Chapter 5

Nanofluidics: Shear Viscosity of Two Component Fluids in Nano-Channels

The work presented in this chapter describes a theoretical picture of the effects of confinement of a two component fluid, to a narrow channel having width of the order of nanometer. The effect of confinement on one component fluid confined to a nanochannel has been successfully studied by Tankeshwar and Srivastava [54-55] which shows that a significant change occurs in the viscosity of a one component fluid with variation in the channel width if the channel in which the fluid is confined is of micro/nano sized width. It has been shown that the viscosity of the fluid gets enhanced when width of the channel is reduced to a few nanometers.

In the present work, the effects of confinement on the shear viscosity of a two component fluid have been studied when the fluid is confined to a narrow channel having width of the order of a few atomic diameters. The effects of variations of mass and concentration on the shear viscosity with respect to variation in the width of confining channel for an isotopic two component fluid have also been studied when
the isotopic fluid is confined to a nanochannel. It has been found that on macro scales there is no appreciable change in the shear viscosity of a two component fluid with respect to variation in the channel width. However, as the channel width is reduced to a few hundreds of the atomic diameter the effects of confinement start surfacing. As width of the channel is reduced further transport properties of the fluid start showing an unusual behaviour. This unusual behaviour becomes more and more prominent with further decrease in the channel width.

5.1 Generalities

Tankeshwar and Srivastava [55] have recently studied the effect of confinement on the diffusion coefficient of a fluid in a direction perpendicular to the confining walls. A new model has been proposed by them which is based on the consideration that the confining wall influences the motion of each individual particle of fluid. The model has the advantage that the structural complexity of the fluid enters indirectly and thus it can be applied to complex liquids. This model is very useful for studying the effect of confinement on the shear viscosity of a two component fluid confined in a nanochannel.

The Model

Following the model proposed earlier for the diffusive motion in liquid [76,80], the constituent particles of a fluid were regarded as harmonic oscillators and following considerations have been made. (i) The configuration space of a many-body system is divided into a number of cells. Each cell is characterized by a fixed configuration associated with the local minima on the potential energy hyper-surface of the system. (ii) Within the cell the liquid configuration executes harmonic motion about local minima which are described by a fixed frequency or spectrum of frequencies. (iii) The
A particle in the nanochannel
system jumps between cells with a certain jump frequency $\tau^{-1}$. These considerations have provided a useful understanding of the time evolution of velocity auto-correlation function and self-diffusion coefficients of one-component [76], two component [77] and three-component [78] fluids and are useful for the stress auto correlation function and shear viscosity of the fluids under confinement as well [56]. The above model has also been applied to the system of a molten salt confined to two charged walls [79]. In order to understand the direct effect of confinement on atomic motion, in the first instance only non-structural walls are considered. The walls first affect the amplitude of the harmonic motion of the particles in a given cell which are closer to the wall in the direction of confinement. This in turn affects the motion in the $z$-direction of neighboring particles. Thus particles find themselves in a compression-like situation if the width of channel is of nano/micro size. Due to this the second consideration regarding the concept of fixed frequency is no longer valid and one has to study the locally defined frequency. To study the effect of confinement on the frequency and amplitude of single harmonic oscillator executing motion in the $z$-direction following relation can be considered.

$$z(t) = A \sin(\omega t), \quad (5.1.1)$$

where, $A$ is the amplitude when the liquid is not under confinement. When a particle in a given cell is confined, there occurs a decrease in its amplitude. Let this decrease be $d$. If at $t=t_1$ the particle reaches the maxima (confining wall) then,

$$z(t_1) = A - d = A \sin(\omega t_1), \quad (5.1.2)$$

which gives,

$$t_1 = \frac{1}{\omega} \sin^{-1}(1 - \frac{d}{A}), \quad (5.1.3)$$

This change in amplitude results in a change in frequency of the particle. This new frequency of the particle can be given as,

$$\Omega = \frac{\pi \omega}{2 \sin^{-1}(1 - \frac{d}{A})}. \quad (5.1.4)$$
From the above expression it is obvious that when the compression \( \frac{d}{A} \) becomes zero, the frequency remains unchanged, and for definite positive compression the new frequency is higher than the old frequency. In a channel the compression will vary with distance from the wall as a function of \( z \) and let it be represented by \( c(z) \). The expression for the frequency is then modified to

\[
\Omega = \frac{\pi \omega}{2 \sin^{-1}(1 - c(z))}, \tag{5.1.5}
\]

### 5.2 Shear Viscosity

Shear viscosity of the fluid can be expressed in terms of Green Kubo expression \([1,20]\) which relates it to the transverse stress auto correlation function \( S(t) \), expressed by Eq.(2.1.27). The stress auto correlation function is an ensemble average of product of momentum current at two different times. The SAC function involves potential and kinetic parts. Evaluation of the \( S(t) \) and hence of shear viscosity of a two component fluid is a many body problem involving complications. However, many functional forms, semi-microscopic model have been provided in literature \([1,20,75-76]\). Following the model proposed earlier \([75]\) for the diffusive motion in liquid we consider that the SAC function for a two component fluid for the situation where the fluid has been confined to a narrow channel can be modeled to have the following functional form

\[
S(t) = S_0 \text{sech} \left( \frac{t}{\tau_1} \right) \cosh \left( \frac{t}{\tau_2} \right), \tag{5.2.1}
\]

where, \( \tau_1 \) and \( \tau_2 \) are two parameters such that \( \tau_2 \leq \tau_1 \). The first parameter \( \tau_1 \) represents the decays of the correlation function in an exponential (fluid like) manner having structural origin whereas \( \tau_2 \) takes care of the any dynamical feedback like phenomena dominant at high density. Comparison of short time expansion of Eq.(2.1.27) with the exact short time expansion of \( S(t) \) provides,

\[
\tau_1 = 2 \left[ \frac{S_1}{S_2 - \frac{S_2}{S_0}} \right]^{-\frac{1}{2}}, \tag{5.2.2}
\]
and

$$\tau_2 = 2 \left[ \frac{S_4}{S_2} - \frac{S_3}{S_0} \right]^{-\frac{1}{2}}. \quad (5.2.3)$$

$S_0$, $S_2$ and $S_4$ in Eq. (5.2.2) and Eq. (5.2.3) are the zeroth, second and fourth frequency sum rules of the stress auto correlation function. The expressions for these sum rules are already known [63,70] for one and two component fluids. It has been found that the condition $\tau_2 < \tau_1$ is satisfied for most of the densities and temperatures of inert fluids. For $\tau_1 = \tau_2$ the correlation function remains constant resulting in infinite viscosity of the system which leads to ideal solidification. The model mentioned here has been applied to a system of inert fluid and provided reasonably good results judged by comparison with simulation/experimental results [76].

The atomic motion inside the fluid, which gets affected under confinement directly affects the dynamical relaxation $\tau_2$. The dynamical relaxation which appears as a result of collective phenomena is affected because of local confinement and becomes a function of $z$. In analogy with Eq. (5.1.5) the new value of local relaxation time is provided by the following expression.

$$\tau_2^{-1}(z) = \frac{\pi \tau_2^{-1}(z = 0)}{2 \sin^{-1}[1 - c(z)]}. \quad (5.2.4)$$

In Eq. (5.2.4), $c(z)$ represents compression in the confining channel and is a function of the distance $z$ from the wall of the channel. Following the exponential law for fall of effect of wall on atomic motion then $c(z)$, which gives a measure of compression, is expected to be of the form

$$c(z) = \exp[-(l - z)]. \quad (5.2.5)$$

From Eq. (5.2.4) it can be clearly observed that when compression $c(z)$ becomes zero, $\tau_2^{-1}(z)$ or the relaxation time remains unchanged. Also it can be seen that for a definite positive compression the new relaxation time is more than the old relaxation time. $\tau_2^{-1}(z)$ actually represents the new value of local frequency frequency of oscillations of the constituent particles of fluid. Therefore, $\tau_2^{-1}(z)$ also gives an idea about...
the modification of frequency of oscillations of the fluid with respect to variation in the channel width when the fluid is confined to a nanochannel. The average value of relaxation time which can be used in the expression for $S(t)$, can be given as,

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

(5.2.6)

In Eq. (5.2.5) and Eq. (5.2.6), $2l$ represents width of the channel in $z$ direction measured in the units of atomic diameter. The effect of walls (at $z = -l$ and $l$) is expected to decrease as one moves away from them and shall reduce to zero at the center of the channel ($z = 0$). From Eq. (2.1.27) and Eq. (5.2.1), expression for the coefficient of shear viscosity for a two component fluid confined in a nanochannel can be obtained as,

$$
\eta = \frac{\pi}{2} \frac{n_S}{k_B T} \tau_1 \sec \left( \frac{\pi \tau_1}{2 \tau_2} \right).
$$

(5.2.7)

In Eq. (5.2.7) $n_i = \frac{N_i}{V}$ is the number density of the two constituents of the two component fluid.

### 5.3 Results and Discussion

As mentioned in the earlier section, the confined geometry causes a modification in the frequency of oscillations of constituent particles of the fluid. This further leads to a change in shear viscosity of the confined fluid. Therefore, in order to study the effect of confinement on the shear viscosity of a two component fluid which is confined to a narrow channel having width of the order of a few nanometers, firstly the effect of confinement on the frequency of oscillations of constituent particles of the two component fluids has been studied. Eq. (5.2.6) represents the average value of modified frequency $\Omega$, where $\Omega = \tau_2^{-1}$. $\Omega$ has been studied when width of the channel is decreased to a few atomic diameters from the larger values. It has been found that the effect of wall decreases as one moves away from the walls of the channel.
To study the effect of confined geometry on viscosity within the above model, a system of spherical particles has been considered in which the particles are interacting via Lennard-Jones (LJ) potential. In order to calculate the shear viscosity one requires the values of $\tau_1$ and $\tau_2(z = 0)$ when fluid is not subjected to any confinement. The values for these can be obtained from zeroth, second and fourth sum rules of stress auto correlation function for a two component fluid, results of which are available [70]. The effect of confined geometry on the shear viscosity of a two component liquid mixture has been studied for an equimolar Ar-Kr mixture of density $1.84\text{gm/cm}^3$ at $121.7\text{K}$.

Fig.5.1 represents a graph between the normalised oscillation frequency and width of the nanochannel. This figure shows the variation in the frequency of oscillations of constituent particles of the fluid with respect to the variation in the width of
Figure 5.2: Behaviour of the time relaxation of TSAC function at different widths (shown by long arrows) of the channel to which the fluid is confined (in one direction only).

confining channel. In the figure $l$ represents width of the nanochannel measured in the units of atomic diameter. It can be observed that for the widths up to about 200 atomic diameters, $\Omega$ remains practically unaffected. As width of the nanochannel is decreased further, the confinement starts affecting the frequency, appreciably. $\Omega$ starts increasing with further decrease in the width. As the width is decreased below 100 atomic diameters, the frequency $\Omega$ starts experiencing sharper increase. When the width of channel is reduced to about 25 atomic diameters, $\Omega$ increases very rapidly. In the figure $\Omega_0$ is the unaffected frequency for channel widths equal to or greater than 200 atomic diameters. This behaviour of frequency when the fluid is under confinement, has a direct influence on the time relaxation of TSAC function which
further affects the shear viscosity of the system.

Fig. 5.2 shows the manner in which TSAC function decays with time. The quantities written with arrows on each curve represent different widths of the narrow channel in which the liquid has been confined. These widths are taken in the units of atomic diameter. It is quite clear from the figure that the decay process of TSAC function with respect to time gets slowed down with the decreasing widths of the confining channel. For the widths around 30 atomic diameters the decay becomes appreciably slow. As width of the channel is reduced below this value the curve starts becoming flat and directs one to conclude that for further reduction in the channel width it will become more flat. This means that the short time interactions among the particles tend to become long time interactions. This transformation of short time behaviour into the long time behaviour of TSAC function leads to a phase transition like situation in the confined liquid. Due to this one can expect an enhancement in shear viscosity of the fluid when width of the channel is reduced to a few nanometers.

It is found that the shear viscosity of Ar-Kr mixture increases with the decreasing width of the nanochannel. It is also observed that for widths greater than or equal to 200 atomic diameters there is no appreciable effect on the shear viscosity of the considered fluid. However, as the width is reduced below 200 atomic diameters the effect of confinement starts surfacing and shear viscosity of the two component fluid starts increasing. This study successfully explains the behaviour of a liquid confined in the carbon nanotubes as reported by Koga et al [47, 74].

Fig. 5.3 shows the variation in the shear viscosity of a two component and an equimolar Ar-Kr mixture. It can be observed from the figure that when width of the confining channel of Ar-Kr fluid is equal to or greater than 200 times the atomic diameter, the shear viscosity of the fluid is almost same as that of the bulk sample which means that for these widths the effect of confinement on the Ar-Kr fluid is negligible. As width of the walls of confining channel is reduced further, shear viscosity
of the fluid starts increasing. This increase in the shear viscosity becomes sharper and sharper with further decrease in the width. When width of the channel gets reduced to 50 atomic diameters enhancement in the viscosity becomes quite prominent. Below this width the liquid becomes more and more viscous. As the width of the confining channel is reduced to about 25 times the atomic diameter rise in the shear viscosity of fluid becomes very sharp. This shows that the fluid tends to freeze as width of the confining channel is reduced. In the figure $\eta$ represents the shear viscosity of Ar-Kr fluid and is in the units of $10^{-5}$ Pa s and $l$ is the width of confining channel measured in the units of atomic diameter.

Figure 5.3: Behaviour of shear viscosity of an equimolar Ar-Kr mixture with respect to variation in width of the channel to which the fluid is confined (in one direction only).
5.3.1 Mass and Concentration Dependence

To understand the mass and concentration dependence of a two component fluid, an isotopic liquid mixture, confined to a channel, has been considered which has two types of species differing only in respect of their masses. It has been found that for bulk systems, the zeroth sum rule of the transverse stress auto correlation (TSAC) function is independent of the effects of changes of mass and concentration of constituents of the isotopic liquid mixture. However, second and fourth sum rules of the TSAC function for such a system depend upon mass as well as the concentration. The mass and concentration dependence of, the second frequency sum rule is given as

\[ S_2(m_1, m_2) = \left[ 1 + (1 - x)^{m_1/m_2} \right] S_2(m_1). \] (5.3.1)

where \( x = \frac{N_1}{N} \) is the concentration of particles with mass \( m_1 \). The mass and concentration dependence of the fourth frequency sum rule is given as

\[ S_4(m_1, m_2) = \left[ x(1 + x) + (1 - x)(2 - x)^{m_1^2/m_2^2} + 2x(1 - x)^{m_1^2/m_2^2} \right] S_4(m_1). \] (5.3.2)

The dependence of viscosity on mass and concentration is studied by examining the variation of shear viscosity of the isotopic fluid with respect to change in width of the nanochannel for different mass ratios and at different values of \( x \). For this study, a one component Lennard-Jones (LJ) fluid has been considered at reduced number density \( n^* = 0.844 \) and reduced temperature \( T^* = 0.73 \). \( n^* = n\sigma^3 \) and \( T^* = \frac{k_B T}{\epsilon} \). Here, \( n \) is the number density, \( k_B \) is Boltzmann’s constant, \( T \) is absolute temperature whereas, \( \sigma \) and \( \epsilon \) are respectively, the atomic diameter and depth of the Lennard-Jones potential. The zeroth, second and fourth frequency sum rules for a pure LJ fluid have been computed numerically by using the corresponding expressions [63].

The values (in reduced units) of \( S_0, S_2(m_1) \) and \( S_4(m_1) \) are 19.54, 6.81 and 17.42, respectively. It has been considered that the two types of species in the isotopic LJ
fluid interact via same potential. It has been observed that the values of $\tau_1$ and $\tau_2$ depend upon $S_0$, $S_2$ and $S_4$ out of which $S_2$ and $S_4$ further depend upon mass and concentration of constituent particles of the fluid. Hence the values of $\tau_1$ and $\tau_2$ also depend upon mass and concentration of constituent particles of the isotopic fluid. Due to this the shear viscosity which also depends upon the frequency sum rules gets affected. The variation in the shear viscosity for the fluid under confinement has been studied separately for different mass ratios of two type species in the fluid as well as for different values of concentrations of one type of species in the fluid. Figures 5.3, 5.4 and 5.5 represent the variation in shear viscosity for different mass ratios, when the concentration of one type of components of the fluid has been kept constant. Figures 5.6, 5.7 and 5.8 represent the variation in shear viscosity with respect to the channel width for different concentrations when the mass ratio has been kept constant. In these figures, $\eta$ is in the units of $10^{-3}$Pa s and the channel width $l$ is in the units of atomic diameter.

Fig. 5.4 represents the variation in shear viscosity $\eta$ of the isotopic LJ fluid with respect to the varying channel width $l$. It can be seen from the figure that for larger channel widths, the effect of confinement is negligible. For smaller channel widths, an enhancement in the shear viscosity can be observed which increases with the decrease in channel width. This effect continues further with the decreasing channel width. Enhancement of viscosity with the decreasing channel width is calculated for various mass ratios given in the figure keeping the concentration $x$ constant. It is found that the increase in the shear viscosity becomes sharper and sharper with decreasing channel width. This phenomenon explains that as the channel width is reduced the fluid has a tendency to freeze thereby leading to a phase transition in the fluid. It is clear from various curves plotted in the figure that the tendency of fluid to undergo such phase transition increases as the mass ratio of the constituent species is increased.

Figure 5.5 shows the variation in the shear viscosity of the isotopic fluid with
Figure 5.4: Behaviour of shear viscosity of an isotopic LJ fluid with respect to variation in width of the confining channel (in one direction only) for $x=0.25$.

Figure 5.5: Behaviour of shear viscosity of an isotopic LJ fluid with respect to variation in width of the confining channel (in one direction only) for $x=0.50$. 
Figure 5.6: Behaviour of shear viscosity of an isotopic LJ fluid with respect to variation in width of the confining channel (in one direction only) for $x=0.75$.

Figure 5.7: Behaviour of shear viscosity of an isotopic LJ fluid with respect to variation in width of the confining channel (in one direction only) for $m_2/m_1 = 2$. 
Figure 5.8: Behaviour of shear viscosity of an isotopic LJ fluid with respect to variation in width of the confining channel (in one direction only) for $m_2/m_1 = 5$.

Figure 5.9: Behaviour of shear viscosity of an isotopic LJ fluid with respect to variation in width of the confining channel (in one direction only) for $m_2/m_1 = 10$.
respect to the variation in the channel width when the concentration of particles belonging to mass \( m_1 \) is equal to the concentration of particles belonging to mass \( m_2 \) in the fluid i.e. at \( x=0.50 \). It can be observed in the figure that just like the case for \( x=0.25 \), the isotopic fluid has a tendency to freeze with decreasing channel width. This can be seen that the gap between the curves for different mass ratios is less as compared to Fig.5.3. This means that the increase in tendency of fluid to freeze with the decreasing channel width for increasing mass ratios becomes slower.

Figure 5.6 represents the variation in shear viscosity of the isotopic LJ fluid with respect to the variation in the channel width when the concentration of particles belonging to mass \( m_1 \) exceeds the concentration of particles belonging to mass \( m_2 \) in the fluid i.e. when \( x=0.75 \). It can be observed from the figure that the gap between the curves in this case is quite small as compared to figures 5.3 and 5.4 and they almost overlap when the channel width is about 25 times the atomic diameter. This means that when concentration of the lighter particles is more in the fluid the increase in tendency to freeze at more narrow channel becomes less prominent with the increasing mass ratio of constituent particles of the liquid mixture.

Figure 5.7 represents the variation in shear viscosity of the isotopic LJ fluid with respect to the variation in channel width when the concentration of particles belonging to mass \( m_1 \) in the isotopic fluid is increased. The curves have been plotted for \( c=0.25 \), \( c=0.50 \) and \( c=0.75 \), at \( m_2/m_1 = 2.0 \). It has been found that gap between the curves is very less and they almost overlap. This shows that increase in the tendency of confined liquid to freeze is not affected by the increase in concentration for mass ratio of the order of 2.

Figures 5.8 and 5.9 represent the behaviour of shear viscosity of the isotopic fluid with respect to variation in the channel width at different concentrations for a fixed mass ratio i.e. for \( m_2/m_1 = 5.0 \) and \( m_2/m_1 = 10.0 \), respectively. It can be observed from these two figures that gaps among various curves increases. This means that