

Details about pressure calculation in molecular dynamic analysis

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Abstract Numerical modeling of nano/micro devices needs measurement of thermo-fluid properties in molecular simulations. Therefore, special attention has been paid to the method of numerical measurement of fluid properties. Details about pressure calculation in a molecular system and its sensitivity to approximations made are studied in this paper. Convergence behavior of kinetic and potential parts of pressure and the effect of cut-off distance on pressure calculation in different bin sizes are studied. Finally a method is introduced for the correct calculation of pressure. This method is based on the assumption that macroscopic properties should be independent from the bin sizes.

Keywords: Nano fluid, Molecular Dynamics, Pressure, Bin size, Sampling

1. Introduction

Although continuum model generally applied to describe fluid flows is practically useful, it does not talk about all details that are significant in molecular scale. Following the rapid development of computational facilities in recent years, trend toward the analysis of nano/microfluid flows is sharply risen. Numerical modeling of nano/micro devices needs measurement of thermo-fluid properties in molecular simulations. Therefore, special attention has been paid to the method of numerical measurement of fluid properties. Molecular Dynamics (MD) is a deterministic method for estimating molecules' positions. Molecular forces are the cause of motion; many potential functions have been defined to represent these forces (see e.g. Leach 1999 and Sadus 2002). Extracting the macroscopic properties like velocity, temperature and pressure from microscopic data has been a challenging issue for scientists. Macroscopic properties at any point of a molecular domain can be extracted via sampling and averaging of molecular behaviors within a small region around that point, called a bin (Karniadakis et al. 2002). A unique formulation for determining each of the macroscopic properties can be found in the

literature. To extract macroscopic properties, these formulations must be applied correctly. In this paper, we study pressure calculation in a molecular dynamic system. Convergence behavior of kinetic and potential parts of pressure and the effect of cut-off distance on pressure calculation in different bin sizes were studied. Finally we introduce a method for the correct calculation of pressure. This method is based on the assumption that macroscopic properties should be independent from the bin sizes.

2. Molecular dynamics

In molecular dynamics, motions of molecules are predicted using Newton's second law. Intermolecular forces between fluid-fluid molecules are calculated using the Lennard-Jones 12-6 potential equation. (Rapaport 2004)

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (1)$$

In this equation, $U(r_{ij})$ is the Lennard-Jones potential, r_{ij} is the distance between two interacting Molecules i and j , and σ_{ij} and ϵ_{ij} are distance characteristic length and energy scale. Derivative of $L-J$ potential equation with

respect to r_{ij} is used to calculate intermolecular forces.

$$f_{ij} = \frac{48\epsilon}{\sigma^2} \left[\left(\frac{\sigma}{r_{ij}} \right)^{14} - \frac{1}{2} \left(\frac{\sigma}{r_{ij}} \right)^8 \right] \quad (2)$$

Usually, this equation is enforced within a cut off distance to optimize the computational cost. In this paper, we chose cut off distance of $r_c=2.5\sigma$ which is usually used in other references. To save computational time, the Lennard-Jones potential is truncated at this cut off distance.

3. Pressure formula

In a microscopic system, pressure is calculated from the summation of forces on all atoms according to the virial equation. For pair-additive force fields this equation is usually written as

$$P = \frac{NK_B T}{V} + \frac{1}{6V} \left[\sum_{i=1}^N \sum_{j \neq i}^N r_{ij} \cdot f_{ij} \right] \quad (3)$$

Where N is the number of molecules exist in the computational domain, k_B is Boltzmann's constant, V and T are volume and temperature of the computational domain, and f_{ij} is force between molecule i and j .

This equation is formed from two different terms. First term is called kinetic term that contains temperature of computational domain. In microscopic view, Temperature equation is defined as

$$T = \frac{m_{Ar}}{3N_{bin}k_B} \sum_{n=1}^{N_{bin}} \sum_{i=1}^3 (V_{n,i} - \bar{V}_i)^2 \quad (4)$$

Where n denotes the molecule number in the bin, $i=1, 2, 3$ denotes the $x, y,$ and z component of the atomic velocity $V_{n,i}$, \bar{V}_i is the i -th component of the mean flow velocity, and m is the atom mass. Mean velocity can be obtained from any of the several averaging methods like SAM (Tysanner and Garcia 2004), CAM (Tysanner and Garcia 2005) or SMC (Karimian et al. 2011) that reduces statistical errors in its calculation. In this paper, SMC method is used to calculate mean velocity. Temperature is related to the kinetic

energy of molecules in microscopic view. This term is always positive. Second term includes the effect of forces between the molecules; this term is called potential term. Kinetic term is always positive but potential term may be positive or negative. Zero force exists between two molecules at a distance of $2^{1/6}\sigma$ based on L-J potential model. If the distance between two molecules is higher than this value, the sign of pair-additive force will be negative and the molecules attract each other. This is vice versa when the distance between two molecules is less than this value.

In this paper, we use a code, which is written in FORTRAN language. Also, this code has been used in previous works and the accuracy of computed macroscopic properties has been studied on those papers. (Karimian et al. 2011, Karimian and Namvar 2012, Namvar and Karimian 2012, and Karimian and Izadi 2013) calculation of pressure is added to this code to extract the pressure value.

Our experience shows that some precautions should be taken in calculation of pressure in the molecular flow. In this paper, details about the pressure calculation and considerations that should be taken into account will be discussed in detail.

4. Pressure calculation

In this paper we would like to study the behavior of kinetic and potential parts of pressure equation. For this purpose, consider a cubic region with its molecules in equilibrium. We know that pressure would be the same all over this region. The size of this cube is $L=45 \text{ \AA}$ and it contains $N=1728$ mono atomic noble gas molecules of Argon. Atomic diameter of Argon is $\sigma=3.4 \text{ \AA}$ and its energy parameter is $\epsilon=1.67 \times 10^{-21} \text{ J}$. Periodic boundary condition is applied in all directions. Argon molecules are initially arranged in a lattice form of FCC. MD simulation of Argon molecules starts from the initial temperature of 120K, and mean velocities of zero. Equation of motion is integrated over time with $\Delta t=10^{-15}$ sec, using Verlet scheme. The number of molecules is constant during the simulation. Macroscopic properties at any point of a molecular domain

can be extracted via sampling and averaging of molecular behavior within a control region around that point, called a bin. Four bins with different sizes are selected for sampling and averaging of flow parameters. The larger one fits the whole cube and contains all argon molecules. The other bins have smaller sizes equal to $\frac{3}{4}$, $\frac{1}{2}$ and $\frac{1}{4}$ of the whole cube, respectively, and are located as shown in Figure 1. The pressure calculated within these bins should be the same. It is based on the assumption that macroscopic properties should be independent from the bin sizes. We would like to know if this is true, and if not under what conditions this will happen. Molecular dynamics simulation is continued for 30,000 time steps of 10^{-15} sec, where equilibrium is reached. Figures 2 and 3 show convergence history of kinetic and potential shares of pressure for the four bins, respectively.

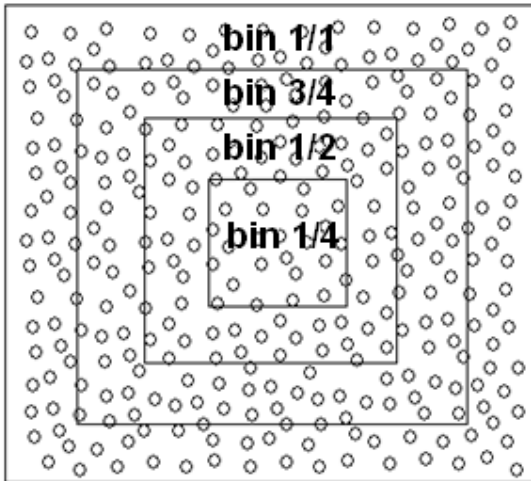


Fig. 1. Bin sizes for pressure calculation in a periodic stationary molecular flow

As shown in fig.2, the kinetic share of pressure converges to the same value of 27 MPa in all of the four different bins. Kinetic part of pressure equation is based solely on the properties of atoms, and in contrast to the potential part, it is independent of interaction with other molecules. Potential share of pressure is calculated with different approaches. In the first approach, potential share of pressure in each bin is set equal to the summation of all pair-additive forces multiplied by the distance between molecules

within each bin. In this approach, no cut-off distance is assumed for the molecules. The reason to include even far molecules in pressure calculation is that although the pair-additive force between these molecules is very small, when the distance between them is multiplied, the result can be very different. Figures 3 and 4 show the convergence rate of potential share of pressure and the total pressure, respectively for all four bins.

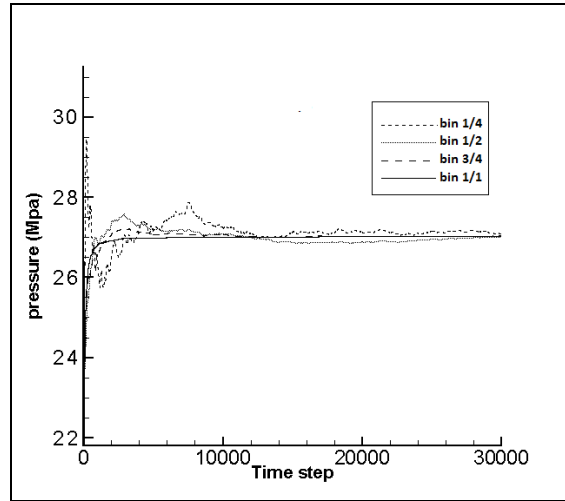


Fig. 2. Convergence rate of Kinetic part of pressure in different bins

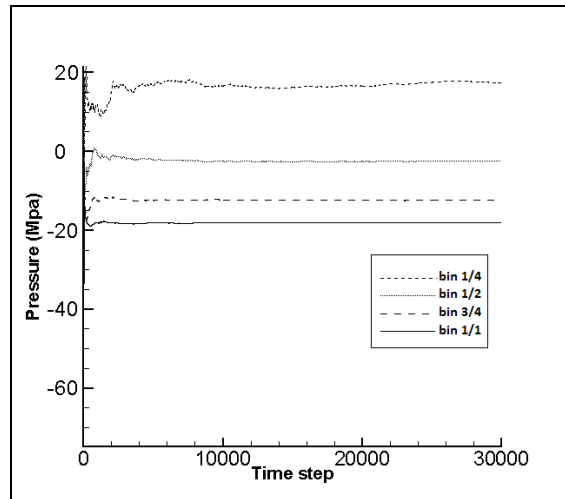


Fig. 3. Convergence rate of Potential part of pressure in different bins; cut-off not included

As seen, potential share of pressure converges to different values and even different signs in each bin. To examine the effect of cut-off distance, pressure is evaluated in each bin using all molecules within the bin and taking

into consideration the cut-off distance for these molecules. Convergence rate of pressure calculated with this approach is shown in fig. 5. Although this result is better than that of Fig. 4, unfortunately pressure still converges to different values in each bin.

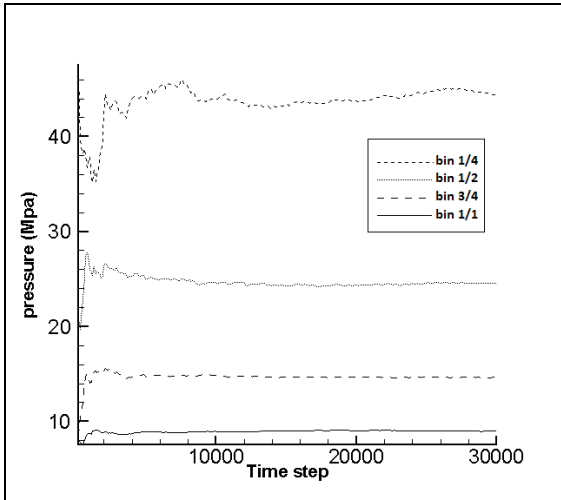


Fig. 4. Convergence rate of pressure in different bins; cut-off not included

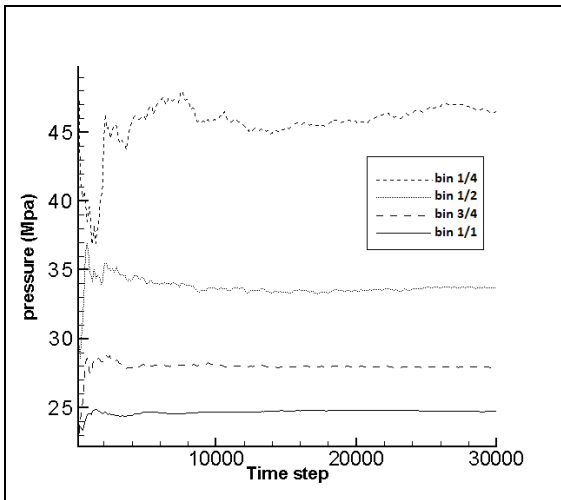


Fig. 5. Convergence rate of pressure in different bins; cut-off included

In the above simulations, although interactions between molecules in a bin (inner molecules) are taken into account, yet correct results have not been obtained. A careful review of our calculations revealed that molecules within the cut-off distances of inner molecules that fall outside of the bin (outer molecules) are not included in calculation procedure. Therefore, forces between these molecules have been

excluded from our calculations. Note that our algorithm was devised to work merely on inner molecules. Therefore, in our third approach the algorithm was modified to include intermolecular forces between inner molecules and outer molecules located in their cut-off distance as well. Obviously, these outer molecules are located in the vicinity of the bin's outer boundary, and therefore their inclusion will add significant cost to our computation. Convergence rate of pressure calculated with this approach in all of four bins are shown in figure 6. As seen, pressure is converging to the same value in the bins at the equilibrium state, although there are some oscillations in pressure value for the $\frac{1}{4}$ and $\frac{1}{2}$ bins. These oscillations and the small differences between pressure values at equilibrium state are due to another issue that is the bin size. Notice that the number of molecules, which are located inside the bin, has an important role in pressure calculation. Passing molecules through the bin boundaries should not have a big effect on extracted macroscopic properties. More details about the effect of bin size on sampling and averaging can be found in Karimian and Izadi (2013). At the end of this section, it can be concluded that with the third approach described above one can calculate pressure value in a molecular system using a proper bin size.

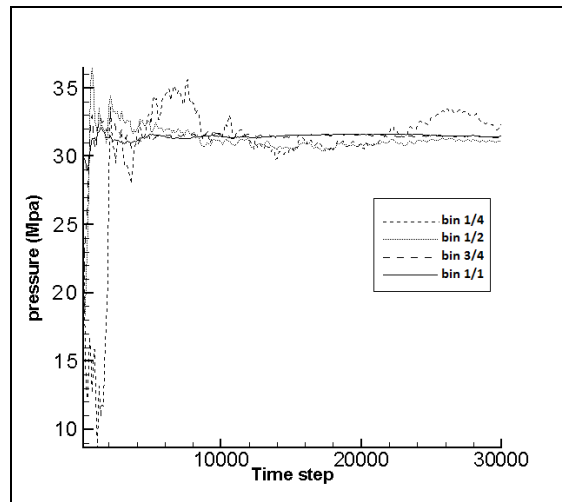


Fig. 6. Convergence rate of pressure in different bins; cut-off included; outer molecules within the cut-off distance of inner molecules included

To verify the result which is obtained from our MD code, this simulation is also done by LAMMPS code for the largest bin size. As shown in fig 7, pressures obtained from both codes are converging to the same value at the equilibrium state with less than 3 percent difference, which is very good. Although, it can be seen that there are some oscillations in pressure value obtained from LAMMPS. These oscillations are due to the different approaches used in LAMMPS for averaging and calculating methods.

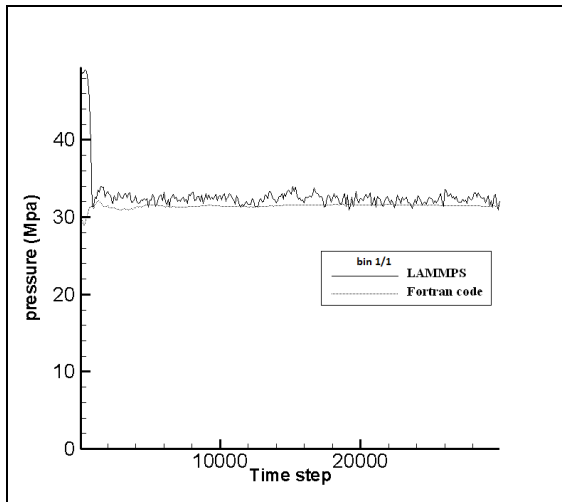


Fig. 7. Comparison of Convergence rates of pressure in bin 1/1 which are obtained from LAMMPS software and our Fortran code

5. Conclusion

Details about pressure calculation in a molecular system and its sensitivity to approximations made were studied in this paper. A method was defined for calculating the pressure correctly by comparing it on different size of bins. This method was based on the assumption that macroscopic properties should be independent from the bin sizes. It was shown that special care should be given to the implementation of cut-off region near the boundaries in order to calculate pressure correctly.

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