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Molecular Dynamics Studies on Nanoscale Gas Transport

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Synonyms

Nanoscale gas transport; Shear-driven flow; Surface force effects; Tangential momentum accommodation coefficient

Definition

Gas transport in nano-confinements can significantly deviate from the kinetic theory predictions due to surface force effects. Kinetic theory-based approaches based on the assumption of dynamic similarity between nanoscale confined and rarefied flows in low-pressure environments by simply matching the Knudsen and Mach numbers are incomplete. Molecular dynamics simulations of nanoscale gas flows in the early transition and free-molecular flow regimes reveal that *the wall force field penetration depth* should be considered as an important length scale in nano-confined gas flows, in addition to the channel dimensions and gas mean free path.

Overview

Gas flows in micron and nanoscale domains are frequently encountered in the components of microelectromechanical systems and microfluidic devices. Gas flow in such small scales cannot be described using the continuum hypothesis, and the Knudsen number, Kn (ratio of the gas mean free path, l, to the characteristic flow dimension, H), emerges as a measure of the degree of rarefaction. Depending on the local Knudsen number, the flow is considered to be in the continuum ($Kn \leq 0.001$), slip ($0.001 \leq Kn \leq 0.1$), transition ($0.1 \leq Kn \leq 10$), and free-molecular ($Kn > 10$) flow regimes [1].

Rarefied gas flows can be characterized using the Reynolds (Re), Mach (M), and Knudsen (Kn) numbers. These three parameters are interdependent for ideal gas flows. Hence, matching two dimensionless groups, preferably the Kn and M, can maintain the dynamic similarity for rarefied gas flows [2]. However, nanoscale gas flows also experience surface force field effects. Hence, "dynamic similarity" of gas flows in low-pressure environments (i.e., large λ) and nanoscale domains is questionable. Within regions experiencing the wall force field, the transport could significantly deviate from the kinetic theory predictions. As a result, analyses of fluid behavior near a surface require proper investigations of the wall force field effects.

This entry presents the deviations of nanoscale confined shear-driven gas flows from kinetic theory predictions. Subsequently, results proved that the dynamic similarity between the rarefied and nanoscale confined gas flows is *incomplete*. Importance of wall force field effects is clearly

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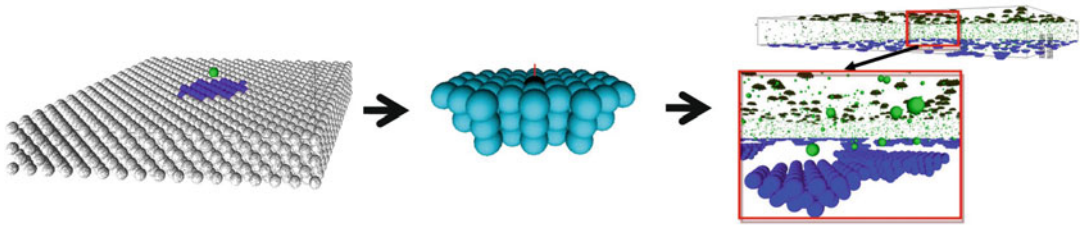

Fig. 1 Illustration of the SWMD procedure

indicated, and *the wall force field penetration depth* is introduced as an important length scale in addition to the channel dimension and gas mean free path in nano-confined gas flows.

Basic Methodology

Smart Wall Molecular Dynamics

Wall force field effects can be directly accounted within a deterministic computational process by molecular dynamics (MD) method, which is suitable for simulating very small volumes of liquid flow, or solid domains with dimensions on the order of 10 nm or less. Although liquid transport in nano-channels has been studied extensively using MD, the method becomes inefficient for simulating gas flows due to the large intermolecular distances that require relatively large domains. Thus, literature on MD simulations of rarefied gas flows is rather limited.

Gas states evolve through intermolecular collisions separated by ballistic motion of particles characterized by the "mean free path (λ)." In order to allow intermolecular collisions, gas simulation domains should be on the order of λ in the lateral and axial directions. This requirement results in relatively large simulation volumes for classical MD, which necessitates modeling of a large number of gas molecules and excessively large number of wall molecules. In order to address this computational difficulty, a smart wall MD (SWMD) algorithm is developed [3]. For Lennard-Jones (L-J) molecules interacting with FCC wall structures ((1,0,0) plane facing the fluid), the SWMD utilizes 74 wall molecules as a stencil for fluid–surface interactions (Fig. 1). Due to the cutoff distance of the L-J potentials, 74 wall molecules stencil can produce the force field of an infinite wall, significantly reducing the memory requirements for MD simulations [3].

Three-Dimensional MD for Nanoscale Gas Flows

Argon gas flow confined between two infinite plates that are a distance H apart is considered as illustrated in Fig. 2. Periodic boundary conditions are applied in the axial (x) and lateral (z) directions. Shear-driven flow is obtained by moving the top and bottom channel walls in opposite directions with a characteristic velocity of $U_W = M\sqrt{\gamma k_b T/m}$ where M is the Mach number, γ is the adiabatic index (5/3 for monatomic molecules), k_b is the Boltzmann constant (1.3806×10^{-23} J K^{-1}), T (298 K) is the temperature, and m is the mass of gas molecules. Mass for an argon molecule is $m = 6.63 \times 10^{-26}$ kg, its molecular diameter is $\sigma = 0.3405$ nm, and the depth of the potential well for argon is $\varepsilon = 119.8 \times k_b$. For simplicity, the walls have molecular mass and diameter equivalent to argon ($m_{\text{wall}} = m_{\text{Ar}}$, $\sigma_{\text{wall}} = \sigma_{\text{Ar}}$) with FCC (face-centered cubic) structure, and (1,0,0) plane faces the gas molecules.

Lennard-Jones (L-J) 6–12 potential was utilized to model van der Waals interactions between gas–gas and gas–wall molecules. The truncated (6–12) Lennard-Jones (L-J) potential is given as

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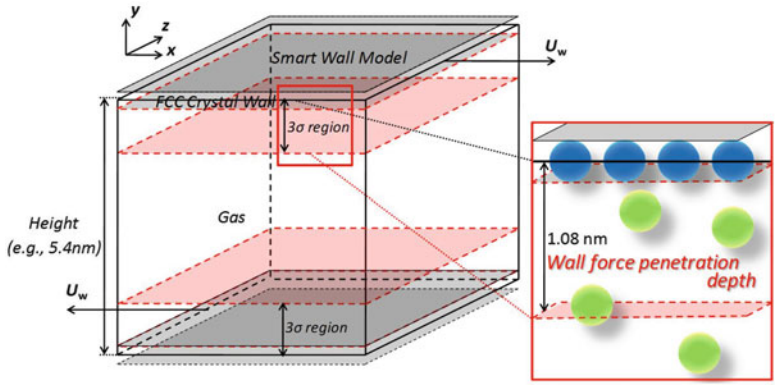

Fig. 2 Sketch of the simulation domain with explanation of the wall force penetration depth

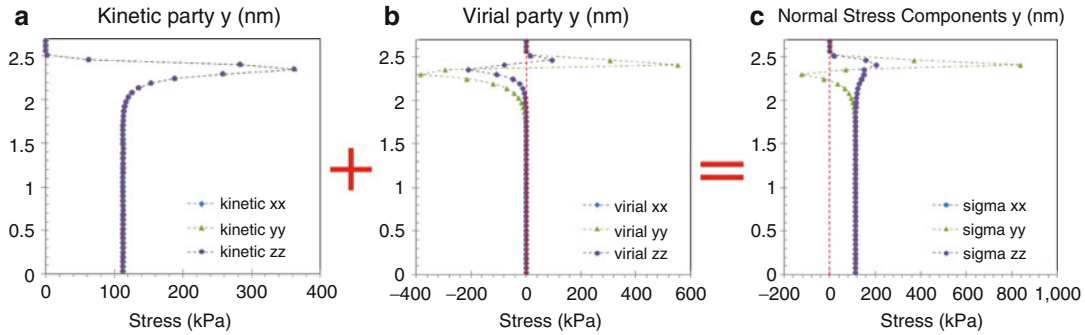

Fig. 3 Kinetic (**a**) and virial (**b**) components of the normal stress distribution (**c**) for the dilute gas case

$$V_{\text{truncated}}(r_{ij}) = 4\varepsilon\left(\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right) - \left(\left(\frac{\sigma}{r_c}\right)^{12} - \left(\frac{\sigma}{r_c}\right)^{6}\right)\right) \quad (1)$$

where r_{ij} is the intermolecular distance, ε is the depth of the potential well, σ is the molecular diameter, and r_c is the cutoff radius. In this study $r_c = 1.08$ nm is used, which is approximately equal to 3.17σ for argon molecules.

Key Research Findings

Gas in a Nanoscale Confinement

Equilibrium MD method is employed to resolve the density and stress variations within the static gas domain. Argon is simulated in a nano-channel of 5.4 nm in height and 54 nm in length and width at 298 K and 1.896 kg/m^3 corresponding to dilute gas state. Comparison of the mean free path to the channel height results in $Kn = 10$. The potential strength for gas–wall interactions is chosen to be the same with that of gas–gas molecular interactions resulting in $\varepsilon_{\text{wall-Ar}}/\varepsilon_{\text{Ar-Ar}}$ ratio of unity ($\varepsilon_{wf}/\varepsilon_{ff}=1$).

Inside the wall force penetration depth, solid walls induce body forces on fluid molecules, which result in surface-induced stresses. Stresses generated by the surface–particle interactions are identified as the "surface virial," which create anisotropic normal stresses for dilute and dense gas phases

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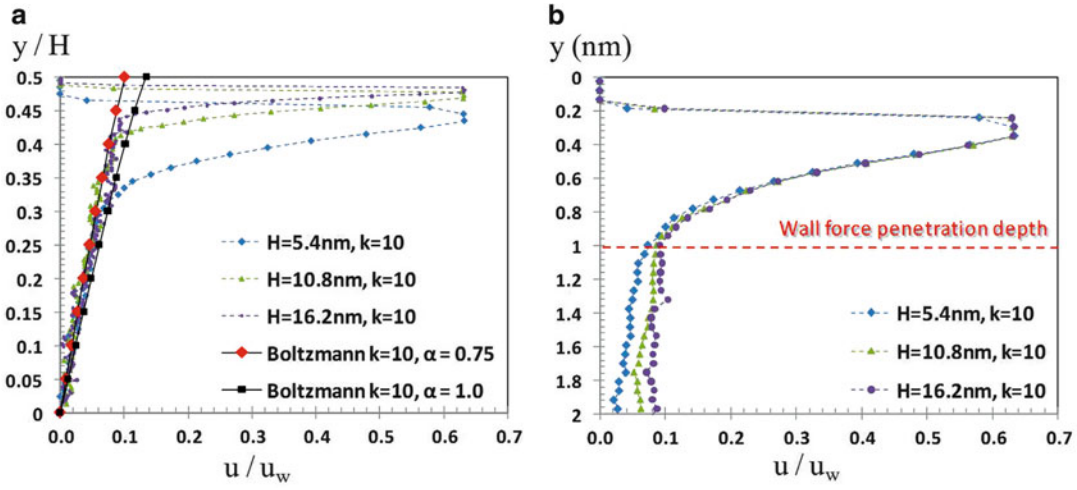

Fig. 4 Normalized velocity profiles of $k = 10$ flows with constant wall velocity of 64 m/s (**a**) as a function of the normalized channel height (y/H) and (**b**) within 2 nm distance from the walls

while the normal stresses became isotropic and recover the thermodynamic pressure sufficiently away from the surfaces [4]. Figure 3c shows the distribution of three mutually orthogonal components of normal stresses of dilute gas within the nano-channel. The kinetic and virial contributions of Irving–Kirkwood expression [5] are given separately in Fig. 3a, b. In the bulk portion of the channel, pressure can be calculated as the average of the three normal stress components, and the pressure field predicted using the computed density and temperature using ideal gas law matches the computed pressure distribution exactly. Due to the anisotropic normal stress distribution, it is impossible to define pressure in the near-wall region of nanoscale confined fluids. These observations are also valid for flow cases [6].

Shear-Driven Nanoscale Gas Flows

The SWMD simulations of shear-driven argon gas flows in nano-channels are performed to reveal the surface effects for flows in the transition and free-molecular flow regimes. Fluid behavior in the wall force penetration region is found to depend mostly on the properties of the surface–gas pair. Investigation is started with *a specific gas–surface pair* ($\varepsilon_{wf}/\varepsilon_{ff} = 1$) to validate independency of the near-wall fluid behavior on channel dimensions (H) and flow dynamics (Kn) [6]. In order to show this, two different sets of simulations are conducted. In the first set of simulations, channel height and density are varied to compare the results of k $= 10$ ($k = \sqrt{\pi}/2Kn$) flow in different height nano-channels, and dimensional effects on dynamically similar flow conditions are studied. In the other set, the channel height is varied, while the local pressure and temperature are kept constant that k is varied from early transition to free-molecular flow regime. Thus, k dependency of the surface influence is investigated. Next, surface effects are studied as a function of the surface–gas potential strength ratio ($\varepsilon_{wf}/\varepsilon_{ff}$) [7]. In this case, two different sets of molecular dynamics simulations at $k = 1$ and $k = 10$ with surface–gas pair interaction strength ratios of $1 \leq \varepsilon_{wf}/\varepsilon_{ff} \leq 6$ are performed.

Significant wall force field effects are found on the velocity, density, shear stress distributions in the near-wall region that extends approximately three molecular diameters from each surface for van der Waals interactions. Within this *wall force penetration depth*, a density buildup with a single peak point is observed. Exactly matching the earlier static case, normal components of the stress tensor are anisotropic and dominated by the surface virial. For a specific gas–surface pair ($\varepsilon_{wf}/\varepsilon_{ff} = 1$), results show that the density and normal stress variations are scalable by the bulk density and

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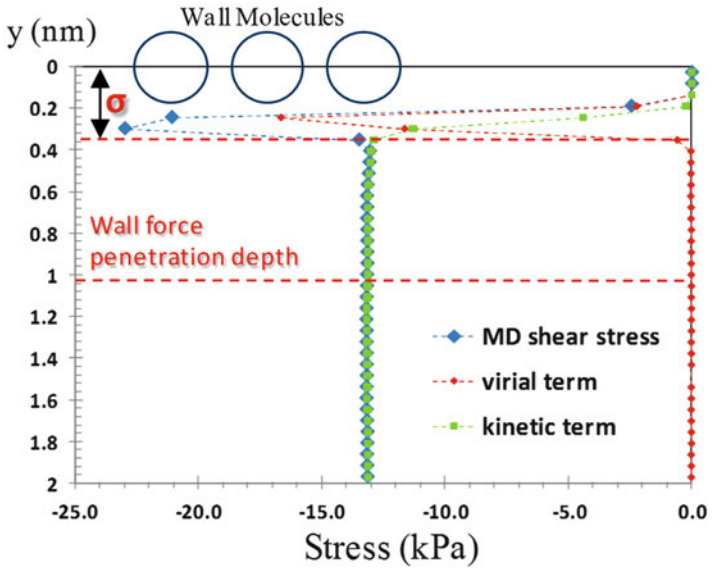

Fig. 5 Virial and kinetic components of shear stress distribution in 5.4 nm height nano-channel for $k = 10$ flow

pressure and their behavior are unaffected by the shear-driven flow, channel dimensions, and gas rarefaction (Kn). Velocity profiles show sudden increase within this region. Near-wall gas velocity is independent of the channel dimensions and density for a specific gas–surface pair however varies as a function of the Knudsen number due to the rarefaction effects. Outside the "near-wall" region, pressure is defined by the ideal gas law, and the velocity distribution is predicted by kinetic theory based on the Boltzmann equation using tangential momentum accommodation coefficient (TMAC) of the corresponding gas–surface pair.

Figure 4a shows the gas velocity profiles of $k = 10$ flows confined in 5.4, 10.8, and 16.2 nm height channels through the nondimensional height (y/H). For these dynamically similar flows, influence of the surface forces differs with the ratio of the wall force penetration depth to channel height. The MD-based velocity profiles agree well with the kinetic theory predictions from [8] in the middle of the channels. Better match between the MD results and linearized Boltzmann solutions using TMAC value of $\alpha = 0.75$ is observed for all cases. The zoomed velocity profiles within 2 nm from the top wall in Fig. 4b show identical velocity variations in the near-wall region despite different shear rates in the bulk region and different channel heights.

Figure 5 demonstrates shear stress variation for $k = 10$ flow inside 5.4 nm channel as the sum of its kinetic and virial contributions. Shear stress is constant in the bulk and shows variations within 0.34 nm (~s) from wall. Shear stress is defined by the kinetic term in most of the domain, while the surface virial increases starting from one sigma distance from the wall till the gas density reduces to zero due to the impenetrable wall zone. Therefore, near-wall spatial variations of shear stress are induced by the surface force field effects and the wall motion.

The TMAC (α) values are predicted by comparing the bulk shear stress value found using 3D SWMD simulations, with the theoretical shear stress value at the given k. Figure 6a shows that the shear stress results for $k = 10$ flow match the kinetic theory for $\alpha = 0.75$. For consistency, velocity profiles in the bulk flow region must also match the linearized Boltzmann solution of $\alpha = 0.75$. Figure 6b shows the MD-predicted and linearized Boltzmann velocity profiles at $k = 10$ for $\alpha = 0.75$ and $\alpha = 1.0$. Clearly, the shear stress induced by FCC walls and the corresponding bulk flow velocity profiles match the linearized Boltzmann solution better for $\alpha = 0.75$ than the $\alpha = 1$ case.

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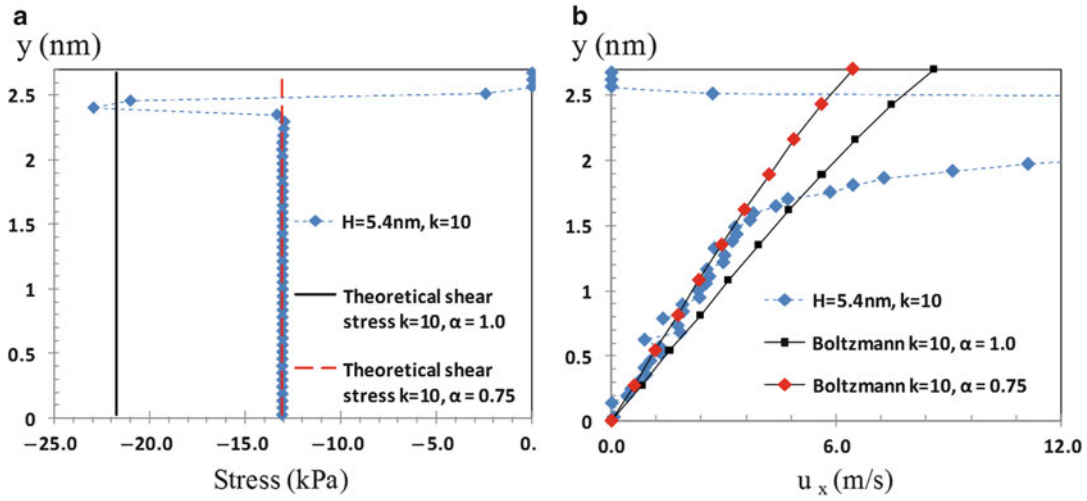

Fig. 6 (**a**) MD shear stress profile of 5.4 nm height channel at $k = 10$ flow with wall velocity of 64 m/s and the corresponding theoretical shear stress results for TMAC values of $\alpha = 1.0$ and 0.75. (**b**) A zoomed version of the $k = 10$ flow velocity distributions of MD results and linearized Boltzmann solutions at $\alpha = 1.0$ and 0.75

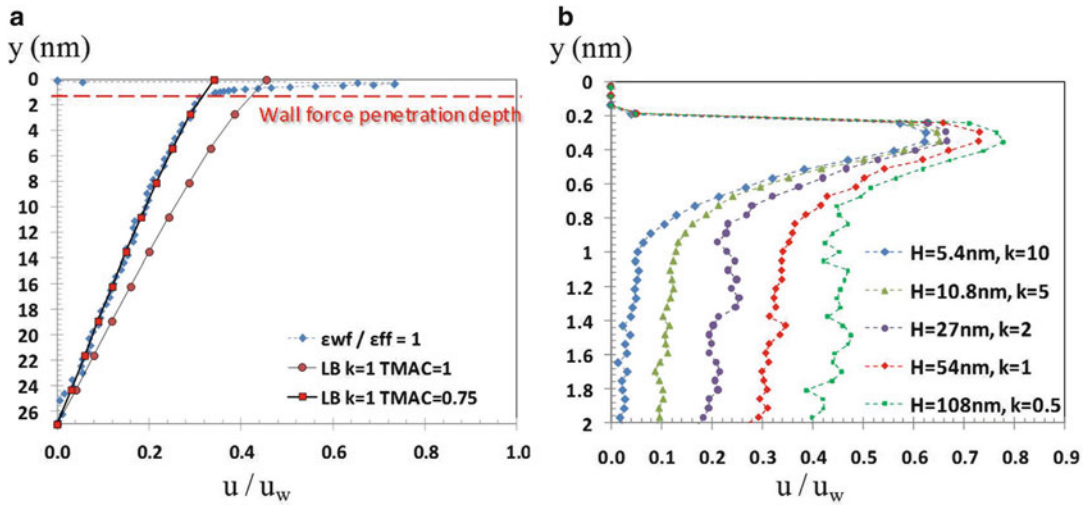

Fig. 7 (**a**) Velocity profile for $k = 1$ flow in half of the 54 nm height channel with linearized Boltzmann solutions using TMAC = 1.0 and 0.75. (**b**) Velocity profiles for various k flows within 2 nm distance from the top wall. The wall velocity is 64 m/s

Next, argon gas flows at standard condition created in different height channels, corresponding to $k = 10$, 5, 2, 1, and 0.5 flows. Figure 7a gives the velocity profile for $k = 1$ flow (H = 54 nm) in half of the channel and the linearized Boltzmann solution for $k = 1$ flow with $\alpha = 1.0$ and 0.75. MD result clearly agrees better with the theory using $\alpha = 0.75$ in the bulk region, while deviations from the kinetic theory solution are still observed inside the force penetration depth. Even though these deviations are confined in the 3σ region and their influence extends only 4 % of the domain for 54 nm height channel, effect of the surface forces is observed indirectly in the bulk velocity by means of the TMAC value, which is a property of the gas–surface pair. Therefore, without a prior knowledge of TMAC, it will not be possible to predict the correct bulk velocity field using kinetic theory. Figure 7b shows the velocity profiles for various k flows within 2 nm distance from the top

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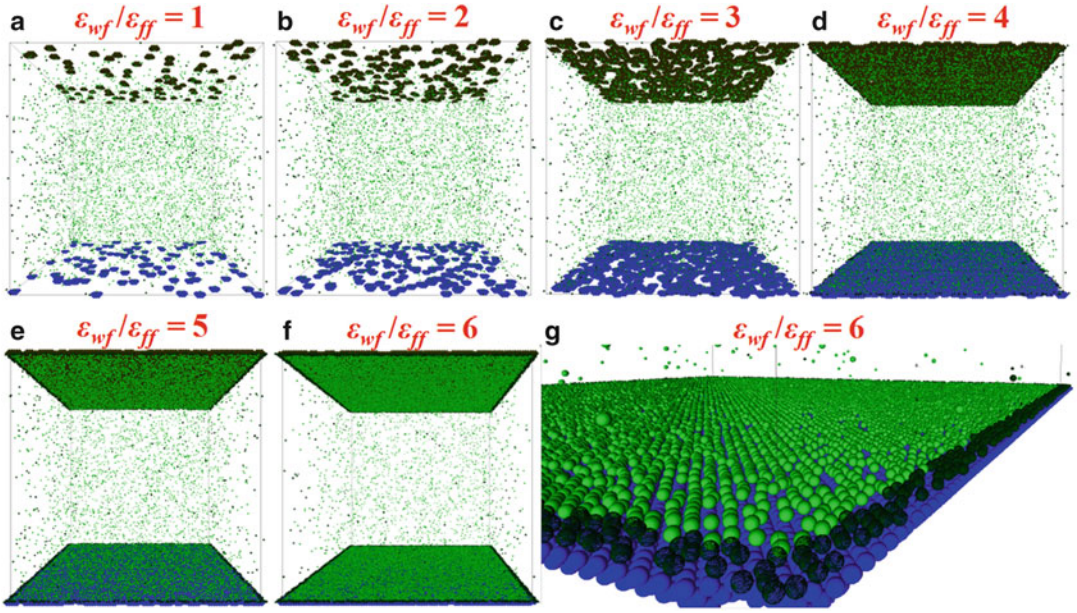

Fig. 8 (**a**–**f**) Snapshots of argon gas flows at $k = 1$ with various $\varepsilon_{wf}/\varepsilon_{ff}$ values. All simulations are confined in 54 × 54 × 54 nm domains at 298 K and 113.4 kPa. (**g**) shows adsorbed argon gas layer on the bottom surface for the $\varepsilon_{wf}/\varepsilon_{ff} = 6$ case

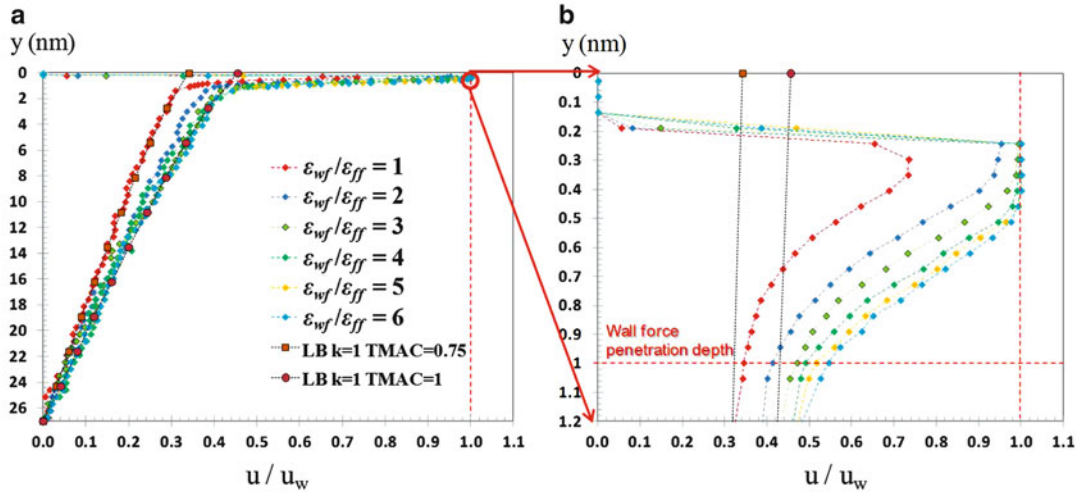

Fig. 9 Velocity profiles for k=1 flow with different $\varepsilon_{wf}/\varepsilon_{ff}$ values (**a**) in the half of the 54 nm height channel and (**b**) within 1.2 nm distance from the walls. Velocity profiles are normalized with the constant wall velocity of 64 m/s

wall. Different profiles inside the force penetration depth show effects of the Knudsen number on the near-wall velocity profiles. Velocities in the near-wall region increase with reduction in *Kn*.

The TMAC values are predicted as a function of Kn using similar approach shown in the discussions of Fig. 6, and the TMAC value for argon gas flow at k = 0.5, 1, 2, 5, and 10 is predicted to be $\alpha = 0.75$. As a result, atomically smooth FCC crystal walls with (1,0,0) plane facing the gas resulted in TMAC = 0.75, independent of the Knudsen number in the transition and free-molecular flow regimes for the specified gas–surface pair ($\varepsilon_{wf}/\varepsilon_{ff} = 1$) [6].

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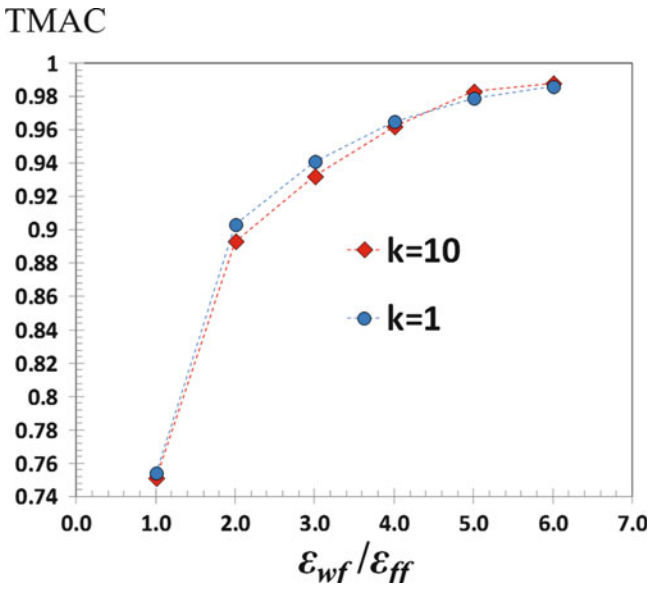

Fig. 10 TMAC variation of $k = 1$ and $k = 10$ flows as a function of the normalized gas–wall potential strength ratio $\varepsilon_{wf}/\varepsilon_{ff}$

Simulation domains of $k = 1$ gas flows in 54 nm height channel at different $\varepsilon_{wf}/\varepsilon_{ff}$ values are shown in Fig. 8. Increased $\varepsilon_{wf}/\varepsilon_{ff}$ results in increased gas density, leading towards monolayer adsorption on surfaces. Regardless of the Knudsen number, density profile in the near-wall region is determined by the $\varepsilon_{wf}/\varepsilon_{ff}$ value. Increase in $\varepsilon_{wf}/\varepsilon_{ff}$ increases the bulk velocity, which reaches to the LB solution of $\alpha = 1$ for $\varepsilon_{wf}/\varepsilon_{ff} \geq 3$ cases (Fig. 9a). The near-wall velocity profile given in Fig. 9b shows reduced gas slip and eventually velocity stick with increased $\varepsilon_{wf}/\varepsilon_{ff}$.

Using the previously described approach, the TMAC values of $k = 1$ and $k = 10$ flows for various $\varepsilon_{wf}/\varepsilon_{ff}$ cases are calculated. Starting with the value of 0.75 for $\varepsilon_{wf}/\varepsilon_{ff} = 1$, TMAC increases with increased ε_{wf} and approaches unity for $\varepsilon_{wf}/\varepsilon_{ff} \geq 3$. TMAC variations for $k = 1$ and $k = 10$ flows for the studied cases are plotted in Fig. 10. TMAC variations as a function of $\varepsilon_{wf}/\varepsilon_{ff}$ are shown to be independent of the Knudsen number [7].

Overall the results show that the wall force field penetration depth is an additional length scale for gas flows in nano-channels, breaking dynamic similarity between rarefied and nanoscale gas flows solely based on the Knudsen and Mach numbers. Hence, one should define a new dimensionless parameter as the ratio of the force field penetration depth to the characteristic channel dimension, where wall effects cannot be neglected for large values of this dimensionless parameter. Additionally, the calculated tangential momentum accommodation coefficients for a specific gas–surface couple were found to be constant regardless of different base pressure, channel height, wall velocity, and Knudsen number. Results of different gas–surface couples reveal that TMAC is only dependent on the gas–surface couple properties and independent of the Knudsen number.

Future Directions for Research

Compressibility effects should be studied by considering non-isothermal flow conditions.

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Cross-References

- ▶ DSMC Simulations of Microscale Gas Flows
- ▶ Gas Flow in Nanochannels
- ▶ Inter-Atomic Potential
- ▶ Knudsen Number
- ▶ Mach Number
- ▶ Mean Free Path
- ▶ Micro- and Nanoscale Gas Dynamics
- ▶ Micro- and Nanoscale Gas Fluidics
- ▶ Molecular Dynamics Simulation Method
- ▶ Monte Carlo Method
- ▶ Nanochannels
- ▶ Pressure-Driven Single Phase Gas Flows
- ▶ Rarefaction Parameter
- ▶ Rarefied Gas Dynamics
- ▶ Shear-Driven Flow
- ▶ Shear-Driven Micro- and Nanofluidics
- ▶ Shear Flows
- ▶ Wall Shear Stress

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