

# A kinetic model for collisional effects in dense adsorbed gas layers

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**Abstract.** The effects of adsorbed gas layers on gas-surface interaction is investigated by a kinetic model based on the Enskog-Vlasov equation. The onset of collisional effects in the gas layer is studied by equilibrium simulations. The effects of adsorption on the gas-wall friction forces is investigated in a simple Couette flow geometry. It is shown that gas adsorption might reduce tangential stresses, as indicated by molecular dynamics based studies. Finally an example is produced in which the two-dimensional Enskog-Vlasov equation is solved to simulate the formation of a liquid film on the walls of a planar channel.

## INTRODUCTION

In gaseous flows past hydrophilic surfaces, the attractive forces between gas and solid lattice atoms/molecules cause the gas species residence time and surface density to increase. If gas-wall interaction is sufficiently strong, an adsorbed gas layer forms on the surface. The layer thickness amounts to a few molecular diameters but the density may become high enough to give raise to collisional effects and fluid-like behavior [1]. Gas-gas interaction in surface layers does affect accommodation coefficients, as shown in a few studies based on molecular dynamics (MD) simulations [2, 3]. Although the study of adsorbed gas layers and thin liquid films has been extensively studied [4], modeling flows consisting of dense adsorbed gas layers interacting with a rarefied gas is made difficult by the large difference between the space/time scales of the two flow regions. The adoption of hybrid methods which combine MD simulations for the gas-surface interaction with DSMC schemes is a powerful but still computationally expensive tool [2, 5]. The aim of the present study is to show that a reasonably accurate and unified description of the dense adsorbed layer and the rarefied gas region far from the solid surface can be obtained by a kinetic equation which combines an Enskog-like collision term with a mean field term which takes into account long range attractive gas-gas and gas-solid interactions [6]. The kinetic equation can be solved numerically by a DSMC scheme [6] which provides not only macroscopic quantities profiles but also accommodation coefficients and their dependence on the problem physical parameters, in good agreement with MD simulations [6]. The paper is organized as follows. After a description of the mathematical model, the onset of gas-gas interaction in adsorbed layers is studied by the properties of absorption isotherms, obtained from equilibrium solutions of the kinetic model. The effects of adsorbed layers of gas-surface interaction are then studied by applying the model to a simple one-dimensional Couette flow. Finally, an application of the model to a two-dimensional flow in which condensation on cold wall produces a liquid layer is presented and discussed.

## MODEL DESCRIPTION

Following Refs. [6], 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:

$$\phi^{(11)}(\rho) = \begin{cases} +\infty & \rho < \sigma_1 \\ \psi^{(11)}(\rho) & \rho \geq \sigma_1 \end{cases} \quad \phi^{(12)}(\rho) = \begin{cases} +\infty & \rho < \sigma_{12} \\ \psi^{(12)}(\rho) & \rho \geq \sigma_{12} \end{cases} \quad (1)$$

As shown above,  $\phi^{(11)}$  and  $\phi^{(12)}$  are obtained by superposing the soft tails,  $\psi^{(11)}(\rho)$  and  $\psi^{(12)}(\rho)$ , to hard sphere potential determined by the hard sphere diameters  $\sigma_1$  and  $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ , respectively. The adoption of simplifying assumptions about pair correlations [6], allows the derivation of the following kinetic equation for the one-particle distribution function  $f(\mathbf{r}, \mathbf{v}|t)$  of fluid molecules:

$$\frac{\partial f}{\partial t} + \mathbf{v} \circ \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}(\mathbf{r}|t)}{m_1} \circ \frac{\partial f}{\partial \mathbf{v}} = C^{(11)}(f, f) + C^{(12)}(f_w, f) \quad (2)$$

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

$$C^{(11)}(f, f) = \sigma_1^2 \int \left\{ \chi^{(11)}(\mathbf{r}, \mathbf{r} + \sigma_1 \hat{\mathbf{k}}) f(\mathbf{r} + \sigma_1 \hat{\mathbf{k}}, \mathbf{v}_1^*|t) f(\mathbf{r}, \mathbf{v}^*|t) - \chi^{(11)}(\mathbf{r}, \mathbf{r} - \sigma_1 \hat{\mathbf{k}}) f(\mathbf{r} - \sigma_1 \hat{\mathbf{k}}, \mathbf{v}_1|t) f(\mathbf{r}, \mathbf{v}|t) \right\} (\mathbf{v}_r \circ \hat{\mathbf{k}})^+ d\mathbf{v}_1 d^2 \hat{\mathbf{k}} \quad (3)$$

$$C^{(12)}(f_w, f) = \sigma_{12}^2 \int \left\{ \chi^{(12)}(\mathbf{r}, \mathbf{r} + \sigma_{12} \hat{\mathbf{k}}) f_w(\mathbf{r} + \sigma_{12} \hat{\mathbf{k}}, \mathbf{v}_1^*|t) f(\mathbf{r}, \mathbf{v}^*|t) - \chi^{(12)}(\mathbf{r}, \mathbf{r} - \sigma_{12} \hat{\mathbf{k}}) f_w(\mathbf{r} - \sigma_{12} \hat{\mathbf{k}}, \mathbf{v}_1|t) f(\mathbf{r}, \mathbf{v}|t) \right\} (\mathbf{v}_r \circ \hat{\mathbf{k}})^+ d\mathbf{v}_1 d^2 \hat{\mathbf{k}} \quad (4)$$

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  $\mathbf{F}(\mathbf{r}|t)$  is defined as

$$\mathbf{F}(\mathbf{r}|t) = \mathbf{F}^{(11)}(\mathbf{r}|t) + \mathbf{F}^{(12)}(\mathbf{r}) \quad (5)$$

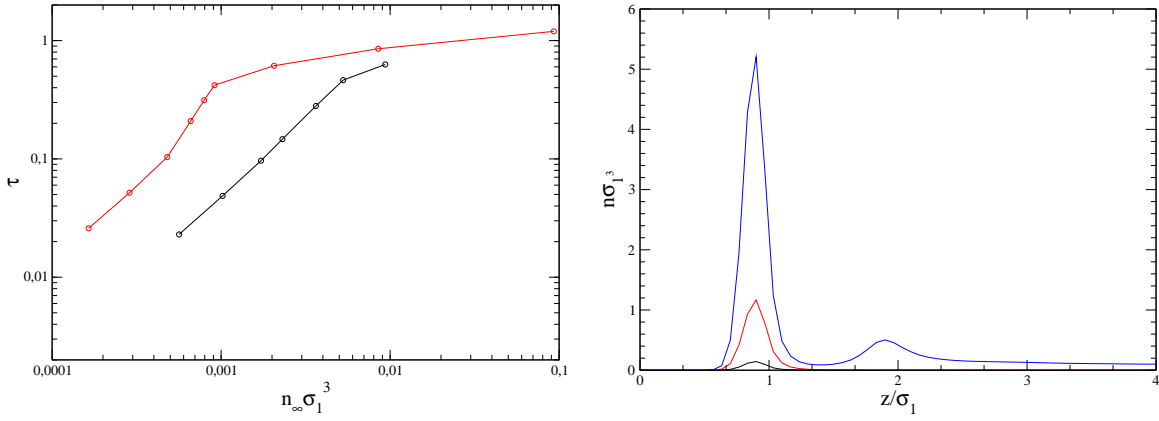
$$\mathbf{F}^{(11)}(\mathbf{r}|t) = \int_{\|\mathbf{r}_1 - \mathbf{r}\| > \sigma_1} \frac{d\phi^{(11)}}{d\rho} \frac{\mathbf{r}_1 - \mathbf{r}}{\|\mathbf{r}_1 - \mathbf{r}\|} n(\mathbf{r}_1|t) d\mathbf{r}_1 \quad \mathbf{F}^{(12)}(\mathbf{r}) = \int_{\|\mathbf{r}_1 - \mathbf{r}\| > \sigma_{12}} \frac{d\phi^{(12)}}{d\rho} \frac{\mathbf{r}_1 - \mathbf{r}}{\|\mathbf{r}_1 - \mathbf{r}\|} n_w(\mathbf{r}_1) d\mathbf{r}_1 \quad (6)$$

being  $\mathbf{F}^{(11)}(\mathbf{r}|t)$  and  $\mathbf{F}^{(12)}(\mathbf{r})$  the contributions of fluid-fluid and fluid-wall long range interaction. In absence of long range spatial correlations,  $\mathbf{F}^{(11)}(\mathbf{r}|t)$  and  $\mathbf{F}^{(12)}(\mathbf{r})$  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-wall 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  $\mathbf{F}^{(12)}(\mathbf{r})$  generated by the long range potential tails of wall atoms, when the distance  $\rho$  exceeds  $\sigma_{12}$ . 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

$$f_w(\mathbf{r}, \mathbf{v}) = \frac{n_w(\mathbf{r})}{[2\pi R_2 T_w(\mathbf{r})]^{3/2}} \exp \left\{ -\frac{[\mathbf{v} - \mathbf{u}_w(\mathbf{r})]^2}{2R_2 T_w(\mathbf{r})} \right\} \quad (7)$$

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  $k_B/m_2$ , 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 [7]:

$$\chi^{(12)}(n_w) = \frac{1}{2} \frac{2 - \eta_{12}}{(1 - \eta_{12})^3}, \quad \eta_{12} = \frac{\pi}{6} n_w \sigma_{12}^3 \quad (8)$$



**FIGURE 1.** Equilibrium simulations. **Left** - Surface density,  $\tau$ , versus the reduced gas density,  $n_\infty \sigma_1^3$ , and gas-wall interaction strength. Model parameters setting:  $m_2/m_1 = 2$ ,  $\sigma_2/\sigma_1 = 1.0$ ,  $\bar{\phi}^{(11)}/k_B T_w = 1.0$ ,  $n_w \pi \sigma_{11}^3/6 = 0.7$ .  $\bar{\phi}^{(12)}/k_B T_w = 5.0$  (red);  $\bar{\phi}^{(12)}/k_B T_w = 4.0$  (black). **Right** - Reduced density profiles in the vicinity of the wall:  $\tau = 0.026$  (black), 0.212 (red), 1.19 (blue).

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 [6].

## EQUILIBRIUM AND COUETTE FLOW: RESULTS AND DISCUSSION

The onset of collisional effects in adsorbed gas layers can be easily studied by examining the properties of equilibrium solutions of the model outlined above. In equilibrium conditions the solid wall, at temperature  $T_w$ , is in contact with a gas at rest. The number density of the gas far from the wall is  $n_\infty$ . The combined action of the attractive mean field  $\mathbf{F}(\mathbf{r})$  and the collective repulsive effect of hard sphere collisions, described by the term  $C^{(12)}$ , causes the formation of a gas layer whose density depends on  $n_\infty$ , once  $T_w$ , the gas-gas and the gas-wall interaction parameters have been specified. The fraction  $\tau(n_\infty)$  of wall area covered by adsorbed gas molecules can be defined as

$$\tau = \frac{\pi}{4} \int_0^\delta n(z) dz \quad (9)$$

being  $\delta$  the adsorbed gas layer thickness. The behavior of the function  $\tau(n_\infty)$  is very useful to assess the importance of gas-gas interactions in the adsorbed gas layer. The function values have been obtained by solving a one-dimensional version of Eq. (2). More precisely, equilibrium solutions have been obtained for a gas filling the gap between two parallel plates. The nominal walls separation is denoted by  $2L_z$  and the motion of the fluid is observed in a Cartesian reference frame whose  $x_1$  and  $y_1$  axis are parallel to the walls, whereas the coordinate  $z_1$  spans the gap between the walls. The origin  $O$  of the reference frame is located at distance  $L_z$  from the walls. It is assumed that walls are composed by spherical molecules having a diameter  $\sigma_2$ , mass  $m_2$  and number density  $n_2(z_1)$  given by the following expression:

$$n_2(z_1) = \begin{cases} n_w & |z_1| > L_z \\ 0 & |z_1| \leq L_z \end{cases} \quad (10)$$

$n_w$  being the constant value of the number density of wall atoms. The equilibrium velocity distribution function of wall atoms is given by the following expression

$$f_w(z_1, \mathbf{v}_2) = \begin{cases} \frac{n_w}{(2\pi R_2 T_w)} \exp\left[-\frac{\mathbf{v}_2^2}{2R_2 T_w}\right] & z_1 \leq -L_z \\ \frac{n_w}{(2\pi R_2 T_w)} \exp\left[-\frac{\mathbf{v}_2^2}{2R_2 T_w}\right] & z_1 \geq L_z \end{cases} \quad (11)$$

In the simple one-dimensional geometry considered here, the force field  $\mathbf{F}$  reduces to the component  $F_z(z_1)$  normal to the plates. The gas-wall force field  $F_z^{(12)}$  has been derived by the exponential tail

$$\psi^{(12)}(\rho) = -\bar{\phi}^{(12)} \exp[(\rho - \sigma_{12})/\lambda_{12}] \quad (12)$$

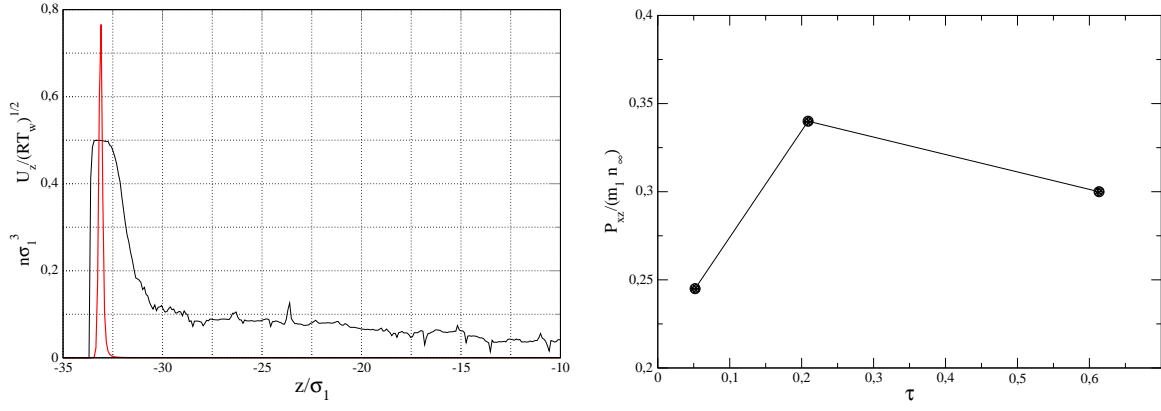
whereas the algebraic tail

$$\psi^{(11)}(\rho) = -\bar{\phi}^{(11)} \left( \frac{\rho}{\sigma_1} \right)^{-\gamma^{(11)}} \quad (13)$$

has been used to model long range gas-gas interaction. In Eqs. (12)-(13),  $-\bar{\phi}^{(12)}$  and  $-\bar{\phi}^{(11)}$  are the depths of the potential wells. The parameters  $\lambda_{12}$  and  $\gamma^{(11)}$  tune the potential ranges. In all the computations shown below  $\gamma^{(11)}$  has been set equal to 6 in order to match the attractive tail of the Lennard-Jones potential. Elementary manipulations of Eqs. (6) allow reducing the computation of mean fields to one-dimensional integrals [6]. Steady solutions of Eq. (2) have been sought as long time limit of unsteady solutions by the DSMC extension described in Ref.[8]. Figure 1 shows the behavior of the function  $\tau(n_\infty)$  for the values 4.0 and 5.0 of the gas-wall interaction parameter  $\bar{\phi}^{(12)}/k_B T_w$ . The remaining model parameters have been set as follows:  $m_2/m_1 = 2$ ,  $\sigma_2/\sigma_1 = 1.0$ ,  $\bar{\phi}^{(11)}/k_B T_w = 1.0$ ,  $n_w \pi \sigma_1^3/6 = 0.7$ . The absorption isotherm curve exhibits a typical behavior [9]. At low gas density,  $\tau$  grows rapidly in response to an increase of  $n_\infty$ . The initial grow rate might be more rapid than a linear one because the attractive action (if any) of the adsorbed gas atoms might superpose to the gas-solid force field. At higher values of the density the curve saturates because the self-interaction of adsorbed gas atoms prevents or slows further adsorption down. Hence, the value of  $\tau$  where the two curves bend toward saturation marks the region where collisional effects are important. It is interesting to note that such value depends weakly on  $\bar{\phi}^{(12)}/k_B T_w$ . In order to investigate the effects of gas adsorption on the gas-surface interaction in dilute gas flows, the Couette flow of a monatomic gas has been studied by solving Eq. (2). The one dimensional form of the equation has been used in the same geometry described above for equilibrium simulations. The gas-wall interaction has been modified by adding opposite bulk velocities  $\pm U_w$ , along  $x$  direction, to walls occupying the half spaces  $z_1 < -L_z$  and  $z_1 > L_z$ . The flow field simulations have been performed by setting  $U_w/\sqrt{RT_w} = 0.5$ . The Knudsen number  $1/(\sqrt{2}\pi n_\infty \sigma_1^2 L_z)$  has been set equal to 5.0. The density value in the rarefied region has been changed following the saturation curves. For each value of the gas density, the channel width has been selected to obtain the desired Knudsen number. A typical velocity profile in the vicinity of the wall is shown in Figure 2 for the case  $\tau \approx 0.21$  along with the reduced density profile. In the rarefied region the velocity profile shows the typical linear behavior. The velocity slip is quite pronounced because of the relatively large value of the Knudsen number. At a distance of about  $3\sigma_1$  from the density peak, the velocity starts quickly growing till it reaches the wall velocity value, indicating that the adsorbed layer has the same velocity of the wall. This is not surprising since the adsorbed layer is composed by atoms which have interacted for a long time with the solid wall. The overall characteristics of gas-wall friction forces are best understood by examining the behavior of the tangential stress per particle  $P_{xz}/(m_1 n_\infty)$ , being  $n_\infty$  the nearly constant value of the density in the dilute gas region. As show in Figure 2b, the behavior of the above quantity is not monotonic. When surface density is increased, the tangential stress grows at first, but decreases slightly when the surface density  $\tau$  curve bends toward saturation. A closer examination of the behavior of density profiles and residence time (i.e. the time an atom spends in the adsorbed layer region), which are not here reported, shows that tangential stress decreases when the density profile shows the formation of a second atomic layer. This layer is less tightly bounded to the solid as indicated by the parallel drop of average residence time. It is interesting to note that similar results have been described in Ref.[10] where the effects of gas adsorption on accommodation coefficients have been studied by MD simulation.

## CONDENSATION IN MICROCHANNELS: RESULTS AND DISCUSSION

The capability of the kinetic model to deal with dense adsorbate gas layer is further supported by studying the gas flows through a two-dimensional microchannel in which condensation on a cold wall takes place. A main point of the numerical code which solve the two-dimensional version of Eq. (2) is the computation of the self-consistent force field,  $\mathbf{F}(\mathbf{r}|t)$ . Unlike the one-dimensional case, it is not possible to find an analytic expression of the force field for a generic potential. Therefore  $\mathbf{F}(\mathbf{r}|t)$  has been computed by numerical integration. More precisely, the integration over



**FIGURE 2.** Couette flow simulations. **Left** - Reduced density (red) and mean velocity profile (black). **Right** - Tangential stress tensor per unit mass as a function of surface density  $\tau$ . Model parameters setting:  $m_2/m_1 = 2$ ,  $\sigma_2/\sigma_1 = 1.0$ ,  $\bar{\phi}^{(11)}/k_B T_w = 1.0$ ,  $n_w \pi \sigma_{11}^3/6 = 0.7$ ,  $\bar{\phi}^{(12)}/k_B T_w = 5.0$ ,  $U_w/\sqrt{RT_w} = 0.5$ .

$z_1$  is first carried out with a generalized Romberg method, thus reducing Eq. (2) to

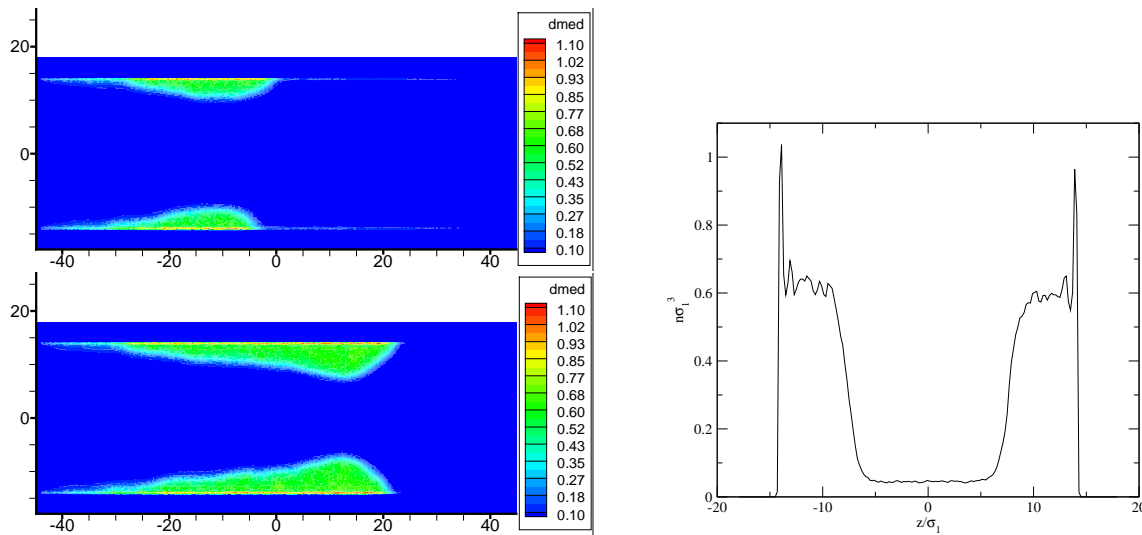
$$\mathbf{F}(x, y|t) = \int [(x_1 - x)\mathbf{i} + (y_1 - y)\mathbf{j}] n(x_1, y_1|t) \mathcal{S}(x_1 - x, y_1 - y) dx_1 dy_1 \quad (14)$$

where the component along the  $z$  axis,  $F_z$ , is equal to zero by symmetry. Eq. 14 is then integrated with a simple mid-point quadrature formula. It is worth noticing that in Eq. 14 the kernel  $\mathcal{S}(x_1 - x, y_1 - y)$  depends on the chosen potential, but not on the actual value of the density field. This fact makes possible to compute the kernel  $\mathcal{S}$  only once for a suitable range of the variables  $x_1 - x$  and  $y_1 - y$ . In principle, each particle feels the force field generated by all the particles in the domain. Hence, if  $N_c$  is the total number of physical cells, the computation of the force field would have a computational cost of the order of  $N_c^2$ . In practice, to reduce the problem to a feasible size, we introduce a cut-off distance and include in the computation of the force field only the contribution of the cells inside the cut-off region.

In the computations shown below, we have chosen algebraic tails for both the gas-gas and gas-wall attractive potentials with parameters  $\bar{\phi}^{(11)}/k_B T_0 = 1$ ,  $\gamma^{(11)} = 6$  and  $\bar{\phi}^{(12)}/k_B T_0 = 1.5$ ,  $\gamma^{(12)} = 6$  respectively, being  $T_0$  a reference temperature. The cut-off distance for the force-field computation has been set equal to three molecular diameters. The channel has a width of  $30\sigma_1$  and a length of  $90\sigma_1$  and it has been divided into  $180 \times 360$  uniform cells. The inlet is connected with an infinite reservoir whereas vacuum is assumed to exist at the outlet. The reduced gas density,  $\pi/6\sigma_1^3 n_0$ , and temperature,  $T_r/T_0$ , in the reservoir are equal to 0.015 and 0.8, respectively. For condensation to occur, the temperature of the channel walls,  $T_w/T_0$ , has to be lower than the critical temperature of the gas which, for the chosen parameters of the gas-gas potential, is  $T_c \approx 0.75$ . We have set  $T_w/T_0 = 0.7$ , i.e 9% below  $T_c$ . The gas inside the channel has been initialized with the temperature of the reservoir. The simulation has been performed for a time interval from  $(RT_0)^{1/2}/\sigma_1 t = 0$  to  $(RT_0)^{1/2}/\sigma_1 t = 1000$ . Starting from  $t = 40$  the time interval has been divided in 16 sub-intervals, each of width 60, and time averaged macroscopic quantities have been computed over each sub-interval. The number of particles has been set initially to 100000 but it has reached the value of 500000 at  $t = 1000$  because of the gas condensation along the channel walls. Fig. 3 shows the averaged density in the channel in the time intervals  $\Delta t = 460 - 520$  (upper left panel) and  $\Delta t = 940 - 1000$  (lower left panel), respectively, along with the density profile over the vertical plane at  $x = 13$  (right panel). It is apparent that liquid layers form over the channel walls and their width grows as the simulation proceeds. It is worth pointing out that the phase transition takes place spontaneously, without the need to explicitly track the interface. The results presented are only preliminary but they clearly show that the proposed kinetic model has the capability to describe multiphase flows.

## CONCLUSIONS

In the present work, a kinetic model is proposed to study the effects of dense adsorbate layers on rarefied gas flows. The kinetic model is an extension of the Enskog theory of dense fluids and has the capability of handling both the



**FIGURE 3.** Gas flow in a two-dimensional microchannel. **Upper left panel** - Density field at  $\Delta t = 460 - 520$ . **Lower left panel** - Density field at  $\Delta t = 940 - 1000$ . **Right panel** - Density profile for  $x = 13$  at  $\Delta t = 940 - 1000$ . Model parameters setting:  $\bar{\phi}^{(11)}/k_B T_0 = 1$ ,  $\gamma^{(11)} = 6$ ,  $\bar{\phi}^{(12)}/k_B T_0 = 1.5$ ,  $\gamma^{(12)} = 6$ ,  $T_w/T_0 = 0.7$ ,  $\pi/6\sigma_1^3 n_0 = 0.015$ ,  $T_r/T_0 = 0.8$ .

gas and the adsorbed layers in a unified manner. Moreover, it can be efficiently solved with a DSMC code with a computational cost which is negligible with respect to MD simulations. Equilibrium solutions of the kinetic model provides the absorptions isotherm curves which clearly show the existence of a threshold value of the gas density beyond which the collisional effects in adsorbed layers influence significantly the overall dynamics of the gas. This is further confirmed by the tangential stress behaviour in the Couette flow which is shown to be a non-monotonic function of the gas density. In addition, preliminary simulations prove that the kinetic model is able to describe a gas flow through a two-dimensional microchannel in which condensation occurs. The results also suggest that a sufficiently intense gas-surface interaction might produce even denser multi-layer structures which behaves as a two-dimensional fluids [1].

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the support received from European Space Agency within the framework of the project “Application of Macroscopic Theory and Development of Gas-Kinetic Theory of Surface Phase for Gas/Surface Interactions in Hypersonic Flows”.

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