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Comparison of Molecular Dynamics and Kinetic Modeling of Gas-Surface Interaction

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Abstract. The interaction of a dilute monatomic gas with a solid surface is studied by Molecular Dynamics (MD) simulations and by numerical solutions of a recently proposed kinetic model. Following previous investigations, the heat transport between parallel walls and Couette flow have been adopted as test problems. The distribution functions of re-emitted atoms and the accommodation coefficients obtained from the two techniques are compared in different flow conditions. It is shown that the kinetic model predictions are close to MD results.

Keywords: gas surface interactions, accommodation coefficients, Enskog equation, Monte Carlo, Molecular Dynamics simulations

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INTRODUCTION

A drawback of phenomenological gas-surface scattering kernels [1] is represented by the difficulty of establishing relationships between the models coefficients (often accommodation coefficients) and the fundamental physical parameters determining the interaction between gas and wall molecules. In absence of such relationships, tuning of the model coefficients should be repeated on any change of physical conditions. The need of a deeper understanding of gas-wall interaction has triggered a large number of studies in which molecular dynamics (MD) techniques have been used to investigate the dynamics of atoms and molecules in proximity of a solid wall whose atomic structure is explicitly taken into account. Simulations of atomic beams scattering from surfaces [2] have shown typical lobular reemission patterns [3] which are not well approximated by Maxwell’s kernel [1]. Thermal and momentum accommodation coefficients of various atomic and molecular gases in contact with metal surfaces have been obtained [4, 5]. Furthermore, the distribution function of scattered molecules has been obtained and compared with Maxwell’s model predictions [5] for various values of the molecular interaction parameters [6]. Although notable efforts have been made to reproduce MD results by simpler unifying models [4, 5, 7], the proposed methods still rely on phenomenological coefficients to be fitted to MD data. Hence, molecular dynamics simulations remain the only tool for a treatment of gas-wall interaction based on first principles. The computational effort associated with atomistic simulations can be reduced by the development of hybrid simulation methods [5, 8] in which the use of MD is limited to the calculation of the motion of wall atoms/molecules and of the gas atoms/molecules interacting with walls. Atomic/molecular interactions in the gas phase are computed by DSMC [9]. Although feasible, hybrid simulations still remain computationally demanding, since MD limits the rate of the faster Monte Carlo algorithm.

Recently, a kinetic model [10] for fluid-wall interaction has been proposed to replace the detailed deterministic MD calculation of atomic/molecular interaction with a kinetic equation derived from Enskog’s theory of dense fluids [11]. The structure of the resulting kinetic equation is not simple, but it can be solved numerically by the same Monte Carlo method used to compute interactions in the gas phase, thus eliminating the need of hybrid numerical methods. As is well known, Enskog’s theory is not free from phenomenological elements whose validity and limitations have to be carefully assessed. Accordingly, the aim of the present paper is to present an analysis of the kinetic model capabilities through comparisons with the results of MD simulations of a monatomic gas interacting with a solid. Comparisons are organized around the study of two specific applications: (a) the heat transfer in a monatomic gas confined between two infinite parallel plates kept at different temperatures, and (b) a simple Couette flow. The shapes of the distribution function of impinging and re-emitted atoms as well as the accommodation coefficients of energy and momentum have been determined from MD and the kinetic model for various values of flow parameters. Unlike previous MD investigations [4, 12, 13], gas-gas interaction has been suppressed in order to highlight the effects of gas-wall interaction.
Following Refs. [10], we consider a system composed by a monatomic fluid interacting with solid walls. Fluid molecules have mass \( m_1 \) and nominal diameter \( \sigma_1 \), whereas \( m_2 \) and \( \sigma_2 \) are the mass and nominal diameter of wall molecules, respectively. Fluid-fluid and fluid-wall interaction forces are obtained from the potentials \( \phi^{(11)}(\rho) \) and \( \phi^{(12)}(\rho) \) given by the following expressions:

\[
\phi^{(11)}(\rho) = \begin{cases} 
\frac{1}{\rho - \sigma_1} \rho < \sigma_1 \\
\rho \geq \sigma_1
\end{cases}
\phi^{(12)}(\rho) = \begin{cases} 
\frac{1}{\rho - \sigma_2} \rho < \sigma_2 \\
\rho \geq \sigma_2
\end{cases}
\]  

As shown above, \( \phi^{(11)} \) and \( \phi^{(12)} \) are obtained by superposing a soft tail to hard sphere potential determined by the hard sphere diameters \( \sigma_1 \) and \( \sigma_2 = (\sigma_1 + \sigma_2)/2 \). The adoption of simplifying assumptions about pair correlations [10] allows the derivation of the following kinetic equation for the one-particle distribution function \( f(\mathbf{r}, \mathbf{v}|t) \) of fluid molecules:

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \frac{\mathbf{F}(\mathbf{r}|t)}{m_1} \cdot \frac{\partial f}{\partial \mathbf{v}} = C^{(11)}(f,f) + C^{(12)}(f_w,f)
\]

The terms \( C^{(11)}(f,f) \) and \( C^{(12)}(f_w,f) \) represent the hard sphere collision integrals defined by the expression

\[
C^{(11)}(f,f) = \sigma_1^2 \int \left\{ \chi^{(11)}(\mathbf{r}, \mathbf{r} + \sigma_1 \hat{\mathbf{k}}) f(\mathbf{r} + \sigma_1 \hat{\mathbf{k}}, \mathbf{v}_1|t) f(\mathbf{r}, \mathbf{v}|t) - \chi^{(11)}(\mathbf{r}, \mathbf{r} - \sigma_1 \hat{\mathbf{k}}) f(\mathbf{r} - \sigma_1 \hat{\mathbf{k}}, \mathbf{v}_1|t) f(\mathbf{r}, \mathbf{v}|t) \right\} (\mathbf{v}, \cdot \hat{\mathbf{k}})^+ d\mathbf{v}_1 d^2\hat{\mathbf{k}}
\]

\[
C^{(12)}(f_w,f) = \sigma_2^2 \int \left\{ \chi^{(12)}(\mathbf{r}, \mathbf{r} + \sigma_2 \hat{\mathbf{k}}) f_w(\mathbf{r} + \sigma_2 \hat{\mathbf{k}}, \mathbf{v}_1|t) f(\mathbf{r}, \mathbf{v}|t) - \chi^{(12)}(\mathbf{r}, \mathbf{r} - \sigma_2 \hat{\mathbf{k}}) f_w(\mathbf{r} - \sigma_2 \hat{\mathbf{k}}, \mathbf{v}_1|t) f(\mathbf{r}, \mathbf{v}|t) \right\} (\mathbf{v}, \cdot \hat{\mathbf{k}})^+ d\mathbf{v}_1 d^2\hat{\mathbf{k}}
\]

where \( f_w \) is the distribution function of wall molecules. The contact values of the correlation function are represented by \( \chi^{(11)} \), for pairs formed by two fluid molecules, and by \( \chi^{(12)} \), for pairs formed by one gas and one wall molecule. The self-consistent force field \( F(\mathbf{r}|t) \) is defined as

\[
F(\mathbf{r}|t) = F^{(11)}(\mathbf{r}|t) + F^{(12)}(\mathbf{r})
\]

\[
F^{(11)}(\mathbf{r}|t) = \int_{|\mathbf{r}_1 - \mathbf{r}| > \sigma_1} d\phi^{(11)} \frac{\mathbf{r}_1 - \mathbf{r}}{|\mathbf{r}_1 - \mathbf{r}|} n(\mathbf{r}_1|t) d\mathbf{r}_1 \quad F^{(12)}(\mathbf{r}) = \int_{|\mathbf{r}_1 - \mathbf{r}| > \sigma_2} d\phi^{(12)} \frac{\mathbf{r}_1 - \mathbf{r}}{|\mathbf{r}_1 - \mathbf{r}|} n_w(\mathbf{r}_1) d\mathbf{r}_1
\]

being \( F^{(11)}(\mathbf{r}|t) \) and \( F^{(12)}(\mathbf{r}) \) the contributions of fluid-fluid and fluid-wall long range interaction. In absence of long range spatial correlations, \( F^{(11)}(\mathbf{r}|t) \) and \( F^{(12)}(\mathbf{r}) \) are linear functionals of the fluid number density \( n(\mathbf{r}|t) \) and wall number density \( n_w(\mathbf{r}) \), respectively. It is worth stressing that, in the framework of the present model, fluid-fluid interaction is not present in the form of a boundary condition, but it is taken into account through an explicit, although approximate, microscopic model. In particular, it is assumed that the motion of a gas atom in the vicinity of the wall is determined by the stationary force field \( F^{(12)}(\mathbf{r}) \) generated by the long range potential tails of wall atoms, when the distance \( \rho \) exceeds \( \sigma_2 \). At shorter distances, the effect of intense repulsive forces is added by the collision integral \( C^{(12)}(f,f_w) \) which describes binary elastic collisions between gas and wall molecules. It is therefore assumed that repulsion on a gas molecule is caused just by the closest wall molecule. However, the collective effect of nearby wall molecules on the frequency of binary encounters is felt through \( \chi^{(12)} \). Although no explicit assumption is made about the interaction among wall atoms, it is assumed that walls are in a prescribed state of equilibrium which is not altered by the interaction with the gas phase. Hence, the velocity distribution function \( f_w \) will take the following form

\[
f_w(\mathbf{r}, \mathbf{v}) = \frac{n_w(\mathbf{r})}{(2\pi R_2 T_w(\mathbf{r}))^{3/2}} \exp \left\{ -\frac{[\mathbf{v} - \mathbf{u}_w(\mathbf{r})]^2}{2R_2 T_w(\mathbf{r})} \right\}
\]

being \( n_w(\mathbf{r}) \), \( T_w(\mathbf{r}) \) and \( \mathbf{u}_w(\mathbf{r}) \) the wall atoms number density, temperature and mean velocity, respectively. The gas constant \( R_2 \) is defined as \( \frac{k_B}{m_2} \), where \( k_B \) is the Boltzmann constant. Although good approximations are available for the computation of \( \chi^{(11)} \), the calculation of the fluid-wall pair correlation function is more problematic. For the sake of
simplicity, it has been assumed that excluded volume effects are determined solely by wall molecules through their number density \( n_w \). The specific form of \( \chi^{(12)}(n_w) \) is taken from an approximate expression for the contact value of the pair correlation function of a single component hard sphere gas in uniform equilibrium [14]:

\[
\chi^{(12)}(n_w) = \frac{1}{2} \frac{2 - \eta_{12}}{(1 - \eta_{12})^3}, \quad \eta_{12} = \frac{\pi}{6} n_w \sigma_{12}^3
\]

where \( \eta_{12} \) is the volume fraction occupied by hard sphere cores. Eq. (8) provides a very accurate approximation of the contact value of the uniform equilibrium pair correlation function in a single component hard sphere gas, but its use in the present context is questionable. However, the physical consequences of the above assumption are quite reasonable. Actually, it is easily shown that, in the presence of a wall density gradient, the hard sphere term produces a net repulsive force proportional to \( \chi^{(12)}(n_w) \) and strong enough to confine the fluid [10].

**MOLECULAR DYNAMICS MODEL**

Our MD model to study the one-dimensional heat flow in a microchannel consists of two parallel plates of length \( L_y \) at a distance \( L_x \) apart from each other, and of gas molecules confined between these two walls. Both plates have their own temperature, \( T_c \) (cold wall) and \( T_h \) (hot wall) respectively, where this temperature is uniform on the plate surface and constant in time. The cold wall is kept at constant temperature of 300K. Different temperatures are considered for the hot wall, resulting in temperature ratios \( T_h/T_c \) varying and taking the following values: 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0. The gas consists of spherical particles of diameter \( \sigma_1 \) and mass \( m_1 \), at temperature \( T_{ref} \). The density of the gas can be expressed as \( n_1 \), being the number of particles per unit of volume, or using a reduced density \( \eta \), which also takes the particle sizes into account and is related to the number density as \( \eta = \pi n_1 \sigma_1^3 / 6 \). The distance between the plates, in the \( x \)-direction, is always such that both plates are only a few mean free paths \( \lambda \) apart.

In MD, the Lennard-Jones (LJ) potential is used to model the explicit interactions between the gas-gas, gas-wall and wall-wall molecules [15]. The LJ potential serves our purpose of studying the dependency of the accommodation coefficient on the gas-wall interactions and it is given by the relation:

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

where \( \varepsilon \) is the interaction strength and \( \sigma \) is the core diameter. This LJ potentials are especially appropriate for noble gases but it captures also the essence of all systems and can thus in principle be used for metals [16, 17].

The parameters used in our MD model are expressed in reduced units. The system consists of the following reduced units: the unit for length \( \sigma^* \), the unit for mass \( m^* \) and the unit for energy \( \varepsilon^* \). Other units can be derived out of these
choices [15, 18]. The two walls consisting of 18000 particles each forming a face centered cubic (fcc) lattice are placed in a box of size 80.00σ×46.89σ×46.89σ and are separated from each other in x direction (L_x = 32σ). We name one wall hot (h) and the other one cold (c). The total number of gas particles in the box is 1300 corresponding to a number density n_1 = 0.01σ^-3 simulated. The temperature of the two plates (T_c and T_h) can be controlled by coupling them to a heat bath. The mass and the size of wall particles are taken as unity: m_w = m_m*, and σ_w = 1σ.*

The thermal problem and the Couette flow is going to be investigated for two systems: a Xenon gas and an Argon gas confined between two Platinum walls. In case of a Couette flow, walls are moving with relative velocity 2u_w. The speed ratio is defined as S_w = u_w/√(2k_B T/m_1), where m_1 is the mass of the gas molecule. The following speed ratios are considered in the simulations: S_w = 0.1 and S_w = 0.25. The fluid/wall mass and radius ratios are the following: for Xe-Pt: m_1/m_2 = 0.673, σ_1/σ_2 = 1.62, and for Ar-Pt: m_1/m_2 = 0.20, σ_1/σ_2 = 1.35. The other parameters like the interaction strength (ε) and the position of the minima (σ) in the LJ potential were taken to correspond with the gas-wall interaction parameters considered by Yamamoto in [4, 5]. Yamamoto et al. used the Morse potential to describe the Xe-Pt and Ar-Pt gas-wall interactions and the shape of this potential is different than the LJ potential as we can see in figure 1a. The units of our MD simulations [15] [ε*, σ*] are given by ε*/k_B = 628.58K and σ* = 2.523Å. The set of parameters for the LJ potential used in our MD simulations is the following: ε_Xe-Pt = 0.5076ε* (ε_Xe-Pt/k_B = 319.1K), σ_Xe-Pt = 1.13σ*, ε_Ar-Pt = 0.2132ε* (ε_Ar-Pt/k_B = 134.7K), σ_Ar-Pt = 1.62σ*. The walls are kept together by a relatively strong interaction strength ε_{Pt-Pt} = 6.0ε* in the LJ potential. For the gas-gas interactions ε has been set equal to zero, corresponding to free molecular flow. Every MD simulation consists of two parts. In the first part the system is run until equilibrium is reached, and in the second part the macroscopic quantities are obtained. These simulations consist of 5000000 time steps and were executed on 8 cpu’s of an AMD Athlon 1800+ Beowulf cluster.

RESULTS

Equation (2) provides an approximate description of the fluid both in its gas and liquid phase. In the dilute gas limit, the field $F^{(1)}$ becomes negligible, whereas the collision term $C^{(1)}(f, f')$ takes the usual form of the Boltzmann collision term for a hard sphere gas. In this case, the space and time scales of gas-surface interaction are much shorter than
the mean free time and path in the gas phase. Hence, it is possible to compute the gas motion solving the Boltzmann equation by a traditional DSMC scheme in which walls are represented by smooth and structureless surfaces. However, when a gas molecule hits a wall its motion is computed by the following linear and one-dimensional version of Eq. (2), till it is re-emitted into the gas phase:

$$\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + \frac{F_x^{(12)}(x)}{m_1} \frac{\partial f}{\partial v_x} = C^{(12)}(f_w, f)$$

with

$$F_x^{(12)}(x) = 2\pi \phi^{(12)}(\sigma_{12}^{(12)}) \left[ \int_{|x-x'|>\sigma_{12}} (x'-x) n_w(x') |r| dx' + \int_{|x-x'|\leq\sigma_{12}} (x-x) n_w(x') dx' \right]$$

Eq. (10) is solved in the one dimensional domain (−σ_{12}, σ_{12}). The coordinate x spans the direction normal to the wall whose density profile is approximated as a step function n_w(x) = \pi_w[1 - H(x)], being H(x) the Heaviside function and π_w the constant wall density value. The adopted numerical scheme is a simple variant of the DSMC scheme for dense gases described in Ref. [19]. In a typical application the algorithm computes \(2 - 5 \times 10^4\) trajectories per second on 2.2 GHz dual core CPU. If T_{ref} is a reference temperature value, σ_1, σ_1/√(k_B T_{ref}) and m_1 can be adopted as units for length, time and mass, respectively. The gas-surface interaction model is then characterized by the following dimensionless parameters: \(\sigma_{12}/\sigma_1, \phi^{(12)}/k_B T_{ref}, \gamma^{(12)}, m_2/m_1, \eta_w = \frac{\pi_w}{m_w} \sigma_1^3\). The nature and number of additional parameters depend on the problem at hand. In the case of the heat transfer problem, the temperature ratios \(T_c/T_{ref}\) and \(T_h/T_c\) have to be added to the parameters listed above, being \(T_c\) and \(T_h\) the temperatures of the cold and hot walls. In the case of Couette flow, it is assumed that the walls are kept at the same temperature \(T_w\) and move with opposite velocities ±u_c. Hence, the temperature ratio \(T_w/T_{ref}\) and \(S_w = \frac{u_w}{\sqrt{2k_B T_w}}\) are the additional parameters. The following procedure has been followed to match model gas-surface interaction parameters to MD potentials: the depth of the potential well \(\Phi^{(12)}\) has been set equal to the corresponding MD potential, the exponent \(\gamma^{(12)}\) has been set equal to 6 to match the LJ attractive tail, the ratio \(\sigma_{12}/\sigma_1\) has been set equal to one while \(\eta_w\) has been set equal to 0.7 (reasonable for solid platinum, used in MD simulation). Specifying the above parameters completely specifies the mean field \(F_x^{(12)}(x)\). The strength of the repulsive effects has been tuned through the parameter \(\eta_{12}\), which has been considered as an independent parameter, slightly forcing the model structure. The reference temperature \(T_{ref}\) has been set equal to 300 K in all simulations. The comparison of kinetic model and MD results has been mostly based on accommodation coefficients of kinetic energy, \(\alpha_k\), normal momentum \(\alpha_n\) and tangential momentum \(\alpha_t\). However, the distribution functions of impinging and re-emitted molecules have also been obtained. Figures 1b and 1c present the reduced distribution functions of normal and tangential velocity components of impinging and re-emitted Xe atoms scattered from a Pt surface in the case of the heat transfer problem. The kinetic model and MD results are in good agreement. Moreover, the distribution functions of impinging and outgoing atoms are well represented by anisotropic Maxwellians, in agreement with previous findings [4]. Figure 2 summarizes the results of computed accommodation coefficients for the Ar – Pt system. Energy and normal momentum accommodation have been obtained from heat transfer simulations whereas tangential momentum accommodation coefficients have been obtained from Couette flow simulations. In Figure 2a and 2b the kinetic model results have been compared with MD results obtained by Yamamoto et al.. It should be observed that \(\eta_{12}\) is the only adjustable model parameter and the choice \(\eta_{12} = 0.7\) allows to obtain results close to all MD accommodation coefficients, except at low value of \(T_h/T_c\). Changing the shape of gas-solid potential from Morse’s to Lennard-Jones’s, as described in section 3, modifies the behavior of the system. A series of MD simulations has been performed by suppressing gas-gas interaction thus obtaining \(\alpha_k, \alpha_n\) and \(\alpha_t\) in free molecular flow conditions. In the heat transfer configuration, accommodation coefficients have been computed at both walls. As shown in Figure 2c and 2d, the LJ potential produces slightly lower values of the normal accommodation coefficient whereas the \(\alpha_k, \alpha_n\) are higher than those computed from Morse potential. Changing \(\eta_{12}\) to 0.575 reduces the repulsive effects of the hard sphere term and allows the kinetic model to produce good predictions of \(\alpha_k, \alpha_n\) and \(\alpha_t\) at the cold wall. However, the model overestimates \(\alpha_k\) and \(\alpha_t\) at the hot wall, although the qualitative behavior is correctly captured. When the Xe – Pt system is considered, the mass ratio and potential parameters are changed accordingly. As shown in Figures 3a and 3b, the comparison with Yamamoto’s results shows that the kinetic model can correctly predict \(\alpha_k\) by setting \(\eta_{12} = 0.5\). However, \(\alpha_n\) is again overestimated and \(\alpha_t\) is slightly below MD values. The behavior is confirmed by the free molecular simulations of the heat transfer with LJ gas-solid interaction, whose results are shown in Figures 3c and 3d. In this case, \(\eta_{12}\) has been kept equal to 0.5. Again, \(\alpha_k\) at the cold wall is very well predicted for all temperature ratios. At the hot wall the model predicts a slightly lower value of \(\alpha_k\) but the behavior is the correct one.
FIGURE 3. Comparison of kinetic model and MD predictions for accommodation coefficients for Xe – Pt system. (a) $\alpha_n$ and $\alpha_e$ as a function of $T_h/T_c$, from heat transfer simulations. Lines markings are the same as Figure 2. MD data from Ref. [13]. (b) $\alpha_t$ as a function of $S_w$ from Couette flow simulations. Lines markings are the same as Figures 3a, 3b. MD data from Ref. [12]. (c) $\alpha_n$ and $\alpha_e$ as function of $T_h/T_c$ from free molecular heat transfer simulations. Lines markings are the same as Figure 2c.

CONCLUSIONS

A model for the interaction of a monatomic gas with a solid surface has been formulated in the framework of the kinetic theory of dense fluids. The model is able to predict accommodation coefficients and it is easily translated into an efficient DSMC scheme. The comparison with MD simulations shows that, for a given system, quantitative agreement with all accommodation coefficients is not always obtained. However, discrepancies are not large and qualitative behaviors always match. Further research activity will be devoted to improving the model capabilities.

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