The effect of system boundaries on the mean free path for confined gases

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The mean free path of rarefied gases is accurately determined using Molecular Dynamics simulations. The simulations are carried out on isothermal argon gas (Lennard-Jones fluid) over a range of rarefaction levels under various confinements (unbounded gas, parallel reflective wall and explicit solid platinum wall bounded gas) in a nanoscale domain. The system is also analyzed independently in constitutive sub-systems to calculate the corresponding local mean free paths. Our studies which predominate in the transition regime substantiate the boundary limiting effect on mean free paths owing to the sharp diminution in molecular free paths near the planar boundaries. These studies provide insight to the transport phenomena of rarefied gases through nanochannels which have established their potential in microscale and nanoscale heat transfer applications. © *2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4824634]

I. INTRODUCTION

Recent advancements in micro/nanodevice technology connote the significance of nanochannels involving motion of fluids. These include mechanical systems like the micropumps, micro heat exchangers, microturbines, etc. In micro/nanoscale gas flows, the levels of rarefaction rely primarily on the non- dimensional Knudsen number (Kn), defined as the ratio of gas mean free path (λ) to the characteristic dimension (L). For a nano-sized channel, accurate determination of mean free path (MFP) over a range of rarefaction levels is one of the key parameters for the calculation of various molecular transport phenomena.

Accurate modeling of gas flows in nano sized structure is crucial for prediction of properties of these system. At the the molecular level computations MFP is an important parameter that governs the physical properties.[1] Generally, the flow properties are calculated by approximating the MFP using the theoretical models.[2,3] The theoretical models that dictate MFP calculate the bulk value and do not give any information regarding the variation with linear dimension, if any.[4,5] However there have been attempts to portray the variation of confined fluid with reflective wall boundary.[6,7] Furthermore, using the idea of local MFP there have also been attempts to predict the slip phenomenon.[8,9]

Dongari *et al.* have used the product of velocity after collision and time between adjacent collisions to calculate the distance between collisions for reflective wall confinements. Nevertheless, this approach fails when continuous potential fields are present as MFP is a function of position of molecules. When the gas is bounded with solid wall, the variation of number density of fluid atoms near the wall is significant.[10,11] In this study the attempt is to calculate the mean free path by tracking the trajectory of a molecule and detecting collisions.

In the present study, Molecular Dynamics (MD) method has been employed to calculate MFP of rarefied gas under different conditions. A single monatomic gas is at kept at a constant temperature and the MFP is obtained for different boundary conditions and rarefaction levels. The domain size and
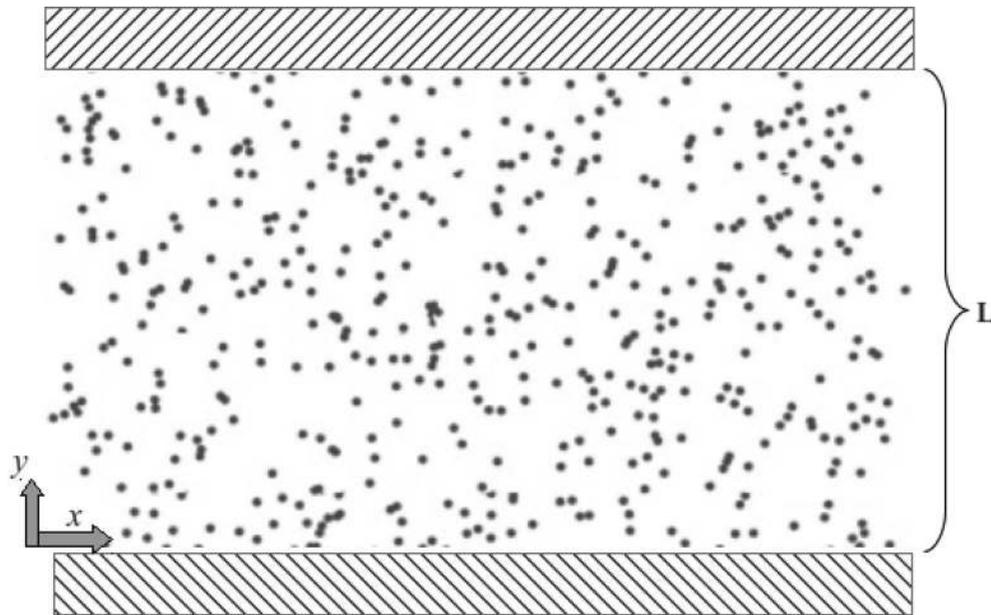
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FIG. 1.   Skematic representation of the argon atoms and solid surface. The characteristic dimension is also shown.

number density of atoms are selected so as to keep the rarefaction levels in the transition regime. In this study, the MFP is calculated by tracking the trajectory of each molecule and identifying collisions in the domain, which has periodic boundary conditions. The MFP thus obtained is compared with the MFP obtained by different mathematical models. Finally, The variation of MFP along the characteristic dimension for reflective and explicit boundary conditions is also compared at different rarefaction levels.

II. METHODOLOGY

A. Simulation model

A three dimensional system containing a monoatomic gas (argon) is the primary simulation domain. The interactions are modeled with Lennard-Jones (LJ) potential with a cut-off distance equal to three times the diameter of molecule.[12] Hard sphere diameter σ, is chosen to be 0.340 nm, where σ is the characteristic length parameter in LJ potential. The Ar-Ar interaction strength is taken to be 0.996 KJ/mol.[13] The fluid molecules are spatially distributed in a domain of size 1000 nm^3 with an initial Gaussian velocity distribution corresponding to a temperature of 300 K. For the unbounded gas, periodic boundary conditions (PBC) are employed in all three directions. The walls are modeled at either extremes of the domain in y direction (Fig. 1).

For the solid wall, Platinum atoms of thickness 1 nm are placed on either sides ensuring a parallel infinite wall boundary. The interaction strength for Pt - Pt interaction is taken to be 31.36 KJ/mol and for Pt - Ar interaction is taken to be 0.658 KJ/mol at a characteristic length of 0.294 nm.[13] The temperature of walls is maintained at 300 K using a Berendsen thermostat by controlling transitional degrees of freedom of wall atoms. The simulation domain is filled with argon gas with a number density ranging from 0.2 to 2.8 atoms/nm ^{3}. For the confined gas, this number density range corresponds to a Knudsen number range of 0.07 to 1.0, when the kinetic theory model is used to calculate the MFP. The total simulation run for data collection is for 50 ns. Velocity of the centre of mass of the system is periodically set to zero so as to nullify any net unbalanced force on the system. Parallel algorithm for classical MD with short range forces was used for simulations.[14]

B. Detecting collisions

Identification of intermolecular collisions is inevitable in calculating MFP. The time step size of 2 fs assures that all the collisions are captured. In the beginning, the system is allowed to relax to the equilibrium state. The position, velocity and timestep of the atoms are recorded at every timestep. A cubic collision domain of side length of about 3σ is chosen around every atom and all the atoms (neighbors) in the vicinity of the atom under consideration, within the collision domain are tested out for the occurrence of collisions. The intermolecular distance of σ or lesser registers a collision. For highly rarefied gases, since collisions are predominantly binary in nature, the odds of multiple simultaneous collisions between atoms are neglected.

C. Calculating molecular free path

The MFP of each molecule is calculated by averaging the distance they travel between collisions. In the case of simulation domains with PBCs, atoms escaping from the domains reappear at the opposite boundary. If a collision is detected immediately after reappearance, that collision is neglected for the calculation of MFP to avoid the error due to the imposed PBC. Thus, sufficient data is collected from the bulk fluid to get a stable calculated value of MFP.

III. RESULTS AND DISCUSSION

A. Unbounded gases

The ideal gas behavior is simulated by limiting the cut off distance to less than σ (3 Å) and thereby negating the influence of potential field during interaction. Accordingly well established kinetic theory results can be compared with the simulation results and check the credibility of calculations. For this, argon gas at 300 K is simulated with periodic boundary conditions.

1. Velocity distribution

The velocity distribution obtained from the MD simulation of 2785 atoms at a temperature of 300 K is shown in Fig. 2. When density and temperature are assigned to an ideal gas, then the velocity distribution will tend to the Maxwell's velocity distribution.[15] The velocity distribution obtained from simulation is conforming with the Maxwell's velocity distribution and it confirms the accuracy of the simulation model. As expected, the ideal behavior of argon gas is emulated in accordance with the kinetic theory and can be furthered to bounded gas simulations also.

2. Mean free path of ideal gas

To further validate the MD model, MFP of the gas is calculated and compared to the theoretical values. From kinetic theory, the MFP of gases can be approximated to

$$\lambda_K = 1/(\sqrt{2}\pi d^2 n), \tag{1}$$

where d is the hard sphere diameter and n is the number density. The variation of MFP with the number density of atoms for the ideal gas (λ_{Id}) is shown in Fig. 3. The graph affirms that MFP is inversely proportional to the number density of the gas atoms. This shows that the simulation model could simulate ideal gas behavior and calculated MFP accurately matches with the MFP predicted with the kinetic theory approach (λ_K). The MFP calculations are compared with another method of calculation, which uses velocity after collision and the time period between collisions (λ_{VT}).[7] The values obtained from both the methods yield the same result and it shows that the trajectory tracing method can be effectively used even with PBC.

Furthermore, it can be observed that when the real gas behavior is introduced to the atoms, MFP computed from MD simulations (λ_{Rl}) do not differ much from the ideal gas behavior for the selected rarefaction levels. The comparison of real gas behavior with ideal gas for bulk fluid is shown in Fig. 4.
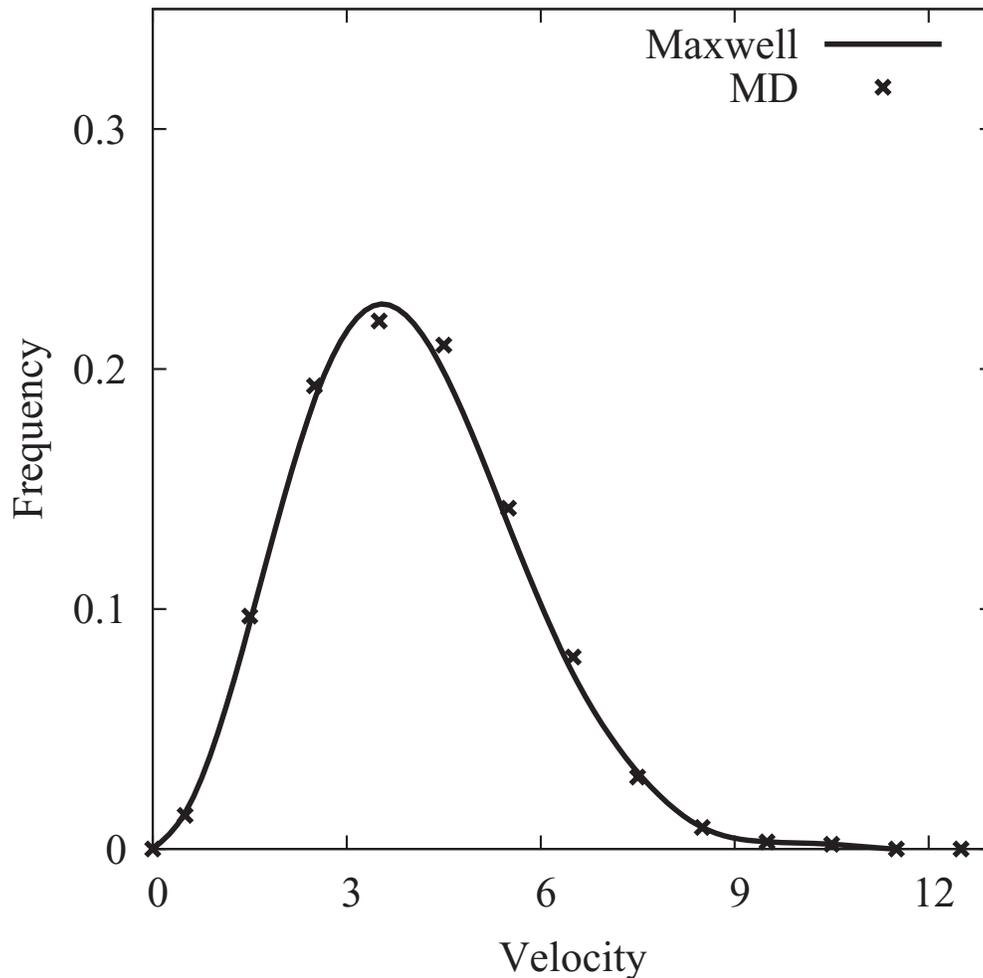
FIG. 2. Comparison of Maxwell's velocity distribution and velocity distribution obtained from MD simulations at T=300 K, 2785 atoms

B. Ideal gas with reflective wall boundaries

The MFP of argon gas with reflective wall bounding surfaces is calculated to study the effect of wall boundary with MFP and its variation with rarefaction levels. It is observed that the average MFP shows a deviation from the theoretically calculated MFP and the deviation augments with increase in rarefaction (Fig. 4). The reflective wall changes the direction of normal component of velocity when the molecule crosses the boundary. This has two effects, the molecule crossing the boundary registers a collision and a slight increase in number density than the bulk portion as the molecules are redirected to the bulk fluid. Consequently, the presence of wall will increase the chances of fluid molecule undergoing a collision near the wall. This effect becomes more significant when the rarefaction levels of the fluid increases.

C. Viscosity MFP

Cercingani suggests that for particles with extended potentials, the mean free path can be expressed in terms of the viscosity by the following operational definition.[5,15] It is given as
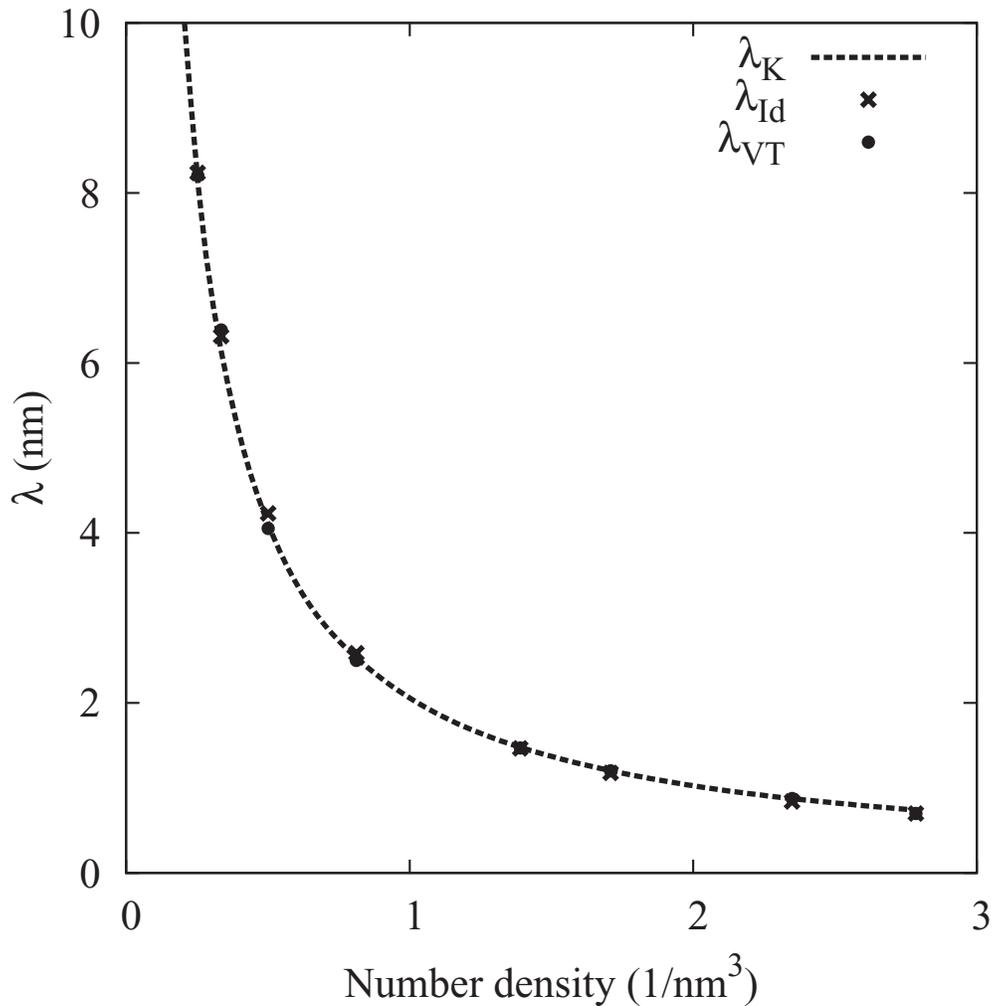
$$\lambda_v = \frac{v}{\rho}\sqrt{\frac{\pi m}{2k_B T}}, \tag{2}$$

FIG. 3.   Variation of MFP with argon atom number density for unconfined ideal gas at 300 K. The curve represents the kinetic theory model (λ_K) and the dots represent the results obtained from MD simulation (λ_{VT} and λ_{Id}).

where k_B is the Boltzmann's constant and T is the temperature. The subscript v suggests that MFP is in terms of viscosity. Figure 4 shows the comparison of MFP for ideal gas (λ_{Id}), MFP for real gas (λ_{Rl}), MFP for reflective wall boundary (λ_R) and viscosity MFP (λ_v). The viscosity of argon gas was selected from experimentally obtained data at a constant temperature.[16] This suggests that the viscous effect imposed by the wall is noticeable as a net reduction in the effective mean free path of the gas at the bulk.

D. Variation of MFP along characteristic dimension

Figure 5 compares the variation of MFP along the characteristic length for a range of rarefaction levels for reflective and explicit wall models. The MFP in a bin is normalized with the average value of MFP obtained from MD. For better understanding of rarefaction level, the corresponding Knudsen number is also shown and Kn is calculated as, $Kn = 1/(\sqrt{2}\pi d^2 nL)$. Thus, for a moderately rarefied gas confined between smooth, flat and hard surfaces, viscosity MFP model can be effectively used to predict the MFP.
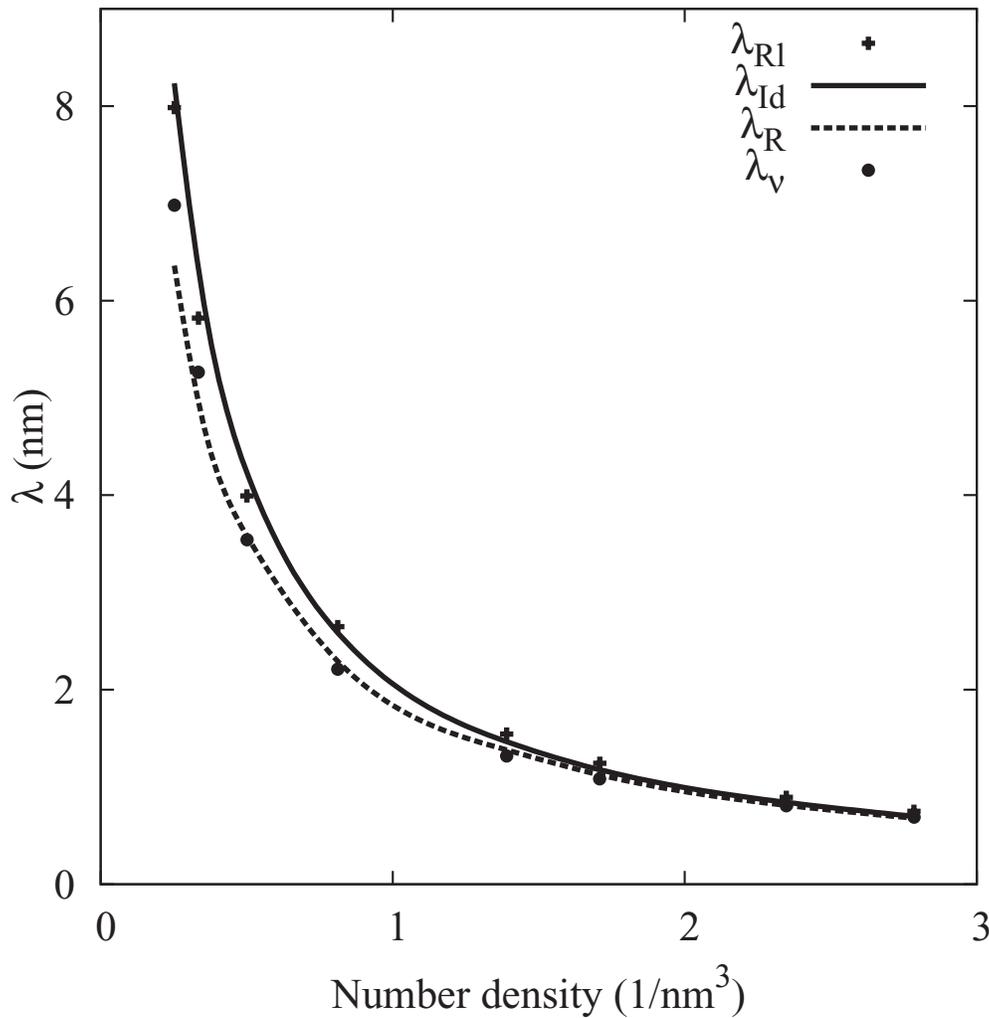
FIG. 4. The comparison of MFP for ideal gas (λ_{Id}), MFP for real gas (λ_{Rl}), MFP for reflective wall boundary (λ_R) and viscosity MFP (λ_ν)

1. Reflective wall

It can be observed that the variation of normalized MFP shows similar variation with reflective wall boundary. For reflective wall, the MFP shows a slightly lower value than the bulk average near boundary. The fluid molecules near the wall are more probable to register a collision. However, it can be noticed that the variation of normalized MFP along characteristic dimension do not vary with the rarefaction levels.

### 2. Mean free path of real argon gas in solid platinum wall confinement

To study the effect of real wall environment the the fluid domain is provided with explicit wall boundary in the *y*-direction. The characteristic dimension is kept same as in the reflective wall confinement. In this case, simulations are carried out by considering solid-solid, solid-fluid and fluid-fluid interactions. The solid-solid interactions are limited to 2.5σ limit and all other interactions with 3σ limit. For explicit wall model, the collision with the wall is identified by defining a plane near the wall which is located at a molecular diameter distance away from the wall. When an atom crosses the plane towards the wall a collision is registered. When a gas atom interacting with the solid surface it is more probable to have multiple simultaneous collisions with the wall atoms. These simultaneous
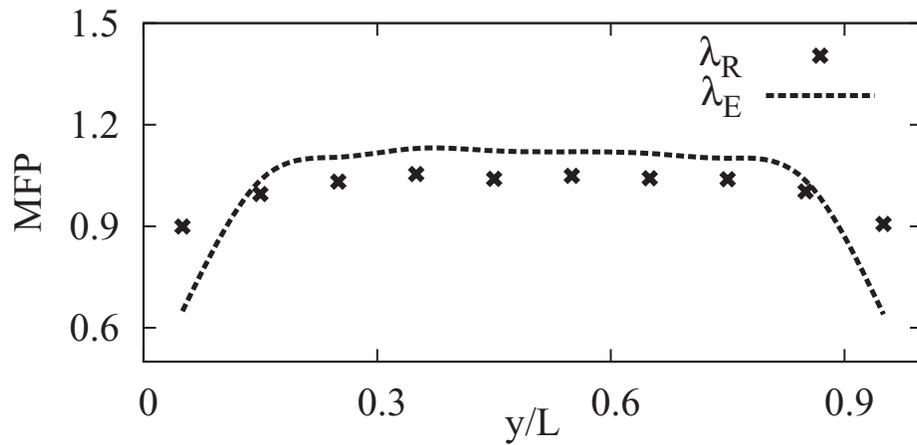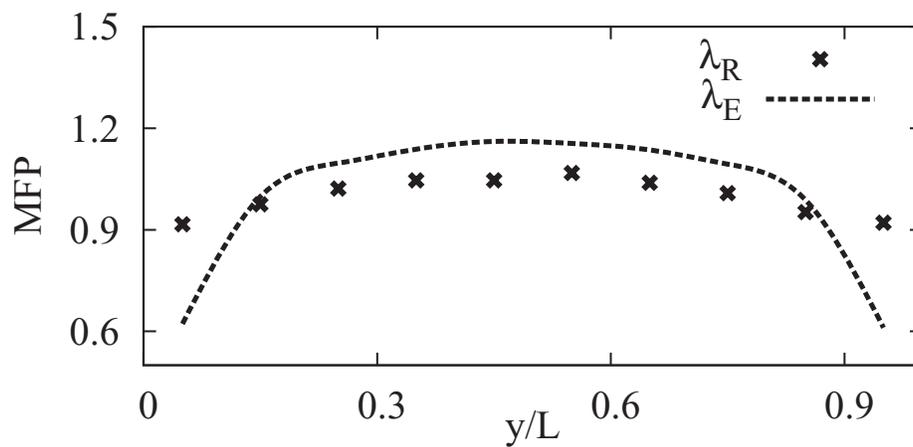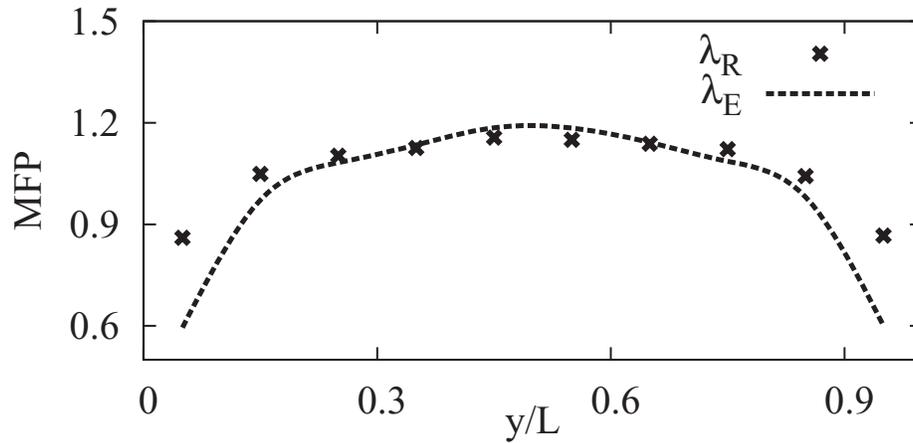
FIG. 5. Comparison of mean free paths obtained for confined gas under reflective wall (λ_R) and solid platinum wall (λ_E). (a) Kn = 0.15; (b) Kn = 0.4; (c) Kn = 0.8.

collisions, if any, are neglected; unless otherwise unrealistic values of MFP are obtained near the wall boundary.

For explicit wall model also shows a reduction in MFP near the wall (λ_E). In this study, as the average MFP in the system domain is used to normalize the MFPs, there is a reduction in the MFP near the wall and subsequently the MFP in the middle portion is higher than the average value. For moderately dilute gases, corresponding to the transition regime, the reduction in MFP near the walls is significantly higher than that for the reflective wall boundary. This behavior can be attributed to the increase in the relative number of atoms near the surface as compared to that at the bulk. When number density decreases, fluid-fluid interaction decreases and the effect of surface potential is significant. This behavior becomes less significant as the gas atom number density increases while keeping all other parameters invariant.

It is interesting to note that the reduction in MFP near the wall, compared to the region away from the wall, is significant at lower number densities. As the rarefaction levels increases the Knudsen layer also increases and the variation of MFP extends deeper into the middle portion. Tang *et al.*[9] have also observed a similar variation of local MFPs between two plates. Apparently, it can be presumed that the variation in MFP is significant for the accurate determination of thermo-physical properties that are directly related to MFP.

IV. CONCLUSION

Numerical Molecular Dynamics simulations are accomplished to accurately calculate the mean free path of argon gas in slip and transition regimes. The calculation of speed distribution and mean free path from the simulation of ideal gas behavior validates the accuracy of the MD model. The MFP is calculated by averaging the inter-collision distances of each molecule incorporating the effect of periodic boundary condition. The MFP calculated for real gases do not vary much from that of ideal gases at moderate rarefaction levels. Introduction of reflective wall boundaries results in the premature termination of atomic trajectories and hence MFP decreases near the boundary. The viscosity dependent MFP is in fair agreement with the results obtained from MD for reflective wall confinements. For explicit wall model, the variation of MFP is steeper near the boundary and it changes with number density.

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