Molecular free path distribution in rarefied gases

Nishanth Dongari, Yonghao Zhang and Jason M Reese

Department of Mechanical Engineering, University of Strathclyde, Glasgow G1 1XJ, UK

E-mail: `nishanth.dongari@strath.ac.uk`

PACS numbers: 47.45.-n, 47.61.Cb, 47.11.Mn

Abstract. We present the results of investigations into the distribution of molecular free paths in rarefied gases using molecular dynamics simulations. Our tests on a range of different gas densities and confinements (unbounded, single bounding wall, and parallel bounding walls) indicate that the molecules perform Lévy-type flights, irrespective of the presence of a bounding wall. The free paths most closely follow a power-law distribution. Simulations of gases confined by planar surfaces indicate that the local molecular mean free path varies sharply close to a solid surface. These results may yield new insight into diffusive transport in rarefied gases, in particular, the constitutive behaviour of gas flows in micro and nanoscale devices.

Submitted to: *J. Phys. D: Appl. Phys.*

1. Introduction

Rarefied gases often display non-standard fluid behaviour, as demonstrated in numerous experiments [1]. The key parameter indicating the rarefaction of the gas (and the degree of departure from quasi-equilibrium fluid mechanics) is the Knudsen number, Kn, defined as the ratio of the gas molecular mean free path λ to the characteristic system length scale L. Understanding the behaviour of gases over a wide range of Kn is key to the design of future micro and nanoscale devices and to the manipulation of materials at the molecular scale.

While bulk gas flow properties, such as the average mass flowrate along a micro channel, can be experimentally measured, interpretation of a single integral flow parameter in terms of the components making up the flow model is problematic. Any deviation of an integral quantity from its value calculated using conventional macroscopic fluid mechanics could be ascribed to multiple and competing causes, e.g. deficiencies in the bounding surface slip model, the effect of Knudsen layers, non-linear constitutive behaviour in the bulk, etc. *A posteriori* fitting of macroscopic theories to the experimental data with the aid of tuning parameters is unlikely to be physically realistic, or general enough, although it is widely practised [1].

In this situation, and in order to shed light on the molecular phenomena that determine the macroscopic behaviour, simulating rarefied gases determinstically comes to the fore. Simulation methods such as Molecular Dynamics (MD) can allow us to assess fundamental molecular properties of the gas — the inter-molecular collision rate, the velocity distribution, the distribution of free paths between collisions — over a range of rarefied conditions, and in both unconfined and confined spaces [2]. MD is the most appropriate method as it is deterministic, allowing for realistic molecular behaviour, i.e. molecular attractions, repulsions, movements and scatterings.

This paper presents the results of numerical MD experiments on simple rarefied gases. We highlight the substantively different behaviour of the molecular free paths, collision rates, and mean free path profiles from their classical equilibrium counterparts. In particular, we show that Lévy-type or power-law descriptions better describe the rarefied gas behaviour. As the diffusive transport coefficients of gases can be interpreted in terms of the collisions of molecules, and of the free paths of the molecules between collisions [3, 4], our results may yield new insight into the fluid mechanics of the rarefied case. This work may also be relevant to the construction of particle-mesh simulations (e.g. the DSMC method) of rarefied flows in micro and nano systems.

2. Methodology

2.1. Molecular dynamics modelling

We use the open source software OpenFOAM [5], which includes the MD routines implemented by Macpherson *et al* [6, 7], although modified as we describe below. Monatomic Lennard-Jones molecules are simulated, such that the short-range repulsive/long-range attractive potential between two molecules separated by a distance r is:

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6} \right], \tag{1}$$

where ϵ is related to the interaction strength of the molecules and σ is the hard-sphere diameter of the gas molecules [4] (see also section 2.2 below). We investigate Neon gas, which has $\sigma = 2.5830 \times 10^{-10}$ m, $\epsilon = 7.1957 \times 10^{-22}$ J, and a molar mass $m = 20.180$ kg/kmol. The molecules are spatially distributed in a domain of interest with a random initial Gaussian velocity distribution corresponding to a prescribed gas temperature [3]. They are then allowed to relax to their steady-state configuration before we take measurements.

All interactions between nonbonded particles should be calculated but, since the LJ potential vanishes at larger r, only the interactions between molecules within a certain cutoff radius r_c need to be evaluated in the MD simulation. We choose a cut-off radius of $r_c = 2.5\sigma$, as any larger value has a negligible effect on our results but increases the computational cost of the simulations. The equations of molecular motion are integrated using a leapfrog scheme [7] with a step size of 0.005τ, where $\tau = (m\sigma^2/\epsilon)$ ($\sim 10^{-12}$ s). The spatially-resolved flow parameters are written at intervals of 20τ, and the total run time of the simulations to relax to steady-state is at least 3000τ (in the extreme rarefied case we test, up to 50000τ).

In order to record the free paths of individual molecules in MD simulations, conventionally each molecule's travelled distance between two successive collisions is required. But this can only be recorded when collisions occur and, in simulations with periodic boundaries, it is not appropriate to directly measure the travelled distance of the molecule as a difference between its current position and the position of its last collision. Instead, we obtain the molecular free path as $l = (t_C - t_{LC})Sp_C$, where t_C is the current simulated time, t_{LC} is set to the current simulation time when a collision occurs (so it holds the time of the last occurring collision), and Sp_C is the current speed of the molecule. These molecular attributes, t_{LC} and Sp_C, we implemented into the MD solver in OpenFOAM, along with the attribute *col* that keeps track of whether a target molecule is currently undergoing a collision. The latter is activated (set to 1) when the target molecule is within r_{col} of any other molecule (see section 2.2 below). It is deactivated (set to 0) if it is currently activated and the target molecule is greater than r_{col} from any other molecule.

This new method records the molecular free paths in every time step, and its major advantage is that we can calculate the probability that molecules travel a distance without experiencing a collision, i.e. the free path distribution function. The simple average of these free paths of all simulated molecules is the mean free path. Additionally, the collision handling algorithm allows the evaluation of multiple collisions, i.e. collision events which involve three or more molecules simultaneously. This means the dilute gas assumption employed in deriving the Boltzmann equation can be explored.

2.2. The collision radius

We need to identify the occurrence of inter-molecular collisions in the MD simulations. While the instance of a collision is unambiguous only if the molecular interaction is a step potential (i.e. hard-sphere molecules), the time step required for simulations in that case would need to be vanishingly small in order to capture the collision instant reliably [2]. For the continuous and more physically-realistic LJ potential that we use, we instead declare a collision to have occurred if two molecules are closer together than a distance r_{col}. Molecules in the simulation start to exchange momentum as soon as they are within the MD cut-off distance r_c, and they start to repel each other when they are closer than σ. Hence, the closeness parameter r_{col} must lie between 2.5σ and σ.

An appropriate value for r_{col} can be evaluated through MD simulations to obtain the mean free path for unconfined Neon gas — $\lambda_{Ne} = (\mu/\rho)(\pi/2RT)^{1/2}$, where μ is the gas dynamic viscosity, ρ is gas density, R is specific gas constant and T is temperature — at standard (i.e. non-rarefied) conditions. While computationally time-consuming at standard gas densities, this is also an effective way of validating the MD technique overall. At STP, the expression above give a λ_{Ne} of 1.233×10^{-7} m [4]. Using $r_{col} = \sigma$, the MD simulation retrieves this mean free path value within 1% (see section 3.1.1). As a sensitivity check, if we use $r_{col} = 2.5\sigma$ our MD simulation result is 15% less than the theoretical mean free path value. So the appropriate value for r_{col} is σ, and all the simulations in this paper have been carried out using this value.

3. Results and Discussion

3.1. Unconfined gases

Collision rate probabilities, the distribution of free path lengths, and the steady state mean free path (MFP) for different rarefied gas conditions are simulated using MD in an unconfined cubic domain.

3.1.1. Mean free path To validate our MD method, and as noted in section 2.2 above, we first use it to deduce the unconfined value of the mean free path of Neon gas at standard conditions. We simulate a cubic spatial geometry with periodic boundary conditions, i.e. if a molecule leaves the domain, it is reintroduced on the opposite side of the domain, retaining the same velocity. The side-length of this simulation domain is chosen to be the MFP of Neon at STP conditions, and the domain is filled with 51505 molecules to achieve a gas density of 0.9011 kg/m^3.

Figure 1(a) shows the recorded MFP as the simulation progresses in time. The MD measurements relax to an MFP value of 1.221×10^{-7} m, that differs from the theoretical value of MFP by only 0.96%. The simulations also recorded the number of binary inter-molecular collisions (by discounting a molecule as undergoing a binary collision if its counterpart molecule is already undergoing a collision, i.e. a molecule with $col = 0$ cannot collide with a molecule with $col = 1$). At standard density, binary collisions

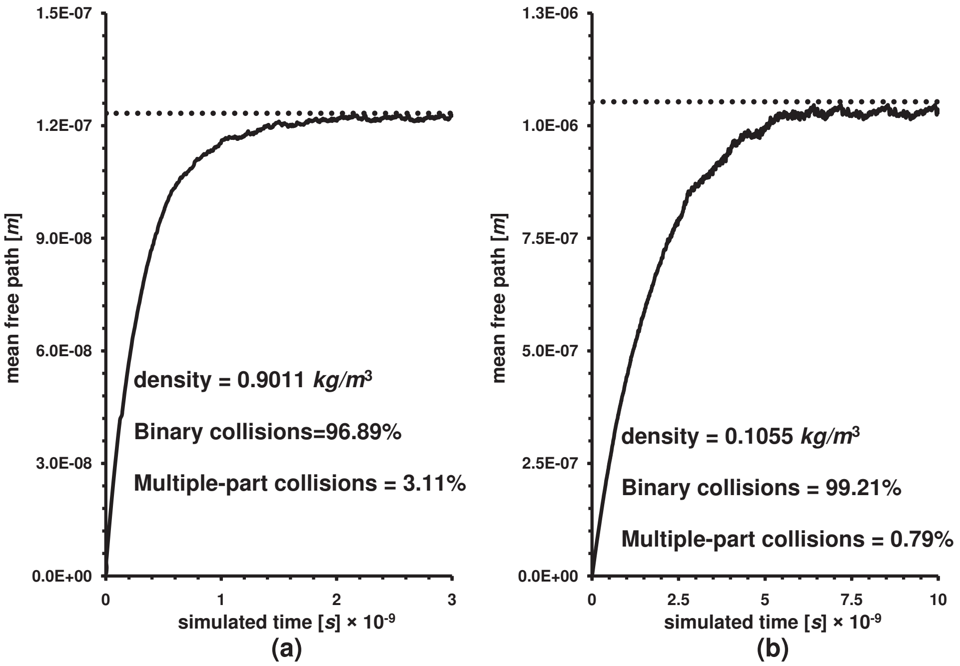

Figure 1. Relaxation to steady-state of the measured mean free path as the simulation progresses, for gas densities of (a) 0.9011 kg/m^3 and (b) 0.1055 kg/m^3. The theoretical values of the mean free path in each case are given by the straight dotted lines [4].

account for 96.92% of all collisions, the remainder being multiple-molecule collisions. If only binary collisions are allowed to contribute to the MFP measurement we retrieve an MFP of 1.262×10^{-7} m, which is close to the kinetic value of 1.255×10^{-7} m given through [3]:

$$\lambda_k = \frac{m/N_{Av}}{\pi \rho \sigma^2 \sqrt{2}}, \tag{2}$$

where $N_{Av} = 6.0221415 \times 10^{23}$ is Avogadro's number. This indicates that the kinetic theory description of MFP is accurate if collisions are purely binary, as expected.

We then test a rarefied case: Neon gas of density 0.1055kg/m^3. The side-lengths of the simulation cubic domain were increased to $2.5\lambda_{Ne}$, and the simulations run up to 10×10^{-9} s of problem time because, with a reduced frequency of inter-molecular collisions, the steady-state MFP is reached more slowly. Figure 1(b) shows the MFP measurements from the simulations. As expected in this rarefied case, the equilibrium kinetic value of MFP given by (2) differs more markedly from the deterministically-simulated MFP, in this case by about 2.31%. More than 99% of the inter-molecular collisions are binary, and fluctuations in the steady-state MFP value increased.

3.1.2. Collision rates and free path distributions Besides the value of the mean free path, the distribution of individual molecular free paths is also of interest [3]. For a group of similar gas molecules moving at speed $\overline{v}$ with a collision rate of $\dot{\theta}_v$, the molecular mean free path is $\lambda = \overline{v}/\dot{\theta}_v$. If the gas molecules are in thermodynamic equilibrium, then the distribution of free path lengths, $\psi(r)$, can be derived as [3]:

$$\psi(r) = \lambda^{-1}p(r) \qquad \text{with} \qquad p(r) = \exp(-r/\lambda), \tag{3}$$

where $p(r)$ is the probability of a molecule traveling distance r without experiencing any collision with other moving molecules in the group. If the gas is not bounded, the MFP of the gas molecule ensemble is then simply $\int_0^\infty r\psi(r)dr = \lambda$. By *thermodynamic equilibrium* we mean that the probability of a certain microscopic state, averaged over the details of the interactions, does not change in time or space [8]. So (3) is only valid under equilibrium conditions, i.e. if $\dot{\theta}_v$ is constant or fluctuations in $\dot{\theta}_v$ are negligible.

Figure 2 shows the variation of collision rate per unit number density with MD simulation time, for gas densities of 0.9011 kg/m^3 and 0.1055 kg/m^3. At atmospheric density conditions, Fig. 2(a), the mean and standard deviation of the collision rate are 4.1×10^{-11} and 9.49×10^{-12}, respectively, so the temporal fluctuations are low. For the rarefied case, Fig. 2(b), the fluctuations are significantly higher and the ratio of standard deviation to the mean of collision rate is around 0.77. This indicates that the thermodynamic equilibrium assumption of a collision rate constant in time is not valid in rarefied conditions. Consequently, the probability distribution of free paths is not necessarily exponential in form in the rarefied case.

Our MD results allow us to test other forms of distribution function for the rarefied case. We note that non-equilibrium transport is often better described using Lévy or power-law statistics [9, 10]. Montroll & Scher [10] pointed out that a finite moment of the probability distribution function implies an exponential character of the randomness. A distribution function with diverging higher-order moments, such as the standard deviation, is essential to non-equilibrium transport. In transient photoconductivity experiments, and the adsorption of ions in semiconductors, concentration distributions may have a long tail such that the standard deviation is diverging [11]. This long-tail problem is common to various flows in non-uniform media, in many fields such as chemical engineering and environmental sciences [12].

Montroll & Scher [10] and Schlesinger [13] showed theoretically that anomalous transport is characteristic of a distribution function with diverging higher-order moments, e.g. a power-law (PL) form for the distribution function. Second moments (i.e. the standard deviation) diverge for many PL functions used to describe the probability density distribution of electrons in photoconductivity experiments.

We hypothesize that the molecular free paths in a rarefied gas follow a power-law (PL) probability distribution function. We therefore investigate the following molecular free path distribution function [16]:

$$\psi(r) = C(a + r)^{-n}, \tag{4}$$

where a and C are constants with positive values determined through the zeroth and first moments. A gas has a finite MFP value, so the first moment of the distribution function is required to be finite. The range of values for the exponent n can be obtained

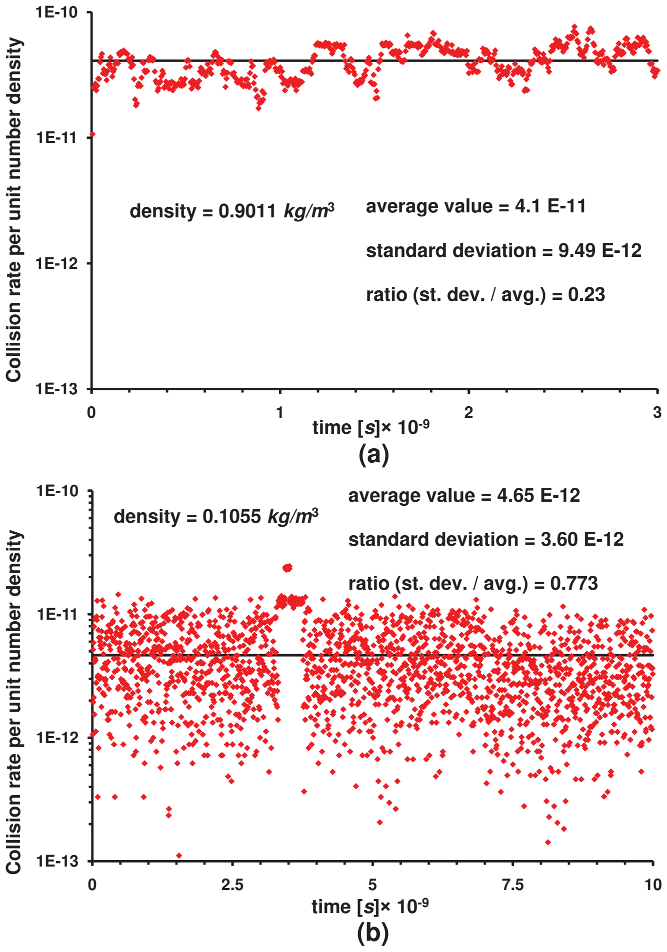

Figure 2. Collision rate per unit number density as a function of simulation time, for gas densities (a) 0.9011 kg/m^3 and (b) 0.1055 kg/m^3. The mean values of all samples are indicated by the straight lines.

by making one of the higher-order moments divergent. Zeroth and first moments are given as follows:

$$1 = \int_0^\infty C(a+r)^{-n} dr, \tag{5}$$

$$\lambda = \int_0^\infty Cr(a+r)^{-n} dr. \tag{6}$$

Equation (5) requires the probability to range only from zero to one; (6) defines the unconfined MFP value. It then follows that $C = (n-1)a^{n-1}$ and $a = \lambda(n-2)$. If $n > 2$ then $a > 0$, otherwise the distribution function is negative. The standard deviation (second moment) of the distribution function (4) diverges only for $n \leq 3$; so $2 < n \leq 3$. If we wish to make the i^{th} moment diverging, then $\max(n) = i+1$. If $n \to \infty$, the distribution function will have finite moments, which is the condition required of an equilibrium distribution function of exponential form. For a finite n, the distribution function describes a system deviating from equilibrium. So n acts as a decisive parameter to define the extent of deviation from equilibrium.

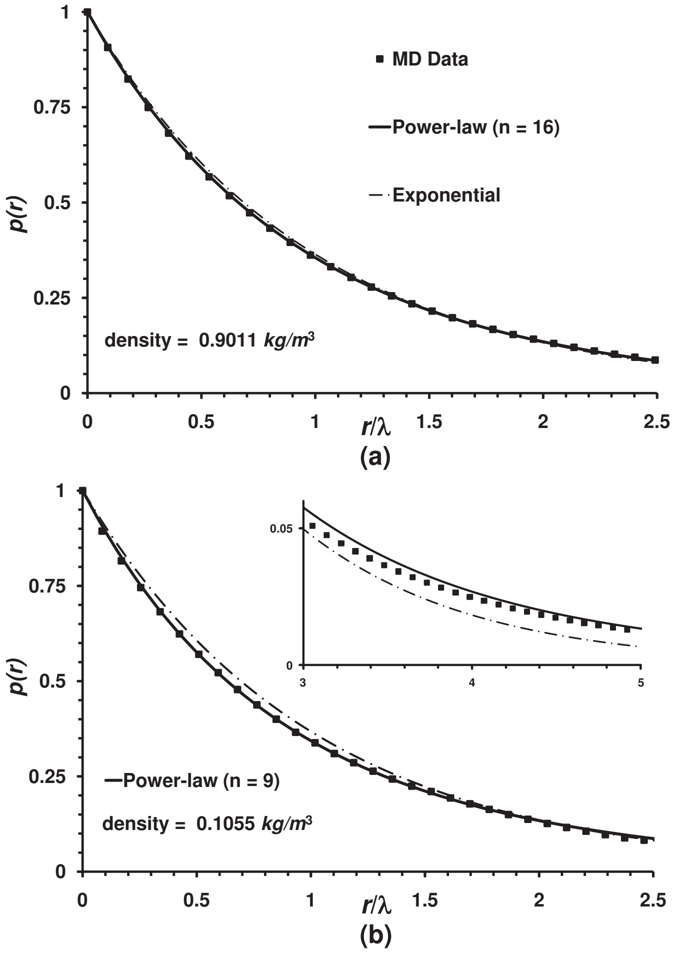

Figure 3. Probability molecules experience a collisionless travelling distance r/λ, in Neon gas of density (a) 0.9011 kg/m^3 and (b) 0.1055 kg/m^3. Molecular dynamics measurements are compared with the exponential and power-law distribution functions. Power-law exponent n values are 16 and 9 in cases (a) and (b), respectively.

Figure 3 presents our MD results for the probability a molecule travels a distance r/λ without experiencing a collision, at both atmospheric and rarefied conditions (where λ refers to the theoretical MFP at the corresponding densities). At atmospheric density, both MD measurements and the power-law model agree well with the classical exponential distribution function. In this case $n = 16$ is used in the power-law model to fit the MD data, and this larger value of n conveys that the system is quite close to equilibrium. Minor deviations from the exponential distribution are noticed, and this is probably due to the consideration of multiple particle collisions.

However, in the low density case, Fig. 3(b), the deviations between the MD measurements and the classical distribution function are significant, with the discrepancies relatively higher at the longer free paths (see inset of this figure). The power-law model with an exponent n value of 9 gives good agreement with the MD data, and this decrease in n illustrates that the system is relatively more non-equilibrium.

Both the MD data and the power-law function predict a long tail to the distribution function, while classically there is a much faster decay of free paths. A faster decay indicates the system does not have many longer flights of molecules, and it follows the Brownian motion described by Einstein [14]. However, this is only valid for times much larger than a characteristic time that, in turn, is much larger than the times characterising molecular collisions: this condition may not be fulfilled under rarefied conditions. The MD data show longer Lévy-type free flights of molecules, and the long tail of the distribution function implies higher-order moments are diverging.

3.2. Confined gases

The mean free path of the gas molecule ensemble approaches the theoretically predicted value only if the gas is unbounded (i.e. $r = 0 \rightarrow \infty$). If a solid bounding surface is included in the system, some molecules will hit the surface and their free flight paths will be terminated. The MFP of all the gas molecules in the system will therefore be reduced due to this boundary limiting effect. Stops [15] derived such a geometry-dependent MFP but used the classical exponential free path distribution function; Dongari *et al* [16] have developed this further using the PL distribution (4).

We now make MD measurements of the MFP of gas molecules when bounding planar surfaces are part of the system, and compare our simulation results with other geometry-dependent MFP models [15, 16]. All our simulations are in a six-sided configuration, with two sides reflective bounding surfaces, and the other two pairs of sides periodic boundaries. This replicates a parallel plate configuration, with infinite width and length. The reflective surfaces are specular, i.e. the tangential velocity of molecules colliding with them is maintained, while the molecular normal velocity changes sign. Molecular reflections on the planar surfaces are recorded by setting t_{LC} to the current simulated time, as for gas inter-molecular collisions.

We investigate gases confined by both single and parallel planar surfaces: a gas molecule's collision with a surface terminates that molecule's free path, so the local MFP should be shortened in the near-wall region. In the single-surface case, we use domain side lengths of λ_{Ne} in the directions of the periodic boundaries, and $2\lambda_{Ne}$ in the bounding surface directions. One of the reflective wall surfaces is required to simulate the bulk of the gas, so all reflected molecules at this surface are set to have experienced a collisionless travel of one mean free path. This is done by setting $t_{LC} = t_C - \lambda_{Ne}/Sp_C$. The gas is represented by 102950 simulation particles, and the sampling of the local MFP, λ_{eff}, variation across the system is made over 2 nanoseconds of problem time, taken after 3 nanoseconds relaxation.

Figure 4 shows the variation of the normalized local MFP $\beta = \lambda_{\text{eff}}/\lambda_{Ne}$ with normalized distance from the bounding surface y/λ_{Ne}. The MD data agrees with the PL model for the free path (with an exponent $n = 3$), although minor deviations are noticed in the bulk region. Both the MD measurements and the PL results have a sharp gradient close to the surface, while the conventional exponential model has shallower

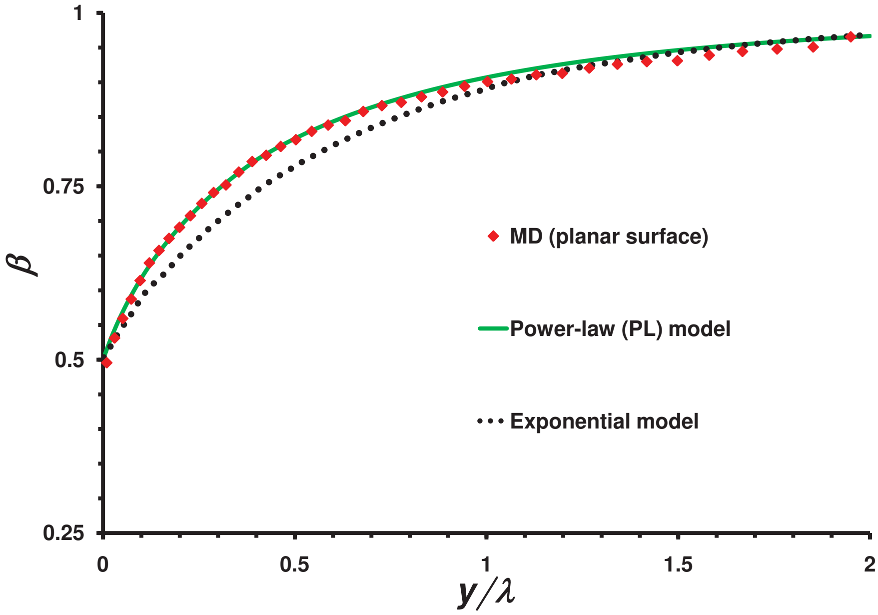

Figure 4. Variation of normalized mean free path, $\beta = \lambda_{\text{eff}}/\lambda_{Ne}$, with normalized distance from the surface, for the planar single-surface case. Comparison of MD simulation data with power-law (PL) [16] and exponential [15] MFP models.

gradients and underpredicts the MFP values in the wall vicinity. All three solutions agree on the MFP value in the bulk region, as expected.

For the parallel-surface case, a similar geometry is used and the Knudsen number is tuned by changing the gas density value. Results for the normalized local MFP between the two parallel surfaces are presented in Fig. 5. The total simulation time varied from 5 to 20 nanoseconds, based on the degree of rarefaction. At $Kn = 0.2$, the PL model with an exponent $n = 3$ is in fair agreement with the MD data in the near-wall region but deviates slightly in the bulk region. The exponential model underpredicts the MD data near-wall but shows fair agreement in the bulk. As the value of Kn increases the exponential model fails to predict the local MFP in the wall region, as well as in the bulk (so the exponential model results are not shown for comparison at $Kn = 2$). The MFP values predicted by the PL model compare very well to the MD data for both $Kn = 0.5$ and 1, although it overpredicts for $Kn = 1$ in the bulk. By $Kn = 2$ the PL model shows significant deviations from the simulation data and overpredicts in the near-wall region, although there is fair agreement in the bulk region. The MD data shows a relatively sharper gradient of effective MFP in the near-wall region, than the theoretical predictions.

4. Conclusion

The results of numerical molecular dynamics (MD) experiments support the argument that the molecular behaviour of rarefied gases is better described by Lévy or power-

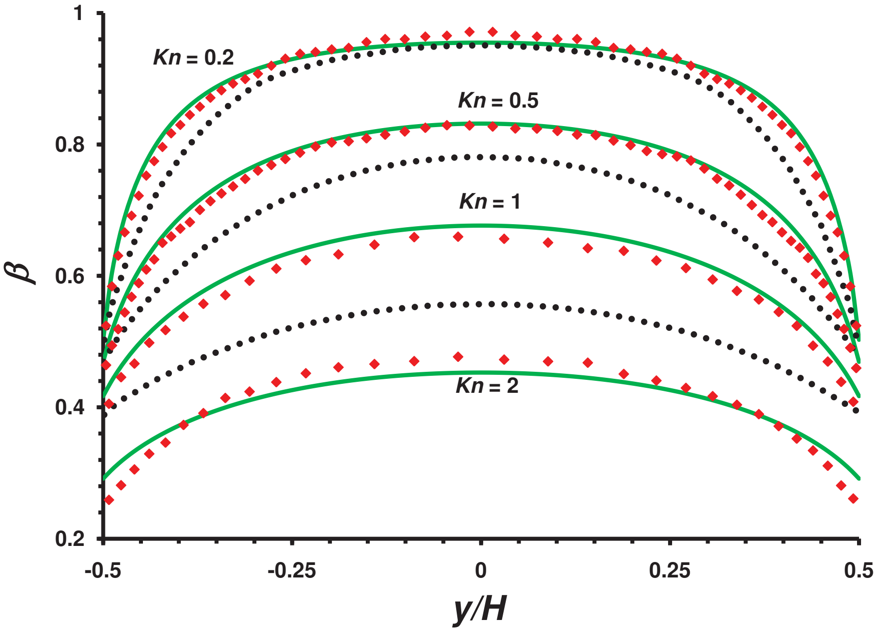

Figure 5. Variation of normalized mean free path, $\beta = \lambda_{\mathrm{eff}}/\lambda_{Ne}$, with normalized distance from a surface, for the planar parallel-surfaces case. Comparison of molecular dynamics simulation data with power-law (PL) [16] and exponential [15] effective local MFP models for Knudsen numbers ranging from the slip to the continuum-transition regimes. Symbols and lines are as in Fig. 4.

law types of distribution functions than the classical exponential function (or variations thereof). Inter-molecular collision rate fluctuations are significantly high in the rarefied case, which highlights the non-equilibrium nature of the gas. The MD-measured probability distribution of molecular free paths is distinguished by having a long tail that is not present in the classical distribution function.

The MD simulations in this paper are for simple geometries with planar surfaces, and for isothermal gases with no flow. It is important to explore further any new description of the molecular behaviour of rarefied gases through simulations of gases in complex geometries, with specular-diffusive and explicit walls, and also for non-isothermal cases.

Confirmation of this power-law behaviour of rarefied gases may help in the development of both new constitutive models for rarefied gases in micro and nano systems, and particle-mesh methods (such as the DSMC technique) that require a mesh that relates to the (local) molecular mean free path.

Acknowledgments

The authors would like to thank Matthew Borg of the University of Strathclyde, and Erik Arlemark of the Technische Universiteit Eindhoven, for very useful discussions. The research leading to these results has received funding from the European

Community's Seventh Framework Programme FP7/2007-2013 under grant agreement ITN GASMEMS no. 215504. JMR would like to thank the Royal Academy of Engineering and the Leverhulme Trust for support through a Senior Research Fellowship.

References

[1] Karniadakis G, Beskok A and Aluru N 2005 *Microflows and Nanoflows: Fundamentals and Simulation* (Springer)

[2] Rapaport D C 2004 *The Art of Molecular Dynamics Simulation* (2nd ed. Academic Press)

[3] Kennard E H 1938 *Kinetic Theory of Gases with an Introduction to Statistical Mechanics* (McGraw-Hill, New York)

[4] Cercignani C 2000 *Rarefied Gas Dynamics: from Basic Concepts to Actual Calculations* (Cambridge University Press, New York)

[5] OpenFOAM, The Open Source CFD Toolbox, http://www.opencfd.co.uk.

[6] Macpherson G B and Reese J M 2008 *Mol. Sim.* **34** 97

[7] Macpherson G B, Borg M K and Reese J M 2007 *Mol. Sim.* **33** 1199

[8] Cercignani C 1990 *Mathematical Methods in Kinetic Theory* (Plenum Press, New York)

[9] Fa K S and Lenzi E K 2003 *Phys. Rev. E* **67** 061105

[10] Montroll E W and Scher H 1973 *J. Stat. Phys.* **9** 101

[11] Scharfe M E 1970 *Phys. Rev. B* **2 (12)** 5025

[12] Grolimund D, Borkovec M, Federer P and Sticher H 1995 *Environ. Sci. Techno.* **29** 2317

[13] Shlesinger M F 1974 *J. Stat. Phys.* **10** 421

[14] Einstein A 1956 *Investigations on the Theory of Brownian Movement* (Dover, New York)

[15] Stops D W 1970 *J. Phys. D: App. Phys.* **29** 685

[16] Dongari N, Zhang Y H and Reese J M 2010 *Proc. ASME ICNMM2010 (Montreal)* 30743