A Kinetic Model for Fluid-Wall Interaction

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Summary

• Motivation
• Kinetic model structure and basic equations.
• Application to test problems and comparison with MD results
• Concluding remarks
Motivation

The traditional approach to gas-surface interaction modeling is based on phenomenological scattering kernels in the form (Maxwell, Cercignani-Lampis...)

$$(v \circ n)f(r, v|t) = \int_{v_1 \circ n < 0} K_w(v_1 \rightarrow v)|v_1 \circ n|f(r, v_1|t) dv_1 \quad v \circ n > 0 \quad (1)$$

- **Advantages:** theoretical and computational simplicity
- **Disadvantages:** they contain a few free parameters (typically accommodation coefficients). Their relationships with fundamental interaction properties (intermolecular potentials) can be determined with great difficulty. More often they are fitted to match experimental results, but tuning has to be repeated if physical conditions change.

Modeling gas-surface interaction by solving the microscopic dynamics of wall and gas atoms/molecules is possible by Molecular Dynamics (MD) techniques.

- **Advantages:** model is based on fundamental interaction properties.
- **Disadvantages:** only numerical approach is possible; computationally expensive
A Kinetic Model?

Computational efforts can be reduced by hybrid simulation methods in which DSMC is used to describe collisions in the gas phase whereas MD use is limited to describe interactions among wall atoms/molecules and interactions between wall and gas atoms/molecules [Yamamoto (2006), Nedea et al. (2006)].

- For rarefied gas flows hybrid methods are still quite demanding in terms of computational resources.

An alternative approach to fluid-wall interaction can be based on the use of a kinetic equation which describes “collisions” between fluid and wall atoms/molecules.

- **Advantages**: based on fundamental interaction properties, solved by DSMC (no hybrid method is necessary), approximate solutions possible.

- **Disadvantages**: complex mathematical structure, numerical treatment necessary.
The idea is not new

1. Cercignani (1988) has shown that Cercignani-Lampis model can be derived by modeling the motion of gas molecules adsorbed into the solid matrix by a Fokker-Planck equation.

2. More recently, Pozhar and Gubbins (1991,1993) have proposed a rather general kinetic formulation of non-uniform dense fluids in which the fluid-wall interaction is described by a collision integral.

However

1. The Fokker-Planck equation does not take into account non-local effects of molecular interaction which play a very important role in the vicinity of the solid boundary.

2. Non-local effects are correctly included in the treatment described by Pozhar and Gubbins, but wall molecules are given an infinite mass thus limiting the model capabilities in predicting the correct momentum and energy exchanges between the wall and the fluid phase.
Kinetic Model Structure and Basic Equations

- We consider a monatomic gas whose atoms have mass $m_1$
- The gas phase interacts with walls whose atoms have mass $m_2$
- It is assumed that atoms in the gas and solid phases interact pairwise through a potential $\phi_{12}(\rho)$ in the form

$$\phi_{12}(\rho) = \begin{cases} +\infty & \rho < \sigma_{12} \\ -\overline{\phi}_{12}\left(\frac{\rho}{\sigma_{12}}\right)^{-\gamma_{12}} & \rho \geq \sigma_{12} \end{cases}$$

(2)

- $\phi_{12}(\rho)$ depends only on the distance $\rho$ between the centers of two interacting atoms and it results from the superposition of a repulsive hard sphere potential and a soft tail.
- The hard sphere diameter is defined as $\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$, being $\sigma_1$ and $\sigma_2$ the hard sphere diameters of gas and wall atoms, respectively.
- The behavior of the soft potential tail is determined by the right limit of $\phi_{12}(\rho)$ at $\rho = \sigma_{12}$, $-\overline{\phi}_{12}$, and by the value of the positive exponent $\gamma_{12}$. 
Neglecting atomic interactions in the gas phase, the following equation holds

\[
\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \circ \nabla_{\mathbf{r}_1} f_1 = \nabla_{\mathbf{v}_1} \circ \left[ \int_{\rho > \sigma_{12}} \hat{k} \frac{d\phi_{12}}{d\rho} f_{12}(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2|t) \, d\mathbf{r}_2 \, d\mathbf{v}_2 \right] + \\
\sigma_{12}^2 \int \left[ f_{12}(\mathbf{r}_1, \mathbf{v}_1^*, \mathbf{r}_1 + \sigma_{12} \hat{k}, \mathbf{v}_2^*|t) - f_{12}(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1 - \sigma_{12} \hat{k}, \mathbf{v}_2|t) \right] (\mathbf{v}_r \circ \hat{k})^+ \, d\mathbf{v}_2 \, d^2\hat{k}
\]  

(3)

- \( f_1(\mathbf{r}_1, \mathbf{v}_1|t) \) denotes the one-particle distribution function of velocities \( \mathbf{v}_1 \) of gas atoms at spatial location \( \mathbf{r}_1 \) at time \( t \).
- \( f_{12}(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2|t) \) is the distribution function of pairs formed by one gas atom, having position \( \mathbf{r}_1 \) and velocity \( \mathbf{v}_1 \), and one wall atom located at \( \mathbf{r}_2 \) with velocity \( \mathbf{v}_2 \).
- The first integral at r.h.s of Eq. (3) represents the soft tail contribution to the rate of change of \( f_1 \), being \( \rho = ||\mathbf{r}_2 - \mathbf{r}_1|| \) and \( \hat{k} \) the unit vector \( \frac{\mathbf{r}_1 - \mathbf{r}_2}{\rho} \).
- The contribution of hard collisions is given by the second integral where \( \mathbf{v}_1^* \) and \( \mathbf{v}_2^* \) are the post-collisional velocity vectors in a hard sphere impact, \( \mathbf{v}_r \) is the relative velocity \( \mathbf{v}_2 - \mathbf{v}_1 \). The integral over \( \hat{k} \) is limited to the hemisphere where the condition \( \mathbf{v}_r \circ \hat{k} > 0 \) holds.
Within the limits of the assumptions described above, Eq.(3) is exact but not closed, since it also involves the pair distribution function $f_{12}(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2|t)$.

- Closure is obtained by the following assumptions on pair correlations:
  1. The first term at $r.h.s$ of Eq. (3) gives the total force exerted by wall atoms on gas atoms when the interatomic distance is larger than $\sigma_{12}$. Since spatial correlations are expected to decay rapidly, it is not unreasonable to ignore correlations completely by writing

$$f_{12}(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2|t) = f_1(\mathbf{r}_1, \mathbf{v}_1|t)f_2(\mathbf{r}_2, \mathbf{v}_2|t)$$ (4)

  2. In the hard sphere collision integral, short range correlations are taken into account but, following Enskog, they are assumed to be velocity independent. Accordingly, the pair distribution function at contact is written as:

$$f_{12}(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1 - \sigma_{12}\hat{\mathbf{k}}, \mathbf{v}_2|t) = \chi_{12}(\mathbf{r}_1, \mathbf{r}_1 - \sigma_{12}\hat{\mathbf{k}})f_1(\mathbf{r}_1, \mathbf{v}_1|t)f_2(\mathbf{r}_1 - \sigma_{12}\hat{\mathbf{k}}, \mathbf{v}_2|t)$$ (5)

In Eq. (5), $\chi_{12}(\mathbf{r}_1, \mathbf{r}_1 - \sigma_{12})$ is the pair correlation function at contact, which takes spatial correlation and excluded volume effects into account[Enskog (1921)].
A rigorous derivation of $\chi_{12}$ would be difficult, therefore:

- it is assumed that excluded volume effects are determined solely by wall molecules through their number density $n_2(r_2)$.

- The specific form of $\chi_{12}(n_2)$ 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:

$$\chi_{12}(n_2) = \frac{1}{2} \frac{2 - \eta_2}{(1 - \eta_2)^3}, \quad \eta_2 = \frac{\pi}{6} n_2 \sigma_2^3$$  \hspace{1cm} (6)

where $\eta_2$ is the reduced density (or volume fraction) in the solid phase.

- The expression given above is easily derived from the approximate equation of state of a hard sphere gas proposed by Carnahan and Starling (1969).

- Although Eq. (6) provides a very accurate approximation of the contact value of the uniform equilibrium pair correlation function in a single component hard sphere gas, its use in the present context is highly questionable.
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 $f_2$ will take the following form

$$f_2(r_2, v_2) = \frac{n_2(r_2)}{[2\pi R_2 T_2(r_2)]^{3/2}} \exp \left\{ -\frac{[v_2 - u_2(r_2)]^2}{2R_2 T_2(r_2)} \right\}$$

(7)

being $n_2(r_2)$, $T_2(r_2)$ and $u_2(r_2)$ 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.

Substituting the expressions in Eqs. (4,5) into Eq.(3) leads to following linear integro-differential equation for $f_1$:

$$\frac{\partial f_1}{\partial t} + v_1 \cdot \nabla r_1 f_1 + \frac{F_{12}}{m_1} \cdot \nabla v_1 f_1 = \sigma_{12}^2 \int \chi_{12} \left[ n_2(r_1 + \sigma_{12} \hat{k}) \right] f_1(r_1, v^*_1|t) f_2(r_1 + \sigma_{12} \hat{k}, v^*_2|t) - \chi_{12} \left[ n_2(r_1 - \sigma_{12} \hat{k}) \right] f_1(r_1, v_1|t) f_2(r_1 - \sigma_{12} \hat{k}, v_2|t) \right\} (v_r \cdot \hat{k})^+ d\nu_2 d^2\hat{k}$$

(8)

$$F_{12}(r_1) = -\int_{\rho > \sigma_{12}} \frac{r_1 - r_2}{\rho} \frac{d\phi_{12}}{d\rho} n_2(r_2) dr_2$$

(9)
Test Problems

P1 Heat transport in a collisionless gas confined between two parallel plates kept at different temperatures.

P2 Couette flow in a collisionless gas to obtain

- Profiles of macroscopic quantities
- Shapes of velocity distribution function
- Accommodation coefficients for:
  1. kinetic energy and normal momentum (from problem P1)
  2. tangential momentum accommodation coefficient (from problem P2)
1D Equation for Test Problems

- In both problems listed above a collisionless gas fills the gap between two parallel infinite plates represented by the following density profile:

\[
n_2(z_1) = \begin{cases} 
n_w & |z_1| > L_z \\
0 & |z_1| \leq L_z 
\end{cases} \tag{10}
\]

\(n_w\) being the constant value of the number density of wall atoms.

- The equilibrium velocity distribution function of wall atoms is given by the following expressions

\[
f_2(z_1, v_2) = \begin{cases} 
\frac{n_w}{(2\pi R_T T_L)} \exp \left[ -\frac{v_2^2}{2 R_T T_L} \right] & z_1 \leq -L_z \\
\frac{n_w}{(2\pi R_T T_R)} \exp \left[ -\frac{v_2^2}{2 R_T T_R} \right] & z_1 \geq L_z 
\end{cases} \quad \text{Heat Transport}
\]

\[
f_2(z_1, v_2) = \begin{cases} 
\frac{n_w}{(2\pi R_T T_L)} \exp \left[ -\frac{(v_2-u_L \hat{x})^2}{2 R_T T_L} \right] & z_1 \leq -L_z \\
\frac{n_w}{(2\pi R_T T_R)} \exp \left[ -\frac{v_2+u_L \hat{x})^2}{2 R_T T_L} \right] & z_1 \geq L_z 
\end{cases} \quad \text{Couette Flow}
\]
• In the simple one-dimensional geometry considered here, the force field $F_{12}$ reduces to the component $F_z^{(12)}(z_1)$ normal to the plates.

$$F_z^{(12)}(z_1) = 2\pi \bar{\phi}_{12} \left[ \sigma_{12}^{\gamma_1} \int_{|z_1 - z_2| > \sigma_{12}} \left( \frac{(z_2 - z_1)n_2(z_2)}{|z_1 - z_2|^{\gamma_1}} \right) dz_2 + \int_{|z_1 - z_2| \leq \sigma_{12}} \left( \frac{(z_2 - z_1)n_2(z_2)}{|z_1 - z_2|^{\gamma_1}} \right) dz_2 \right]$$  \hspace{1cm} (11)

• Since walls cannot produce spatial gradients of fluid properties along $x_1$ or $y_1$ directions, the following one-dimensional form of Eq. (8) can be used to study the problem:

$$\frac{\partial f_1}{\partial t} + v_{1z} \frac{\partial f_1}{\partial z_1} + \frac{F_z^{(12)}(z_1)}{m_1} \frac{\partial f_1}{\partial v_{1z}} = C_{12}(f_2, f_1) \hspace{1cm} (12)$$

$$C_{12}(f_2, f_1) = \sigma_{12}^2 \int \{ \chi_{12} [n_2(z_1 + \sigma_{12}k_z)] f_2(z_1 + \sigma_{12}k_z, v_2^*)f_1(z_1, v_1^*|t) - \chi_{12} [n_2(z_1 - \sigma_{12}k_z)] f_2(z_1 - \sigma_{12}k_z, v_2)f(z_1, v_1|t) \} (\nu_r \circ \hat{k})^+ d\nu_2 d^2\hat{k} \hspace{1cm} (13)$$
Numerical Method

Eq. (12) has been solved numerically by a variant of a DSMC scheme for the non-linear Enskog and Enskog-Vlasov kinetic equation [Frezzotti (1997)].

- Steady solutions of Eq. (12) are sought as long time limit of unsteady solutions.
- Each simulation is started by filling the gap between the walls uniformly with $N_p$ particles whose velocities are distributed according with a Maxwellian having temperature $T_L$ and bulk velocity equal to zero.
- After the onset of steady flow conditions, particle properties are sampled and time averaged to obtain the macroscopic quantities of interest as well as the distribution function.

It should be observed that the existence of steady solutions is not obvious because, in general, gas atoms can diffuse through the solid under the action of random collisions. However, the equation of balance of linear momentum shows that the non-local structure of $C_{12}(f_2, f_1)$ produces a net force where $n_2$ profile is not uniform.

- The force generated by hard sphere collisions repels atoms approaching the walls. The intensity of repulsion is proportional to $n_w \chi_{12}(n_w)$ and it becomes strong enough to confine the fluid within the gap, when $n_w$ has the typical values of a solid substance.
Comparison with MD results

- The results obtained from the numerical solution of Eq. 12 have been compared to the results of MD studies of test problems (1) and (2).

- Numerical data have been collected from the following investigations of rare gases (Xe and Ar) flows in contact with metal plates (Pt):


• Interaction potentials used in MD studies are not the same used to derive the kinetic model.

• Yamamoto adopted a Morse potentials in the form

\[ \phi(Xe-Pt)(\rho) = \epsilon(Xe-Pt) \{ exp \left[ -2\sigma(Xe-Pt)(\rho - \rho_0) \right] - 2exp \left[ -\sigma(Xe-Pt)(\rho - \rho_0) \right] \} \]

\[ \phi(Ar-Pt)(\rho) = \epsilon(Ar-Pt) \{ exp \left[ -2\sigma(Ar-Pt)(\rho - \rho_0) \right] - 1 \}^2 \] (14)

• Interactions among wall atoms simulated through Lennard-Jones potential.

• Gas phase not collisionless \( Kn = 0.2 - 10 \). DSMC scheme adopted to account for atomic interactions in the gas. Small effects of \( Kn \) on accommodation coefficients.

• In Ref. [4] Lennard-Jones potential has been used to describe \( Ar - Pt \) interaction (with a very different \( \epsilon(Ar-Pt) \)). Walls simulated by arrays of non-interacting atoms, individually tethered to fixed points by springs.

• Gas phase not collisionless. MD algorithm adopted to account for atomic interactions in the gas.
If $\sigma_1$, $\sigma_1/\sqrt{R_1T_w}$ and $m_1$ are adopted as units of length, time and mass, solutions of Eq. (12) can be shown to depend on the following non-dimensional parameters:

$$\eta_w = \frac{\pi \sigma_2^3 \eta_w^2}{6}, \quad \frac{\tau_{12}}{k_B T_w}, \quad \gamma_{12} \quad \frac{\sigma_2}{\sigma_1}, \quad \frac{m_2}{m_1}, \quad \frac{T_L}{T_w}, \quad \frac{T_R}{T_L}, \quad S_w = \frac{u_w}{\sqrt{2R_1T_w}}.$$

<table>
<thead>
<tr>
<th>System</th>
<th>$\eta_w$</th>
<th>$\frac{\tau_{12}}{k_B T_w}$</th>
<th>$\frac{\sigma_2}{\sigma_1}$</th>
<th>$\frac{m_2}{m_1}$</th>
<th>$\frac{T_L}{T_w}$</th>
<th>$\frac{T_R}{T_L}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Xe - Pt$</td>
<td>0.5, 0.7</td>
<td>1.4896, 1.064</td>
<td>1.0</td>
<td>1.486</td>
<td>1.0</td>
<td>1.2 - 4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$Ar - Pt$</td>
<td>0.5, 0.7</td>
<td>0.6286, 0.449</td>
<td>1.0</td>
<td>4.883</td>
<td>1.0</td>
<td>1.2 - 4.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Problem 1 - Heat Transport - $T_w = 300^\circ K$, $\gamma_{12} = 6$**

<table>
<thead>
<tr>
<th>System</th>
<th>$\eta_w$</th>
<th>$\frac{\tau_{12}}{k_B T_w}$</th>
<th>$\frac{\sigma_2}{\sigma_1}$</th>
<th>$\frac{m_2}{m_1}$</th>
<th>$\frac{T_L}{T_w}$</th>
<th>$\frac{T_R}{T_L}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Xe - Pt$</td>
<td>0.5, 0.7</td>
<td>0.0, 1.4896, 1.064</td>
<td>1.0</td>
<td>1.486</td>
<td>1.0</td>
<td>1.0</td>
<td>0.1 - 2.5</td>
</tr>
<tr>
<td>$Ar - Pt$</td>
<td>0.5, 0.7</td>
<td>0.0, 0.6286, 0.449</td>
<td>1.0</td>
<td>4.883</td>
<td>1.0</td>
<td>1.0</td>
<td>0.1 - 0.5</td>
</tr>
</tbody>
</table>

**Problem 2 - Couette Flow A - $T_w = 300^\circ K$, $\gamma_{12} = 6$**

<table>
<thead>
<tr>
<th>System</th>
<th>$\eta_w$</th>
<th>$\frac{\tau_{12}}{k_B T_w}$</th>
<th>$\frac{\sigma_2}{\sigma_1}$</th>
<th>$\frac{m_2}{m_1}$</th>
<th>$\frac{T_L}{T_w}$</th>
<th>$\frac{T_R}{T_L}$</th>
<th>$S_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ar - Pt$</td>
<td>0.7</td>
<td>0.2158, 0.449</td>
<td>1.0</td>
<td>4.883</td>
<td>0.333 - 1.333</td>
<td>1.0</td>
<td>0.224</td>
</tr>
</tbody>
</table>
Heat Transfer between Parallel Plates, Xe-Pt

\[ \frac{T_R}{T_L} = 2.0, \frac{m_2}{m_1} = 1.486, \sigma_1 = \sigma_2 = 1, \phi_{12} = 1.064, k_B T_L, L_z = 10 \sigma_1, \eta_w = 0.7 \]
Heat Transfer between Parallel Plates, Xe-Pt

\[ \frac{T_R}{T_L} = 2.0, \frac{m_2}{m_1} = 1.486, \sigma_1 = \sigma_2 = 1, \phi_{12} = 1.064k_B T_L, L_z = 10\sigma_1, \eta_w = 0.7 \]
Heat Transfer between Parallel Plates

\[ \frac{T_g}{T_L} \text{ Vs. } \frac{T_R}{T_L} \]
The accommodation coefficient of the molecular property $\phi(v)$ has been computed from the following general expression:

$$\alpha_\psi = \frac{\int_{v_z<0} \psi(v)|v_z|f(v) \, dv - \int_{v_z>0} \psi(v)|v_z|f(v) \, dv}{\int_{v_z<0} \psi(v)|v_z|f(v) \, dv - \int_{v_z>0} \psi(v)|v_z|f_w(v) \, dv}$$  \hspace{1cm} (16)

The moments appearing in Eq. (16) have been computed by sampling gas particles in the central slice of the computational domain where both the short and long range interaction with walls are negligible.
Heat Transfer between Parallel Plates, Xe-Pt
Energy and Normal Momentum Accommodation Coefficients

\[ \alpha_{v_x} - \text{EV - Xe - } \eta_w = 0.5 \]
\[ \alpha_E - \text{EV - Xe - } \eta_w = 0.5 \]
\[ \alpha_{v_x} - \text{EV - Xe - } \eta_w = 0.7 \]
\[ \alpha_E - \text{EV - Xe - } \eta_w = 0.7 \]
\[ \alpha_{v_x} - \text{MD - Xe} \]
\[ \alpha_E - \text{MD - Xe} \]
Heat Transfer between Parallel Plates, Ar-Pt
Energy and Normal Momentum Accommodation Coefficients
Couette Flow - Xe-Pt

\[ \frac{m_2}{m_1} = 1.486, \quad \sigma_1 = \sigma_2, \quad S_w = 0.5 \]
Couette Flow, Ar-Pt - Reduced Distribution Functions

\( \frac{m_2}{m_1} = 4.883, \sigma_1 = \sigma_2 = 1, \eta_0 = 0.7, \phi_{12} = 0.449 k_B T_w, S_w = 0.5 \)
Couette Flow, Xe-Pt - Reduced Distribution Functions

$m_2/m_1 = 1.486, \sigma_1 = \sigma_2 = 1, \eta_0 = 0.5, \phi_{12} = 1.4896 k_B T_w, S_w = 2.5
Tangential Momentum Accommodation Coefficients

Xe-Pt, Ar-Pt

\( \alpha_t \)

\( \phi_{12} = 1.064, \eta_w = 0.7 \)
\( \phi_{12} = 1.486, \eta_w = 0.5 \)
\( \phi_{12} = 0.0, \eta_w = 0.5 \)
\( \phi_{12} = 0.0, \eta_w = 0.7 \)

MD - Yamamoto (1997, 2001)

\( \phi_{13} = 0.449, \eta_w = 0.7 \)
\( \phi_{12} = 0.2158, \eta_w = 0.7 \)

Exp. fit of MD data (Cao et al. 2005)
Conclusions

- A simple kinetic model of fluid-wall interaction has been developed along the guidelines of the kinetic theory of dense fluids.

- Model predictions for test problems are close to (or not far from) the results of MD simulations.

- Future activity will concentrate on:
  1. Extend the data base of MD simulations
  2. Development of better models for pair correlations.
  3. Coupling with DSMC simulations of gases and liquids [Frezzotti & Gibelli (2006)]
  4. Extension to diatomic gas species.