

**Molecular dynamics investigation of
nanobubble formation and their role in
thermophysical and thermochemical
behaviour of polar and nonpolar liquids**

**A Thesis Submitted for the
Degree of Doctor of Philosophy**

By

Hamidreza Hassanloo

**Department of Mechanical and Aerospace
Engineering, Brunel University London**

2026

Acknowledgement

First and foremost, I would like to express my deepest gratitude to my beloved parents. Their unconditional love, endless sacrifices, patience, and unwavering belief in me have been the foundation of everything I have achieved. Their encouragement, moral support, and prayers have been my greatest strength throughout this journey.

I would like to extend my sincere appreciation to my supervisor for his invaluable guidance, continuous support, and insightful discussions throughout the course of this research. His expertise, constructive feedback, and commitment to academic excellence have significantly shaped this work and my development as a researcher. I am truly grateful for his mentorship and encouragement.

Finally, I would like to acknowledge all friends and well-wishers who supported me, directly or indirectly, during this PhD journey. Their encouragement and understanding have meant a great deal to me.

Abstract

The rapid increase in atmospheric greenhouse gas concentrations, particularly CO₂ emissions from anthropogenic activities, poses a significant global challenge requiring urgent mitigation. Key strategies include improving energy efficiency through advanced thermal management and heat-transfer technologies, developing engineered working fluids, and deploying next-generation fuels alongside carbon capture and storage (CCS) technologies. Growing attention is being directed toward nanoparticle incorporation and nanoscale mechanisms to advance these strategies by enhancing fluid and fuel properties, accelerating hydrate formation, and improving overall process efficiency. Nanobubbles (NBs), defined as gaseous cavities smaller than 1 μm , exhibit exceptional stability, high surface-to-volume ratios, and the capacity for free radical generation, highlighting their potential in energy, power, and environmental applications. A fundamental understanding of NB nucleation and behaviour is essential to elucidate their effects on the thermophysical properties of host liquids and on key processes such as CO₂ hydrate formation and combustion, which are difficult to capture experimentally. Classical and reactive molecular simulation techniques provide a rigorous approach for probing the influence of NBs on intrinsic material behaviour, process kinetics, and reaction pathways at the molecular scale. Integrating data-driven approaches with molecular dynamics (MD) simulations enables systematic characterization of NB dynamic behaviour and properties. This study investigates the possible formation and effects of NBs generated by nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), and hydrogen (H₂) on the thermophysical properties of four host liquids, including dodecane, isooctane, water, and methanol, examines solid–liquid–gas interactions in graphene-enhanced water and methanol nanofluids (NFs), explores the phase transition and thermal behaviour of NB-enhanced dodecane and its combustion processes, and evaluates their potential impact on CO₂ hydrate formation using classical and reactive MD simulations. Furthermore, the DBSCA (density-based spatial clustering of applications with

noise) algorithm was utilised to analyse the formed NB clusters, assessing their size, density, and motion over time in water and methanol as polar and alcoholic host liquids. The findings reveal that the formation of NBs reduces the density of polar and alcoholic liquids due to the establishment of a nanolayer. The presence of NBs and dispersed graphene increases the viscosity of water-based NFs but decreases viscosity in graphene-methanol NFs containing two-atom gases. Under optimal thermodynamic conditions, NBs markedly enhance hydrate formation by providing hydrophobic nucleation sites, generating local concentration gradients, and accelerating clathrate kinetics, with hydrogen and nitrogen NBs further promoting growth through rapid core-to-solution diffusion. Low temperatures suppress molecular mobility and hinder these effects. At elevated pressures, NBs exhibit a dual role, with a pressure-dependent shift from NB-induced interfacial ordering to bulk-phase interactions. In organic host liquids, NB formation and coalescence are governed by molecular interactions between the host liquid and the dispersed gas, as demonstrated by oxygen forming NB in dodecane but not in isooctane. The presence of NBs, particularly hydrogen NB, depresses the liquid-to-solid transition temperature of dodecane and enhances both thermal conductivity and specific heat capacity, with nitrogen NB yielding the highest thermal conductivity increase of approximately 14%. Nitrogen and hydrogen NBs also exhibit excellent stability over a wide temperature range, making them promising candidates for high-temperature applications. Furthermore, nitrogen NB reduce the activation energy to 52.89 kcal/mol in samples with a density of 0.17 g/mL by promoting the formation of intermediates and radicals, thereby accelerating dodecane consumption, whereas oxygen NB increase the activation energy to 66.93 kcal/mol under the same conditions.

Keywords:

Nanobubbles; Alcoholic and Polar liquids; Organic liquids; Classical molecular dynamics simulations; ReaxFF molecular dynamics simulations; Graphene nanofluids; CO₂ hydrate; Combustion mechanism; Thermophysical properties; Unsupervised machine learning.

Contents

Chapter 1	Introduction	1
1.1	Introduction.....	2
1.2	Statement of the problem	5
1.3	Aim and objectives of this Study	6
1.4	Structure of this thesis.....	8
Chapter 2	Literature Review.....	10
2.1	Introduction.....	11
2.2	Formation and generation of NBs.....	13
2.3	Measurements of NBs.....	20
2.4	Characteristics and stability of NBs.....	24
2.5	Applications of NBs.....	32
2.6	Summary	36
Chapter 3	Research Methodology	40
3.1	Introduction.....	41
3.2	Molecular dynamics simulation.....	42
3.3	Force fields and potentials	46
3.4	MD simulation workflow.....	57
3.4.1	System initialization.....	57
3.4.2	Ensembles	59
3.5	Property evaluation and validation	62
3.5.1	Property evaluation	62
3.5.2	Validation.....	65
3.6	Cluster analysis	65
3.7	Summary	70

Chapter 4 NBs in Polar and Alcoholic Environments 73

4.1	Introduction.....	74
4.2	Pure polar and alcoholic media.....	74
4.2.1	Characteristics of NBs	74
4.2.2	Thermophysical properties.....	86
4.3	Graphene-reinforced environment.....	90
4.3.1	NB nucleation and behaviour.....	90
4.3.2	Thermophysical properties.....	97
4.4	CO ₂ hydrate kinetics	108
4.4.1	Effects of NB type	108
4.4.2	Impacts of temperature and NB	118
4.4.3	Influences of pressure and NB.....	123
4.5	Summary	126

Chapter 5 NBs in Non-Polar Host Liquids 128

5.1	Introduction.....	129
5.2	Formation, coalescence and effects of bulk NBs.....	129
5.2.1	Impact of host liquids and gas types	129
5.2.2	Effect of gas content	140
5.2.3	Effect of temperature	145
5.3	Phase transition and thermal behaviour	150
5.3.1	Phase transition	150
5.3.2	Thermal behaviour	162
5.4	Combustion mechanism of nanobubbled dodecane.....	166
5.4.1	Effects of NB Type	166
5.4.2	Impacts of temperature	174

5.4.3	Influences of sample density.....	178
5.5	Summary	185
Chapter 6	Conclusion & Future Work	187
6.1	Conclusion	188
6.1.1	Polar and alcoholic environments.....	188
6.1.2	Non-polar host liquids.....	190
6.2	Future work.....	192
Chapter 7	Bibliography	195

List of Table

Table 1. <i>Harmonic bond coefficients for methanol molecule.</i>	50
Table 2. <i>Harmonic angle coefficients for methanol molecule.</i>	51
Table 3. <i>OPLS dihedral coefficients for methanol molecule.</i>	51
Table 4. <i>Interaction coefficients of atoms in water, methanol, and dissolved Gases.</i>	53
Table 5. <i>Interaction coefficients of atoms in dodecane and isooctane.</i>	54
Table 6. <i>The comparison of inherent properties calculated by MD simulation and experimental values under the environmental condition [166-170].</i>	65
Table 7. <i>Obtained information for the four detected nanobubbles formed in the water/nitrogen sample at 3 ns.</i>	69
Table 8. <i>Obtained information for the detected nanobubble formed in the water/nitrogen sample at 13 ns.</i>	70
Table 9. <i>Radius and density of the final formed NBs in methanol sample.</i>	82
Table 10. <i>The average total energy between dissolved gas and methanol molecules.</i>	100
Table 11. <i>The viscosity (Pa.s) of G-water and G-methanol NFs with varying mass fractions of scattered nitrogen gas.</i>	102
Table 12. <i>The ratio of specific heat capacity between graphene-water and graphene-methanol nanofluids, relative to their respective pure fluids, for different weight fractions of dissolved gas.</i>	107
Table 13. <i>Linear fit slopes of potential energy evolution for nanobubbled and non-nanobubbled samples.</i>	118
Table 14. <i>The structural features of the prepared organic samples.</i>	131
Table 15. <i>The viscosity of dodecane and isooctane-based samples (Pa.s) with various dissolved gas.</i>	136
Table 16. <i>The diffusion coefficient of dodecane and isooctane-based samples with various dissolved gas ($\times 10^{-9} \text{ m}^2/\text{s}$).</i>	138
Table 17. <i>Comparison of thermal conductivity (λ) values of dodecane obtained from molecular dynamics simulations with corresponding experimental data at 25 °C and 1 atm [204].</i>	156
Table 18. <i>The most common reaction leading to water production within the pure, oxygen (ONB), hydrogen (HNB), and nitrogen (NNB) nanobubbled samples (the numbers on the arrows indicate the frequency of a reaction).</i>	171
Table 19. <i>Three most unique consumption of CH_3 and C_2H_5 in hydrogen nanobubbled samples at densities of 0.08 g/mL and 0.25 g/mL.</i>	182

List of Figure

Figure 1. <i>Molecular structures of dodecane and isooctane, highlighting distinct carbon atom types in isooctane.</i>	55
Figure 2. <i>Methodological framework for studying NBs, involving temporal atom coordinate extraction through MD simulation, unsupervised ML for NB detection, comprehensive characterization of NBs, and elucidation of underlying behavioural mechanisms.</i>	68
Figure 3. <i>Snapshot of the water/nitrogen sample at 3 ns, illustrating the arrangement of atoms and the distribution of nitrogen within the water medium.</i>	69
Figure 4. <i>(left) Snapshot of the water/nitrogen sample at 13 ns, capturing the positions of the formed nanobubbles for further analysis and extraction, (right) the size of formed NB through scattering the position of atoms.</i>	70
Figure 5. <i>Overview of the research framework</i>	72
Figure 6. <i>Initial structure of the dispersed gas in (a) methanol and (b) water.</i>	75
Figure 7. <i>Snapshots at 1 ns (top) and evolution of the number of formed (bottom) nitrogen (left), oxygen (centre), and hydrogen (right) NBs in water over time.</i>	76
Figure 8. <i>Snapshot of formed nitrogen (left), oxygen (centre) and hydrogen (right) NBs in methanol at 1 ns.</i>	76
Figure 9. <i>The average of total energy between nitrogen-nitrogen (left) oxygen-host liquid (centre) and carbon dioxide- carbon dioxide molecules (right) in water and methanol.</i>	78
Figure 10. <i>The number of scattered nitrogen (left), oxygen (centre), and hydrogen (right) in water host.</i>	78
Figure 11. <i>Density (top) and the radius of formed (bottom) nitrogen (left), oxygen (centre), and hydrogen (right) NBs in water.</i>	80
Figure 12. <i>The mechanism of coalescence of nitrogen NB in water host medium.</i>	81
Figure 13. <i>The movement of average centre of final formed nitrogen (lift), oxygen (centre), and hydrogen NB (right) in water host liquid at 298.15 K from 1 ns to 13 ns every 0.5 ns.</i>	81
Figure 14. <i>(a) Number of formed nitrogen NBs, (b) radius of the NBs, (c) number of gas atoms inside the formed NBs, and (d) density of the nitrogen NBs at 343.15 K in water host.</i>	83
Figure 15. <i>The number of nitrogen (left), oxygen (centre) and hydrogen (right) gas atoms inside the formed NBs in water sample at 298.15 K.</i>	84
Figure 16. <i>The average of total energy between nitrogen gas and water (left) and between nitrogen gas atoms (right) in two different temperatures.</i>	84
Figure 17. <i>The movement of the average centre of final formed nitrogen NB in methanol sample at 298.15 K (left) and 323.15 K (right) in the final 2.5 ns of the simulation at 0.5 ns intervals (start point is marked as star).</i>	85
Figure 18. <i>Density of prepared samples with various gases.</i>	86

Figure 19. Number densities of the host liquid molecules around the formed NB in (left) water and (right) methanol samples.	87
Figure 20. The viscosity of samples containing dissolved gases in water (left) and methanol (right).	88
Figure 21. The average of total energy between carbon dioxide and hydrogen molecules with water molecules.	89
Figure 22. The average of van der Waals energy of methanol mixtures.	90
Figure 23. Sequential snapshots illustrating the process of (a) initial site formation of oxygen (green) NBs on the G surface (red), (b) coalescence on the graphene surface, (c) movement of the formed NB to the edge of G, (d, e) adsorption of oxygen on the lower surface and migration to the unoccupied edge, and (f) encapsulation of the NB core by the G shell within the water NF.	92
Figure 24. Temporal snapshots illustrating the formation and behavior of nitrogen (pink) NBs in nitrogen/G-water NF over time.	93
Figure 25. Snapshot of the morphology of (a) hydrogen (cyan) and (b) carbon dioxide (brown) G-water NFs at 13.4 ns.	93
Figure 26. At 13.4 ns, a visual representation captures the formation of NB in the G-methanol NF.	94
Figure 27. The average of the total energy between oxygen (left), nitrogen (centre), and hydrogen (right) with G in water and methanol.	95
Figure 28. Temporal evolution of nitrogen (yellow) cluster formation, movement, and disappearance with lower mass fractions of dissolved nitrogen gas within a G-water NF. ...	96
Figure 29. Behaviour of dissolved nitrogen gas in G-methanol NF with lower mass fraction.	97
Figure 30. Viscosity of G-water/scattered gas (left) and G-methanol/dissolved gas (right) NFs.	98
Figure 31. The average of total energy between dissolved gases and water molecules.	99
Figure 32. The average total energy between dissolved gas and methanol molecules in bubbled (left) and the average van der Waals energy of non-bubbled methanol NFs.	101
Figure 33. The van der Waals energy of nitrogen/G-water NFs (left) and nitrogen/G-methanol NFs (right) at different mass fractions of scattered gas.	102
Figure 34. Specific heat capacity of samples compared to the host mediums.	103
Figure 35. The radial distribution function (RDF) of the same mass fraction dissolved gas in water samples with G nanosheet.	105
Figure 36. The radial distribution function (RDF) of the different mass fraction of dissolved nitrogen gas in water (left) and methanol (right) NFs with G nanosheet.	108

Figure 37. Initial configuration of (a) a non-nanobubble and (b) a nanobubble-containing water-carbon dioxide sample, including a hydrate seed.	110
Figure 38. Number of formed hydrate cages: (a) small, large, and total cages at 28.35 ns; (b) small cages, (c) large cages, and (d) total cages over the course of 85 ns at 2 MPa and 260 K.	111
Figure 39. Snapshots of (a) WG, (b) HNB with diffused hydrogen atoms (green) in the solution, (c) CDNB, (d) ONB, and (e) NNB samples at 28.35 ns at 2 MPa and 260 K.	114
Figure 40. Four-order structural parameter of various samples.	116
Figure 41. Temporal evolution of potential energy for the pure water-gas sample (WG) and nanobubbled samples (CDNB, ONB, NNB, and HNB).	118
Figure 42. Number of formed hydrate cages: (a) small, (b) large, and (c) total cages over time at 2 MPa and 240 K; (d) comparison of the number of formed cages at 85 ns between 240 K and 260 K at 2 MPa.	120
Figure 43. RDF of (a) hydrogen-carbon dioxide and (b) hydrogen-water in the HNB sample at 39.06 ns.	122
Figure 44. (a) F_4 parameter of CDNB at two different temperature and (b) the number of total formed rings and cages at 240 K for CDNB at two different times.	123
Figure 45. The number of formed hydrate cages: (a) small, (b) large, and (c) total cages at 10 MPa and 260 K.	125
Figure 46. Initial configuration of the scattered gas in the (a) dodecane and (b) isooctane samples.	131
Figure 47. Formation process of (a, b, c, d) nitrogen and (e, f, g, h) oxygen NBs in PCM host after 1, 1.5, 4.75, and 10 ns (from left to right).	133
Figure 48. Formed hydrogen NBs in dodecane at (a) 0.5, (b) 1, and (c) 10 ns.	133
Figure 49. Formed nitrogen NBs in (a) dodecane and (b) isooctane samples at 1.5 ns.	134
Figure 50. The NBs formed in (a, b, c, d) dodecane and (e, f, g, h) isooctane samples with different gases at the end of simulation.	134
Figure 51. The average of the total energy between oxygen and host liquids.	135
Figure 52. (a) Coulomb energy of the carbon dioxide and nitrogen system. (b) Van der Waals energy of nitrogen and oxygen samples. Note that the negative sign shows the attractive force and the absolute amount of it should be used for comparing.	137
Figure 53. Distribution of carbon dioxide and oxygen molecular in isooctane-based fluid at the 13.4 ns.	138
Figure 54. Specific heat capacity of samples compared to the host mediums.	139
Figure 55. The radial distribution function (RDF) of nitrogen gas in (a) isooctane and (b) dodecane samples.	141

Figure 56. <i>Viscosity of obtained samples with different gas weight fractions and host liquids.</i>	141
Figure 57. <i>Absolute amount of attractive energy of samples with various content of scattered gas in (a) dodecane and (b) isooctane.</i>	142
Figure 58. <i>The RDF for the gas-liquid interactions of the prepared (a) dodecane and (b) isooctane samples with different nitrogen concentration.</i>	142
Figure 59. <i>Comparison of specific heat capacity of mixtures with different gas weight fraction.</i>	143
Figure 60. <i>The average of (a) pairwise energy of dodecane sample, and (b) the total energy between gas and host liquid in isooctane sample.</i>	144
Figure 61. <i>Snapshots of the formed NBs in dodecane sample at (a) 298.15 K and (b) 343.15 K at 0.5 ns.</i>	145
Figure 62. <i>Snapshots of the formed NBs in isooctane sample at (a) 298.15 K and (b) 343.15 K at 0.5 ns.</i>	146
Figure 63. <i>Snapshots of the formed NBs (a) at higher temperature at 1.5 ns, (b) at lower temperature at 1.5 ns and (c) at 4.75 ns in dodecane.</i>	146
Figure 64. <i>Snapshots of formed NBs in (a, b) dodecane and (c, d) isooctane (a, c) at lower and (b, d) higher temperature.</i>	147
Figure 65. <i>Absolute amount of van der Waals energy of (a) dodecane and (b) isooctane at different temperatures.</i>	148
Figure 66. <i>The specific heat capacity of prepared samples at different temperature.</i>	149
Figure 67. <i>(a) Pairwise energy of isooctane and (b) coulomb energy of dodecane samples at 298.15 K and 343.15 K.</i>	150
Figure 68. <i>Initial configurations of the simulated systems: (a) pure dodecane sample, (b) nanobubble-containing sample, and (c) cross-sectional view of the nanobubble-containing sample.</i>	151
Figure 69. <i>Snapshots of NBs in solidified dodecane: (a) nitrogen, (b) oxygen, and (c) hydrogen NBs.</i>	151
Figure 70. <i>Diffusion coefficient and density of (a) pure dodecane, (b,e) hydrogen, (c,f) oxygen, and (d,g) nitrogen nanobubble-containing samples.</i>	153
Figure 71. <i>The temperature gradient of pure dodecane along the x-axis direction.</i>	155
Figure 72. <i>(a) Comparison of thermal conductivity between nanobubbled samples and pure dodecane, (b) RDF between dodecane molecules, and (c) RDF between nitrogen and hydrogen nanobubble molecules and dodecane molecules at 253.15 K.</i>	159
Figure 73. <i>(a) Vibrational density of states (VDOS) of the pure sample and nanobubbled samples, and distribution of coordination numbers for the three highest fractions of hydrogen</i>	

<i>and carbon atoms in dodecane, the host medium, for (b) the pure sample and (c) the sample with nitrogen NB.</i>	161
Figure 74. (a) Comparison of the specific heat capacity of nanobubble-containing samples to the pure dodecane sample, and (b) pairwise energy of the samples at 253.15 K.	162
Figure 75. Snapshots of (a) nitrogen, (b) oxygen, and (c) hydrogen NBs in dodecane at 275.15 K.	163
Figure 76. Snapshots of (a) nitrogen, (b) oxygen, and (c) hydrogen NBs in dodecane at 443.15 K.	163
Figure 77. Comparison of the thermal conductivity of nanobubble-containing samples with that of pure dodecane at 443.15 K.	164
Figure 78. Comparison of the viscosity of nanobubble-containing samples with that of pure dodecane at (a) 275.15 K and (b) 443.15 K.	165
Figure 79. Mean square displacement of pure and nanobubble-containing samples at (a) 275.15 K and (b) 443.15 K.	166
Figure 80. Initial configuration of (a) a pure sample containing dodecane ($C_{12}H_{26}$) and oxygen molecules, featuring red carbon atoms, blue hydrogen atoms, and green oxygen atoms, and (b) a nanobubbled sample, orange NB atoms.	167
Figure 81. Time evolution of (a) the number of dodecane molecules in pure and nanobubbled samples, and the number of chemical species, oxygen, and nanobubbles molecules within (b) nitrogen, (c) pure, (d) hydrogen, and (e) oxygen nanobubbled samples.	169
Figure 82. The three most produced chemical species at 2000 K after 2000 ps within (a) pure, (b) oxygen, (c) hydrogen, and (d) nitrogen nanobubbled samples.	170
Figure 83. Reaction network of intermediates and radicals originating from the introduced nitrogen nanobubbles that result in water production.	171
Figure 84. Reaction paths of formation C_2H_4 within (a) pure and (b) hydrogen nanobubbled sample.	174
Figure 85. Reaction paths of formation CH_3 within (a) pure and (b) oxygen nanobubbled sample.	174
Figure 86. Arrhenius parameters extracted from fitted rate constants $\ln(k)$ versus temperature for (a) pure, (b) hydrogen, (c) nitrogen, and (d) oxygen nanobubbled samples at a density of 0.17 g/mL.	176
Figure 87. Number of total chemical and carbon species after 2 ps within (a) pure, (b) hydrogen, (c) nitrogen, and (d) oxygen samples.	178
Figure 88. (a) Time evolution of the number of dodecane molecules, and (b) average pairwise energy within hydrogen nanobubbled samples across various densities.	179
Figure 89. Arrhenius parameters derived from fitted rate constants $\ln(k)$ versus temperature for hydrogen nanobubbled samples at (a) 0.085 g/mL and (b) 0.25 g/mL densities.	180

Figure 90. *The total number of chemical species and the top five products in hydrogen nanobubbled samples at densities of (a) 0.08 g/mL and (b) 0.25 g/mL, measured at 2000 K after 2000 ps.*181

Figure 91. *The reaction pathways and the frequency of the conversions in the formation of CH₂O within samples with densities of (a) 0.08 g/mL and (b) 0.25 g/mL, and H₂O within samples with densities of (d) 0.08 g/mL and (e) 0.25 g/mL within hydrogen nanobubbled sample (the numbers in the circles indicate the frequency of a reaction).....*184

List of peer-reviewed journal articles from this thesis

1. **H. Hassanloo** and X. Wang, "*Formation, coalescence and behaviour of bulk nanobubbles in dodecane and isooctane and their thermophysical properties: A comprehensive molecular study*," **Fuel**, vol. 358, p. 130254, 2024.
2. **H. Hassanloo** and X. Wang, "*Unveiling the inherent properties and impact of ultrafine nanobubbles in polar and alcoholic media through unsupervised machine learning and atomic insight*," **International Journal of Thermofluids**, p. 100734, 2024.
3. **H. Hassanloo** and X. Wang, "*Nanobubbles in graphene-based nanofluids: Unraveling the mechanisms behind nucleation, behaviour and thermophysical properties using a molecular approach*," **Fuel**, vol. 375, p. 132517, 2024.
4. **H. Hassanloo** and X. Wang, "*Combustion mechanism of nanobubbled dodecane: A reactive molecular study*," **Fuel**, vol. 374, p. 132486, 2024.
5. **H. Hassanloo**, X. Wang and Y. Yang, "*Characterising phase transition and thermal behaviour of phase change material with nanobubbles: A comparative molecular dynamics study*," **International Communications in Heat and Mass Transfer**, vol. 171, p. 110113, 2026.
6. **H. Hassanloo** and X. Wang, "*Molecular dynamics study on the mechanisms of ultrafine bubbles in CO₂ hydrate formation*," **Journal of CO₂ Utilization**, vol. 105, p. 103335, 2026.

Chapter 1 Introduction

1.1 Introduction

The accelerating rise in atmospheric greenhouse gases, particularly carbon dioxide (CO_2), driven by anthropogenic activities, represents a critical global challenge, necessitating urgent and integrated mitigation strategies. Among these strategies, significant emphasis has been placed on enhancing energy efficiency through advanced thermal management and heat transfer technologies, particularly via the development of engineered working fluids, alongside the deployment of next-generation fuels and carbon capture and storage (CCS) technologies [1-5]. In combination with other complementary approaches, these efforts form a robust framework for reducing greenhouse gas emissions and facilitating the transition toward a sustainable, net-zero energy future.

Within this framework, improving thermal-fluid performance has emerged as a key research direction. Significant efforts have been devoted to replacing conventional thermal fluids with alternatives exhibiting superior thermophysical properties. Notably, nanoscale phenomena have a significant impact on these attributes, as nanoparticles or nanoscale mechanisms govern fluid properties such as viscosity, density, and rheological behaviour [6, 7]. This influence could be amplified when gases are introduced into working fluids, particularly in industrial processes like electrochemical reactions used in energy conversion and storage, where gaseous byproducts such as hydrogen and oxygen often emerge, potentially leading to alterations in the thermophysical properties of the host liquid [8-10]. This alteration becomes even more pronounced when these gases tend to give rise to nanobubbles (NBs) [11].

Beyond thermal systems, decarbonisation efforts must also address the fuel sector, as the global reliance on fossil fuels such as diesel, petroleum, natural gas, and coal remains a major contributor to greenhouse gas emissions. These non-renewable resources are not only limited

in availability but also fundamentally conflict with the Paris Agreement's objective of achieving a decarbonised society by the end of this century [12-14]. Alternative fuels, including ammonia and hydrogen, hold great potential for decarbonisation [15, 16], but their widespread adoption is constrained by intrinsic limitations, as hydrogen's high reactivity raises safety concerns during storage and combustion, while ammonia exhibits a slow reaction rate and a tendency to generate NO_x emissions [17, 18]. By contrast, blended fuels, such as methanol–ammonia mixtures and hydrogen-enriched NB fuels, represent a promising decarbonisation pathway, as the deliberate tuning of physicochemical fuel properties and combustion characteristics, thereby leading to improved engine performance and overall system efficiency [19-21] .

In parallel with advances in thermal-fluid engineering and fuel innovation, carbon management technologies have become indispensable components of climate mitigation strategies. CCS technologies not only offer substantial reductions in greenhouse gas emissions but also provide broader economic and environmental benefits essential for the transition to net-zero energy systems [3]. Among all CCS technologies, CO₂ hydrate stands out as a novel approach that not only enables effective carbon capture but also offers valuable applications such as gas storage, transportation, and use as a secondary refrigerant, owing to its high dissociation enthalpy and environmentally friendly properties [22]. However, the inherently slow kinetics of hydrate nucleation and growth remain major technical barriers. Although physical enhancement methods such as pressurisation, cooling, and agitation have been applied, these approaches are often energy-intensive, difficult to scale, and economically impractical. Consequently, chemical additives have gained attention as more efficient alternatives for accelerating hydrate formation [23, 24]. More recently, NBs have emerged as a promising enhancement strategy, demonstrating significant potential in

promoting natural gas hydrate formation and offering a low-energy, scalable, and efficient pathway for improving hydrate kinetics [25].

NBs are nanoscale gas-filled cavities with a spherical cap shape, typically less than 1 μm in diameter, that exist either as surface-bound structures or as dispersed entities within bulk liquids [26-28]. Owing to their unique interfacial and physicochemical characteristics, including exceptional long-term stability, capability for free radical generation, high surface-to-volume ratio, electrically charged gas-liquid interfaces, and enhanced mass transfer capability, NBs exhibit behaviour that deviate from classical bubble dynamics and conventional theoretical predictions [29-34]. These distinctive properties enable NBs to persist in host liquids for extended durations and resist coalescence and dissolution [35]. As a result, NBs have emerged as a powerful nanoscale platform for liquid-phase optimisation, offering significant potential for enhancing transport phenomena, reaction kinetics, and process efficiency across a wide range of industrial applications, including energy sectors [36-38], fuel technologies [20, 21, 39], and environmental engineering [40].

The existence of stable NBs has now been experimentally confirmed, and over the past two decades, their production and application have garnered exponentially increasing attention. Industries are already harnessing the potential of NBs, with projections indicating that the market in Europe will grow to €145 million by 2030 [37].

1.2 Statement of the problem

Although the long-term existence of NBs has been experimentally confirmed, investigating these tiny bubbles through experimental techniques [41-43] presents significant challenges. Some methods struggle to distinguish NBs from other nanoscale contaminants, and the fundamental processes governing their behaviour and inherent properties remain elusive [44, 45]. One of the most intriguing and extraordinary aspects of these tiny bubbles is their exceptional stability, defying the predictions of the Epstein-Plesset theory, enabling them to persist in host liquids for extended periods and significantly influencing practical applications [33, 34]. Their deviation from conventional continuum theories adds further complexity to NB research, especially when studying bulk NBs, which, unlike surface-bound NBs, are affected by Brownian motion [27, 46, 47].

Furthermore, experimental evidence has confirmed that NBs possess the potential to alter the inherent properties of host liquids and even influence reaction processes such as combustion. For instance, the presence of CO₂ NBs in food fluids has been shown to impact their thermophysical properties [11]. Additionally, improvements in engine power output and brake-specific fuel consumption (BSFC) have been observed in gasoline engines using a hydrogen nanobubble-gasoline blend, compared to conventional gasoline, under specific engine load conditions [20]. However, experimental methods face limitations in fully clarifying the mechanisms by which NBs impact the inherent properties of host liquids and influence reaction processes at the nanoscale. Moreover, the potential applications of NBs in nature-based engineering processes, such as gas hydrate formation, remain largely unexplored. Most studies in this area have focused on chemical additives or methane-based host liquid systems, leaving a significant knowledge gap concerning the potential role of different types of NBs in CCS processes.

In conjunction with experimental techniques, molecular approaches such as molecular dynamics (MD) simulations provide critical insights into the molecular-level behaviours and nanoscopic effects of tiny bubbles. However, most studies have focused on the fundamental properties of surface NBs or pre-defined bulk NBs, primarily in water as the host liquid [48-51], leaving the nucleation, dynamic behaviour, and application-relevant properties of bulk NBs largely unexplored [52]. Furthermore, the behaviour and potential effects of NBs in organic and alcoholic environments remain largely uninvestigated, and their influence on combustion and other reaction mechanisms has not been elucidated at the molecular level. This limited understanding has created a critical gap between fundamental knowledge and engineering applications, as existing studies predominantly focus on the intrinsic behaviour of NBs without sufficiently accounting for their impact on the thermophysical properties of nanobubbled systems. Consequently, current fundamental insights cannot be readily translated to industrial processes, including thermal energy management, reaction engineering, and carbon capture. Bridging this gap requires comprehensive molecular-level investigations of NB systems under industrially relevant conditions and processes, encompassing diverse host liquids, to directly connect fundamental mechanisms with practical engineering outcomes.

1.3 Aim and objectives of this Study

This study bridges the gap between fundamental NB science and industrial applications by systematically investigating NB nucleation, behaviour, and functional impacts in thermally, chemically, and kinetically relevant processes. The research focuses on the role of NBs in the thermophysical and transport properties of host liquids, reaction mechanisms and combustion characteristics in nanobubbled fuels, as well as their implications for advanced carbon capture strategies. Specifically, the thesis investigates NB-engineered working fluids

for thermal energy management, NB-assisted combustion through reactive molecular modeling, and NB-driven carbon capture mechanisms, including CO₂ hydrate nucleation and growth as a hydrate-based carbon sequestration mechanism. Furthermore, recognising the complexity of real industrial systems, the research extends to multiphase environments by investigating NB formation and behaviour in solid–liquid–gas systems, such as graphene-reinforced nanofluids.

To enable a systematic and transferable investigation, this thesis focuses on four industrially relevant host liquids representing distinct molecular and functional classes, namely dodecane, isooctane, water, and methanol. Dodecane and isooctane were selected as representative organic liquids due to their strong relevance to thermal energy systems and fuel applications. Dodecane’s high boiling point and thermal stability make it particularly suitable for high-temperature heat transfer, thermal energy storage, and phase change applications, while its lubricating properties and biodegradability support sustainable industrial use as an alternative to conventional hydrocarbon solvents [53-56]. Isooctane, as a high-octane reference fuel, provides a reliable platform for investigating NB nucleation and its effects on fuel properties, owing to its cleaner and more efficient combustion compared to lower-octane fuels [57].

Water and methanol were selected as polar and alcoholic host liquids due to their central roles in industrial processes, renewable energy systems, and carbon capture applications. Water serves as a fundamental working fluid in thermal management, electrochemical energy systems, hydrogen production, and gas hydrate formation, making it essential for studies related to energy conversion and carbon sequestration technologies [58]. Methanol, recognised for its considerable hydrogen storage capacity, serves as a valuable renewable energy carrier and an alternative fuel [59, 60]. Collectively, these liquids enable a

comprehensive evaluation of NB behaviour across diverse environments, ensuring the applicability of results to energy, combustion, and carbon capture technologies.

1.4 Structure of this thesis

This thesis presents a comprehensive molecular-level investigation of NBs in both polar and non-polar liquids, focusing on their formation, stability, behaviour, and impact on thermophysical properties, reaction pathways in combustion processes, and the kinetics of CO₂ hydrate formation and growth. Chapter 1 introduces the research background, objectives, and significance, outlining the need to understand the influence of NBs on inherent fluid properties, combustion processes, and hydrate formation mechanisms. Chapter 2 follows with a detailed literature review, critically examining previous studies on NB generation, detection, stability, characteristics and applications, while identifying the key knowledge gaps that this research aims to address. Chapter 3 describes the research methodology, highlighting MD simulations as the core computational approach and introducing complementary techniques, such as unsupervised machine learning, to systematically analyse NB behaviour and interactions at the molecular level.

Building on this methodology, Chapter 4 focuses on the study of NBs in polar and alcoholic environments. Initially, a hybrid approach combining MD simulations with unsupervised machine learning is used to assess NB formation and intrinsic properties, such as NB density over time, resulting from dissolved gases, including hydrogen, nitrogen, oxygen, and carbon dioxide, as well as to evaluate their effects on solvent properties, such as viscosity. The study then explores the impact of complex solid–liquid–gas interactions in graphene-reinforced, water- and methanol-based nanofluids on the formation of NBs and their effects on thermophysical properties and molecular structures. Finally, this chapter examines the molecular-level influence of different types of NBs on CO₂ hydrate formation and growth,

providing insight into their potential roles in hydrate inhibition or promotion under different thermodynamic conditions.

Chapter 5 extends the investigation to organic host liquids. Classical MD simulations are employed to study the formation, behaviour, and effects of NBs on the thermophysical properties of dodecane and isooctane, systematically analysing the influence of gas type, dissolved gas fraction, and system temperature. Furthermore, the impact of NBs on phase transitions and the thermal behaviour of dodecane as a phase change material (PCM) was investigated. Recognising the importance of chemical interactions in combustion processes, the study then applies the ReaxFF reactive molecular approach to evaluate the impacts of stably formed hydrogen, nitrogen, and oxygen NBs on the combustion characteristics of dodecane, considering variations in NB type, temperature, and sample density.

In conclusion, Chapter 6 summarises the key findings of the thesis and discusses their scientific and practical implications. Further research gaps and questions and potential future work resulted from this study are also discussed in this chapter.

Chapter 2

Literature Review

2.1 Introduction

In the 1940s, researchers first hypothesized the presence of small gas nuclei, microscopic pockets of gas, within the blood and tissues of animals, especially under low-pressure conditions. These gas nuclei could, theoretically, be eliminated through processes such as centrifugation, filtration, boiling, or by applying high hydrostatic pressure. It was suggested that these nuclei might achieve stability by attaching to the walls of hydrophobic, conical crevices, a concept hinting at the potential ubiquity of nanoscale gas bubbles in nature. However, direct observation of these nanoscale bubbles remained elusive, likely due to the limitations of detection methods available at the time [41, 61]. In 1950, Epstein and Plesset introduced a pivotal theoretical model that describes the growth or shrinkage of gas bubbles in a liquid-gas solution based on the solution's saturation level. Grounded in diffusion theory and the Laplace equation, this model posits that gas transport from the bubble adheres to the diffusion equation. The rate of change of the bubble radius R over time t , in spherical geometry, is expressed as [46]:

$$\frac{dR}{dt} = -\frac{D\Delta c}{\rho} \left(\frac{1}{R} + \frac{1}{\sqrt{\pi Dt}} \right) \quad (2.1)$$

where D represents the diffusion constant of the dissolved gas in water, while ρ denotes the gas density. The concentration difference Δc is defined as $c_b - c_\infty$, where c_b refers to the dissolved gas concentration near the bubble and c_∞ is the concentration in the far field. By substituting $c_b = \frac{P_b}{K_H}$ (with $P_b = P_o + \frac{2\gamma}{R}$ being the gas pressure inside the bubble, γ as surface tension, and K_H as Henry's constant), the concentration difference can be expressed as:

$$\Delta c = \left(P_o + \frac{2\gamma}{R} \right) \frac{1}{K_H} - c_\infty \quad (2.2)$$

Based on previous reports applying the Epstein–Plesset theory, a 100 nm radius bubble has been estimated to experience an internal pressure approximately 14.4 times atmospheric pressure and to dissolve in less than one microsecond. This conclusion implied that stable nanoscale gas bubbles could not persist in liquid environments, leading to limited research on this topic in subsequent years [41]. However, in 1994, Parker et al. [62] reintroduced the concept of NBs, aiming to provide a compelling explanation for the long-range attractive forces observed between two hydrophobic surfaces submerged in aqueous solutions marked a significant turning point in the understanding of NBs, shifting focus to their interactions and implications in various contexts. More notably, direct observations of bulk NBs and surface NBs were first reported by the research groups of Hu [28] and Higashitani [63] in the early 2000s.

NBs, which are defined as gaseous cavities with diameters smaller than 1 μm , can be classified into two main categories: surface NBs and bulk NBs. Surface NBs typically exhibit heights ranging from greater than 10 nm to less than 100 nm, along with contact line pinning from 50 to 500 nm. In contrast, “bulk NBs,” also known as “ultrafine bubbles,” are generally spherical, gas-filled structures with diameters less than 1000 nm exhibit unique properties that make them become versatile sensing materials with applications spanning diverse industrial and chemical processes [26, 64].

This chapter analyses the current literature on NBs, focusing on both experimental and simulation-based studies that explore their formation, detection, characteristics and stability, as well as applications. These studies significantly contribute to the understanding of NB behaviour and properties, highlighting the factors influencing their generation and persistence. Additionally, this research showcases the promising applications of NBs across

fields such as medicine, environmental science, water treatment, and powering energy-related applications where their unique properties present innovative potential.

2.2 Formation and generation of NBs

NB formation in solutions can follow two primary pathways. The first involves the appearance of a new phase, a gas bubble phase, emerging from the liquid phase. This phase change is typically a first-order phase transition that begins through a process called nucleation. The second pathway involves the collapse or shrinkage of microbubbles, which can result in the formation of stable NBs under certain conditions [41].

In the nucleation process, the formation of bubbles within a solution signifies the transition to a new thermodynamic phase (gas) from a liquid that typically exists in a metastable state. Classical nucleation theory posits that the nucleation rate is determined by the Gibbs free energy associated with the formation of this new phase, which is described by an exponential relationship that incorporates the Boltzmann constant and the temperature. In the case of homogeneous nucleation, the free energy required to form a spherical bubble nucleus in an oversaturated gas solution can be expressed as follows [41]:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_{lg} + 4\pi r^2 \gamma \quad (2.3)$$

where r represents the radius of the nucleus, γ denotes the surface tension at the gas/liquid interface, and ΔG_{lg} , which is referred to as G_v in some references [65], represents the volumetric energy associated with a unit volume of gas, indicating the difference in Gibbs free energy per unit volume between the bulk liquid and the gas nuclei at the same pressure. ΔG_{lg} or G_v becomes negative under thermodynamically favorable conditions, which

encourages nucleation. In contrast, the liquid-vapor surface tension γ is always positive and therefore works against nucleation. For small radii r , the surface energy term typically prevails. However, when the bubble reaches a critical radius $r^* = \frac{-2\gamma}{G_v(\Delta G_{lg})}$, the derivative $\frac{dG}{dr} \big|_{r>r^*} < 0$, indicating that the bubble will begin to grow. In a molecular study, Weijs et al. [65] investigate the formation of NBs in systems where gas is uniformly dissolved in the host liquid. They observed that as the gas concentration in the liquid increases, the magnitude of G_v also rises, making it increasingly favorable for the system to contain gas atoms in the gas phase rather than in the dissolved state. This increase in G_v reduces the value of the critical radius r^* , eventually becoming small enough that the spontaneously forming tiny bubbles are sufficiently large (where $r > r^*$) to overcome the surface energy penalty and continue growing. Homogeneous nucleation is often a slow process due to the high energy barrier created by the surface free energy term ($4\pi r^2\gamma$), which dominates over the bulk free energy term (r^3) for small nuclei. This results in a positive Gibbs free energy change, preventing bubble growth. Consequently, bubble formation typically occurs via heterogeneous nucleation, facilitated by surfaces or impurities that reduce the nucleus surface area and, in turn, the energy barrier. This makes heterogeneous nucleation more likely and significantly faster. In oversaturated solutions, this principle governs NB generation, achieved by dissolving excess gas or via gas-evolution reactions like hydrogen or oxygen evolution [41].

Generally, spherical bubbles in liquids are inherently unstable. They may grow by inward diffusion of gas from their surroundings and eventually be removed by buoyant forces, or they may shrink as gas diffuses outward, leading to their disappearance. However, during bubble collapse, an intermediate NB stage may occur, providing a pathway for microbubbles to shrink into NBs and achieve stability. It has been observed that NBs form shortly after

microbubble generation in water. When the water is saturated with microbubbles, it appears milky. After production halts, the microbubbles gradually rise and vanish, leaving clear water, where NBs of 100-200 nm are detectable, suggesting that NBs may form as a residual byproduct of microbubble formation [66]. Jin et al. [66, 67] used dark field microscopy (DFM) to track microbubbles before they burst, observing that microbubbles larger than 50 μm aggregated and burst rapidly, while those between 10 and 50 μm shrank and formed NBs through Brownian motion.

It is crucial to acknowledge that the demand for efficient production of NBs is primarily driven by specific applications. To enable industrialisation and broaden the potential applications of NBs in the wider market, it is essential to develop methods that are cost-effective, simple, efficient, stable, and scalable for generating gaseous NBs. Different approaches are employed for producing surface and bulk NBs, each tailored to the specific requirements of the application [68]. Electrolysis is one of the methods used to generate NBs, taking advantage of electrochemical reactions at the electrodes, such as during the electrolysis of salt solutions. Specifically, oxygen and hydrogen NBs can be produced at designated electrodes during water electrolysis in the presence of acid or base. As recently reported by Postnikov et al. [69], one effective and straightforward method for producing bulk NBs of controlled size is alternating polarity electrolysis of water. Molecular simulations explored the diffusion-driven evolution of electrolytic NBs on wettability-patterned nanoelectrodes. These electrodes, with hydrophobic islands as nucleation sites, promote NB growth in the pinning mode. A critical current density was identified, distinguishing stable from unstable NBs. At sub-threshold current densities, NBs grow to equilibrium, maintaining a nanoscale size. However, above the threshold, NBs experience unchecked growth and may eventually detach due to buoyancy [70].

When gas is dissolved or mixed in a liquid, a rapid pressure change, known as cavitation, leads to the formation of gas bubbles in areas of lower pressure. There are two main types of pressure reduction mechanisms in fluid flow: hydrodynamic cavitation and acoustic cavitation [68]. Hydrodynamic cavitation occurs in flowing fluids when the local pressure drops below a critical threshold. In this process, microbubbles rise quickly to the gas-liquid interface and burst, while NBs remain in the solution due to their slower ascent. As a result, generating NBs can be time-consuming, and precisely controlling the size of cavitation bubbles is difficult [71]. On the other hand, acoustic cavitation involves the creation of bubbles through exposure to sound waves with alternating positive and negative pressure. During this process, nucleation and expansion of bubbles occur under negative pressure, while the bubbles contract under positive pressure conditions [68, 72]. Contrary to earlier beliefs that NBs could only form in gas-oversaturated environments, it has been proposed that bulk NBs can also be generated through decompression and can remain stable in an unsaturated gas environment for extended periods [41, 73]. It has also been reported that extremely high-frequency vibrations can nucleate nanoscale bubbles through localised heating. This occurs when the temperature in specific regions surpasses the liquid's boiling point. The heating arises from energy dissipation into the liquid through viscous dissipation near vibrating surfaces, a phenomenon that becomes significant when the liquid film thickness is smaller than the Stokes boundary layer height. The boundary layer height depends on the liquid's density (ρ), dynamic viscosity (μ), and the angular vibrational frequency (ω). High acoustothermal heat fluxes can be generated for small amounts of liquid subjected to high-frequency vibrations, reaching levels as high as $\sim 10^9$ W/m² for nanofilms of water vibrated at 100 GHz. This intense heat flux can rapidly bring the liquid to the liquid–vapor spinodal region, triggering explosive bubble nucleation or boiling. This vibration-driven boiling phenomenon has the potential to replace laser-irradiation-driven phase

changes in various applications. Molecular dynamics (MD) simulations have been employed to study the acoustothermal nucleation of surface NBs. In these simulations, a nanoscale water film supported by a solid surface was modeled. Bubble formation was observed to occur when liquid molecules overcame the attraction from the solid surface (work of adhesion), surpassing an energy barrier to form vapor-filled regions. The mechanism of nucleation is influenced by two modes through which liquid molecules gain energy: (1) an increase in molecular kinetic energy due to viscous dissipation, leading to boiling, and (2) an increase in potential energy from film tensioning caused by surface vibrations, resulting in cavitation [74-76]. The cavitation threshold is the critical external tensile pressure that triggers the unstable growth of bubbles. Experimental findings indicate that surface NBs remain stable down to -6 MPa, contrasting with the classical Blake threshold, which predicts instability for bulk bubbles below -0.6 MPa. Three-dimensional MD simulations, involving a supersaturated water phase doped with N_2 and subjected to pressure reductions over 0.1 ns, were employed to investigate cavitation. Stability was observed at -7.5 MPa but lost at -10.5 MPa, identifying a cavitation threshold near -9.18 MPa. This finding was further supported by theoretical modeling [77].

Previous methods for generating NBs often face challenges such as high energy consumption, inflexibility, and operational complexity. A more streamlined and efficient technique involves compressing the target gas into a liquid, releasing it through specially designed nozzles, and nucleating tiny bubbles, which can lead to NB formation. Porous materials like ceramic membranes are particularly effective, acting as an array of micro-orifices to produce a cloud of bubbles with varying sizes, enabling efficient and scalable NB generation. Ceramic membranes with nanometer-scale uniform pores have been shown to produce NBs, offering solutions to challenges such as high energy use and inefficiency in bubble generation. Widely applied as bubbling diffusers in processes like wastewater

treatment and landfill leachate management, these membranes typically produce millimeter-scale bubbles, with the smallest reported size being 0.51 mm. Injecting air through nanoporous ceramic tubes at varying pressures influences bubble size, zeta potential (ZP), solution pH, and dissolved oxygen. Higher air pressure decreases bubble size and dissolved oxygen, but increases solution pH, ZP, and NB stability. These properties are determined by pore size and applied pressure, showcasing the membrane's effectiveness in enhancing and controlling NB generation [68, 78].

Novel and effective methods have been developed to produce concentrated and stable bulk NBs with high uniformity, owing to their various industrial and medical applications [79]. Lipid NBs are one of these novel approaches for producing bulk NBs. These NBs, formed through lipid encapsulation, consist of a lipid shell surrounding a gas core. The lipid shell provides mechanical resistance, raising the pressure at which the gas condenses, protecting the core up to approximately 0.8 atm. The lipid layers enhance the stability of these nanosized bubbles, preventing dissolution and making them more durable compared to the less stable 'open' bulk NBs produced by other methods [80, 81]. Coarse-grained MD simulations using a Martini-based nitrogen model were employed to study lipid NBs, revealing radius-dependent phase separation in lipid monolayers that becomes maximal at the planar gas–water interface [82]. The generation of bulk NBs using external electric or magnetic fields is another novel approach that has only recently gained attention. Pulsed magnetic fields can induce bulk NBs by perturbing the van der Waals interactions and hydrogen-bond network of water, creating local conditions that favour the clustering of dissolved gas molecules and the formation of stable bubbles. To explore this phenomenon, a novel water treatment system employing an alternating magnetic field was investigated for its potential to generate NBs [83]. Complementing this, nonequilibrium molecular dynamics (NEMD) simulations showed that applying a static electric field to water with

dissolved propane causes the gas molecules to cluster and form NBs, resembling Ostwald ripening, particularly under stronger fields [84].

The solvent exchange process has been proven to be a convenient and effective method for forming surface NBs and nanodroplets, and this approach has also been adopted to produce BNBs. During the solvent exchange process for generating surface NBs, the substrate is initially in contact with a gas/oil-saturated solution (i.e., ethanol), which is gradually substituted with a poor solvent (i.e., water), leading to the formation of long-lived surface NBs. Both ethanol and water are either saturated or oversaturated with air or a specific gas, promoting nucleation [85]. In the case of bulk NBs, oversaturation occurs during the mixing of ethanol and water because gas is more soluble in each component individually than in the combined mixture. Specifically, at equilibrium, the total amount of dissolved gas in the individual volumes of ethanol and water exceeds the equilibrium amount of dissolved gas when the two are mixed. This results in supersaturation of dissolved gases, primarily nitrogen (N_2) and oxygen (O_2) from the atmosphere, which creates the conditions for nucleation and the formation of bulk NBs [43]. MD simulations were employed to investigate the dynamic characteristics of the solvent exchange process in the production of NBs. A quasi-two-dimensional simulation box, measuring $22.4 \times 2.24 \times H$ nm³, was constructed, where the height (H) of the box fluctuated under a given pressure. Periodic boundary conditions were applied in the x and y directions, while the z direction was constrained by two solid substrates consisting of frozen solid molecules arranged on an FCC lattice. The bottom substrate was fixed during the simulations. The simulations modeled solvent exchange between a good solvent (solvent I) and a poor solvent (solvent II). To replicate the process of solvent exchange in contact with a bulk solution of solvent II containing dissolved gas, a source region was incorporated into the simulation box to act as an infinite reservoir, controlling gas concentration far from the substrates. Solvent exchange

occurred through molecular diffusion. The simulations revealed that, in the initial stage of solvent exchange, an interface forms between the interchanging solvents with differing gas solubilities. This interface progressively moves toward the substrate as the exchange process advances. Gas molecules were observed to diffuse in a directed manner against the concentration gradient, driven by the solubility gradient across the moving solvent-solvent interface. This directed diffusion resulted in significant gas retention and the development of a localized gas oversaturation near the substrate, far exceeding that of the bulk solution. In the second stage of solvent exchange, the localized gas oversaturation near the substrate led to bubble nucleation, either on the solid surface or within the bulk solution. The specific nucleation site was determined by the substrate's hydrophobicity and the degree of local gas oversaturation [86].

2.3 Measurements of NBs

Differentiating between bulk NBs, nanodroplets, and nanoparticles presents significant challenges, particularly in identifying parameters such as hydraulic diameter, concentration, and size distribution of NBs. While the detection of colloidal systems is relatively straightforward, accurately determining the precise nature of these nanoscale entities is far more complex. This difficulty has often led to misinterpretations, where nanodroplets or nanoparticles have been mistakenly classified as NBs. Such mischaracterisations highlight the need for more precise analytical methods and a deeper understanding of the fundamental distinctions between these nanoscale structures. Furthermore, existing characterisation techniques face substantial limitations, making it difficult to directly measure properties like gas density within bulk NBs [42, 45].

Bubble concentrations commonly reported in medical and industrial applications typically range from 10^6 to $10^{10}/\text{cm}^3$. These concentrations are detectable using standard optical methods. Light scattering methods play a pivotal role in NB research and are widely used for detecting and characterizing colloidal particles. The advent of advanced and user-friendly dynamic light scattering (DLS) equipment has significantly contributed to the growth of the NB field. Later, nanoparticle tracking analysis (NTA) gained popularity for providing more detailed size distribution data. A simple yet practical light scattering technique involves using a laser pointer to illuminate a water sample and visually observe the scattered light, often employed to detect presumed NBs. However, light scattering alone cannot distinguish between gaseous bubbles, solid particles, or droplets. To address this limitation, optical methods based on phase contrast are utilized to determine whether the refractive index (RI) of the particle is higher (as with solid particles or liquid droplets) or lower (as with gaseous bubbles) than that of water [42, 45, 87].

In addition to DLS and NTA, electron microscopy (EM) offers exceptionally high resolution, making it a powerful tool for detecting and characterizing micro- and NBs. However, EM has several drawbacks, including high costs, extensive training requirements, and time-intensive procedures. Moreover, sample preparation and imaging processes can potentially alter or affect the results. Various sample preparation and imaging techniques are employed in EM, with cryogenic methods (Cryo-EM) and liquid transmission electron microscopy (TEM) being the most prominent. Cryo-EM addresses the challenge of maintaining sample integrity by rapidly freezing "wet" samples before imaging. This process effectively locks bubbles in place, allowing them to be visualized with scanning electron microscopy (SEM) or TEM. Beyond Cryo-EM, liquid TEM provides another valuable technique for studying native dispersions with high resolution. This method enables differentiation between bubbles, droplets, and solid particles. However, one significant limitation of liquid TEM is

that the electron beam can deliver excessive energy to small liquid volumes, often resulting in the formation of hydrogen bubbles through radiolysis. Despite these challenges, both Cryo-EM and liquid TEM remain essential tools for advancing the understanding of NBs [87, 88].

In holography and phase-contrast microscopy methods, transmitted light passing through a liquid sample carries phase information that is not provided by scattered light alone. When light encounters a solid particle, it slows down, causing a phase shift compared to the light that bypasses the particle. For gaseous bubbles, however, the phase shift occurs in the opposite direction. Analog phase-contrast microscopy is a well-established technique, often used to study biological specimens, and has also been applied to study NBs and microbubbles immobilized in gels. While it is a qualitative technique, phase-contrast microscopy is typically used for observing stationary samples. In contrast, digital holographic microscopy (DHM) methods offer a way to quantify the refractive index (RI) of individual particles, making them particularly useful for detecting bubbles. The use of digital holography to image NBs was first reported by Bunkin [89]. Additionally, DHM provides the ability to determine both the hydrodynamic and optical sizes of particles, droplets, or bubbles, using just a few image frames. This capability makes it possible to monitor real-time changes in the optical properties of these entities, offering valuable insights into their behaviour and dynamics [42].

Unlike other techniques used to study NBs, which often lack spatial resolution or focus solely on bubble content rather than shape in the case of surface NBs, Atomic Force Microscopy (AFM) emerges as a distinctive mechanical method capable of determining NB shape. AFM-based approaches have provided significant insights into the interactions between AFM tips and NBs, as well as the deformation behaviour of NBs during

experimental measurements. The interaction between the AFM tip and a NB leads to mutual deformation of the bubble surface and the AFM cantilever throughout contact. Analysis of force-distance curves during these interactions allows estimation of NB stiffness from the linear portions of the curves. The stiffness is comparable to the surface tension of water, confirming that NBs are exceptionally soft and likely filled with gas. This demonstrates AFM's unique ability to reveal detailed structural and mechanical properties of NBs [90].

Resonance mass measurement, an advanced acoustic technique, provides an innovative and precise method for distinguishing NBs from nanoparticles by leveraging their density differences. As a liquid containing particles passes through a resonator, the resonant frequency shifts based on the density of the particles relative to the liquid. Particles denser than the liquid, such as solid nanoparticles, cause the resonance frequency to decrease due to their negative buoyancy mass. In contrast, less dense particles, like NBs, increase the resonance frequency due to their positive buoyancy mass. This variation in frequency directly corresponds to the buoyancy mass of the particles, enabling accurate differentiation. By harnessing this capability, resonance mass measurement offers a powerful tool for identifying and characterising NBs, even in complex systems, with exceptional precision and reliability [45].

Innovative techniques like vibrational spectroscopy, including infrared and Raman spectroscopy, offer promising avenues for detecting NBs. The molecular vibrations of certain gases differ depending on whether they are in the gaseous state or dissolved in water, providing a basis for bubble detection in aqueous environments [91-93]. However, when multiple gases or molecules are present in both gaseous and liquid states, interpreting vibrational spectra can become complex and ambiguous. As a result, vibrational spectroscopy is best suited for systems with simple chemical compositions [42].

In summary, a range of complementary techniques is available for the detection and characterisation of NBs, each with distinct advantages and limitations. Light scattering techniques such as DLS and NTA are widely used for size analysis but cannot distinguish between bubbles, droplets, and solid particles. Optical methods such as DHM enable quantitative, real-time measurements, although complex data processing is required. Electron microscopy techniques, such as TEM and Cryo-EM, offer high-resolution direct imaging but are limited by potential artefacts introduced during sample preparation or irradiation. Atomic force microscopy provides unique mechanical and morphological insights, while resonance mass measurement enables highly sensitive differentiation based on density. Vibrational spectroscopy offers chemical specificity but is generally restricted to simpler systems.

2.4 Characteristics and stability of NBs

The unique features of NBs make them promising candidates for various applications. Their extraordinary properties have attracted significant research interest, establishing NBs as a fascinating topic in the field. Unlike regular bubbles, NBs are exceptionally small yet offer a much larger surface area for a given gas volume. This increased surface area is crucial in industrial applications reliant on surface interactions. For example, NBs provide substantially greater contact areas in water, enhancing aerobic bacterial activity with oxygen or anaerobic processes with nitrogen. This property also benefits practical applications, such as improving carbon dioxide uptake by algae or oxygen availability to plant roots and aerobic bacteria in soil remediation. The enhanced surface area of NBs boosts gas mass transfer and reaction efficiency, making them highly effective for industrial and environmental processes [94].

NBs can generate reactive radicals in the host medium, making them highly valuable for sonochemistry applications. As cavitation nuclei activators, NBs facilitate cavitation, which can be classified into two types: homogeneous cavitation, occurring in a metastable pure liquid, and heterogeneous cavitation, triggered by impurities such as solid particles or gas-filled pockets that serve as nucleation sites. The tensile strength of pure water is theoretically very high, and the cavitation threshold, the minimum acoustic amplitude required for cavitation, is inversely related to the gas concentration in the liquid. As gas concentration increases, the cavitation threshold decreases. NBs significantly enhance acoustic cavitation by lowering this threshold, thereby amplifying the chemical effects of cavitation. During cavitation, successive sound cycles cause bubbles to grow to a critical size and collapse, releasing a tremendous amount of energy. This collapse leads to the thermal dissociation of surrounding water molecules, producing reactive radicals such as H and OH. The presence of these radicals has been detected in nanobubbled samples, underscoring their potential in chemical reactions [95].

The most distinctive feature of bulk NBs is their extraordinary longevity. Unlike microbubbles, which typically last only a few seconds, NBs have been shown to persist for weeks or even months. According to Stoke's Law, the rising speed of a bubble is directly proportional to its size and inversely proportional to the viscosity of the surrounding medium [96].

$$V_r = \frac{d^2 g (\rho_l - \rho_g)}{18 \mu_l} \quad (2.4)$$

Where d represents the bubble diameter, g is the acceleration due to gravity, μ_l denotes the viscosity of the surrounding medium, and ρ_l and ρ_g are the densities of the host liquid and the gas bubble, respectively. Compared to conventional bubbles, MBs and NBs have

significantly smaller diameters, allowing them to remain suspended in the host medium for extended periods. This prolonged stagnation enhances their survival in the surrounding liquid, leading to a higher collision rate and increased opportunities for interaction with other ultrafine particles in the base fluid.

As gas solubility increases with pressure, the higher Laplace pressure, $\Delta P = \frac{2\gamma}{R}$, leads to smaller bubbles, while simultaneously increasing the concentration of dissolved gas in the surrounding medium. The concept of Laplace Pressure Bubble Catastrophe (LPBC) can be explained by applying a small perturbation to a bubble in equilibrium with an infinitely large reservoir of host liquid. Two possible outcomes arise: if the bubble slightly enlarges, the Laplace pressure decreases, reducing the solubility of gas in the surrounding liquid. This causes more gas to diffuse into the bubble, resulting in continuous growth and preventing the bubble from returning to equilibrium with the reservoir. Conversely, if the bubble shrinks slightly, the gas solubility in the host liquid increases, leading to further shrinkage in a cycle that continues until the bubble disappears, unable to regain equilibrium. This phenomenon, known as LPBC, demonstrates the inherent thermodynamic instability of bubbles, especially smaller ones, which either grow uncontrollably and rise to the surface due to buoyant forces or shrink and vanish [26]. For NBs to maintain thermodynamic stability, both chemical and mechanical stability are essential. Mechanical equilibrium involves balancing the forces acting on the NBs with their internal pressure, while chemical equilibrium is governed by Henry's law (Eqs. 2.1 and 2.2). Several theories have been proposed to explain NB stability, emphasising the importance of both mechanical and diffusive stability in preserving the integrity of these tiny bubbles.

The skin model has been proposed as a representation of cavitation nuclei for more than five decades [97, 98]. In this model, the surface of a gas bubble is entirely covered by an organic

layer or surfactant. This organic coating acts as a mechanical barrier, preventing the diffusion of gas from the bubble. Initially, the gas bubble's surface is only partially covered by the organic layer. As gas dissolves from the bubble into the surrounding liquid, the bubble shrinks in size. Eventually, this shrinking stops when the bubble becomes fully encased in the organic layer. However, achieving complete coverage of the bubble surface is challenging, particularly if the organic material is in a solid form [95, 99].

As another model proposed five decades ago, the particle crevice model suggests that a gas 'bubble' is trapped within a crevice on the surface of a solid particle or impurity. In this model, the gas interface within the crevice adopts a concave shape, leading to reduced internal gas pressure due to surface tension. This stabilisation prevents the gas "bubble" from dissolving. However, the model assumes that the primary structure of the "particle" is a solid rather than a gas "bubble," which seems to contradict experimental resonance mass measurements of stable bulk NBs. The previous findings suggest that the bubble mass is primarily gaseous, challenging the assumptions of the particle crevice model [95, 100].

High zeta potential (ZP) on the surface of NBs is one of their distinctive characteristics, distinguishing them from larger bubbles. It has been reported that ZP plays a crucial role in tiny bubble systems, significantly influencing the interfacial properties that govern their interaction mechanisms. The surface charge of nanoparticles in a colloidal solution is analysed using a technique known as ZP measurement. A charged surface on suspended materials attracts oppositely charged ions, forming a thin layer called the Stern layer, where the ions are tightly bound to the particle's surface. Beyond the Stern layer, free ions are loosely distributed around the suspended particle due to Coulomb forces, creating an outer region referred to as the diffuse layer. Together, the Stern layer and diffuse layer form the electrical double layer (EDL) around the particle or NB. Within the diffuse layer, an

imaginary boundary called the "slipping plane" is defined. Ions within this boundary move along with the bubble, while ions outside the boundary remain stationary. The electrical potential at this slipping plane is referred to as the ZP. Zeta potential is determined by measuring the velocity of charged particles under an applied electric field, using the Smoluchowski equation [101, 102]:

$$\zeta = \frac{4\pi\mu}{\varepsilon} U \quad (2.5)$$

in which ζ is ZP (V), μ is the viscosity of base fluid (Pa.s), ε is the permittivity of the medium (F.m⁻¹), and U is the electrophoretic mobility ((m/s).(V/m)⁻¹). The electrophoretic mobility, U , is calculated using:

$$U = \frac{v}{V/L} \quad (2.6)$$

where v is the speed of particle (m.s⁻¹), V is the voltage (V), and L is the distance of the electrodes (m).

The high zeta potential of NBs ensures electrostatic repulsion between neighboring particles, preventing the coalescence of adjacent bubbles. According to the electrostatic repulsion model, the negative charge on the bubble's surface generates an electrostatic repulsion that can counterbalance the Laplace pressure caused by surface tension. This balance may inhibit gas diffusion from the bubble, contributing to the stability of bulk NBs. In this model, the pressure inside the bubble (p_g) is expressed by the following equation [95]:

$$p_g = p_o + \frac{2\gamma}{R} - \frac{\epsilon \zeta^2}{R^2} \quad (2.7)$$

where p_o represents the liquid pressure outside the bubble (equal to 1 atm), γ denotes the surface tension, R is the bubble radius, ϵ is the dielectric constant, and ζ is the zeta potential of the bubble (equal to -40 mV). The final term in Eq. 2.7 represents the repulsive pressure resulting from the electrostatic forces on the charged surface of a bubble. However, numerical calculations have shown that the magnitude of this electrostatic repulsive pressure is more than an order of magnitude smaller than the second term, which corresponds to the Laplace pressure. As a result, the electrostatic repulsive pressure is insufficient to counterbalance the Laplace pressure [95]. Furthermore, it has been observed that when the bubble radius is smaller than $10 \mu\text{m}$, the zeta potential at the bubble interface experiences a significant change. As the bubble radius decreases below $1 \mu\text{m}$, the ion concentration at the interface gradually increases with bubble contraction, resulting in a rise in zeta potential. Once the bubble radius reaches 100 nm , the zeta potential stabilizes, suggesting that this model cannot fully account for the stability of individual NBs [45].

Molecular-level approaches are also employed to investigate the stability of NBs. H. Weijis et al. [65] proposed diffusive shielding as a potential mechanism for stabilising bulk NB clusters. To examine this idea, they conducted a numerical study using quasi-2D molecular dynamics simulations of a Lennard-Jones binary liquid. Two initial configurations were prepared for the study: one featuring a pre-existing bulk NB and another with gas molecules dispersed throughout the medium. Their findings revealed that nucleation occurred at high concentrations of dispersed gas. Additionally, they concluded that NBs need to remain in close proximity to each other to maintain a saturated environment, thereby preventing complete dissolution. The effect of the maximum distance between bubbles (L) and bubble

radius (R) on the stability of bulk NBs was investigated by Hong et al. [103] using numerical simulations conducted with the GROMACS program. A simulation box was prepared by dispersing a large number of water molecules, and a bulk NB was formed by removing a group of water molecules from the simulation box. The interactions between water molecules were simulated using the CHARMM27 force field with a cutoff radius of 1.2 nm. It was found that stability can be achieved when the maximum distance (L^*) between bubbles is proportional to $R^{4/3}$, where R is the bubble radius. The stability of vapor NBs in bulk liquid was studied theoretically, and the critical bubble size was determined using macroscale thermodynamic equations [104]. Below this critical size, the system destabilises, causing a sharp drop in pressure. This size was verified through MD simulations using the Lennard-Jones model of argon, which showed that stronger molecular attraction plays a significant role in the pressure drop. As the Laplace pressure on the curved bubble interface fails to counterbalance the pressure difference across the interface, the bubbles become unstable. Therefore, vapor bubbles larger than the critical diameter remain stable, as long as the pressure difference across the phase interface is large enough to balance the Laplace pressure. The stability of nitrogen NBs under different concentrations of nitrogen molecules was investigated using MD simulations [105]. Stable N_2 NBs were not detected when the N_2 concentration was below a critical threshold. Under these conditions, all N_2 molecules diffused freely in water, representing a dispersed state. However, when the nitrogen concentration exceeded the critical value, the NBs rapidly grew in size, signifying a transition to an assembled state. This shift from dispersed to assembled states occurred due to a slight increase in concentration, achieved by introducing just ten additional nitrogen molecules into the system. These findings highlight the high sensitivity of N_2 NB stability to changes in nitrogen concentration. It was further observed that the density of N_2 within NBs was significantly higher than that of dispersed N_2 . Gao et al. [106] employed all-atom

(AA) and coarse-grained (CG) MD simulations to investigate the stabilisation of predefined oxygen and nitrogen NBs in water as the host liquid. It was observed that the gas inside the NBs exhibits ultrahigh pressure (in the MPa range), and the internal density, in the range of hundreds of kilograms per cubic meter, was found to be a key factor enhancing NB stability. Additionally, it was noted that the internal density of the NBs varies with bubble size, with smaller NBs exhibiting higher internal densities. At the NB interface, the hydrogen bonds formed between water molecules were weakened, leading to a reduction in surface tension. Furthermore, the gas molecules within the NBs were found to exhibit behaviour similar to confined diffusion, which contributes to the stabilisation of the NBs.

Overall, NBs exhibit unique properties such as a large surface-area-to-volume ratio, which enhances gas–liquid interfacial interactions and significantly improves gas mass transfer. NBs also play an important role in sonochemistry by acting as cavitation nuclei, lowering the cavitation threshold, and intensifying acoustic cavitation, which generates reactive radicals such as H and OH through water molecule dissociation. A key distinguishing feature of bulk NBs is their extraordinary longevity compared to microbubbles, which is influenced by factors such as reduced buoyant rise velocity. The stability of NBs has been attributed to a combination of mechanical and chemical equilibrium, with proposed explanations including the skin model involving surfactant layers, the particle crevice model, and electrostatic repulsion due to high zeta potential, although these models alone are insufficient to fully explain the observed stability. Molecular-level simulations suggest additional mechanisms such as diffusive shielding and critical size- or concentration-dependent stability, while internal NB characteristics such as high gas density, elevated internal pressure, and weakened interfacial hydrogen bonding further contribute to their persistence in liquid media.

2.5 Applications of NBs

Interest and activity in the field of NBs are growing rapidly, despite the limited research on bulk NBs. This momentum is reflected in efforts to establish an ISO standard for fine bubbles (ISO/TC281), the expanding membership of the Fine Bubble Industry Association (FBIA), and the increasing number of patents in the field. These developments underscore the rising recognition of NBs' unique properties and their potential across diverse applications [26].

One of the most notable properties of NBs is their extremely low-rise velocity and remarkable longevity, which contribute to their effectiveness in various fields. These characteristics allow NBs to remain suspended in water for extended periods, enhancing gas dissolution and transfer efficiency [26]. An interesting application of this property is in agriculture, particularly in enhancing plant growth. Michailidi et al. [107] investigated the effects of NBs on tomato plants by using four plastic cells filled with a standard volume of soil, each containing a tomato seed. The plants were watered daily with equal amounts of water, but different types of water were tested: pure water, oxygen-enriched water, air-enriched water, and nitrogen-enriched water. The study found that nitrogen NBs had the most significant positive impact on plant growth, followed by air NBs, while oxygen-enriched water had the least effect. These results demonstrate the potential of NB technology, leveraging their low-rise velocity and enhanced gas transfer capabilities, to improve agricultural productivity.

Beyond agriculture, NBs have also shown immense potential in medicine, particularly in diagnostics and drug delivery. A prominent application in this domain is the use of NBs as contrast agents in ultrasound imaging, a widely adopted diagnostic tool. Within the

ultrasound field, NBs undergo alternating compression and expansion, generating distinct and strong echo signals that are significantly more pronounced than those from surrounding tissues. This property makes NBs highly effective as contrast agents, with their smaller size and greater stability enabling them to penetrate blood vessel walls and reach specific regions for precise imaging. In addition to their diagnostic role, NBs have proven valuable in therapeutic applications, particularly for drug delivery. Their high mass transfer efficiency allows them to act as carriers for targeted drug delivery. Under the influence of magnetic fields or ultrasound energy, NBs exhibit magnetic responsiveness and explosive behaviour. These effects facilitate self-destruction and increase cell membrane permeability, both of which are critical for effective drug delivery [108]. A notable example of nanobubble-based drug delivery was demonstrated by Sanlier et al. [109], who developed an innovative dual-drug system for targeted therapy against non-small cell lung cancer. This system combines magnetic-targeting and ultrasound-responsive properties. Drug release from the NBs was triggered by applying a magnetic field and ultrasound energy, resulting in effective therapeutic outcomes. These advancements highlight the immense potential of NB in revolutionizing medical diagnostics and treatments.

Another significant application of NBs lies in flotation processes, which are extensively utilized in industries such as wastewater treatment, mining, and oil recovery [96]. The efficiency of flotation has been shown to improve significantly with the miniaturisation of bubbles. Studies have demonstrated that NBs enhance the flotation performance of fine coal particles and various minerals. Bulk NBs increase the collision probability with particles due to their reduced inertia, allowing Brownian motion to dominate their movement when their size is below approximately 1000 nm. This increased collision probability is proposed to facilitate the attachment of NBs to particles, transitioning them into surface NBs upon

contact [110]. The influence of bulk NBs on mineral flotation is further attributed to the positive roles played by surface NBs. Two primary mechanisms have been identified [110]:

1. Induced Agglomeration of Mineral Particles: Experimental studies and theoretical calculations have confirmed that surface NBs enhance the attractive forces between hydrophobic particles, promoting their agglomeration.
2. Improved Wetting Film Rupture: The wetting films between a particle covered with surface NBs and a conventional bubble rupture at a greater thickness compared to systems without surface NBs. This facilitates the attachment of particles to bubbles more effectively.

The role of surface NBs in improving particle attachment has also been supported by the work of Zhou et al. [111].

NBs also show strong potential in enhanced oil recovery (EOR). Although not yet widely adopted in industrial practice, their unique physicochemical properties suggest significant benefits across recovery stages. Studies indicate that gas-lift efficiency can be improved when sufficient microbubbles or nanobubbles are present in downhole environments [107]. In particular, CO₂ NBs have demonstrated the ability to suppress channeling and gravity override, enhance oil displacement, modify reservoir wettability, and increase interfacial activity. By reducing interfacial tension and improving sweep efficiency, CO₂ NBs offer a promising strategy for improving oil recovery performance [112].

NBs can also play a pivotal role in energy and power applications due to their ability to modify thermophysical and thermochemical properties, thereby enhancing process efficiency, sustainability, and progress toward net-zero emission targets. When dispersed in liquids, NBs act as functional nano-additives, altering key thermophysical parameters, such

as viscosity, which are critical for renewable and thermal energy systems [11]. In bioenergy processes, their presence has been shown to enhance biofuel production from renewable biomass by accelerating bacterial activity and metabolic processes [38]. Furthermore, the incorporation of NBs into conventional fuels, including diesel, biodiesel, gasoline, and alcohol, has been explored as a practical approach to improving combustion characteristics, reducing emissions, and increasing fuel conversion efficiency [20, 21, 39].

In addition to improving energy efficiency and fuel performance, NBs have shown promise in supporting global carbon reduction efforts. Carbon capture and storage (CCS) technologies are critical for achieving carbon peaking and long-term decarbonisation goals. Among all CCS technologies, CO₂ hydrate stands out as a novel approach that not only enables effective carbon capture but also offers valuable applications such as gas storage, transportation, and use as a secondary refrigerant, owing to its high dissociation enthalpy and environmentally friendly properties [22]. Clathrate hydrates are ice-like crystalline solid inclusion compounds formed when water molecules act as hosts, encapsulating guest gas species within a hydrogen-bonded lattice under specific pressure–temperature conditions. These structures consist of various cage topologies required to occupy three-dimensional space, with three primary hydrate families classified according to the size of the largest guest molecules. The stability of clathrate hydrates is primarily governed by short-range attractive interactions between the guest molecules, often paradoxically hydrophobic, and the surrounding water cages. Additionally, hydrogen bonding and other intermolecular interactions contribute to the structural and dynamic properties of the hydrates. In the context of CO₂ hydrates, the formation kinetics involve nucleation followed by crystal growth. However, the inherently slow rates of hydrate nucleation and growth present significant challenges. While physical methods such as pressurization, cooling, and agitation have been employed to enhance formation, these approaches are typically energy-intensive, limited in

scalability, and economically impractical [23, 24]. Recent studies have shown that NBs can act as efficient promoters for CO₂ hydrate nucleation, providing a cost-effective strategy to accelerate formation and improve overall CCS performance [113].

Beyond their role in fluids and fuels, the interaction between NBs and advanced nanomaterials, particularly graphene, has opened new opportunities across various applications. Graphene (G), a two-dimensional carbon material with exceptional mechanical strength, high thermal conductivity, large surface area, and excellent chemical stability, has emerged as a versatile material for sensing and electrochemical applications, owing to its unique electronic structure and intrinsic properties [114-122]. In industrial electrochemical processes, gaseous byproducts such as hydrogen, oxygen, and carbon dioxide are commonly generated, particularly during water splitting and fuel cell operation [10]. Consequently, the interactions between G and dissolved gases, especially in the form of NBs, are of considerable importance, as NBs can induce morphological changes in G and influence the thermophysical properties of engineered fluids [123]. Graphene nanobubbles (GNBs), capable of trapping gas volumes, offer promising applications in nanoscale engineering, though conventional fabrication methods often require specialized equipment or extreme conditions [123, 124]. An et al. [123] produced GNBs via water splitting under a high potential, generating hydrogen and oxygen NBs within graphene layers, which were detected using tapping-mode atomic force microscopy. Remarkably, the hydrogen stored in the GNBs exceeded the theoretical binding capacity, demonstrating promising potential for meeting hydrogen storage targets established by the U.S. Department of Energy.

2.6 Summary

Existing research has primarily concentrated on the fundamental properties of NBs while largely overlooking their engineering applications. Even in fundamental studies, which often

rely on molecular approaches to examine NB behaviour and characteristics, several challenges persist. These include the significant computational demands posed by large simulation boxes in MD studies and the complexities associated with managing the extensive datasets generated. To address these difficulties, researchers frequently adopt simplifying assumptions, such as fixing the center of pre-defined NBs, to enable more detailed investigations of NB behaviour [106]. However, such assumptions can compromise the accuracy of these studies, limiting their ability to capture the true dynamics and motion of NBs in real-world scenarios. Machine learning (ML) has become a transformative tool for handling the extensive datasets generated by atomistic and molecular simulations across various scientific disciplines, such as materials science, solid-state physics, biophysics, and biochemistry. Despite its broad applicability, ML remains underutilized in NB studies which can be integrated with MD simulations as part of hybrid approaches, providing valuable insights into NB behaviour and dynamics and addressing many of the challenges faced in NB research.

Moreover, research has predominantly examined the interactions of NBs with fixed solid particles [125] or pure liquid environments without nanoparticles [50]. However, in real-world industrial scenarios, dispersed solid particles freely interact with their surroundings, particularly with host liquids. These interactions trigger nanoscale mechanisms that influence the thermophysical properties of the medium, which are critical for practical applications.

Furthermore, despite these advancements, most studies have concentrated on water as the host liquid, overlooking organic liquids such as dodecane and isooctane, which are promising candidates for renewable energy applications. In addition, the potential effects of NBs on reaction processes and CO₂ hydrate formation and growth remain largely unexplored,

leaving a significant gap in understanding their role in complex chemical and industrial systems.

In this thesis, four host liquids, water, methanol, dodecane, and isooctane, were selected and categorized into two groups: polar and alcoholic host liquids, comprising water and methanol, and organic host liquids, including dodecane and isooctane.

For polar and alcoholic host liquids, a hybrid methodology was employed, combining MD simulations with unsupervised machine learning techniques to assess the potential for NB formation resulting from the dissolution of gases such as nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and hydrogen (H_2). These gases are widely used in chemical processes and industrial applications, including water splitting [126] and enhanced oil recovery [127]. This research not only investigates the intrinsic characteristics of the formed NBs but also examines their influence on the thermophysical properties of host liquids, which are critical for fluid applications. In parallel, graphene (G)-based nanofluids (NFs) were investigated due to their significantly higher thermal conductivity compared to metal oxide NFs, even at lower concentrations [128]. For instance, G-reinforced methanol-based NFs exhibit properties that are particularly advantageous for energy applications, such as their potential use as working fluids in solar energy systems. The possibility of NB formation through the dissolution of these gases in two potential graphene-based NFs, namely water and methanol-based fluids, is also examined. Furthermore, the behaviour and thermophysical properties of these G-NFs were investigated using MD simulations to integrate both fundamental aspects and engineering applications of such complex fluids, with the aim of gaining a deeper understanding of the role of NBs in complex fluids in the presence of solid–liquid–gas interactions. Moreover, given the critical role of molecular interactions between novel additives and the hydrate phase, as well as the potential of nanobubble-enriched water to

enhance CO₂ hydrate nucleation and growth, this study also explores the influence of four types of NBs, i.e. hydrogen, nitrogen, oxygen, and carbon dioxide, on CO₂ hydrate formation and growth using a molecular-level approach, which have not been fully explored in literature. The investigation focuses on the effects of NB type, the combined impact of temperature and NBs, and the interactive influence of pressure and NBs on the kinetics of hydrate formation and growth.

For organic host liquids, the nucleation, coalescence, and behaviour of NBs formed from the scattered CO₂, O₂, N₂, and H₂ gases in dodecane and isooctane samples, along with their effects on the thermophysical properties of the samples, were investigated using classical molecular dynamics simulations. Additionally, the effects of different NB types on the phase transition and thermal behaviour of nanobubbled dodecane as a phase change material, as well as their influence on thermophysical properties and atomic structure, were also investigated. Furthermore, the effects of stable NBs on the combustion process of dodecane were examined, focusing on blended fuels incorporating stable NBs. For the first time, ReaxFF molecular approach was used to investigate the impact of three types of stable NBs, hydrogen, nitrogen, and oxygen, on the combustion characteristics of dodecane and reaction pathways, assessing the effects of NB type, temperature, and sample density on combustion characteristics.

Chapter 3 Research Methodology

3.1 Introduction

Exploring NBs through experimental techniques [41-43] presents formidable challenges, as some methods struggle to distinguish NBs from other nanoscale contaminants, and the fundamental processes governing NB behaviour and inherent properties remain elusive [44, 45]. One of the most intriguing and extraordinary aspects of these tiny bubbles is their exceptional stability, defying the predictions of the Epstein-Plesset theory, enabling them to persist in host liquids for extended periods and significantly influencing practical applications [33, 34]. Their divergence from conventional continuum theories adds further complexity to the investigation of NBs. This complexity is accentuated when dealing with bulk NBs, which, unlike surface-bound NBs, are influenced by Brownian motion [27, 46, 47]. In tandem with experimental techniques, computational nanoscience and molecular approaches such as MD simulations offer a means to attain a molecular-level understanding of the characteristics, behaviours, and impact of these nanoscopic bubbles.

Computational nanoscience serves as an indispensable research tool, facilitating the modeling, comprehension, and prediction of nanoscale phenomena. It employs various methods, including classical and reactive molecular dynamics, density functional approaches, and fully correlated wave functions, to solve physical problems at different levels of sophistication. In quantum mechanics (QM), the Schrödinger equation is solved to elucidate molecular interactions, potential energy surfaces, and charge distributions. Among QM-based techniques, *ab initio* molecular dynamics (AIMD) stands out, rooted in density functional theory (DFT). AIMD combines classical nuclear dynamics with quantum electron dynamics, providing a powerful approach for simulating complex systems, albeit with smaller accessible correlation lengths and relaxation times compared to classical molecular dynamics. While AIMD offers a deeper understanding of quantum behaviours, it demands

substantial computational resources, limiting its performance, especially in simulating multicomponent liquids [129-132]. In contrast, molecular dynamics, treating atoms and bonds as a balls-and-springs and using Newtown's second law and different potentials to calculate the atomic interactions and predict the motions of atoms enables researchers to study the complex system from molecular approaches. In the first place, molecular topology and interaction potential are defined. Then initial positions, velocities, and simulation conditions are defined. By using the selected potentials and the equation of motion, tangible parameters like per-atom energies (potential and kinetic) are calculated to use directly or in other methods like Green-Kubo to clarify the atomic mechanism behind the bulk behavior of materials and their thermophysical properties [133, 134].

3.2 Molecular dynamics simulation

Molecular Dynamics simulations are based on the fundamental principles of classical mechanics, specifically Newton's equations of motion, which govern the trajectories of atoms and molecules in a system. The core principle of MD is to calculate the positions and velocities of particles at each time step, given their initial conditions and the forces acting on them. If the mass of molecule i is denoted by m_i , and the total force acting on it, resulting from interactions with surrounding molecules and any external fields, is represented by f_i , then the motion of the particle is governed by Newton's second law of motion [135]:

$$m_i \frac{d^2 r_i}{dt^2} = f_i \quad (3.1)$$

In a system consisting of N molecules, there are N coupled equations of motion, each describing the movement of an individual molecule. These molecules interact with each other through forces, making the system highly complex. However, differential equations

like the one in Eq. 3.1 are not well-suited for direct numerical solutions on a computer. Computers are much more efficient at solving algebraic equations than differential ones. Therefore, to enable computational analysis, Eq. 3.1 must be transformed into an algebraic form. This is achieved by approximating the second-order differential term in Eq. 3.1 using a Taylor series expansion, which converts the differential equation into an algebraic equation as follow [135]:

$$x(t + h) = x(t) + h \frac{dx(t)}{dt} + \frac{1}{2!} h^2 \frac{d^2x(t)}{dt^2} + \dots \quad (3.2)$$

Equation 3.2 indicates that the position x at time $t + h$ can be represented as a series expansion, including position x at time t , the first-order differential, the second-order differential, and higher-order terms, each multiplied by an appropriate constant. If x changes only marginally over the time interval, the higher-order differential terms can be neglected for sufficiently small of the time interval h . To approximate the second-order differential term in Eq. 3.1 algebraically, another form of the Taylor series expansion is applied [135]:

$$x(t - h) = x(t) - h \frac{dx(t)}{dt} + \frac{1}{2!} h^2 \frac{d^2x(t)}{dt^2} - \dots \quad (3.3)$$

By eliminating the first-order differential term from Eqs. 3.2 and 3.3, the second-order differential term can be expressed as [135]:

$$\frac{d^2x(t)}{dt^2} = \frac{x(t + h) - 2x(t) + x(t - h)}{h^2} + O(h^2) \quad (3.4)$$

The final term on the right-hand side of this equation represents the error in the approximation. In this case, terms of order higher than h^2 are neglected [135].

$$\frac{d^2x(t)}{dt^2} = \frac{x(t + h) - 2x(t) + x(t - h)}{h^2} \quad (3.5)$$

This expression is known as the "central difference approximation." Using this approximation, and with the notation $r_i = (x_i, y_i, z_i)$ for the position of molecule i and $f_i = (f_{xi}, f_{yi}, f_{zi})$ for the force acting on particle i , the equation for the x -component of Newton's equation of motion can be written as [135]:

$$x_i(t + h) = 2x_i(t) - x_i(t - h) + \frac{h^2}{m_i} f_{xi}(t) \quad (3.6)$$

Similar equations hold for the other components of the system. Since Eq. 3.6 is an algebraic equation, the molecular position at the next time step can be determined using the current and previous positions, along with the present force. In a system consisting of N molecules, this results in a set of $3N$ algebraic equations that describe the motion of the molecules. These equations are solved computationally, allowing the molecular motion to be tracked over time. Notably, Eq. 3.6 does not require velocity terms to compute the molecular position at the next time step. This approach is known as the "Verlet" method. If the velocity is needed, it can be calculated using the central difference approximation, as follows [135]:

$$v_i(t) = \frac{r_i(t + h) - r_i(t - h)}{2h} \quad (3.7)$$

This approximation is derived by eliminating the second-order differential terms from Eqs. 3.2 and 3.3. Although velocities are unnecessary for evaluating the position at the next time step, a scheme that simultaneously employs both positions and velocities may be preferable for maintaining a constant system temperature. By considering the first- and second-order differentials of the position, which correspond to velocity and acceleration, neglecting the differential terms of third order and higher in Eq. 3.2 results in the following equation [135]:

$$r_i(t + h) = r_i(t) + hV_i(t) + \frac{h^2}{2! m_i} f_i(t) \quad (3.8)$$

This equation determines the position of the molecules, but since the velocity term appears on the right-hand side, an additional equation is required to define the velocity. The first-order differential of velocity corresponds to the acceleration, given by [135]:

$$v_i(t + h) = v_i(t) + \frac{h}{m_i} f_i(t) \quad (3.9)$$

To improve accuracy, the force term in Eq. 3.9 is slightly adjusted, leading to the following equation [135]:

$$v_i(t + h) = v_i(t) + \frac{h}{2m_i} (f_i(t) + f_i(t + h)) \quad (3.10)$$

The approach that employs Eqs. 3.8 and 3.10 to determine the motion of molecules is referred to as the "velocity Verlet" method. The velocity Verlet method offers significant advantages in simulation stability and accuracy [135].

Consider an alternative approach, where the first-order differential of position represents velocity and the first-order differential of velocity represents acceleration, and applying the central difference approximation to these differentials results in the following equations [135]:

$$r_i(t + h) = r_i(t) + hv_i(t + \frac{h}{2}) \quad (3.11)$$

$$v_i(t + h/2) = v_i(t - h/2) + \frac{h}{m_i} f_i(t) \quad (3.12)$$

The method of calculating the positions and velocities of molecules using Eqs. 3.11 and 3.12 is known as the "leapfrog" method. This name comes from the sequential process of first evaluating the positions and forces, and then the velocities, in an alternating or "leapfrog" manner with respect to the time steps [135].

The selection of an appropriate intermolecular interaction model is a fundamental aspect of any MD simulation, as it governs the interactions between particles within the system. Once a suitable energy model has been established, the simulation proceeds through several essential stages. Initially, the system configuration is specified by defining the positions and velocities of the particles. This is followed by an equilibration phase, during which the system evolves from its initial state while thermodynamic and structural properties are monitored until equilibrium is attained. For heterogeneous systems, the equilibration process may require multiple stages to achieve a stable state. Following equilibration, the production phase is initiated, in which the main computational tasks, including force calculations and integration of the equations of motion, are performed. During this stage, system properties are evaluated, and atomic configurations are recorded at regular intervals for subsequent analysis. Finally, upon completion of the simulation, the generated data are analysed to extract additional properties and to investigate the structural evolution of the system over time [135].

3.3 Force fields and potentials

In MD simulations, interatomic and intermolecular potential energies are defined and parameterised using force fields. These are mathematical models that relate potential energy to the spatial coordinates of atoms. The parameters within force fields are typically derived by fitting to experimental data or results from QM calculations. Force fields can be broadly categorised into two types: classical and reactive. Classical force fields are designed for all-atom systems, where individual atoms serve as the basic units, and atom connections are fixed. These models do not account for chemical reactions, making them distinct from coarse-grained force fields, which simplify systems by using "pseudo-atoms" to represent

groups of atoms. Examples of classical force fields include those commonly used for simulating stable molecular systems without bond-breaking or formation. In contrast, reactive force fields, such as ReaxFF, are formulated to accommodate chemical reactions. These models incorporate bond-order terms, enabling them to dynamically adjust to bond-breaking and formation during a simulation. By bridging the gap between QM methods and classical MD, reactive force fields offer a balanced trade-off between computational efficiency and simulation accuracy, making them particularly useful for studying systems where chemical reactivity plays a critical role [136].

Classical force fields are constructed based on defined atom types, with each atom characterised by specific properties. Over time, numerous force fields have been developed, each varying in complexity and tailored to specific types of molecular systems. Fundamentally, a classical force field is composed of two main components: intramolecular potentials, which describe interactions within a molecule, and intermolecular potentials, which govern interactions between different molecules [136].

$$E = E_{\text{intramolecular}} + E_{\text{intermolecular}} \quad (3.13)$$

$$E_{\text{intramolecular}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} \quad (3.14)$$

The terms, listed from right to left, represent bond, angle, and torsion potentials. The bond potential is typically used for covalent species, with bond stretching often modeled by a simple harmonic function. This approach assumes the bond remains intact and is only suitable for describing bond stretching near its equilibrium state [137]. However, the Morse potential provides a more accurate representation of a molecule's vibrational structure.

Unlike the harmonic oscillator approximation, it explicitly accounts for bond-breaking processes and incorporates the anharmonic nature of bonds, offering improved predictive capabilities [138].

$$E_{bond-Harmonic}(r) = K(r - r_0)^2 \quad (3.15)$$

$$E_{bond-Morse}(r) = D_e(1 - e^{-\alpha(r-r_e)})^2 \quad (3.16)$$

where K is the spring constant, r_0 and r_e are the equilibrium bond distances, D_e is the well depth, and α represents the width of the potential.

The angle potential is a three-body interaction that describes the angular vibrations between three adjacent atoms connected by covalent bonds. Some of the most frequently used angle potentials include the harmonic, CHARMM [139], and cosine [140] models. It is worth noting that both bond stretching and angle bending are typically considered high-frequency motions in molecular dynamics simulations. The harmonic potential is ideal for systems where bonded atoms oscillate around equilibrium positions, while the CHARMM potential is suited for large hydrocarbons and biomolecular systems, particularly with restrictions on the movement of the second and third atoms. The cosine potential, on the other hand, is periodic and smooth, making it versatile for a wide range of conditions [136].

$$E_{angle-Harmonic}(\theta) = K(\theta - \theta_0)^2 \quad (3.17)$$

$$E_{angle-CHARMM}(\theta) = K(\theta - \theta_0)^2 + K_{UB}(r - r_{UB})^2 \quad (3.18)$$

$$E_{angle-Cosine}(\theta) = \frac{1}{2}K[\cos(\theta) - \cos(\theta_0)]^2 \quad (3.19)$$

Where K is the bending constant, θ_0 is the equilibrium bond angle, K_{UB} and r_{UB} are the constants for the Urey–Bradley term and the equilibrium bond length, respectively.

The dihedral angle potential and the improper torsion potential are two key types of torsional energy in classical force fields. The dihedral angle potential describes the angular interaction between the planes formed by the first three and last three atoms in a consecutively bonded set of four atoms. This 4-body interaction governs the rotation around a bond, playing a critical role in determining the structure and stability of a molecule, as torsional motions are generally more flexible. Proper modeling of dihedral angles is vital for capturing molecular rigidity and accurately simulating the conformational changes due to bond rotations. The parameters for dihedral potentials are usually derived from *ab initio* calculations and further refined using experimental data, such as molecular geometries and vibrational spectra. On the other hand, the improper torsion potential models out-of-plane motions involving three atoms surrounding a central fourth atom. This potential is crucial for maintaining chirality in tetrahedral structures or ensuring the planarity of specific atoms. Common types of dihedral potentials include the OPLS potential, which provides high precision for dihedral potential barriers and is widely used for studying polymer properties within the OPLS model. Improper torsion potentials, such as harmonic potentials, are utilized to preserve the planarity of molecular structures. Additionally, Fourier potentials, frequently applied in the OPLS-AA force field, are particularly effective for modeling the behavior of alkanes [136].

$$E_{dihedral-OPLS}(\varphi) = K_1[1 + \cos(\varphi)] + \frac{1}{2}K_2[1 - \cos(2\varphi)] + \frac{1}{2}K_3[1 + \cos(3\varphi)] + \frac{1}{2}K_4[1 - \cos(4\varphi)] \quad (3.20)$$

where K_1 , K_2 , K_3 , and K_4 are the bending constants.

In this study, harmonic potential was used to represent the bonds and angles within water molecules and gas atoms. The equilibrium lengths for the bonds between water, nitrogen,

oxygen, and hydrogen atoms were set at 0.9572 Å, 1.09 Å, 1.21 Å, and 0.74 Å, respectively. The equilibrium angle for water molecules was set at 104.52 degrees. For the carbon dioxide/water sample, which consists of two oxygen atoms and one carbon atom, two angles were considered. One angle was related to the water molecule, while the other angle pertained to the linear structure of carbon dioxide, with an equilibrium angle of 180 degrees. To maintain the bond lengths and angles, the Shake algorithm was utilised for the bonds between atoms within water and dissolved gases, as well as for the angles within water molecules. However, the carbon dioxide atoms were allowed to have an energy of angle with a harmonic style to accurately capture the structure of carbon dioxide. However, unlike the water atoms, the methanol atoms utilised the harmonic style for both the bond and angles without any restrictions. This allowed for more flexibility in the configuration of the methanol molecule. Additionally, the OPLS style was employed to describe the dihedral interactions within the methanol molecule, enabling the calculation of dihedral energy. Table 1, 2, and 3 provides the coefficients for the harmonic bond, angle, and OPLS dihedral terms in the methanol molecule, specifying the parameters used in the simulation for accurate representation of the molecular interactions. Furthermore, the angles, dihedrals, and impropers within the organic host liquid molecules were characterized using the Class 2 potential style. Additionally, hybrid approaches were employed in systems with different types of bonds and angles. For example, in the carbon dioxide/dodecane system, a hybrid angle style combining Class 2 and harmonic potentials was used.

Table 1. *Harmonic bond coefficients for methanol molecule.*

K (kcal/mol/Å ²)	r_0 (Å)	Elements
553	0.9600	OH-HO

320	1.41	OH-CT
340	1.09	CT-HC

Table 2. *Harmonic angle coefficients for methanol molecule.*

K (kcal/mol/radian ²)	θ_0 (degrees)	Elements
55	108.5	CT-OH-HO
35	109.5	OH-CT-HC
33	107.8	HC-CT-HC

Table 3. *OPLS dihedral coefficients for methanol molecule.*

K1(kcal/mol)	K2(kcal/mol)	K3 (kcal/mol)	K4 (kcal/mol)	Elements
0.0000	0.0000	0.4500	0.0000	HO-OH-CT-HC

Intermolecular potentials include both van der Waals and electrostatic interactions, which are fundamental to understanding molecular behaviour in simulations. The van der Waals interaction occurs between nonbonded atoms, resulting from a balance between attractive and repulsive forces. The attractive component arises from the interaction between induced dipoles, which follows a r^{-6} relationship, while the repulsive component is due to the overlap of electron clouds when atoms come into close proximity. The most widely used model for van der Waals interactions is the 12-6 Lennard-Jones (LJ) potential. In MD simulations, dimensionless reduced units are commonly used, with scaling factors for mass (m), length (σ), and energy (ϵ). The parameters ϵ and σ for atom pairs are often determined

using the Lorentz-Berthelot combining rules, with the depth of the interaction well given by the geometric mean. The repulsive part of the LJ potential, represented by r^{-12} , is the most commonly used, but it can cause instabilities when atoms approach one another closely. In some cases, the 9-6 Lennard-Jones potential, like in the COMPASS force field, is used as an alternative. On the other hand, the Coulombic potential describes the long-range electrostatic interactions between charged atoms. These interactions depend on the electronic density of each atom and the surrounding environment, though accurately reducing this density for MD simulations can be complex. To manage this, partial atomic charges are often derived by fitting to experimental thermodynamic data or ab initio calculations. Electronegativity values are assigned to atoms and used to calculate the Coulombic potential. For systems with significant polarisation effects, such as water (H_2O), polarisable force fields like SPC, SPC/E, TIP3P, TIP4P, and TIP5P are used to capture the liquid's structure more accurately. Because electrostatic interactions involve long-range forces, they cannot be computed directly in real space. Instead, methods such as the Ewald algorithm, particle-particle particle-mesh (PPPM) algorithm, and multi-level summation method (MSM) are employed to compute these interactions efficiently in reciprocal space [136].

Among various models used for simulating water interactions, the TIP4P/2005 (lj/cut/tip4p/long) water model stands out for its ability to reproduce key properties of water, including density, viscosity, thermal expansion coefficient, isothermal compressibility, and self-diffusion coefficient [106]. This model treats water molecules as rigid, non-polarizable entities with fixed bond lengths and angles. In addition, the TIP4P/Ice potential was employed to describe water interactions during the hydrate formation process. The general form of the TIP4P model is shown in Equation 3.21, which captures intermolecular interactions with high fidelity [141], while the specific interaction parameters for each model are provided in Table 4.

$$E=4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \sum_{i,j} \frac{q_i q_j}{r_{ij}} \quad (3.21)$$

where ε represents the well depth, σ denotes the distance, and q is the charge. Nitrogen, hydrogen, and oxygen molecules exhibit no overall charge, and the LJ/cut potential was used to model their interactions, with an 8.5-angstrom cutoff radius. For carbon dioxide, partial charges of -0.3256 and 0.6512 were assigned to the oxygen and carbon atoms, respectively, and the lj/cut/coul/long potential was applied, using the same cutoff radius. To model interactions within the methanol molecule, the OPLS (lj/cut/coul/long) potential [142] was utilised, employing a 12-angstrom cutoff radius. The mix arithmetic rule was employed to determine the potential interactions between different atoms in the simulation. For the computation of long-range Coulombic interactions, the PPPM/TIP4P solver was utilised in the water sample, while the PPPM (Particle-Particle Particle-Mesh) solver was used in the methanol sample. The specific Lennard-Jones parameters for each gas species and host liquids, including the well depth (ε) and the characteristic length (σ), are presented in Table 4.

Table 4. *Interaction coefficients of atoms in water, methanol, and dissolved Gases.*

Molecule	Elements	Epsilon (kcal/mol)	Sigma (Å)	Charge	Reference
Water (TIP4P/2005)	O	0.1852	3.1589	-1.1128	[143]
	H	0	0	0.5564	
methanol	O(H)	0.1700000304	3.1199999534	-0.683	[142]
	CT	0.065999966	3.5000001502	0.145	
	H(C)	0.0300002576	2.4999982005	0.04	

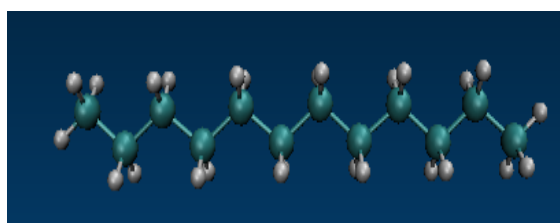
	H(O)	0	0	0.418	
Oxygen	O	0.09538	3.094	0	[144]
Nitrogen	N	0.07217	3.2973	0	[145]
Hydrogen	H	0.01988	2.7200	0	[146]
Carbon	C	0.0559	2.757	0.6512	
dioxide	O	0.15999	3.033	-0.3256	[147]
Water	O	0.21084	3.1668	-1.1794	
(TIP4P/Ice)	H	0	0	0.5897	[148]

The interactions between dodecane and isooctane molecules, as organic host liquids, were described using the condensed-phase optimised molecular potentials for atomistic simulation studies (COMPASS) potential [149] (lj/class2/coul/long) with parameterised values as shown in Table 5.

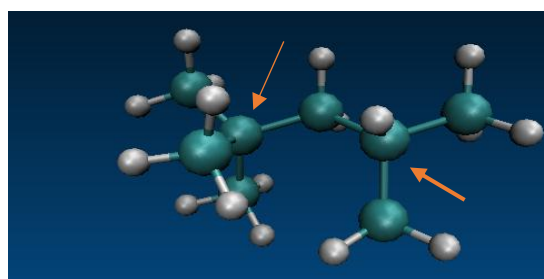
Table 5. *Interaction coefficients of atoms in dodecane and isooctane.*

Molecule	Elements	Epsilon (kcal/mol)	Sigma (Å)	Charge	Reference
Dodecane	C* (c4)	0.062	3.854	-0.106	[149]
	H	0.023	2.878	0.053	
Isooctane	C* (c44)	0.02	3.854	0	
	C* (c4)	0.062	3.854	-0.106	
	C* (c43)	0.04	3.854	-0.053	
	H	0.023	2.878	0.053	

* In the COMPASS potential, carbon atom types are typically denoted as C4x, where 'x' represents a specific carbon atom type. Each carbon atom type is assigned unique parameters in the input file to accurately describe its interactions in the simulation. Figure 1 illustrates the molecular structure of dodecane and isooctane. In dodecane, carbon atoms form linear chains and are bonded to a maximum of two other carbon atoms (C4). On the other hand, in isooctane, two carbon atoms are bonded to three or four other carbon atoms, while six carbon atoms are bonded to two other carbon atoms. This indicates that in the isooctane structure, two carbon atom types differ from the C4 carbon atom that is bonded to a maximum of two other carbon atoms and these two different carbon atoms are bonded to three and four other carbon atoms.



Dodecane



Isooctane

Figure 1. *Molecular structures of dodecane and isooctane, highlighting distinct carbon atom types in isooctane.*

Unlike the permanent bonds in classical force fields, the reactive force field dynamically adapts to the current configurations of atoms, allowing bonds to break and form as atoms move. Reactive force fields, such as ReaxFF, are significantly more complex than classical force fields. Their parameters are typically provided in tables or documents rather than as analytical expressions. These force fields enable the dynamic simulation of bond formation and breaking, making them ideal for studying chemical reactions [136].

The ReaxFF force field defines each element as a distinct atom type and has been expanded to encompass interactions among covalent, metallic, and ionic elements throughout the periodic table. Utilising a bond-order formalism alongside polarisable charge descriptions, ReaxFF effectively models both chemical reactions and static interactions, enabling its application across diverse material systems [136, 150]. The energy contributions to the ReaxFF potential can be delineated as follows [151, 152]:

$$E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdWaals} + E_{Coulomb} + E_{Specific} \quad (3.22)$$

where E_{bond} represents the energy associated with bond formation, which varies continuously with interatomic distance. E_{over} imposes an energy penalty to prevent atom overcoordination, based on atomic valence rules. E_{angle} and E_{tors} denote the energies linked to three-body valence angle strain and four-body torsional angle strain, respectively. $E_{Coulomb}$ and $E_{vdWaals}$ account for electrostatic and dispersive contributions across all atoms, independent of connectivity or bond order, whereas $E_{Specific}$ integrates system-specific terms customised to capture unique properties. The ReaxFF potential, as described in Equation 3.22, encompasses both bond-order-dependent energy, $E_{bond} + E_{over} + E_{angle} + E_{tors}$, and non-bonding interactions or bond-order-independent energy, $E_{vdWaals} + E_{Coulomb}$. The ReaxFF force field utilises bond strength measurements based on the Tersoff method, employing bond order (BO) as a key parameter. This bond order reflects contributions from σ bonds, π bonds, and double- π bonds, and varies according to the distances between atoms and is expressed as [151, 152]:

$$\begin{aligned} BO_{ij} &= BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} \\ &= \exp [p_{bo1} \cdot (r_{ij}/r_o^{\sigma})^{p_{bo2}}] + \exp [p_{bo3} \cdot (r_{ij}/r_o^{\pi})^{p_{bo4}}] + \exp [p_{bo5} \cdot (r_{ij}/r_o^{\pi\pi})^{p_{bo6}}] \end{aligned} \quad (3.23)$$

where BO is the bond order between atoms i and j , r_{ij} is interatomic distance, and r_0^σ , r_0^π , and $r_0^{\pi\pi}$ correspond to the equilibrium bond lengths of the σ bond, π bond, and double- π bond, respectively. The terms from p_{bo1} to p_{bo6} are parameters used to model the bonds. In this study, the C/H/O/N-2019 ReaxFF potentials [153], incorporating parameters for carbon, hydrogen, and oxygen from the widely used C/H/O-2016 potential [154] for studying hydrocarbon combustion, alongside interactions for nitrogen atoms, were employed to investigate the combustion of nanobubbled dodecane fuel. Furthermore, the Tersoff potential [155] was adopted to simulate interactions between carbon atoms within the graphene sheet, and the arithmetic mixing method was used for intermolecular interactions [156].

3.4 MD simulation workflow

3.4.1 System initialization

To perform a simulation, an MD box is first defined, and the positions and velocities of atoms are initialized. Atomic positions are typically assigned based on a lattice structure, with lattice constants set according to experimentally reported values or theoretical calculations. This approach is standard for crystalline materials such as metals and semiconductors. For non-crystalline systems, particularly liquids, atomic positions may be assigned randomly. However, random placement can lead to undesirable atomic overlap. Therefore, structural relaxation is usually performed prior to the main simulation, and an energy minimization step is carried out to optimize the initial configuration [135, 157].

In addition to defining the initial atomic configuration, the simulation box and its boundary conditions must also be specified. The simulation box is defined with a finite size, and due to the surface effect, atoms or molecules located at the boundaries have fewer neighbours than those inside the box; thus, the dynamic behaviour of boundary atoms deviates

significantly from that of atoms in the interior. A common approach to addressing this surface effect is the application of periodic boundary conditions (PBCs), which are among the most widely used boundary conditions in MD simulations. The use of PBCs provides two main advantages. First, each atom in the primary simulation cell interacts not only with other atoms within the cell but also with their periodic images in neighboring virtual cells. As a result, boundary atoms experience a coordination environment similar to that of interior atoms, effectively eliminating surface effects. Second, when an atom leaves the primary simulation cell from one side, its periodic image enters from the opposite side. Therefore, the total number of atoms within the simulation cell remains constant, which is a common requirement in most MD simulations [157].

In principle, the initial atomic velocities may be chosen arbitrarily, provided that the overall stability of the system is maintained. As the simulation proceeds, these velocities will evolve and relax toward physically meaningful values consistent with the specified thermodynamic conditions and applied constraints. However, for improved efficiency and numerical stability, it is advantageous to initialize atomic velocities according to an appropriate statistical distribution. Since most simulations are conducted at a specific non-zero temperature, a common and physically justified approach is to sample initial velocities from the Maxwell–Boltzmann distribution corresponding to the desired temperature, which can guarantee a quick relaxation of the initial system [157].

3.4.2 Ensembles

In MD simulations, ensembles play a crucial role in defining the thermodynamic conditions of a system, ensuring the simulation results align with real-world experimental and physical scenarios. By using ensembles, simulations can replicate specific macroscopic states such as constant temperature, pressure, or energy, each corresponding to distinct thermodynamic conditions. The commonly used ensembles are the NVE ensemble (microcanonical), the NVT ensemble (canonical), and the NPT ensemble (isothermal-isobaric).

In the NVE ensemble, the number of atoms (N), system volume (V), and total energy (E) remain constant. Within this framework, the system's temperature (T) and pressure (P) are allowed to fluctuate around their average values. The system is completely isolated from its surroundings, with no exchange of energy or particles, ensuring the preservation of statistical equilibrium [157].

In the NVT ensemble, the number of atoms (N), system volume (V), and temperature (T) are held constant, while the total energy (E) and pressure (P) are not fixed and instead fluctuate around their average values. This ensemble represents a closed system that can exchange thermal energy with its surrounding environment. Various methods are employed to create the canonical ensemble and maintain a constant temperature. Simple approaches include velocity scaling and coupling the system to a heat bath. Additionally, advanced techniques such as Nosé-Hoover thermostat can be used to regulate the temperature effectively.

The simplest approach to maintaining a constant temperature involves scaling the particle velocities. In this ensemble, the kinetic energy per particle is expressed as follows:

$$\langle K \rangle = \frac{1}{2N} \left\langle \sum_i m_i \vec{v}_i \vec{v}_i \right\rangle \quad (3.24)$$

where N is the number of particles, m_i is the mass of a particle, and $\vec{v}_i$ is the velocity of a particle. By using the theory of kinetic gas:

$$\langle K \rangle = \frac{3}{2} kT \quad (3.25)$$

in which k is the Boltzmann constant. By equating equation 3.24 and 3.25, the temperature can be calculated as:

$$T = \frac{1}{3Nk} \left\langle \sum_i m_i \vec{v}_i \vec{v}_i \right\rangle \quad (3.26)$$

By using equation 3.26, the actual temperature T_A can be obtained at any moment for the ensemble. Therefore, the velocities can be scaled in relation to the actual temperature and the target temperature T_D .

$$\left. \begin{aligned} v_{ix}^{new} &= \sqrt{\frac{T_D}{T_A}} v_{ix} \\ v_{iy}^{new} &= \sqrt{\frac{T_D}{T_A}} v_{iy} \\ v_{iz}^{new} &= \sqrt{\frac{T_D}{T_A}} v_{iz} \end{aligned} \right\} \quad (3.27)$$

The Nosé-Hoover thermostat was initially introduced by Nosé through the extended-system method. A more simplified version of this thermostat was subsequently proposed by both Nose and Hoover in parallel, which has since become the most commonly used formulation. This version is now typically known as the Nose-Hoover thermostat. Nosé introduced an additional coordinate, s , in the Lagrangian of a classical N -body system. This additional degree of freedom can be regarded as the frictional term in the Langevin equation, and it

functions as a “thermal bath” to slow down or accelerate particles until the system temperature reaches the target value (ζ), with an effective “mass” Q . The potential energy associated with s is given by $(3N+1) k_B T \ln s$, where $(3N+1)$ represents the total degrees of freedom, with $3N$ corresponding to the actual system and an additional degree of freedom from s . The equations of motion for the atoms or molecules of an MD system coupled with the Nosé-Hoover thermostat are as follows [157]:

$$m_i \frac{d^2 r_i}{dt^2} = f_i - \zeta m_i v_i \quad (3.28)$$

$$\frac{d\zeta(t)}{dt} = \frac{1}{Q} \left[\sum_{i=1}^N m_i \frac{v_i^2}{2} - \frac{3N+1}{2} k_B T \right] \quad (3.29)$$

In the NPT ensemble, the number of atoms (N), system pressure (P), and temperature (T) are kept constant. The system is coupled with external thermostat and barostat, while particle exchange with the environment is not permitted. Maintaining a controlled pressure in MD simulations is essential for various scenarios. For example, in contrast to the NVE ensemble, the NPT ensemble allows for energy and density fluctuations, enabling the study of processes with large energy changes, such as crystal nucleation and phase separation. Controlled pressure also aids in examining system behaviors under finite rates of heating, cooling, compression, and expansion, such as the glass transition during liquid cooling and bubble formation when a liquid is heated.

3.5 Property evaluation and validation

3.5.1 Property evaluation

A comprehensive evaluation of the studied system was performed by calculating structural, transport, and energetic properties from molecular dynamics simulation outputs. Viscosity and the diffusion coefficient were determined to quantify transport behaviour, while the radial distribution function was used to characterize structural organization. Energetic properties were analyzed through molecular interaction energies extracted from the MD output, and the specific heat capacity was computed. The corresponding mathematical formulations for the transport and structural properties, along with explanatory descriptions for the energetic contributions, are presented in this section. In addition to these properties, which were used in most studied samples, further analyses such as the F_4 parameter, vibrational density of states, thermal conductivity, and activation energy were performed for selected cases and are discussed in the relevant case-specific sections.

The Green-Kubo method was used to calculate the viscosity (μ) of the prepared samples, employing the following equation [158]:

$$\mu_{\alpha\beta}(t) = \frac{V}{k_B T} \int_0^t \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t') \rangle dt' \quad (3.30)$$

where V represents the volume of the particle system, T denotes temperature, k_B is the Boltzmann constant, $\langle \dots \rangle$ signifies averaging over the ensemble employing the three distinct off-diagonal pressure tensor elements (P_{xy} , P_{yz} , P_{xz}) for $\alpha\beta=x, y, z$, and t' and t represent time. The instantaneous value of the pressure tensor used in the Green-Kubo method is calculated at each time step, as described by the following equation [158]:

$$P_{\alpha\beta}(t) = \frac{\sum_{i=1}^K m_i u_{i\alpha}(t) u_{i\beta}(t)}{V} + \frac{\sum_{i=1}^{K'} r_{i\alpha}(t) f_{i\beta}(t)}{V} \quad (3.31)$$

in which the pressure tensor value at time t , denoted as $P_{\alpha\beta}$, m_i represents the mass of atom i , $u_{i\alpha}$ and $u_{i\beta}$ are the velocities of atom i in the α and β directions, and $r_{i\alpha}$ and $f_{i\beta}$ are the position and force vector components of atom i . This calculation involves K atoms in the central simulation box. Additionally, when periodic boundary conditions are applied along with the minimum image convention, the sum is extended to encompass periodic image (ghost) atoms located outside of the central simulation box, denoted as K' .

The diffusion coefficient D can be expressed in terms of the velocity autocorrelation function (VACF) as follow [159]:

$$D = \frac{1}{2} \int_0^\infty \xi(t) dt \quad (3.32)$$

where $\xi(t)$ denotes the velocity autocorrelation function. An alternative approach for determining the diffusion coefficient is based on the Einstein relation, which was also employed in this study. In this framework, the diffusion coefficient is obtained from the mean squared displacement (MSD) of particles and is given by [159]:

$$D = \frac{1}{6t} \left\langle \left[\sum_{i=1}^N \vec{r}_i(t) - \vec{r}_i(0) \right]^2 \right\rangle \quad (3.33)$$

where N is the total number of particles in the system and $\vec{r}_i$ represents the position vector of the i -th particle.

The radial distribution function (RDF) can be calculated by using the following equation [160]:

$$x_v x_\xi \rho g_{v\xi}(r) = \frac{1}{N} \left\langle \sum_{i=1}^{N_v} \sum_{j=1}^{N_\xi} \delta(r + r_i - r_j) \right\rangle \quad (3.34)$$

in which x , ρ , $g(r)$, N , v , and ξ are mole fraction, density, RDF, the number of total atoms, and the types of chemicals, respectively.

The specific heat capacity at constant volume can be computed using the following equation [161]:

$$C_v = \frac{\langle \delta E^2 \rangle}{K_B T^2} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{K_B T^2} \quad (3.35)$$

where $\langle E^2 \rangle - \langle E \rangle^2$ is the fluctuation of energy, K_B is Boltzmann constant and T corresponds to the temperature.

All simulations in this study were performed using the open-source LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package [162]. LAMMPS provides a wide range of built-in commands for calculating system properties, such as density, which can be readily obtained using internal compute functions. In addition, it allows detailed analysis of molecular interaction energies, including total energy contributions. The compute group/group command was used to evaluate total energy and force interactions between two groups of atoms. Other molecular interaction analyses were also performed using appropriate built-in commands. These analyses were employed to gain a deeper understanding of the observed mechanisms and system behaviour. Visualization was performed with Ovito software [163], clathrate formation analyzed using the open-source GRADE code after processing the trajectories with a custom-developed script for compatibility [164], and the reaction network was generated using ReacNetGenerator [165].

3.5.2 Validation

Molecular approaches utilize Newton's second law to predict atomic motion, with various potentials serving as the foundation for calculating the forces acting on each atom. Therefore, the selection of an appropriate potential to describe intermolecular interactions is crucial in any MD simulation. Initially, the viscosity, density, and diffusion coefficient of pure host liquids were calculated using MD simulations, and the resulting values were compared with experimental data to ensure that the chosen potential accurately captures the dynamic behaviour of these liquids. The results show good agreement with experimental measurements, as shown in Table 6.

Table 6. *The comparison of inherent properties calculated by MD simulation and experimental values under the environmental condition [166-170].*

Liquids	Number of atoms	Potential	Density (g/mL)	Viscosity (Pa.s)	Diffusion Coefficient(m ² /s)
Methanol	156000	OPLS	0.77	0.00052	2.52×10^{-9}
		Experimental	0.79	0.00053	2.44×10^{-9}
Water	177000	TIP4P/2005	0.98	0.000096	2.30×10^{-9}
		Experimental	0.99	0.000089	2.30×10^{-9}
Dodecane	190000	Compass	0.73876	0.00127	1.06×10^{-9}
		Experimental	0.746	0.00134	0.871×10^{-9}
Isooctane	166400	Compass	0.678	0.000375	2.59×10^{-9}
		Experimental	0.687	0.000474	-----

3.6 Cluster analysis

Researchers face significant challenges in MD simulations, not only due to the computational demands of large simulation boxes but also because of the substantial volumes of data these simulations generate. To manage this complexity, certain assumptions, such as fixing the center of pre-defined NBs, are often employed to simplify analyses of NB behaviour [106]. While these assumptions facilitate detailed investigations, they may

compromise the accuracy of analyses related to NB motion and dynamics, potentially failing to capture their real-world behaviour.

Machine learning (ML) has emerged as a transformative tool for addressing the challenges posed by large datasets generated in atomistic and molecular simulations across fields such as materials science, solid-state physics, biophysics, and biochemistry. ML encompasses three primary categories. Supervised learning relies on input-output pairs for predictions, commonly used in material and molecular property forecasting. In reinforcement learning, models learn through continuous interaction with their environment, without initial data. Unsupervised learning primarily focuses on extracting valuable insights solely from input data, commonly applied in molecular simulations to generate compact descriptors, including clustering and low-dimensional collective methods, for analysing molecular trajectories [171].

A more systematic and data-driven approach, involving the nucleation of various NBs in diverse liquid hosts, holds the potential to yield profound insights into the characteristics and mechanisms governing the nucleation and subsequent behaviour of bulk NBs and their impact on the inherent properties of host liquids. In this study, a hybrid methodology is employed, combining MD simulations with unsupervised machine learning techniques to evaluate the probability of NB formation resulting from the dissolution of gases in pure water and methanol host liquids.

Utilising a molecular approach, the study delved into the exploration of thermophysical properties and the tracking of atomic motion over time. The temporal and spatial data collected from MD simulations were subsequently utilised in a high-throughput screening process to identify clusters of NBs formed through the scattered gases within the host liquids.

This screening involved an assessment of the gas atom count within these clusters, as well as their density, radius, and motion over time, as shown in Figure 2.

Machine learning is commonly employed for tasks such as classifying data into distinct categories (classification) or forecasting numerical values (regression). Classification entails assigning labels or categories to input data by discerning patterns within the dataset, while regression involves predicting continuous numerical values based on input features. ML techniques are applicable for categorising or analysing extensive datasets derived from MD simulations, including those spanning long simulation durations and featuring numerous atoms. Clustering, an unsupervised machine learning technique, is employed to divide a set of particles into meaningful subgroups (clusters) by minimizing similarities between clusters and maximising within-cluster similarities. DBSCAN (density-based spatial clustering of applications with noise), a well-established density-based clustering algorithm known for its ability to identify clusters, is utilised [172]. Derived from MD simulations, the dataset, including particle positions within the system, serves as input for an in-house code developed using this efficient algorithm, facilitating the analysis of NB characteristics via trajectory data and offering insights into the influence of molecular interactions on their behaviour.

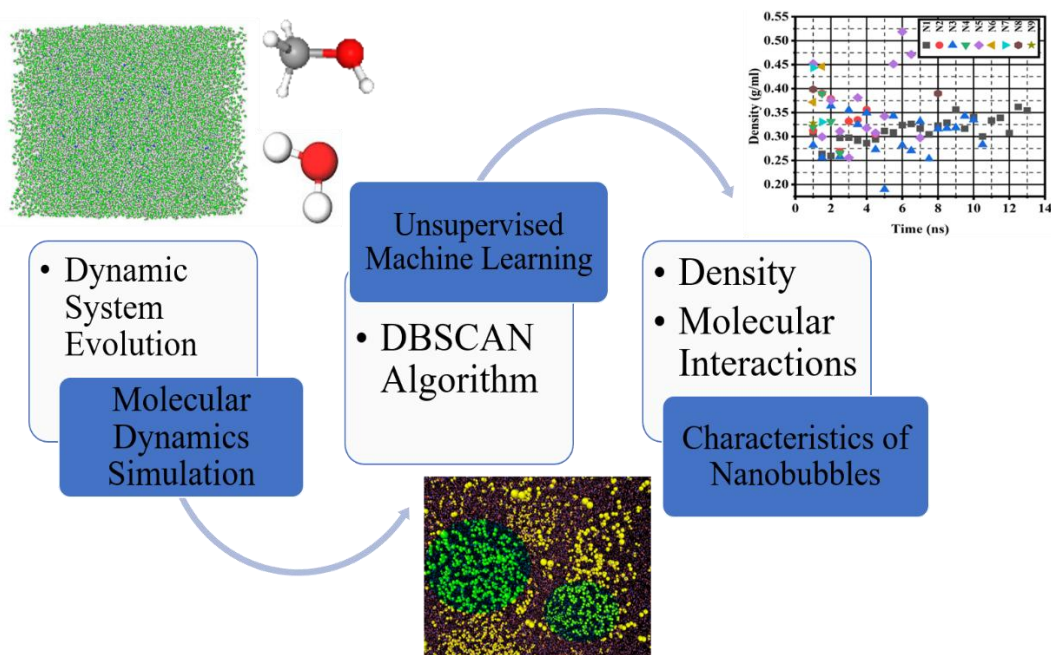


Figure 2. *Methodological framework for studying NBs, involving temporal atom coordinate extraction through MD simulation, unsupervised ML for NB detection, comprehensive characterization of NBs, and elucidation of underlying behavioural mechanisms.*

The positions of atoms were recorded at intervals of 0.05 ns, capturing the coordinates along the x, y, and z axes. These recorded positions were saved in a file, which served as raw input for an in-house developed code. This code utilised the unsupervised DBSCAN algorithm to detect clusters, determine the number of atoms within each cluster, and measure their sizes. The obtained cluster information was then utilized to calculate the density of the formed NBs within the host liquids.

To ensure the accuracy of the developed in-house code based on the unsupervised algorithm, two validation approaches were implemented. The first approach involved comparing the number of detected clusters with the observed number within the simulation box. Additionally, the information obtained, such as the center of the formed NBs, was manually verified by examining the atom positions using OVITO software. For instance, Figure 3

displays a snapshot of the nitrogen-water sample at 3 ns, while Table 7 provides the corresponding information obtained at this time point.

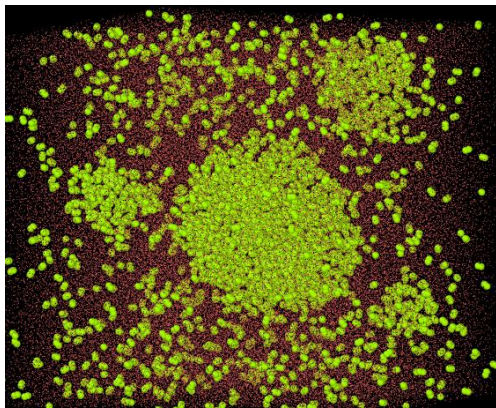


Figure 3. *Snapshot of the water/nitrogen sample at 3 ns, illustrating the arrangement of atoms and the distribution of nitrogen within the water medium.*

Table 7. *Obtained information for the four detected nanobubbles formed in the water/nitrogen sample at 3 ns.*

Estimated number of clusters: 4 Estimated number of noise points: 2051	Cordinate of center: [-10.0348494 5.66119534 -3.66446478] radius: 33.37151430540012		
	number of atoms: 1992		
	density of cluster: 0.2974747550524732		
	Cordinate of center: [-21.8004686 -42.3024046 42.3252682] radius: 20.078849984488656		
	number of atoms: 484		
	density of cluster: 0.3318313246215827		
	Cordinate of center: [38.2764896 28.58753812 7.61406198] radius: 14.836569959815511		
	number of atoms: 209		
	density of cluster: 0.3551683713228059		
	Cordinate of center: [-38.17857238 -39.76491905 -33.3032581] radius: 13.282173105896488		
	number of atoms: 108		
	density of cluster: 0.2558025510368237		

In the second approach, the positions of the formed NBs were utilised as 3D scatter data in space to create a cluster. This cluster was then projected to measure its radius, which was subsequently compared with the radius obtained from the unsupervised method. Figure 4 showcases a snapshot of the water/nitrogen sample at 13 ns, where the position of the formed

NB is scattered in space. Additionally, it displays the projection of this NB, allowing for a direct comparison with the obtained information.

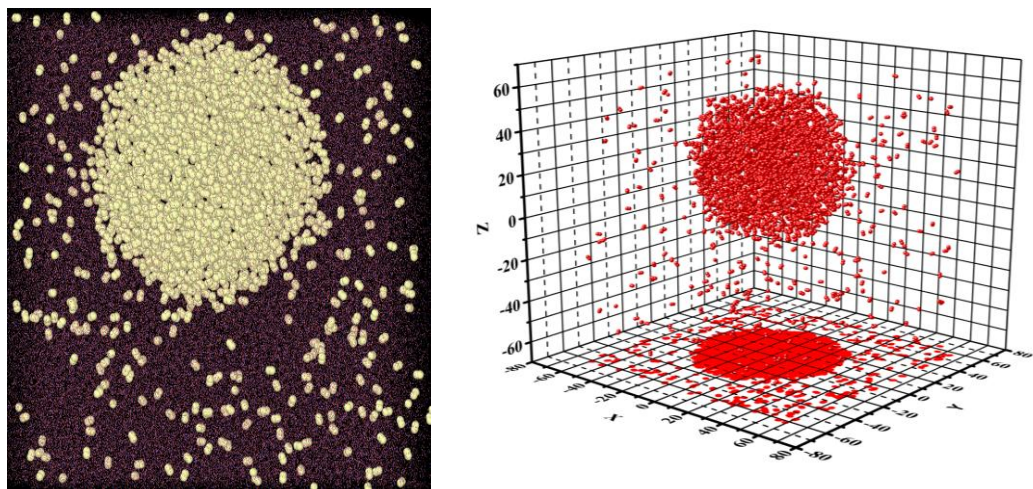


Figure 4. (left) Snapshot of the water/nitrogen sample at 13 ns, capturing the positions of the formed nanobubbles for further analysis and extraction, (right) the size of formed NB through scattering the position of atoms.

Table 8. Obtained information for the detected nanobubble formed in the water/nitrogen sample at 13 ns.

Estimated number of clusters: 1	Cordinate of center: [-2.66669681 1.77050567 22.37164779]
Estimated number of noise points: 644	radius: 40.3649599795429
	number of atoms: 4200
	density of cluster: 0.35442490832121165

3.7 Summary

This chapter outlines the computational methods employed in this study to investigate the behaviour of NBs in different environments using MD simulations. Molecular dynamics provides an atomistic framework for analysing the time evolution of molecular systems by numerically solving Newton’s equations of motion. This approach enables a detailed

examination of microscopic interactions, structural dynamics, and transport phenomena at the molecular scale.

The initial configurations of the simulated systems and their corresponding parameters are presented to define the molecular setups used in this study. Several force fields and potential models were employed to accurately represent intermolecular and intramolecular interactions within the systems. The COMPASS and OPLS-AA force fields were utilised to describe interactions in organic and alcohol-based molecular systems, while gas-phase interactions were modelled using the Lennard–Jones potential to capture interactions between non-bonded atoms. In addition, the reactive force field ReaxFF was applied in simulations where chemical reactions, including bond formation and bond breaking processes, needed to be represented explicitly, particularly in studies involving combustion processes and reactive environments. For water-based systems, different variants of the TIP4P water model were employed to provide an accurate representation of water structure, hydrogen bonding, and intermolecular interactions. The MD simulation procedure was also carefully defined, including the selection of appropriate thermodynamic ensembles to investigate system behaviour under controlled temperature and pressure conditions. Furthermore, key simulation parameters, such as the integration time step and the total simulation time, were systematically determined to ensure numerical stability and to capture the relevant physical processes with sufficient temporal resolution.

A range of statistical mechanical approaches were applied to evaluate the intrinsic properties of the simulated systems. In particular, the Green–Kubo formalism was employed to calculate viscosity from equilibrium molecular dynamics simulations through the time integration of the stress autocorrelation function. In addition, key thermodynamic and transport properties, including density and the diffusion coefficient, were also calculated and subsequently

compared with reported experimental values in order to validate the selected potential models and the applied MD simulation procedure.

In addition to the applied approaches, the methods employed for post-processing and data analysis were also defined to systematically evaluate the simulation outputs and to extract the relevant structural and dynamic properties of the simulated systems.

An overview of the research framework adopted in this thesis is presented in Figure 5, highlighting the classification of host liquids, the molecular interaction potentials employed, and the main phenomena investigated.

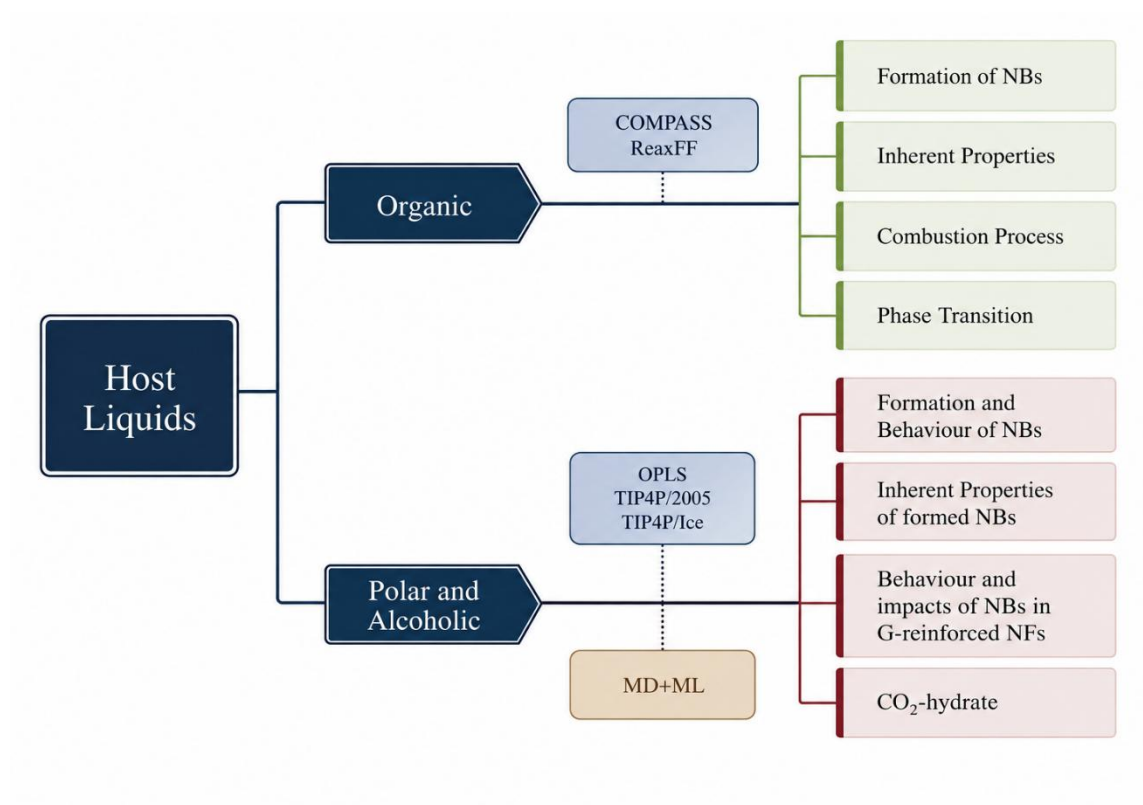


Figure 5. Overview of the research framework

Chapter 4
NBs in Polar and Alcoholic
Environments

4.1 Introduction

In this chapter, the formation and potential generation of NBs through the dissolution of gases, namely oxygen (O_2), hydrogen (H_2), nitrogen (N_2), and carbon dioxide (CO_2), in two candidate working fluids for renewable energy, i.e. water and methanol, were thoroughly examined, along with their properties, behaviour, and impact on the fundamental attributes of the host liquids. Additionally, the potential formation of NBs from these dissolved gases in graphene-reinforced water- and methanol-based NFs was also examined. The thermophysical properties and behaviour of these NFs were analysed using MD simulations, integrating both fundamental insights and engineering applications. This comprehensive approach aims to provide a deeper understanding of the role of NBs in complex fluids, particularly in the context of solid–liquid–gas interactions. Moreover, the potential role of nanobubble-enriched water in enhancing CO_2 hydrate nucleation and growth has also been explored. By leveraging advanced methodologies and incorporating diverse NBs, this chapter also aims to support the development of more efficient and promising strategies for CO_2 capture, a key pillar of sustainable climate mitigation.

4.2 Pure polar and alcoholic media

4.2.1 Characteristics of NBs

To investigate the formation, coalescence, and behaviour of NBs in pure polar and alcoholic media, water and methanol were used as solvents to dissolve nitrogen, oxygen, carbon dioxide, and hydrogen gases. Samples with a 6%-weight fraction of dissolved gases were prepared by scattering 2422, 2120, and 1542 nitrogen, oxygen, and carbon dioxide molecules, respectively, in 59000 water molecules. To achieve the same gas weight fraction in methanol, 1899 nitrogen, 1662 oxygen, and 2231 carbon dioxide molecules were dispersed in 26000, 26000, and 48000 methanol molecules, respectively. Due to its small

mass fraction, different weight fraction of hydrogen gas were used. Samples containing 59000 water molecules and 26000 methanol molecules housed 2422 and 1905 hydrogen molecules, respectively, scattered within them. The initial configuration of the prepared samples is presented in Figure 6. All prepared samples were equilibrated for 1.7 ns in both the NPT and NVT ensembles, followed by a 10 ns simulation in the NVE ensemble, employing a 1 fs time step.

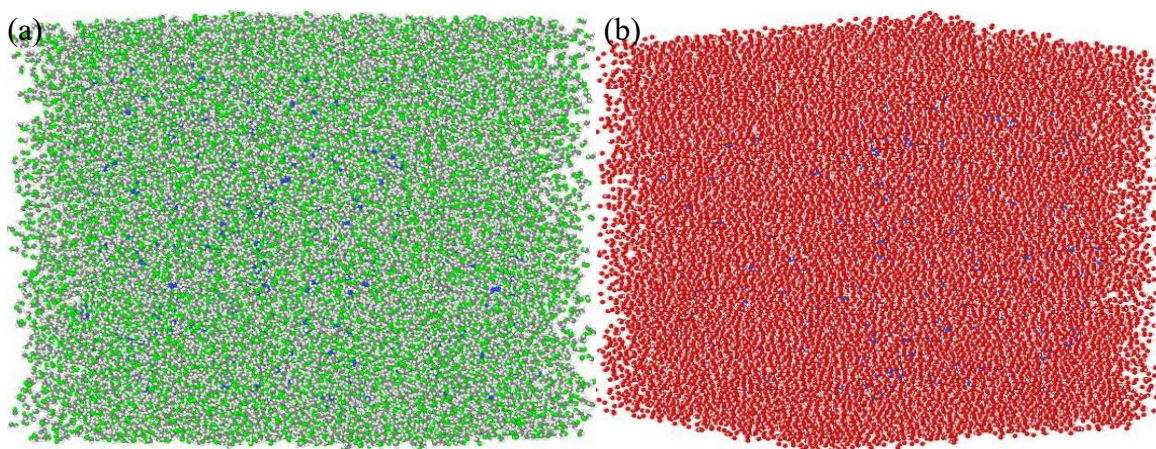


Figure 6. *Initial structure of the dispersed gas in (a) methanol and (b) water*

It was observed at 298.15 K and 1 atm that nitrogen, oxygen, and hydrogen can form NBs in water. The formation of NBs begins with the emergence of nucleation sites within the host liquid. Figure 7 visually depicts the formation of NBs within the host liquids at 1 ns. Furthermore, it illustrates the temporal evolution of the number of bulk NBs formed in the host liquid over time. It is clear that for the same weight fraction of the dissolved gases the number of nucleation sites highly depends on the type of the scattered gas. Nine nitrogen NBs were formed initially while only 2 oxygen NBs were formed in water at 1 ns. The nucleation process in hydrogen/water sample is driven by 1 nucleation site.

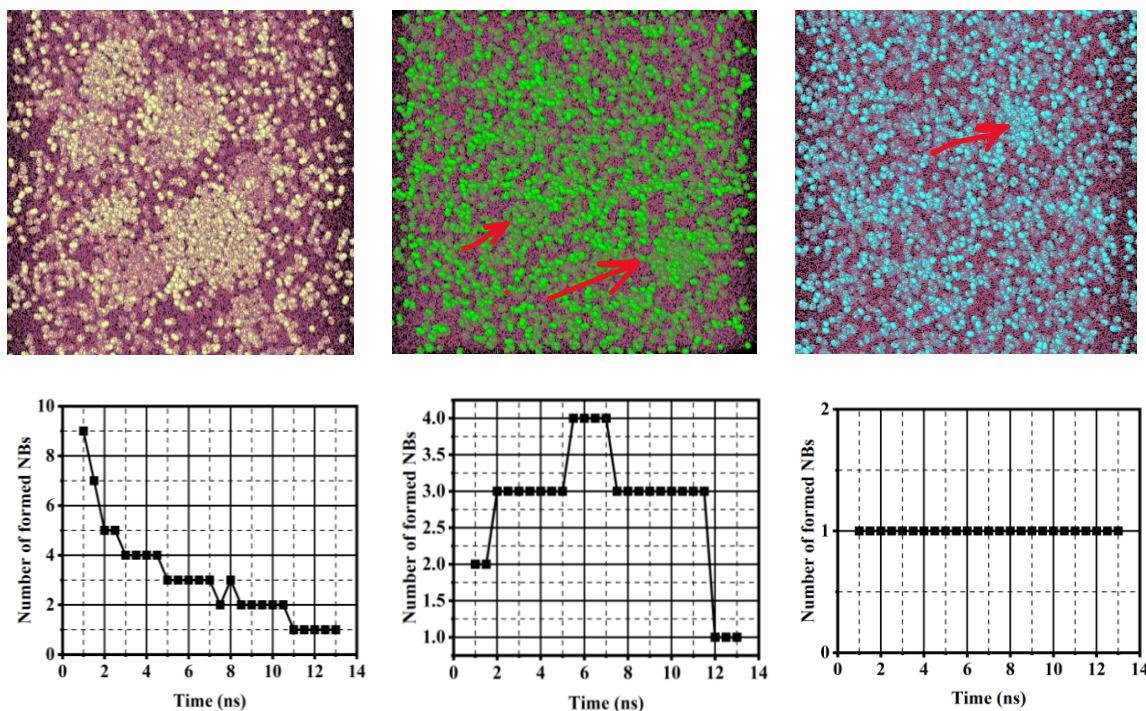


Figure 7. Snapshots at 1 ns (top) and evolution of the number of formed (bottom) nitrogen (left), oxygen (centre), and hydrogen (right) NBs in water over time.

In contrast to the water host liquid, oxygen does not exhibit the formation of NBs in methanol as illustrated in Figure 8. Notably, the nucleation of nitrogen NBs commenced with the presence of 2 NBs in methanol at 1 ns. This observation underscores the significant influence of the host liquid on the nucleation of NBs.

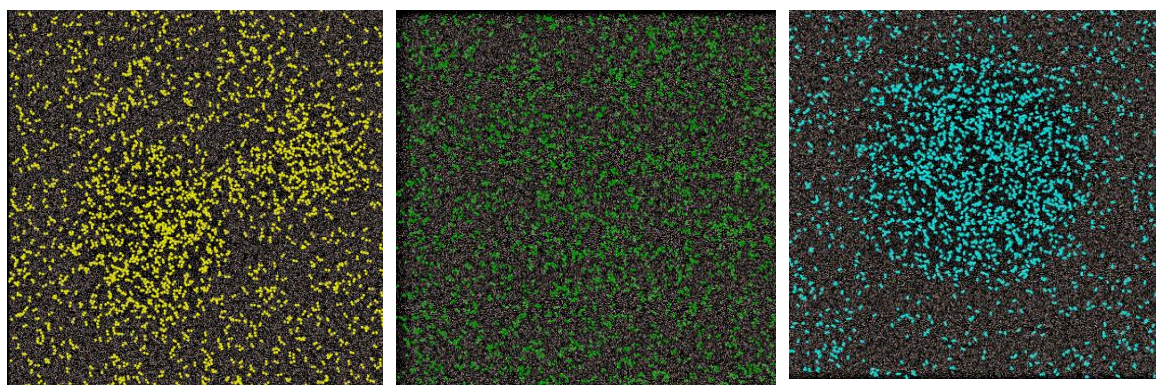


Figure 8. Snapshot of formed nitrogen (left), oxygen (centre) and hydrogen (right) NBs in methanol at 1 ns.

Water molecules have a stronger attraction to each other than methanol molecules due to their ability to form hydrogen bonds [173]. In the case of water, the limited availability of interaction sites between dissolved gas molecules and water molecules results in a more substantial attractive force among nitrogen molecules, as depicted in Figure 9. Consequently, the nucleation of nitrogen within a water host liquid occurs with a higher number of nucleation sites. Conversely, in methanol, the weaker intermolecular forces between methanol molecules enable stronger attractive interactions with dissolved oxygen gas. This strong attraction prevents oxygen molecules from aggregating to form nanobubbles (NBs) in a methanol host liquid, in contrast to water. It should also be noted that the Lorentz–Berthelot mixing rules were employed to define cross-interactions throughout this study. While this is a widely used and well-established approach in classical molecular simulations, it may influence the system behaviour. Furthermore, it's worth noting that carbon dioxide is unable to form NBs in both water and methanol. This is illustrated in Figure 9, where a substantial repulsive force between carbon dioxide molecules prevents their aggregation within the host liquids. Moreover, it is interesting that the majority of the dissolved nitrogen gas exist in the form of NB, only 27.41% of dispersed nitrogen gas remains scattered, after 13 ns in water. However, 34.11% of dissolved hydrogen gas exist in the form of NB in the polar host (Figure 10). Therefore, the nucleation morphology and formation of NBs are affected by the solubility of the dissolved gas. Although the solubility of hydrogen is less than oxygen [174], only one nucleation site was observed in hydrogen/water sample. This suggests that solubility alone may not fully explain the observed differences in nucleation behaviour. One possible contributing factor could be intermolecular interactions between dissolved gas species[173, 175] , which are reflected in their interaction coefficients in Table 4. Oxygen molecules exhibit comparatively stronger intermolecular attractions than

hydrogen molecules, which could promote aggregation and result in multiple nucleation sites.

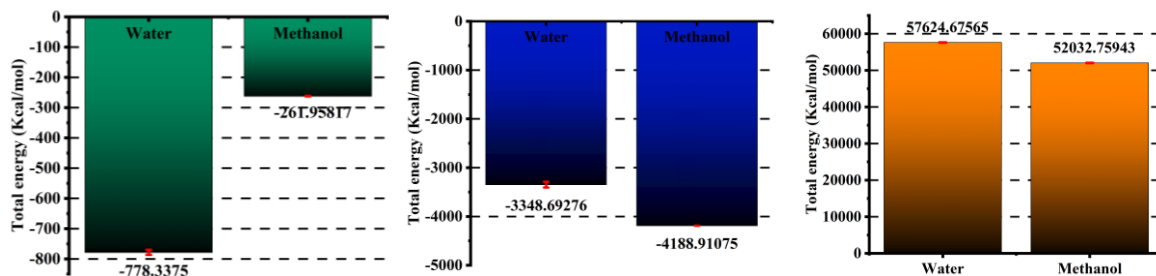


Figure 9. The average of total energy between nitrogen-nitrogen (left) oxygen-host liquid (centre) and carbon dioxide- carbon dioxide molecules (right) in water and methanol.

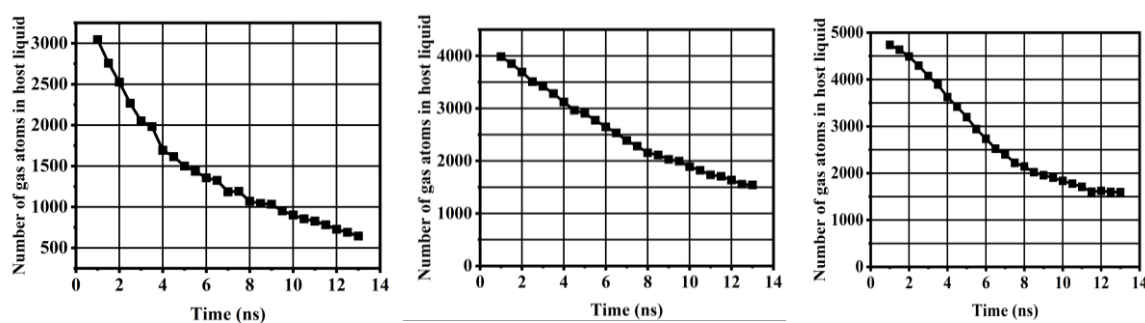


Figure 10. The number of scattered nitrogen (left), oxygen (centre), and hydrogen (right) in water host.

The temporal evolution of NB density was analysed and calculated using unsupervised machine learning, as illustrated in Figure 11. Notably, the density of these generated NBs is significantly greater than the density of the gas present in the gas phase. Upon comparing the density of the formed NBs with their respective sizes, as shown in Figure 11, an intriguing pattern emerges. It becomes evident that the density of NBs increases as their size decreases. For instance, consider the case of nitrogen NB N5, which exhibits its highest density at 6 ns when it boasts its smallest size. Similarly, oxygen NB N3 showcases its peak density at 6 ns when it boasts its smallest size. In the case of hydrogen NBs, it was observed that the highest density occurred at 7 ns, coinciding with the smallest size of the

formed hydrogen NB at 1 ns. This behaviour could be attributed to intermolecular interactions, which significantly affect the density of the formed NBs. As reflected in Table 4, intermolecular interactions between hydrogen atoms are significantly weaker than oxygen and nitrogen. As a result, when hydrogen gas atoms diffuse into the NB, they don't come closer together in the same manner as nitrogen and oxygen atoms. Consequently, hydrogen NBs do not exhibit the same trend of increasing density as their size decreases, in contrast to nitrogen and oxygen NBs. The density of NBs is a key factor contributing to their high stability within the host liquid [27]. To maintain NB stability, a sufficient concentration of scattered gas molecules must be present in the samples. In the interaction between gas atoms and formed NBs, attractive forces act upon both the NB and gas atom. Given that gas atoms are lighter than bulk NBs, gas atoms draw closer and are absorbed by the NB. This same mechanism can be extended to two bulk NBs. In this scenario, the NBs exert attractive forces on each other, causing the smaller NB to move more rapidly and approach the larger NB. Subsequently, as illustrated in Figure 12, the nearest gas atoms are initially absorbed and subsequently fully merge into the larger NB. In nanoscale systems, particle coarsening is governed by two primary pathways: Ostwald ripening and Smoluchowski ripening. Ostwald ripening involves larger particle growth and smaller particle reduction. Gas molecules detach from smaller particles and diffuse through the continuous phase, joining larger nanoparticles. Conversely, Smoluchowski ripening results from collisions among nanoparticles in motion through the continuous phase. Brownian motion induces random movements of NBs suspended in host liquid, causing collisions and subsequent coalescence. As a result, this process enlarges the average diameter of NBs while reducing their overall count [176]. During the coalescence process, atoms within the smaller NB deform it and establish a "bridge" with the larger NB, which could be driven by intermolecular interactions. As it is discussed, the attractive interaction leads to the movement of the formed NBs within the

prepared samples. Brownian motion could also play a role in increasing the stability of NBs. This motion arises from the random interactions of molecules in the surrounding medium. In contrast to macro and microscale bubbles, where buoyant forces act to push them upward due to density differences, Brownian motion introduces random molecular collisions that can move formed NBs in various directions, including downwards. This random movement could be sufficiently robust to counteract the buoyant force acting on NBs, effectively keeping them suspended within the liquid medium. The movement of average centre of final formed NB in water host liquid over time is depicted in Figure 13.

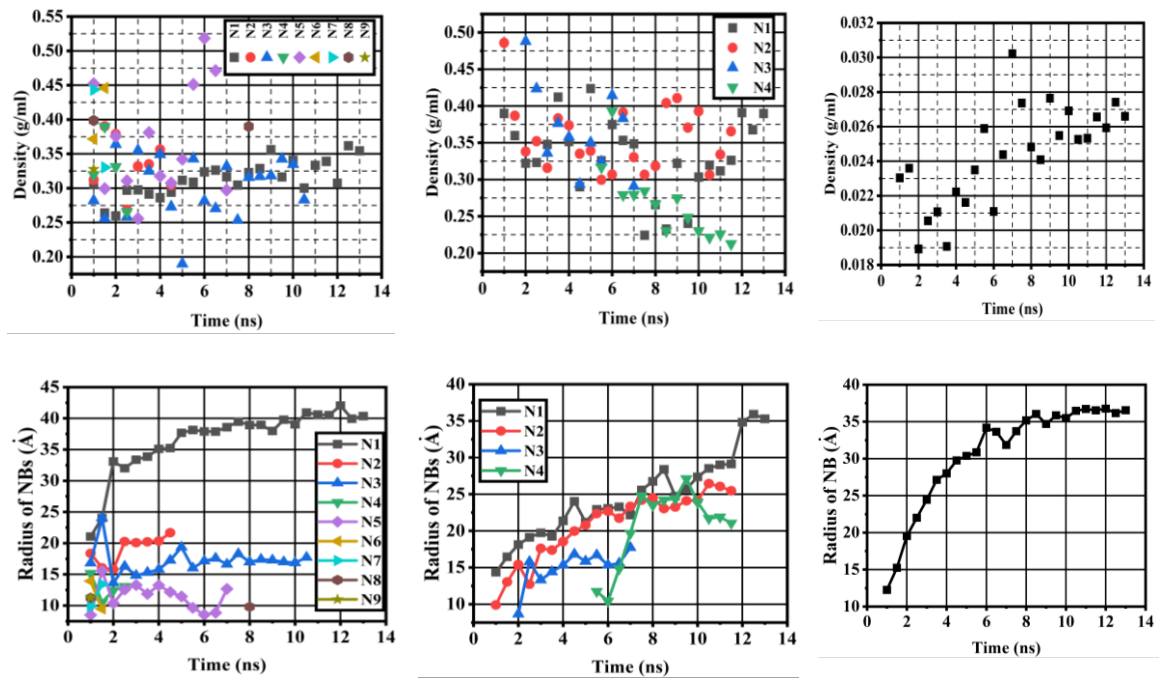
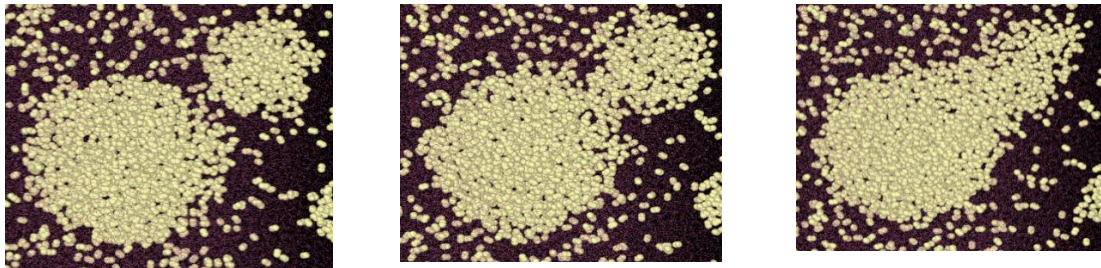


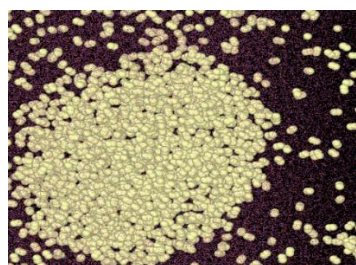
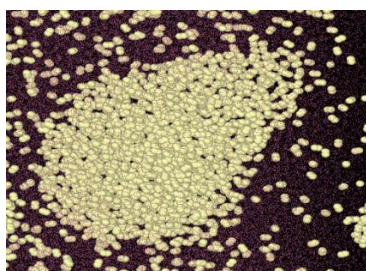
Figure 11. *Density (top) and the radius of formed (bottom) nitrogen (left), oxygen (centre), and hydrogen (right) NBs in water.*



4.7 ns

4.75 ns

4.8 ns



4.85 ns

4.9 ns

Figure 12. *The mechanism of coalescence of nitrogen NB in water host medium.*

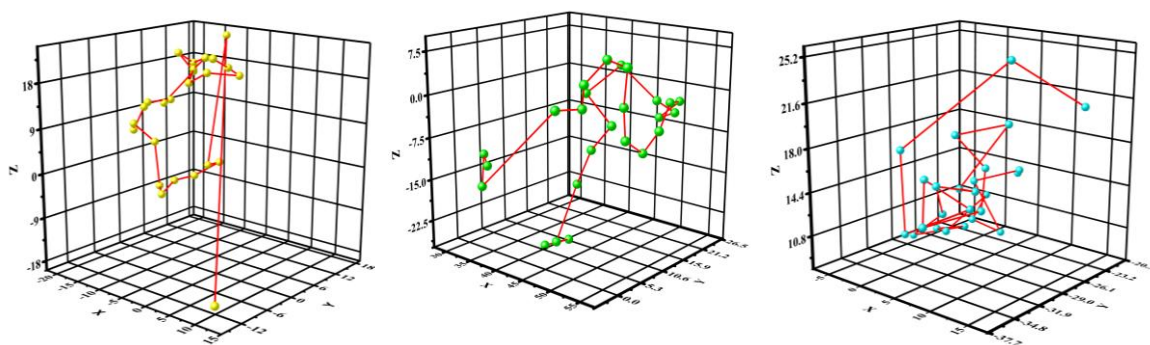


Figure 13. *The movement of average centre of final formed nitrogen (left), oxygen (centre), and hydrogen NB (right) in water host liquid at 298.15 K from 1 ns to 13 ns every 0.5 ns.*

The final radius and density of the formed nitrogen and hydrogen NBs in methanol sample have been shown in Table 9. The comparison of obtained results for the formed NB in methanol (Table 9) and water (Figure 11) reveal that the formed NBs in methanol host have bigger size and lower density than those generated in water. This finding reflects the potential influence of the host liquid type on the characteristics of the formed NBs.

Table 9. *Radius and density of the final formed NBs in methanol sample.*

	Nitrogen	Hydrogen
Radius (Å)	48.510389	55.01482
Density (g/ml)	0.124979	0.007203

Temperature plays a pivotal role in shaping the formation and stability of NBs within a host fluid. It exerts its influence by impacting various factors: firstly, the solubility of gases in the fluid is significantly affected by temperature, which subsequently could affect the behaviour of NBs. Secondly, temperature governs molecular motion and interactions, and may consequently influence the formation and properties of NBs. Notably, the dissolution of nitrogen gas in the host liquids has exhibited intriguing behaviour, particularly in the formation of NBs at room temperature. This intriguing phenomenon has spurred further investigation into the influence of temperature on the nucleation and characteristics of nitrogen NBs in both water and methanol. To unravel these complexities, an investigation was conducted using dispersed nitrogen gas in polar and alcoholic host liquids at equal weight fractions, with examinations carried out at elevated temperatures of 343.15 K and 323.15 K for water and methanol, respectively.

Figure 14 illustrates the number, radius, number of gas atoms and density of formed NBs in water host liquid at 343.15 K. Upon comparing Figure 14 to Figures 7 and Figure 15, it becomes apparent that at higher temperature, nucleation is initiated by a smaller number of nucleation sites, which contain a higher concentration of gas atoms. As it was discussed, at room temperature nucleation is driven by 9 nucleation sites that the biggest one contains 515 gas atoms in the NB with 21.06 Å radius. While at higher temperature, nucleation starts with 4 clusters and the biggest one is made up by 3007 gas atoms inside the NB with 49.18 Å radius. It means that at higher temperature gas atoms have a greater tendency to be present in the form of NBs in the host liquid. In addition, it can be seen that the coalescence process

in the sample at elevated temperature finishes sooner. At higher temperatures, the viscosity of the fluid decreases, making it easier for NBs to move and coalesce.

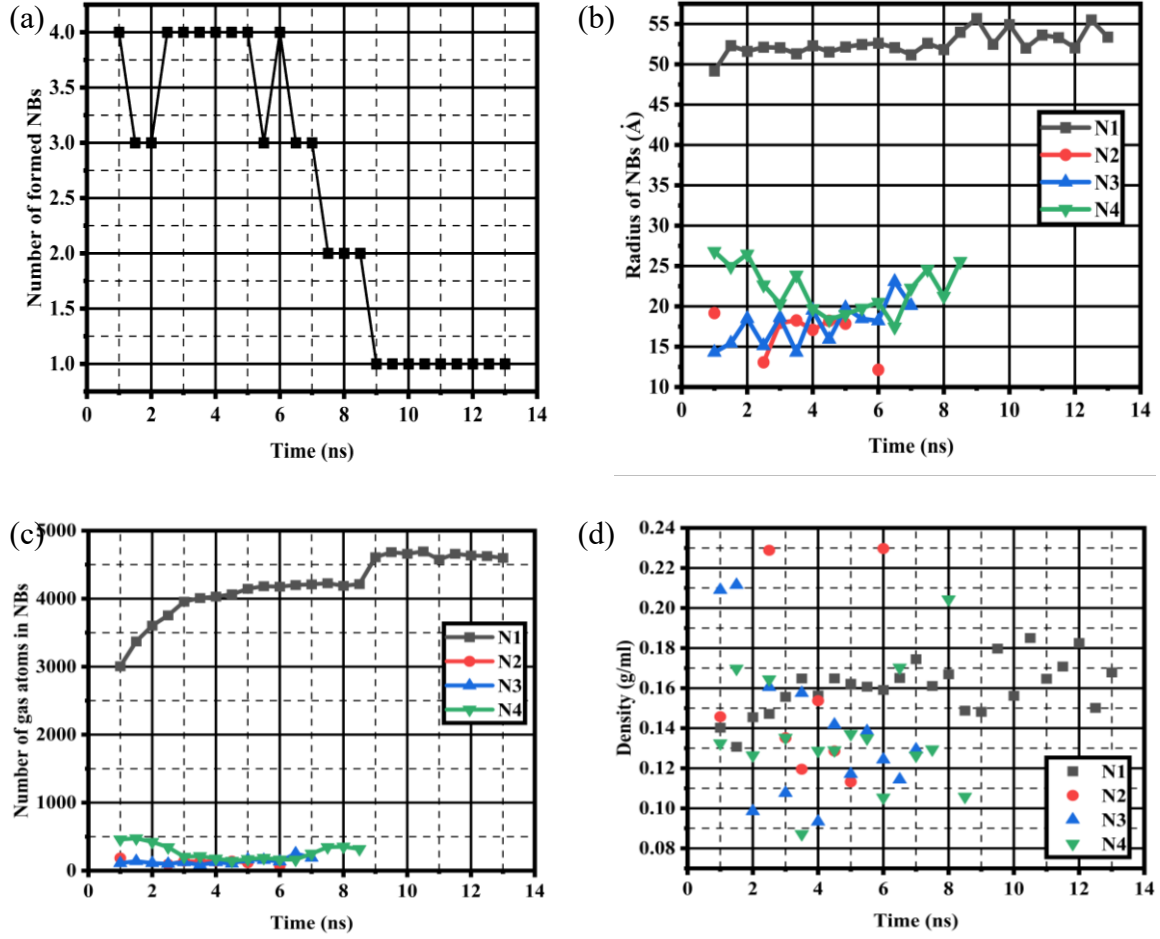


Figure 14. (a) Number of formed nitrogen NBs, (b) radius of the NBs, (c) number of gas atoms inside the formed NBs, and (d) density of the nitrogen NBs at 343.15 K in water host.

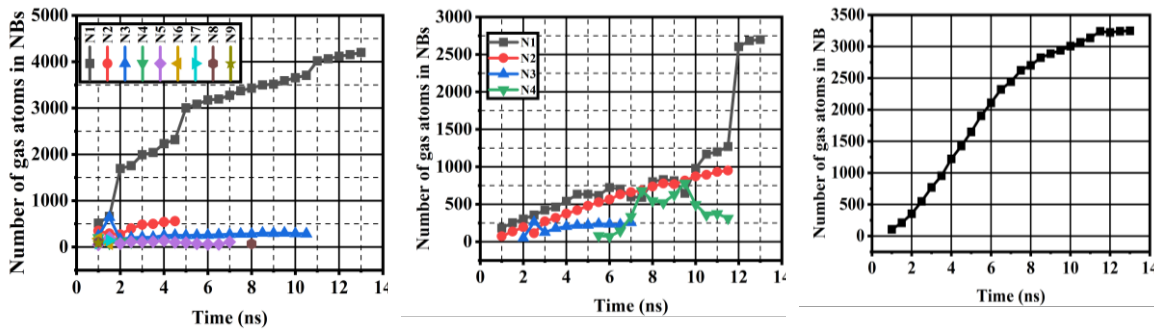


Figure 15. *The number of nitrogen (left), oxygen (centre) and hydrogen (right) gas atoms inside the formed NBs in water sample at 298.15 K.*

Figure 16 presents the average total interaction energy between gas and host liquid atoms at two different temperatures. The results show that the magnitude of the total interaction energy decreases with increasing temperature. Furthermore, at the higher temperature, a lower density of nanobubbles is observed compared with the lower-temperature case. Additionally, Figure 16 shows that the total interaction energy between gas atoms decreases with increasing temperature. These results indicate temperature-dependent variations in both interaction energies and nanobubble density in the investigated systems.

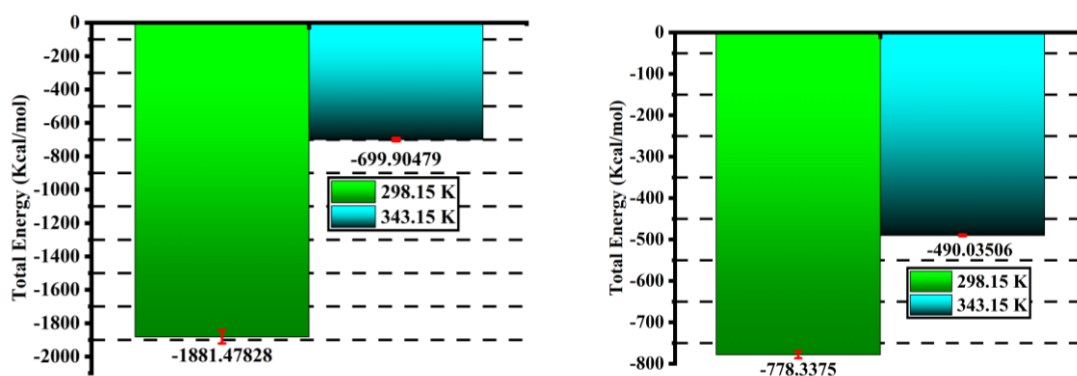


Figure 16. *The average of total energy between nitrogen gas and water (left) and between nitrogen gas atoms (right) in two different temperatures.*

Density and radius of the formed NBs in alcoholic sample at 323.15 K were measured at 0.081 g/ml and 53.30 Å, respectively. By comparing the obtained results with Table 9, it is clear that like water sample, properties of the formed NB are affected by temperature in the alcoholic sample, too. Furthermore, the dynamic of the formed NB in methanol host is also affected by temperature. Figure 17 showcases a sequence of snapshots at intervals of 0.5 ns, depicting the behaviour of the movement of average centre of final formed nitrogen NB in methanol sample at 298.15 and 323.15 K during the last 2.5 ns. It is evident that the formed

NBs in methanol tend to rise to the surface at higher temperature, leading to reduction in the stability of the formed NB. As previously discussed, intermolecular forces, a significant factor influencing Brownian motion, contribute to the motion of molecules and formed NBs. Additionally, NBs suspended within a liquid encounter force like drag force, which arises due to viscosity. Viscosity characterizes a fluid's resistance to flow, where higher viscosity leads to increased drag force acting on a suspended object. When the fluid's viscosity rises, the drag force on a NB intensifies, impeding its movement. Conversely, an elevated fluid temperature leads to decreased viscosity, reducing the drag force exerted on a suspended NB. In the methanol sample, owing to its lower viscosity compared to water, temperature changes exert a greater influence on the balance of forces acting on the NB, causing the NB to rise.

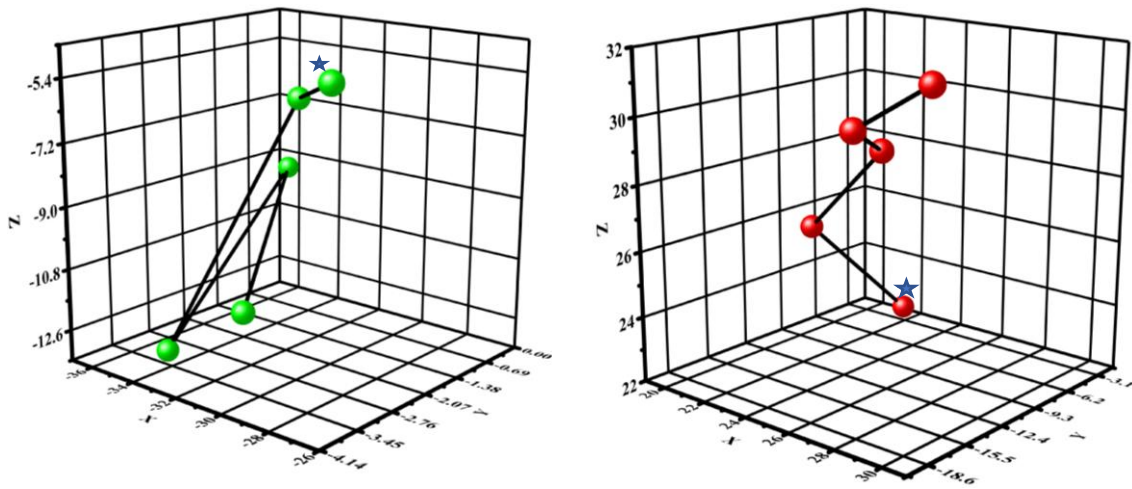


Figure 17. *The movement of the average centre of final formed nitrogen NB in methanol sample at 298.15 K (left) and 323.15 K (right) in the final 2.5 ns of the simulation at 0.5 ns intervals (start point is marked as star).*

4.2.2 Thermophysical properties

Gas molecules, upon dissolving in a liquid, occupy the interstitial spaces between the liquid molecules, thereby expanding the solution's overall volume. This presence also disrupts the interactions among the liquid molecules, contributing to a subsequent decrease in density. Illustrated in Figure 18 are the density alterations observed in the prepared samples, depicting a decline in the host liquid's density following gas dissolution. Furthermore, the emergence of NBs in the sample intensifies this density decrease, notably showcasing that hydrogen NBs exhibit the lowest density among the prepared samples.

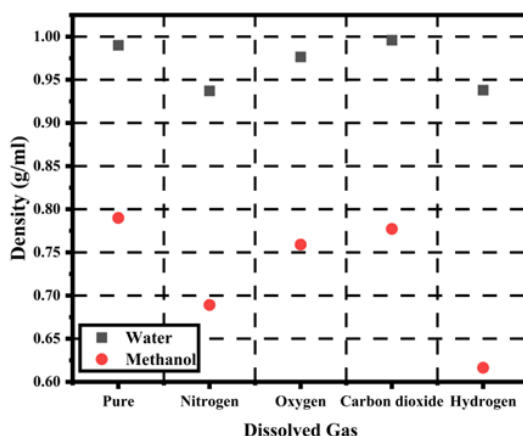


Figure 18. *Density of prepared samples with various gases.*

When a NB nucleates in a host solvent, gas molecules could form weak attractive interactions with host solvent molecules at the NB surface, which may cause the bubble surface to become coated with a layer of host liquid molecules. This means that the base fluid molecules in the nanolayer around the NB take up more space than if they were randomly distributed in the solution. In other words, the nanolayer contributes to a larger volume and lower density of the solution. Therefore, the interfacial layer between the NB and base fluid contains a smaller number of host liquid molecules. Figure 19 shows the

change of host liquid molecules near the NBs for various NB formed in the polar and alcoholic samples. It can be observed that the interfacial layer has a lower concentration of solvent molecules compared to the bulk liquid, and as the distance from the NB increases, the concentration of solvent molecules increases that can be concluded the presence of this layer disrupts the organisation of molecules and results in a decrease in density.

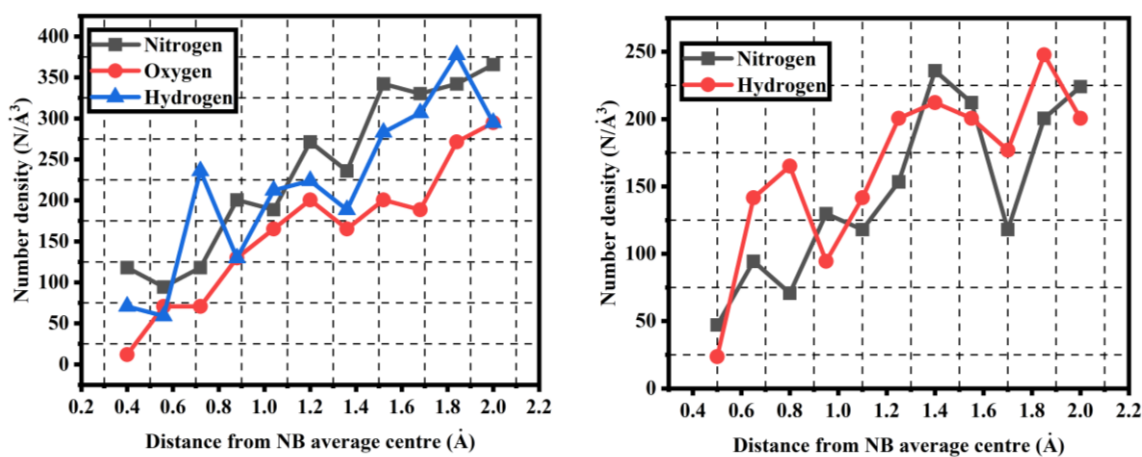


Figure 19. Number densities of the host liquid molecules around the formed NB in (left) water and (right) methanol samples.

In Figure 20, the viscosity of samples containing dissolved gases in both water and methanol is depicted. The results reveal a notable contrast between the two host liquids. In the case of water-based samples, the inclusion of dissolved gases, including oxygen, nitrogen, carbon dioxide, and hydrogen, leads to an increase in viscosity compared to the pure host liquid. This trend aligns with previous research demonstrating that the viscosity of water tends to rise with gas dissolution [9]. Conversely, for methanol-based sample, a distinct behaviour is observed. Dissolution of nitrogen, hydrogen, oxygen, and carbon dioxide in methanol results in a reduction in viscosity compared to pure methanol [177]. This disparity in behaviour

between water and methanol highlights the significant influence of the host liquid type on the viscosity of gas-containing fluid samples.

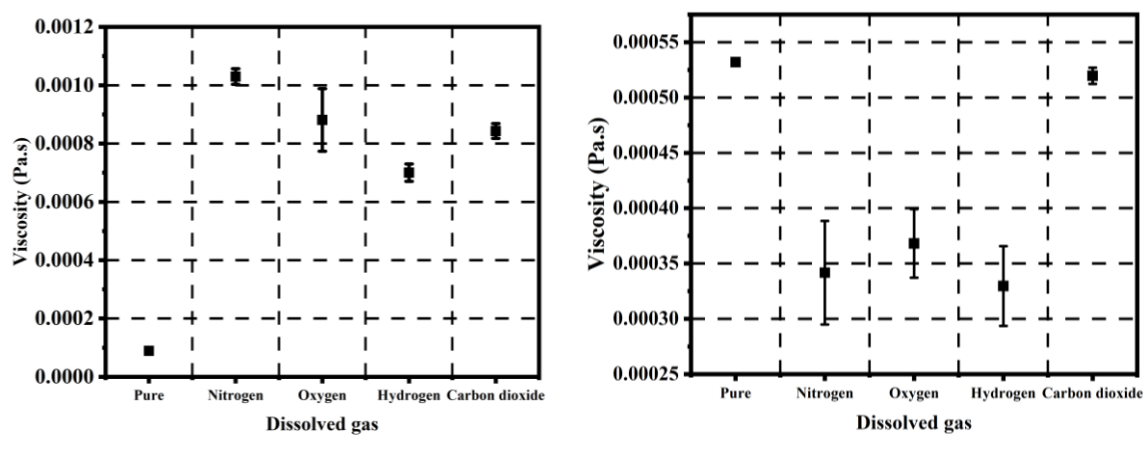


Figure 20. The viscosity of samples containing dissolved gases in water (left) and methanol (right).

Figure 20 demonstrates that the viscosity of the water-based sample increased significantly when nitrogen was dissolved, followed by oxygen and then carbon dioxide. The addition of hydrogen resulted in the smallest increase in viscosity. For the same weight fraction of dissolved gases, including nitrogen, oxygen, and carbon dioxide, it was observed that nitrogen and oxygen could form NBs within the water host medium. It was observed that, Figure 11, the density of these formed NBs was significantly higher than that of the gas in the gas phase and near the liquid phase. Consequently, these NBs may act as obstacles, hindering molecular movement and thereby increasing resistance to motion, which in turn increased viscosity. As depicted in Figure 11, the radius of the nitrogen-formed NB (40.36 Å) was larger than that of the oxygen-formed NBs (35.28 Å), further impacting the freedom of movement and resulting in the nitrogen nanobubble-containing water sample exhibiting higher viscosity than the oxygen-containing one. However, the viscosity of the hydrogen nanobubble-containing water system was lower than that of the carbon dioxide–water system, in which no nanobubbles were observed. As shown in Figure 11, the density of hydrogen NBs was lower than that of oxygen NBs, suggesting that NBs with higher densities

may exert a greater influence on flow behaviour than those with lower densities. Furthermore, variations in intermolecular interaction energies were observed upon dissolving the gases in the water-based samples, as illustrated in Figure 21, with the carbon dioxide–water system exhibiting a more negative interaction energy than the hydrogen–water system.

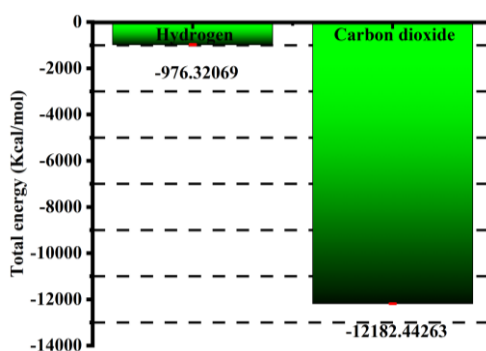


Figure 21. *The average of total energy between carbon dioxide and hydrogen molecules with water molecules.*

As Figure 20 illustrates, among methanol samples, the most significant reduction in viscosity was observed in the hydrogen and nitrogen systems, followed by the oxygen system, while the addition of carbon dioxide resulted in the smallest decrease in viscosity. Notably, nitrogen was found to form a NB within the methanol host liquid. However, when comparing the density of the formed NB in methanol (0.125 g/mL) as shown in Table 9 with those formed in water (0.354 g/mL) as shown in Figure 11, differences are observed between the two systems. Variations in intermolecular interaction energies are also observed among the investigated methanol based-mixtures, as shown in Figure 22, where the van der Waals energy differs between the studied systems.

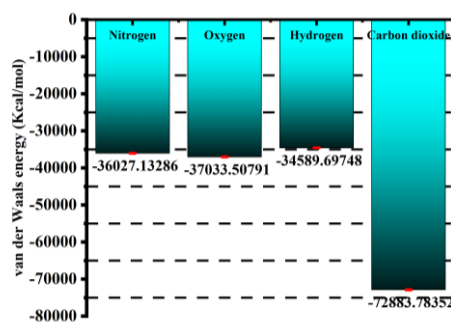


Figure 22. *The average of van der Waals energy of methanol mixtures.*

At 343.15 K, the viscosity of the nitrogen-water mixture was measured at 0.00053 Pa.s, while the nitrogen-methanol mixture at 323.15 K exhibited a viscosity of 0.00017 Pa.s. These findings indicate a decrease in viscosity compared to the viscosity of nitrogen samples at 298.15 K, as illustrated in Figure 20. Additionally, with the increase in temperature, the kinetic energy of fluid molecules intensifies, causing them to move more rapidly and disperse. Furthermore, at elevated temperatures, the density measurements for nitrogen samples in water and methanol were recorded as 0.81 and 0.63 g/ml, respectively.

4.3 Graphene-reinforced environment

4.3.1 NB nucleation and behaviour

Graphene–water and graphene–methanol nanofluids were modeled in cubic simulation boxes of dimensions 15 nm × 15 nm × 15 nm, each containing a 9.5 nm × 9.5 nm graphene sheet (G) composed of 3588 carbon atoms. For the graphene–water nanofluid, the system additionally included 2422 nitrogen molecules, 2120 oxygen molecules, 2422 hydrogen molecules, 1542 carbon dioxide molecules, and 98000 water molecules. Similarly, the graphene–methanol nanofluid system contained 2110 nitrogen molecules, 2120 hydrogen molecules, 1850 oxygen molecules, 1342 carbon dioxide molecules, and 48,000 methanol molecules. The prepared samples underwent relaxation and equilibration processes in different ensembles, including NPT for 1.7 ns and NVT for the same duration, to reach an

equilibrium state at 298.15 K and 1 atm. Subsequently, the simulations were extended for an additional 10 ns in the NVE ensemble to study the behavior of G, NBs and the thermophysical properties of the G-based NFs, employing a time step of 1 fs.

In G-water NF containing oxygen, the initial stage involves the adsorption of oxygen molecules onto the G surface, leading to the formation of nucleation sites (Figure 23a). Subsequently, these sites migrate and coalesce on the G surface, promoting the growth of NBs primarily at the edges of G, consequently inducing a gradual bending of the G structure (Figure 23b and c). The absorption process continues, and absorbed oxygen atoms on the lower surface migrate toward edges that are free of absorbed gas atoms (Figure 23d and 23e). Eventually, the oxygen-covered edges merge, and the oxygen atoms form a NB. This leads to a structure in which a NB core is surrounded by a graphene shell inside the water-based NF (Fig. 23f).

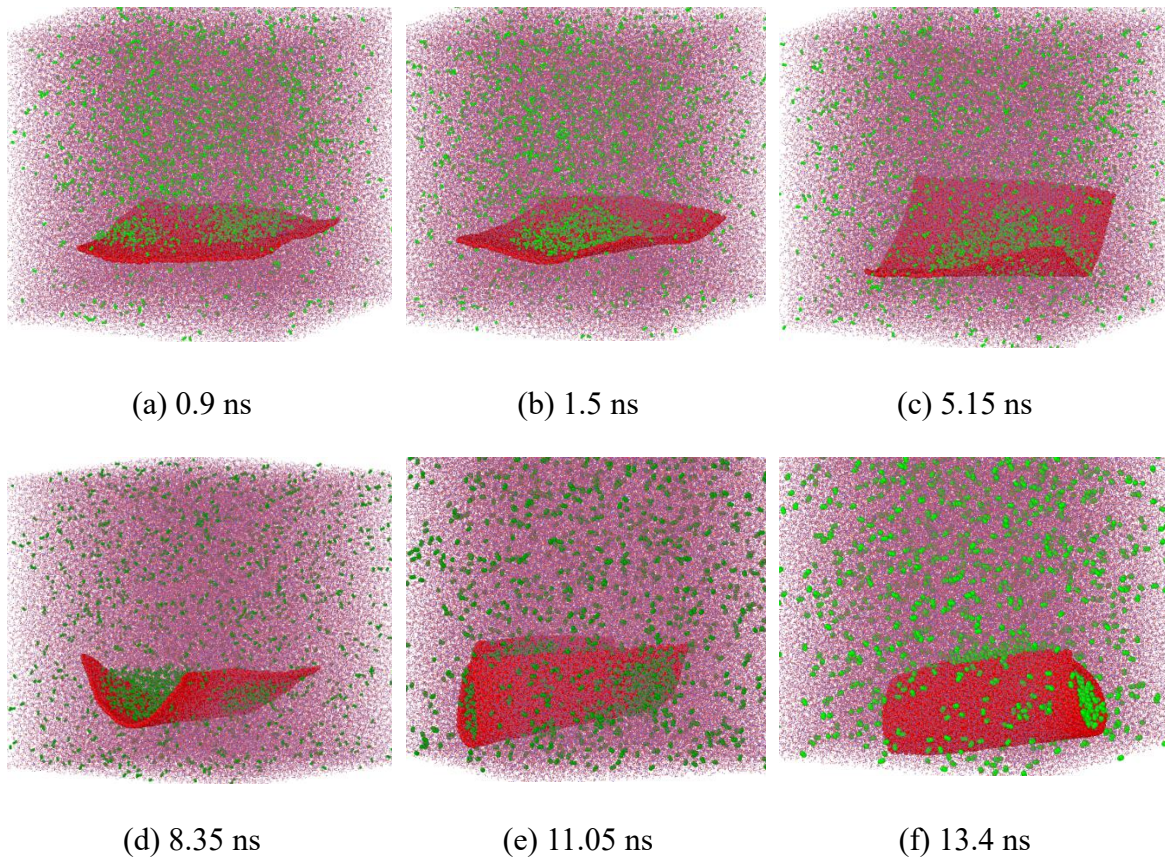


Figure 23. *Sequential snapshots illustrating the process of (a) initial site formation of oxygen (green) NBs on the G surface (red), (b) coalescence on the graphene surface, (c) movement of the formed NB to the edge of G, (d, e) adsorption of oxygen on the lower surface and migration to the unoccupied edge, and (f) encapsulation of the NB core by the G shell within the water NF.*

In nitrogen-water NF, NB nucleation occurs on both G surface and in bulk fluid (Figure 24a). Surface and bulk NBs merge, and nitrogen bulk NBs absorb into G from the unoccupied edge of G, converging with G surface NBs. This leads to a core-shell structure with a G shell encapsulating the NB core (Figure 24b-e). Notably, nitrogen/graphene-water NF contains both GNBs and bulk NBs (Figure 24f).

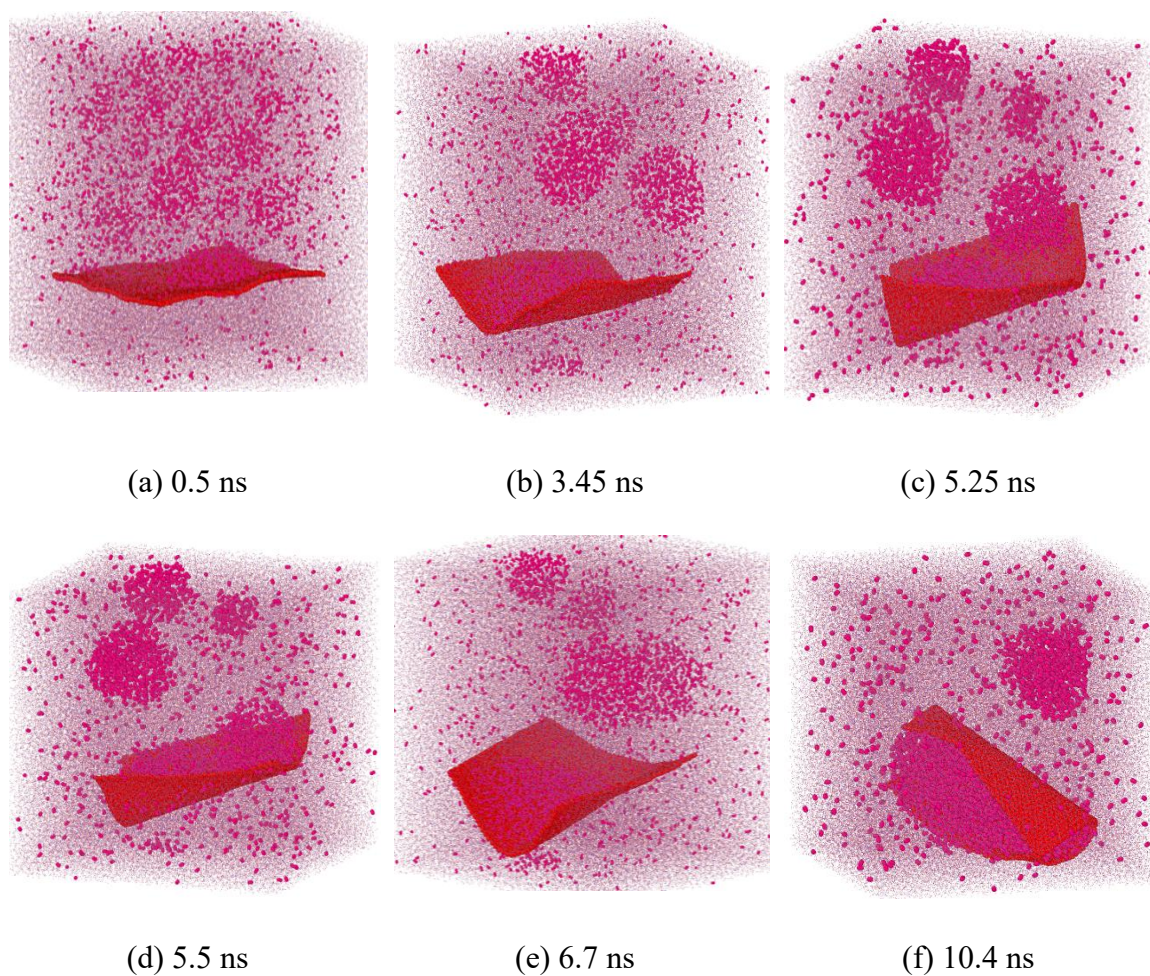


Figure 24. *Temporal snapshots illustrating the formation and behavior of nitrogen (pink) NBs in nitrogen/G-water NF over time.*

The process of GNB formation in the hydrogen sample is similar to that in the oxygen sample, involving the creation of a GNB (Figure 25a). However, the behaviour of carbon dioxide is distinct, as no NBs were observed on the surface or within the bulk host fluid. The G sheet remained unbent, and only some carbon dioxide atoms were absorbed on the surface of G without NB formation (Figure 25b).

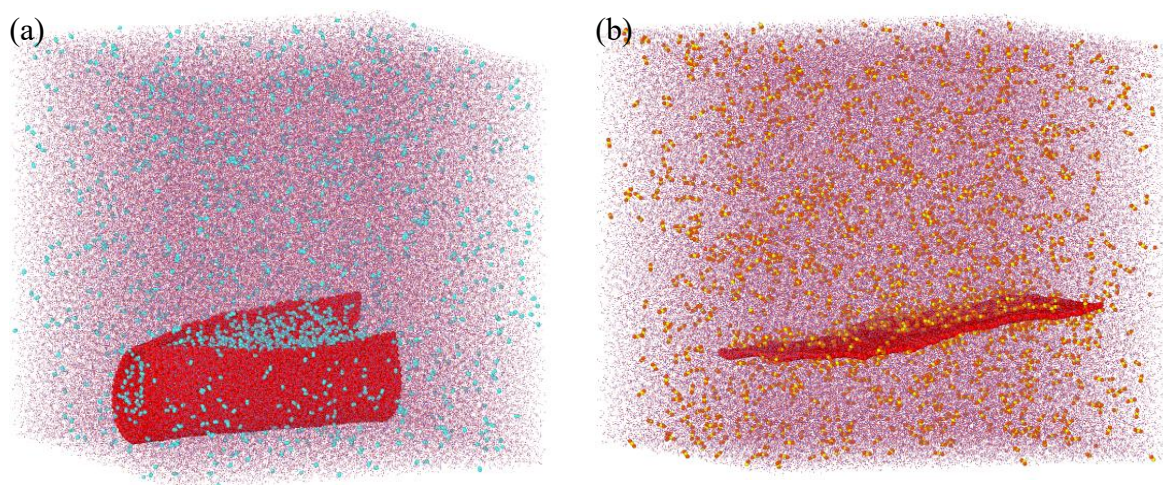


Figure 25. *Snapshot of the morphology of (a) hydrogen (cyan) and (b) carbon dioxide (brown) G-water NFs at 13.4 ns.*

To gain a deeper understanding of the observed intriguing behaviour during the formation of graphene NBs in water-based NFs, comparative investigation was conducted using equivalent samples prepared in methanol as the host fluid under identical conditions. This comparative approach provides valuable insights into the underlying mechanisms behind these behaviours, facilitating a better understanding of the formation process in different fluid environments.

As depicted in Figure 26b and c, the behaviour of nitrogen and hydrogen in methanol host fluids differs from that observed in water-based NFs. In these cases, nitrogen and hydrogen

molecules are not adsorbed onto the G surface, and the nucleation process occurs within the bulk of the host fluid. Furthermore, the formed nitrogen and hydrogen NBs within the host medium do not adsorb onto the graphene surface. An intriguing finding is related to the behaviour of oxygen-G/methanol, where no surface or bulk NBs were observed, contrasting the observations in water-based samples (Figure 26a). Similarly, the behaviour of dissolved carbon dioxide in the G-methanol NF mimicked that of oxygen, with no surface or bulk NBs observed (Figure 26d).

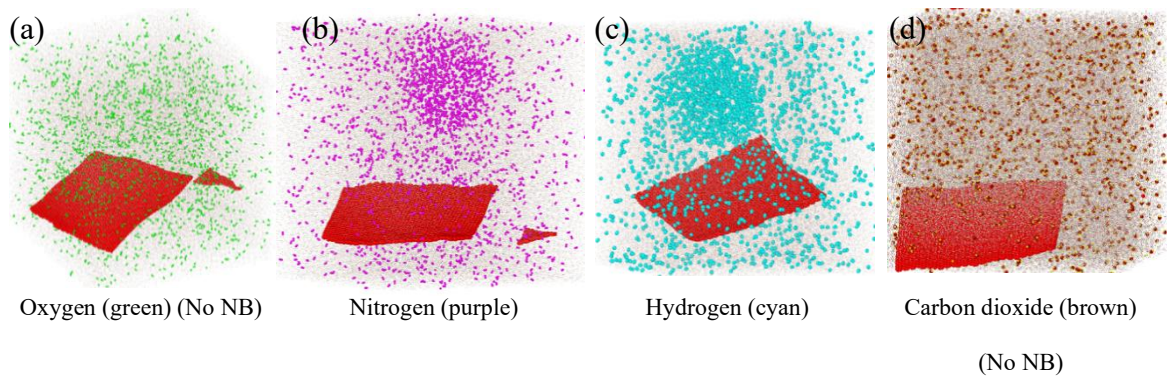


Figure 26. *At 13.4 ns, a visual representation captures the formation of NB in the G-methanol NF.*

Graphene's unique electronic structure, determined by its arrangement of π orbitals, forms a bonding network across its hexagonal lattice of carbon atoms. These π bonds, originating from the overlap of carbon atom 2p orbitals, create a widespread electron system, enabling rapid movement and high mobility. When graphene wrinkles or crumples, the bonding environment of the carbon atoms shifts. This change leads to the formation of non-covalent bonds with graphene and nearby molecules, ions, or particles [178, 179]. In water samples, the polar nature of water molecules, with a partial positive charge on hydrogen atoms and a partial negative charge on oxygen atoms, leads to strong hydrogen bonding between water molecules. This strong intermolecular force results in a high level of interaction among water molecules, leaving fewer interaction points available for other particles. On the other hand,

the intermolecular forces in methanol are weaker compared to water, allowing for interactions with other molecules as well. When G and gases are dispersed in water, strong water–water interactions limit their interaction with the surrounding medium, resulting in a significant molecular interaction between gas molecules and graphene. This promotes the adsorption of gas molecules onto the graphene surface in water. However, in the case of methanol, the weaker interactions between solvent molecules create more available interaction sites for dispersed species, which reduces the molecular interaction between gas molecules and G in methanol. As a result, gas molecules do not adsorb onto the G surface in methanol. Figure 27 illustrates the average total energy between oxygen, nitrogen, and hydrogen with G in water and methanol.

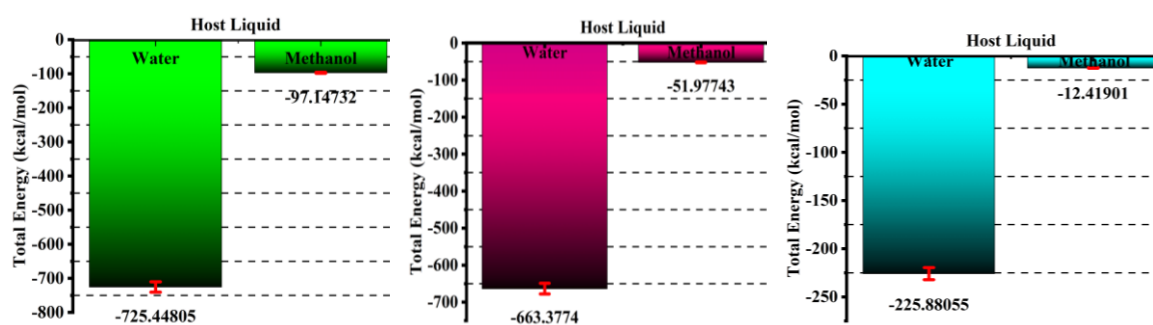


Figure 27. *The average of the total energy between oxygen (left), nitrogen (centre), and hydrogen (right) with G in water and methanol.*

To gain insights into the underlying mechanisms behind the observed behaviour in G-NFs containing dissolved gases, particularly nitrogen, which exhibited intriguing behaviour in both water and methanol-based fluids, a lower mass fraction of dissolved nitrogen, by scattering 605 molecules and 530 molecules in G-water and G-methanol NFs respectively, was investigated in graphene NFs. In the water-based sample, the lower mass fraction resulted in the absence of bulk nucleation, with only a small cluster of nitrogen gas atoms being absorbed onto the G surface (Figure 28). This surface cluster exhibited mobility but

eventually dissipated, indicating the absence of NBs in both the surface and bulk forms. Interestingly, in the methanol-based fluid, no nucleation occurred at all (Figure 29), emphasizing the influence of dissolved gas concentration on the nucleation process.

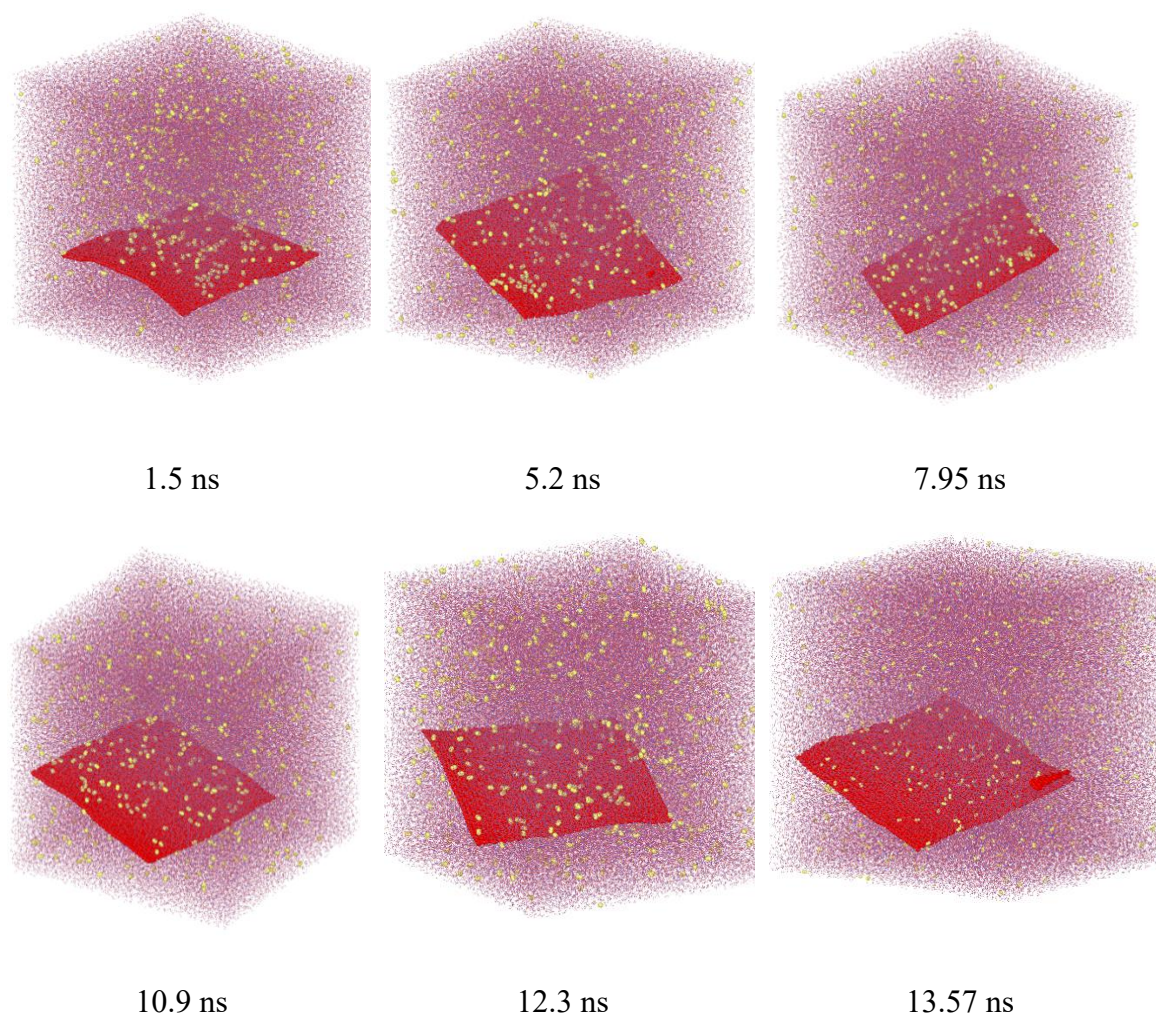


Figure 28. *Temporal evolution of nitrogen (yellow) cluster formation, movement, and disappearance with lower mass fractions of dissolved nitrogen gas within a G-water NF.*

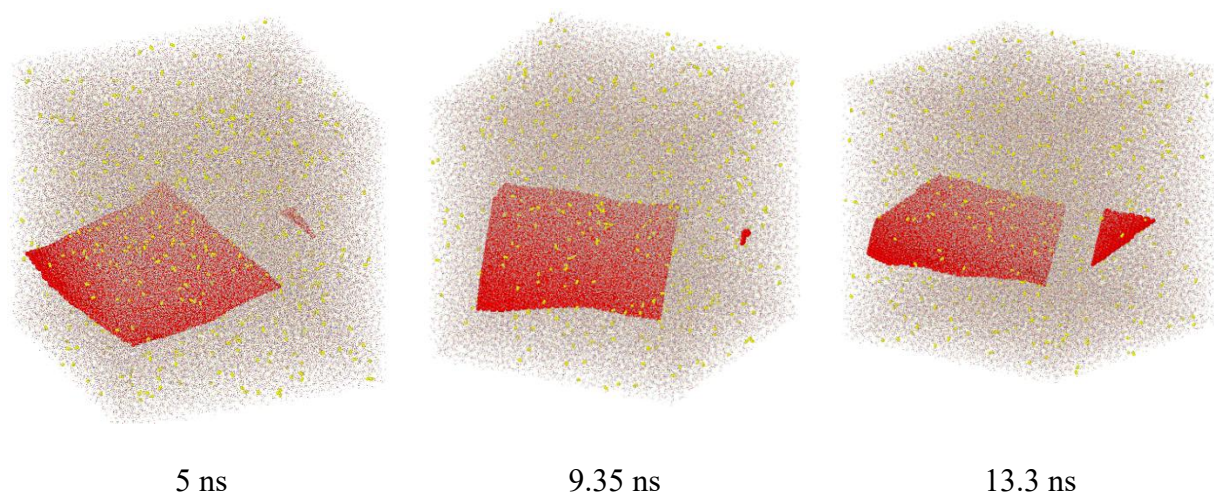


Figure 29. *Behaviour of dissolved nitrogen gas in G-methanol NF with lower mass fraction.*

The investigation of G behaviour in water-based fluids with various mass fraction of dissolved nitrogen gas revealed that, despite the formation of surface gas clusters at a lower mass fraction, no bending or deformation of the G surface was observed. Further analysis of the nitrogen behaviour on the G surface at higher mass fraction sample indicated that nitrogen gas atoms preferentially occupied the G edges. Nitrogen gas atoms were drawn together through intermolecular interactions [173, 175], acting in a manner similar to a bonding agent, which promoted their aggregation and bonding at the G edges (Figure 24). This mechanism may contribute to the stability of NBs formed on the G surface in the water-based NF.

4.3.2 Thermophysical properties

Figure 30 illustrates the viscosity of G-based NFs with dissolved gases in water and methanol. The results show that the inclusion of suspended G and dissolved gases, such as oxygen, nitrogen, carbon dioxide, and hydrogen, increases the viscosity of water NFs compared to the pure host liquids. Interestingly, in the case of methanol NFs, the dissolution

of nitrogen, hydrogen, oxygen, and G results in a reduction in viscosity as opposed to pure methanol. Notably, the addition of carbon dioxide along with graphene to methanol causes an increase in viscosity. These findings are consistent with earlier research indicating that the viscosity of water tends to rise upon the incorporation of graphene [128] and gas dissolution [9]. However, there is a distinction between water and methanol. Unlike water fluid, it has been observed that the dissolution of gas in methanol actually leads to a decrease in viscosity [177]. Similar to the water, the presence of graphene increases the viscosity of methanol [180]. Consequently, it can be inferred that, for a given mass fraction of the prepared additive, the viscosity of methanol NFs is significantly influenced by the specific type of dissolved gas. In water-based NFs incorporating graphene, the highest viscosity is achieved with nitrogen, followed by carbon dioxide, whereas the oxygen/G-water combination exhibits the lowest viscosity. In contrast, for methanol-based NFs containing G, the sample with carbon dioxide and G exhibits the highest viscosity, while the presence of oxygen molecules results in the lowest viscosity.

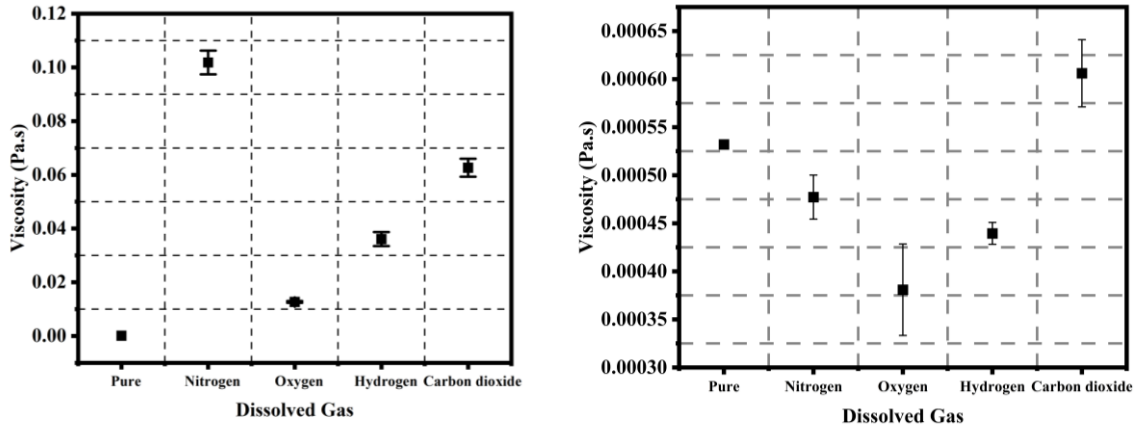


Figure 30. *Viscosity of G-water/scattered gas (left) and G-methanol/dissolved gas (right) NFs.*

The viscosity of NFs may be influenced by molecular motion and intermolecular interactions within the system. The presence of dispersed phases may affect the movement of molecules in the base fluid, which may contribute to changes in viscosity. In the nitrogen–G water system, as shown in Figure 24, the existence of GNBs, along with bulk NBs formed in the host liquid, suggests that bulk NBs may act as obstacles to molecular motion, resulting in increased resistance to flow and higher viscosity. Moreover, variations in interaction energy were observed among the systems without bulk nanobubbles, including the CO₂ system (without nanobubbles) and the O₂ and H₂ systems containing GNBs, as shown in Figure 31, with the water–CO₂ system exhibiting the most negative total interaction energy among these systems.

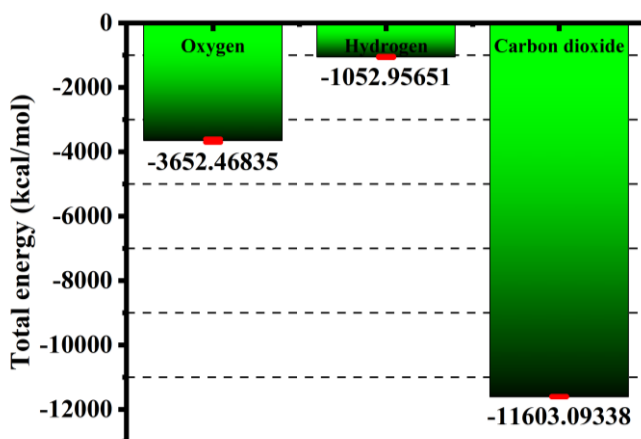


Figure 31. *The average of total energy between dissolved gases and water molecules.*

The joining of G edges may be influenced by intermolecular interactions arising from dissolved gases, as previously discussed. The strength of these interactions depends on the type of molecules and is reflected in the interaction coefficients listed in Table 4. Examining the morphology of suspended G in water with dissolved oxygen and hydrogen provides insights into the behaviour of the absorbed molecules and their impact on the joining of G

edges (Figure 23). The intermolecular interactions associated with absorbed oxygen molecules may promote a more complete joining of G edges. In contrast, weaker interactions in the hydrogen case may result in partial joining of G edges (Figure 25), with one edge remaining exposed to the surrounding environment. This difference may affect the extent of interaction between fluid molecules and the G surface in the hydrogen–G/water and oxygen–G/water systems. The hydrogen–G/water system shows higher viscosity compared to the oxygen-containing system.

The viscosity of the carbon dioxide/G-methanol NF was found to be the highest, followed by the nitrogen/G-methanol NF, while the oxygen/G-methanol sample exhibited the lowest viscosity. To further examine the effect of dissolved gases, additional simulations were performed for non-bubbled methanol systems with identical mass fractions containing only oxygen and carbon dioxide. This analysis shows reductions of 30.82% and 2.44% in viscosity upon inclusion of oxygen and carbon dioxide, respectively. The average total interaction energy between methanol molecules and the dissolved gases, presented in Table 10, indicates more negative values for the CO₂-containing system compared with the oxygen-containing system, reflecting differences in intermolecular interactions among the systems. The results highlight variations in both viscosity and interaction energy depending on the type of dissolved gas present.

Table 10. *The average total energy between dissolved gas and methanol molecules.*

Dissolved gas	Total energy (Kcal/mol)
Oxygen	- 4188.91
Carbon dioxide	- 13158.47

In the nitrogen- and hydrogen/G-methanol samples, NB formation is observed, whereas no NBs are detected in the oxygen-containing system. The nitrogen and hydrogen systems also exhibit higher viscosity compared with the oxygen system (Figure 30). In parallel, differences in interaction energies are observed across the G-methanol systems, with the hydrogen–methanol interaction energy having lower magnitude than in the nitrogen-containing system, while the carbon dioxide system shows more negative van der Waals interaction energies compared with the oxygen system (Figure 32).

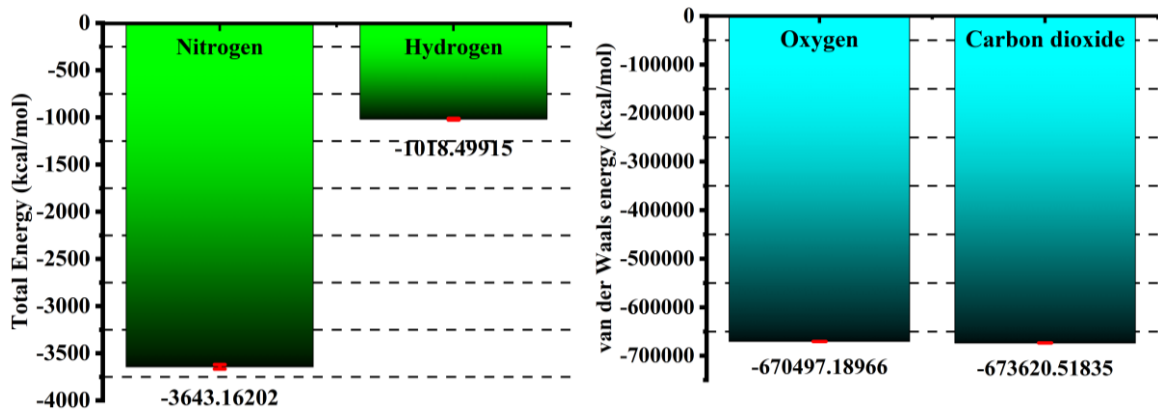


Figure 32. *The average total energy between dissolved gas and methanol molecules in bubbled (left) and the average van der Waals energy of non-bubbled methanol NFs.*

The influence of a lower mass fraction of dissolved nitrogen in G-based NFs on viscosity was investigated. Table 11 presents the influence of mass fraction of dissolved nitrogen gas on the viscosity of G-based water and methanol-based NFs.

Table 11. *The viscosity (Pa.s) of G-water and G-methanol NFs with varying mass fractions of scattered nitrogen gas.*

Host liquid	Lower mass fraction	Higher mass fraction
Water	0.10097	0.10183
Methanol	0.000637	0.000576

As indicated in Table 11, an augmentation in the mass fraction of dissolved gas yields a rise in the viscosity of water-based NFs and a decline in methanol-based NFs. This trend mirrors previous findings observed for both water [9] and methanol [181] NFs. Furthermore, variations in van der Waals energy were observed with changes in the dissolved gas content, as illustrated in Figure 33. The results suggest that increasing the mass fraction of dissolved nitrogen gas may contribute to an increase in the van der Waals energy of the water-based NF and a decrease in the van der Waals energy of the methanol-based NF.

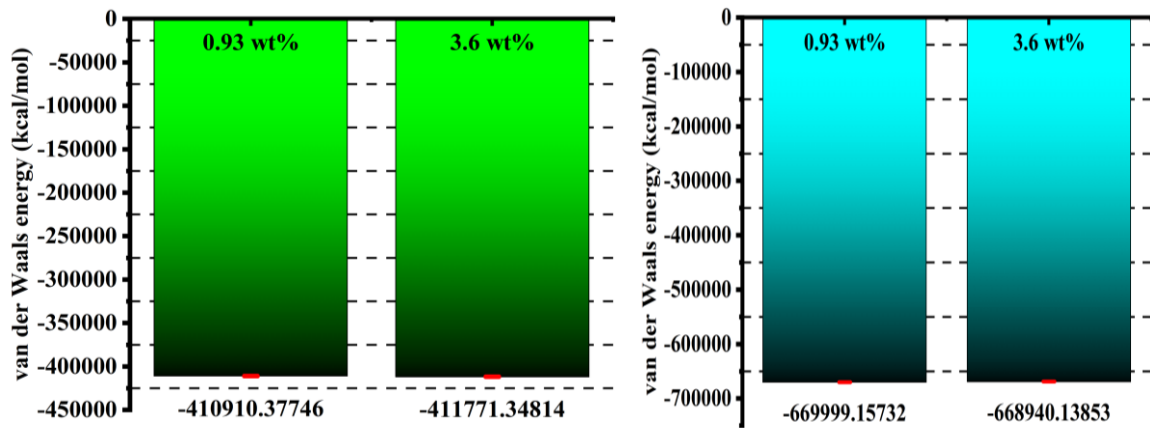


Figure 33. *The van der Waals energy of nitrogen/G-water NFs (left) and nitrogen/G-methanol NFs (right) at different mass fractions of scattered gas.*

Heat capacity is a fundamental property that quantifies the amount of heat energy a substance can absorb to raise its temperature by 1 degree Celsius. In energy applications, efficient heat transfer is of paramount importance. One way to optimise the heat transfer performance of NFs is by modifying their heat capacity. By accurately calculating the heat capacity of NFs using appropriate equations and methodologies, it becomes possible to assess their ability to store and release thermal energy effectively. To quantify the heat storage capacity, the specific heat capacity at constant volume was computed using Eq. 3.35. Figure 34 illustrates the ratio of specific heat capacities between G-based NFs with dissolved gases in water and methanol to the specific heat capacities of their corresponding pure host liquids. The results highlight that incorporating G and dissolved gases in water-based NFs leads to a decrease in their specific heat capacity, corroborating prior studies [128].

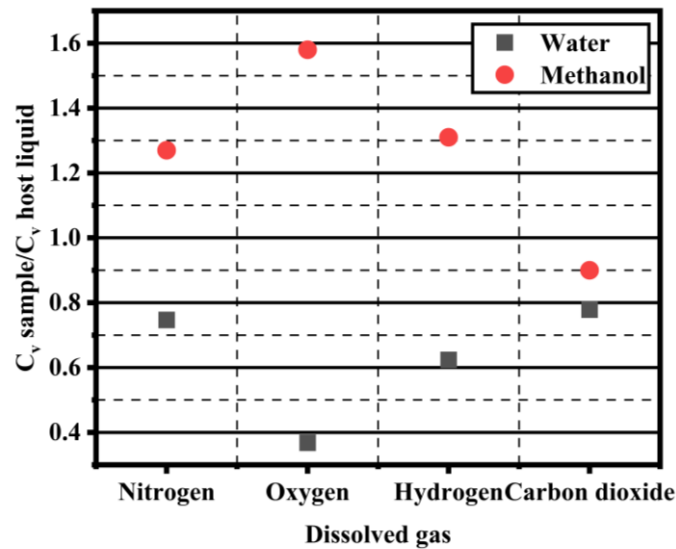


Figure 34. *Specific heat capacity of samples compared to the host mediums.*

Water exhibits a high heat capacity attributed to its distinctive molecular structure and the presence of hydrogen bonding, allowing it to absorb and retain a considerable amount of heat energy. However, with the introduction of G and gases to form water NFs, the overall heat capacity diminishes as graphene possesses a lower specific heat capacity compared to

water. This decline can be attributed to the altered molecular interactions and the influence of G on the thermal properties of the NFs. Consequently, the specific heat capacity of the NFs is influenced by both the intrinsic properties of the host liquid and the presence of G and dissolved gases. The oxygen sample exhibited the largest reduction in heat capacity, while the carbon dioxide and nitrogen samples displayed comparatively smaller reductions compared to the oxygen-G/water NF. The Radial Distribution Function (RDF) provides valuable insights into the spatial distribution of particles and their probabilities at varying distances from a reference particle that can be calculated by using Eq. 3.34.

Graphene can enhance heat transfer within the system, which directly influences the overall energy and heat capacity, Eq. 3.35. Increased impurities surrounding graphene may lead to a decrease in energy distribution within the system. Figure 35 visually represents the RDF between the G nanosheet and dissolved gases, in NFs with the same mass fraction of dissolved gases, with the oxygen sample showing a higher peak, indicating a greater number of oxygen atoms surrounding the dispersed G in water. This disparity in peak heights suggests variations in the order structure of the systems, which can explain the observed differences in specific heat capacity among the samples. When oxygen is dissolved in water, it introduces additional complexity to the system by forming a gas-filled layer around G, which disrupts the heat transfer process and leads to a decrease in heat capacity. In the nitrogen NF, this layer exists to a lesser extent compared to the oxygen sample, resulting in a less pronounced effect on the heat capacity. As a result, the specific heat capacity of the nitrogen NF is higher than that of the oxygen NF. In the carbon dioxide sample, the G nanosheet remains relatively free from an extensive gas layer, allowing for a smoother and more efficient heat transfer process. This absence of a significant gas layer contributes to a higher heat capacity compared to the nitrogen sample. Therefore, the observed differences

in heat capacity can be attributed to the variations in the order structure of the samples induced by the presence of dissolved gases surrounding the graphene nanosheet.

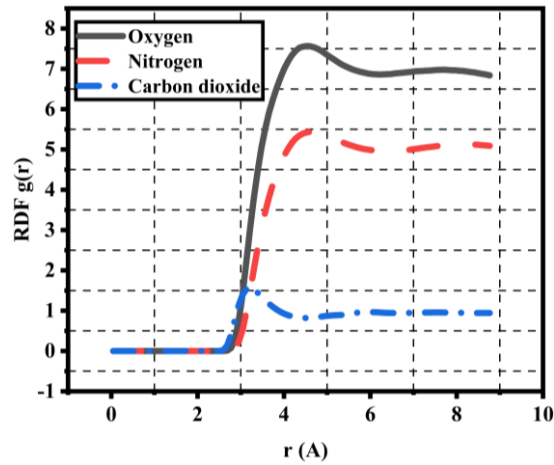


Figure 35. The radial distribution function (RDF) of the same mass fraction dissolved gas in water samples with G nanosheet.

In contrast to water-based NFs, where the addition of G and dissolved gases decreases the specific heat capacity, the specific heat capacity of methanol host liquids increases with addition of nitrogen, oxygen, and hydrogen compared to pure methanol. This difference in heat capacity between water and methanol can be attributed to their distinct intermolecular interactions. The enhancement of heat capacity in NFs can be explained by three mechanisms [182]. Firstly, NPs have a higher heat capacity compared to their bulk counterparts due to the discretization of the phonon spectra and the modification of the phonon density of states. Secondly, the high surface area per unit mass of NPs induces an increase in the interfacial thermal resistance (ITR) between the NPs and the surrounding fluid molecules. This increase in ITR acts as additional thermal storage. Lastly, the presence of a solid-like layer formed by the nanolayering of liquid molecules around the NPs enhances the specific heat capacity due to the smaller intermolecular spacing compared to the bare fluid. As discussed earlier, methanol provides more interaction sites for the added

nanomaterials, resulting in increased solid-liquid interactions. Furthermore, it has been demonstrated that NFs characterized by weak atomic bonding at the particle-fluid interface exhibit high thermal resistance, which could explain the enhanced specific heat capacity observed in the methanol-based fluid.

The introduction of oxygen gas into the G-methanol NF produced the most notable enhancement in specific heat capacity, followed by the hydrogen addition. In the absence of NBs, the intermolecular forces between oxygen molecules and methanol were comparatively weaker when contrasted with the interactions between carbon dioxide and methanol, Table 10, possibly allowing greater mobility of oxygen molecules within the solution. This augmented molecular mobility could lead to heightened collision frequency and interactions between molecules. In the G-methanol sample containing NBs, hydrogen gas has a lower molecular weight, which promotes faster molecular motion. The enhanced molecular motion of hydrogen gas molecules allows them to effectively participate in heat transfer processes, contributing to the overall improvement in specific heat capacity. Moreover, the presence of NBs in the G-methanol NFs leads to higher specific heat capacity compared to non-bubbled carbon dioxide sample. NBs create additional interfaces between the gas phase and the liquid phase, increasing the interfacial thermal resistance. This results in a higher specific heat capacity in nano-bubbled G-methanol NFs. The hydrogen and nitrogen samples, where NBs were formed, exhibit a higher improvement in specific heat capacity than carbon dioxide sample due to the presence of these additional interfaces. However, it is worth noting that oxygen, despite not forming NBs, may still contribute to enhanced intermolecular interactions resulting in improvement in specific heat capacity. This underscores the influence of the dissolved gas type on the specific heat capacity of the nanofluids and indicates that molecular-level interactions may contribute to the observed differences. By examining the specific heat capacity of NFs at different mass fractions, a comprehensive

understanding of the heat transfer behaviour in these samples was obtained. Table 12 uncovers a fascinating relationship between the mass fraction of dissolved nitrogen in water-based and methanol-based GNFs. Notably, the ratio of specific heat capacity exhibits distinct trends with increasing mass fraction, depending on the solvent. In water-based NFs, an increase in the mass fraction of dissolved gas leads to a decrease in specific heat capacity, while the opposite trend is observed in methanol-based NFs.

Table 12. *The ratio of specific heat capacity between graphene-water and graphene-methanol nanofluids, relative to their respective pure fluids, for different weight fractions of dissolved gas.*

Nanofluid based liquid	Lower weight fraction	Higher weight fraction
Water	1.09	0.747
Methanol	1.13	1.27

The remarkable thermal conductivity of G, owing to its unique lattice structure, facilitates enhanced heat transfer when introduced into a fluid. This augmentation in heat transfer efficiency enables the fluid to proficiently absorb and disseminate thermal energy, culminating in an elevation of heat capacity. Furthermore, the substantial surface area relative to graphene's mass creates an abundance of intermolecular interaction sites within the fluid. These interactions bolster energy absorption and storage, thereby contributing to an elevated heat capacity. In water-based NFs, an intriguing observation arises while manipulating the mass fraction of dissolved gas. Elevated fractions of dissolved gas leads to the formation of additional gas layers around the graphene, as demonstrated by the RDF peak in Figure 36. Additionally, the creation of graphene nanobubble in water-based NF, resulting from higher gas mass fractions, leads to the folding of G. This folding diminishes interaction sites, subsequently leading to reduced heat capacity. Conversely, in methanol-based NFs, an escalation in the dissolved gas mass fraction induces the formation of bulk

NB. Notably, unlike water samples, this NB remains distanced from the G sheet in methanol. This spatial configuration diminishes the likelihood of gas atoms existing around the G in methanol-based NF, RDF peak in Figure 36. The outcome is an increased heat capacity of G-methanol NFs as the dissolved gas mass fraction is augmented.

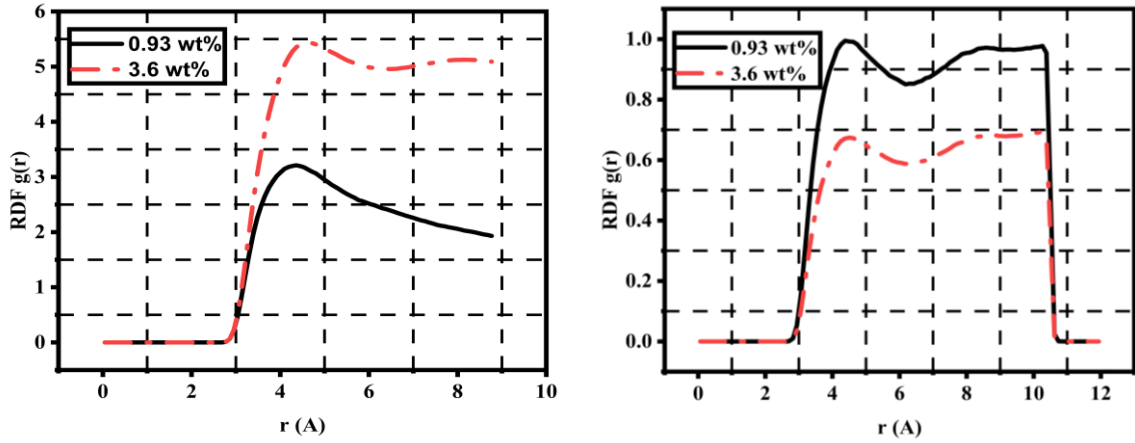


Figure 36. The radial distribution function (RDF) of the different mass fraction of dissolved nitrogen gas in water (left) and methanol (right) NFs with G nanosheet.

4.4 CO₂ hydrate kinetics

4.4.1 Effects of NB type

In the development of carbon capture, utilization, and storage (CCUS) technologies, the formation of CO₂ hydrates represents a promising approach for long-term CO₂ sequestration. CO₂ hydrate is a non-stoichiometric, ice-like crystalline compound formed under conditions of high pressure and low temperature, in which CO₂ molecules are trapped within a hydrogen-bonded network of water molecules. Among the various hydrate structures, the most prevalent is structure I (sI) CO₂ hydrate. Each unit cell of sI hydrate contains two types of cavities: six large cages ($6 \times 6^2 5^{12}$) and two small cages (2×5^{12}). These cages, stabilized by the water lattice, act as hosts for CO₂ guest molecules. Given the molecular size of CO₂ (approximately 5.12 Å), it can be accommodated not only in the large ($5^{12} 6^2$) and small (5^{12})

cages of the sI hydrate but also in the small cages of structure II (sII), the small and medium ($4^35^66^3$) cages of structure H (sH), and the small cages in semi-clathrate hydrates [23, 183].

To investigate the influence of NBs on the hydrate formation process, a CO₂–water solution was prepared by randomly distributing 7015 water molecules and 1220 CO₂ molecules within a simulation cell measuring $6.8 \times 6.03 \times 7.3$ nm. A hydrate seed, constructed as a $2 \times 5 \times 6$ -unit cell slab, was positioned at the center of the simulation box. The CO₂–water solution was subsequently placed on both sides of the hydrate seed, forming the surrounding solution phase. NBs containing equal mole fractions of four gases, CO₂, N₂, O₂, and H₂, were then incorporated into the CO₂–water system to establish the initial configuration of the nanobubble-enhanced model, as illustrated in Figure 37. Each sample was equilibrated under the NVT ensemble for 40 picoseconds (ps) with a 1 fs timestep, including the hydrate seeds. Due to the memory effect, these seeds serve as pre-nucleation sites that accelerate hydrate formation and growth. The memory effect refers to the phenomenon whereby gas hydrates nucleate more readily or rapidly in water with a prior history of hydrate formation compared to fresh water without such history [184]. Thus, even if hydrate structures are disrupted during the NVT equilibration, the presence of seeds continues to facilitate hydrate formation, allowing researchers to effectively study the influence of nano additives on hydrate nucleation and growth. Subsequently, samples were subjected to the NPT ensemble under desired thermodynamic conditions for at least 85 ns to investigate the effects of different types of NBs, as well as the combined influences of NBs with temperature and pressure on clathrate hydrate formation and growth.

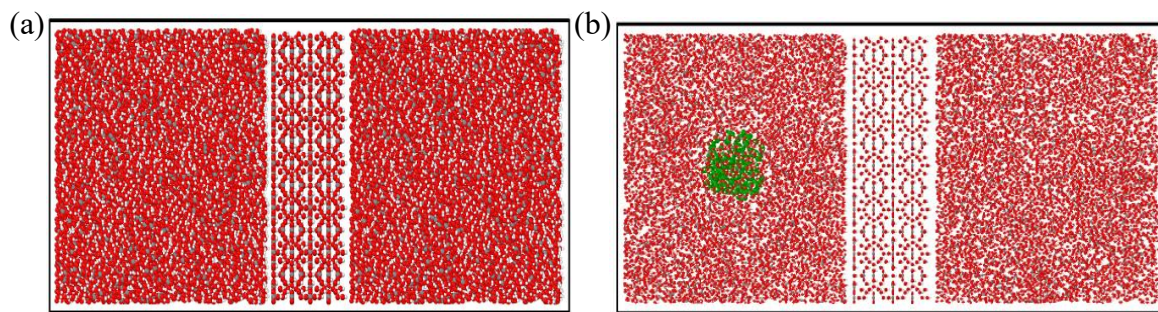


Figure 37. *Initial configuration of (a) a non-nanobubble and (b) a nanobubble-containing water-carbon dioxide sample, including a hydrate seed.*

The number of the two dominant formed cages, 5^{12} and 6^25^{12} , along with the total number of these cages during the initial stage at 28.35 ns is shown in Figure 38a for the water-gas sample without a NB (WG), as well as for samples containing NBs of carbon dioxide (CDNB), oxygen (ONB), nitrogen (NNB), and hydrogen (HNB) at 2MPa and 260 K. The temporal evolution of the 5^{12} cages, 6^25^{12} cages, and the total number of formed cages over time is also presented in Figures 38b-d, respectively. As illustrated in Figure 38d, by 85 ns, all nanobubbled samples exhibited a higher total number of formed cages compared to the non-nanobubbled sample, with the HNB sample showing the highest overall formation, followed by NNB, ONB, and CDNB. A closer analysis of Figure 38d reveals that the enhancement in cage formation due to ONB, NNB, and HNB emerges earlier, whereas the impact of CDNB becomes pronounced only after approximately 60 ns. This delayed response suggests a lag in the structural influence of CDNB on hydrate growth. Further insights from Figure 38a, focusing on the initial stage at 28.35 ns, shows that the presence of NBs, including CDNB, promotes the formation of large cages (6^25^{12}). However, the number of small cages (5^{12}) in the CDNB system is notably lower compared to the NNB and HNB samples.

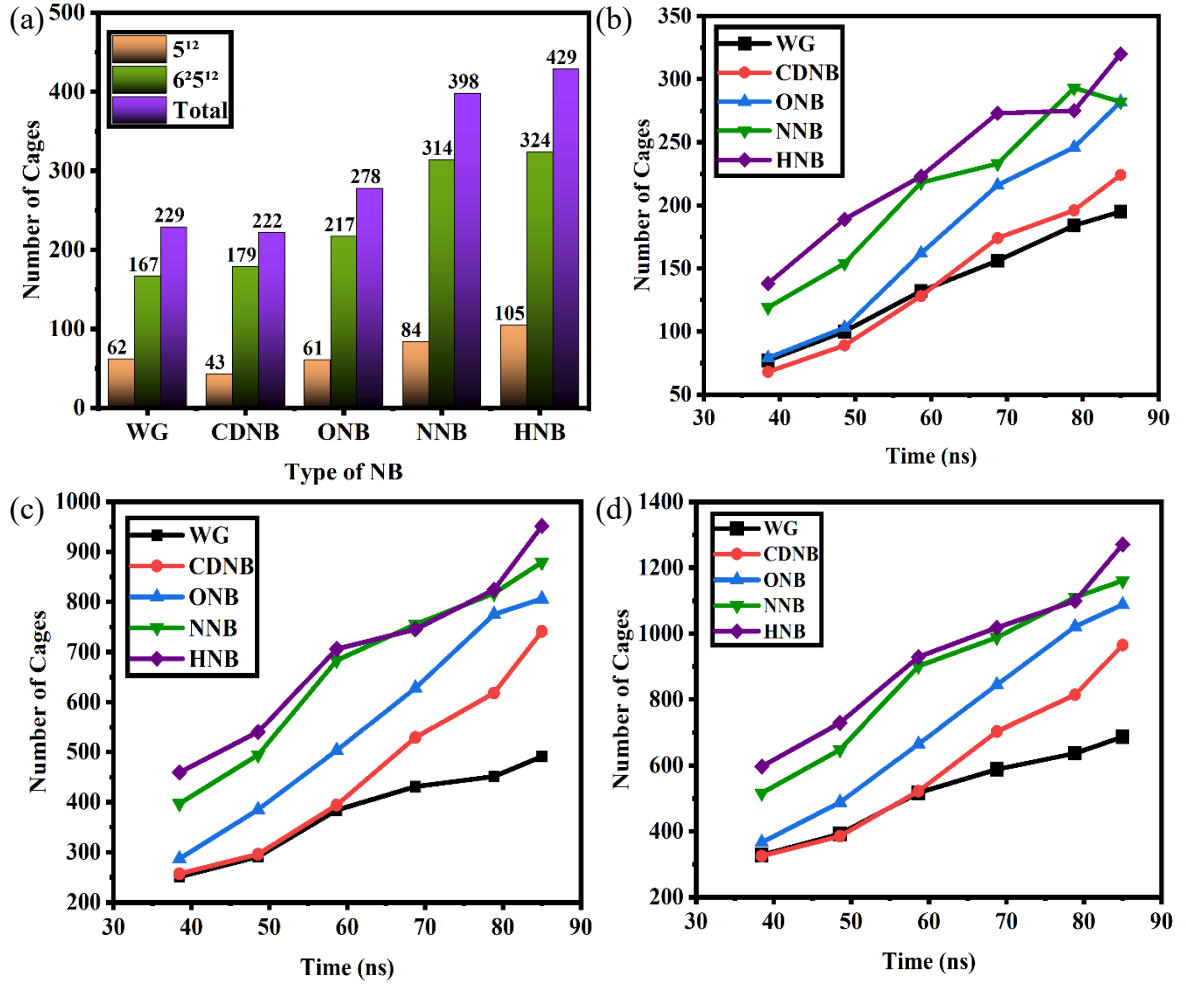


Figure 38. Number of formed hydrate cages: (a) small, large, and total cages at 28.35 ns; (b) small cages, (c) large cages, and (d) total cages over the course of 85 ns at 2 MPa and 260 K.

Analysis of non-nanobubbled aqueous CO₂ samples reveals that, over time, CO₂ molecules tend to self-associate within the bulk solution, forming dispersed molecular clusters. As illustrated in Figure 39a, three distinct clusters are observed at 28.35 ns. These clusters appear to induce a local reorganization of surrounding water molecules into more ordered hydrogen-bonding networks, thereby facilitating the formation of clathrate cages. This observation supports the hypothesis that molecular aggregation enhances local structural order and plays a key role in initiating phase transformation. From the perspective of several nucleation theories, the formation of CO₂ hydrate is driven by the ordered arrangement of water molecules and the

localized ordering of gas molecules. This concept is specifically emphasized in both the labile cluster nucleation hypothesis and the local structuring nucleation theory. MD studies on CO₂ hydrate formation have introduced the blob nucleation mechanism, which proposes that guest molecules initially concentrate into dense regions (blobs) that are in equilibrium with the surrounding solution. These blobs then induce the formation of water cages, giving rise to a clathrate nucleus. This mechanism integrates key elements of both the local structuring and labile cluster hypotheses [23, 185].

In contrast, hydrogen-, oxygen-, and nitrogen-nanobubbled samples show no evidence of pure CO₂ clustering in the bulk solution. Instead, due to the pronounced hydrophobicity of these gases, CO₂ molecules preferentially migrate toward and adsorb onto the NB surfaces, as depicted in Figure 39b-e. These hydrophobic surfaces act as accelerator spots that promote concentration gradients and enhance the kinetics of clathrate formation. More importantly, their presence not only drives CO₂ accumulation at well-defined interfacial regions but also reduces the likelihood of random, spontaneous nucleation events in the bulk solution. By guiding CO₂ molecules toward energetically favorable aggregation sites, the system minimizes stochasticity in both spatial and temporal aspects of nucleation, resulting in a more directed and efficient clathrate formation process. Interestingly, CO₂-nanobubbled (CDNB) samples exhibit a hybrid behaviour. In addition to CO₂ molecules adsorbed at the nanobubble interfaces, dispersed CO₂ clusters are also observed within the bulk solution, as shown in Figure 39c. This dual behaviour is likely due to CO₂'s relatively lower hydrophobicity compared to hydrogen, nitrogen, and oxygen, which allows more CO₂ molecules to remain dissolved in the aqueous phase than in other nanobubble-containing samples. As illustrated in Figure 38a, the number of large cages formed shows a decreasing trend from HNB to NNB, followed by ONB, and finally CDNB. This pattern can be attributed to differences in the hydrophobicity of the NB gases. Hydrogen and nitrogen, being more hydrophobic than oxygen and carbon dioxide, drive a greater number

of CO₂ molecules to rapidly adsorb onto their NB surfaces during the early stages. This adsorption generates a steeper concentration gradient and promotes the formation of larger CO₂-rich blobs, which enhance local water structuring and facilitate clathrate formation. In comparison to the WG sample, the CDNB sample allows a portion of CO₂ molecules to adsorb onto the nanobubble surfaces. As a result, more water molecules remain available in the bulk solution for the remaining CO₂, which generally tends to form larger hydrate cages. This leads to a higher number of large cages in the CDNB sample compared to the WG sample.

At the early stage of the hydration process, as illustrated in Figure 38a, the number of small cages formed in the HNB and NNB samples is significantly higher than in the other samples, suggesting that additional mechanisms may also contribute to hydrate formation. As previously discussed, dissolved CO₂ molecules tend to adsorb onto the surfaces of these NBs. However, due to the small molecular size of hydrogen and nitrogen, a limited number of these gas molecules can diffuse, or "breathe", into the solution from the NB core. The presence of small-molecule gases such as H₂ and N₂ has been reported in an experimental study to significantly enhance the CO₂ hydrate formation process. Specifically, hydrogen was found to influence the initial morphology of CO₂ hydrate films. Raman spectroscopy results further revealed that the presence of hydrogen produced a looser hydrate film structure, which improved mass transfer and supported the continued growth of the hydrate layer. Similarly, nitrogen has been shown to play a comparable role; however, its participation in mixed CO₂/N₂ hydrate formation induces adaptive changes in the film's growth behaviour [186]. A similarly loose hydrate structure has also been reported in molecular dynamics simulations of CO₂ hydrates confined within porous media [187, 188]. In addition, the presence of small guest molecules such as H₂ and N₂ promotes the formation of small hydrate cages during the early stages of hydrate growth. In contrast, this mechanism is absent in CDNB samples. In the CDNB system, hydrate formation initially favors the development and growth of larger cages. However, as the system

becomes more structurally organized and thermodynamically favorable over time, the formation of smaller cages is progressively enhanced. This delayed but sustained nucleation ultimately leads to a continuous increase in the total number of hydrate cages formed in the CDNB sample than WG sample.

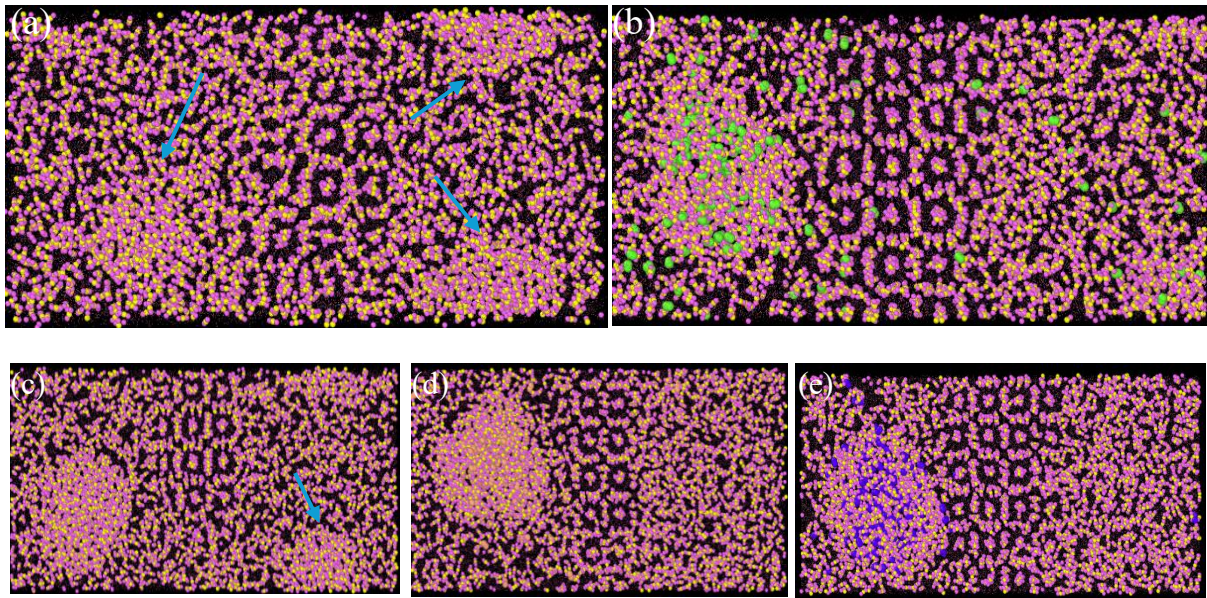


Figure 39. Snapshots of (a) WG, (b) HNB with diffused hydrogen atoms (green) in the solution, (c) CDNB, (d) ONB, and (e) NNB samples at 28.35 ns at 2 MPa and 260 K.

The four-body order parameter, commonly denoted as F_4 , is a valuable tool in MD simulations for characterizing the local structural arrangement of water molecules, particularly during clathrate hydrate formation. It is especially effective in distinguishing between water molecules that participate in the formation of hydrate cages and those that remain in bulk liquid water. By quantifying the degree of local structural ordering within the water network, the F_4 parameter offers important insights into the nucleation and growth mechanisms of CO_2 hydrates. As a classical order parameter, F_4 is defined by the following equation, and its theoretical values range from approximately -0.4 to 0.7 . In this range, typical values for the ice, liquid water, and hydrate phases are around -0.4 , -0.04 , and 0.7 , respectively [183].

$$F_4 = \frac{1}{n} \sum_{i=1}^n \cos 3\varphi_i \quad (4.3)$$

where φ_i represents the dihedral angle formed between the oxygen atoms of two adjacent water molecules and their outermost hydrogen atoms, while n denotes the number of oxygen atoms pairs between H₂O molecules within a distance of 0.35 nm.

Figure 40 illustrates the F_4 parameter for the water–gas sample without NBs and for samples containing various NBs. Over time, the F_4 values of the nanobubbled samples consistently exceeded those of the pure water–gas sample, indicating that NBs promote the nucleation and growth of CO₂ hydrate at 260 K and 2 MPa. Notably, from the initial stage at 28.35 ns, samples containing the more hydrophobic diatomic gases exhibited higher F_4 values compared to the non-nanobubbled sample, suggesting enhanced local structural ordering around water molecules. A closer examination reveals that during the initial and intermediate stages, the F_4 parameter of the non-nanobubbled sample remained higher than that of the CDNB sample. This indicates that the presence of CDNB initially inhibits hydrate nucleation, likely due to the reduced formation of small 5¹² cages in this sample, as previously discussed. However, as time progresses and structural ordering improves, the conditions become more favorable for the formation of small cages. Consequently, the CDNB system overcomes its initial lag and ultimately enhances CO₂ hydrate growth.

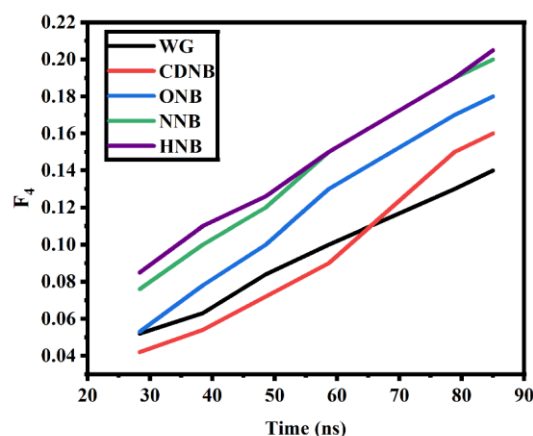


Figure 40. *Four-order structural parameter of various samples.*

Potential energy is commonly used as an indicator of structural transitions, such as hydrate growth or dissociation. Under constant temperature conditions, the average kinetic energy of the sample remains stable. Consequently, changes in the total energy primarily reflect variations in potential energy, which arise from interatomic interactions, including van der Waals forces, electrostatic interactions, and hydrogen bonding. During hydrate formation, water and gas molecules reorganize into an energetically favorable, crystalline structure composed of host water cages enclosing guest gas molecules. This transition to a more ordered phase is exothermic, leading to a net decrease in the sample's potential energy. As a result, a downward trend in potential energy over time is often interpreted as a clear signature of hydrate nucleation and growth, indicating increased structural stabilization of the sample [189].

The variation in potential energy for the different samples is illustrated in Figure 41. It is evident that the addition of NBs significantly alters the potential energy profile compared to the pure water–gas sample. Specifically, samples with higher NB surface hydrophobicity exhibit a more rapid decline in potential energy, indicating that increased hydrophobicity enhances the exothermic nature of hydrate formation. This behaviour suggests that NBs actively promote and accelerate hydrate nucleation and growth. To quantify the rate of hydrate

formation, the slope of the potential energy curve was determined through linear fitting, with results presented in Table 13. The data reveal that hydrogen and nitrogen NB samples, which possess higher surface hydrophobicity, exhibit the steepest energy decline, reflecting faster hydrate formation. This enhancement is attributed to favorable gas aggregation and structural ordering at the hydrophobic NB interfaces. As previously discussed, the CDNB sample shows a delayed onset of hydrate promotion during the early stages. However, as the simulation progresses, the sample becomes increasingly ordered, with enhanced hydrogen bonding, ultimately promoting hydrate formation at later times.

It is generally anticipated that, upon complete hydrate formation, the sample's potential energy would reach a plateau indicative of a fully converted, energetically minimized hydrate structure. However, in the present simulations, the potential energy profiles do not completely level off, indicating that a fraction of water molecules remains in the non-hydrated state. This outcome is unsurprising, given the large size of the simulated samples using the all-atom approach and the limited duration of accessible simulation timescales. Full conversion of all water molecules to hydrate likely requires microsecond timescales or longer, well beyond the nanosecond scale employed in this study. Nevertheless, the comparative analysis presented here provides valuable insights into the underlying mechanisms of hydrate formation and highlights the influence of NB properties on nucleation behaviour. These findings contribute to a deeper molecular-level understanding of hydrate nucleation and growth pathways. Such insights are essential for a better understanding of the hydrate process, for advancing hydrate-based technologies in carbon capture and storage, and for optimising hydrate formation and inhibition strategies.

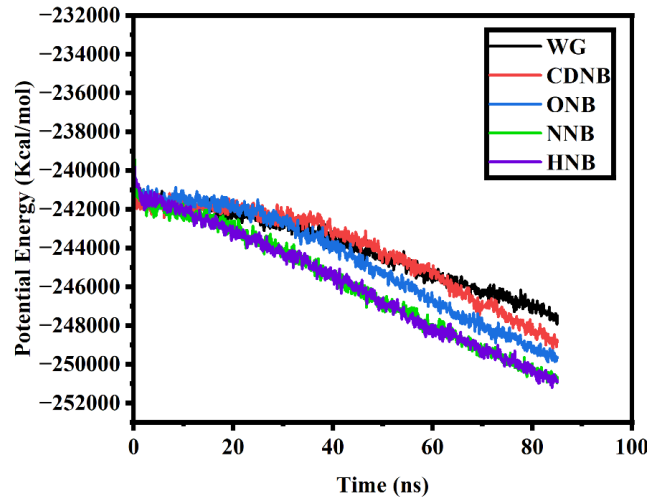


Figure 41. Temporal evolution of potential energy for the pure water–gas sample (WG) and nanobubbled samples (CDNB, ONB, NNB, and HNB).

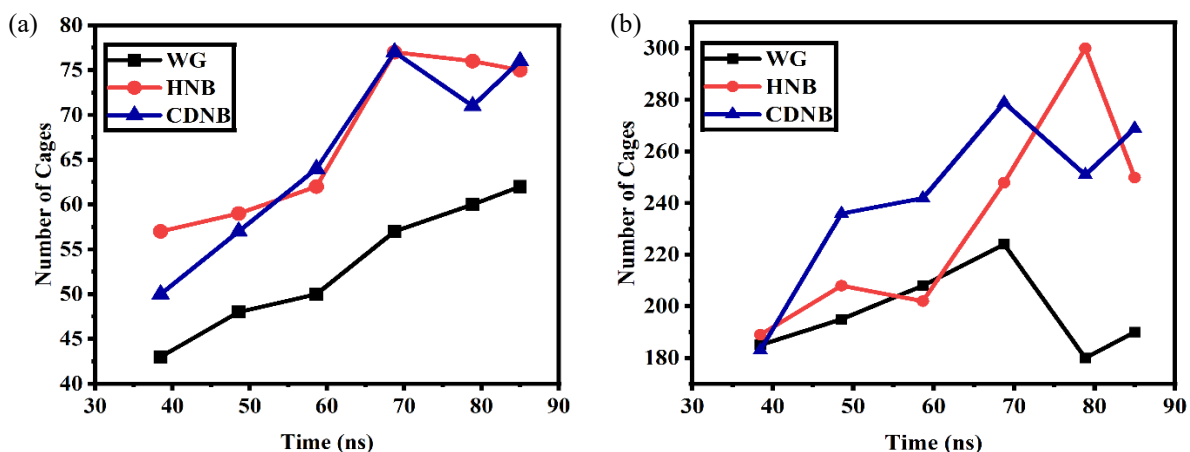
Table 13. Linear fit slopes of potential energy evolution for nanobubbled and non-nanobubbled samples.

Sample	WG	CDNB	ONB	NNB	HNB
Slope	-77.19	-89.77	-111.81	-118.40	-119.80

4.4.2 Impacts of temperature and NB

To investigate the dual impact of NBs and temperature on CO₂ hydrate formation, three samples, HNB, CDNB, and WG, were analysed at a pressure of 2 MPa and temperatures of 240 K and 260 K. The temporal evolution of the two dominant hydrate cages, 5¹² and 6²5¹², the total number of formed cages over time at 240 K, and the comparison of total cage formation at both temperatures at 85 ns are presented in Figures 42a-d, respectively. As shown in Figure 42c, by 85 ns, the nanobubble-containing samples exhibited a higher total number of formed cages

compared to the non-nanobubbled sample at 240 K. However, Figure 42d reveals that at 260 K, the presence of NBs has an even greater effect on cage formation than at 240 K. Additionally, the cage formation process at 260 K appears to be more sensitive to the type of NB, as the number of formed cages in the presence of HNB is significantly higher than in the presence of CDNB. In contrast, at 240 K, the samples are less sensitive to the type of NB, particularly in the formation of 5^{12} cages, as shown in Figure 42a, since there is only a small difference in the total number of formed cages between the HNB and CDNB samples. A comparison of Figures 38d and 42c, which illustrate the total number of cages formed over time at 260 K and 240 K, respectively, reveals distinct differences in hydrate formation dynamics. At 260 K, cage formation exhibits a continuous and steady increase throughout the simulation, indicating a stable growth process. In contrast, the trend at 240 K is notably less consistent. For instance, in the CDNB sample, a decline in the total number of cages is observed around 80 ns, followed by a subsequent recovery. This fluctuation suggests that cage formation at 240 K is comparatively less consistent and more prone to disruption than at 260 K.



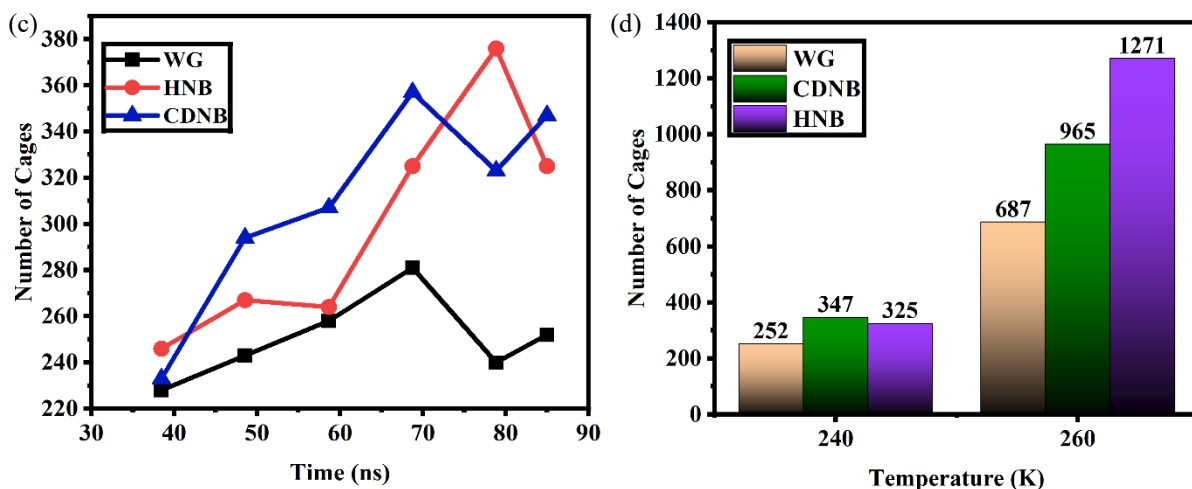


Figure 42. Number of formed hydrate cages: (a) small, (b) large, and (c) total cages over time at 2 MPa and 240 K; (d) comparison of the number of formed cages at 85 ns between 240 K and 260 K at 2 MPa.

As previously discussed, at 260 K and 2 MPa, the formation of blob-like structures was observed in the WG sample. While nanobubbled samples benefited from the hydrophobic surfaces of the NBs, which acted as catalytic interfaces, reducing the stochastic nature of blob nucleation in both space and time, thereby promoting CO₂ hydrate formation. Additionally, HNB was found to further enhance cage formation through a "breathing" mechanism, wherein dynamic gas exchange between the NB and the surrounding solution facilitates hydrate cage formation. All of these enhancement mechanisms are strongly dependent on atomic mobility. As the temperature decreases, atomic motion becomes increasingly restricted, limiting the activation of these mechanisms. For instance, at 240 K, the cage formation process showed reduced sensitivity to the type of NB and its surface hydrophobicity. As CO₂ molecules preferentially migrate and aggregate at more hydrophobic interfaces, sufficient mobility, which is more restricted at lower temperatures, is required for this behaviour to occur. As a result, the influence of NB type on hydrate formation becomes less pronounced at 240 K compared to 260 K.

Figure 43a presents the RDF between hydrogen and dissolved CO₂ at two temperatures, i.e. 240 K and 260 K, evaluated at 39.06 ns, representing a mid-stage of hydrate growth where the sample has dynamically evolved and is poised for further structural development. The RDF at 260 K exhibits a more pronounced peak compared to that at 240 K, indicating a higher probability of finding CO₂ molecules around hydrogen atoms. This suggests that CO₂ molecules are more favorably positioned near hydrogen at 260 K. Furthermore, Figure 43b shows the RDF between hydrogen and water at these two temperatures. The hydrogen–water RDF at 260 K displays a higher peak than at 240 K, indicating more interaction between hydrogen and water at the higher temperature. This enhanced "breathing" mechanism at 260 K suggests increased molecular mobility, further confirming that reduced mobility at lower temperatures can limit interaction and hinder the hydrate formation process. These observations highlight the significance of temperature in hydrate nucleation and growth. Specifically, 260 K appears to offer more favorable conditions, under the given pressure, for promoting hydrate formation due to an optimal balance between molecular mobility and intermolecular interactions. However, further increases in temperature may disrupt this balance, as enhanced atomic motion can overcome hydrogen bonding and other intermolecular forces, ultimately inhibiting cage formation. This underscores the existence of an optimal thermodynamic window for hydrate formation, where both molecular mobility and interaction strength are well balanced.

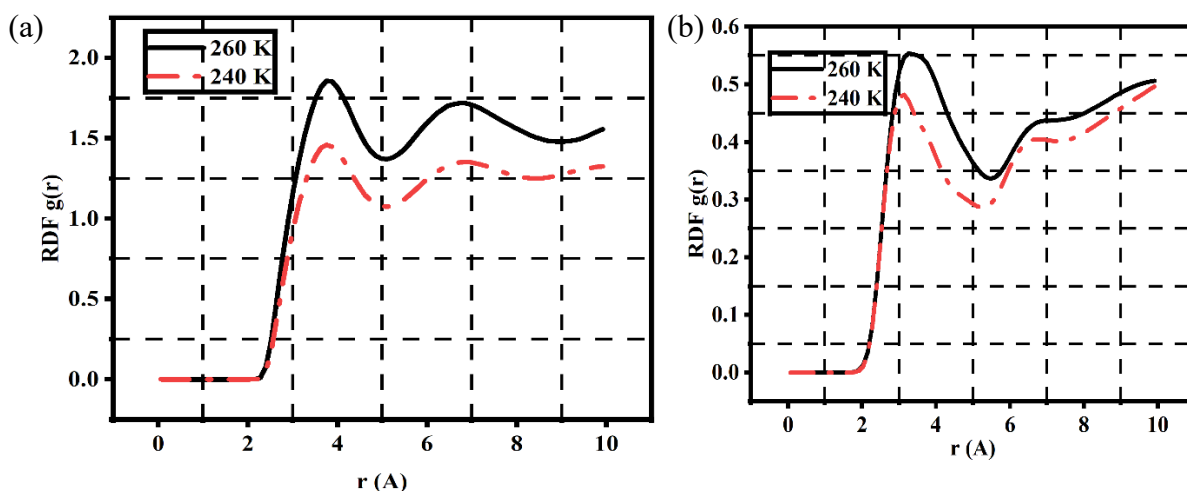


Figure 43. *RDF of (a) hydrogen-carbon dioxide and (b) hydrogen-water in the HNB sample at 39.06 ns.*

As observed at 240 K, hydrate formation appears to be less sensitive to the hydrophobicity of NBs. Notably, the number of formed cages in the presence of CDNB is slightly higher than in other samples at this temperature, as illustrated in Figure 42d. A comparison of the cage formation trends at 240 K and 260 K (Figures 38d and 42c), reveals distinct differences in growth behaviour. At 260 K, cage formation shows a continuous and steady increase over time, indicating a stable and sustained growth process. In contrast, at 240 K, the trend is less consistent. Specifically, in the CDNB sample, the total number of formed cages decreases between 68.75 ns and 78.85 ns before partially recovering, suggesting unstable growth dynamics at the lower temperature. Further comparison of the F_4 parameter for CDNB samples at both temperatures (Figure 44a), reveals that at 240 K, the F_4 value increases within the same time window (68.75 to 78.85 ns) as at 260 K. To better understand this behaviour, the total number of formed rings and cups, fundamental structural units in hydrate formation, was examined. Initially, rings are formed between water molecules, followed by their assembly into cups. The combination of these cups ultimately results in the formation of complete hydrate cages. This suggests that the rise in the F_4 parameter at 240 K is primarily due to the

accumulation of these substructures (Figure 44b), which fail to complete the cage architecture under kinetically limited conditions. The inability of cups and rings to transition into complete cages at 240 K is likely due to kinetic hindrance, which disrupts stable cage growth. Some partially formed cages may even revert back to cup structures due to discontinuous growth. In contrast, at 260 K, the system overcomes this kinetic barrier more effectively, allowing cups to convert more readily into fully formed cages. These findings highlight the existence of an optimal kinetic and thermodynamic window for hydrate formation, where both molecular mobility and interaction strength are balanced to support sustained cage growth.

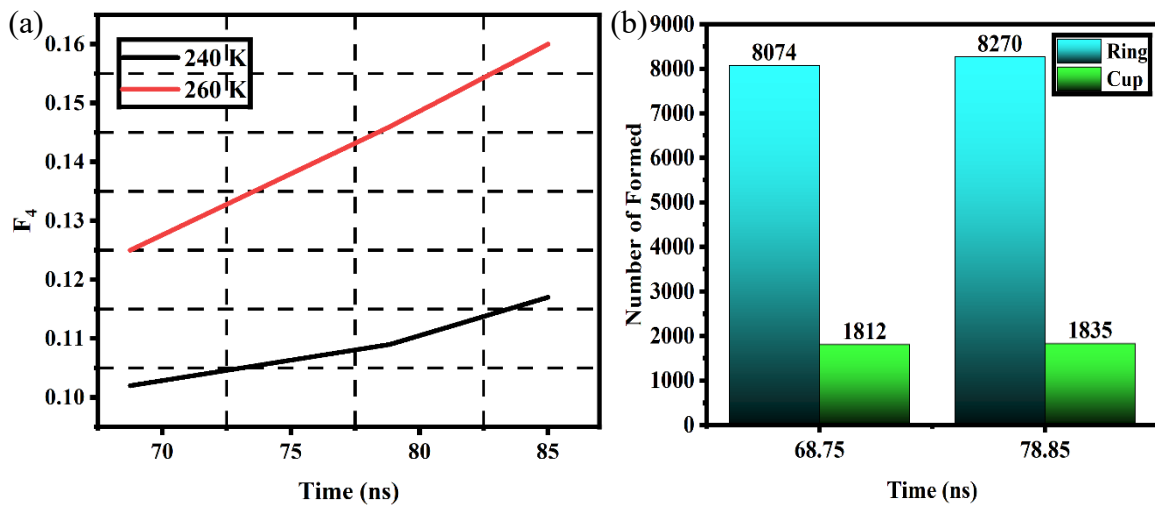


Figure 44. (a) F_4 parameter of CDNB at two different temperature and (b) the number of total formed rings and cages at 240 K for CDNB at two different times.

4.4.3 Influences of pressure and NB

The influence of pressure and the presence of NBs on CO_2 hydrate formation investigated using three distinct samples. WG served as the nanobubble-free reference, while CDNB and HNB represented nanobubble-containing samples, all studied under conditions of 10 MPa and 260 K. The temporal evolution of the two dominant hydrate cages, 5^{12} and 6^25^{12} , as well as the total

number of cages formed over time at 10 MPa and 260 K, are illustrated in Figures 45a-c, respectively. As illustrated in Figure 45c, after 85 ns, the total number of formed cages in the HNB sample is slightly higher than in the WG sample. Notably, in contrast to the results at lower pressure (2 MPa), shown in Figure 38d, the total number of formed cages in the CDNB sample is lower than in the nanobubble-free WG sample. This behaviour indicates the dual role of NBs, which can act as both promoters and inhibitors of hydrate formation [113].

Increasing the pressure in both nanobubbled and non-nanobubbled samples results in higher sample density and stronger molecular interactions. In the non-nanobubbled sample, this pressure-induced densification enhances interactions between molecules, especially between water molecules, creating a more favorable environment for hydrate nucleation, particularly for the formation of small 5^{12} cages. In contrast, in samples containing-nanobubble samples, the increased pressure also densifies the nanobubble itself, intensifying molecular interactions within it. This behaviour reduces the availability of active interaction sites at the gas–liquid interface, particularly on the nanobubble surface, which typically plays a catalytic role in organizing the local molecular structure for hydrate formation, as previously discussed. Interestingly, the presence of carbon dioxide NB significantly reduces the formation of hydrate cages at elevated pressures. At lower pressures, the intermolecular interactions between solution molecules, particularly water–water and water–CO₂, are relatively weak and insufficient to induce the local structural ordering required for hydrate nucleation. In this regime, the presence of a CDNB plays a beneficial role by providing a gas–liquid interface that helps organize water molecules into more ordered, hydrogen-bonded structures, effectively lowering the growth barrier for hydrate cages. However, as pressure increases, the intensified molecular interactions between CO₂ and water in the bulk become strong enough to promote local ordering and hydrate formation without the need for interfacial assistance. In this high-pressure regime, the role of the CDNB shifts. Instead of promoting structural order, the NB

becomes disruptive. It introduces disorder, potentially disturbing the hydrogen-bond network formed through enhanced bulk interactions, a network that would otherwise facilitate hydrate cage formation. As a result, at higher pressures, the NB no longer serves as a catalytic site for atomic structure ordering but instead acts as a structural obstacle, impeding hydrate formation. Furthermore, at lower pressure, the presence of HNB (Figure 38d) significantly enhances hydrate cage formation compared to non-nanobubbled samples, indicating a strong promotive effect. However, as pressure increases, this effect diminishes, and the difference in the number of formed cages between hydrogen nanobubbled and non-nanobubbled samples becomes much less pronounced. These observations underscore a pressure-dependent shift in the dominant mechanism of hydrate nucleation, from nanobubble-induced ordering at low pressure to bulk interaction- driven ordering at high pressure.

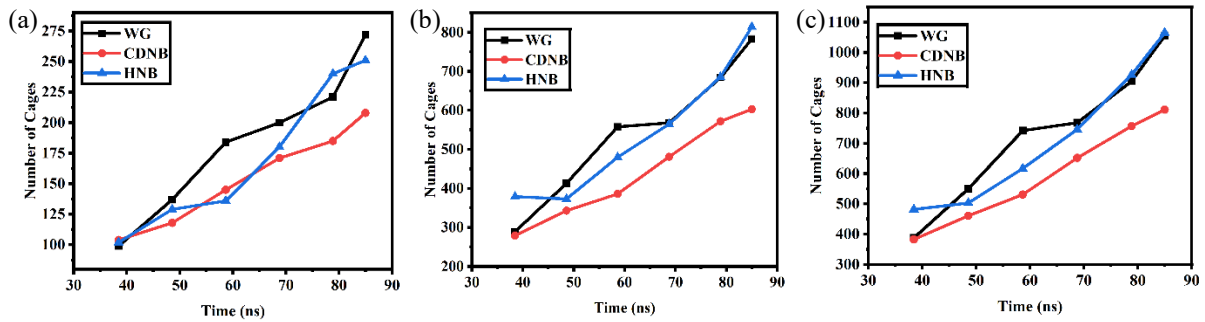


Figure 45. The number of formed hydrate cages: (a) small, (b) large, and (c) total cages at 10 MPa and 260 K.

4.5 Summary

This chapter presented the results obtained from MD simulations conducted to investigate the nucleation behaviour of NBs and their influence on the inherent properties of polar and alcoholic host liquids, as well as their potential role in carbon dioxide hydrate formation. The study further examined the intrinsic properties of NBs by integrating MD simulations with ML techniques to analyse their temporal behaviour in both water and methanol systems. The results obtained from these simulations provide important insights into the mechanisms governing NB nucleation, their stability, and their impacts on thermophysical properties, as well as their potential influence on hydrate formation process.

The initial part of the study examined NBs nucleation in pure water and methanol systems. The results demonstrated distinct nucleation behaviour in the two solvents, water and methanol, due to differences in their intermolecular interaction characteristics. It was reported that the density of the formed NBs was higher than that of gas in its conventional gaseous state, and this density, which depends on NB size, plays an important role in determining their stability within the liquid environments. In systems with a higher density of NBs, the viscosity of the host liquids was primarily influenced by the presence of NBs. In contrast, when the NB density was lower, molecular interactions within the liquid phase played a more dominant role in governing the viscosity behaviour. Furthermore, NB formation was observed to influence the structural parameters of molecular arrangements in the liquid phase, which consequently affected the density of the samples.

The second part of the chapter investigated NB behaviour in solid–liquid–gas interaction environments within graphene-reinforced water- and methanol-based nanofluids. The results suggest that liquid–liquid interactions governed the solid–gas interactions and influenced the

morphology of the dispersed graphene sheets. These interactions subsequently affected NB nucleation and behaviour, and the resulting morphological changes also affected the thermophysical properties of the systems, including their specific heat capacity.

The final section focused on the potential role of NBs in the formation of carbon dioxide hydrates. The simulation results indicated that, under optimal thermodynamic conditions, NBs provided hydrophobic sites that accelerated the ordering of water molecules. Furthermore, NBs composed of smaller atoms, such as hydrogen, were found to further enhance hydrate cage formation through a “breathing” mechanism, compared to NBs composed of larger atoms.

Chapter 5

NBs in Non-Polar Host Liquids

5.1 Introduction

This chapter systematically investigates the formation, stability, and functional effects of NBs in organic host liquids across both thermal energy storage and combustion contexts at the molecular scale. The first part of the chapter examines the formation mechanisms, behaviour, and thermophysical impacts of bulk NBs in dodecane and isooctane using classical MD simulations, with particular emphasis on the roles of gas species, gas weight fraction, and temperature. The second part focuses on the influence of NBs on the phase transition and thermal behaviour of dodecane. Finally, recognising the critical role of chemical interactions in blended fuels and the potential of nanobubble-enriched fuels to enhance combustion performance, the last part of this chapter explores the effects of NBs on the combustion characteristics of dodecane. This is achieved using a ReaxFF molecular dynamics approach to analyse the influence of nanobubble type, temperature, and sample density on combustion behaviour.

5.2 Formation, coalescence and effects of bulk NBs

5.2.1 Impact of host liquids and gas types

To investigate the nucleation and behaviour of NBs in organic host liquids, molecular dynamics simulations were performed for different gas–liquid systems in isooctane and dodecane. Three gases, nitrogen, oxygen, and carbon dioxide, were dispersed in dodecane and isooctane at a consistent mass fraction of 6 wt%. However, due to the low molecular mass of hydrogen, a distinct mass-fraction formulation was considered for hydrogen-containing systems. For the nitrogen–dodecane system, an initial configuration was generated by randomly dispersing 1941 nitrogen molecules and 5000 dodecane molecules within a cubic simulation box of dimensions 12.44 nm × 12.44 nm × 12.44 nm. Additional configurations of the same system were prepared by independently introducing 1699 oxygen

molecules and 1948 hydrogen molecules within the same initial box dimensions. To avoid artefacts associated with periodic boundary conditions in bonded interactions, the simulation domain was subsequently expanded to $15\text{ nm} \times 15\text{ nm} \times 15\text{ nm}$. This ensured that the bond/angle/dihedral (BAD) interaction extent remained smaller than half of the box length, as required for accurate molecular dynamics simulations in LAMMPS. In the enlarged system, 8700 dodecane molecules and 2150 carbon dioxide molecules were incorporated to represent gas–liquid mixtures under consistent thermodynamic conditions. For the isooctane-based systems, 1640 nitrogen molecules, 1436 oxygen molecules, and 1646 hydrogen molecules were initially dispersed within a $12.248\text{ nm} \times 12.248\text{ nm} \times 12.248\text{ nm}$ simulation box containing 6300 isooctane molecules. Consistent with the dodecane system, the simulation box was subsequently expanded to $15\text{ nm} \times 15\text{ nm} \times 15\text{ nm}$ to accommodate 1988 carbon dioxide molecules and 12,000 isooctane molecules. This enlargement ensured proper treatment of periodic images and satisfaction of the BAD interaction criterion, thereby guaranteeing accurate representation of molecular interactions and nanobubble behaviour. Table 14 and Figure 46 illustrate the constructional parameters and initial structure of prepared samples, respectively. All prepared samples were relaxed for 1.7 ns in the NPT ensemble, followed by 1.7 ns in the NVT ensemble, to reach equilibrium under the environmental condition. Subsequently, 10 ns simulations were performed in the NVE ensemble, using a 1 fs time step, to investigate the behaviour of NBs and the thermophysical properties of treated dodecane and isooctane.

Table 14. *The structural features of the prepared organic samples.*

Sample	Number of molecules		Sample	Number of molecules	
	Gas	Host liquid		Gas	Host liquid
Nitrogen/ Dodecane	1941	5000	Nitrogen/ Isooctane	1640	6300
Oxygen/Dodecane	1699	5000	Oxygen/ Isooctane	1436	6300
Carbon dioxide/Dodecane	2150	8000	Carbon dioxide/ Isooctane	1988	12000
Hydrogen/Dodecane	1948	5000	Hydrogen/ Isooctane	1646	6300

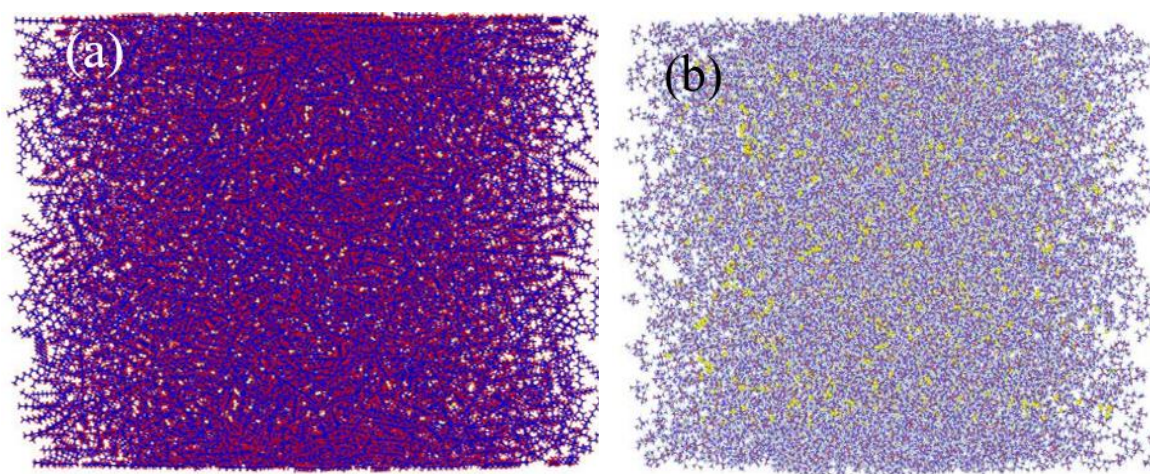


Figure 46. *Initial configuration of the scattered gas in the (a) dodecane and (b) isooctane samples.*

As shown in Figures 47 and 48, nitrogen, oxygen, and hydrogen were observed to form NBs within 13.4 ns in the dodecane host liquid, while nitrogen and hydrogen were able to form NBs in the isooctane host. In contrast, carbon dioxide did not form any NBs in either liquid host. Once the initial nucleation sites appear in the host liquids, small NBs start to coalesce to form a larger bubble. In an experimental study, it was observed that huge amount of

dissolved nitrogen molecules can form NBs in the host liquid and majority of the dispersed gas exists in the form of NBs and nearly there were not any homogenous forms of it in the surrounded medium [92].

The comparison of the results over time in Figures 47 and 48 also suggests that the dynamics of bubble formation and coalescence are affected by the properties of the dispersed gases. It is clear in Figure 47 that considerable nitrogen gas atoms start to agglomerate and form a big NB with 4 child NBs in the host liquid at 1 ns. It can be observed that the child NBs start to join the mother NB and this process takes about 0.5 ns. However, the oxygen atoms only start to create small NBs at 1.5 ns. Unlike the oxygen atoms, majority of nitrogen atoms exist in the form of bulk NB in the dodecane after 4.75 ns. Therefore, for the same amount of scattered gas, the speed of coalescence process of nitrogen atoms in dodecane sample is higher than that of oxygen atoms. The behaviour of scattered hydrogen in Figure 48 indicates that the bubble dynamics is very dependent on the type of dispersed gas. It can be observed that at 1 ns the majority of the scattered hydrogen atoms already generate a tangible NB in dodecane sample. So, it can be concluded the speed of the formation and coalescence of NBs could depend on the type of gas atoms and their molecular interactions.

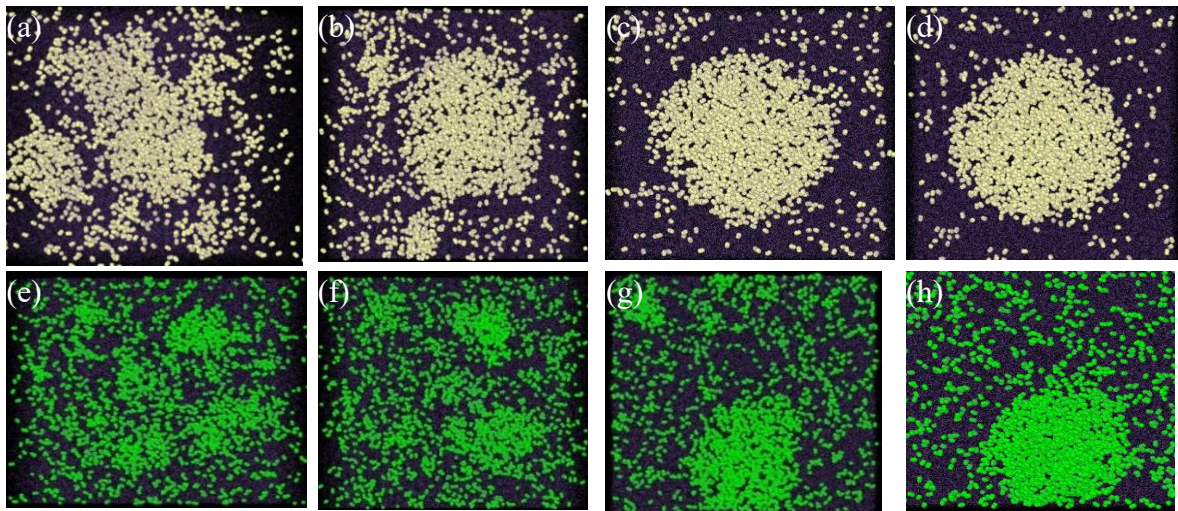


Figure 47. *Formation process of (a, b, c, d) nitrogen and (e, f, g, h) oxygen NBs in PCM host after 1, 1.5, 4.75, and 10 ns (from left to right).*

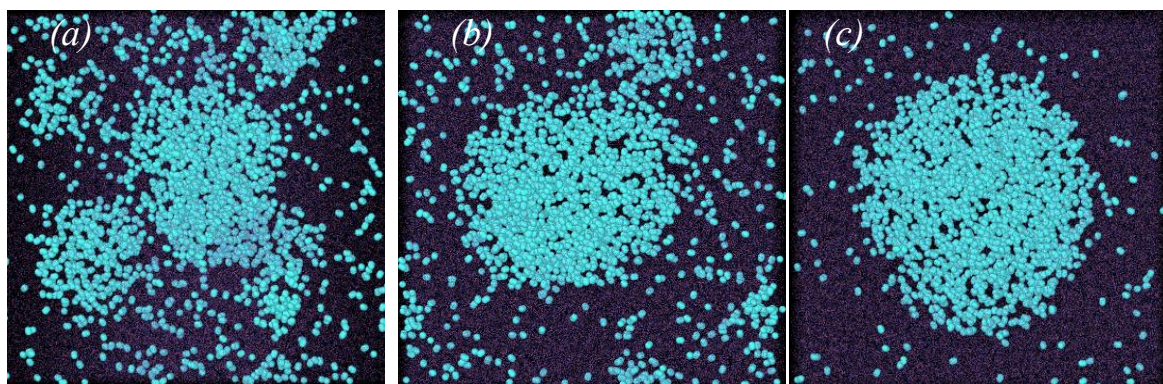


Figure 48. *Formed hydrogen NBs in dodecane at (a) 0.5, (b) 1, and (c) 10 ns.*

It is found that at 1.5 ns the majority amount of nitrogen atoms in dodecane exist in a large NB. However, for the same weight fraction of this type of atoms, small NBs in isooctane can be observed at 1.5 ns, as shown in Figure 49. The most interesting observation is that oxygen atoms could not form any NBs in the isooctane sample, while a large oxygen NB can be observed in dodecane at the end of simulation, as shown in Figure 50. Therefore, the formation of NBs is also affected by the properties of host liquids. Further examination of oxygen interactions with dodecane and isooctane, as illustrated in Figure 51, highlights the possible inhibiting effect of stronger attractive forces between oxygen and isooctane molecules. These stronger interactions may prevent oxygen molecules from clustering in the isooctane system, in contrast to dodecane.

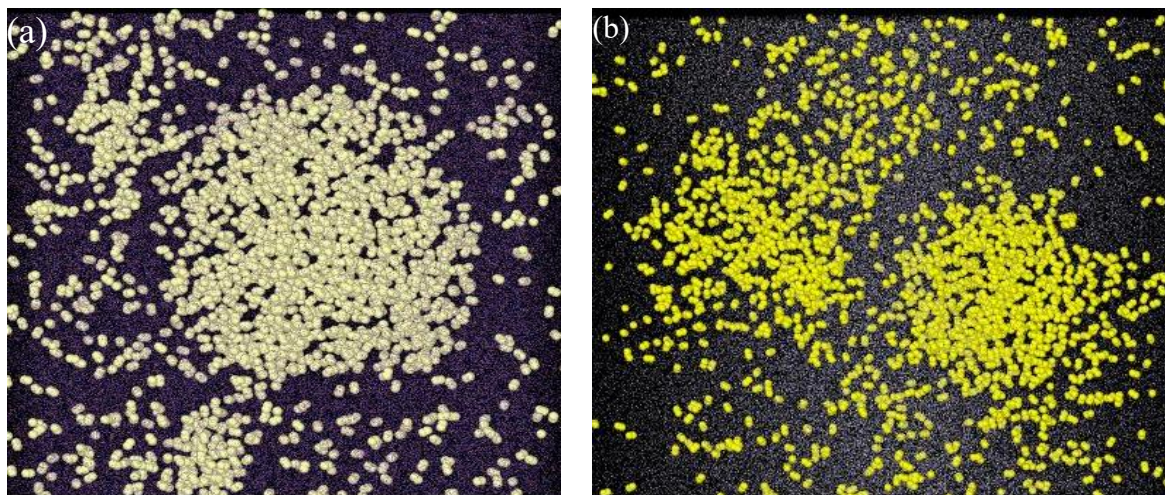


Figure 49. Formed nitrogen NBs in (a) dodecane and (b) isooctane samples at 1.5 ns.

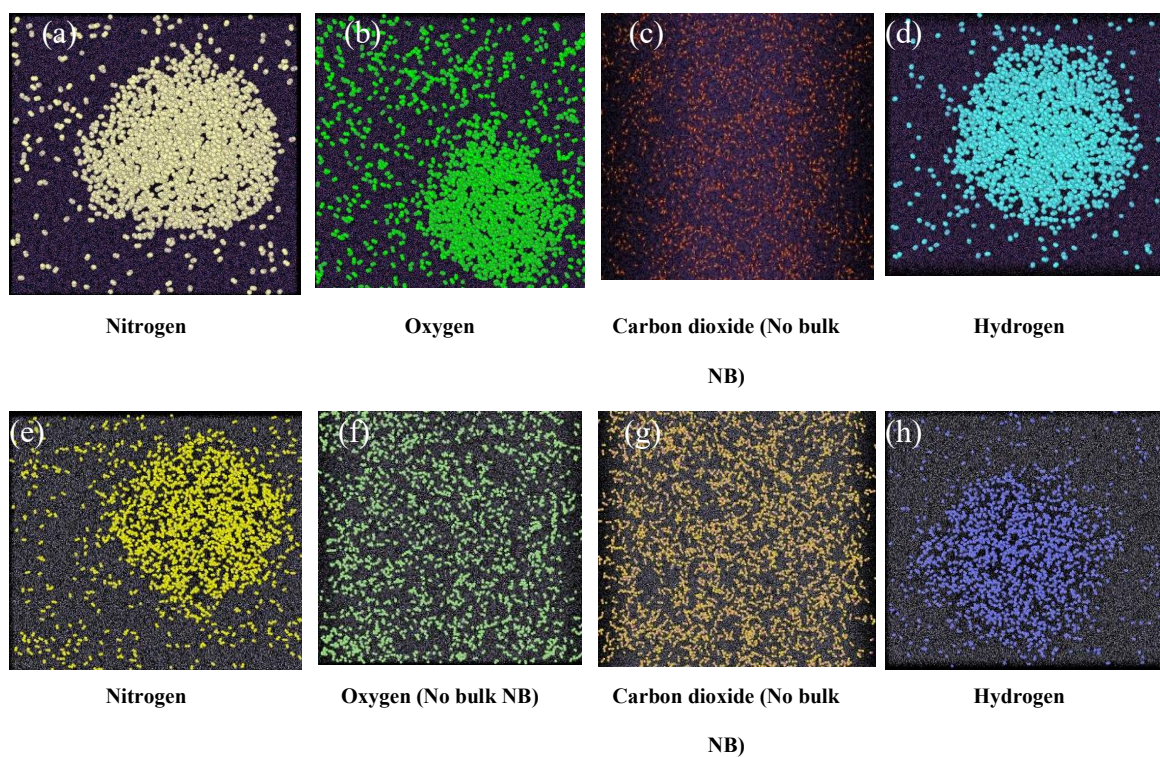


Figure 50. The NBs formed in (a, b, c, d) dodecane and (e, f, g, h) isooctane samples with different gases at the end of simulation.

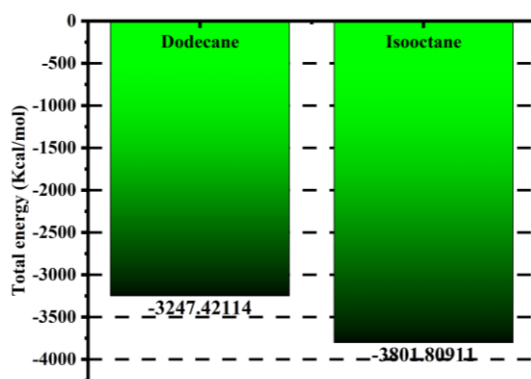


Figure 51. *The average of the total energy between oxygen and host liquids.*

As the transport properties play an important role in the industrial applications of working liquids, the effect of the scattered gas and NBs on the viscosity, specific heat capacity, and diffusion coefficient of the obtained samples were studied after investigating the dynamics of NBs in order to understand the potential of NBs for industrial applications.

Viscosity shows the resistance of materials against the flow and can affect the efficiency of heat transfer as well as the energy consumption of the designed system. Green-Kubo method, Eq. 3.33-3.34, was used to calculate the viscosity of the prepared samples.

Table 15 shows the viscosity of the obtained samples. It can be seen that the viscosity of prepared samples decreases by dissolving carbon dioxide, nitrogen, and hydrogen gases, compared to the pure dodecane (Table 6). However, scattering oxygen atoms in dodecane causes an increase in the viscosity, compared to the pure dodecane. The biggest drop in the viscosity of the dodecane sample is caused by the addition of CO₂ gas, which reduces the viscosity by 20.47% compared to pure dodecane.

Table 15. *The viscosity of dodecane and isooctane-based samples (Pa.s) with various dissolved gas.*

Host Liquids	CO ₂	N ₂	O ₂	H ₂
Dodecane	0.00101	0.00103	0.00153	0.00113
Isooctane	0.000541	0.00049	0.000445	0.000487

Figure 52(a) compares the Coulombic energy of dodecane samples containing dissolved carbon dioxide and nitrogen. The results indicate that the Coulombic energy of the CO₂/dodecane system was higher than that of the nitrogen-containing system at the same mass fraction. Figure 52(b) illustrates the van der Waals interaction energy of dodecane samples containing dissolved oxygen and nitrogen, where differences in attractive interactions were observed among the systems. The oxygen/dodecane system exhibited a higher van der Waals interaction energy than the nitrogen-containing system.

As observed in Figure 50, both nitrogen and oxygen can form NBs in the dodecane system. A comparison of the sizes of the generated NBs at 13.4 ns shows that, although the diameter of the nitrogen NB (8 nm) is larger than that of the oxygen NB (7 nm), the viscosity of the oxygen-containing dodecane system is more affected, as shown in Table 15. This suggests that the viscosity of the prepared samples may be influenced more strongly by the gas type than by the near-equal size of the generated NB. A comparison of the viscosity of the hydrogen/dodecane and nitrogen/dodecane samples (Table 15) suggests that gas type may also play a more important role than the weight fraction of the scattered gas in influencing viscosity. In particular, the hydrogen/dodecane sample shows a higher viscosity than the nitrogen/dodecane sample, despite having a lower scattered gas weight fraction.

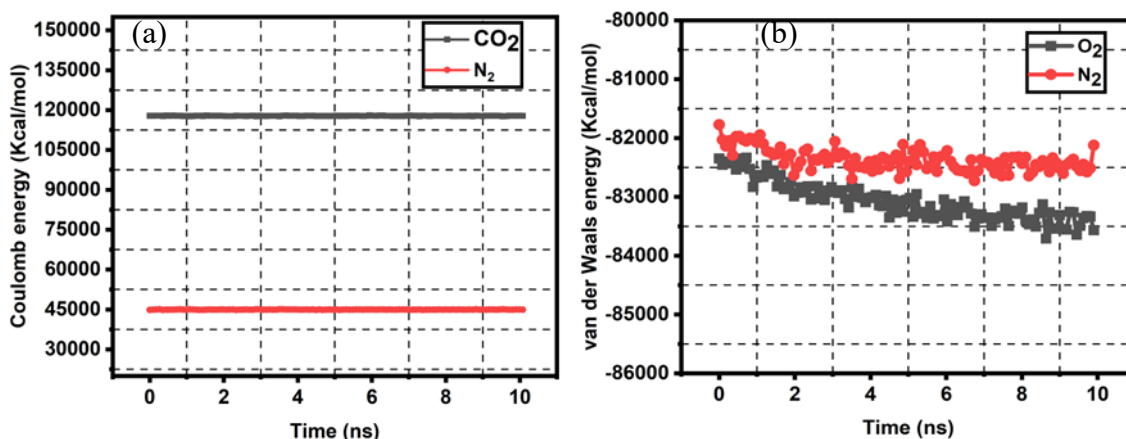


Figure 52. (a) Coulomb energy of the carbon dioxide and nitrogen system. (b) Van der Waals energy of nitrogen and oxygen samples. Note that the negative sign shows the attractive force and the absolute amount of it should be used for comparing.

Unlike the dodecane, the viscosity of isooctane increases when adding carbon dioxide, nitrogen, and hydrogen gases, as shown in Table 15. More specifically, the addition of carbon dioxide produces the highest viscosity, while the addition of oxygen leads to the lowest viscosity of the isooctane mixture. As it was discussed, carbon dioxide and oxygen could not form NB in the isooctane host, however investigating the distribution of CO₂ atoms in isooctane at the end of the simulation time, which is shown in Figure 53, indicates that carbon dioxide atoms form clusters containing a small number of atoms, for example a cluster with three carbon dioxide atoms, inside the host liquid. Since the number of atoms in these clusters is very small, they cannot be considered as NBs, but their presence may affect the movement of atoms, which could act like the scattered obstacles in the path of movement

of atoms that reduce their freedom of movement and increases the viscosity of the CO₂/isooctane sample.

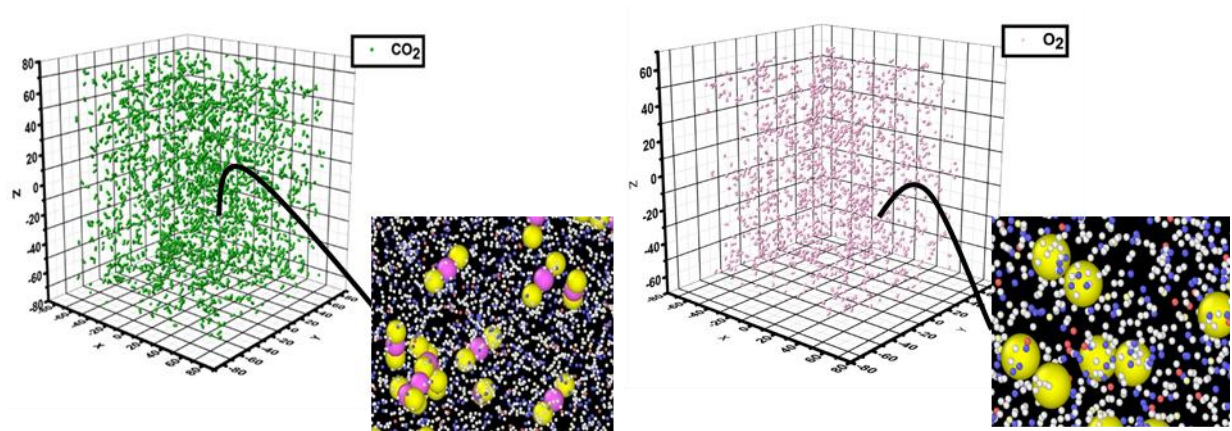


Figure 53. Distribution of carbon dioxide and oxygen molecular in isooctane-based fluid at the 13.4 ns.

Table 16 shows the diffusion coefficient of the prepared samples. The comparison of the diffusion coefficient of dodecane samples with oxygen and nitrogen gases, reveals that for the same weight fraction of the scattered gas, the diffusion coefficient of nitrogen sample with larger NB is lower than oxygen one. This suggests that the diffusion coefficient may decrease with increasing NB size in the sample.

Table 16. The diffusion coefficient of dodecane and isooctane-based samples with various dissolved gas ($\times 10^{-9} \text{ m}^2/\text{s}$).

Host Liquids	CO ₂	N ₂	O ₂	H ₂
Dodecane	1.24	0.772	0.808	0.8438
Isooctane	2.034	2.055	2.1531	2.4712

The specific heat capacity at constant volume was calculated using equation 3.35 to measure the heat storage capacity. Heat capacity is defined as the energy required to raise the system's temperature by 1 K and, therefore, serves as an indicator of the energy stored within the system. The comparison of the specific heat capacity of the prepared samples, Figure 54,

indicates that the addition of nitrogen, oxygen, carbon dioxide, and hydrogen to the dodecane and isooctane leads to an increase in specific heat capacity of host liquids, except the oxygen/isooctane sample. In addition, it can be observed that the addition of hydrogen in dodecane leads to highest increase of specific heat capacity while carbon dioxide results in least increase. It is found that the addition of hydrogen, carbon dioxide, and nitrogen only leads to a slight increase of specific heat capacity with $C_{v,\text{sample}}/C_{v,\text{base}}$ isooctane liquid around 1.1. More importantly, it is noted that the addition of oxygen in isooctane decreases specific heat capacity. Therefore, the change in specific heat capacity appears to depend not only on the host liquid but also on the scattered gas. More investigating the behaviour of samples at nano-scale and the effects of NBs formation on the specific isochoric heat capacity reveals that samples containing NBs have higher specific heat capacity than samples without NBs, like oxygen/isooctane sample. This behaviour may be explained by molecular interactions. In systems where favourable interactions promote NB formation, increased particle collisions may contribute to enhanced thermal properties and a higher isochoric specific heat capacity of the bubbly samples [190].

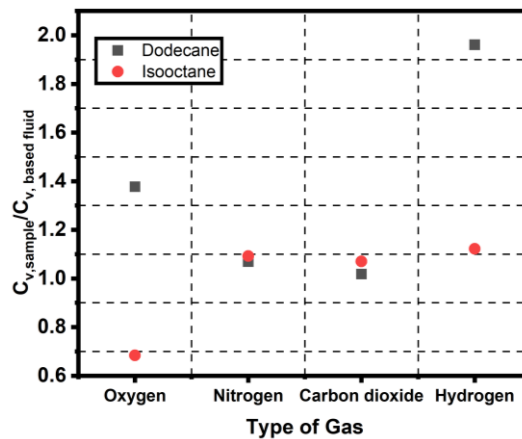


Figure 54. *Specific heat capacity of samples compared to the host mediums.*

5.2.2 Effect of gas content

In order to study the effects of concentration of the dissolved gas on the formation mechanism and transport properties, 485 and 410 nitrogen molecules were dissolved in the dodecane and isooctane hosts, respectively, to obtain samples with gas weight fraction of 1.57%. Unlike the samples with higher gas weight fraction, as shown in the previous section, no bulk NBs can be observed in 13.4 ns.

The radial distribution function (RDF), which represents the probability of atoms existing at a distance r around specific atoms, was calculated using equation 3.34. The RDFs for gas-gas interactions in samples with varying concentrations of dissolved gas are depicted in Figure 55. Within Figure 55, a notable trend emerges in the RDF concerning different gas weight fractions. In cases with higher gas weight fractions, a distinct RDF peak is evident, indicating the presence of a considerable number of gas atoms in close proximity, likely forming gas clusters. Following this peak, a gradual decline in the RDF is observed, implying an increased availability of gas atoms for potential NB formation. Conversely, lower gas weight fractions result in a less pronounced RDF peak, suggesting a diminished number of gas atoms in close proximity. Moreover, a significant drop in the RDF is noticeable, signifying an insufficient quantity of gas atoms surrounding the cluster to facilitate NB formation.

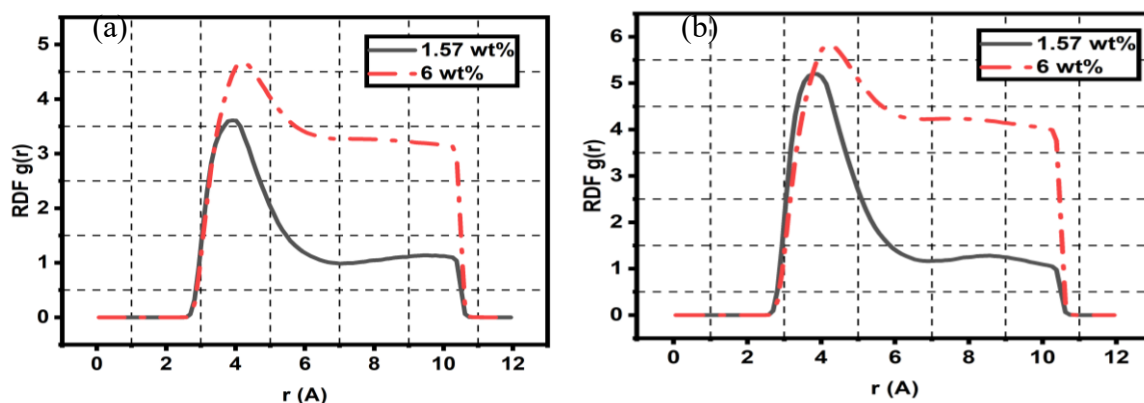


Figure 55. *The radial distribution function (RDF) of nitrogen gas in (a) isooctane and (b) dodecane samples.*

It was reported that the viscosity of carbon-based liquids is affected by the dissolved gas in such a way that increasing its concentration reduces the viscosity of the fluids [191]. As shown in Figure 56, by increasing the concentration of the dissolved gas, the viscosity of the prepared samples decreases.

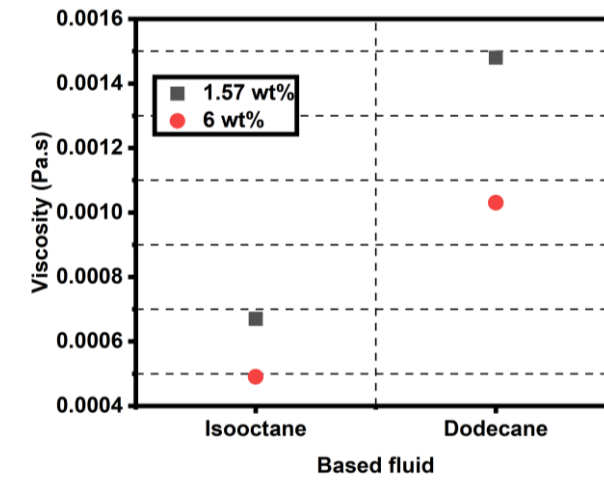


Figure 56. *Viscosity of obtained samples with different gas weight fractions and host liquids.*

Variations in van der Waals energy were also observed across the investigated samples at different gas concentrations. Figure 57 presents the van der Waals energy of the samples at various gas mass fractions. The results suggest that increasing the gas mass fraction is associated with a decrease in the van der Waals energy in both liquids.

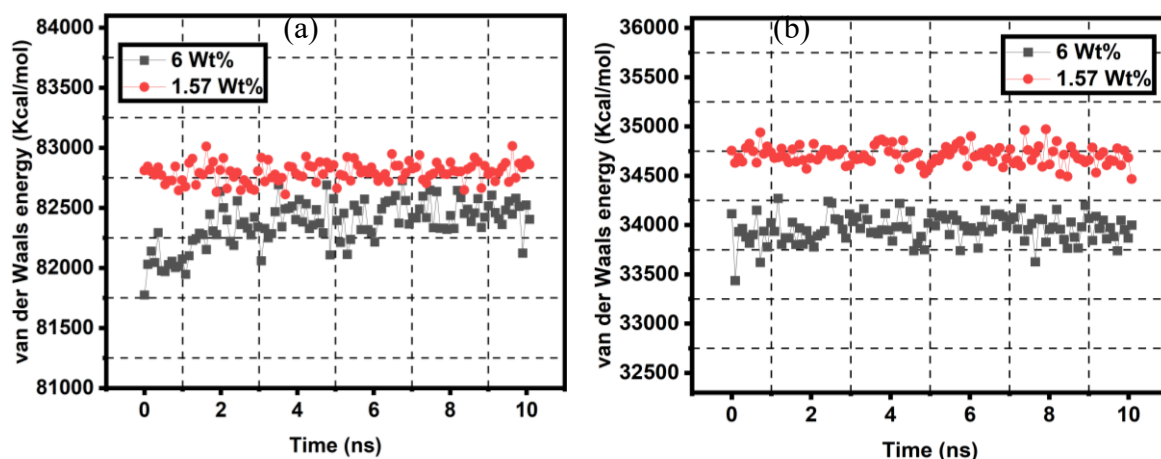


Figure 57. Absolute amount of attractive energy of samples with various content of scattered gas in (a) dodecane and (b) isooctane.

Figure 58 shows the RDF for liquid-gas. The results indicate that increasing the gas weight fraction significantly reduces the RDF. Therefore, the number of gas atoms surrounding the liquid atoms tends to decrease with increasing gas weight fraction, which may enhance their mobility and contribute to a higher diffusion coefficient. It was observed that the diffusion coefficient of the prepared samples is increased by 12.91 % and 1.45 % for isooctane and dodecane samples, respectively, when the gas weight fraction increased from 1.57 to 6 wt%, Table 16 shows the diffusion coefficient of 6 wt% of nitrogen samples.

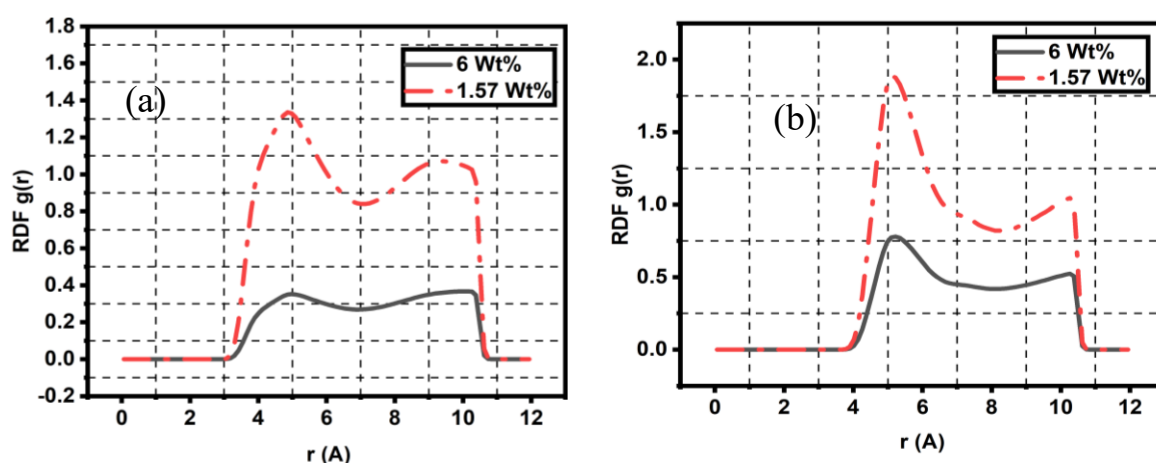


Figure 58. The RDF for the gas-liquid interactions of the prepared (a) dodecane and (b) isooctane samples with different nitrogen concentration.

Figure 59 compares the specific heat capacity of mixtures with different gas weight fraction. It is noted for the prepared dodecane samples with the increase in gas weight fraction, the specific heat capacity is lowered. In contrast, the prepared isooctane sample at lower gas weight fraction has much lower heat capacity compared to the base isooctane, while a higher gas weight fraction at 6 wt% slightly increases the specific heat capacity. This behaviour has been observed in an experimental study in which by increasing the weight fraction of dispersed materials in dispersive medium, the heat capacity increases initially and then decreases [192]. It is proposed that there is an optimal weight fraction that a higher or lower weight fraction can lead to the reduction of the specific heat capacity [55]. Therefore, the results shown in Figure 59 indicate that dodecane may have a lower optimal weight fraction for additives than isooctane, as increasing the weight fraction of the scattered gas above 1.57 wt% appears to reduce the specific heat capacity.

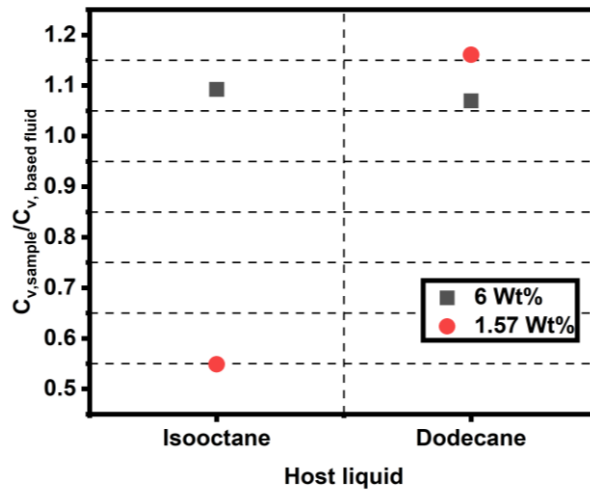


Figure 59. Comparison of specific heat capacity of mixtures with different gas weight fraction.

Figure 60 shows the average pairwise energy of dodecane samples and total energy between gas and liquid in isooctane samples. It can be seen in Figure 60a that, by increasing the

weight fraction of the scattered gas in dodecane samples, the pairwise energy of the system decreases, which could lead to a reduction in specific heat capacity. In addition, it was suggested that three mechanisms play important roles in enhancing heat capacity of base fluids by adding additives, including the increase in surface energy, a high thermal resistance between base fluid and nanoparticles, and semi solidification of liquid layers around the dispersed nanoparticles in host liquids [192]. Scrutinizing the attractive force between nitrogen and isooctane molecules reveals that by rising the weight fraction of the dispersed gas from 1.57 to 6 wt%, the attractive force between host liquid and scattered gas atoms is increased by 60%, which could lead to the increase in heat capacity of isooctane host mixture. Hu et al. [193] found that by increasing the weight fraction of scattered nanoparticles in eutectic salt-silica nanofluid for solar energy storage, the heat capacity is improved initially and then decreased. Their analysis confirmed that by increasing the weight fraction of dispersed particles, the potential energy of the system is increased to the optimum point and the further increase in the weight fraction of the additive leads to the decrease in both potential energy and heat capacity.

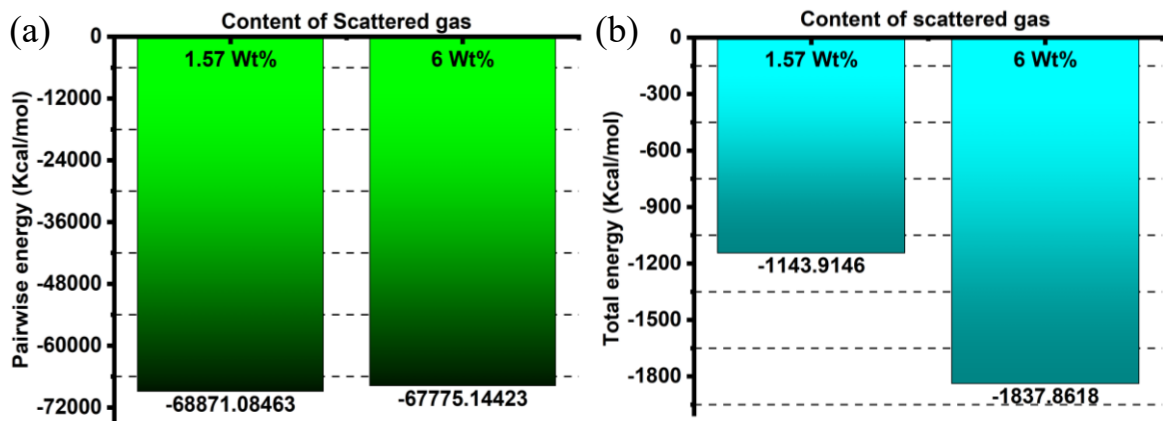


Figure 60. The average of (a) pairwise energy of dodecane sample, and (b) the total energy between gas and host liquid in isooctane sample.

5.2.3 Effect of temperature

Samples with the same weight fraction of the dispersed gas were studied at two different temperatures, 298.15 and 343.15 K. The number of initial clusters formed at higher temperature is less than that at the lower temperature, however the size of initial clusters at higher temperature samples is larger. Figures 61 and 62 show the snapshots of the formed NBs in dodecane sample at 298.15 K and 343.15 K at 0.5 ns. It is noted that three and two clusters are formed in dodecane and isooctane samples, respectively, at 343.15 K. In contrast, more small clusters have been observed at lower temperature.

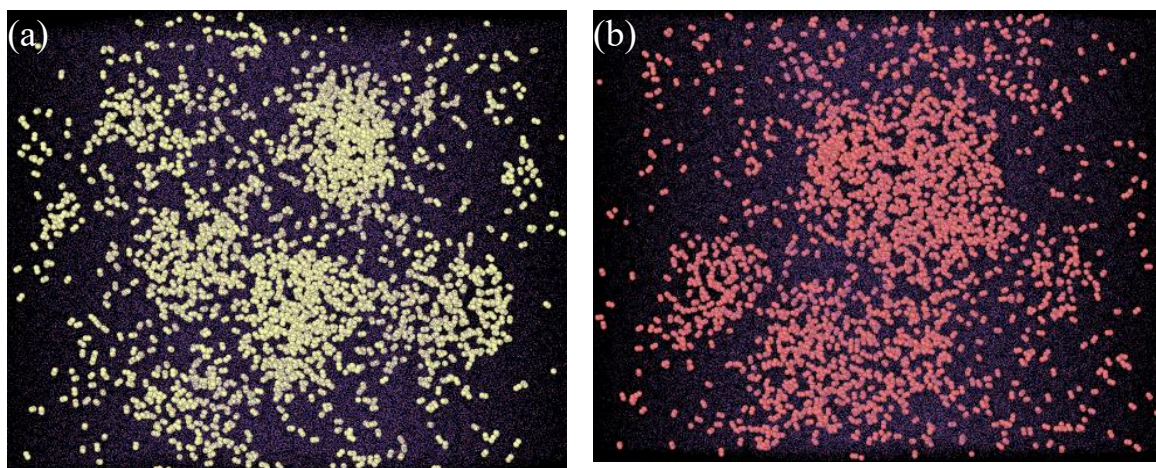


Figure 61. Snapshots of the formed NBs in dodecane sample at (a) 298.15 K and (b) 343.15 K at 0.5 ns.

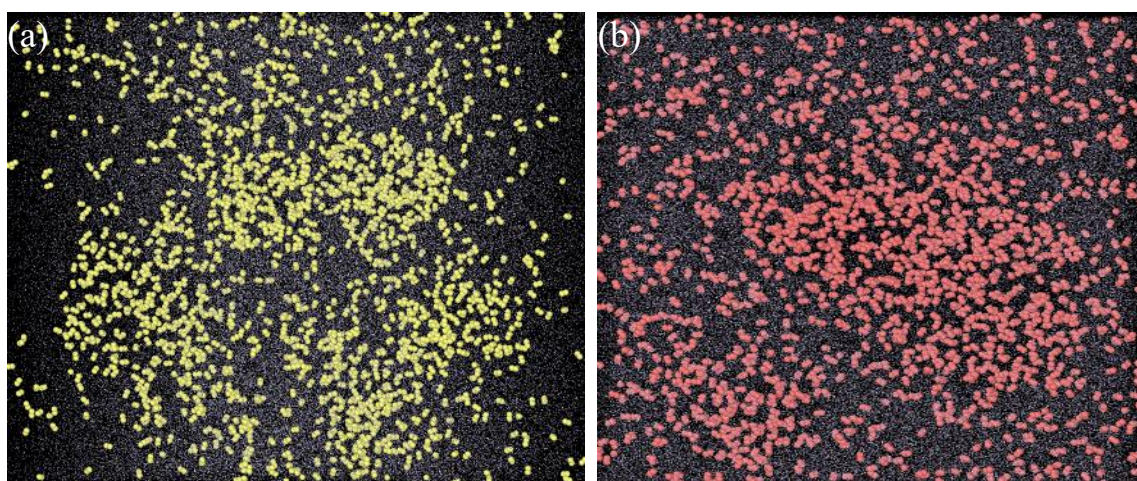


Figure 62. *Snapshots of the formed NBs in isooctane sample at (a) 298.15 K and (b) 343.15 K at 0.5 ns.*

Figure 63 shows the snapshots of the formed NBs at higher temperature at 1.5 ns and lower temperature at 1.5 ns and 4.75 ns. The results indicate that the coalescence process of the formed NBs is faster at higher temperature than at lower temperature, as it completes at 1.5 ns in the higher-temperature sample, whereas it takes 4.75 ns in the lower-temperature sample.

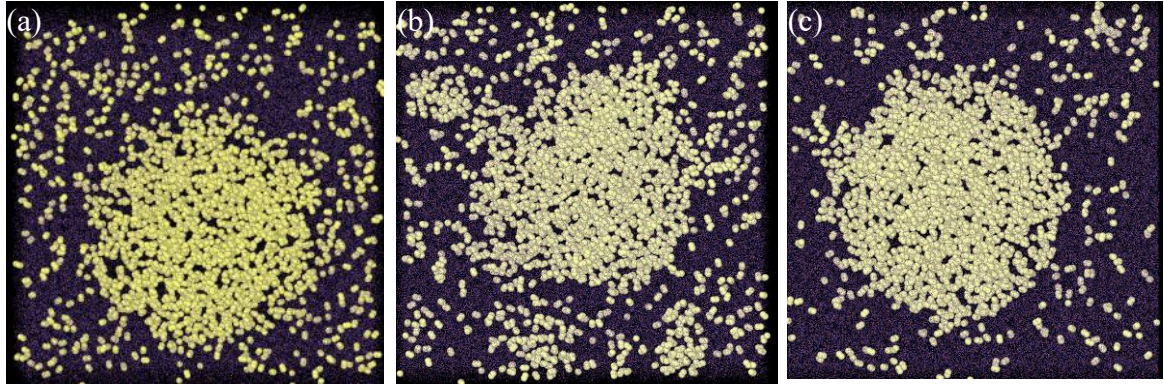


Figure 63. *Snapshots of the formed NBs (a) at higher temperature at 1.5 ns, (b) at lower temperature at 1.5 ns and (c) at 4.75 ns in dodecane.*

Figure 64 shows the snapshots of formed NBs in dodecane and isooctane at lower and higher temperature, and indicates that the size of the formed NBs at 13.4 ns is roughly the same for each combination. Therefore, it can be concluded that temperature doesn't have significant effect on the size of the formed NBs in a long period of time, however as it does affect the coalescence process at initial time.

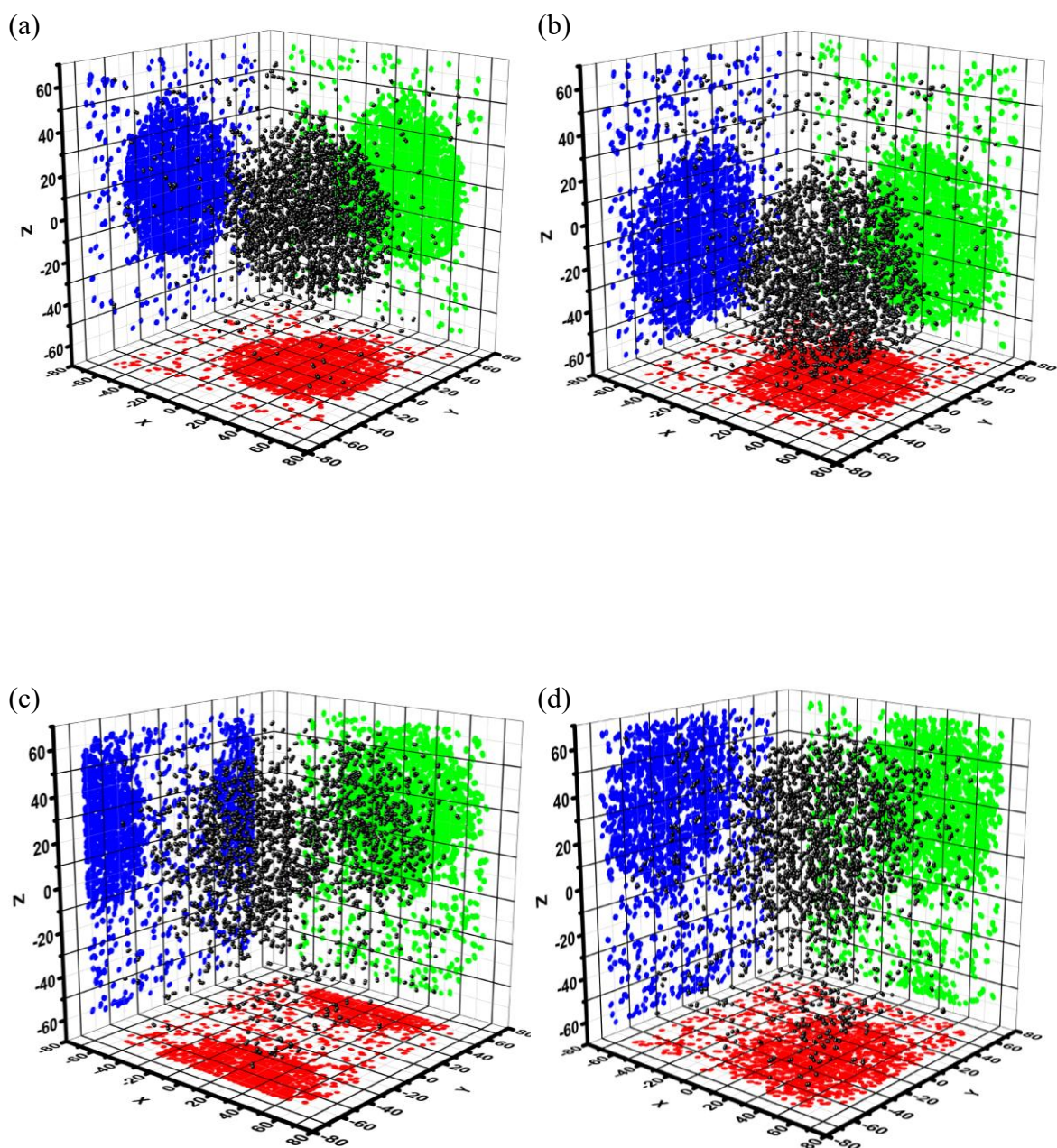


Figure 64. Snapshots of formed NBs in (a, b) dodecane and (c, d) isooctane (a, c) at lower and (b, d) higher temperature.

Compared with the viscosity of the samples at ambient temperature (Table 15), an increase in temperature results in a reduction in viscosity of 21.93% and 49.65% for the studied dodecane and isooctane samples, respectively. It follows the general trend that the viscosity of liquids decreases with the increase of temperature [191]. However, the results suggest that the type of host liquid plays an important role in the viscosity of the prepared samples,

and in this case, the viscosity of the isooctane sample shows a higher sensitivity to temperature changes. Furthermore, as shown in Figure 65, the van der Waals energy of the system varies with temperature, with lower values observed at higher temperatures.

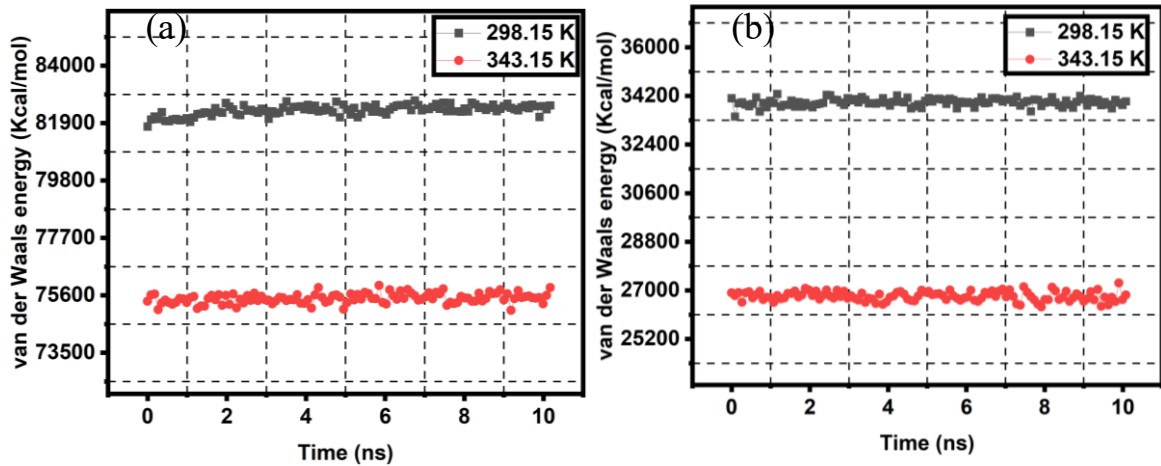


Figure 65. Absolute amount of van der Waals energy of (a) dodecane and (b) isooctane at different temperatures.

It is also observed that the diffusion coefficient of the prepared samples is increased by 102.92% and 112.43% for isooctane and dodecane samples, respectively, when the temperature is increased from 298.15 K to 343.15 K.

Understanding of the effect of temperature on thermal properties, especially the specific heat capacity, is vital as they can influence the application of materials. Generally speaking, heat capacity decreases with the increase in temperature [194]. Figure 66 compares the specific heat capacity of prepared samples at different temperature. The specific isochoric heat capacity of isooctane sample is decreased by increasing temperature, while the specific heat capacity of dodecane sample shows an opposite trend that it increases with the increase in temperature. Similar trend has been observed by other researchers that specific heat capacity of PCM-based mixture can be increased at higher temperature [193, 195, 196].

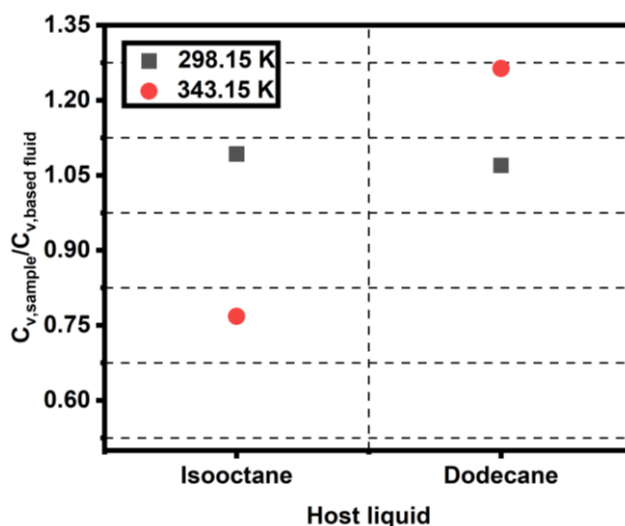


Figure 66. The specific heat capacity of prepared samples at different temperature.

Figure 67 shows the pairwise energy of isooctane and Coulomb energy of dodecane samples at 298.15 K and 343.15 K. In the isooctane sample, a decrease in non-bonded stored energy is observed with increasing temperature. In the dodecane sample, changes in Coulomb energy are observed with temperature. Variations in specific heat capacity are also observed across the systems at the investigated temperatures. These results show temperature-dependent changes in both interaction energies and specific heat capacity.

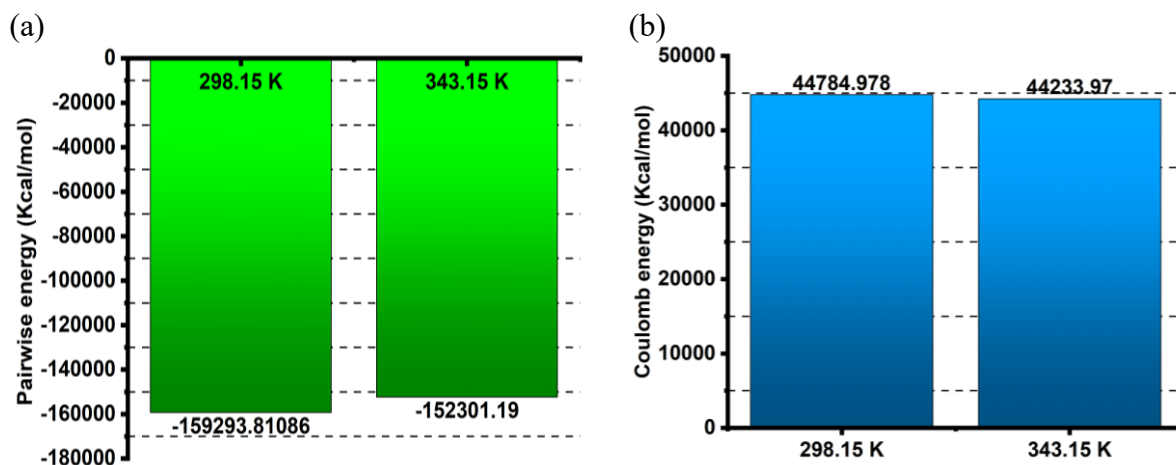


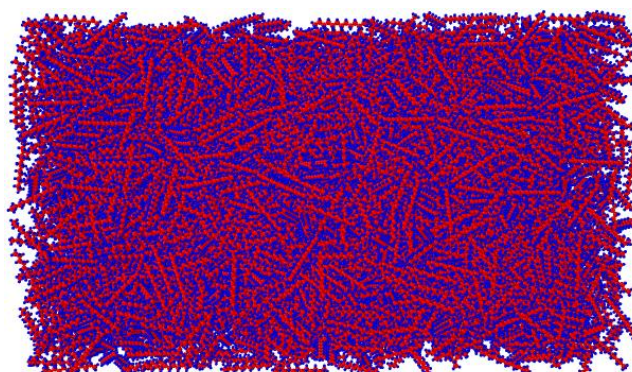
Figure 67. (a) Pairwise energy of isooctane and (b) coulomb energy of dodecane samples at 298.15 K and 343.15 K.

5.3 Phase transition and thermal behaviour

5.3.1 Phase transition

A pure phase-change model was constructed by randomly placing 5000 dodecane molecules within a simulation cell measuring $18.2 \times 10.46 \times 10.46 \text{ nm}^3$. NBs with a diameter of 2 nm, composed of nitrogen, hydrogen, and oxygen, were incorporated into the pure dodecane sample to establish the initial configuration of the nanobubble-enhanced PCM, as illustrated in Figure 68. Each nanobubble-laden sample was equilibrated for 5 ns under the isothermal–isobaric (NPT) ensemble at 298 K and 1 bar with a 1 fs timestep, followed by an additional 1.5 ns equilibration under the canonical (NVT) ensemble at the same temperature. The equilibrated samples were subsequently subjected to additional NPT simulations under target thermodynamic conditions to investigate their phase transition characteristics and thermal behaviour. Furthermore, after reaching the desired state and achieving equilibrium at constant volume, the inherent properties were evaluated using simulations performed in the microcanonical (NVE) ensemble.

(a)



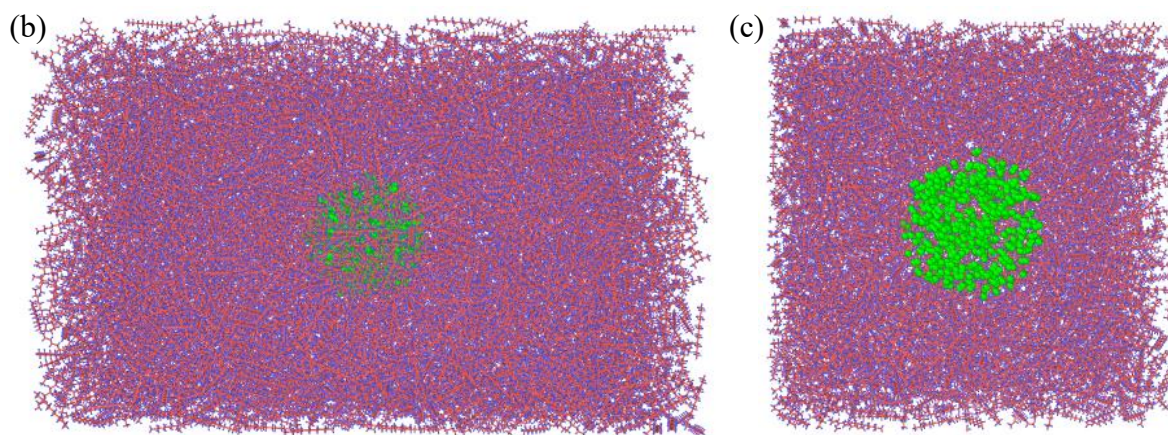


Figure 68. *Initial configurations of the simulated systems: (a) pure dodecane sample, (b) nanobubble-containing sample, and (c) cross-sectional view of the nanobubble-containing sample.*

The equilibrated dodecane samples with NB under environmental conditions underwent a solidification process, during which the temperature was reduced from 298.15 K to 253.15 K over a period of 3.5 ns to investigate the influence of NB type on the phase transition behaviour. Following the cooling phase, the resulting samples were subjected to simulations under the NVT and NVE ensembles to evaluate their inherent properties including thermal conductivity. It was observed that NBs remained stable throughout the solidification process, as illustrated in Figure 69.

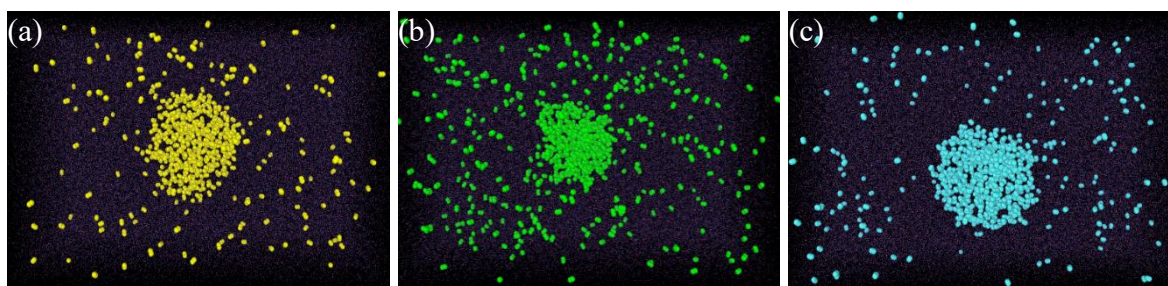


Figure 69. Snapshots of NBs in solidified dodecane: (a) nitrogen, (b) oxygen, and (c) hydrogen NBs.

The diffusion coefficient serves as a sensitive probe of the liquid–solid transition, as its temperature dependence differs strongly between phases. In the liquid regime, molecular mobility decreases rapidly upon cooling, whereas in the solid regime, mobility is nearly frozen and exhibits only weak temperature dependence. Consequently, a change in the slope

of the diffusion–temperature profile is taken as an indication of the onset of phase change [197]. In Figure 70a (main panel), this behaviour is illustrated for pure dodecane. The diffusion coefficient was found to decrease steadily with temperature until approximately 262.5 K, at which point a change in slope was identified by piecewise linear fitting. Below this temperature, the coefficient remains nearly constant, indicating that molecular mobility is greatly reduced in the solid phase. Confirmation of this transition was obtained from the system density shown in the inset of Figure 70a. A sharp discontinuity in density was detected at 263.5 K, despite constant temperature, which is characteristic of a first-order phase transition. This observation verifies that the slope change in the diffusion profile corresponds to solidification. The freezing point determined by MD simulations, 263.5 K, is in close agreement with the experimentally reported value of 263.6 K [198]. The influence of NBs is presented in Figures 70b–d, where the diffusion coefficient–temperature dependence of dodecane with different NBs was investigated to obtain an initial estimate of the phase transition temperature. In the liquid regime, a continuous decrease in the diffusion coefficient is observed, followed by a reduced slope at lower temperatures, indicating the onset of solidification. To refine this estimate, the corresponding sample densities are shown in Figures 70e–g. In each case, a distinct discontinuity in density was detected at the transition point, providing a more precise determination of the freezing temperature. A consistent depression of the transition temperature is observed in all NB-containing samples compared with pure dodecane, with the largest shift induced by hydrogen NB. The observed freezing point depression in dodecane can be attributed to the dynamic disruption induced by the NBs. Diffusion coefficient analysis shows a significant reduction in molecular mobility in the nanobubble-containing system compared to pure dodecane, indicating that the liquid dynamics are kinetically suppressed. This suppression traps the system in a

metastable, supercooled state, as the reduced mobility prevents the molecular rearrangements needed for crystal growth.

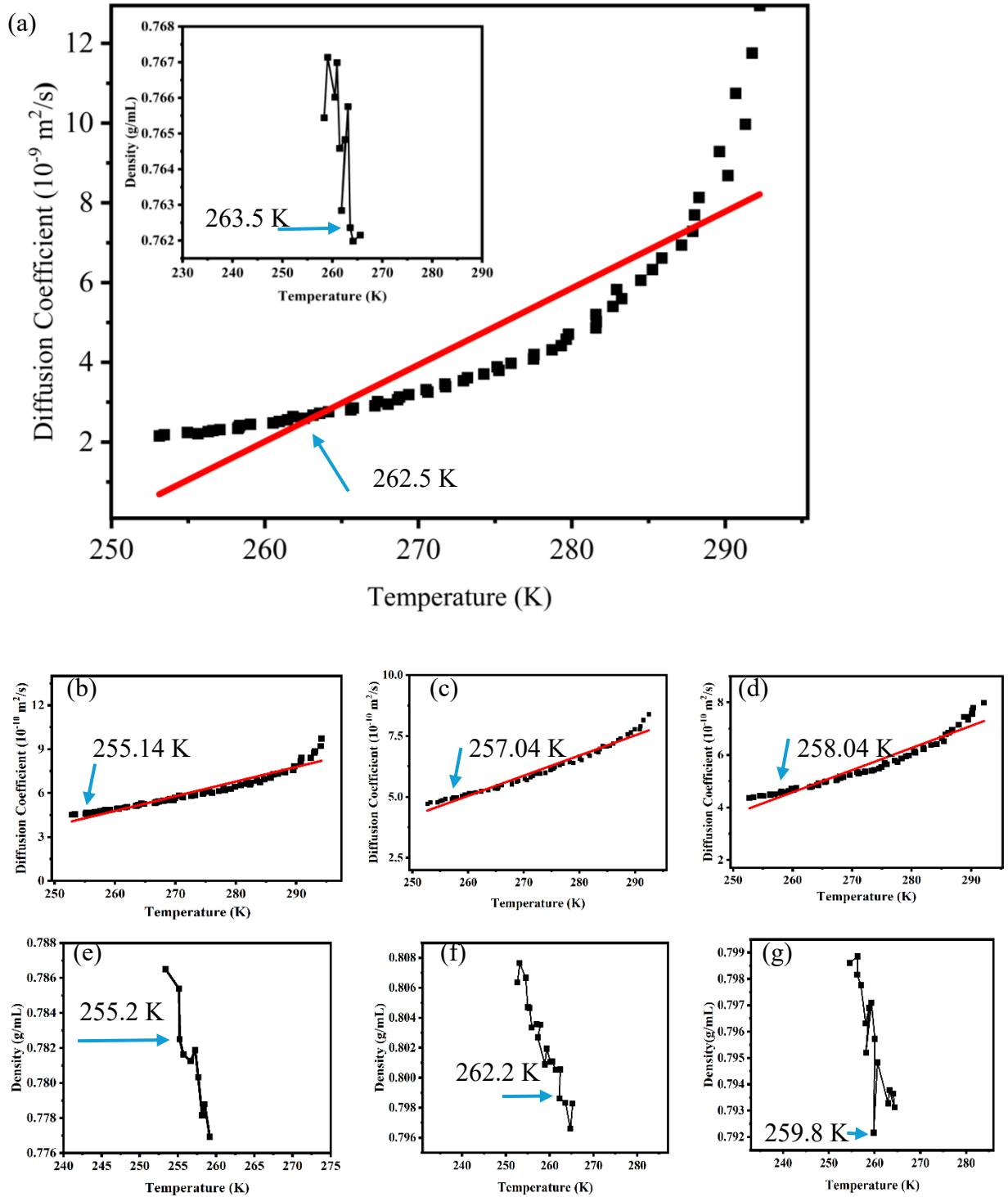


Figure 70. Diffusion coefficient and density of (a) pure dodecane, (b,e) hydrogen, (c,f) oxygen, and (d,g) nitrogen nanobubble-containing samples.

Due to the ongoing debate regarding the most reliable molecular dynamics approach for evaluating thermal conductivity [199], both equilibrium and non-equilibrium methods were employed to ensure the robustness of the results. In the non-equilibrium simulations, thermostatted regions at the two cell boundaries served as heat sources, while a centrally located region acted as a heat sink, establishing a steady-state heat flow under microcanonical (NVE) conditions. A constant heat flux Q was imposed between the sources and the sink. The simulation cell was partitioned into slabs along the heat-flow direction, and the time-averaged temperature of each slab was recorded to construct a temperature profile. The thermal conductivity k was then obtained from Fourier's law as follow [200]:

$$k = \frac{dQ/dt}{A(\frac{dT}{dx_1} + \frac{dT}{dx_2})} \quad (5.1)$$

where dQ/dt denotes the rate of heat addition or extraction at the heat source and sink, A is the cross-sectional area of the simulation box normal to the heat flux direction, and $\frac{dT}{dx_1}$ and $\frac{dT}{dx_2}$ represent the temperature gradients on either side of the heat source or sink. The temperature gradient profile of the pure dodecane system is illustrated in Figure 71.

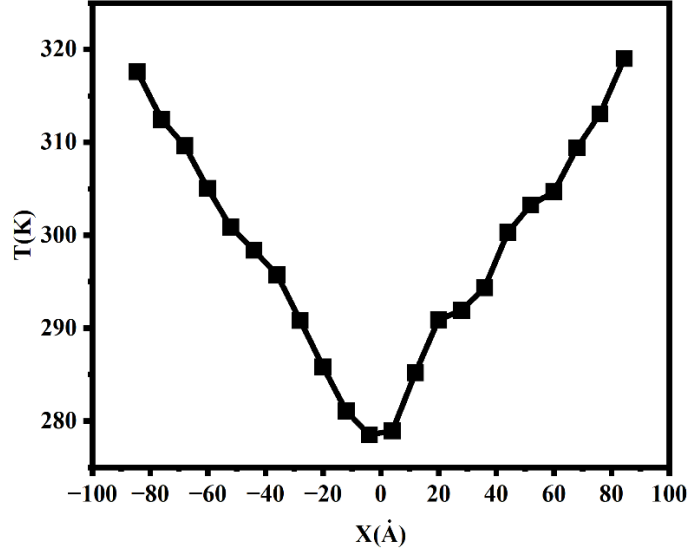


Figure 71. *The temperature gradient of pure dodecane along the x-axis direction.*

In equilibrium molecular dynamics simulations, the Green–Kubo formalism was employed to calculate the thermal conductivity. Specifically, the heat flux vectors and their time-dependent autocorrelations were computed throughout the simulation, and the thermal conductivity was determined by integrating the heat flux autocorrelation function over time, as expressed by the following equation [201].

$$\lambda = \frac{V}{K_B T^2} \int_0^\infty \langle J(0) \cdot J(t) \rangle dt \quad (5.2)$$

In this equation, $J(t)$ represents the heat flux vector at time t , V and T denote the system volume and temperature, respectively, and K_B is the Boltzmann constant. The calculated thermal conductivity, along with the corresponding experimental values, are summarized in Table 17. As shown, the non-equilibrium method adopted in this study shows better agreement with experimental thermal conductivity data than the equilibrium approach. The discrepancy arises from methodological differences. The Green–Kubo method is highly sensitive to long averaging times and noise in the autocorrelation tail and also requires

species-specific partial enthalpy calculations [202, 203]. In contrast, the NEMD method determines thermal conductivity directly from an imposed heat flux and the resulting temperature gradient.

Table 17. *Comparison of thermal conductivity (λ) values of dodecane obtained from molecular dynamics simulations with corresponding experimental data at 25 °C and 1 atm [204].*

	Experimental	Simulation	
		Non-equilibrium	Equilibrium
$\lambda(W/m.K)$	0.1413	0.16	0.26

Figure 72a illustrates a comparison of the thermal conductivity of nanobubbled dodecane samples with that of the pure one at 253.15 K. As shown, all nanobubbled systems exhibit enhanced thermal conductivity relative to the pure sample. The smallest improvement, approximately 8%, is observed with the presence of oxygen NB (ONB), while the nitrogen NB (NNB) results in the greatest enhancement, reaching nearly 14%. A similar enhancement has been reported in an experimental study, where the introduction of NBs was found to increase thermal conductivity by up to 11% [205].

In solids, heat transfer predominantly occurs via conduction, where energy is transmitted through lattice and intermolecular interactions. A higher degree of structural order facilitates more efficient energy propagation by minimizing phonon scattering and resistance, thereby enhancing thermal conductivity. The radial distribution function (RDF) is a fundamental tool used to characterize the spatial arrangement of atoms, representing the probability of finding a particle at a specific distance from a reference particle. RDFs are widely applied to analyse the structural organization of various materials, including crystalline solids, amorphous

phases, and liquids. By capturing variations in particle density as a function of distance, the RDF provides critical insight into intermolecular arrangements, making it essential for investigating the atomic structure and degree of order within materials. Highly ordered materials, such as crystalline solids, exhibit RDFs with sharp and pronounced peaks, indicative of regular and consistent interatomic separations. In contrast, disordered or less-ordered materials, including amorphous solids, display broader and less intense peaks, reflecting their inherently random atomic configurations [206]. The global structural organization of the dodecane matrix in both pure and nanobubble-containing samples was characterized by computing the RDF between dodecane molecules, as presented in Figure 72b. A notable observation from these RDF profiles is that all nanobubbled dodecane samples exhibit higher peak intensities compared to the pure dodecane sample. This clearly demonstrates that the presence of nanoscale bubbles, regardless of the specific gas (oxygen, nitrogen, or hydrogen), induces a more ordered crystalline arrangement within the solid dodecane matrix at 253.15 K. The resulting enhancement in global order implies a reduction in structural defects, which are known to serve as phonon-scattering centers and thereby limit thermal conductivity. Further analysis revealed nuanced differences among the nanobubbled samples. While the oxygen nanobubble-containing sample showed an increase in structural ordering relative to pure dodecane, its RDF peak height was lower than those observed for the nitrogen and hydrogen nanobubble-containing samples. This suggests a comparatively less effective templating or ordering influence of oxygen NB on the dodecane matrix. In contrast, the nitrogen and hydrogen nanobubbled samples exhibited similarly high RDF peak intensities, indicating that both gases promote a comparable degree of global ordering within the solid dodecane structure. To gain deeper insight into the local interactions at the nitrogen and hydrogen nanobubble–dodecane interface, the RDF between these bubble molecules and the surrounding dodecane molecules was computed, as shown in Figure 72c.

This analysis revealed distinct differences in local ordering induced by nitrogen and hydrogen NBs. Specifically, the nitrogen nanobubble-containing sample exhibited a significantly higher RDF peak than the hydrogen NB sample, indicating that dodecane molecules are more locally ordered and densely packed around nitrogen NB. This enhanced local order likely yields superior heat transfer performance compared to hydrogen NB.

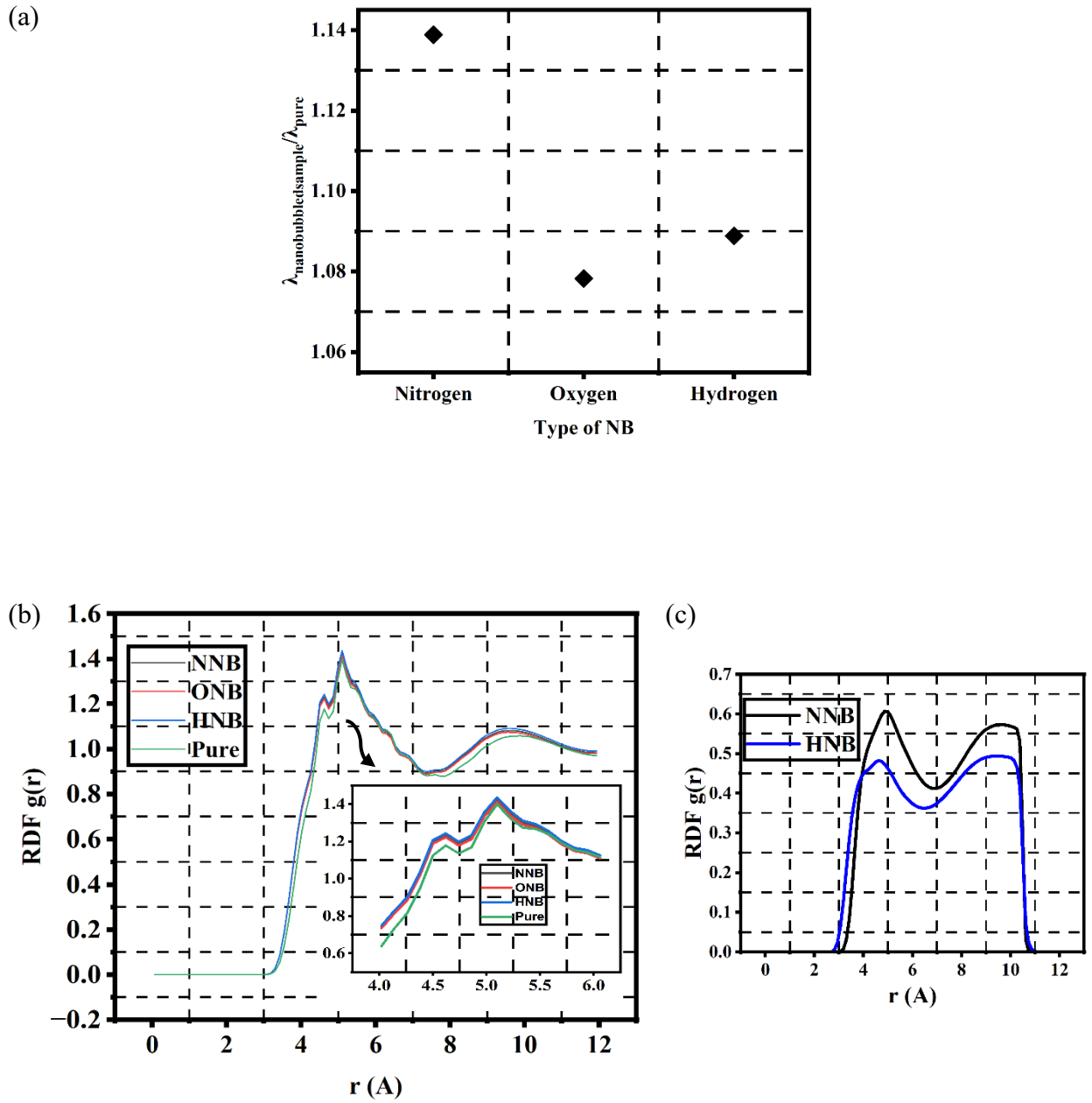
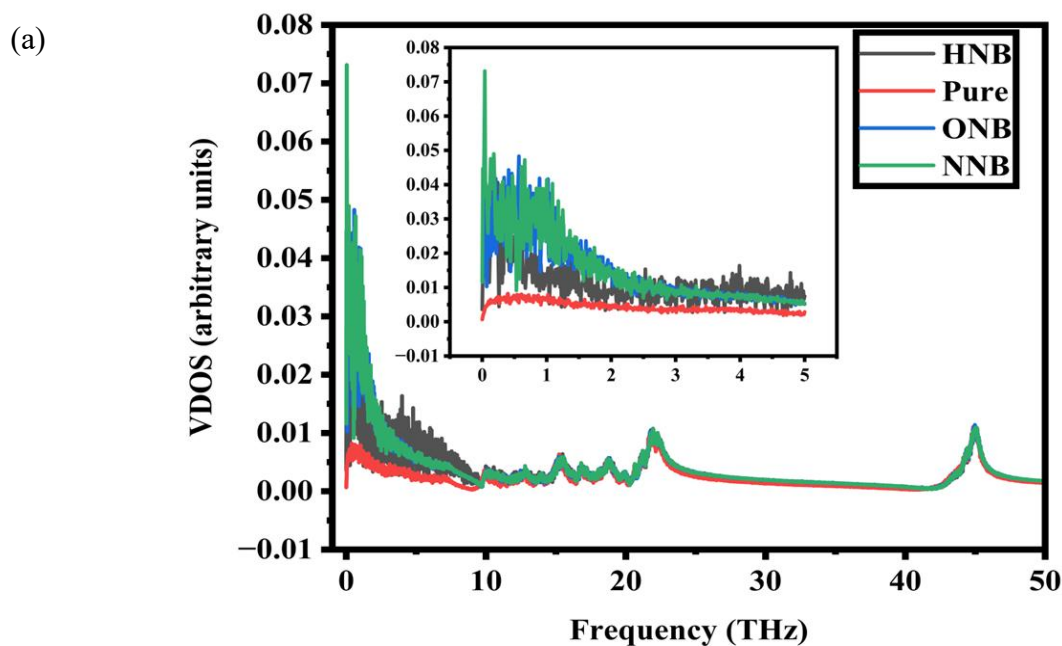


Figure 72. (a) Comparison of thermal conductivity between nanobubbled samples and pure dodecane, (b) RDF between dodecane molecules, and (c) RDF between nitrogen and hydrogen nanobubble molecules and dodecane molecules at 253.15 K.

In addition to the structural insights obtained from the radial distribution function, which characterizes local atomic arrangements and ordering, the vibrational density of states (VDOS) is examined to capture the dynamic aspects of energy transport. The VDOS, obtained through the Fourier transform of the mass-weighted velocity autocorrelation function (VACF), provides the distribution of vibrational modes within the system and establishes a direct connection to phonon dynamics that govern thermal conductivity. Of particular importance is the vibrational matching between nano-additives and the host medium, which predominantly occurs in the low-frequency region [207]. The VDOS of the pure sample and of the samples containing NBs are presented in Figure 73a. Compared to the pure sample, the addition of NBs leads to an enhancement of vibrational modes at lower frequencies and enhancement in the population of low-frequency phonon modes. This effect is most pronounced for nitrogen NB, suggesting that nitrogen NB promotes more efficient low-frequency phonon interactions and potentially enhances thermal transport more effectively.

The enhancement of dynamic vibrational modes in the atomic structure, together with the more locally ordered and densely packed arrangement revealed by the RDF analysis, results in nanobubbled samples exhibiting higher thermal conductivity than the pure system. This combined effect is most pronounced in the case of nitrogen NB, leading to the highest thermal conductivity among the investigated samples. To further analyse the structure of the NNB sample and compare it with the pure sample, the coordination number (CN) was investigated. The CN, which denotes the number of nearest-neighbour atoms or ions

surrounding a central atom in a crystal or amorphous solid, was determined using the Voronoi tessellation method, providing more detailed insights into the atomic structure of the prepared samples. Figures 73b and 73c illustrate the CN distribution of hydrogen and carbon atoms in dodecane, the host medium, for pure and NNB samples, focusing on the three highest CN fractions. The figures reveal that at least 26.61% of atoms in the NNB sample possess a CN of 17 or higher, compared to only 12.86% in the pure sample. A further analysis of all CN fractions with values of 17 or higher indicates 47.48% in the NNB sample and 38.63% in the pure sample, confirming a more densely packed molecular environment in NNB sample. This denser packing enhances vibrational coupling between neighbouring atoms, thereby facilitating more efficient energy transfer.



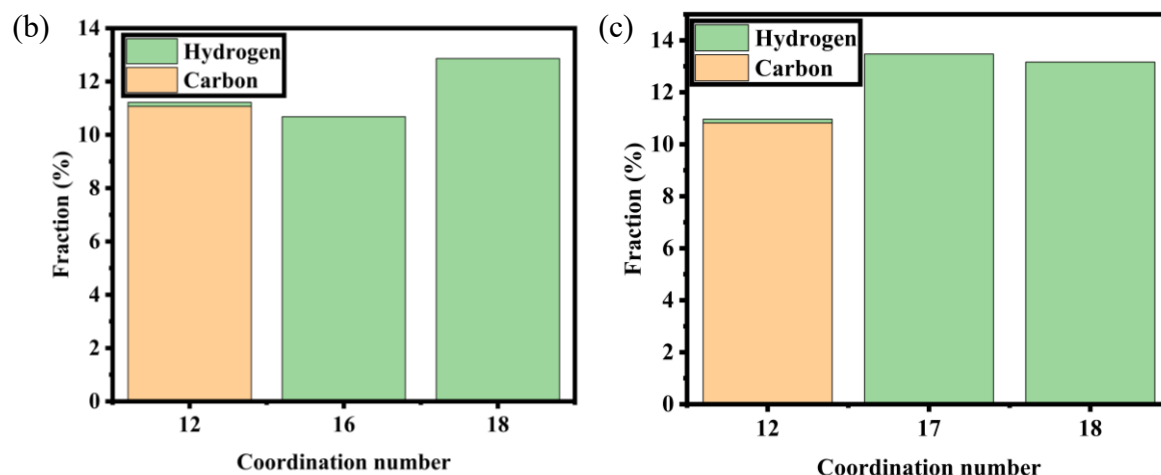


Figure 73. (a) *Vibrational density of states (VDOS) of the pure sample and nanobubbled samples, and distribution of coordination numbers for the three highest fractions of hydrogen and carbon atoms in dodecane, the host medium, for (b) the pure sample and (c) the sample with nitrogen NB.*

The comparison of the specific heat capacity of the prepared NB samples to that of the pure sample, shown as $C_{v,nanobubbledsample}/C_{v,pure}$ in Figure 74a, indicates that the addition of NBs to dodecane leads to an increase in the specific heat capacity of the dodecane matrix at 253.15 K. The highest enhancement was observed for NNB, while the lowest improvement was recorded for HNB. Specific heat capacity is closely related to the strength and nature of intermolecular interactions. Stronger interactions and more complex molecular structures typically lead to higher specific heat capacities, as more energy is needed to disrupt and overcome these interactions and increase molecular motion and temperature. As shown in Figure 74b, analysis of the pairwise interaction energy at 253.15 K indicates that the addition of NBs enhances intermolecular interactions across the samples. Among them, NNB exhibits the greatest increase in pairwise energy, suggesting the strongest intermolecular interactions, while HNB shows the smallest increase.

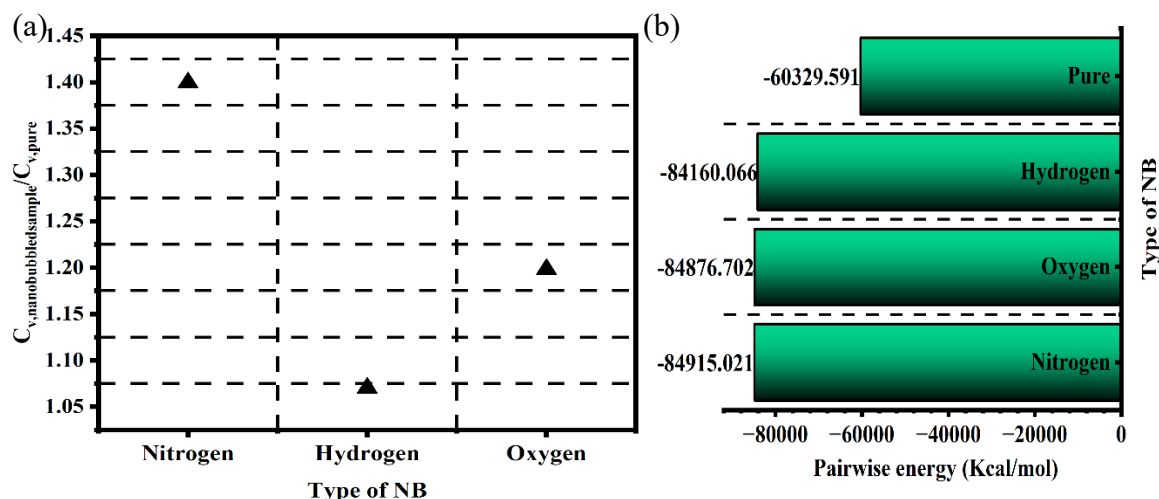


Figure 74. (a) Comparison of the specific heat capacity of nanobubble-containing samples to the pure dodecane sample, and (b) pairwise energy of the samples at 253.15 K.

5.3.2 Thermal behaviour

Understanding the thermal behaviour of host liquids containing NBs is essential for enhancing their performance in heat transfer and thermal management systems. The interactions between NBs and the surrounding liquid medium can significantly influence the thermophysical properties of the system. Temperature acts as a global parameter that strongly affects bubble dynamics and stability. Previous studies have shown that surface NBs can remain stable even near the boiling point of host liquids such as water, largely due to surface pinning effects [208]. This suggests that NBs, especially in bulk liquids, may exhibit distinct thermal stability.

The equilibrated samples under environmental conditions were subjected to separate thermal conditions to investigate their response at non-ambient temperatures. To study high-temperature effects, the equilibrated systems were heated to 443.15 K under the NPT ensemble, while low-temperature behaviour was assessed by cooling the systems to 275.15 K, both temperatures lying outside, but close to, the boiling and solidification points of dodecane, over a 3.5 ns simulation period to investigate the influence of temperature on NB

behaviour. Following this, the samples were subjected to additional simulations under the NVT and NVE ensembles to evaluate their inherent properties, including thermal conductivity. As illustrated in Figure 75, nitrogen, oxygen, and hydrogen NBs remain stable at 275.15 K. However, at the elevated temperature of 443.15 K, only nitrogen and hydrogen NBs retain their stability, as shown in Figure 76, while oxygen NBs disappear. The higher solubility of O₂ in dodecane, compared with N₂ and H₂ [209], along with the increased molecular mobility at elevated temperatures, allows oxygen NB to disperse into the host liquid. In contrast, nitrogen and hydrogen interact more weakly with dodecane, as reflected by the smaller Lennard–Jones well depths in Table 4, resulting in lower solubility and enabling them to persist as NBs under the same conditions. These results indicate that nitrogen and hydrogen NBs are more suitable candidates for high-temperature applications and could potentially be utilized across a wide temperature range.

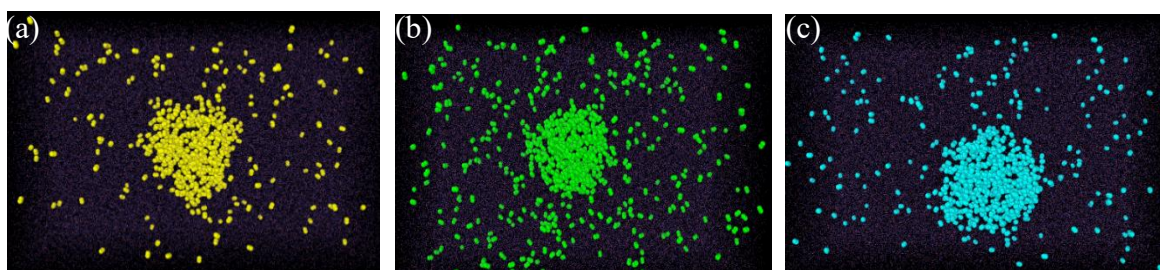


Figure 75. Snapshots of (a) nitrogen, (b) oxygen, and (c) hydrogen NBs in dodecane at 275.15 K.

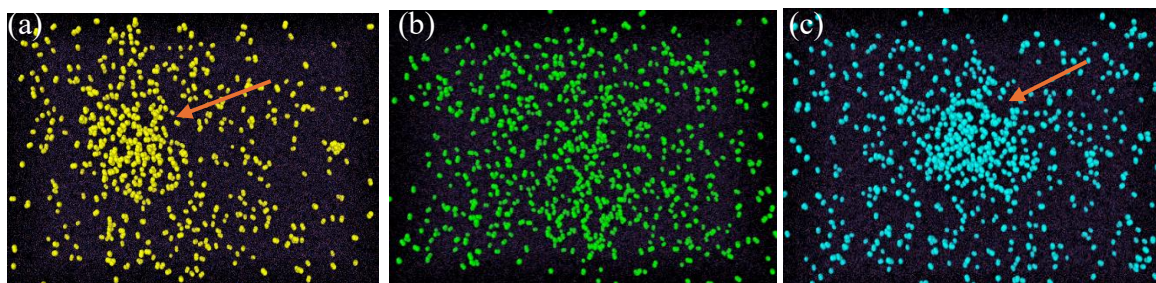


Figure 76. Snapshots of (a) nitrogen, (b) oxygen, and (c) hydrogen NBs in dodecane at 443.15 K.

As discussed in the previous section, the presence of NBs at lower temperatures enhances molecular orientation and contributes to an increase in thermal conductivity. To further explore this phenomenon, the thermal conductivity of hydrogen and nitrogen NBs, both of which remain stable at 443.15 K, was calculated. The results, presented in Figure 77, demonstrate that the presence of NBs at elevated temperatures can significantly enhance thermal conductivity, confirming their positive impact on heat transfer performance.

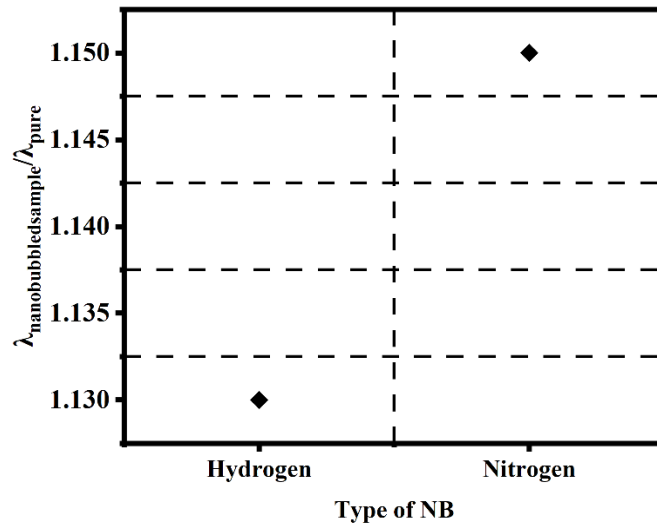


Figure 77. *Comparison of the thermal conductivity of nanobubble-containing samples with that of pure dodecane at 443.15 K.*

Viscosity reflects a material's resistance to flow and plays a crucial role in determining the efficiency of heat transfer and the overall energy consumption of a system. As illustrated in Figure 78, the introduction of NBs into the host liquid, both at low and high temperatures, results in an increased viscosity compared to pure dodecane. At 275.15 K, the highest viscosity was observed in the sample containing hydrogen NB, followed by nitrogen and then oxygen. Conversely, at 443.15 K, the nitrogen NB sample exhibited the highest viscosity, followed by hydrogen. These variations highlight the influence of NB type and temperature on the rheological behaviour of the fluid.

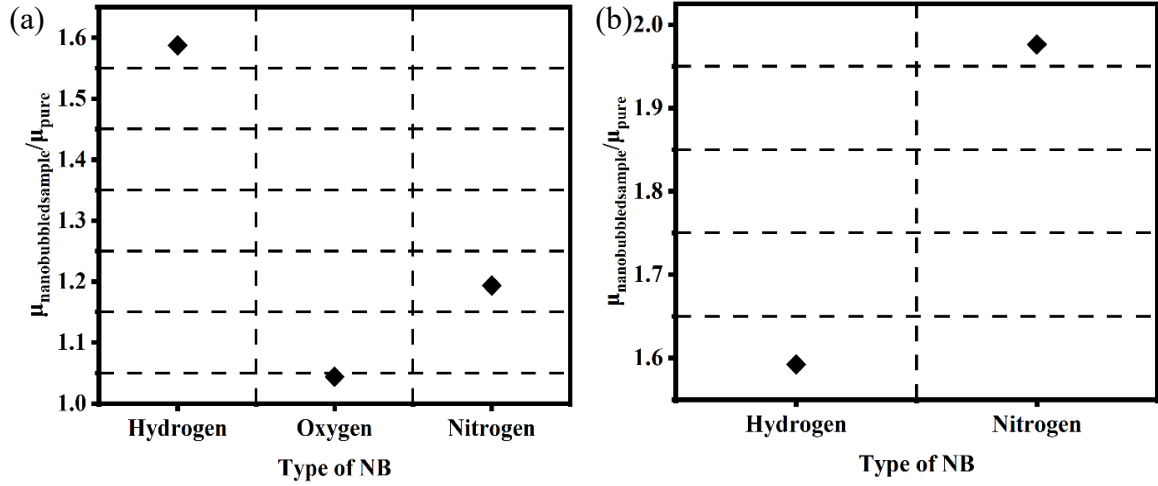


Figure 78. Comparison of the viscosity of nanobubble-containing samples with that of pure dodecane at (a) 275.15 K and (b) 443.15 K.

Mean Square Deviation (MSD) is a fundamental metric used to quantify the average squared displacement of atoms or molecules from their initial positions over time. It provides critical insight into atomic mobility and is widely employed to characterize diffusion behaviour in materials. In the context of phase change materials (PCMs), MSD analysis is particularly valuable for evaluating atomic movement, offering a deeper understanding of the material's thermal and dynamic properties. MSD is mathematically defined as the time-averaged deviation of a particle's position from its reference position, and can be expressed as follows [197]:

$$\text{MSD}(t) = \frac{1}{N} \langle \sum_{i=1}^N |r_i(t) - r_i(0)|^2 \rangle \quad (5.3)$$

in which N is the total number of atoms, and $r_i(t)$ and $r_i(0)$ represent the position vectors of the i^{th} atom at time t and at the initial moment, respectively, with positions given in angstroms. The MSD of the samples at 274.15 K and 443.15 K is presented in Figure 79. As observed, the MSD values of the nanobubbled samples are lower than those of the pure dodecane sample at both temperatures, indicating reduced atomic mobility due to the

presence of NBs. At 274.15 K, the HNB sample exhibits the lowest MSD, followed by the NNB and ONB samples. At 443.15 K, the NNB sample shows a lower MSD compared to the HNB sample. This difference can be explained by the fact that hydrogen atoms, being lighter than nitrogen atoms, experience a greater increase in velocity when the temperature increases. As a result, atoms in the HNB sample move more freely at higher temperatures. Overall, NBs act as obstacles in the path of atomic movement, restricting mobility and contributing to the increased viscosity observed in nanobubbled samples.

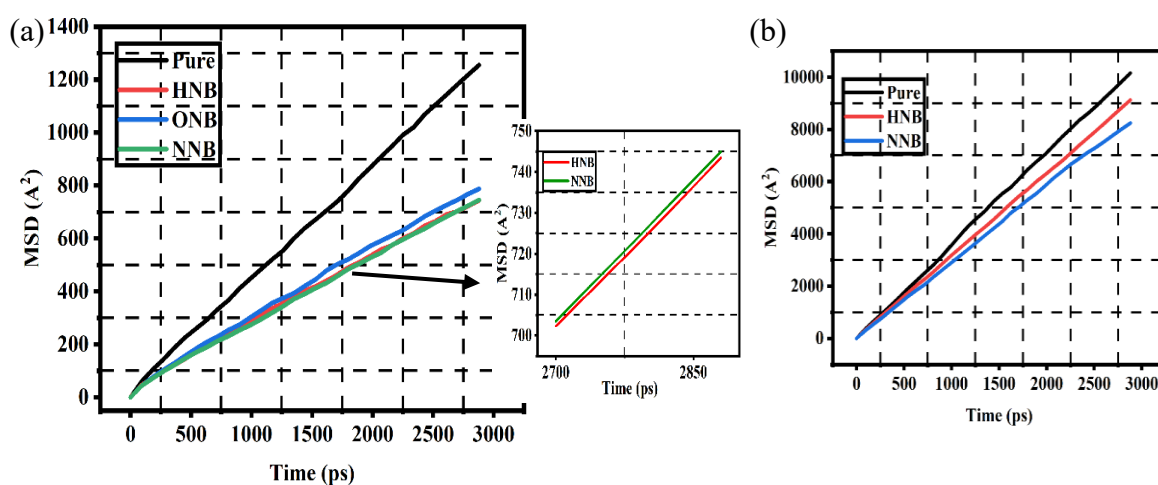


Figure 79. Mean square displacement of pure and nanobubble-containing samples at (a) 275.15 K and (b) 443.15 K.

5.4 Combustion mechanism of nanobubbled dodecane

5.4.1 Effects of NB Type

To investigate the effects of NBs on the combustion process of dodecane, a stoichiometric sample was prepared by randomly distributing 100 dodecane molecules and 1850 oxygen molecules within a cubic box with a side length of 90.64 Å in three dimensions, resulting in a sample density of 0.17 g/mL. NBs of three different types, each with a radius of 3 nm, were introduced into the pure sample. The box dimensions were adjusted to 95.05 Å, 93.80

Å, and 90.91 Å for samples containing oxygen, nitrogen, and hydrogen NBs, respectively. These NBs contained 365 oxygen molecules, 295 nitrogen molecules, and 345 hydrogen molecules. The initial configuration of the prepared samples is illustrated in Figure 80. Each prepared sample was studied with three different initial structures. Additionally, hydrogen NB samples were examined at three different densities to elucidate the impact of the sample density on the combustion characteristics of nanobubbled dodecane fuel. All prepared samples underwent a relaxation process for 300 picoseconds (ps) in the NVT ensemble, followed by heating to the desired temperature. Subsequently, a combustion process was investigated over 2000 ps with a timestep of 0.1 fs.

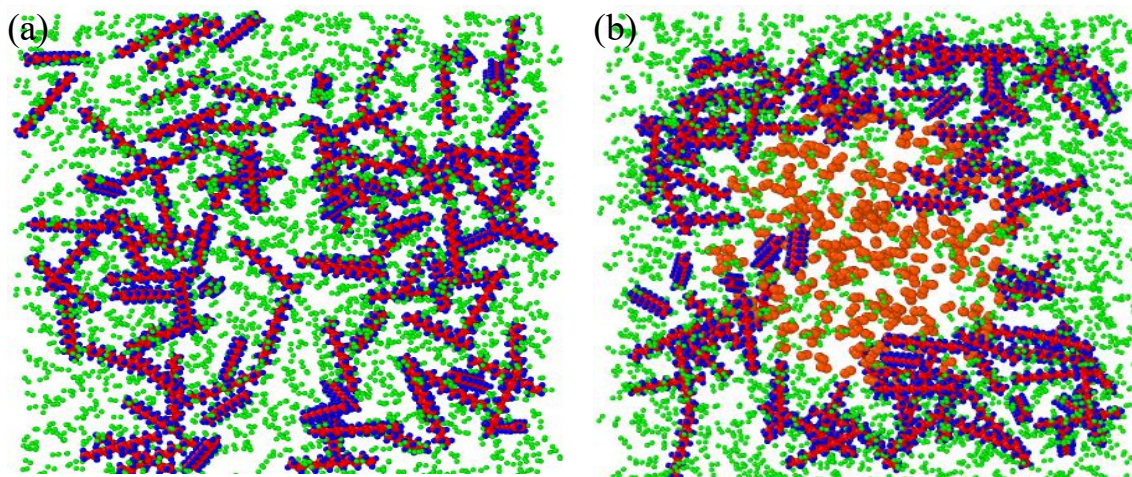


Figure 80. *Initial configuration of (a) a pure sample containing dodecane ($C_{12}H_{26}$) and oxygen molecules, featuring red carbon atoms, blue hydrogen atoms, and green oxygen atoms, and (b) a nanobubbled sample, orange NB atoms.*

Figure 81a illustrates the time evolution of the number of dodecane molecules in pure and nanobubbled samples. It can be seen that the presence of nitrogen and hydrogen NBs accelerates the consumption of dodecane molecules, whereas the addition of oxygen NB leads to a decrease in dodecane consumption compared to the pure sample.

To delve deeper into the initial stages of the combustion process, an examination was conducted regarding the number of chemical species and molecules at the combustion temperature for 60 ps. Figure 81c illustrates the number of oxygen molecules and chemical species in the pure sample. Notably, no reaction was observed before reaching the desired temperature. However, despite the constant number of oxygen molecules, there was a noticeable increase in the number of chemical species at the combustion temperature over time. Further analysis of the formed species unveiled that the reaction commenced with the thermal decomposition of $C_{12}H_{26}$ to $C_{10}H_{21}$ and C_2H_5 . This decomposition process proceeded with the formed species decomposing into C_8H_{17} and C_2H_4 . In Figure 81d, the number of chemical species and molecules in the hydrogen nanobubbled sample, inclusive of dodecane, oxygen, and hydrogen, is shown. Before reaching the desired combustion temperature, no reaction occurred. As the temperature reached the desired level, an increase in the number of chemical species was observed, while the number of hydrogen and oxygen molecules remained constant. The reaction initiation in this sample commenced with the thermal decomposition of $C_{12}H_{26}$. Likewise, the oxygen nanobubbled sample followed a similar trajectory to the pure and hydrogen nanobubbled samples, where the reaction commenced with the decomposition of the hydrocarbon fuel.

Conversely, within the nitrogen nanobubbled sample (Figure 81b), reactions occurred near the desired temperature. Oxygen molecules reacted with nitrogen molecules, yielding the formation of N_2O_2 (dioxohydrazine). Additionally, interactions between nitrogen molecules and dodecane molecules resulted in the formation of $C_{12}H_{26}N_2$, at temperatures near 2000 K, which converted into $C_{12}H_{25}$ and HN_2 . This unique behaviour suggests that the reaction process in the nitrogen nanobubbled sample initiated through molecule reactions and formation of intermediates and radicals, rather than thermal decomposition, thereby accelerating the consumption of dodecane.

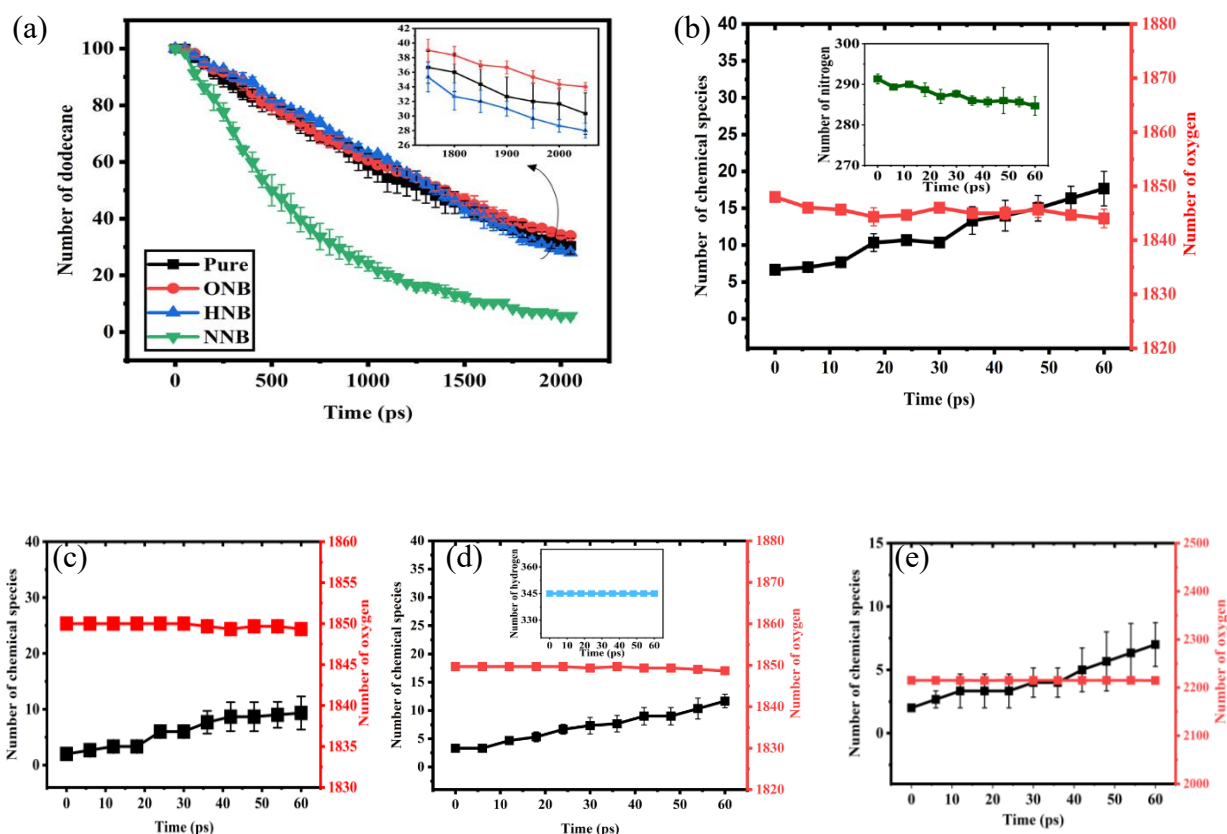


Figure 81. Time evolution of (a) the number of dodecane molecules in pure and nanobubbled samples, and the number of chemical species, oxygen, and nanobubbles molecules within (b) nitrogen, (c) pure, (d) hydrogen, and (e) oxygen nanobubbled samples.

Figure 82 displays the three most abundant chemical species at 2000 K at the conclusion of the simulation period. C_2H_4 , C_3H_6 , and CH_3 are the predominant species created in the pure, oxygen, and hydrogen nanobubbled samples. Conversely, water was the most produced species in the nitrogen nanobubbled sample. In addition to the species shown in Figure 82, other chemical species such as CO and H_2O were detected in the pure, oxygen, and hydrogen nanobubbled samples. Moreover, compounds like CO , NO_2 , and NO were also found in the nitrogen nanobubbled sample as well.

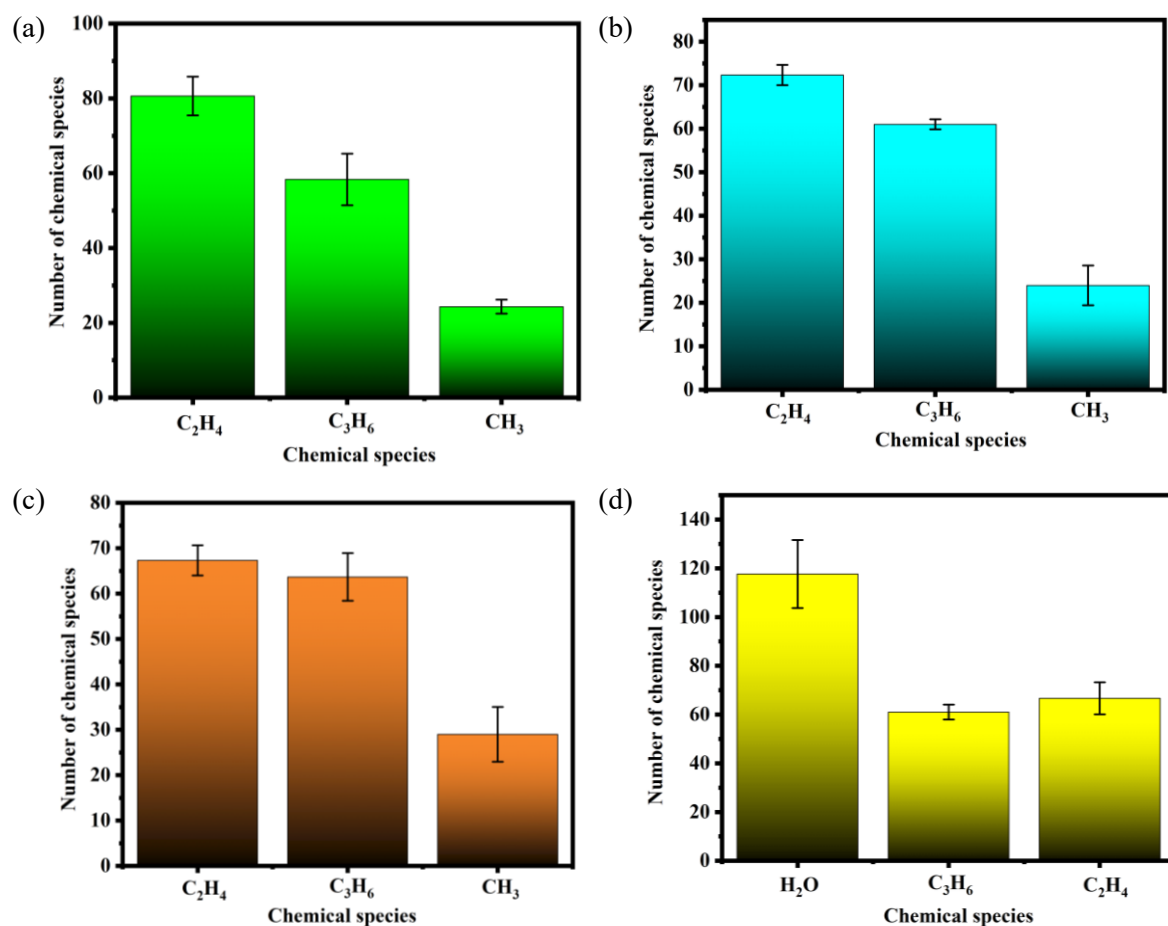
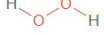
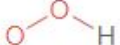
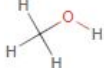
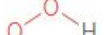
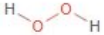
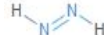


Figure 82. *The three most produced chemical species at 2000 K after 2000 ps within (a) pure, (b) oxygen, (c) hydrogen, and (d) nitrogen nanobubbled samples.*

The most significant distinction in the produced chemical species among the prepared samples lies in the production of water, within the nitrogen nanobubbled sample exhibiting the highest quantity. Further analysis of water production in the prepared samples shows that the hydrogen nanobubbled sample had the second highest water production, whereas the oxygen nanobubbled sample recorded the lowest amount of water production. To elucidate the mechanism underlying the influence of NBs on water formation, the reaction network was investigated [165]. Table 18 illustrates the most frequent reaction pathway resulting in the production of water within the prepared samples, with a notable emphasis on the reaction involving OH, which is particularly prominent in the nitrogen NB sample, primarily originating from H₂O₂ introduced by the nitrogen NB. Additionally, Figure 83 provides

further insight into the influence of blended nitrogen NB on the reaction path of the formation of intermediates and radicals.

Table 18. *The most common reaction leading to water production within the pure, oxygen (ONB), hydrogen (HNB), and nitrogen (NNB) nanobubbled samples (the numbers on the arrows indicate the frequency of a reaction).*

Pure	 	$\xrightarrow{4}$			$\xrightarrow{3}$			$\xrightarrow{1}$	
ONB	 	$\xrightarrow{3}$			$\xrightarrow{1}$			$\xrightarrow{1}$	
HNB	 	$\xrightarrow{11}$		 	$\xrightarrow{10}$			$\xrightarrow{2}$	
NNB	 	$\xrightarrow{82}$			$\xrightarrow{36}$			$\xrightarrow{35}$	

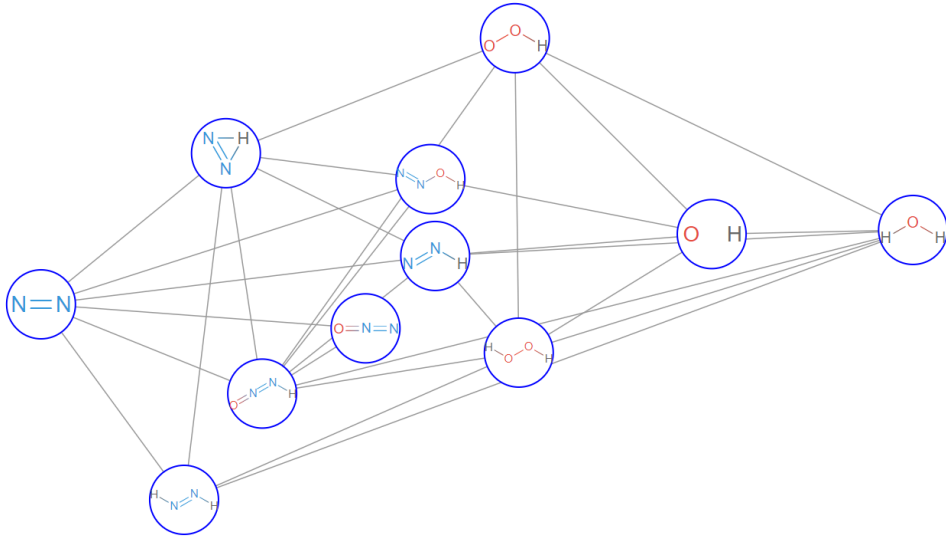


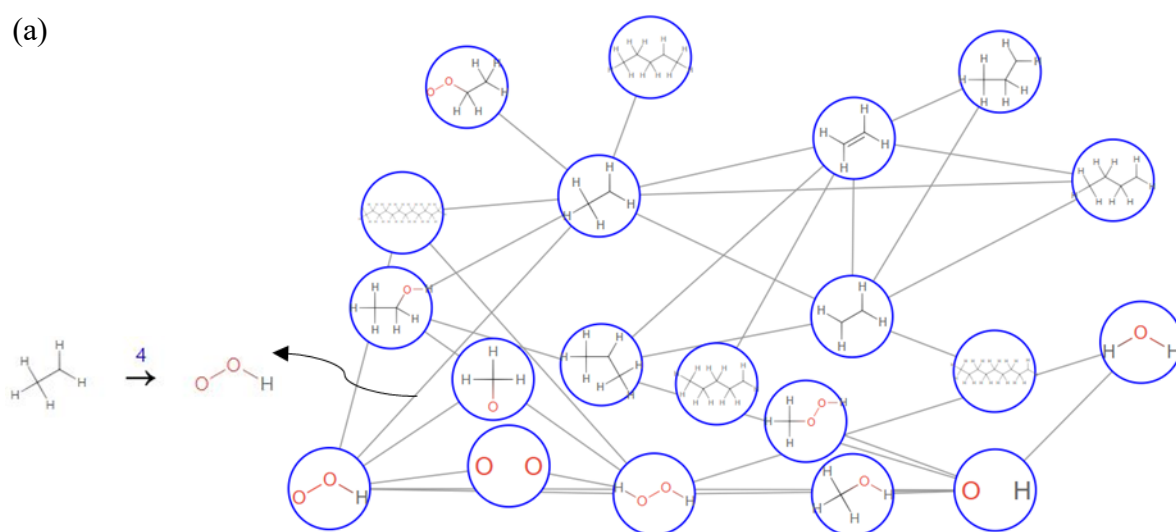
Figure 83. *Reaction network of intermediates and radicals originating from the introduced nitrogen nanobubbles that result in water production.*

Differences between the reaction pathways in the pure sample and the oxygen NB sample are highlighted in Table 18. The pure sample notably features the incorporation of hydrogen atoms from the dodecane structure into water molecules as the second most frequent reaction. Detailed tracking of hydrogen atoms in the fuel structure reveals this pathway: $C_{12}H_{26} \rightarrow C_{10}H_{21} \rightarrow C_7H_{15} \rightarrow C_4H_9 \rightarrow CH_3 \rightarrow CH_2O \rightarrow H_2O$, demonstrating that hydrogen from dodecane thermal decomposition contributes to the formation of water. In contrast, this reaction pathway is absent in the oxygen nanobubbled sample. Furthermore, the comparison of dodecane consumption in Figure 81a indicates higher dodecane consumption in the pure sample compared to the oxygen nanobubbled sample. The introduction of oxygen NB, which increase the availability of oxygen in the sample, can act as heat sinks by absorbing energy from the combustion process, thereby lowering reaction rates and decomposition of dodecane. Moreover, oxygen NB can quench radical species involved in combustion reactions, decreasing the frequency of chain reactions and reducing overall reaction rates. Additionally, the presence of excess oxygen molecules can dilute the concentration of fuel molecules in the combustion mixture, resulting in fewer fuel molecules available to participate in combustion reactions and consequently leading to slower reaction rates.

Figure 82 highlights that water is the predominant product in the nitrogen nanobubbled sample, while the formation of C_2 - C_3 -C species prevails in the pure, hydrogen, and oxygen nanobubbled samples. It's crucial to note that a pivotal stage in the formation of soot during the oxidation of rich hydrocarbon fuels involves the recombination reactions of carbon-containing fragments, leading to the generation of species with two or more carbon atoms [210]. Within the neat dodecane sample and samples with hydrogen, and oxygen nanobubbles, C_2H_4 , C_3H_6 , and CH_3 exhibit the highest production levels. Interestingly, when comparing the production of C_2H_4 and CH_3 in these three samples as predominant products,

it's observed that the addition of oxygen and hydrogen to the pure sample decreases the formation of C_2H_4 , with the lowest amount recorded for hydrogen nanobubbled samples. Conversely, the production of CH_3 increases, with the highest amount observed for the oxygen nanobubbled sample.

An examination of the reaction pathways and their frequencies leading to the production of C_2H_4 in pure and hydrogen nanobubbled samples, as shown in Figure 84a and b, highlights the significant role of C_2H_5 in the formation of C_2H_4 . Notably, in the hydrogen nanobubbled sample (Figure 84b), more C_2H_5 intermediates convert to HO_2 radicals compared to the pure sample. This increased conversion leads to the production of more water molecules and fewer C_2H_4 molecules in the hydrogen nanobubbled sample than in the pure sample. Furthermore, scrutinizing the reaction pathway for the formation of CH_3 in pure and oxygen nanobubbled samples (Figure 85a and b) reveals the important role of CH_3O_2 as the most frequent reaction in CH_3 formation. Interestingly, in the oxygen nanobubbled sample, more CH_3O_2 converts to CH_3 compared to the pure sample. Consequently, blending NBs with the host fuel alters the production quantity by affecting the production and reaction of intermediates and radicals, thereby influencing the combustion process.



(b)

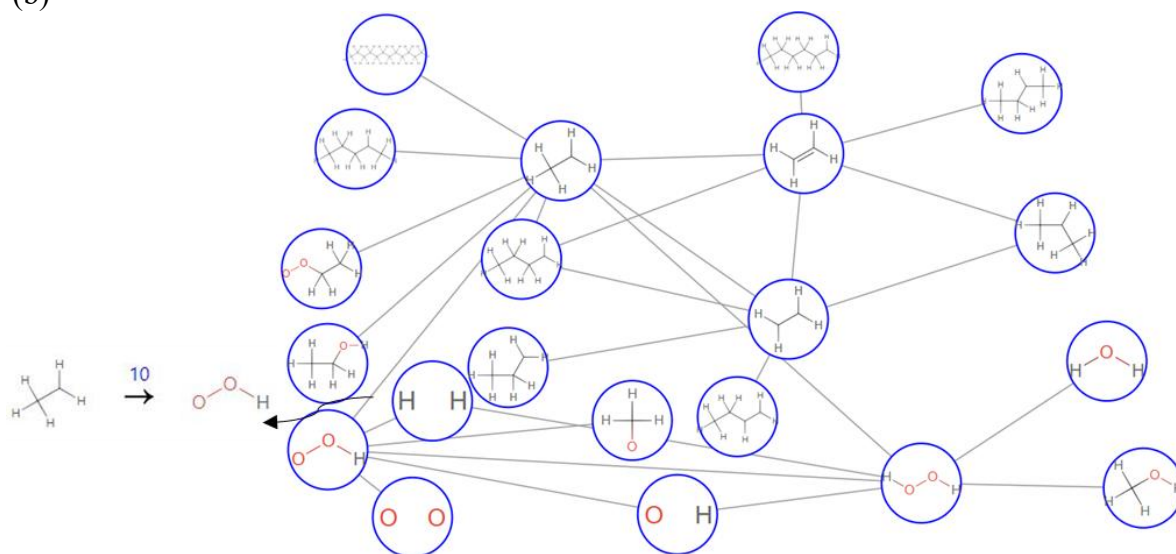
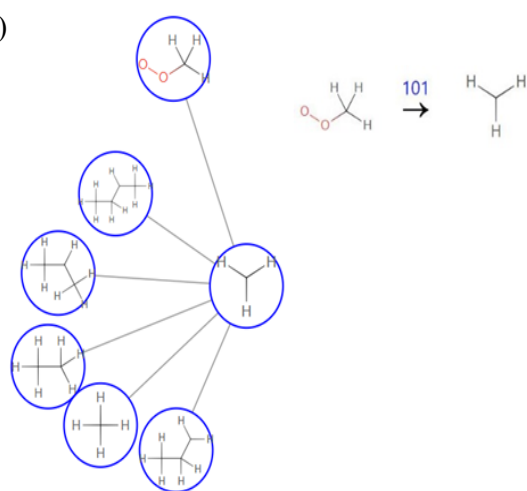


Figure 84. *Reaction paths of formation C_2H_4 within (a) pure and (b) hydrogen nanobubbled sample.*

(a)



(b)

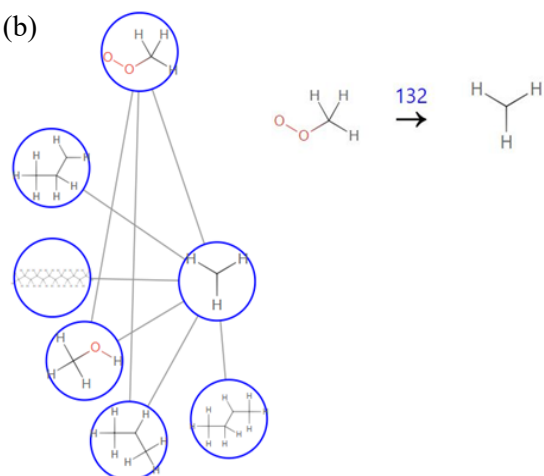


Figure 85. *Reaction paths of formation CH_3 within (a) pure and (b) oxygen nanobubbled sample.*

5.4.2 Impacts of temperature

In order to explore the influence of temperature variations on the combustion process, an investigation was conducted within the temperature range of 1800 K to 2400 K, with 200 K intervals, under the sample's density of 0.17 g/mL, with three different initial configurations

for each temperature, totaling 48 simulations. The investigation entailed tracking the evolution of dodecane over a 200 ps timeframe to determine the reaction rate constant and activation energy. The reaction rate constant at each temperature is determined using the following integrated first-order rate law equation [211]:

$$kt = \ln(N_0) - \ln(N_t) \quad (5.4)$$

where N_0 represents the initial number of dodecane molecules, N_t denotes the number of molecules at any given time t , and k stands for the rate constant. The rate constants obtained at various temperatures were utilized to construct the Arrhenius plot for the dodecane molecules. The activation energy and pre-exponential factor can be calculated using the Arrhenius equation, which is described as follow [211]:

$$k = Ae^{\frac{-E_a}{RT}} \quad (5.5)$$

in which E_a signifies the activation energy, A represents the pre-exponential factor, and R is the universal gas constant. Therefore, the values of A and E_a can be determined by plotting the logarithm of the reaction rate constant against the inverse of temperature, as depicted in Figure 86. It is evident that the reaction rate increases with an increase in reaction temperature. The activation energy extracted from Figure 86 for dodecane at 0.17 g/mL is 63.76 kcal/mol, aligning with the previous study's reported value of 63.68 kcal/mol [212]. Additionally, for the hydrogen nanobubbled sample, an activation energy of 62.73 kcal/mol was observed, whereas for the nitrogen nanobubbled sample, it was 52.89 kcal/mol, and for the oxygen nanobubbled sample, it was 66.93 kcal/mol. This comparison suggests that nitrogen and hydrogen NBs decrease the activation energy of fuel, while the incorporation of oxygen NB increases it.

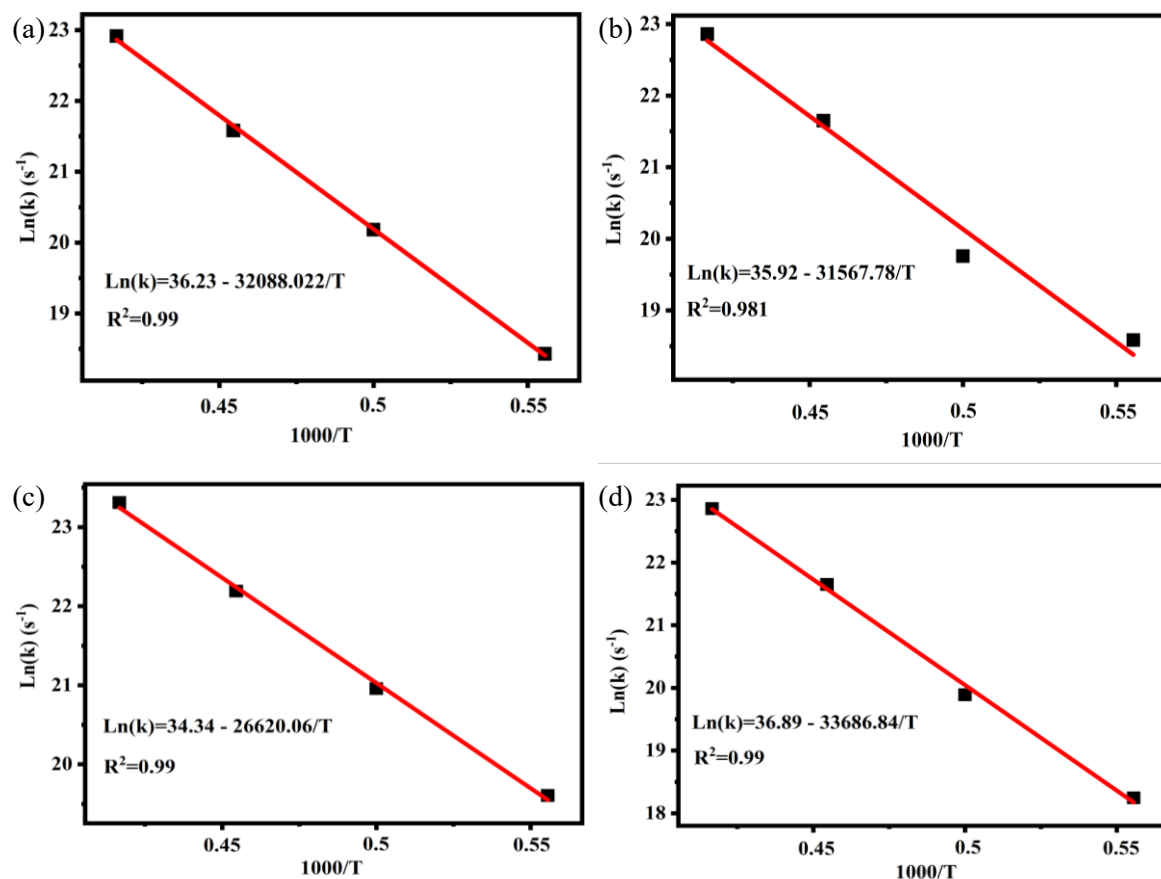


Figure 86. Arrhenius parameters extracted from fitted rate constants $\ln(k)$ versus temperature for (a) pure, (b) hydrogen, (c) nitrogen, and (d) oxygen nanobubbled samples at a density of 0.17 g/mL.

To deepen the understanding of the effects of temperature and NBs on the initial stages of the combustion process, the total number of chemical and carbon species at 2 ps at temperatures of 1800 K and 2400 K was depicted in Figure 87. It was observed that an increase in temperature was associated with a higher consumption of dodecane and the production of more carbon-based species in both the pure sample and the nanobubbled samples. At elevated temperatures, fuel molecules became more susceptible to thermal decomposition, resulting in their breakdown into smaller, more reactive fragments that readily participated in combustion reactions. However, an investigation into the rate of increase in the emergence of carbon-based species with rising temperatures revealed that the

rate of emergence of carbon-based species in the fuel within the pure sample, hydrogen, nitrogen, and oxygen nanobubbled samples was increased by 1033%, 766%, 283%, and 221.08%, respectively, when the temperature was raised from 1800 K to 2400 K. The comparison of the initial stages at 2 ps of the pure sample at lower and higher temperatures (Figure 87) showed that in the pure sample, increasing the temperature accelerated carbon decomposition into smaller carbon-based species more than nanobubbled samples. Therefore, it can be concluded that the existence of NBs decreases the thermal decomposition of fuel at the initial stages. However, in nitrogen nanobubbled samples, increasing the temperature also led to an increase in the number of noncarbon-based intermediates and radicals, as the amount of HN_2 and N_2O_2 at the higher temperature increased by 253.03% and 175.18%, respectively, compared to the lower temperature that accelerated the consumption of fuel molecules during the combustion process, as by the end of 200 ps, 93% of the fuel had been consumed in the nitrogen nanobubbled sample at 2400 K, while 83.34% of the fuel had been consumed in the neat dodecane sample. The hydrogen nanobubbled sample experiences an increase in both carbon-based and noncarbon-based intermediates and radicals as the temperature increases, similar to the nitrogen nanobubbled sample, resulting in a decrease in activation energy. A comparison of Figures 87a and 87d reveals that the total number of species and carbon-based species in the oxygen nanobubbled sample at higher temperatures is less than that in the neat dodecane sample. As discussed and illustrated in Figure 87, the presence of NBs decreases the rate of carbon decomposition at higher temperatures compared to the pure sample. In contrast to the pure sample, where increasing temperature provide more heat for fuel thermal decomposition, in the nanobubbled samples, part of this heat is absorbed by the NB atoms. In the case of nitrogen and hydrogen nanobubbled samples, this results in an increase in noncarbon-based intermediates and radicals, a phenomenon that is not observed in the oxygen nanobubbled

samples. This indicates that oxygen atoms from the introduced NB into the fuel acts as a heat sink, thereby increasing the activation energy.

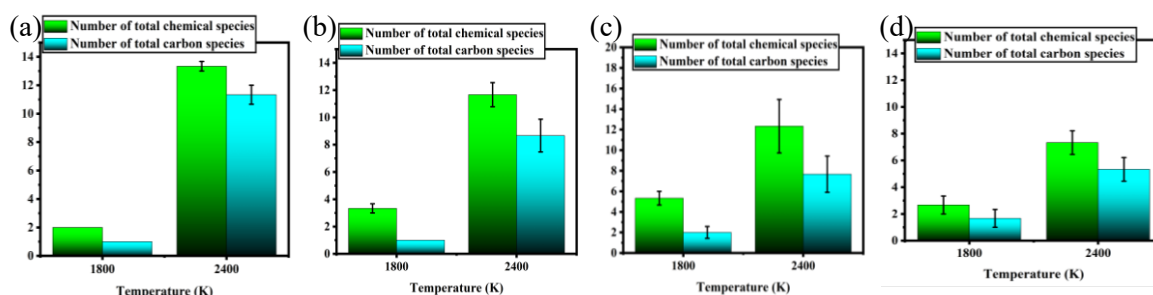


Figure 87. Number of total chemical and carbon species after 2 ps within (a) pure, (b) hydrogen, (c) nitrogen, and (d) oxygen samples.

5.4.3 Influences of sample density

Molecular collisions and bonding reactions play crucial roles in pyrolysis and combustion processes. The change in sample density can serve as an approximation for different chemical species concentrations in macro studies [213]. Additionally, due to the importance of hydrogen engines fueled with a mixture of hydrogen and other fuels, three samples containing hydrogen NBs with various densities were prepared. Each sample consisted of 100 dodecane molecules and 1850 oxygen molecules, along with hydrogen NBs with a radius of 3 nm. These components were randomly distributed within cubic boxes with side lengths of 116.88 Å, 90.91 Å, and 79.95 Å to achieve hydrogen nanobubbled samples densities with 0.08 g/mL, 0.17 g/mL, and 0.25 g/mL, respectively to investigate the combustion process over a duration of 2000 ps.

Figure 88a displays the time evolution of the number of dodecane molecules, illustrating that as density increases, more dodecane is consumed over time. This phenomenon can be attributed to the closer proximity of atoms as density rises, resulting in stronger interactions between them. As depicted in Figure 88b, this in turn results in elevated pairwise energy,

leading to more frequent and energetic collisions among atoms. Consequently, during combustion processes, the increased energy facilitates more efficient reactions, thereby driving increased fuel consumption rates over time.

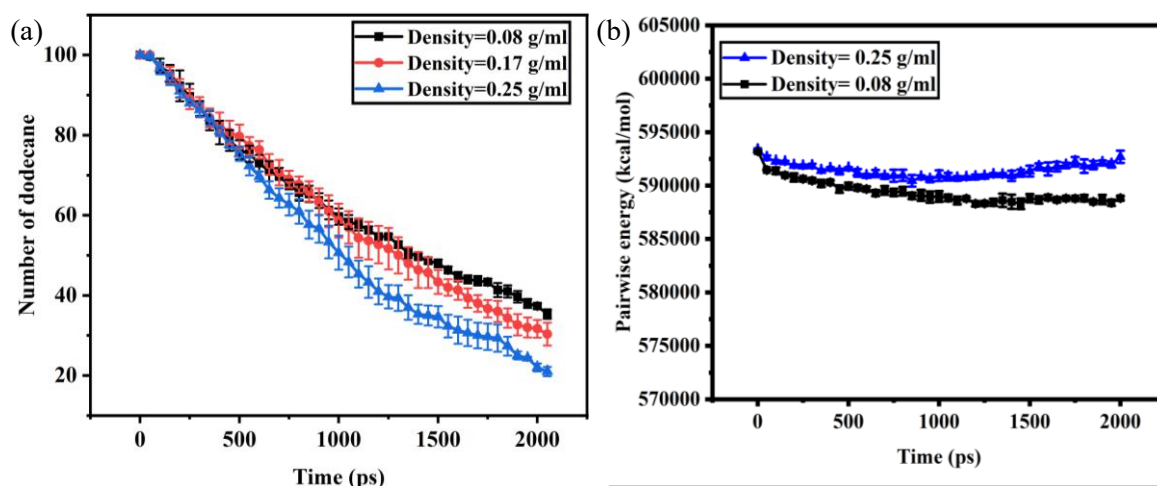


Figure 88. (a) Time evolution of the number of dodecane molecules, and (b) average pairwise energy within hydrogen nanobubbled samples across various densities.

As noted, an increase in density leads to higher fuel consumption over time. However, a detailed analysis of Figure 88a indicates that in the initial stages of combustion, the density of the sample does not significantly affect the combustion process. But as time progresses, for example, after 1000 ps as shown in Figure 88a, the density of the samples starts to significantly influence the rate of fuel consumption. In chemical reactions, molecules must surmount specific energy barriers to initiate reactions. The activation energy for a hydrogen nanobubbled sample at a density of 0.17 g/mL was previously calculated to be 62.73 kcal/mol. Using the same method, the activation energies for hydrogen nanobubbled samples at densities of 0.08 g/mL and 0.25 g/mL were determined to be 60.84 kcal/mol and 66.72 kcal/mol, respectively, as illustrated in Figure 89. It can be observed that as the density of the sample increases, the activation energy also rises. Therefore, in denser systems, molecular interactions can generate additional or higher energy barriers. These barriers arise because molecules must find more precise orientations for reactions, given the increased

number of neighbouring molecules and the resulting interaction forces. The close proximity of many molecules requiring them to overcome additional rotational or translational energy barriers. Once these barriers are overcome, the more energetic collisions among atoms in denser samples lead to increased fuel consumption over time.

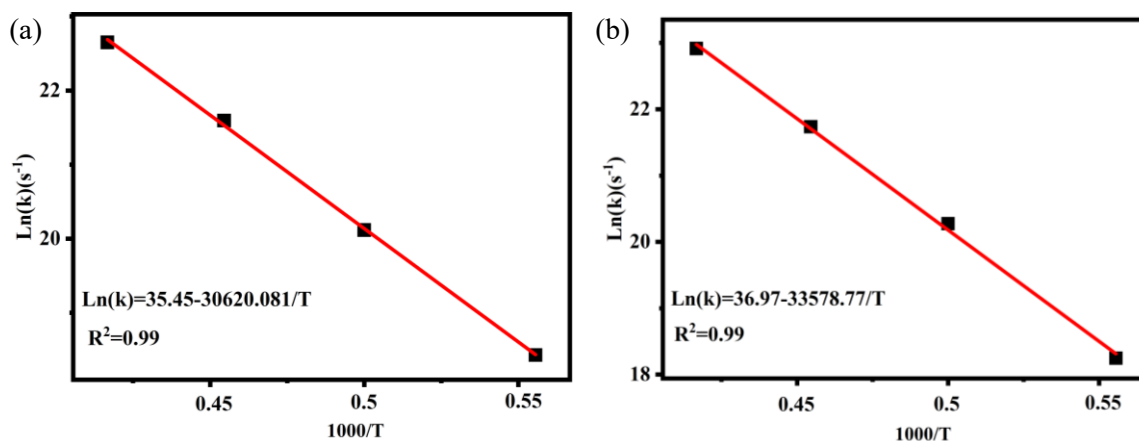


Figure 89. Arrhenius parameters derived from fitted rate constants $\ln(k)$ versus temperature for hydrogen nanobubbled samples at (a) 0.085 g/mL and (b) 0.25 g/mL densities.

Figures 90a and b depict the total number of chemical species and the five dominant products for hydrogen nanobubbled samples with densities of 0.08 g/mL and 0.25 g/mL, respectively. These figures confirm that the number of chemical species increases with density. This rise can be attributed to the enhanced rate of molecular collisions; as density increases, molecules are forced closer together, boosting the frequency of collisions. Additionally, higher densities modify thermodynamic conditions like pressure, potentially shifting reaction equilibria and facilitating the formation of a more diverse array of chemical species. In both samples, the primary products include C_3H_6 , C_2H_4 , and C_4H_8 . However, the sample with a density of 0.08 g/mL predominantly features CH_3 and C_2H_5 , whereas H_2O and CH_2O are more prevalent in the sample with a higher density.

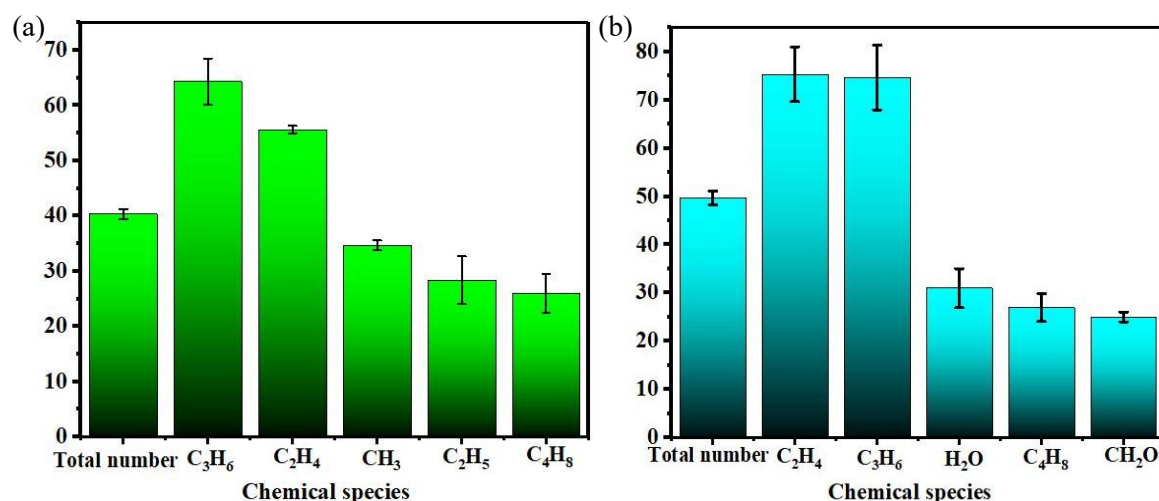


Figure 90. The total number of chemical species and the top five products in hydrogen nanobubbled samples at densities of (a) 0.08 g/mL and (b) 0.25 g/mL, measured at 2000 K after 2000 ps.

Table 19 illustrates the three most unique consumption path of CH_3 and C_2H_5 , which are among the top five chemical species observed at lower densities, for hydrogen nanobubbled samples at a density of 0.08 g/mL and 0.25 g/mL. As it can be seen in the higher density sample, more CH_3 is converted to CH_4O (methanol), CH_3O (methoxy groups), and C_2H_6O (ethanol), which can be attributed to pressure-related effect on reaction dynamics and thermodynamics. High pressure, compressing molecules within a smaller volume, significantly boosts the frequency of molecular collisions, thereby enhancing the reactivity of CH_3 groups with other molecules. Furthermore, from the data presented in the table, it is also observed that the conversion of C_2H_5 to C_2H_4 (ethylene) is more frequent under high pressure. Additionally, the formation of HO_2 (hydroperoxide) is accelerated under these high-pressure conditions. Likewise, the likelihood of producing C_2H_6O (ethanol) increases in environments where reactants are densely packed, resulting in more CH_3 and C_2H_5 being consumed over time in higher density samples compared to lower density one.

Table 19. Three most unique consumption of CH_3 and C_2H_5 in hydrogen nanobubbled samples at densities of 0.08 g/mL and 0.25 g/mL.

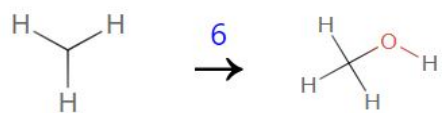
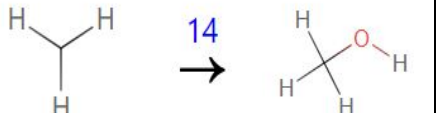
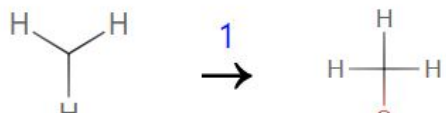
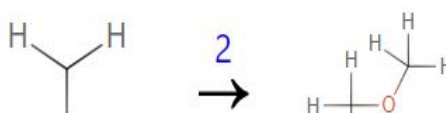
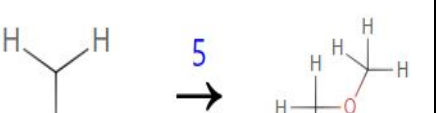
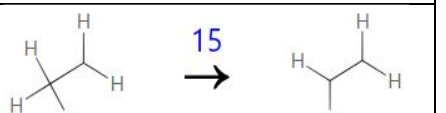
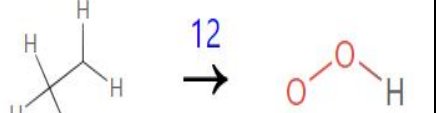
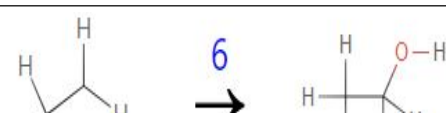
Species	Density of sample (g/mL)	
	0.08	0.25
CH_3		
		
		
C_2H_5		
		
		

Figure 91 illustrates the reaction pathways leading to the formation of CH_2O and H_2O , ranking among the top five products in higher density conditions in both lower and higher density hydrogen nanobubbled samples. Observations highlight the crucial roles of CH_3O and OH radicals in forming CH_2O and H_2O , respectively. In the higher density hydrogen nanobubbled sample, a notable increase in the conversion of CH_3O to CH_2O is observed. This enhancement is attributed to the elevated pressure, which not only increases the

collision frequency among molecules but also boosts the overall reaction rate and the likelihood of engaging specific pathways that lead to CH_2O formation. Additionally, an increased production of OH radicals was observed under these high-pressure conditions, thereby increasing their probability of reacting to form water. This highlights the acute sensitivity of radical-driven reactions to changes in pressure and concentration in combustion environments, which serves to accelerate and refine pathways to product formation, such as the efficient conversion of hydroxyl radicals into water within the higher hydrogen nanobubbled sample.

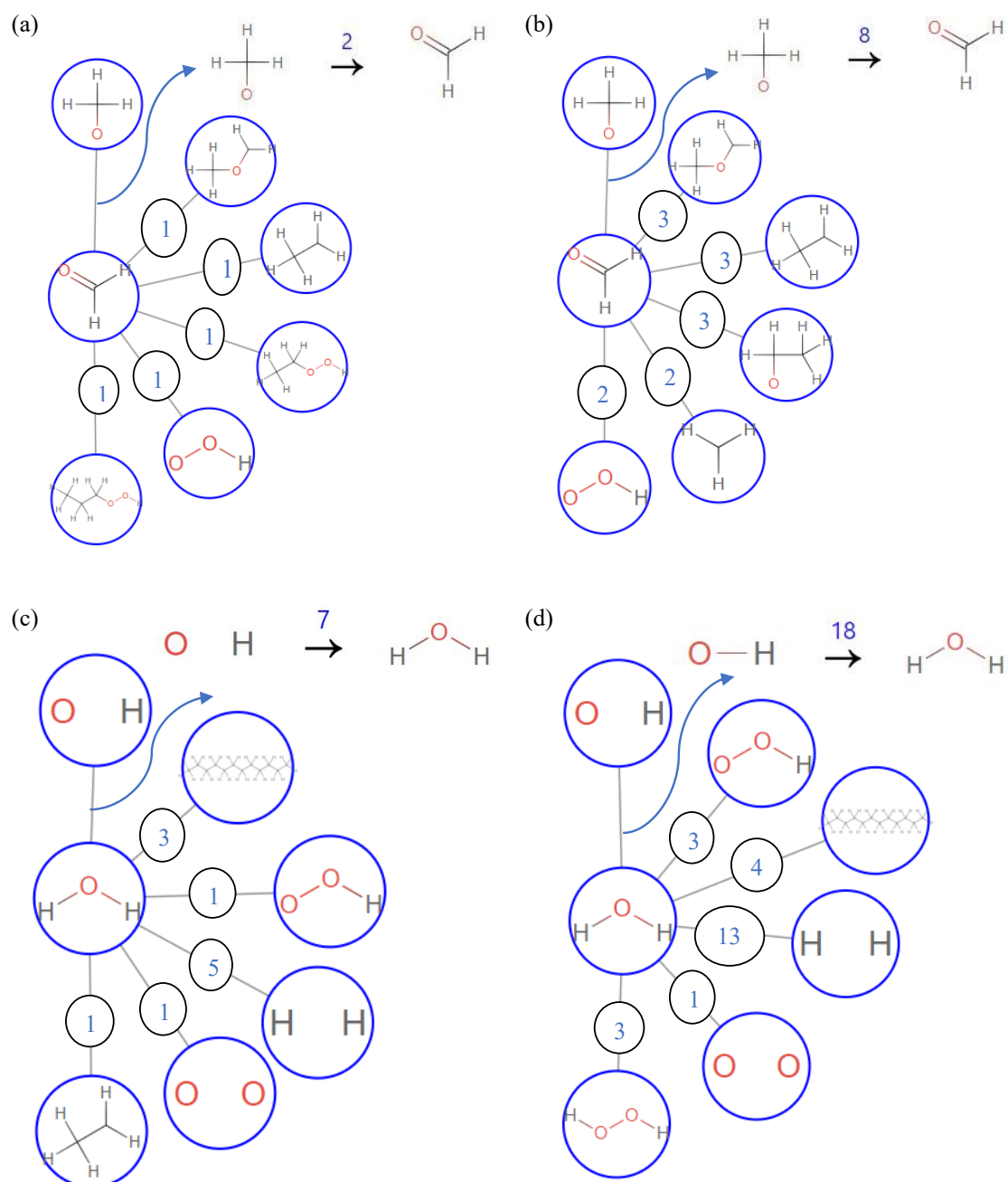


Figure 91. The reaction pathways and the frequency of the conversions in the formation of CH_2O within samples with densities of (a) 0.08 g/mL and (b) 0.25 g/mL, and H_2O within samples with densities of (d) 0.08 g/mL and (e) 0.25 g/mL within hydrogen nanobubbled sample (the numbers in the circles indicate the frequency of a reaction).

5.5 Summary

This chapter presents a comprehensive MD simulations study aimed at understanding the formation of NBs and their thermophysical and thermochemical effects in different non-polar liquids. The study focuses on investigating NBs formation and behaviour in hydrocarbon environments, as well as examining their influence on phase transition and combustion reaction processes. The simulation results provide valuable insights into the molecular-level mechanisms governing the role of NBs in modifying liquid properties, thermal behaviour, and combustion characteristics.

Initially, the formation of NBs in dodecane and isooctane and their effects on the inherent properties of these liquids, including viscosity and specific heat capacity, were investigated. The results revealed that molecular interactions play a crucial role in the nucleation and coalescence behaviour of NBs, governing their formation and determining the extent to which they modify the inherent thermophysical properties of the host liquids.

The influence of NBs on the phase transition and thermal behaviour of dodecane was then investigated. The results indicate that the presence of NBs suppresses the phase transition temperature of the system. In addition, NBs promote a more ordered molecular arrangement in the solid phase and enhance the vibrational density of states (VDOS), thereby contributing to improved thermal conductivity.

Finally, the thermochemical effects of NBs were investigated using reactive molecular dynamics simulations to study the combustion behaviour of dodecane–oxygen systems in both pure conditions and in the presence of formed NBs. The results demonstrate that NBs significantly affect the combustion process by altering the activation energy, affecting fuel consumption, and influencing the formation of intermediates and reactive radicals. In

addition, although an increase in system density raises the activation energy, it also enhances molecular collisions, thereby promoting fuel consumption during combustion.

Chapter 6

Conclusion & Future Work

6.1 Conclusion

This study employs molecular dynamics (MD) simulations to investigate the nucleation behaviour and intrinsic properties of nanobubbles (NBs) in water and methanol, representing polar and alcoholic host liquids, respectively, and to provide atomic-level insights into their impact on the thermophysical properties of these media. MD simulations were further used to examine the effects of solid–liquid–gas interactions on NB formation in graphene-based water and methanol nanofluids, offering valuable insights into their nucleation mechanisms and their impact on the inherent properties of these nanofluids. In parallel, molecular modeling approaches were applied to assess the role of various NBs on CO₂ hydrate formation under diverse thermodynamic conditions. For organic host liquids, the study focused on the formation, coalescence, and behaviour of NBs composed of different gases in dodecane, as a phase change material and fuel, and in isooctane, as a high-octane fuel host, evaluating their impact on the thermophysical properties of these organic liquids through MD simulations. Moreover, the effects of different NB types on the phase transition, thermal behaviour, and atomic structure of dodecane across various temperature ranges were investigated. Finally, the influences of NB type, temperature, and sample density on the combustion process of dodecane fuel were analysed using the ReaxFF reactive force field.

6.1.1 Polar and alcoholic environments

The results for polar and alcoholic environments reveal that the nucleation of NBs depends on the interaction between solvent molecules and the dissolved gas. The interaction between dispersed gases and host mediums is affected by the competition of solvent molecules for available intermolecular interaction sites. As a result, dissolved gases exhibit different behaviours in different solvents, as reflected by the observations that oxygen can form NB in polar host but cannot form any NBs in methanol. Moreover, the density of nitrogen NB

formed differs between water and methanol, with observed values of 0.354 g/ml in water and 0.125 g/ml in methanol. The size and density of NBs play a crucial role in their longevity in the host medium. As the size of NBs decreases, their density increases, leading to a higher surface area-to-volume ratio compared to larger gas bubbles. The smallest NB can deform during a coalescence process due to the presence of intermolecular forces, which can facilitate the formation of a bridge-like shape. Moreover, the presence of these formed NBs has an impact on the density of the surrounding liquid. In water, the dissolution of nitrogen and hydrogen led to reductions of 6.4% and 5.91%, respectively, and in the methanol-based sample, the most substantial density decrease occurred during hydrogen dissolution, reaching 22.22%, attributed to the nanolayer formed around the NBs disrupting liquid molecule interactions. Notably, the viscosity of the host liquid is influenced by the presence of high-density NBs, as evidenced by the highest viscosities observed in nitrogen and oxygen nanobubbled water samples at 0.0013 and 0.00088 Pa.s, respectively. It was also found that at elevated temperatures, nucleation is initiated by a smaller number of nucleation sites with a higher concentration of gas atoms.

For graphene-reinforced water- and methanol-based nanofluids, it was observed that the interaction between host liquids and dispersed gas species significantly influences nanobubble formation and graphene morphology. In polar-based nanofluids strong interactions between water molecules promote the formation of graphene nanobubbles. Conversely, in methanol-based nanofluids, weaker molecular interactions result in the absence of graphene nanobubbles, with only bulk NBs forming. Furthermore, the introduction of additive particles in host liquids increases the viscosity of water-based nanofluids, a phenomenon influenced by the morphology of graphene NBs. Specific heat capacity exhibits contrasting trends between water- and methanol-based nanofluids, which can be attributed to the presence of gas-filled nanolayers surrounding graphene. In water-

based nanofluids, increasing the dissolved gas mass enhances the formation of graphene nanobubbles. This leads to graphene folding and the creation of a gas layer around it, which reduces the specific heat capacity. On the other hand, in methanol-based nanofluids, an elevated dissolved gas mass promotes the formation of bulk nanobubbles. This diminishes the concentration of gas atoms near graphene, thereby increasing the heat capacity of graphene-methanol nanofluids.

The findings for CO₂ hydrate process at 2 MPa and 260 K indicate that under optimal thermodynamic conditions, the hydrophobic surfaces of NBs act as nucleation spots, attracting CO₂ molecules and enhancing local concentration gradients. This interfacial accumulation not only accelerates hydrate formation kinetics but also reduces the occurrence of stochastic nucleation events in the bulk phase, leading to more efficient and directed clathrate growth. Furthermore, the diffusion of small guest molecules such as H₂ and N₂ from the NB core further enhances the formation of hydrate cages. However, this enhancement is highly dependent on molecular mobility; under sub-optimal conditions, particularly at a lower temperature (240 K), restricted atomic motion suppresses these mechanisms, diminishing the influence of NB type and surface characteristics. A pressure-dependent dual role of NBs is also observed when the system pressure increases from 2 MPa to 10 MPa. While CO₂ NBs promote hydrate formation at optimal pressures by inducing local structural ordering, they become disruptive at higher pressures. In this regime, strong bulk molecular interactions dominate hydrate nucleation, while the presence of carbon dioxide NBs introduces disorder that hinders, rather than promotes, cage formation.

6.1.2 Non-polar host liquids

In organic host liquids, the formation of NBs and the speed of the coalescence process strongly depend on the type of the host liquids and dispersed gases. For instance, oxygen

can form NBs in a dodecane host but fails to generate any NBs in the isooctane sample. . NB nucleation is also highly dependent on the weight fraction of dispersed gases; as the weight fraction decreases, the probability of NB formation diminishes. Specific heat capacity is closely tied to the weight fraction of the dispersed gas and the type of host fluid. In dodecane, which consists of long-chain molecules, the stored energy in the system decreases as the weight fraction of dispersed gas increases, resulting in reduced heat capacity. Conversely, in isooctane samples, an increase in the weight fraction of the scattered gas, leading to a rise in specific heat capacity. Increasing temperature enhances the coalescence process; however, its effect on specific isochoric heat capacity depends heavily on the host liquid and additives.

The results also demonstrate that NBs significantly affect the phase transition process by markedly reducing molecular mobility. This reduction kinetically suppresses liquid-phase dynamics, effectively trapping the system in a metastable, supercooled state. Consequently, the molecular rearrangements required for crystal growth are impeded, resulting in a depression of the liquid-to-solid transition temperature. Furthermore, analysis of the radial distribution function reveals that the presence of NBs in the dodecane matrix promotes a more ordered crystalline structure while simultaneously increasing the population of low-frequency phonon modes, thereby enhancing thermal conductivity. Additionally, the presence of NBs enhances molecular interactions, thereby requiring more energy to initiate molecular motion, which results in an elevated thermal response and an increase in the specific heat capacity of the nanobubble-containing samples. It was also observed that as temperature increased, nitrogen and hydrogen NBs remained stable, whereas the oxygen NB vanished. This demonstrates the superior thermal stability of nitrogen and hydrogen NBs, making them more suitable for high-temperature applications and enabling their use over a wider temperature range. Furthermore, their presence was found to enhance thermal conductivity while simultaneously reducing atomic mobility. As a result, nanobubble-

containing samples exhibited lower mean square displacement compared to the pure sample, along with increased viscosity.

In the combustion process of dodecane, the incorporation of nanobubbles and their specific types significantly influence both the initiation of combustion and its resulting products. In pure, hydrogen, and oxygen nanobubbled samples, combustion is initiated through the thermal decomposition of the fuel, whereas in nitrogen nanobubbled samples, the process is driven by the emergence of intermediates and radicals interacting with the fuel. The higher production of OH radicals, resulting from H_2O_2 introduced by nitrogen nanobubbles, makes water the dominant product in nitrogen nanobubbled samples. In contrast, C_2H_4 is the predominant species in pure, oxygen, and hydrogen nanobubbled samples at a density of 0.17 g/mL and a temperature of 2000 K. The elevated production of intermediates and radicals in nitrogen nanobubbled samples notably reduces the activation energy and boosts fuel consumption. Additionally, increasing temperature leads to more extensive thermal decomposition of fuel in pure samples compared to nanobubbled ones. In hydrogen and nitrogen nanobubbled samples, higher temperatures promote the production of intermediates and radicals, while oxygen nanobubbles in oxygen nanobubbled samples act as a heat sink, significantly increasing activation energy and reducing fuel consumption. In hydrogen nanobubbled samples, increasing density raises the activation energy, as denser systems facilitate molecular interactions that create additional or higher energy barriers. However, once these barriers are overcome, the increased density results in more frequent and energetic reactions, thereby enhancing fuel energy consumption over time.

6.2 Future work

The findings of this research highlight the strong potential of nanobubble-enhanced environments for applications in thermal energy storage and management systems, CO_2

hydrate formation, and combustion processes. Nevertheless, further research is required to fully exploit the capabilities of NBs across a broader range of energy-related and industrial applications. The present results provide a robust scientific foundation for future experimental investigations and contribute to bridging the gap between atomic-scale insights and practical engineering systems.

A critical next step involves extending these investigations to hybrid environments, particularly hybrid nanofluids, which have demonstrated superior enhancement in thermophysical properties, especially thermal conductivity, relative to conventional nanofluids. These systems represent promising host media for NB incorporation. Further work is required to elucidate the nucleation mechanisms, stability criteria, and dynamic behaviour of NBs within such complex fluids, as well as their influence on overall thermophysical performance. In addition, advanced analytical approaches, including the integration of machine learning techniques, are recommended to predict the likelihood of NB formation and to quantify their impact on thermophysical performance under diverse operating conditions. Realising this objective will require comprehensive, high-quality datasets derived from systematic investigations spanning a wide range of governing parameters.

Future research should also prioritize atomistically resolved investigations of nanobubble-mediated combustion under externally applied fields, particularly electric fields known to modulate charge distribution and reactive species transport. Clarifying the coupled effects of NBs and external fields on radical generation, reaction pathways, and transient kinetics will advance mechanistic understanding and enable predictive modeling. These efforts will provide a foundation for the rational design of advanced combustion control strategies and enhanced energy conversion efficiency.

Beyond energy applications, NBs also hold considerable promise in water treatment systems. A fundamental understanding of their behaviour in the presence of impurities, dissolved ions, contaminants, and surfactants is essential. Atomistic-level studies can elucidate nanobubble–solute interactions, including their influence on surfactant self-assembly, adsorption behaviour, and contaminant removal mechanisms. Such insights are crucial for optimizing nanobubble-assisted water treatment technologies.

Chapter 7 Bibliography

- [1] A. Hassan *et al.*, "Thermal management and uniform temperature regulation of photovoltaic modules using hybrid phase change materials-nanofluids system," *Renewable Energy*, vol. 145, pp. 282-293, 2020.
- [2] X. Li, W. Xie, C. Sui, and P.-C. Hsu, "Multispectral thermal management designs for net-zero energy buildings," *ACS Materials Letters*, vol. 2, no. 12, pp. 1624-1643, 2020.
- [3] D. Y. Shu, S. Deutz, B. A. Winter, N. Baumgärtner, L. Leenders, and A. Bardow, "The role of carbon capture and storage to achieve net-zero energy systems: Trade-offs between economics and the environment," *Renewable and Sustainable Energy Reviews*, vol. 178, p. 113246, 2023.
- [4] P. Dimopoulos, C. Bach, P. Soltic, and K. Boulouchos, "Hydrogen–natural gas blends fuelling passenger car engines: combustion, emissions and well-to-wheels assessment," *International journal of hydrogen energy*, vol. 33, no. 23, pp. 7224-7236, 2008.
- [5] G. Simonsen, R. Ravotti, P. O'Neill, and A. Stamatou, "Biobased phase change materials in energy storage and thermal management technologies," *Renewable and Sustainable Energy Reviews*, vol. 184, p. 113546, 2023.
- [6] M. Awais, A. A. Bhuiyan, S. Salehin, M. M. Ehsan, B. Khan, and M. H. Rahman, "Synthesis, heat transport mechanisms and thermophysical properties of nanofluids: A critical overview," *International Journal of Thermofluids*, vol. 10, p. 100086, 2021.
- [7] Z. Said *et al.*, "Recent advances on the fundamental physical phenomena behind stability, dynamic motion, thermophysical properties, heat transport, applications, and challenges of nanofluids," *Physics Reports*, vol. 946, pp. 1-94, 2022.
- [8] W. Wu *et al.*, "Diffusivities in 1-alcohols containing dissolved H₂, He, N₂, CO, or CO₂ close to infinite dilution," *The Journal of Physical Chemistry B*, vol. 123, no. 41, pp. 8777-8790, 2019.
- [9] A. Kumagai, Y. Kawase, and C. Yokoyama, "Falling capillary tube viscometer suitable for liquids at high pressure," *Review of scientific instruments*, vol. 69, no. 3, pp. 1441-1445, 1998.
- [10] G. Graziano, "Forever blowing nanobubbles," *Nature Reviews Chemistry*, vol. 4, no. 10, pp. 506-506, 2020.
- [11] K. Phan, T. Truong, Y. Wang, and B. Bhandari, "Effect of CO₂ nanobubbles incorporation on the viscosity reduction of fruit juice concentrate and vegetable oil," *International Journal of Food Science & Technology*, vol. 56, no. 9, pp. 4278-4286, 2021.

- [12] R. Heinberg and D. Fridley, *Our renewable future: Laying the path for one hundred percent clean energy*. Island Press, 2016.
- [13] J. L. Holechek, H. M. Geli, M. N. Sawalhah, and R. Valdez, "A global assessment: can renewable energy replace fossil fuels by 2050?," *Sustainability*, vol. 14, no. 8, p. 4792, 2022.
- [14] "United Nations. The Paris Agreement," 2015.
- [15] O. B. Inal, B. Zincir, and C. Deniz, "Investigation on the decarbonization of shipping: An approach to hydrogen and ammonia," *International Journal of Hydrogen Energy*, vol. 47, no. 45, pp. 19888-19900, 2022.
- [16] J. D. Ampah, A. A. Yusuf, S. Afrane, C. Jin, and H. Liu, "Reviewing two decades of cleaner alternative marine fuels: Towards IMO's decarbonization of the maritime transport sector," *Journal of Cleaner Production*, vol. 320, p. 128871, 2021.
- [17] L. Kang, W. Pan, J. Zhang, W. Wang, and C. Tang, "A review on ammonia blends combustion for industrial applications," *Fuel*, vol. 332, p. 126150, 2023.
- [18] O. I. Awad, B. Zhou, K. Harrath, and K. Kadirgama, "Characteristics of NH₃/H₂ blend as carbon-free fuels: a review," *International Journal of Hydrogen Energy*, vol. 48, no. 96, pp. 38077-38100, 2023.
- [19] M. Lu *et al.*, "Chemical mechanism of ammonia-methanol combustion and chemical reaction kinetics analysis for different methanol blends," *Fuel*, vol. 341, p. 127697, 2023.
- [20] S. H. Oh, S. H. Yoon, H. Song, J. G. Han, and J.-M. Kim, "Effect of hydrogen nanobubble addition on combustion characteristics of gasoline engine," *International journal of hydrogen energy*, vol. 38, no. 34, pp. 14849-14853, 2013.
- [21] M. Brayek, Z. Driss, M. A. Jemni, A. Damak, and M. S. Abid, "Effect of hydroxygen nanobubble addition on performance characteristics and emission formations of a spark-ignition engine," *Journal of Mechanical Science and Technology*, vol. 37, no. 1, pp. 457-463, 2023.
- [22] Q. Sun and Y. T. Kang, "Review on CO₂ hydrate formation/dissociation and its cold energy application," *Renewable and Sustainable Energy Reviews*, vol. 62, pp. 478-494, 2016.
- [23] F.-P. Liu, A.-R. Li, S.-L. Qing, Z.-D. Luo, and Y.-L. Ma, "Formation kinetics, mechanism of CO₂ hydrate and its applications," *Renewable and Sustainable Energy Reviews*, vol. 159, p. 112221, 2022.
- [24] J. A. Ripmeester and S. Alavi, "Some current challenges in clathrate hydrate science: Nucleation, decomposition and the memory effect,"

Current Opinion in Solid State and Materials Science, vol. 20, no. 6, pp. 344-351, 2016.

- [25] Y. Zhang, L. Zhao, S. Deng, R. Zhao, X. Nie, and Y. Liu, "Effect of nanobubble evolution on hydrate process: a review," *Journal of Thermal Science*, vol. 28, no. 5, pp. 948-961, 2019.
- [26] M. Alheshibri, J. Qian, M. Jehannin, and V. S. Craig, "A history of nanobubbles," *Langmuir*, vol. 32, no. 43, pp. 11086-11100, 2016.
- [27] B. H. Tan, H. An, and C.-D. Ohi, "Stability of surface and bulk nanobubbles," *Current Opinion in Colloid & Interface Science*, vol. 53, p. 101428, 2021.
- [28] S.-T. Lou *et al.*, "Nanobubbles on solid surface imaged by atomic force microscopy," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, vol. 18, no. 5, pp. 2573-2575, 2000.
- [29] A. Gurung, O. Dahl, and K. Jansson, "The fundamental phenomena of nanobubbles and their behavior in wastewater treatment technologies," *Geosystem Engineering*, vol. 19, no. 3, pp. 133-142, 2016.
- [30] S. Liu, J. Li, S. Oshita, M. Kamruzzaman, M. Cui, and W. Fan, "Formation of a hydrogen radical in hydrogen nanobubble water and its effect on copper toxicity in chlorella," *ACS Sustainable Chemistry & Engineering*, vol. 9, no. 33, pp. 11100-11109, 2021.
- [31] W. Xiao and G. Xu, "Mass transfer of nanobubble aeration and its effect on biofilm growth: Microbial activity and structural properties," *Science of the total environment*, vol. 703, p. 134976, 2020.
- [32] Y. Feng *et al.*, "Study of hydrate nucleation and growth aided by micro-nanobubbles: Probing the hydrate memory effect," *Energy*, vol. 290, p. 130228, 2024.
- [33] P. S. Epstein and M. S. Plesset, "On the stability of gas bubbles in liquid-gas solutions," *The Journal of Chemical Physics*, vol. 18, no. 11, pp. 1505-1509, 1950.
- [34] E. D. Michailidi *et al.*, "Bulk nanobubbles: Production and investigation of their formation/stability mechanism," *Journal of colloid and interface science*, vol. 564, pp. 371-380, 2020.
- [35] A. Azevedo, R. Etchepare, S. Calgaroto, and J. Rubio, "Aqueous dispersions of nanobubbles: Generation, properties and features," *Minerals Engineering*, vol. 94, pp. 29-37, 2016.
- [36] S. Gobinath, G. Senthilkumar, and N. Beemkumar, "Air nanobubble-enhanced combustion study using mustard biodiesel in a common rail

- direct injection engine," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 41, no. 15, pp. 1809-1816, 2019.
- [37] A. W. Foudas, R. I. Kosheleva, E. P. Favvas, M. Kostoglou, A. C. Mitropoulos, and G. Z. Kyzas, "Fundamentals and applications of nanobubbles: A review," *Chemical Engineering Research and Design*, vol. 189, pp. 64-86, 2023.
 - [38] X. Wang, Z. Lei, K. Shimizu, Z. Zhang, and D.-J. Lee, "Recent advancements in nanobubble water technology and its application in energy recovery from organic solid wastes towards a greater environmental friendliness of anaerobic digestion system," *Renewable and Sustainable Energy Reviews*, vol. 145, p. 111074, 2021.
 - [39] P. M. Sharif *et al.*, "Nano gas bubbles dissolve in gasoline fuel and its influence on engine combustion performance," in *IOP Conference Series: Materials Science and Engineering*, 2019, vol. 469: IOP Publishing, p. 012062.
 - [40] M. Jia *et al.*, "Nanobubbles in water and wastewater treatment systems: small bubbles making a big difference," *Water Research*, p. 120613, 2023.
 - [41] L. Zhou, S. Wang, L. Zhang, and J. Hu, "Generation and stability of bulk nanobubbles: A review and perspective," *Current Opinion in Colloid & Interface Science*, vol. 53, p. 101439, 2021.
 - [42] F. Eklund, M. Alheshibri, and J. Swenson, "Differentiating bulk nanobubbles from nanodroplets and nanoparticles," *Current Opinion in Colloid & Interface Science*, vol. 53, p. 101427, 2021.
 - [43] M. Alheshibri and V. S. Craig, "Generation of nanoparticles upon mixing ethanol and water; Nanobubbles or Not?," *Journal of colloid and interface science*, vol. 542, pp. 136-143, 2019.
 - [44] A. Häbich, W. Ducker, D. E. Dunstan, and X. Zhang, "Do stable nanobubbles exist in mixtures of organic solvents and water?," *The Journal of Physical Chemistry B*, vol. 114, no. 20, pp. 6962-6967, 2010.
 - [45] L. Sun *et al.*, "Research progress on bulk nanobubbles," *Particuology*, vol. 60, pp. 99-106, 2022.
 - [46] B. H. Tan, H. An, and C.-D. Ohl, "How bulk nanobubbles might survive," *Physical review letters*, vol. 124, no. 13, p. 134503, 2020.
 - [47] D. Lohse and X. Zhang, "Pinning and gas oversaturation imply stable single surface nanobubbles," *Physical Review E*, vol. 91, no. 3, p. 031003, 2015.
 - [48] Y. Lu, L. Yang, Y. Kuang, Y. Song, J. Zhao, and A. K. Sum, "Molecular simulations on the stability and dynamics of bulk nanobubbles in

aqueous environments," *Physical Chemistry Chemical Physics*, vol. 23, no. 48, pp. 27533-27542, 2021.

- [49] S. A. Hewage and J. N. Meegoda, "Molecular dynamics simulation of bulk nanobubbles," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 650, p. 129565, 2022.
- [50] E. Bird, E. Smith, and Z. Liang, "Coalescence characteristics of bulk nanobubbles in water: A molecular dynamics study coupled with theoretical analysis," *Physical Review Fluids*, vol. 6, no. 9, p. 093604, 2021.
- [51] E. Bird, J. Zhou, and Z. Liang, "Coalescence speed of two equal-sized nanobubbles," *Physics of Fluids*, vol. 32, no. 12, 2020.
- [52] A. Angulo, P. van der Linde, H. Gardeniers, M. Modestino, and D. F. Rivas, "Influence of bubbles on the energy conversion efficiency of electrochemical reactors," *Joule*, vol. 4, no. 3, pp. 555-579, 2020.
- [53] A. Jabbarzadeh, P. Harrowell, and R. Tanner, "The structural origin of the complex rheology in thin dodecane films: Three routes to low friction," *Tribology international*, vol. 40, no. 10-12, pp. 1574-1586, 2007.
- [54] L. Zhao *et al.*, "Combined experimental and computational study on the unimolecular decomposition of JP-8 jet fuel surrogates. I. n-Decane (n-C₁₀H₂₂)," *The Journal of Physical Chemistry A*, vol. 121, no. 6, pp. 1261-1280, 2017.
- [55] Y. Song, N. Zhang, Y. Jing, X. Cao, Y. Yuan, and F. Haghighat, "Experimental and numerical investigation on dodecane/expanded graphite shape-stabilized phase change material for cold energy storage," *Energy*, vol. 189, p. 116175, 2019.
- [56] J. R. Darvin, M. S. Hossain, M. Nabil, J. Uertz, and G. Mills, "Concentrated Ag nanoparticles in dodecane as phase change materials for thermal energy storage," *ACS Applied Nano Materials*, vol. 2, no. 10, pp. 6187-6196, 2019.
- [57] M. Ershov, D. Potanin, S. Tarazanov, T. M. Abdellatief, and V. Kapustin, "Blending characteristics of isooctene, MTBE, and TAME as gasoline components," *Energy & Fuels*, vol. 34, no. 3, pp. 2816-2823, 2020.
- [58] P. Bayer, L. Rybach, P. Blum, and R. Brauchler, "Review on life cycle environmental effects of geothermal power generation," *Renewable and Sustainable Energy Reviews*, vol. 26, pp. 446-463, 2013.

- [59] F. Schorn *et al.*, "Methanol as a renewable energy carrier: An assessment of production and transportation costs for selected global locations," *Advances in Applied Energy*, vol. 3, p. 100050, 2021.
- [60] M. A. Ghadikolaei, C. S. Cheung, and K.-F. Yung, "Study of combustion, performance and emissions of a diesel engine fueled with ternary fuel in blended and fumigation modes," *Fuel*, vol. 235, pp. 288-300, 2019.
- [61] A. H. Whiteley, W. D. McElroy, G. H. Warren, and E. N. Harvey, "Bubble formation in animals. V. Denitrogenation," *Journal of Cellular and Comparative Physiology*, vol. 24, no. 3, pp. 257-271, 1944.
- [62] J. L. Parker, P. M. Claesson, and P. Attard, "Bubbles, cavities, and the long-ranged attraction between hydrophobic surfaces," *The Journal of Physical Chemistry*, vol. 98, no. 34, pp. 8468-8480, 1994.
- [63] N. Ishida, T. Inoue, M. Miyahara, and K. Higashitani, "Nano bubbles on a hydrophobic surface in water observed by tapping-mode atomic force microscopy," *Langmuir*, vol. 16, no. 16, pp. 6377-6380, 2000.
- [64] H. Hu *et al.*, "Quasi/non-equilibrium state in nanobubble growth trajectory revealed by in-situ transmission electron microscopy," *Nano Today*, vol. 48, p. 101761, 2023.
- [65] J. H. Weijs, J. R. Seddon, and D. Lohse, "Diffusive shielding stabilizes bulk nanobubble clusters," *ChemPhysChem*, vol. 13, no. 8, pp. 2197-2204, 2012.
- [66] H. S. Alam, P. Sutikno, T. A. F. Soelaiman, and A. T. Sugiarto, "Bulk Nanobubbles: generation using a two-chamber swirling flow nozzle and long-term stability in water," *Journal of Flow Chemistry*, pp. 1-13, 2022.
- [67] J. Jin *et al.*, "Dynamic tracking of bulk nanobubbles from microbubbles shrinkage to collapse," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 589, p. 124430, 2020.
- [68] E. P. Favvas, G. Z. Kyzas, E. K. Efthimiadou, and A. C. Mitropoulos, "Bulk nanobubbles, generation methods and potential applications," *Current Opinion in Colloid & Interface Science*, vol. 54, p. 101455, 2021.
- [69] A. V. Postnikov, I. V. Uvarov, N. V. Penkov, and V. B. Svetovoy, "Collective behavior of bulk nanobubbles produced by alternating polarity electrolysis," *Nanoscale*, vol. 10, no. 1, pp. 428-435, 2018.
- [70] Y. Zhang, X. Zhu, J. A. Wood, and D. Lohse, "Threshold current density for diffusion-controlled stability of electrolytic surface nanobubbles," *Proceedings of the National Academy of Sciences*, vol. 121, no. 21, p. e2321958121, 2024.

- [71] Q. Wang, H. Zhao, N. Qi, Y. Qin, X. Zhang, and Y. Li, "Generation and stability of size-adjustable bulk nanobubbles based on periodic pressure change," *Scientific reports*, vol. 9, no. 1, p. 1118, 2019.
- [72] J. I. Lee, B.-S. Yim, and J.-M. Kim, "Effect of dissolved-gas concentration on bulk nanobubbles generation using ultrasonication," *Scientific Reports*, vol. 10, no. 1, p. 18816, 2020.
- [73] Z. Fang *et al.*, "Formation and stability of surface/bulk nanobubbles produced by decompression at lower gas concentration," *The Journal of Physical Chemistry C*, vol. 122, no. 39, pp. 22418-22423, 2018.
- [74] R. Pillai, M. K. Borg, and J. M. Reese, "Acoustothermal atomization of water nanofilms," *Physical review letters*, vol. 121, no. 10, p. 104502, 2018.
- [75] O. Manor, A. R. Rezk, J. R. Friend, and L. Y. Yeo, "Dynamics of liquid films exposed to high-frequency surface vibration," *Physical Review E*, vol. 91, no. 5, p. 053015, 2015.
- [76] S. Datta, R. Pillai, M. K. Borg, and K. Sefiane, "Acoustothermal nucleation of surface nanobubbles," *Nano Letters*, vol. 21, no. 3, pp. 1267-1273, 2021.
- [77] D. Dockar, M. K. Borg, and J. M. Reese, "Mechanical stability of surface nanobubbles," *Langmuir*, vol. 35, no. 29, pp. 9325-9333, 2018.
- [78] A. K. A. Ahmed *et al.*, "Generation of nanobubbles by ceramic membrane filters: The dependence of bubble size and zeta potential on surface coating, pore size and injected gas pressure," *Chemosphere*, vol. 203, pp. 327-335, 2018.
- [79] J. Jin, Z. Feng, F. Yang, and N. Gu, "Bulk nanobubbles fabricated by repeated compression of microbubbles," *Langmuir*, vol. 35, no. 12, pp. 4238-4245, 2019.
- [80] J. Du, X.-Y. Li, H. Hu, L. Xu, S.-P. Yang, and F.-H. Li, "Preparation and imaging investigation of dual-targeted C3F8-filled PLGA nanobubbles as a novel ultrasound contrast agent for breast cancer," *Scientific Reports*, vol. 8, no. 1, p. 3887, 2018.
- [81] M. Alheshibri and V. S. Craig, "Armoured nanobubbles; ultrasound contrast agents under pressure," *Journal of colloid and interface science*, vol. 537, pp. 123-131, 2019.
- [82] X. Lin, F. Tian, and S.-J. Marrink, "Martini coarse-grained nitrogen gas model for lipid nanobubble simulations," 2021.
- [83] N. V.-Y. Quach, A. Li, and J. C. Earthman, "Interaction of calcium carbonate with nanobubbles produced in an alternating magnetic field,"

ACS Applied Materials & Interfaces, vol. 12, no. 39, pp. 43714-43719, 2020.

- [84] M. R. Ghaani, P. G. Kusalik, and N. J. English, "Massive generation of metastable bulk nanobubbles in water by external electric fields," *Science advances*, vol. 6, no. 14, p. eaaz0094, 2020.
- [85] D. Lohse and X. Zhang, "Surface nanobubbles and nanodroplets," *Reviews of modern physics*, vol. 87, no. 3, pp. 981-1035, 2015.
- [86] Q. Xiao, Y. Liu, Z. Guo, Z. Liu, D. Lohse, and X. Zhang, "Solvent exchange leading to nanobubble nucleation: A molecular dynamics study," *Langmuir*, vol. 33, no. 32, pp. 8090-8096, 2017.
- [87] G. Han, S. Chen, S. Su, Y. Huang, B. Liu, and H. Sun, "A review and perspective on micro and nanobubbles: What They Are and Why They Matter," *Minerals Engineering*, vol. 189, p. 107906, 2022.
- [88] M. Li, L. Tonggu, X. Zhan, T. L. Mega, and L. Wang, "Cryo-EM visualization of nanobubbles in aqueous solutions," *Langmuir*, vol. 32, no. 43, pp. 11111-11115, 2016.
- [89] N. Bunkin, A. Shkirin, P. Ignatiev, L. Chaikov, I. Burkhanov, and A. Starosvetskij, "Nanobubble clusters of dissolved gas in aqueous solutions of electrolyte. I. Experimental proof," *The Journal of chemical physics*, vol. 137, no. 5, 2012.
- [90] W. Walczyk and H. Schönherr, "Characterization of the interaction between AFM tips and surface nanobubbles," *Langmuir*, vol. 30, no. 24, pp. 7112-7126, 2014.
- [91] X. H. Zhang, A. Khan, and W. A. Ducker, "A nanoscale gas state," *Physical review letters*, vol. 98, no. 13, p. 136101, 2007.
- [92] K. Ohgaki, N. Q. Khanh, Y. Joden, A. Tsuji, and T. Nakagawa, "Physicochemical approach to nanobubble solutions," *Chemical Engineering Science*, vol. 65, no. 3, pp. 1296-1300, 2010.
- [93] T. Uchida, K. Yamazaki, and K. Gohara, "Generation of micro-and nano-bubbles in water by dissociation of gas hydrates," *Korean Journal of Chemical Engineering*, vol. 33, pp. 1749-1755, 2016.
- [94] "<https://www.acniti.com/technology/different-bubbles-sizes-and-why-it-matters-to-the-properties/>." (accessed.
- [95] K. Yasui, T. Tuziuti, and W. Kanematsu, "Mysteries of bulk nanobubbles (ultrafine bubbles); stability and radical formation," *Ultrasonics sonochemistry*, vol. 48, pp. 259-266, 2018.

- [96] W. Shen *et al.*, "Microbubble and nanobubble-based gas flotation for oily wastewater treatment: a review," *Environmental Reviews*, vol. 30, no. 3, pp. 359-379, 2022.
- [97] R. E. Apfel, "The role of impurities in cavitation-threshold determination," *The Journal of the Acoustical Society of America*, vol. 48, no. 5B, pp. 1179-1186, 1970.
- [98] L. A. Crum, "Tensile strength of water," *Nature*, vol. 278, no. 5700, pp. 148-149, 1979.
- [99] K. YASUI, "Mechanism for stability of ultrafine bubbles," *Japanese Journal of Multiphase Flow*, vol. 30, no. 1, pp. 19-26, 2016.
- [100] H. Kobayashi, S. Maeda, M. Kashiwa, and T. Fujita, "Measurement and identification of ultrafine bubbles by resonant mass measurement method," in *International Conference on Optical Particle Characterization (OPC 2014)*, 2014, vol. 9232: SPIE, pp. 147-151.
- [101] F. Y. Ushikubo *et al.*, "Zeta-potential of micro-and/or nano-bubbles in water produced by some kinds of gases," *IFAC Proceedings Volumes*, vol. 43, no. 26, pp. 283-288, 2010.
- [102] A. J. Shnoudeh *et al.*, "Synthesis, characterization, and applications of metal nanoparticles," in *Biomaterials and bionanotechnology*: Elsevier, 2019, pp. 527-612.
- [103] S.-N. Hong, S.-H. Choe, U.-G. Jong, M.-S. Pak, and C.-J. Yu, "The maximum interbubble distance in relation to the radius of spherical stable nanobubble in liquid water: A molecular dynamics study," *Fluid Phase Equilibria*, vol. 487, pp. 45-51, 2019.
- [104] S. Mi, C. Hou, and W. Ge, "Theoretical study on the stability of nanobubbles and its verification in molecular dynamics simulation," *Particuology*, vol. 87, pp. 99-105, 2024.
- [105] M. Zhang, Y.-s. Tu, and H.-p. Fang, "Concentration of nitrogen molecules needed by nitrogen nanobubbles existing in bulk water," *Applied Mathematics and Mechanics*, vol. 34, no. 12, pp. 1433-1438, 2013.
- [106] Z. Gao, W. Wu, W. Sun, and B. Wang, "Understanding the stabilization of a bulk nanobubble: A molecular dynamics analysis," *Langmuir*, vol. 37, no. 38, pp. 11281-11291, 2021.
- [107] E. D. Michailidi, G. Bomis, A. Varoutoglou, E. K. Efthimiadou, A. C. Mitropoulos, and E. P. Favvas, "Fundamentals and applications of nanobubbles," in *Interface science and technology*, vol. 30: Elsevier, 2019, pp. 69-99.

- [108] Y. Wang and T. Wang, "Preparation method and application of nanobubbles: a review," *Coatings*, vol. 13, no. 9, p. 1510, 2023.
- [109] Ş. H. Şanlıer *et al.*, "Development of ultrasound-triggered and magnetic-targeted nanobubble system for dual-drug delivery," *Journal of pharmaceutical sciences*, vol. 108, no. 3, pp. 1272-1283, 2019.
- [110] C. Li and H. Zhang, "A review of bulk nanobubbles and their roles in flotation of fine particles," *Powder Technology*, vol. 395, pp. 618-633, 2022.
- [111] Z. Zhou, Z. Xu, and J. Finch, "On the role of cavitation in particle collection during flotation-a critical review," *Minerals Engineering*, vol. 7, no. 9, pp. 1073-1084, 1994.
- [112] L. Cai *et al.*, "Investigating the potential of CO₂ nanobubble systems for enhanced oil recovery in extra-low-permeability reservoirs," *Nanomaterials*, vol. 14, no. 15, p. 1280, 2024.
- [113] M. Pan, P. Naeiji, and N. J. English, "Study of CO₂-hydrate formation in contact with bulk nanobubbles: An investigation from experiment and molecular-dynamics simulations," *Journal of Colloid and Interface Science*, vol. 685, pp. 415-426, 2025.
- [114] K. Khanafer and K. Vafai, "A review on the applications of nanofluids in solar energy field," *Renewable energy*, vol. 123, pp. 398-406, 2018.
- [115] A. A. Balandin *et al.*, "Superior thermal conductivity of single-layer graphene," *Nano letters*, vol. 8, no. 3, pp. 902-907, 2008.
- [116] C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene," *science*, vol. 321, no. 5887, pp. 385-388, 2008.
- [117] K. I. Bolotin *et al.*, "Ultrahigh electron mobility in suspended graphene," *Solid state communications*, vol. 146, no. 9-10, pp. 351-355, 2008.
- [118] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, "Graphene-based ultracapacitors," *Nano letters*, vol. 8, no. 10, pp. 3498-3502, 2008.
- [119] S. Gadipelli and Z. X. Guo, "Graphene-based materials: Synthesis and gas sorption, storage and separation," *Progress in Materials Science*, vol. 69, pp. 1-60, 2015.
- [120] P. Kanti, A. A. Minea, K. Sharma, and M. Revanasiddappa, "Improved thermophysical properties of Graphene Ionanofluid as heat transfer fluids for thermal applications," *Journal of Ionic Liquids*, vol. 2, no. 2, p. 100038, 2022.
- [121] F. Yavari and N. Koratkar, "Graphene-based chemical sensors," *The journal of physical chemistry letters*, vol. 3, no. 13, pp. 1746-1753, 2012.

- [122] Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay, and Y. Lin, "Graphene based electrochemical sensors and biosensors: a review," *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, vol. 22, no. 10, pp. 1027-1036, 2010.
- [123] H. An, B. H. Tan, J. G. S. Moo, S. Liu, M. Pumera, and C.-D. Ohl, "Graphene nanobubbles produced by water splitting," *Nano letters*, vol. 17, no. 5, pp. 2833-2838, 2017.
- [124] G. Zamborlini *et al.*, "Nanobubbles at GPa pressure under graphene," *Nano letters*, vol. 15, no. 9, pp. 6162-6169, 2015.
- [125] Z.-X. Qu, B.-S. Wang, and J.-W. Jiang, "The Gas in Graphene Bubbles: An Improved van der Waals Equation Description," *The Journal of Physical Chemistry C*, vol. 127, no. 19, pp. 9205-9212, 2023.
- [126] C. Bie, L. Wang, and J. Yu, "Challenges for photocatalytic overall water splitting," *Chem*, vol. 8, no. 6, pp. 1567-1574, 2022.
- [127] F. D. Tovar, M. A. Barrufet, and D. S. Schechter, "Enhanced oil recovery in the wolfcamp shale by carbon dioxide or nitrogen injection: An experimental investigation," *SPE Journal*, vol. 26, no. 01, pp. 515-537, 2021.
- [128] K. Elsaid *et al.*, "Thermophysical properties of graphene-based nanofluids," *International Journal of Thermofluids*, vol. 10, p. 100073, 2021.
- [129] R. Bader, "Quantum topology of molecular charge distributions. III. The mechanics of an atom in a molecule," *The Journal of Chemical Physics*, vol. 73, no. 6, pp. 2871-2883, 1980.
- [130] D. J. Tannor *et al.*, "Accurate first principles calculation of molecular charge distributions and solvation energies from ab initio quantum mechanics and continuum dielectric theory," *Journal of the American Chemical Society*, vol. 116, no. 26, pp. 11875-11882, 1994.
- [131] K. Varga and J. A. Driscoll, *Computational nanoscience: Applications for molecules, clusters, and solids*. Cambridge University Press, 2011.
- [132] I. Balyakin, A. Yuryev, B. Gelchinski, and A. Rempel, "Ab initio molecular dynamics and high-dimensional neural network potential study of VZrNbHfTa melt," *Journal of Physics: Condensed Matter*, vol. 32, no. 21, p. 214006, 2020.
- [133] W. G. Hoover, D. J. Evans, R. B. Hickman, A. J. Ladd, W. T. Ashurst, and B. Moran, "Lennard-Jones triple-point bulk and shear viscosities. Green-Kubo theory, Hamiltonian mechanics, and nonequilibrium molecular dynamics," *Physical Review A*, vol. 22, no. 4, p. 1690, 1980.

- [134] M. P. Allen, "Introduction to molecular dynamics simulation," *Computational soft matter: from synthetic polymers to proteins*, vol. 23, no. 1, pp. 1-28, 2004.
- [135] A. Satoh, *Introduction to practice of molecular simulation: molecular dynamics, Monte Carlo, Brownian dynamics, Lattice Boltzmann and dissipative particle dynamics*. Elsevier, 2010.
- [136] Q. Mao, M. Feng, X. Z. Jiang, Y. Ren, K. H. Luo, and A. C. van Duin, "Classical and reactive molecular dynamics: Principles and applications in combustion and energy systems," *Progress in Energy and Combustion Science*, vol. 97, p. 101084, 2023.
- [137] A. C. Van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard, "ReaxFF: a reactive force field for hydrocarbons," *The Journal of Physical Chemistry A*, vol. 105, no. 41, pp. 9396-9409, 2001.
- [138] P. M. Morse, "Diatomic molecules according to the wave mechanics. II. Vibrational levels," *Physical review*, vol. 34, no. 1, p. 57, 1929.
- [139] B. R. Brooks, R. E. Bruccoleri, B. D. Olafson, D. J. States, S. a. Swaminathan, and M. Karplus, "CHARMM: a program for macromolecular energy, minimization, and dynamics calculations," *Journal of computational chemistry*, vol. 4, no. 2, pp. 187-217, 1983.
- [140] M. J. Abraham *et al.*, "GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers," *SoftwareX*, vol. 1, pp. 19-25, 2015.
- [141] S. H. Lee and J. Kim, "Transport properties of bulk water at 243–550 K: A comparative molecular dynamics simulation study using SPC/E, TIP4P, and TIP4P/2005 water models," *Molecular physics*, vol. 117, no. 14, pp. 1926-1933, 2019.
- [142] W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, "Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids," *Journal of the american chemical society*, vol. 118, no. 45, pp. 11225-11236, 1996.
- [143] A. Zaragoza *et al.*, "Molecular dynamics study of nanoconfined TIP4P/2005 water: how confinement and temperature affect diffusion and viscosity," *Physical Chemistry Chemical Physics*, vol. 21, no. 25, pp. 13653-13667, 2019.
- [144] S. Jain and L. Qiao, "Molecular dynamics simulations of the surface tension of oxygen-supersaturated water," *AIP Advances*, vol. 7, no. 4, 2017.

- [145] K. Chae and A. Violi, "Mutual diffusion coefficients of heptane isomers in nitrogen: A molecular dynamics study," *The Journal of chemical physics*, vol. 134, no. 4, 2011.
- [146] Q. Yang and C. Zhong, "Molecular simulation of adsorption and diffusion of hydrogen in metal– organic frameworks," *The Journal of Physical Chemistry B*, vol. 109, no. 24, pp. 11862-11864, 2005.
- [147] C. Sun, B. Wen, and B. Bai, "Application of nanoporous graphene membranes in natural gas processing: Molecular simulations of CH₄/CO₂, CH₄/H₂S and CH₄/N₂ separation," *Chemical engineering science*, vol. 138, pp. 616-621, 2015.
- [148] A. Guerra, S. Mathews, J. T. Su, M. Marić, P. Servio, and A. D. Rey, "Molecular dynamics predictions of transport properties for carbon dioxide hydrates under pre-nucleation conditions using TIP4P/Ice water and EPM2, TraPPE, and Zhang carbon dioxide potentials," *Journal of Molecular Liquids*, vol. 379, p. 121674, 2023.
- [149] H. Sun, "COMPASS: an ab initio force-field optimized for condensed-phase applications overview with details on alkane and benzene compounds," *The Journal of Physical Chemistry B*, vol. 102, no. 38, pp. 7338-7364, 1998.
- [150] T. P. Senftle *et al.*, "The ReaxFF reactive force-field: development, applications and future directions," *npj Computational Materials*, vol. 2, no. 1, pp. 1-14, 2016.
- [151] J. E. Mueller, A. C. Van Duin, and W. A. Goddard III, "Development and validation of ReaxFF reactive force field for hydrocarbon chemistry catalyzed by nickel," *The Journal of Physical Chemistry C*, vol. 114, no. 11, pp. 4939-4949, 2010.
- [152] M. F. Russo Jr and A. C. Van Duin, "Atomistic-scale simulations of chemical reactions: Bridging from quantum chemistry to engineering," *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 269, no. 14, pp. 1549-1554, 2011.
- [153] M. Kowalik, C. Ashraf, B. Damirchi, D. Akbarian, S. Rajabpour, and A. C. Van Duin, "Atomistic scale analysis of the carbonization process for C/H/O/N-based polymers with the ReaxFF reactive force field," *The Journal of Physical Chemistry B*, vol. 123, no. 25, pp. 5357-5367, 2019.
- [154] C. Ashraf and A. C. Van Duin, "Extension of the ReaxFF combustion force field toward syngas combustion and initial oxidation kinetics," *The Journal of Physical Chemistry A*, vol. 121, no. 5, pp. 1051-1068, 2017.

- [155] J. Tersoff, "Modeling solid-state chemistry: Interatomic potentials for multicomponent systems," *Physical review B*, vol. 39, no. 8, p. 5566, 1989.
- [156] J. Grossman, N. Ferralis, D. Cohen-Tanugi, and S. H. Dave, "Porous materials and methods including nanoporous materials for water filtration," ed: Google Patents, 2014.
- [157] K. Zhou and B. Liu, *Molecular dynamics simulation: fundamentals and applications*. Academic Press, 2022.
- [158] D. Mathas *et al.*, "Evaluation of methods for viscosity simulations of lubricants at different temperatures and pressures: a case study on PAO-2," *Tribology Transactions*, vol. 64, no. 6, pp. 1138-1148, 2021.
- [159] E. Kirova and G. Norman, "Viscosity calculations at molecular dynamics simulations," in *Journal of Physics: Conference Series*, 2015, vol. 653, no. 1: IOP Publishing, p. 012106.
- [160] J.-P. Hansen and I. R. McDonald, *Theory of simple liquids: with applications to soft matter*. Academic press, 2013.
- [161] S. Engelmann and R. Hentschke, "Specific heat capacity enhancement studied in silica doped potassium nitrate via molecular dynamics simulation," *Scientific reports*, vol. 9, no. 1, p. 7606, 2019.
- [162] S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," *Journal of computational physics*, vol. 117, no. 1, pp. 1-19, 1995.
- [163] A. Stukowski, "Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool," *Modelling and simulation in materials science and engineering*, vol. 18, no. 1, p. 015012, 2009.
- [164] F. Mahmoudinobar and C. L. Dias, "GRADE: A code to determine clathrate hydrate structures," *Computer physics communications*, vol. 244, pp. 385-391, 2019.
- [165] J. Zeng, L. Cao, C.-H. Chin, H. Ren, J. Z. Zhang, and T. Zhu, "ReacNetGenerator: an automatic reaction network generator for reactive molecular dynamics simulations," *Physical chemistry chemical physics*, vol. 22, no. 2, pp. 683-691, 2020.
- [166] K. R. Harris and L. A. Woolf, "Pressure and temperature dependence of the self diffusion coefficient of water and oxygen-18 water," *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 76, pp. 377-385, 1980.
- [167] W. S. Price, H. Ide, and Y. Arata, "Solution dynamics in aqueous monohydric alcohol systems," *The Journal of Physical Chemistry A*, vol. 107, no. 24, pp. 4784-4789, 2003.

- [168] A. Pádua, J. Fareleira, J. Calado, and W. Wakeham, "Density and viscosity measurements of 2, 2, 4-trimethylpentane (isooctane) from 198 K to 348 K and up to 100 MPa," *Journal of Chemical & Engineering Data*, vol. 41, no. 6, pp. 1488-1494, 1996.
- [169] P. S. Tofts *et al.*, "Test liquids for quantitative MRI measurements of self-diffusion coefficient in vivo," *Magnetic Resonance in Medicine: An Official Journal of the International Society for Magnetic Resonance in Medicine*, vol. 43, no. 3, pp. 368-374, 2000.
- [170] D. Caudwell, J. Trusler, V. Vesovic, and W. Wakeham, "The viscosity and density of n-dodecane and n-octadecane at pressures up to 200 MPa and temperatures up to 473 K," *International Journal of Thermophysics*, vol. 25, no. 5, pp. 1339-1352, 2004.
- [171] A. Glielmo, B. E. Husic, A. Rodriguez, C. Clementi, F. Noé, and A. Laio, "Unsupervised learning methods for molecular simulation data," *Chemical Reviews*, vol. 121, no. 16, pp. 9722-9758, 2021.
- [172] M. Ester, H.-P. Kriegel, J. Sander, and X. Xu, "A density-based algorithm for discovering clusters in large spatial databases with noise," in *kdd*, 1996, vol. 96, no. 34, pp. 226-231.
- [173] K. Dill and S. Bromberg, *Molecular driving forces: statistical thermodynamics in biology, chemistry, physics, and nanoscience*. Garland Science, 2010.
- [174] L. Gevantman, "Solubility of selected gases in water," *Nitric oxide (NO)*, vol. 308, no. 3.348, pp. 10-4, 2000.
- [175] S. Alavi, *Molecular simulations: fundamentals and practice*. John Wiley & Sons, 2020.
- [176] J. I. Lee, H. S. Huh, J. Y. Park, J.-G. Han, and J.-M. Kim, "Coarsening behavior of bulk nanobubbles in water," *Scientific Reports*, vol. 11, no. 1, p. 19173, 2021.
- [177] M. Kerscher *et al.*, "Thermophysical properties of the energy carrier methanol under the influence of dissolved hydrogen," *International Journal of Hydrogen Energy*, 2023.
- [178] J. Zhan, Z. Lei, and Y. Zhang, "Non-covalent interactions of graphene surface: Mechanisms and applications," *Chem*, 2022.
- [179] S. Deng and V. Berry, "Wrinkled, rippled and crumpled graphene: an overview of formation mechanism, electronic properties, and applications," *Materials Today*, vol. 19, no. 4, pp. 197-212, 2016.
- [180] M. Sarafraz and M. R. Safaei, "Diurnal thermal evaluation of an evacuated tube solar collector (ETSC) charged with graphene

nanoplatelets-methanol nano-suspension," *Renewable energy*, vol. 142, pp. 364-372, 2019.

- [181] C. Turner, "From supercritical carbon dioxide to gas expanded liquids in extraction and chromatography of lipids," *Lipid Technology*, vol. 27, no. 12, pp. 275-277, 2015.
- [182] M. d. R. Rodríguez-Laguna *et al.*, "Mechanisms behind the enhancement of thermal properties of graphene nanofluids," *Nanoscale*, vol. 10, no. 32, pp. 15402-15409, 2018.
- [183] X. Jing, Q. Luo, X. Cui, Q. Wang, Y. Liu, and Z. Fu, "Molecular dynamics simulation of CO₂ hydrate growth in salt water," *Journal of Molecular Liquids*, vol. 366, p. 120237, 2022.
- [184] Y. Wei and N. Maeda, "Mechanisms of the memory effect of clathrate hydrates," *Chemical Engineering Science*, vol. 270, p. 118538, 2023.
- [185] M. Aminnaji *et al.*, "CO₂ Gas hydrate for carbon capture and storage applications–Part 1," *Energy*, vol. 300, p. 131579, 2024.
- [186] Y. Xie *et al.*, "Effects of H₂/N₂ on CO₂ hydrate film growth: Morphology and microstructure," *Chemical Engineering Journal*, vol. 431, p. 134004, 2022.
- [187] X. Zhang, T. Shan, H. Song, J. Li, and Q. Wu, "Molecular dynamics study of the micro-mechanism of CO₂ hydrate formation in the confined space of porous media," *International Journal of Heat and Mass Transfer*, vol. 244, p. 126940, 2025.
- [188] X. Zhang *et al.*, "Molecular insight into the formation mechanism of CO₂ hydrate in a confined space of surface oxidized porous media system," *Fuel*, vol. 404, p. 136254, 2026.
- [189] M. H. Mahmoodi, M. Manteghian, and P. Naeiji, "Study the effect of Ag nanoparticles on the kinetics of CO₂ hydrate growth by molecular dynamics simulation," *Journal of Molecular Liquids*, vol. 343, p. 117668, 2021.
- [190] Y. Yu, C. Zhao, Y. Tao, X. Chen, and Y.-L. He, "Superior thermal energy storage performance of NaCl-SWCNT composite phase change materials: A molecular dynamics approach," *Applied Energy*, vol. 290, p. 116799, 2021.
- [191] H. Dembicki, *Practical petroleum geochemistry for exploration and production*. Elsevier, 2022.
- [192] M. X. Ho and C. Pan, "Optimal concentration of alumina nanoparticles in molten Hitec salt to maximize its specific heat capacity," *International Journal of Heat and Mass Transfer*, vol. 70, pp. 174-184, 2014.

- [193] Y. Hu, Y. He, Z. Zhang, and D. Wen, "Enhanced heat capacity of binary nitrate eutectic salt-silica nanofluid for solar energy storage," *Solar Energy Materials and Solar Cells*, vol. 192, pp. 94-102, 2019.
- [194] S. Engelmann and R. Hentschke, "Specific heat capacity enhancement studied in silica doped potassium nitrate via molecular dynamics simulation," *Scientific reports*, vol. 9, no. 1, pp. 1-14, 2019.
- [195] Z. Rao, S. Wang, and F. Peng, "Molecular dynamics simulations of nano-encapsulated and nanoparticle-enhanced thermal energy storage phase change materials," *International Journal of Heat and Mass Transfer*, vol. 66, pp. 575-584, 2013.
- [196] H. Tafrishi, S. Sadeghzadeh, R. Ahmadi, F. Molaei, F. Yousefi, and H. Hassanloo, "Investigation of tetracosane thermal transport in presence of graphene and carbon nanotube fillers—A molecular dynamics study," *Journal of Energy Storage*, vol. 29, p. 101321, 2020.
- [197] Y. Mao *et al.*, "Molecular dynamics simulation of thermal properties in composite phase change materials based on functionalized graphene and polyethylene glycol," *Journal of Energy Storage*, vol. 94, p. 112104, 2024.
- [198] W. M. Haynes, *CRC handbook of chemistry and physics*. CRC press, 2016.
- [199] P. Boone, H. Babaei, and C. E. Wilmer, "Heat flux for many-body interactions: corrections to LAMMPS," *Journal of chemical theory and computation*, vol. 15, no. 10, pp. 5579-5587, 2019.
- [200] H. Babaei, P. Keblinski, and J. Khodadadi, "Thermal conductivity enhancement of paraffins by increasing the alignment of molecules through adding CNT/graphene," *International Journal of heat and mass transfer*, vol. 58, no. 1-2, pp. 209-216, 2013.
- [201] L. Manjunatha, H. Takamatsu, and J. J. Cannon, "Atomic-level breakdown of Green–Kubo relations provides new insight into the mechanisms of thermal conduction," *Scientific reports*, vol. 11, no. 1, p. 5597, 2021.
- [202] L. d. S. Oliveira and P. A. Greaney, "Method to manage integration error in the Green-Kubo method," *Physical Review E*, vol. 95, no. 2, p. 023308, 2017.
- [203] H. Babaei, P. Keblinski, and J. M. Khodadadi, "Equilibrium molecular dynamics determination of thermal conductivity for multi-component systems," *Journal of Applied Physics*, vol. 112, no. 5, 2012.
- [204] X. Zheng, Y. Bao, D. Qu, J. Wu, G. Qin, and Y. Liu, "Thermal conductivity measurements for long-chain n-alkanes at evaluated

- temperature and pressure: n-dodecane and n-tetradecane," *The Journal of Chemical Thermodynamics*, vol. 162, p. 106566, 2021.
- [205] G. Senthilkumar, M. Purusothaman, C. Rameshkumar, N. Joy, S. Sachin, and K. S. Thanigai, "Generation and characterization of nanobubbles for heat transfer applications," *Materials Today: Proceedings*, vol. 43, pp. 3391-3393, 2021.
 - [206] E. K. Goharshadi, "A review on the radial distribution function: Insights into molecular structure, intermolecular interactions, and thermodynamic properties," *Journal of Molecular Liquids*, p. 127900, 2025.
 - [207] K. Yan, L. Qiu, H. Li, N. Cao, and Y. Feng, "Expanded graphite encapsulation of nitrates for enhanced thermal transport: Mechanism insight and component screening," *Composites Science and Technology*, vol. 259, p. 110957, 2025.
 - [208] M. Li, X. Ma, J. Eisener, P. Pfeiffer, C.-D. Ohl, and C. Sun, "How bulk nanobubbles are stable over a wide range of temperatures," *Journal of Colloid and Interface Science*, vol. 596, pp. 184-198, 2021.
 - [209] R. Battino and P. G. Seybold, "The O₂/N₂ ratio gas solubility mystery," *Journal of Chemical & Engineering Data*, vol. 56, no. 12, pp. 5036-5044, 2011.
 - [210] A. Van Duin and P. S. U. U. P. U. States, "Development, Validation and Application of the ReaxFF Reactive Force Field to Hydrocarbon Oxidation Kinetics," 2019.
 - [211] C. Ashraf, S. Shabnam, A. Jain, Y. Xuan, and A. C. van Duin, "Pyrolysis of binary fuel mixtures at supercritical conditions: A ReaxFF molecular dynamics study," *Fuel*, vol. 235, pp. 194-207, 2019.
 - [212] Q.-D. Wang, J.-B. Wang, J.-Q. Li, N.-X. Tan, and X.-Y. Li, "Reactive molecular dynamics simulation and chemical kinetic modeling of pyrolysis and combustion of n-dodecane," *Combustion and Flame*, vol. 158, no. 2, pp. 217-226, 2011.
 - [213] J. Li, X. Zhang, A. Zhang, and H. Wang, "ReaxFF based molecular dynamics simulation of ethyl butyrate in pyrolysis and combustion," *Chemical Engineering Science*, vol. 284, p. 119528, 2024.