A Kinetic Model for Equilibrium and Non-Equilibrium Structure of the Vapor-Liquid Interface

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Abstract. The Enskog-Vlasov kinetic equation for a dense fluid of spherical molecules interacting by Sutherland potential has been solved numerically to study the vapor-liquid equilibrium by a single kinetic equation. The equilibrium structure of the vapor-liquid interface has been obtained at various temperatures. The linear Enskog-Vlasov equation has also been used to describe the motion of a test particle crossing the vapor liquid boundary. The reemission probability of a gas molecule impinging on the liquid surface is obtained as a function of initial molecular velocity and system temperature.

INTRODUCTION

The traditional kinetic theory treatment of evaporation or condensation processes is limited to the description of the Knudsen layer formed at the boundary between the vapor and the condensed phase. Since in most applications the vapor is dilute, the Boltzmann equation is used to describe the gas motion above the liquid or solid. The interface structure is not resolved and the condensed phase simply acts as a source or sink for vapor molecules. The molecular exchange process is usually described by a phenomenological model which takes the form of an inhomogeneous boundary condition [1] for the distribution function $f(\mathbf{x}, \mathbf{v}|t)$ at location $\mathbf{x}$ on the liquid-vapor interface:

$$\langle \mathbf{v} \cdot \mathbf{n} \rangle f(\mathbf{x}, \mathbf{v}|t) = \langle \mathbf{v} \cdot \mathbf{n} \rangle f_e(\mathbf{v}) + \int_{\langle \mathbf{v}_1 \cdot \mathbf{n} \rangle < 0} R(\mathbf{v}, \mathbf{v}_1) |\langle \mathbf{v}_1 \cdot \mathbf{n} \rangle| f(\mathbf{x}, \mathbf{v}|t) d^3 \mathbf{v}_1, \quad \mathbf{v} \cdot \mathbf{n} > 0$$

(1)

$n$ being the unit vector, normal to the boundary at $\mathbf{x}$, which points from the liquid into the gas region. With very few exceptions, limited to linear theory of weak evaporation/condensation[2], the usual choice for the distribution function $f_e(\mathbf{v})$ of molecules evaporating from the condensed phase is the half range Maxwellian

$$f_e(\mathbf{v}) = \sigma_e \frac{n_w}{(2\pi R T_w)^{3/2}} \exp \left( -\frac{\mathbf{v}^2}{2 R T_w} \right), \quad \mathbf{v} \cdot \mathbf{n} > 0$$

(2)

whereas Maxwell’s gas-surface scattering kernel is the usual choice to describe molecular re-emission from the condensed phase:

$$R(\mathbf{v}, \mathbf{v}_1) = (1 - \sigma_e) \left[ \alpha(\mathbf{v} \cdot \mathbf{n}) \frac{1}{2\pi (R T_w)^2} \exp \left( -\frac{\mathbf{v}^2}{2 R T_w} \right) \delta(\mathbf{v} - \mathbf{v}_1 + 2(\mathbf{v} \cdot \mathbf{n})\mathbf{n}) \right]$$

(3)

In Eqs.(1-3) $n_w$ is the number density of the saturated vapor at the temperature $T_w$. The coefficient $\sigma_e (0 \leq \sigma_e \leq 1)$ gives the fraction of vapor molecules impinging on the interface and absorbed. The total fraction of impinging molecules which are instantaneously re-emitted is $1 - \sigma_e$, $\alpha$ being the probability of diffuse re-emission and $1 - \alpha$ the probability of specular reflection.

The assessment of the model accuracy or the determination of the model parameters requires either (difficult) experimental investigations or a more general theory, capable of describing the structure of the condensed phase as well. In the past few years, molecular dynamics (MD) numerical experiments have been performed to investigate evaporation and condensation processes and estimate evaporation/condensation coefficients[3, 4, 5]. In this work a different approach is followed and an approximate kinetic equation is used to provide a unified description of both phases.

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BASIC EQUATIONS

Following Refs. [6, 7], we consider a fluid composed of spherical and identical molecules of mass \( m \), interacting by Sutherland potential [8]

\[
\phi(r) = \begin{cases} 
\frac{-a^6}{r^6} & r < a \\
-\phi_0 \left( \frac{a}{r} \right)^\gamma & r \geq a
\end{cases}
\]  
(4)

which results from the superposition of a hard sphere potential and an attractive soft potential. The hard sphere diameter is \( a \), whereas \( \phi_0 \) and \( \gamma \) are two positive constants which are related to the depth of the potential well at \( r = a \) and to the range of the soft interaction, respectively. The following exact equation can be derived for the one-particle distribution function [7, 9].

\[
\frac{\partial f_1}{\partial t} + v \circ \nabla_x f_1 = -\nabla_v \circ \left[ \frac{\hbar}{\mu} \frac{\partial \phi}{\partial x} f_2(x, v, x_1, v_1|t) d\v_1 \right] + \\
a^2 \int [f_2(x, v^*, x + \alpha \hat{k}, v_1^*|t) - f_2(x, v, x - \alpha \hat{k}, v_1|t)] (v_r \circ \hat{k})^+ d\v_1 d^2\hat{k}
\]  
(5)

Eq. (5) is exact but of little use, since it also involves the pair distribution function \( f_2(x, v, x_1, v_1|t) \). A closed equation for the one-particle distribution function is obtained by the following two approximations:

(a) In the hard sphere collision integral in Eq. (5), following Enskog [10], it is assumed that

\[
f_2(x, v, x - \alpha \hat{k}, v_1|t) = Y \left[ n \left( x - \frac{\alpha}{2} \hat{k} \right) \right] f_1(x, v|t)f_1(x - \alpha \hat{k}, v_1|t)
\]  
(6)

\( Y(n) \) being the contact value of the pair correlation function in a hard sphere fluid in uniform equilibrium with density \( n \).

(b) Pair correlations are completely neglected in the soft potential contribution in Eq. (5). Accordingly, it is assumed that

\[
f_2(x, v, x_1, v_1|t) = f_1(x, v|t)f_1(x_1, v_1|t)
\]  
(7)

Taking into account Eqs. (6, 7), Eq. (5) takes the form

\[
\frac{\partial f_1}{\partial t} + v \circ \nabla_x f_1 + \frac{F(x|t)}{m} \circ \nabla_v f_1 = C_E(f_1, f_1)
\]  
(8)

\[
F(x|t) = \int_{\|x_1 - x\| > \alpha} \frac{d\phi}{dr} \frac{x_1 - x}{\|x_1 - x\|} n(x_1|t) d\v_1
\]  
(9)

\[
C_E(f_1, f_1) = a^2 \int \left\{ Y \left[ n \left( x + \frac{\alpha}{2} \hat{k} \right) \right] f_1(x + \alpha \hat{k}, v_1^*|t) f_1(x, v^*|t) - \\
y \left[ n \left( x - \frac{\alpha}{2} \hat{k} \right) \right] f_1(x - \alpha \hat{k}, v_1|t) f_1(x, v|t) \right\} (v_r \circ \hat{k})^+ d\v_1 d^2\hat{k}
\]  
(10)

Eq. (8), also named Enskog-Vlasov kinetic equation [6], describes a hard sphere fluid under the action of the self-consistent force field (see Eq. (9)) generated by the soft attractive tail.

EQUILIBRIUM SOLUTIONS

The equation of state of a fluid described by Eq. (8) can be easily shown to have the following generalized van der Waals form [11]:

\[
p = p^{\text{hs}}(n, T) = \frac{2\pi a^3}{3} \frac{\gamma}{\gamma - 3} \phi_0 n^2
\]  
(11)

\[
p^{\text{hs}}(n, T) = nkT \left( 1 + \eta + \eta^2 - \eta^3 \right), \quad \eta = \frac{\pi a^3 n}{6}
\]  
(12)
where $p^{hs}$ denotes the hard sphere contribution to the total pressure $p$. The approximate (but accurate) expression for $p^{hs}$ given in Eq.(12) has been proposed by Carnahan and Starling [12]. Eq.(12) also provides an expression for $Y(n)$[9]

$$Y(n) = \frac{1}{nb} \left( \frac{p^{hs}}{n^k T} - 1 \right) = \frac{1}{2} \left( \frac{2 - \eta}{(1 - \eta)^2} \right)^{1/3}, \quad b = \frac{2\pi a^3}{3} \tag{13}$$

It is easy to check that isotherms given by Eq.(11) have the typical wiggles associated to mean field theories[11], when the temperature $T$ is below the critical temperature $T_c$. The critical parameters associated with Eq.((11) are readily obtained:

$$\eta_c = \frac{\pi a^3 n_c}{6} = 0.130443, \quad T_c = 0.094329 \frac{4\gamma}{\gamma - 3k} \tag{14}$$

The equilibrium properties of the fluid in the vapor-liquid coexistence region have been studied by solving the spatially one-dimensional form of Eq.(8). In this case, elementary manipulations of Eq.(9) lead to the following simplified expression for the $x$ component of the self-consistent force field:

$$F_x(x|x) = 2\pi\phi_a \left[ a^2 \int_{|x-y|>a} \frac{(y-x)n(y|x)}{|x-y|^2} dy + \int_{|y-x| \leq a} (y-x)n(y|x) dy \right] \tag{15}$$

It is interesting to observe that the non-uniform density profile of the fluid in equilibrium at temperature $T < T_c$ obeys the equation[6]

$$kT \frac{dn}{dx} = n(x) F_x(x) + 2\pi a^2 n(x) \int_{-1}^{+1} k_Y \left[ n(x - \frac{a}{2} k) \right] n(x - a k) dk \tag{16}$$

where $F_x$ is given by Eq.(15). The above equation can be obtained by substituting the expression

$$f_1(x, v) = \frac{n(x)}{(2\pi RT)^{3/2}} \exp \left( -\frac{v^2}{2RT} \right) \tag{17}$$

into Eq.(8). A physically meaningful interpretation of Eq.(16) is readily obtained by observing that the term at left hand side can be written as $dP_x^k/dx$, $P_x^k$ being the kinetic contribution to the $P_x$ component of the stress tensor. The integral at right hand side can be shown to be equal to $-dP_x^C/dx$, where the collisional (hard sphere) contribution $P_x^C$ to the stress tensor $P$ is defined as

$$P_x^C = -m a^2 \int dv_1 dv_2 d^2 \hat{k} \int_0^a d\lambda \left[ \hat{v} \hat{n} \left( n(x + \lambda \hat{k} - \frac{a}{2} \hat{k}) \right) \right] \times f_1(x + \lambda \hat{k} - \frac{a}{2} \hat{k}, v_1, t) f_1(x + \lambda \hat{k}, v_2, t)(v, \hat{k})^+ \tag{18}$$
FIGURE 2. (a) Vapor-liquid coexistence curve. Solid line: vapor density \( n_g \); Dashed line: liquid density \( n_l \); rectilinear diameter \((n_g + n_l)/2\); filled □: critical density; Solid straight line: linear regression of rectilinear diameter data. (b) Reciprocal interface thickness \( \Delta_I \) as a function of normalized temperature \( T/T_c \).

When recast in the form

\[
\frac{d}{dx}(p^K_{xx} + p^C_{xx}) = n(x)F_x(x)
\]  

Eq.(16) simply states that a fluid element is in mechanical equilibrium, the self-consistent force field being balanced by the gradient of \( p^K_{xx} + p^C_{xx} \). Eq.(19) also provides a useful check for the accuracy of numerical solutions, as shown below in Fig. 3(a).

A particle scheme[13] has been used to calculate approximate equilibrium solutions of Eq.(8). The spatial domain is a finite symmetric interval \([-L/2,L/2]\) of the \( x \) axis and periodic boundary conditions have been assumed. Each computation is started by arranging a homogeneous liquid slab at temperature \( T \) in the center of an empty computational domain. The system evolution is then computed until the evaporation of part of the liquid brings the liquid and vapor in equilibrium. The system is thermostatted[14] to keep the temperature of the system constant during the transient evaporation phase. In all simulations the soft potential exponent \( \gamma \) has been set equal to 6, to have the same asymptotic behavior of a \( 12-6 \) Lennard-Jones potential[15].

Examples of computed density and self-consistent force field profiles at different temperatures are given in Fig. 1, whereas the constant values of the density in the gas and liquid region are shown in Fig. 2(a) as a function of temperature. The rectilinear diameter [15] \((n_g + n_l)/2\) has also been computed from vapor-liquid coexistence data. As shown in Fig. 2(a), the rectilinear diameter is very well fitted by a straight line which also provides a very good extrapolated estimate of the theoretical critical point, represented by the filled square. The interface width, computed from density profiles, amounts to \( 7 \times 10a \). However, it should be observed that the mechanical effects of the density gradient are felt in a slightly wider region. As a matter of fact, the self-consistent force field, which attracts gas molecules toward the interface, extends a few diameters into the constant density regions, both on the liquid and the vapor side. The response of the interface thickness to temperature changes can be characterized by the reciprocal interface thickness \( \Delta_I^{-1} \), defined as the maximum value of the normalized density gradient

\[
\frac{1}{n_l - n_g} \left| \frac{dn}{dx} \right|
\]  

As shown in Fig. 2(b), increasing \( T \) causes the interface to widen, since the reduction in the density difference between liquid and gas phase also reduces the confining effect of the force field \( F_x \). It is also worth noting that the density profile
in the interface region can be very accurately approximated by a hyperbolic tangent profile

\[
n(x) = n_g + \frac{(n_l - n_g)}{2} \left[ 1 + \tanh \left( \frac{2(x-x_l)}{\Delta I} \right) \right]
\]

as shown in Fig.3(b).

**CONденсАTION СОEFFICIENTS FROM EQUilibrium SIMуLАTIONS**

Equilibrium simulations can also be used to study molecular exchange processes between the gas and the liquid phase, thus providing estimates for evaporation/condensation coefficients and velocity distribution of molecules crossing the interface. The method, also adopted in several MD investigations[4, 5], consists in following the trajectories of a number of molecules which cross the vapor-liquid boundary. A similar technique has been used here to obtain the condensation probability of a gas molecule onto the liquid surface from the mathematical model described above. The motion of a test molecule through the background fluid in equilibrium at temperature \(T\) is studied by solving the linear transport equation

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_x f + \frac{F(x|t)}{m} \cdot \nabla_v f = C_E(\Psi, f)
\]

In Eq.(22) \(f(x,v|t)\) is the distribution function of test molecules, \(\Psi(x,v)\) is the equilibrium Maxwellian distribution function of background molecules, as given by Eq.(17). The equilibrium density profile has been calculated from Eq.(21) by substituting the parameters \(n_g, n_l\) and \(\Delta I\) obtained from the numerical solution of Eq.(8), for each selected temperature value. Eq.(22) has been solved numerically by a simplified version of the Monte Carlo algorithm used to solve the nonlinear one. At the beginning of each calculations, \(N_0^p\) particles are placed in the gas region, close to the interface, right out of the range of the attractive force \(F\) generated by the background fluid. The initial molecular velocities are directed toward the liquid surface, and they can be either set equal to a common value \(v_0\) (mono-energetic pulse) or sampled from a Maxwellian flux density proportional to \(v^2 \exp(-v^2/(2RT))\). Molecules trajectories are generated according to Eq.(22) and the number of back scattered molecules \(N_{bs}(v^0, T|t)\) at time \(t\) is obtained by counting molecules which come back to their initial position, within time \(t\). Whenever a molecule is scattered back to the vapor phase its final velocity \(v_f\), the time \(t_k\) spent in the interface region and its maximum penetration \(\delta_M\) into the condensed phase are recorded. The limit of the ratio \(N_{bs}(v^0, T|t)/N_0^p\) for \(N_0^p \to \infty\) defines the probability \(P_b(v^0, T|t)\) that a vapor molecule with initial velocity \(v^0\) is reflected back its initial position before time \(t\). Fig. 4 shows the time evolution of \(P_b(v^0, T|t)\) for different initial molecular velocities (normalized to \(\sqrt{RT_c}\)) and background fluid.
density and their reemission rate will change slowly. A closer examination of the data shows that backscattered
the initial velocity. On the contrary, molecules whose residence time
also show that the probability
velocities. A possible explanation is that molecules having a low impact velocity are more likely to be reflected by a
molecular desorption goes on for a very long time, as shown by simulations in which the evolution of
In the liquid region, where the product $8^n a^2 Y(n)$ takes a large value, $D$ is accordingly small. Hence the test particles
density and their reemission rate will change slowly. A closer examination of the data shows that backscattered
molecules can be roughly divided into two groups. Actually, the rate of change of $P_r(v^0, T|t)$ exhibits a peak, followed
by a slowly decaying tail (see Figs. 4c, 4d). The peak characteristics depend on the energy of the impinging molecules,
whereas the tail behavior depends on $T$, only. The peak is associated with a group of molecules which is immediately
reflected into the gas phase after a short interaction with the liquid-vapor interface. The analysis is confirmed by the
scatter plot which shows the maximum penetration of an injected molecule into the condensed phase as a function of
the residence time $t_R$ (Fig.5). The data indicate that penetration depth and residence time are strongly correlated
for the group of molecules whose residence times are close to the peak position. The correlation is weaker for
molecules whose residence time is in the tail region. These are absorbed molecules which move along random
walks and suffer many collisions before reemission. The two groups also exhibit a different behavior as far as the
distribution function of the molecular velocities is concerned. Fig. 6 shows the distribution of the velocity component
normal to the liquid surface. Molecules whose residence time $t_R$ value falls in the peak region have a distribution
function which deviates from the equilibrium one, the low velocity region being more populated than the reference
Maxwellian distribution function. The effect, already observed in Refs.[4, 5], is more pronounced for low initial
velocities. A possible explanation is that molecules having a low impact velocity are more likely to be reflected by a
single collision, whereas reflection of more energetic molecules is the result of consecutive collisions which thermalize
the initial velocity. On the contrary, molecules whose residence time $t_R$ is in the tail region have a distribution function
very close to the equilibrium Maxwellian distribution function, irrespective of their initial energy. The curves in Fig.4
also show that the probability $P_r(v^0, T|t)$ is a decreasing function of $v^0$, for fixed $T$. Since the behavior of the tail

\begin{equation}
\frac{3}{8na^2 Y(n)} \sqrt{\frac{\kappa T}{\pi m}}
\end{equation}
of the reemission rate does not depend on $v_0^0$, the decrease is to be attributed to a smaller contribution of the peak. This behavior is quite reasonable since molecules with larger normal velocity component are not easily reflected by a collision. When the initial velocity is fixed and $T$ is increased, the reemission probability $P_r(v^0, T|\tau)$ grows. The explanation is quite straightforward, since both the peak and the tail give a larger contribution. Actually, at higher $T$, for fixed $v_0^0$, a larger number of molecules will be scattered back by a collision with a more energetic molecule. Moreover, the potential barrier created by the self-consistent field is weaker, therefore it is easier for an absorbed molecule to be reemitted toward the gas phase. The slow evolution of $P_r(v^0, T|\tau)$ makes the calculation of a definite value of reemission or condensation probability rather difficult. It is to be observed that, although the “natural” time scale of the process under examination is $\tau$, the decay of the reemission tail has a characteristic time scale which is not small in comparison with the vapor characteristic time $(n_0a^2/RT)^{-1}$. A nominal value for reemission probability is suggested by the time duration of the reemission peak whose duration can be approximately set equal to $10\tau$. Table 1 presents values of the reemission probability at $t = 10\tau$ as a function of initial molecular velocity and background temperature. However, the definition of condensation probability is related to the choice of a time scale which might depend on the particular problem at hand.

REFERENCES

FIGURE 6.  (a) Velocity distribution $v_x f(v_x)$ of reemitted molecules with $t_R < 10 \tau$.  (b) Velocity distribution $v_x f(v_x)$ of reemitted molecules with $t_R > 10 \tau$.  Solid line: Maxwellian distribution; $\circ: v_0^\parallel / \sqrt{RT_e} = 0.407$; $\square: v_0^\parallel / \sqrt{RT_e} = 0.814$; $\diamond: v_0^\parallel / \sqrt{RT_e} = 1.221$; $\triangle: v_0^\parallel / \sqrt{RT_e} = 1.628$; $\triangleleft: v_0^\parallel / \sqrt{RT_e} = 2.0351$.