Variation in Shear viscosity of a Lennard Jones Fluid in a Nanochannel

Rohan Kaushal
Department of Physics, D.A.V. College, Sector-10, Chandigarh (U.T.), India

Abstract
The shear viscosity of a Lennard-Jones fluid in a nanochannel has been studied when it is subjected to a one dimensional wall width variation. A one component fluid has been considered at specific values of reduced temperature T^* and reduced number density n^* and the behaviour of shear viscosity has been studied for the system. The atoms of the fluid are considered to be interacting through Lennard-Jones (LJ) potential. The confining walls of the nano channel are considered to be of non-interacting type. The study shows a change in the shear viscosity of the LJ fluid. It is observed that with a decrease in the width of the nanochannel in one direction, shear viscosity of the fluid increases. This increase in the shear viscosity appears to be sharper when the size of the nanochannel is reduced below 15 atomic diameters.

Introduction
The study of classical fluids has still been helping the researchers in studying various properties of liquids including the phase transitions and transport properties. A lot of work has been done in this regard. However, this has not reduced the interest of the researchers in the study of liquids. Nano scale studies of the physical systems have made the scientists think about the nano scale behaviour of the fluids and this resulted in a shift of attention to study the liquids in nano scale. The fluids are observed to exhibit different properties when these are subjected to the nano scale confined geometries than the properties of the bulk liquids. This study of various properties of fluids when it is confined to the nano scale geometries is popularly called Nanofluidics. Nanofluidics finds many applications in micro cooling devices, use of charged polymers for lubrication, for self-cleaning surfaces, drug delivery systems etc. The properties of the fluids like self-diffusion, shear viscosity and longitudinal viscosity have been studied under the study of transport properties of liquids for the bulk liquids and the liquids confined to nanochannels. [1-11]
The diffusion of fluids in nano scale confinement has been studied by considering various types of nano scale geometries like cylindrical type nanotubes, carbon nanotubes, nanopores etc.[12-13]. Fabrication of nanofluidic devices has become feasible for the practical applications [14]. Tankeshwar et al proposed a dynamical model to study the effect of confinement on the self-diffusion coefficient in Lennard-Jones (LJ) fluids when such a fluid is confined to a channel whose width is reduced to the nanoscale. [15-16]
The study of behaviour of the stress autocorrelation function (SAF) plays an important role in the study of the transport properties of liquids like viscosity. Also computer simulation techniques like equilibrium molecular dynamics (EMD) and non-equilibrium molecular

dynamics (NEMD) have been extensively used to study the transport properties of the fluids for the systems with constituent atoms in equilibrium and not in equilibrium, respectively [8]. In this work the dependence of the shear viscosity of a fluid on the behaviour of its SAF for the transverse case has been exploited to study the behaviour of the shear viscosity with the width of channel when a Lennard-Jones (LJ) fluid is confined to a nanochannel. For this study a LJ system has been considered for a specific state with specific values of reduced density and reduced temperature. Tankeshwar and Srivastava model [16] has been applied to study the shear viscosity of the mentioned fluid system..

Theoretical Framework

The Green Kubo expression relates the shear viscosity of a fluid with the time integral of the SAF (transverse) represented by the function S(t) [17] as follows

$$\eta = \frac{1}{Vk_BT}\int_0^\infty S(t)dt \ , \tag{1}$$

with S(t) defined as,

$$S(t) = < J_{xy}(t)J_{xy}(0) >, \tag{2}$$

and $J_{xy}(t)$ is a dynamical variable which can be expressed mathematically as,

$$J_{xy}(t) = \sum_{i=1}^{N}[m_i v_{iy}(t)\, v_{ix}(t) + x_i(t)F_{iy}(t)]. \tag{3}$$

In Eq. (1), V represents volume of the system whereas, k_B and T are the Boltzmann's constant and absolute temperature, respectively. The angular brackets in Eq. (2) represent the ensemble average. In Eq. (3), N is the total number of particles considered to be present in the system. $x_i(t)$, $v_{ix}(t)$, $v_{iy}(t)$ and $F_{iy}(t)$ are the x component of position, x component of velocity, y component of velocity and y component of force of the i^{th} particle, respectively, at a time t. The SAF S(t) takes care of the interactions among like and unlike particles. The SAF is estimated by studying its short time behaviour. The short time expansion of S(t) is given as follows,

$$S(t) = S_0 - S_2\frac{t^2}{2!} + S_4\frac{t^4}{4!}\ldots\ldots\ldots \ , \tag{4}$$

where S_0, S_2, and S_4 are respectively, the zeroth, second and fourth sum rules of the SAF. For this study we follow a model which was proposed for the atomic motion in liquid [18] and consider the following phenomenological form of the SAF i.e. ,

$$S(t) = S_0\,\mathrm{sech}\left(\frac{t}{\tau_1}\right)\cosh\left(\frac{t}{\tau_2}\right). \tag{5}$$

The two parameters τ_1 and τ_2 are such that $\tau_2 \leq \tau_1$. τ_1 has a structural origin and represents the exponential decay of the correlation function there by showing the fluid like behaviour. τ_2 represents a dynamical feedback like phenomenon which is dominant at high density. Comparing the short time expansion of Eq. (1) with exact short time expansion of the SAF provides,

$$\tau_1 = 2\left[\frac{S_4}{S_2} - \frac{S_2}{S_0}\right]^{-\frac{1}{2}}, \tag{6}$$

and

$$\tau_2 = 2\left[\frac{S_4}{S_2} - 5\frac{S_2}{S_0}\right]^{-\frac{1}{2}}. \quad (7)$$

Expressions for the sum rules used in Eq. (7) and Eq. (8) are known for one component and two component fluids [18]. To study the direct effect of confinement of a fluid when it is placed in a nano sized channel we consider the walls of the nanochannel to be non-structured. Initially, the motion of those constituent atoms is affected by the wall which is closer to it. This further affects the atomic motion in the direction perpendicular to the wall. Since the fluid is confined to a nanochannel this will happen in the direction in which the width of nano channel is varied (say z) if we consider the fluid to be flowing in the x direction due to which the particles are in a compressed like situation. This directly affects the dynamical feedback parameter also known as dynamical relaxation τ_2 . Because of this effect of confinement τ_2 becomes a function of z and can be expressed by the following relation,

$$\tau_2{}^{-1} = \frac{1}{l}\int_0^l \tau_2^{-1}(z)\ dz, \quad (8)$$

with l as the distance of the wall from the centre of the nanochannel in z direction, respectively. This distance is measured in the units of atomic diameters. The effect of wall is expected to get reduced as one move towards the centre of the nanochannel and become zero at the centre. The new value of local frequency now gets modified and can be given as

$$\tau_2{}^{-1} = \frac{\pi\tau_2{}^{-1}(z=0)}{2\sin^{-1}[(1-c(l,z))]}\ , \quad (9)$$

In Eq.(9), $c(l,z)$=exp(-(l-z) and give the measure of compression in z direction.

Following this model the shear viscosity of the LJ fluid can be expressed as

$$\eta = \frac{n\pi}{2k_BT} S_0\tau_1 \sec\left(\frac{\pi}{2}\frac{\tau_1}{\tau_2}\right), \quad (10)$$

n being the number of atoms per unit volume or simply the number density.

Results and Discussions

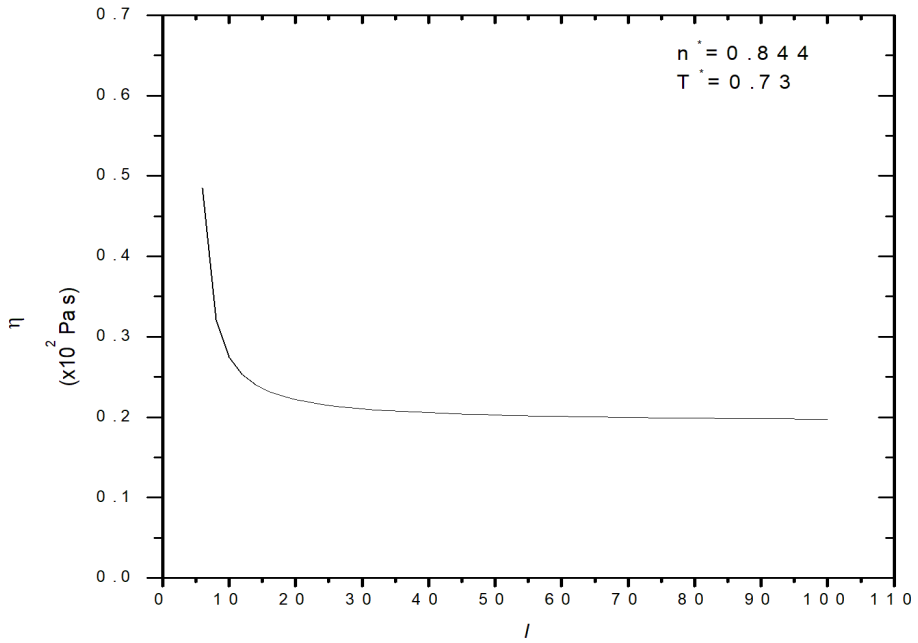
We consider an Ar system in order to study the behaviour of SAF, when it is confined to a nanochannel and its width is varied in one direction. The atoms of the fluid are considered to be interacting with each other through LJ potential which is given as,

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad (11)$$

For Ar system, ε_{Ar} = 120 x $k_{B,}$ where, k_B is Boltzmann's constant and σ_{Ar} = 3.405 Å. Numerical calculations have been carried out for the case for which n^* = 0.844 and T^* = 0.73, where n^* and T^* are reduced density and temperature, respectively, and calculated as $n^* = n\sigma^3$ and $T^* = k_BT/\varepsilon$. Values of the sum rules of the SAF for this system are obtained as given in Table 1.

Table: 1

S_0 (x10^{-43}J^2)	S_{22} (x10^{-17}J^{2}s^{-2})	S_{23} (x10^{-17}J^{2}s^{-2})	S_{42} (x10^{10}J^{2}s^{-4})	$S4_3$ (x10^{10}J^{2}s^{-4})
536.334	685.47	-282.71	279.60	-57.60



Graph 1: Graph of variation in shear viscosity of a Lennard Jones fluid with the varying channel width. The viscosity is measured in Pa s and the channel width in the units of atomic diameter.

Using the numerical values of the sum rules of SAF and Eqs. (5) to (10) the shear viscosity has been calculated with the varying channel widths. It is observed that the shear viscosity of the LJ fluid varies with the variation in channel width. This behaviour of the shear viscosity when width of the nanochannel varies is expressed in Graph 1. It can be observed from the graph that when the width is of the size of 100 atomic diameters the fluid behaves as a bulk fluid. As width of the nanochannel confining the fluid is reduced up to l = 50 no appreciable change occurs in the viscosity. Between l = 50 and l = 40 a mild increasing trend in the shear viscosity comes into picture. When the width of the channel is further reduced up to l = 20 the rate of variation in the shear viscosity increases i.e. the shear viscosity increases at a faster rate. Below l = 20 a sharp increase in the viscosity is observed for a smaller change in the width of the nanochannel. Beyond l = 15 the rate of increase of viscosity becomes rapid and for a further decrease in the channel width the curve depicting the increase in viscosity becomes almost parallel to the Y axis. This indicates the development of a tendency in the fluid for a phase transition from liquid to solid.

Conclusion

The confinement of a fluid in a nanochannel results in a change in its behaviour. The shear viscosity increases with the decreasing width of the nanochannel in one direction. The rate of increase of the shear viscosity is smaller for the broader channel of about 100 atomic diameters and the fluid behaves as a bulk. Around 15 atomic diameter widths the change in the shear viscosity starts becoming sharper and beyond that there is an abrupt increase in the

shear viscosity. This behaviour leads to the conclusion that the fluid system under consideration for this study possesses higher viscosities at narrower channels and shows a tendency of phase transition towards solidification.

References

[1] J.C.T. Eijkel and A. van den Berg, Microfluid Nanofluid (2005) 1: 249-267.

[2] Y. Zhang, H. F. Chan, and K. W. Leong, Adv. Drug Delivery Rev. 65, 104

[3] H. T. Davis, Statistical Mechanics of Phases, Interfaces and Thin Films (VCH, New York, 1995).

[4] J. N. Israelachvili, Intermolecular and Surface Forces: With Applications to Colloidal and Biological Systems (Academic, London, 1985).

[5] J. Mittal, J. Phys. Chem. B. 113 (42), 13800 (2009).

[6] P.J. Cadusch, B.D. Todd, J. Zhang, and P.J. Daivis, J. Phys. A: Math. Theor. 41, 035501 (2008).

[7] R. Kaushal, S. Srivastava, and K. Tankeshwar, Int. J. Nanosci. 8, 543 (2009).

[8] F. Sofos, T. Karakasidis, and A. Liakopoulos, Int. J. Heat Mass Transfer 52, 735 (2009).

[9] J.L. Xu and Z.Q. Zhou, Heat Mass Transfer 40, 859 (2004).

[10] Y.C. Liu, Q. Wang, T. Wu, and L. Zhang, J. Chem. Phys. 123, 234701 (2005).

[11] R. Kaushal and K. Tankeshwar, Phys. Rev. E. 68, 011201 (2003).

[12] I. Goyal, S. Sunita, and K. Tankeshwar, AIP Conf. Proc. 1393, 323 (2011).

[13] S. H. Krishnan and K. G. Ayappa, Journal of Chemical Physics 118 690 (2003).

[14] T. (Ezzat) Keshavarzi, F. Sedaghat, and G. A. Mansoori, Microfluid. Nanofluid. 8, 97 (2010).

[15] H. Anpan *Nanotechnology* 17**,** 2498 (2006).

[16] K. Tankeshwar and Sunita Srivastava, Nanotechnology 18, 485714 (2007).

[17] J. P. Boon and S. Yip, Molecular Hydrodynamics (McGraw Hill, New York), (1980).

[18] R.K. Sharma, K. Tankeshwar and K.N. Pathak, J. Phys. Condens. Matter 7, 537 (1994).