

# Molecular Modeling of Force Driven Gas Flows in Nano-channels

Murat Barisik<sup>1</sup>

<sup>1</sup>Mechanical Engineering Department, Izmir Institute of Technology, Izmir 34469, Turkey

Corresponding author: muratbarisik@iyte.edu.tr

**Abstract:** Nano-scale gas transport plays an important role in many micro/nanotechnology applications where the rarefied gas dynamics based solutions are frequently used by maintaining a “dynamic similarity” between low pressure (rarefied) and nano gas flows. However, such a consideration is incomplete since the surface force field effects dominant in nano-levels induce significant variations. In order to specify the surface force effects on gas transport, we define a new parameter ( $B$ ) as the ratio of force penetration length to the channel height, and studied the length scales and conditions for applicability of current rarefied gas dynamics on nano-scale gas flows. Using Molecular Dynamics, force driven gas flows were characterized as a function of  $B$  parameter and Knudsen number. Results showed that for a negligible value of  $B$  parameter ( $B \rightarrow 0$ ) transport can be described by rarefied gas dynamics in the whole Knudsen range while the velocity profiles are parabolic and the variation of mass flow rate shows the well-known Knudsen minimum around  $Kn=1$ . As the flow dimension decreases,  $B$  becomes a finite value indicating the dominance of surface force effects over rarefaction, and gas velocities and mass transport significantly deviates from the kinetic theory predictions.

*Keywords:* Molecular Dynamics, Argon Gas Flow, Rarefied Gas Dynamics, Kinetic Theory.

## 1 Introduction

Gas flows in nano-channels and pores are observed in several industrial and environmental applications [1-3]. For example, gas separation using nano-membranes can remove carbon dioxide from flue gases to combat global climate change with low capital costs, low energy requirements, and ease in operation [4-7]. Under pressure differences or concentration gradients, nano-engineered composite membranes allow species selective migration of gas molecules through their nano-pores. Carbon nanotubes and carbon based nano-composite materials can capture hydrogen from earth's atmosphere or combustion products [8-9]. Alternatively, these nano-pore systems can provide solid-state hydrogen storage by packing larger quantities of hydrogen into smaller volumes by adsorption [10-15]. Another interesting application is in gas recovery from shale reservoirs enabled by the recent advances in horizontal well fracturing [16-18], where gas transport in shale pore-sizes as small as 5nm is commonly observed [19-22]. Despite these technological developments, existing theoretical and numerical transport models are incapable of explaining the actual flow rates in these nano-scale confinements. Overall, there is a significant knowledge gap and an urgent need for accurate description and understanding of gas transport in nano-scale conduits.

Gas flows in nano-scale conduits encounter substantially different physics than their macroscopic

counterparts due to the (i) rarefaction, (ii) surface force field, and (iii) surface adsorption. Contributions of these effects on gas transport greatly differ depending on the conduit size, gas pressure and gas-surface interactions. Rarefaction is well known and frequently addressed using the kinetic theory based methods by assuming “dynamic similarity” between the low pressure (rarefied) and nano-scale gas flows. However, the surface force field and surface adsorption originating from the van der Waals force interactions of gas and wall molecules can greatly impact transport, and destroy this similitude.

Rarefaction, surface force field, and surface adsorption effects can be investigated using Molecular Dynamics (MD), which is a deterministic computational method. However, MD is most suitable for simulating very small volumes of liquid or solid domains with dimensions on the order of 10nm or less. As a result, liquid transport in nano-channels has been studied extensively using MD. Unlike liquids, gas flows evolve through intermolecular collisions characterized by the mean free path ( $\lambda_{air} \approx 65$  nm at standard conditions) [23]. In order to properly capture the intermolecular collisions and to have a sufficient number of gas molecules for a meaningful statistical ensemble, gas flow simulations using MD require large computational domains dominated by an excessively large number of wall molecules. This is a challenge for classical MD software making them impractical for gas flow simulations. I already addressed this problem by developing a “smart wall” MD (SWMD) algorithm [36], which properly incorporates the force field of a semi-infinite wall. This algorithm significantly reduced the memory requirements and enabled proper MD simulations of nano-scale gas flows for the first time in literature.

Using SWMD, we investigated shear and force-driven nano-channel gas flows in the entire Knudsen regime [23-31]. Simulation results have shown formation of a near wall layer that is several molecular diameters thick. We identified this as the “wall force penetration length” ( $L_f$ ), where the gas density and velocity distributions are under the effect of surface molecular forces. Transport beyond the near-wall region can be considered as the bulk flow region, which exhibits flow physics predictable by KT solutions for a prescribed Tangential Momentum Accommodation Coefficient (TMAC). We have also shown that TMAC is a function of the gas-wall interaction parameter and it is independent of the Knudsen number.

Objective of this study is to explore the length scales and conditions for applicability of “rarefied gas dynamics” on nano-scale gas flows. By defining the ratio of surface force penetration length ( $L_f$ ) to the channel height ( $H$ ) as a new dimensionless parameter ( $B = L_f/H$ ), we will determine the influence of near wall hydrodynamics on the overall gas transport and define validity range of kinetic theory for small scale flows as a function of the  $B$  parameter.

## 2 Three-Dimensional MD Simulation Details

Argon gas flow between two parallel surfaces was modeled using SWMD. We simulated force-driven isothermal flows, which are hydrodynamically similar to pressure-driven gas flows at low Mach numbers ( $Ma$ ). Computational domain was periodic in the stream-wise and lateral directions and extended one mean free path ( $\lambda_{Ar}$ ) in these directions. Thermodynamic state of argon was fixed at 298 K and 113.4kPa, which corresponds to a density of  $\rho_{Ar}=1.896\text{kg/m}^3$  and  $\lambda_{Ar}=54\text{nm}$ . By keeping gas temperature at 298K, pressure was varied to obtain different  $\lambda$  values. Mean molecular spacing for each case was checked, and the thermodynamic states were validated to be dilute gas, obeying the ideal gas law. A constant driving force ( $F_{drive}$ ) was applied on each gas molecule in the stream wise direction, while the magnitude of the force was controlled to maintain  $Ma < 0.1$ , so that gas flow is nearly incompressible.

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

$$V_{truncated}(r_{ij}) = 4\epsilon \left[ \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) - \left( \left( \frac{\sigma}{r_c} \right)^{12} - \left( \frac{\sigma}{r_c} \right)^6 \right) \right], \quad (1)$$

where  $r_{ij}$  is the intermolecular distance,  $\epsilon$  is the depth of the potential well,  $\sigma$  is the molecular diameter and  $r_c$  is the cut-off radius. In this study, we utilized  $r_c=1.08$  nm, which is approximately equal to  $3.17\sigma$  for argon molecules. At this cut-off-distance, the attractive part of the L-J potential was reduced to  $0.00392\epsilon$ . Our algorithm utilized the well-known link cell method to handle particle-particle interactions [32]. Mass for an argon molecule is  $m_{Ar}=6.63 \times 10^{-26}$  kg, its molecular diameter is  $\sigma_{Ar} = 0.3405$  nm and the depth of the potential well for argon is  $\epsilon_{Ar}=119.8 \times kb$ , where  $kb$  is the Boltzmann constant ( $1.3806 \times 10^{-23}$  J K<sup>-1</sup>). Here  $\epsilon_{Ar}$  defines the gas-gas interaction strength, and is identified as  $\epsilon_{ff}$ . Walls were modeled molecularly using Face-Centered Cubic (FCC) structure with (1,0,0) plane facing the gas. For simplicity, walls molecules have mass and diameter equivalent to argon ( $m_{wall}=m_{Ar}$ ,  $\sigma_{wall} = \sigma_{Ar}$ ). Since wall molecules are fixed in the cold wall model, the wall's molecular mass has no effect in momentum exchange between the gas and wall molecules. In addition, the molecular diameter between different species does not vary drastically.

Simulations started from the Maxwell-Boltzmann velocity distribution for gas molecules at 298K. Initial particle distribution was evolved 106 time-steps (4 ns) to reach an isothermal steady state using 4 fs ( $\sim 0.002\tau$ ) time steps, after which,  $8 \times 10^6$  time steps (32 ns) were performed for time averaging. Longer time averaging has also been performed to confirm convergence of density, stress and velocity profiles to steady state. In order to capture variations within the near wall region accurately and using same resolution for each channel case, all simulation domains were divided into slab bins with constant height of 0.054nm in the wall normal direction. Canonical ensemble (NVT, i.e., constant mole, N, volume, V, and temperature, T) was performed by utilizing a thermostat. We employed the Nose-Hoover algorithm as a global thermostat inside the local sub-domains to obtain isothermal conditions at 298 K with a relaxation time of  $\sim 0.2$ ps. Sub-domains have 0.54nm heights through the entire span, which is 10 times larger than the utilized bin size. Local gas temperature was also computed throughout the channels to ensure isothermal conditions were imposed by the thermostat.

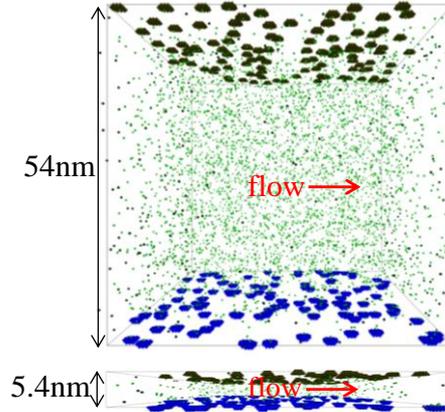


Figure 1: Molecular Dynamics simulations of gas flows inside 54 and 5.4nm height channels.

### 3 Results and Discussion

We studied force driven argon gas flows inside 54nm and 5.4nm height channels (Figure 1) at  $Kn=10$ , 1 and 0.1 flows. Since the surface effects are limited in 54nm cases ( $L_f \approx 1$ nm,  $1$ nm/54nm=2%), velocity profiles from SWMD match Kinetic theory predictions for  $TMAC=0.75$  well as seen from Figure 2.

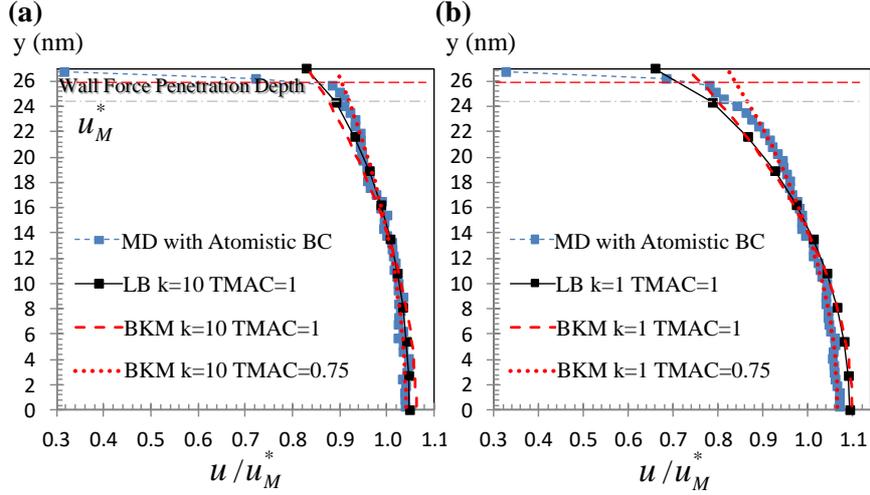


Figure 2: Gas velocity distributions inside 54nm height channel at (a)  $Kn=10$  and (b)  $Kn=1$ . Comparisons were done with Linearized Boltzmann and Beskok&Karniadakis Method [32].

However, the surface forces becomes dominant for the 5.4nm channel ( $1nm/5.4nm=20\%$ ) where the velocity distribution at any  $Kn$  value cannot be described by a parabolic profile (Figure 3). Hence, gas flows in a 5.4nm channel cannot be predicted by a kinetic theory based procedure both in the bulk and near wall regions at any  $Kn$  value through the entire Knudsen regime.

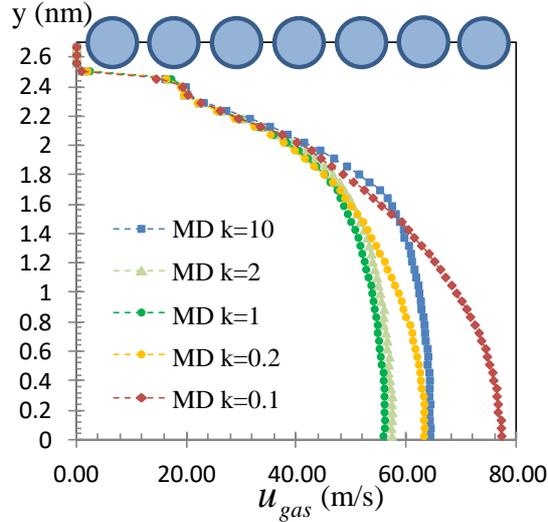


Figure 3: Gas velocity distributions inside 5.4nm height channel at various  $Kn$  numbers.

In order to identify the scale effects, I used my new dimensionless parameter  $B$  ( $B=L_f/H$ ), where the finite values of  $B$  show significance of the wall force-field. I calculated gas mass flow rates in 5.4nm ( $B \approx 0.2$ ) and 54nm ( $B \approx 0.02$ ) channels (Figure 4). For  $B \approx 0.02$  flow in 54nm channel, MD results show great agreement with the kinetic theory based solutions in a wide  $Kn$  range. This validates that MD can successfully model gas flows from slip to free molecular flow regimes.

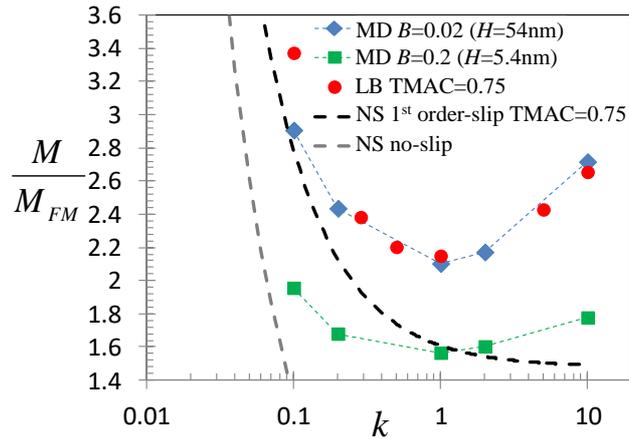


Figure 4. Free-molecular scaling of MD mass flow rates for 54nm and 5.4nm height channels using MD. LB results for TMAC=0.75 are adopted from [33]. Mass flow rate results of Navier-Stokes solution using no-slip and first order-slip boundary conditions are also shown.

Variation of mass flow rate as a function of Kn in Figure 4 shows the well-known “Knudsen’s Minimum”. While the variation of transport observed in LB solution solely depends on the rarefaction level, MD reveals the size effects as a function of B. For the 54nm channel cases, mass transport still varies mostly based on the rarefaction effects defined by Kn since the surface force effects represented by B parameter is negligible ( $B = 0.02$ ). However, in 5.4nm channel B reaches a finite value ( $B \approx 0.2$ ), and the mass flow rates become a function of both rarefaction and nano-scale effects

## 4 Conclusions

We investigated force driven gas flows confined in different height nano-channels, and characterize nano-scale effects on velocity profiles and mass flow rates in the entire Knudsen regime (late slip, transition, and free molecular flow regimes). Near surface molecular forces becomes dominant for finite values of B, and the near wall region interacts with the bulk flow, resulting in completely different velocity profiles and mass transport in nano-channels. Hence, the well-known Knudsen’s minimum in mass transport manifests itself differently for gas nano-flows with finite B values. We have shown that the dimensional limit of kinetic theory based descriptions of gas nano-flows are defined by the B parameter, where dynamic similarity between rarefied and nano-flows are valid only for  $B \rightarrow 0$ , while finite values of B require modeling of the wall force field effects. MD simulations of gas flows enable proper investigations of the non-equilibrium and confinement effects, revealing the influence of wall-force-field and surface adsorption on transport.

## 4 Acknowledgments

Murat Barisik would like to thank H2020 Marie Skłodowska-Curie action CO-FUNDED Brain Circulation Scheme for support under the grant number TÜBİTAK 115C026.

## References

- [1] Majumder M, Chopra N, Hinds BJ (2011) Mass transport through carbon nanotube membranes in three different regimes: ionic diffusion and gas and liquid flow. *ACS nano* 5(5):3867-3877.
- [2] Halonen N, Rautio A, Leino AR, Kyllonen T, Toth G, Lappalainen J, Vajtai R (2010) Three-dimensional carbon nanotube scaffolds as particulate filters and catalyst support membranes. *ACS Nano* 4(4):2003-2008.

- [3] Yoon D, Lee C, Yun J, Jeon W, Cha BJ, Baik S (2012) Enhanced Condensation, Agglomeration, and Rejection of Water Vapor by Superhydrophobic Aligned Multiwalled Carbon Nanotube Membranes. *ACS nano* 6(7):5980-5987.
- [4] Li B, Jiang B, Fauth DJ, Gray ML, Pennline HW, Richards GA (2011) Innovative nano-layered solid sorbents for CO<sub>2</sub> capture. *Chemical Communications* 47(6):1719-1721.
- [5] Venna SR, Carreon MA (2009) Highly permeable zeolite imidazolate framework-8 membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. *Journal of the American Chemical Society* 132(1):76-78.
- [6] Yave W, Car A, Wind J, Peinemann KV (2010) Nanometric thin film membranes manufactured on square meter scale: ultra-thin films for CO<sub>2</sub> capture. *Nanotechnology* 21(39):395301.
- [7] Ho MT, Allinson GW, Wiley DE (2008) Reducing the cost of CO<sub>2</sub> capture from flue gases using membrane technology. *Industrial & Engineering Chemistry Research* 47(5):1562-1568.
- [8] Hijikata T (2002) Research and development of international clean energy network using hydrogen energy (WE-NET), *International Journal of Hydrogen Energy* 27:115-129.
- [9] Momirlan M, Veziroglu TN (2005) The properties of hydrogen as fuel tomorrow in sustainable energy system for a cleaner planet, *International Journal of Hydrogen Energy* 30:795-802.
- [10] Chalk SG, Miller JF (2006) Key challenges and recent progress in batteries, fuel cells, and hydrogen storage for clean energy systems, *Journal of Power Sources*. 159:73-80.
- [11] Furukawa H, Yaghi OM (2009) Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications, *J. Am. Chem. Soc.* 131(25):8875-8883.
- [12] Ma S, Zhou HC (2009) Gas storage in porous metal-organic frameworks for clean energy applications, *Chem. Commun.* 46:44-53.
- [13] Cho JH, Yang SJ, Lee K, Park CR (2011) Si-doping effect on the enhanced hydrogen storage of single walled carbon nanotubes and graphene, *International Journal of Hydrogen Energy*. 36:12286-12295.
- [14] Maruyama S, Kimura T (2000) Molecular Dynamics Simulation of Hydrogen Storage with Single Walled Carbon Nanotubes, *International Mechanical Engineering Congress and Exhibit, Orland, November 5-11.* 37:377-378.
- [15] Firouzi M, Tsotsis TT, Sahimi M (2007) Molecular dynamics simulations of transport and separation of supercritical carbon dioxide-alkane mixtures in supported membranes, *Chemical Engineering Science*. 62:2777-2789.
- [16] King G (2010) Thirty years of gas shale fracturing: what have we learned?. In *SPE Annual Technical Conference and Exhibition*.
- [17] Chong KK, Grieser W, Passman A, Tamayo H, Modeland N, Burke B (2010) A Completions Guide Book to Shale-Play Development: A Review of Successful Approaches toward Shale-Play Stimulation in the Last Two Decades. In *Canadian Unconventional Resources and International Petroleum Conference*. doi:10.2118/133874-MS
- [18] Fisher MK, Heinze JR, Harris CD, Davidson BM, Wright CA, Dunn KP (2004) Optimizing horizontal completion techniques in the Barnett shale using microseismic fracture mapping. In *SPE Annual Technical Conference and Exhibition*. doi:10.2118/90051-MS
- [19] Loucks RG, Reed RM, Ruppel SC, Jarvie DM (2009) Morphology, genesis, and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett Shale. *Journal of Sedimentary Research*, 79(12):848-861.
- [20] King G (2010) Thirty years of gas shale fracturing: what have we learned?. In *SPE Annual Technical Conference and Exhibition*.
- [21] Montgomery SL, Jarvie DM, Bowker KA, Pollastro RM (2005) Mississippian Barnett Shale, Fort Worth basin, north-central Texas: Gas-shale play with multi-trillion cubic foot potential. *AAPG bulletin*, 89(2):155-175. DOI:10.1306/09170404042v.
- [22] Chong KK, Grieser W, Passman A, Tamayo H, Modeland N, Burke B (2010) A Completions Guide Book to Shale-Play Development: A Review of Successful Approaches toward Shale-Play Stimulation in the Last Two Decades. In *Canadian Unconventional Resources and International Petroleum Conference*. doi:10.2118/133874-MS
- [23] Barisik M, Kim B, Beskok A (2010) Smart wall model for molecular dynamics simulations of nanoscale gas flows, *Communications in Computational Physics*. doi:10.4208/cicp.2009.09.118.

- [24]Barisik M, Beskok A (2011) Equilibrium Molecular Dynamics Studies on Nanoscale-confined Fluids. *Microfluidics Nanofluidics* doi:10.1007/s10404-011-0794-5.
- [25]Barisik M, Beskok A (2010) MD Simulations of Nano-Scale Gas Flows: A Case Study of Couette Flow at  $Kn=10$ , in Proceedings of the 27th Symposium on Rarefied Gas Dynamics Pacific Grove, California, July 10-15.
- [26]Barisik M, Beskok A (2013) Encyclopedia of Microfluidics and Nanofluidics: Molecular Dynamics Studies on Nanoscale Gas Transport. Springer, New York. In press.
- [27]Barisik M, Beskok A (2011) Molecular Dynamics Simulations of Shear Driven Gas Flows in Nano-Channels. *Microfluidics Nanofluidics* doi:10.1007/s10404-011-0827-0.
- [28]Barisik M, Beskok A (2012) Surface-Gas Interaction Effects on Nanoscale Gas Flows. *Microfluidics Nanofluidics*, doi:10.1007/s10404-012-1000-0.
- [29]Barisik M, Beskok A (2015) Molecular Free Paths in Nano-Scale Gas Flows. *Microfluidics Nanofluidics*, 18(5-6):1365-1371, Doi 10.1007/s10404-014-1535-3.
- [30]Barisik M, Beskok A (2014) Scale Effects in Gas Nano Flows. *Physics of Fluids*, 26:052003, doi:10.1063/1.4874678.
- [31]Barisik M, Beskok A (2016) ‘Law of the Nano-Wall’ in Nano-Channel Gas Flows. *Microfluidics Nanofluidics*, doi 10.1007/s10404-016-1713-6.
- [32]Karniadakis GE, Beskok A, Aluru N (2005) *Micro Flows and Nano Flows: Fundamentals and Simulation*. Springer-Verlag, New York.
- [33]Sharipov F (2001) Application of the Cercignani-Lampis scattering kernel to channel gas flows. In AIP Conference Proceedings 585:347.