

## Transport properties of fluids in nanochannels: bridging nano to macro

Filippos SOFOS, Theodoros E. KARAKASIDIS\*, Antonios GIANNAKOPOULOS, Antonios LIAKOPOULOS

\* Corresponding author: Tel.: ++30 2421074163; Fax: ++30 2421074169; Email: thkarak@uth.gr  
Hydromechanics and Environmental Engineering Laboratory, University of Thessaly, 38334, Pedion Areos,  
Volos, Greece

**Abstract** A method of calculating transport properties in nanochannels is presented in this work. The Molecular Dynamics simulation of a system of liquid argon flowing in a nanochannel formed by krypton walls was the basis for our analysis concerning transport properties and specifically diffusion coefficient, shear viscosity and thermal conductivity. It is shown that for confined systems, such as nanochannels, if one of the transport properties is known, then the others can be estimated. The simulation results reveal that all properties approach bulk values at relatively small channel widths, at about 6-7nm. Below this critical point, the wall effect on fluid atoms is strong and the transport properties change dramatically. In order to extend the calculations over rough-wall nanochannels, we apply the relation extracted for flat wall channels to channels with walls consisted of successive rectangular protrusions and cavities.

**Keywords:** Nanochannels, Diffusion Coefficient, Shear Viscosity, Thermal Conductivity, Molecular Dynamics.

### 1. Introduction

The present work proposes a universal method of calculating transport properties of fluids, as presented in Giannakopoulos et al. (2011), where the most significant transport properties of fluids (i.e., diffusion coefficient, shear viscosity and thermal conductivity) seem to be connected somehow. We have tried to bridge the gap between the macroscale (bulk) behavior of fluids and their near-atomic scale behavior through an argon flow-simulation system.

The diffusion coefficient of fluids has been successfully calculated for flat channels at the nanoscale (Bitsanis et al. 1987; Murad et al. 1993; Sofos et al. 2009a). In general, diffusion coefficient is found higher in layers close to the center of the channel and decreases for the channel layers adjacent to the walls (Aggarwal et al. 2007; Tankeshwar et al. 2007). As the channel width increases, bulk-like behavior is approached at the interior of the channel. Shear viscosity is usually extracted from the Green-Kubo (GK) method for equilibrium systems (Meier et al. 2001; Pas and Zwolinski 1991; Sofos et al. 2009a; Song

et al. 2003; Yonetani and Kinugawa 2004). However, due to the induced strain rates at nanochannels with dimensions close to the atomic scale, NEMD methods for the calculation of shear viscosity are a good alternative (Akhmatskaya et al. 1997; Liem et al. 1992; Singer et al. 1980; Todd et al. 1995). Thermal conductivity is extracted for equilibrium systems in Evans (1986) and Yonetani and Kinugawa (2004), but as far as non-equilibrium systems at the nanoscale are concerned, it is difficult to be estimated.

The effect of wall roughness on fluid properties, especially the slip length, is currently an intriguing subject in micro- and nano-flows (Cao et al. 2009; Sofos et al. 2009b; Yang 2006). Reports on diffusion coefficient and fluid viscosity for rough-wall channels can be found in Jabbarzadeh et al. (2000), Kim and Darve (2006) and Sofos et al. (2010). However, no reports were made on theoretical calculation of fluid thermal conductivity.

In this work, we present simulation results of argon flow in several nanochannels with flat walls, as well as in channels with one smooth and one rough wall, where the rough wall is

formed by periodically-spaced rectangular protrusions. The flow conditions correspond to the macroscopic equivalent of planar Poiseuille flow, at constant temperature, low pressures and low densities. Having calculated diffusion coefficients and shear viscosity, both for flat and rough-wall nanochannels, we incorporate the “binding” relation from Giannakopoulos et al. (2011) in order to calculate thermal conductivity as a total average value over a rough-wall nanochannel.

## 2. Simulation details

### 2.1. Molecular system model

Non-equilibrium molecular dynamics simulations were performed to simulate flow of liquid argon in flat- and rough-wall nanochannels. Simulation of argon (a monoatomic liquid) flow has been a popular choice in nanofluidics for the ease of computations. The simulations apply to flat-wall nanochannels (of height  $h$  from 0.9 – 15nm), as well as in channels with a rough upper wall and a smooth lower wall (of height  $h$  about 6nm) (cf Fig.1). The periodic roughness of the upper wall has amplitude of about 0.6nm and the protrusion/cavity length  $l$  varies from 0.28nm to 1.7nm. Dimensions of the computational domain in  $x$ - and  $y$ -dimensions are  $L_x \times L_y = 3.1 \times 3.1$  nm.

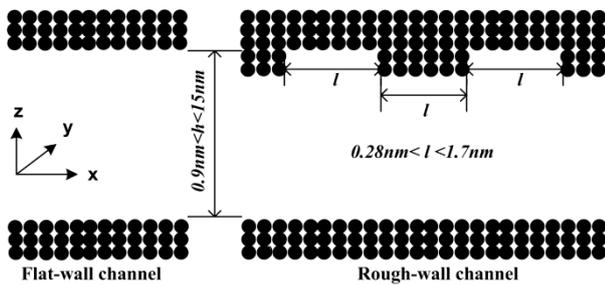


Fig. 1. Schematic of flat and rough-wall channels modeled.

Fluid/fluid, fluid/wall and wall/wall atom interactions are described by Lennard-Jones (LJ) 12-6 potential

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

where the parameters of the Lennard-Jones potential are:  $\sigma = 0.3405$  nm,  $\epsilon/k_B = 119.8$  K, the atomic mass for argon is  $m = 39.95$  a.u. and the cut-off radius is  $r_c = 2.5\sigma$ .

Periodic boundary conditions are considered in  $x$ - and  $y$ -directions. Wall atoms are bound on fcc sites and remain to their original positions due to the effect of an elastic spring force  $\mathbf{F} = -K(\mathbf{r}(t) - \mathbf{r}_{eq})$ , where  $\mathbf{r}(t)$  is the vector position of a wall atom at time  $t$ ,  $\mathbf{r}_{eq}$  is its initial lattice position vector and  $K = 57.15 (\epsilon / \sigma^2)$  is the wall spring constant. Temperature is kept constant at  $T^* = 1$  ( $\epsilon/k_B$ ,  $k_B$  is the Boltzman’s constant) with the application of appropriate Nosé-Hoover thermostats. An external driving force  $F_{ext} = 0.01344 (\epsilon/\sigma)$  is applied along the  $x$ -direction to drive the flow.

The simulation step for the system is  $\Delta t = 0.005\tau$  ( $\tau$  is in units of  $\sqrt{m\sigma^2/\epsilon}$ ). In the beginning, fluid atoms are given appropriate initial velocities in order to reach the desired temperature ( $T^* = 1$ ). The system reaches equilibrium state after a run of  $2 \times 10^6$  time steps. Then, a number of NEMD simulations are performed, each with duration of  $5 \times 10^5$  time steps.

### 2.2. Computation of transport properties

The diffusion coefficient is obtained using the Einstein’s relation (Hansen and MacDonald 1986, Haile 1992)

$$D = \frac{1}{d} \lim_{t \rightarrow \infty} \frac{MSD}{t} \quad (2)$$

where  $\mathbf{r}_j$  is the position vector of the  $j^{th}$  atom,  $d$  is the dimensionality of the system ( $d=1$  for diffusivity calculation in one direction,  $d=2$  in two directions and  $d=3$  in three directions) and  $MSD$  is the Mean Square Displacement, obtained from

$$MSD(t) = \frac{1}{N} \left\langle \sum_{j=1}^N [\mathbf{r}_j(t) - \mathbf{r}_j(0)]^2 \right\rangle \quad (3)$$

Shear viscosity is evaluated as local value at various layers across the  $z$ -direction of the channels. To achieve this, the channel is divided into  $n$  bins in the  $z$ -direction, each one of volume  $V_{bin} = (L_x \times L_y \times (h/n))$ , where  $n=40$ .

Shear viscosity  $\eta_s(z)$  across the  $z$ -direction for a pure fluid is computed by the relation

$$\eta_s(z) = \lim_{F_{ext} \rightarrow 0} - \frac{\langle P_{xz}(z) \rangle}{\dot{\gamma}(z)} \quad (4)$$

where the shear rate  $\dot{\gamma}(z)$  is

$$\dot{\gamma}(z) = \frac{\partial v_x(z)}{\partial z} \quad (5)$$

and  $P_{xz}(z)$  is the off-diagonal component of the microscopic stress tensor  $\mathbf{P}$  across  $z$ -direction, while  $\langle \dots \rangle$  denote time-averaged values.  $P_{xz}$  is given by

$$P_{xz} = \frac{1}{V_{bin}} \left( \sum_{i=1}^N m_i v_i^x v_i^z - \sum_{i=1}^N \sum_{j>1}^N r_{ij}^x \frac{\partial u(\mathbf{r}_{ij})}{\partial r_{ij}^z} \right) \quad (6)$$

where  $u(r_{ij})$  is the LJ potential of atom  $i$  interacting with atom  $j$ ,  $\mathbf{r}_{ij}$  is the distance vector between atoms  $i$  and  $j$ , and  $v_i^j$  is the  $j$ -component ( $j= x, y$  or  $z$ ) of the velocity of atom  $i$  (the mean flow velocity is excluded from  $v_i^x$ ) The above expression for the stress tensor can be separated in a kinetic and a potential energy part. We denote as the kinetic part of the stress tensor  $P_{xz}^{kin}$

$$P_{xz}^{kin} = \sum_{i=1}^N m_i v_i^x v_i^z \quad (7)$$

and the potential energy part  $P_{xz}^{pot}$  as

$$P_{xz}^{pot} = \sum_{i=1}^N \sum_{j>1}^N r_{ij}^x \frac{\partial u(\mathbf{r}_{ij})}{\partial r_{ij}^z} \quad (8)$$

By substituting Eqs. (7-8) into Eq. (6) we obtain the relation for the stress tensor

$$P_{xz} = \frac{1}{V_{bin}} (P_{xz}^{kin} - P_{xz}^{pot}) \quad (9)$$

In order to obtain better statistics and more accurate results for the stress tensor expression (Fernandez et al. 2004), we calculate all three independent off-diagonal elements of the stress tensor and average them as

$$P_{off-diag} = \frac{P_{xz} + P_{xy} + P_{yz}}{3} \quad (10)$$

and, finally, Eq. (4) converts to

$$\eta_s(z) = \lim_{F_{ext} \rightarrow 0} - \frac{\langle P_{off-diag}(z) \rangle}{\dot{\gamma}(z)} \quad (11)$$

Thermal conductivity  $\lambda$  can be calculated as a total value by the integration of the time-autocorrelation function of the microscopic heat flow  $J_q^x$  [19], i.e.,

$$\lambda = \frac{1}{V k_B T^2} \int_0^\infty dt \langle J_q^x(t) \cdot J_q^x(0) \rangle \quad (12)$$

where the microscopic heat flow  $J_q^x$  is given by

$$J_q^x = \frac{1}{2} \sum_{i=1}^N m_i (v_i)^2 v_i^x - \sum_{i=1}^N \sum_{j>1}^N \left[ r_{ij}^x : \frac{\partial u(\mathbf{r}_{ij})}{\partial r_{ij}^x} - \mathbf{I} \cdot u(\mathbf{r}_{ij}) \right] \cdot v_i^x \quad (13)$$

where  $v_i$  is the speed velocity magnitude of atom  $i$  and  $\mathbf{I}$  is the unitary matrix.

In Giannakopoulos et al. (2011), it is proposed that all transport properties above are connected by the relation

$$\lambda = a C_v (\rho D \eta_s)^{1/2} \quad (14)$$

where, for argon at 120 K, the specific heat is  $C_v = 0.523 \frac{\text{kJ}}{\text{kg K}}$ , the density considered in

the simulations is  $\rho = 1078 \frac{\text{kg}}{\text{m}^3}$  and the constant  $a \approx 5 \times 10^6$ .

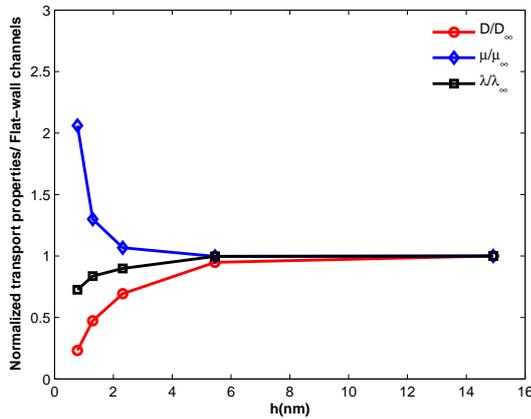
## 3. Results and discussion

### 3.1. Flat-wall nanochannels

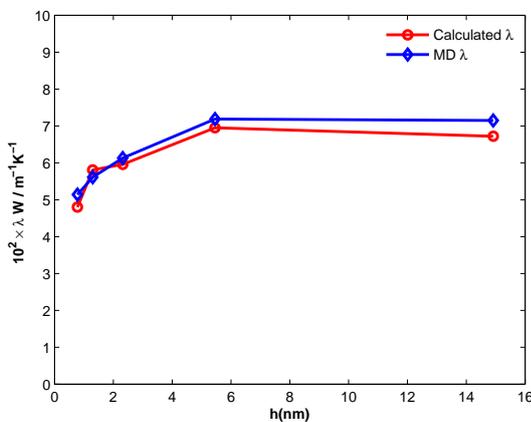
At first, we calculate as total values averaged over the whole nanochannel, diffusion coefficient, shear viscosity and thermal conductivity for all flat-wall nanochannels modelled, of width from 0.9 to 15nm. Bulk values for each one are taken from Fernandez et al. (2004). We observe that all transport properties approach their bulk values at relatively small channel widths, at about 6-7nm (cf. Fig.2). Below this critical point, the wall effect on fluid atoms is strong and the transport properties change dramatically. We

estimate that in a 0.9nm width channel, the diffusion coefficient has been drastically decreased at the 25% of its bulk value, shear viscosity is more than 2.5 times greater than bulk and thermal conductivity retains only a 75% of the bulk value.

If we apply Eq. (14) in order to check its validity on flat-wall, argon flow simulation results taken from Sofos et. al (2009a), the agreement of this approximation with our thermal conductivity NEMD calculations is excellent (cf. Fig.3). We observe that  $\lambda$  has a very small dependence on the relative channel size  $h/\sigma$  and it can be considered to depend point-wise on  $D$ . Indeed, the spatial variation of  $D$  along the channel width is the same with that of  $\lambda$  (lower close to the channel walls).



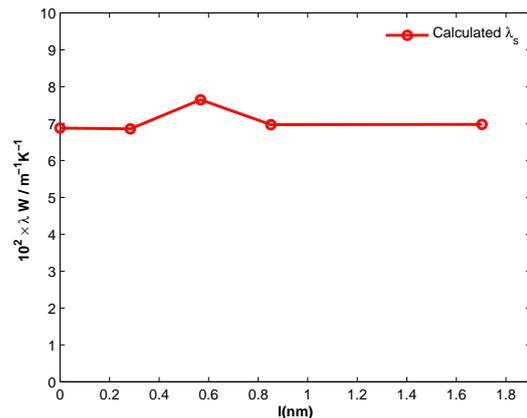
**Fig. 2.** MD calculated transport properties for flat-wall channels (diffusion coefficient,  $D$ , shear viscosity,  $\mu$ , and thermal conductivity,  $\lambda$ ), divided by their respective bulk values  $D_\infty$ ,  $\mu_\infty$  and  $\lambda_\infty$ .



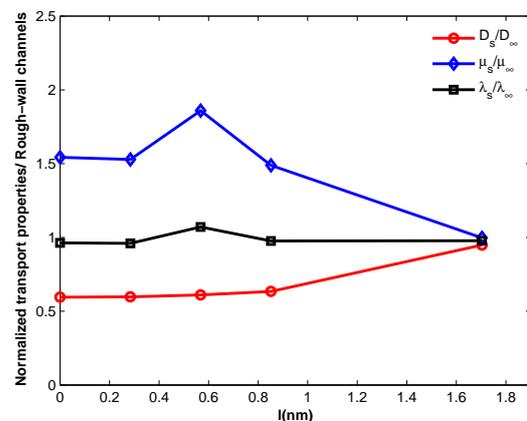
**Fig. 3.** MD calculated thermal conductivity compared to the proposed method according to Eq. (14).

### 3.2. Rough-wall nanochannels

In order to extend the calculations over rough-wall nanochannels, we apply Eq. (14) to our diffusion coefficients and shear viscosity results from channels with walls consisted of successive rectangular protrusions and cavities (Sofos et al. 2010). Figure 4 shows the results for calculated thermal conductivity versus protrusion/cavity length  $l$ . We observe that thermal conductivity is rather stable over the range of protrusion (or, cavity) length studied here. However, it presents an increase in its value for the rough-wall case (about 15%) when the protrusion length is about 0.5nm. At first sight, we could explain this instability due to statistical uncertainties, but, on the other hand, this increase is also occurring for the respective shear viscosity values (cf. Fig.5).



**Fig. 4.** Thermal conductivity according to Eq. (14) for rough-wall nanochannels.



**Fig. 5.** Transport properties according to Eq. (14) for rough-wall nanochannels (diffusion coefficient,  $D$ , shear viscosity,  $\mu$ , and thermal conductivity,  $\lambda$ ), divided by their respective bulk values  $D_\infty$ ,  $\mu_\infty$  and  $\lambda_\infty$ .

It is possible that the specific channel geometry may have induced uncertainties or there may be some kind of transitional behaviour at this case. Figure 5 presents all transport properties divided by their respective bulk values. We observe that thermal conductivity is less affected by the presence of roughness, while, when roughness length is minimum, the diffusion coefficient decreases about 50% and shear viscosity is doubled.

#### 4. Conclusions

The calculation of the diffusion coefficient, shear viscosity and thermal conductivity is of primary interest as it provides details on heat and mass transport not only at the nanoscale but also at the macroscale. In this work, we have presented calculations from non-equilibrium molecular dynamics simulations of liquid argon in flat- and rough-wall nanochannels and connected the results.

We found that there is a clear relation between the diffusion coefficient, shear viscosity and thermal conductivity. If we have knowledge of the size effect on the one transport property, the values of the other properties can be obtained from the proposed relations. These results have been verified by flat-wall nanochannel simulations and are applied in rough-wall nanochannel simulations.

The effect of channel width, as well as protrusion length on transport properties is significant. We found that the diffusion coefficient decreases from its bulk value at small channel widths, as well as near a rough surface with protrusions of small length. In contrast, shear viscosity increases in small channel widths and small roughness lengths, while thermal conductivity has smaller than bulk values as channel dimensions decrease and is not significantly affected by protrusions length. The modified values of transport properties should be taken into account in the design process of nanofluidic systems, since they affect flow characteristics.

To conclude, it is obvious that there are many theoretical and practical aspects in nanochannel liquid flows that have to be studied extensively when it comes to simulating or designing real systems at these scales.

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