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Abstract: In this paper we revisit the derivation of boundary conditions for the Boltzmann Equation. The interaction between the wall atoms and the gas molecules within a thin surface layer is described by a kinetic equation introduced in [9] and used in [1]. This equation includes a Vlasov term and a linear molecule-phonon collision term and is coupled with the Boltzmann equation describing the evolution of the gas in the bulk flow. Boundary conditions are formally derived from this model by using classical tools of kinetic theory such as scaling and systematic asymptotic expansion. In a first step this method is applied to the simplified case of a flat wall. Then it is extented to walls with nanoscale roughness allowing to obtain more complex scattering patterns related to the morphology of the wall. It is proved that the obtained scattering kernels satisfy the classical imposed properties of non-negativeness, normalization and reciprocity introduced by Cercignani [11].

1 Introduction

The Boltzmann equation is a powerful tool to describe phenomena in a gas flow taking place at a the scale of the order of the mean free path, i.e. the micrometric scale (for the air under stantard conditions). For many applications the gas flow takes place in a region bounded by one or several solid bodies. Then boundary conditions have to be prescribed in order to characterize the behavior of the gas close to the wall [11, 28].

The first attempt to propose boundary conditions for the Boltzmann equation goes backs to Maxwell in a paper of 1879 ([26]) where he discusses the way to describe the interaction between a gas and a wall. The first condition he proposed corresponds to a simple gas-solid interaction where we assume that the wall is smooth, and perfectly elastic, so that the particles of gas are specularly reflected. This condition writes

$$f(t,x,v) = f(t,x,v-2\nu\langle\nu,v\rangle) \quad \langle v,\nu\rangle > 0, \tag{1}$$

where ν is the unit vector to the surface at point x and $f(t,x,v)$ is the distribution function of particles that tt time t and position x have the velocity v. Maxwell noticed that this assumption means that the gas can exert any stress on the surface only in the direction of the normal. But this is not physically relevant because in practical situations it can also exert stress in oblique directions. This is why he introduced another type of boundary conditions corresponding to a more complex gas-solid interaction. Physically he supposed that the wall has a stratum in which fixed elastic spheres are placed. Moreover the stratum is assumed to be deep enough so that every molecule going from the gas to the wall must collide ones or more with the spheres. In this case, the particle is reflected into the gas with a velocity taken with a probability whose density corresponds to the equilibrium state of the gas. In that case the boundary condition (known as the perfect accommodation or diffuse reflexion condition) writes

$$f(t,x,v) = \frac{1}{2\pi(RT)}\int_{\langle v',\nu\rangle<0} |\langle v',\nu\rangle|\, f(t,x,v')dv' \, \exp(-\frac{v^2}{2RT}), \quad \langle v,\nu\rangle > 0, \tag{2}$$

where T is the temperature of the wall. Finally Maxwell considered a more complicated intermediate situation which is devoted to be more physically realistic. This model is intermediate between the two previous ones. Maxwell postulated that there is a fraction of the gas which accomdates to the temperature of the solid and another one which is reflected by the solid. In that case the boundary conditions writes

$$\begin{aligned} f(t,x,v) &= (1-\alpha) f(t,x,v-2\nu\langle\nu,v\rangle) \\ &+ \alpha \frac{1}{2\pi(RT)} \int_{\langle v',\nu\rangle<0} |\langle v',\nu\rangle|\, f(t,x,v')dv' \, \exp(-\frac{v^2}{2RT}), \quad \langle v,\nu\rangle > 0, \end{aligned} \tag{3}$$

where T is still the temperature of the wall and $\alpha \in [0,1]$ is called the accomodation coefficient. It represents the tendency of a gas to accomodate to the wall. It means that a fraction of $(1-\alpha)$ of molecules satisfies specular boundary conditions whereas a fraction of α satisfies Maxwell diffuse boundary conditions. When $\alpha = 0$, we recover the specular boundary conditions and when $\alpha = 1$, we recover the diffuse boundary condition. The main drawback of this condition is that it gives the same accommodation coefficient for energy and momentum though it is known that energy and momentum accommodate differently in physical molecule-wall interactions (see for instance [15]). Nevertheless, this condition has been widely used, both for theoretical studies and numerical simulations for practical applications.

More recently, in [14, 11, 12, 13] Cercignani adressed in great details the question of gas-surface interaction and boundary conditions for the Boltzmann equation with a large bibliography. He introduced a general formulation of the boundary conditions

$$f(t,x,v)|\langle\nu,v\rangle|_{|\langle\nu,v\rangle>0} = \int_{\langle\nu,v'\rangle<0} R(v'\to v,x,t) f(t,x,v')|\langle\nu,v'\rangle|dv', \tag{4}$$

where the scattering kernel $R(v'\to v,x,t)$ characterizes the interaction between the molecules of the gas and the molecules of the wall. More precisely $R(v'\to v,x,t)$ represents the probability density that a molecule stricking the wall with a velocity v' at point x and time t is reemitted at the same point with a velocity between v and $v+dv$. To determine the scattering kernel, Cercignani proposed to use either physical or mathematical considerations.
In the physical approach we have to compute as exactly as possible the path of the molecules within the wall. This is anything but easy since such a molecule may experience various events such as elastic scattering, inelastic scattering (including multi-phonon scattering), temporary or permanent adsorption, mobile adsorption (surface diffusion), condensation, reactive interactions. Therefore, in a first attempt, very simplified models have been used to describe the wall and the interactions such as arrays of smooth hard sphere or hard cubes (see the work of Maxwell and the references given in [13]). A more interesting way to approximate the path of molecules within the wall has been proposed by Cercignani. He suggested to use a transport equation for the molecules inside the solid which is regarded as a half-space. This transport equation includes a Vlasov-type term describing the van der Walls forces exerted on the gas molecules by the solid atoms and a linear collision term (of Boltzmann or Fokker-Plank type) describing the scattering by phonons. Nevertheless, the Maxwell condition (3) can be recovered in this way (with a Boltzmann-like collision term) as well as the Cercignani-Lampis condition [15] (with a Fokker-Plank collision term). This latter condition is free from the physically inconsistence of the Maxwell condition indicated above and has been widely used. More recent works come close to the same approach by determining the molecule-wall interactions by means of molecular dynamics simulation [19, 4]. But an intrinsic difficulty in this physical approach is due to our lack of knowledge of the surface layers of solid walls, which leads Cercignani to propose as an alternative that he called the mathematical approach.
The idea of the mathematical approach is to construct a scattering kernel, as simple as possible,

satisfying the following basic (physical) requirements:

(i) Non-negativeness:

$$R(v' \to v, x, t) \geq 0, \tag{5}$$

(ii) Normalization:

$$\int_{\langle v,\nu\rangle>0} R(v' \to v, x, t)\, dv = 1, \tag{6}$$

this property means that the mass flux through the boundary vanishes. It is valid when permanent adsorption is excluded.
(iii) Reciprocity:

$$|\langle v', \nu\rangle|\, M_w(v')\, R(v' \to v, x, t) = |\langle v, \nu\rangle|\, M_w(v)\, R(-v \to -v', x, t), \tag{7}$$

where M_w is a Maxwellian distribution having the temperature of the wall. This last property means that the microscopic dynamics is time reversible, and that the wall is in a local equilibrium state and is not influenced by the incoming molecule. An example of a well-known scattering kernel derived in such a way is the Cercignani-Lampis model.

In the present paper we use the so called physical approach but we start from a somewhat more sophisticated model introduced in [9] and used in [10, 6, 7, 8, 24, 25, 1] for studying gas-surface interaction, nanoflows and surface diffusion. This model, valid for smooth walls, is still a crude approximation of the complex gas surface interaction, but it proved to be remarkably useful to give new insight on these issues. It couples the Boltzmann equation in the bulk flow with a kinetic model inside a very thin surface layer (with width typically less than a nanometer) where the van der Waals forces are taken into account. This model includes a Vlasov term to take into account the part of the interaction potential that depends on the frozen position of the atoms of the solid wall (the long range interactions), and a Boltzmann like linear collision term between molecules and phonons to take into account the thermal fluctuations of the atoms of the solid (short range interactions).
It contains several characteristic times: the characteristic time of the Boltzmann equation in the bulk flow, the characteristic time of the kinetic model in the surface layer, the characteristic time of flight of a molecule through the surface layer, the characteristic molecule-phonon relaxation time. Then using classical tools of kinetic theory such as scaling asymptotic analysis we can derive various models corresponding to different regimes according to the relative value of the characteristic times. Thus in [1] surface kinetic and surface diffusion models have been derived from this three phase model: they describe mobile adsorption and can be interpreted as *non local* boundary conditions. In the present paper, using different scalings, we derive *local* boundary conditions from the same basic three phase model. First, a weak molecule-phonon interaction regime is considered. In that case the particles of the gas quickly cross the surface layer and the classical specular boundary condition is obtained. Then a strong molecule-phonon interaction is investigated. In this situation the particles of the gas slowly cross the surface layer and are thermalized by the wall leading to Maxwell-diffuse boundary conditions. Finally, an intermediate interaction is assumed, and we get a Maxwell-like boundary condition (3), but with a fraction of diffusely evaporated molecules that depends on the velocity. Moreover, the relationship between this coefficient and the surface-molecule interaction potential is formulated. One of the interesting asset of this boundary condition is that it gives different accommodation coefficients for energy and (normal and tangential) momentum, contrary to the original Maxwell condition. Moreover it must be noted that mobile adsorption (see [1]) as well as elastic or inelastic scattering are treated within the same framework. Finally this analysis is extended to a non-smooth wall with nanoscale roughness assumed to be periodic in the directions parallel to the surface. This leads to a scattering kernel with more complex reflexion patterns that depend on the wall morphology.

This paper is organized as follows. Section 2 deals with the presentation of nanoscale kinetic models describing the interaction between a wall and particles in a very simplifed configuration with a flat wall and simplified expression of the potential. In section 3, the boundary conditions are derived under these assumptions by using asymptotic analysis. In section 4, the same analysis is extended to the more realistic case of a wall with nanoscale roughness and a general potential. Section 5 is devoted to some comments on these results and to concluding remarks.

2 Nanoscale kinetic models for gas-surface interaction

In this section we recall the nanoscale models describing a gas flow near a wall introduced in [9] and [1]. In these models the interaction between the wall and the gas molecules through Van der Walls forces are taken into account in a thin *surface layer* (with thickness L typically smaller than one nanometer). In all the following, for the sake of simplicity, we assume that the molecules move in a 2D half-plane [1] and we consider the following configuration: the solid is occupying the half-space $z > L$, the gas phase is constituted by the gas molecules in the half-space $z < 0$, outside of the range of the surface forces, and we consider separately the *surface layer* $0 < z < L$, where the gas molecules move within the range of the surface potential. The gas flow in this surface layer is modelled by the collisionless Boltzmann equation (the size of this layer is much smaller than the mean free path of the molecules), with a Vlasov term to take into account the part of the interaction potential that depends on the frozen position of the atoms of the solid wall (the long range interactions), and a collision term between molecules and phonons to take into account the thermal fluctuations of the atoms of the solid (short range interactions) (see [9] for a physical justification of this approach). Since in many applications the surface potential is an attractive-repulsive potential, some of the molecules in the surface layer have a total energy which is too small to escape from the potential well and are *trapped* in the surface layer. On the other hand some molecules, called the *free* molecules, have enough energy to escape from the potential well and can leave the surface layer and go into the bulk flow.

Both type of molecules (trapped and free) are taken into account in this approach and we give now more details on the model describing their motion in the surface layer.

2.1 The surface potential

We assume that the wall is flat and we use a simplified interaction potential which writes

$$\mathcal{V}(x, z) = W(z), \tag{8}$$

where W is an attractive-repulsive potential, ie;

(H1) $0 \leq W(z)$,

(H2) $\lim_{z \to L} W(z) = +\infty$,

(H3) the potential W is repulsive (i.e. $W'(z) > 0$) for $z_m \leq z < L$ and is attractive ($W'(z) < 0$) for $0 < z < z_m$, and we set $W(z_m) = 0$

(H4) The range of the surface forces is finite and thus, the potential satisfies $W(z) = W_m$ for $z < 0$.

[1] As indicated in [1] we can assume that the molecules move in the 3D half-space $(x, y, z), z < 0$, provided that f is interpreted as the marginal distribution function obtained by integrating the original distribution function with respect to v_y.

This simplified potential allows to uncouple the parallel motion and the normal motion of gas molecules near the solid wall, which makes the mathematical developments much easier. Moreover, though not physically realistic, this potential is sufficient to obtain accurate information on the behavior of the gas near the walls (see [1] for more details). Extension to a more realistic interaction potential is considered in section 4.

It is useful to introduce in the surface layer the following velocity variable, called equivalent velocity:

$$e_z = sign(v_z)\sqrt{v_z^2 + 2W(z)/m}, \tag{9}$$

which is the velocity of a particle whose total energy $\frac{1}{2}mv_z^2 + W(z)$ would be a kinetic energy $\frac{1}{2}me_z^2$ only. We denote by $e = (v_x, e_z)$ the corresponding two dimensional velocity.

It will be more convenient to describe the distribution function of gas molecules in the surface layer as a function of e rather than a function of (v_x, v_z).

Now, we explain how particles can be divided into two different classes: the free particles and the trapped particles. The trajectory of a particle along z is defined (if there is no collision) by the two differential equations $z'(t) = v_z(t)$ and $mv_z'(t) = \partial_z W(z(t))$. Along this trajectory, the total energy $\frac{1}{2}mv_z^2 + W(z)$ is constant. According to the definition of the equivalent velocity e_z (see (9)), we have $\frac{1}{2}me_z^2 = \frac{1}{2}mv_z^2 + W(z)$ which is a constant too. A particle is free if it can leave the surface layer and go into the gas. In this case, the potential reaches the value W_m, and since its kinetic energy $\frac{1}{2}mv_z^2$ is non-negative, this means that $\frac{1}{2}me_z^2 > W_m$, which is equivalent to $|e_z| > \sqrt{\frac{2}{m}W_m}$. The limit position of this particle when it is inside the surface layer is such that it takes a zero velocity. At this point, denoted by $z_-(e_z)$, we have $W(z_-(e(z))) = \frac{1}{2}me_z^2$ (see figure 1).

At the contrary, a particle is trapped if its total energy is lower that W_m, that is to say $|e_z| < \sqrt{\frac{2}{m}W_m}$. In that case, the potential is bounded by $\frac{1}{2}me_z^2 < W_m$, which means that z varies between two limit values $z_+(e_z)$ and $z_-(e_z)$ such that $W(z_\pm(e_z)) = \frac{1}{2}me_z^2$ (see figure 2): the particle cannot escape from the surface layer.

In order to have the same notation for trapped and free particles, we set $z_+(e_z) = 0$ for free particles (that is to say, if $|e_z| > \sqrt{\frac{2}{m}W_m}$). Moreover, for particles with zero total energy, we have $e_z = 0$ and hence the velocity and the potential are zero too, which means that the particle stay at position $z = z_m$. The we set $z_\pm(0) = z_m$ in this case.

With this definition, note that z_+ and z_- are even functions of e_z.

Now, we introduce some notations that are useful to switch between v_z and e_z variables. The velocity of a particle with equivalent velocity e_z located at position $z \in [z_+(e_z), z_-(e_z)]$ is given by

$$v_z(z, e_z) = sign(e_z)\sqrt{e_z^2 - \frac{2}{m}W(z)}, \tag{10}$$

and we have

$$v_z(z_-(e_z), e_z) = v_z(z_-(-e_z), -e_z) = 0. \tag{11}$$

Moreover, for trapped molecules we also have

$$v_z(z_+(e_z), e_z) = v_z(z_+(-e_z), -e_z) = 0. \tag{12}$$

Let us define

$$\sigma(z, e_z) = \frac{1}{|v_z(z, e_z)|} = (e_z^2 - \frac{2}{m}W(z))^{-1/2} \text{ for } |e_z| > \sqrt{2W(z)/m},$$

so that

$$\sigma(z, e_z)\ v_z(z, e_z) = sign(e_z), \tag{13}$$

and also

$$\tau_z(e_z) \quad = \quad \int_{z_+(e_z)}^{z_-(e_z)} \sigma(z,e_z)dz = \int_{z_+(e_z)}^{z_-(e_z)} (e_z^2 - \frac{2}{m}W(z))^{-1/2}dz.$$

As in [18], $\tau_z(e_z)$ can be interpreted as the time for a molecule to cross the surface layer. Moreover, for every $z \in]0,L]$ the application $v_z \to e_z$ is a one-to-one application from $[0,+\infty[$ onto $[\sqrt{\frac{2}{m}W(z)},+\infty[$ and from $]-\infty,0]$ onto $]-\infty,-\sqrt{\frac{2}{m}W(z)}]$. Therefore differentiating (10) leads to

$$dv_z = |e_z|\sigma(z,e_z)de_z. \tag{14}$$

Thus the integral of a given function $\psi(z,v_z)$ with respect to v_z can be transformed as follows:

$$\int_{v_z} \psi(z,v_z)\ dv_z = \int_{|e_z|>\sqrt{\frac{2}{m}W(z)}} \psi(z,v_z(z,e_z))\ |e_z|\sigma(z,e_z)de_z. \tag{15}$$

Moreover, the order of integration in a z-e_z integral can be changed as follows (see figure 3):

$$\begin{aligned} &\int_0^L \left(\int_{|e_z|>\sqrt{\frac{2}{m}W(z)}} \psi(z,v_z(z,e_z))|e_z|\sigma_z(z,e_z)\ de_z \right)\ dz \\ &\qquad = \int_{-\infty}^{+\infty} \left(\int_{z_+(e_z)}^{z_-(e_z)} (\psi(z,v_z(z,e_z))|e_z|\sigma(z,e_z)\ dz \right)\ de_z. \end{aligned} \tag{16}$$

2.2 Molecule-phonon collision term

In this paper we consider the general molecule-phonon collision term

$$Q[\phi](v) = \int_{I\!R^2} K(v,v')\Big(\exp\Big(-\frac{m|v|^2}{2kT}\Big)\phi(v') - \exp\Big(-\frac{m|v'|^2}{2kT}\Big)\phi(v)\Big)\ dv'.$$

With the new velocity variable $e = (v_x, e_z)$ defined in (9), for a given value of z, this operator reads:

$$Q[\phi](z,e) = Q_+[\phi](z,e) - Q_-[\phi](z,e) = \int_{\mathcal{E}(z)} K(z,e,e')\,(G(e)\phi(e') - G(e')\phi(e))\,J_{e'}\ de', \tag{17}$$

where $\mathcal{E}(z) = \{e',\ |e'_z| \geq \sqrt{2W(z)/m}\}$, $J_{e'} = J(z,e'_z) = |e'_z|\sigma(z,e'_z)$, and

$$G(e) = \exp\left(-\frac{m(|v_x|^2 + |e_z|^2)}{2kT}\right). \tag{18}$$

The collision kernel K is such that $k(z, e \to e') = K(z,e,e')G(e')$ is the probability of transition per unit time from the state e to the state e' in a"collision" with a phonon. The dimension of K is $[time/length^2]$ (or, if the molecules move in a 3D plane, of $[time^2/length^3]$). We assume in the following that

$$\begin{aligned} K(z,e,e') &= K(z,e',e), \\ 0 < \nu_0 &\leq K(z,e,e') \leq \nu_1, \qquad (19) \\ K(z,v_x,-e_z,v'_x,-e'_z) &= K(z,v_x,e_z,v'_x,e'_z), \qquad (20) \\ K(z,-v_x,e_z,v'_x,e'_z) &= K(z,v_x,e_z,v'_x,e'_z). \end{aligned}$$

The loss term of the molecule-phonon collision term can be written

$$Q_-[\phi](z,e) = \frac{1}{\tau_{ms}(z,e)}\phi(z,e), \tag{21}$$

where

$$\tau_{ms}(z,e) = \left(\int_{\mathcal{E}(z)} K(z,e,e') G(e') J(z,e'_z) de' \right)^{-1} \tag{22}$$

is a collision time (at point z). It is useful for the sequel to introduce the mean relaxation time $\overline{\tau}_{ms}(e)$ defined as the harmonic mean of $\tau_{ms}(z,e)$ weighted by $\sigma(z,e_z)$:

$$\frac{1}{\overline{\tau}_{ms}(e)} = \frac{\int_0^{z_-(e_z)} \sigma(z,e_z)/\tau_{ms}(z,e)\ dz}{\int_0^{z_-(e_z)} \sigma(z,e_z)\ dz} = \frac{\int_0^{z_-(e_z)} \sigma(z,e_z)/\tau_{ms}(z,e)\ dz}{\tau_z(e_z)}. \tag{23}$$

Using (20), the even parity of σ, G, J and $z_\pm$ with respect to e_z, and the symmetry of $\mathcal{E}(z)$, we have :

$$\tau_{ms}(z,v_x,-e_z) = \tau_{ms}(z,v_x,e_z), \text{ and } \overline{\tau}_{ms}(v_x,-e_z) = \overline{\tau}_{ms}(v_x,e_z).$$

Let us remark that if we assume $K(z,e,e') = 1$, then τ_m does not depends on e and we have:

$$Q[\phi] = \frac{1}{\tau_{ms}(z)} \left(\frac{n[\phi]}{\gamma(z)} G - \phi \right), \tag{24}$$

where $\gamma(z) = \tau_{ms}(z)^{-1} = \int_{\mathcal{E}(z)} G(e') J(z,e'_z) de'$ and $n[\phi] = \int_{\mathcal{E}(z)} \phi(e') J(z,e'_z) de'$, which is quite similar to the BGK-like relaxation term used in [1]. Finally we recall some of the main properties satisfied by the operator Q.

Proposition 1. *The collision term satisfies the following properties*

$$\int_{\mathcal{E}(z)} Q[\phi](e) J_e\ de = 0, \quad \textit{(mass conservation)}, \tag{25}$$

$$Q[\phi] = 0 \ \Leftrightarrow \ \phi = n\ G, \ \textit{(equilibrium)}, \tag{26}$$

$$\int_{\mathcal{E}(z)} Q[\phi](e)\phi(e) \frac{J_e}{G(e)} de \ \leq \ -\nu_0 \gamma(z) \int_{\mathcal{E}(z)} w^2 \frac{J_e}{G} de, \ \textit{(H theorem)}, \tag{27}$$

$$\int_{\mathcal{E}(z)} Q[\phi](e)\psi(e) \frac{J_e}{G(e)} de = \int_{\mathcal{E}(z)} Q[\psi](e)\phi(e) \frac{J_e}{G(e)} de, \ \textit{(symmetry)}\ , \tag{28}$$

where we used the macro-micro decomposition $\phi = q + w$ with $q = n[\phi]G$ and where $w = \phi - q$ satisfies $n[w] = 0$.

2.3 Nanoscale models

The first model introduced in [9] and [1] is the following system of coupled kinetic equations which describes the flow of molecules in the surface layer (where the Van der Waals forces are acting) and outside:

$$\partial_t f + v_x \partial_x f + v_z \partial_z f = 0, \ z < 0 \tag{29}$$

$$f(t,x,0,v_x,v_z)|_{v_z<0} = \phi(t,x,0,v_x,e_z(0,v_z)), \tag{30}$$

$$\partial_t \phi + v_x \partial_x \phi + v_z(z,e_z)\partial_z \phi = Q[\phi], \ z_+(e_z) < z < z_-(e_z), \tag{31}$$

$$\phi(t,x,0,v_x,e_z)_{e_z > \sqrt{2W_m/m}} = f(t,x,0,v_x,v_z(0,e_z)), \tag{32}$$

$$\phi(t,x,z_-(e_z),v_x,e_z) = \phi(t,z_-(-e_z),v_x,-e_z), \tag{33}$$

$$\phi(t,x,z_+(e_z),v_x,e_z) = \phi(t,z_+(-e_z),v_x,-e_z), \ |e_z| < \sqrt{2W_m/m}, \tag{34}$$

where $f = f(t,x,z,v_x,v_z)$ is the distribution function describing the bulk flow and $\phi = \phi(t,x,z,v_x,e_z)$ is the distribution function describing the gas flow inside the surface layer. Let us remark that

since we have chosen to define ϕ as a function of (v_x, e_z) equation (31) does not contain a Vlasov term in the z-direction.

The above model describes the gas-solid interaction at the nanoscale, i.e on a domain $[0, x^*] \times [-z^*, L]$ with x^* and $z^* \approx 1$ nanometer. But on a larger scale in the tangential direction, this model is too complicated and contains stiff terms that would make its numerical solution too much expensive. Thus in [1] the authors derived a limit model obtained by asymptotic analysis when the domain is much larger than the surface layer (that is to say $x^\star \approx z^* \gg L$). In this model, the flow of molecules in the surface layer is described by a one-dimensional kinetic equation which can be considered as a nonlocal boundary condition for the Boltzmann equation in the bulk flow.

But on a larger scale in x and z this last model is still too complicated to manage and it would be interesting to investigate the relation between these nanoscale models and the standard boundary conditions used with the Boltzmann equation in gas kinetic theory.

In the following, we use the nanoscale model (29-34) to derive various boundary conditions for the Boltzmann equation (29), according to convenient scalings.

3 Derivation of boundary conditions: case of a flat wall

In this section, we assume that the characteristic times of the flow in the surface layer (the time for a molecule to cross the surface layer and the relaxation time of molecules by phonons) are much smaller than the characteristic time of evolution of the bulk flow. We derive boundary conditions for the Boltzmann equation in the bulk flow by an asymptotic analysis of system (29-34). The main point in this derivation is to find the solution of a linear kinetic problem which describes, in a first approximation, the motion of the molecules in the surface layer. Unfortunately this problem cannot be solved exactly but approximated solutions can be obtained (see Lemma 1) through an iterative process.

We consider system (29-34) and we introduce the following dimensionless quantities:

$$\tilde{n} = \frac{n}{n^*}, \tilde{v}_x = \frac{v_x}{v^*}, \tilde{v}_z = \frac{v_z}{v^*}, \tilde{e}_z = \frac{e_z}{v^*}, \tilde{f} = \frac{f}{f^*}, \tilde{\phi} = \frac{\phi}{f^*}, \tilde{x} = \frac{x}{l^*},$$
$$\tilde{W} = \frac{W}{W^*}, \tilde{W}_m = \frac{W_m}{W^*}, \tilde{t} = \frac{t}{t_B^*}, \tilde{\tau}_z = \frac{\tau_z}{\tau_z^*}, \tilde{\tau}_{ms} = \frac{\tau_{ms}}{\tau_{ms}^*}, \tilde{K} = \frac{K}{K^*},$$

and $\tilde{z} = \frac{z}{l^*}$ for the Boltzmann equation in the bulk flow, while $\tilde{z} = \frac{z}{L}$ in the surface layer. The reference quantities are the followings: n^* is the reference number density, $v^* = \sqrt{kT/m}$, $f^* = n^*/{v^*}^2$, t_B^* is the reference time of evolution for the Boltzmann equation (29), $l^* = v^* t_B^*$, $\tau_{ms}^* = 1/(K^* {v^*}^2)$ is a reference relaxation time, $\tau_z^* = L/v^*$ is the characteristic time of flight of a molecule through the surface layer, and $W^* = m{v^*}^2/2$.

In order to study different regimes corresponding to different order of magnitude of the characteristic time scales τ_z^*, τ_{ms}^* and t_B^*, we introduce the following nondimensional parameters:

$$\varepsilon = \frac{\tau_{ms}^*}{t_B^*} \qquad \text{and} \qquad \eta = \frac{\tau_{ms}^*}{\tau_z^*}.$$

Then system (29-34) reads in dimensionless form

$$\begin{aligned}
\partial_{\tilde t}\tilde f + \tilde v_x\partial_{\tilde x}\tilde f + \tilde v_z\partial_{\tilde z}\tilde f &= 0,\ \tilde z < 0, && (35)\\
\tilde f(\tilde t,\tilde x,0,\tilde v_x,\tilde v_z)_{\tilde v_z<0} &= \tilde\phi(\tilde t,\tilde x,0,\tilde v_x,\tilde e_z(0,\tilde v_z)), && (36)\\
\partial_{\tilde t}\tilde\phi + \tilde v_x\partial_{\tilde x}\tilde\phi + \frac{\eta}{\varepsilon}\tilde v_z(\tilde z,\tilde e_z)\partial_{\tilde z}\tilde\phi &= \frac{1}{\varepsilon}\tilde Q[\tilde\phi],\ \tilde z_+(\tilde e_z) < \tilde z < \tilde z_-(\tilde e_z), && (37)\\
\tilde\phi(\tilde t,\tilde x,0,\tilde v_x,\tilde e_z)_{\tilde v_z>0} &= \tilde f(\tilde t,\tilde x,0,\tilde v_x,\tilde v_z(0,\tilde e_z)), && (38)\\
\tilde\phi(\tilde t,\tilde x,\tilde z_-(\tilde e_z),\tilde v_x,\tilde e_z) &= \tilde\phi(\tilde t,\tilde z_-(\tilde e_z),\tilde v_x,-\tilde e_z), && (39)\\
\tilde\phi(\tilde t,\tilde x,\tilde z_+(\tilde e_z),\tilde v_x,\tilde e_z) &= \tilde\phi(\tilde t,\tilde z_+(\tilde e_z),\tilde v_x,-\tilde e_z),\ \text{for } |\tilde e_z| < \sqrt{\tilde W_m}. && (40)
\end{aligned}$$

We mention that with this dimensionless variables, a particle of velocity e_z located at z is:

- either trapped if $|\tilde e_{\tilde z}| < \sqrt{\tilde W_m}$, and hence stays between $\tilde z_\pm(\tilde e_{\tilde z})$ defined by $\tilde W(\tilde z_\pm(\tilde e_z)) = \tilde e_z^2$,
- or free if $|\tilde e_z| > \sqrt{\tilde W_m}$, and hence stays on the left-hand-side of $\tilde z_-(\tilde e_z)$ defined by $\tilde W(\tilde z_-(\tilde e_z)) = \tilde e_z^2$. We set $\tilde z_+(\tilde e_{\tilde z}) = 0$ in this case.

We can obtain boundary conditions for the Boltzmann equation through an asymptotic analysis of the above system when $\varepsilon \to 0$. This leads to the following results.

Proposition 2. *Under the hypothesis (8) and (H1-H4), in the limit $\varepsilon \to 0$, the gas-surface interaction depends on the order of magnitude of η and can be described by the following boundary conditions at $z = 0$:*

1. *for $\eta = O(\frac{1}{\varepsilon})$, the boundary condition is the specular reflection*

$$f(t,x,0,v_x,v_z)_{|v_z<0} = f(t,x,0,v_x,-v_z).$$

2. *for $\eta = O(\varepsilon)$, the boundary condition is the reflection with perfect accommodation*

$$f(t,x,0,v_x,v_z)_{|v_z<0} = \kappa(t,x)M(v_x,v_z), \qquad (41)$$

where

$$\kappa(t,x) = \int_{v_z>0}\int v_z f(t,x,0,v_x,v_z)dv_xdv_z \Big/ \int_{v_z>0}\int v_z M(v_x,v_z)dv_xdv_z$$

is such that the mass flux of f through the boundary $z = 0$ is zero, and where $M(v) = \exp\left(-m(v_x^2+v_z^2)/2kT\right)$.

3. *for $\eta = O(1)$, the boundary condition writes, in a first approximation, as a Maxwell-like boundary condition*

$$f(t,x,0,v_x,v_z)_{|v_z<0} = a(v)\beta_1(t,x)M(v) + (1-a(v))f(t,x,0,v_x,-v_z),$$

and

$$\begin{aligned}
a(v) &= 1 - \exp\left(-\frac{2\hat\tau_z(v_z)}{\hat\tau_{ms}(v)}\right) && (42)\\
\beta_1(t,x) &= \int_{v_z>0}\int v_z a(v) f(t,x,0,v_x,v_z)dv_xdv_z \Big/ \int_{v_z>0}\int v_z a(v) M(v_x,v_z)dv_xdv_z,
\end{aligned}$$

with the notations $\hat\tau_z(v_z) = \tau_z(e_z(0,v_z))$ and $\hat\tau_{ms}(v) = \overline{\tau}_{ms}(v_x,e_z(0,v_z))$. This boundary condition ensures a zero mass flux of f at the boundary $z = 0$. Moreover, it can be written under the general form (4) with a scattering kernel $R(v' \to v)$ that satisfies the properties of non-negativeness, normalization and reciprocity.

Proof:
In order to simplify the notations, the tilde ˜ over the dimensionless quantities are dropped in the following. To avoid confusion, we will indicate explicitely when we come back to dimensional quantities.

In order to perform an asymptotic analysis of system (35-40), we look for a solution in the form

$$f = f_\varepsilon = f^0 + \varepsilon f^1 + ..., \quad \phi = \phi_\varepsilon = \phi^0 + \varepsilon \phi^1 + ...$$

This expansion is inserted into (35–40) and we identify the terms of same power of magnitude w.r.t ε. The zeroth-order term f^0 satisfies

$$\begin{aligned} \partial_t f^0 + v_x \partial_x f^0 + v_z \partial_z f^0 &= 0, & (43)\\ f^0(t,x,0,v_x,v_z)_{v_z<0} &= \phi^0(t,x,0,v_x,e_z(0,v_z)). & (44) \end{aligned}$$

However, the zeroth-order term ϕ^0 depends on the order of magnitude of η.

(1) We consider the case $\eta = O(\frac{1}{\varepsilon})$. This means that

$$\tau_z^* \ll \tau_{ms}^* \ll t_B^*,$$

that is to say the free time of flight of a molecule to cross the surface layer is much smaller than the relaxation time of molecules by phonons. Thus the flow of molecules crosses the surface layer so quickly that the relaxation phenomena can be neglected. Then ϕ^0 satisfies the following linear kinetic surface layer (LKSL) problem:

$$\begin{aligned} v_z(z,e_z)\partial_z \phi^0 &= 0, \ \text{ for } z_+(e_z) < z < z_-(e_z), & (45)\\ \phi^0(t,x,0,v_x,e_z)_{e_z>\sqrt{W_m}} &= f^0(t,x,0,v_x,v_z(0,e_z)), & (46)\\ \phi^0(t,x,z_-(e_z),v_x,e_z) &= \phi^0(t,x,z_-(e_z),v_x,-e_z), & (47)\\ \phi^0(t,x,z_+(e_z),v_x,e_z) &= \phi^0(t,x,z_+(e_z),v_x,-e_z), \ \text{ for } |e_z| < \sqrt{W_m}. & (48) \end{aligned}$$

Consider some $v_z < 0$ and the boundary condition (44) where we write $\bar{e}_z = e_z(0,v_z)$:

$$f^0(t,x,0,v_x,v_z)_{v_z<0} = \phi^0(t,x,0,v_x,\bar{e}_z). \quad (49)$$

Since (45) implies that ϕ^0 does not depend on z, we can replace $z = 0$ in the right-hand side of (49) by $z = z_-(e_z)$ to get

$$f^0(t,x,0,v_x,v_z)_{v_z<0} = \phi^0(t,x,z_-(\bar{e}_z),v_x,\bar{e}_z).$$

Moreover (47) and the even parity of z_- imply

$$f^0(t,x,0,v_x,v_z)_{v_z<0} = \phi^0(t,x,z_-(-\bar{e}_z),v_x,-\bar{e}_z).$$

Again, we use the fact that ϕ^0 does not depend on z to get

$$f^0(t,x,0,v_x,v_z)_{v_z<0} = \phi^0(t,x,0,v_x,-\bar{e}_z),$$

where, by definition, $-\bar{e}_z \geq \sqrt{W_m}$. Now we can use (46) to replace the right-hand side of the previous relation and to get the specular boundary condition

$$f^0(t,x,0,v_x,v_z)_{v_z<0} = f^0(t,x,0,v_x,-v_z).$$

We mention that we used $\eta = O(\frac{1}{\varepsilon})$ for simplicity. In fact, we recover the same boundary condition if $\eta = O(\varepsilon^{-\alpha})$, for every positive α.

(2) Now we assume $\eta = O(\varepsilon)$, which implies that

$$\tau^*_{ms} \ll \tau^*_z \ll t^*_B.$$

This means that the relaxation time of molecules by phonons is much smaller than the free time of flight of a molecule to cross the surface layer. In this limit the flow of incoming molecules into the surface layer immediately relaxes toward the equilibrium. Now the LKSL problem satisfied by ϕ^0 reads

$$\begin{aligned}
Q[\phi^0] &= 0, \quad \text{for } z_+(e_z) < z < z_-(e_z), && (50)\\
\phi^0(t,x,0,v_x,e_z)_{e_z>0} &= f^0(t,x,0,v_x,v_z(0,e_z)), && (51)\\
\phi^0(t,x,z_-(e_z),v_x,e_z) &= \phi^0(t,z_-(e_z),v_x,-e_z), && (52)\\
\phi^0(t,x,z_+(e_z),v_x,e_z) &= \phi^0(t,x,z_+(e_z),v_x,-e_z), \text{ for } |e_z| < \sqrt{W_m} && (53)
\end{aligned}$$

which gives

$$\phi^0(t,x,z,v_x,e_z) = \alpha(t,x)G(v_x,e_z), \text{ for } z_+(e_z) < z < z_-(e_z). \tag{54}$$

However, the distribution function ϕ^0 is Maxwellian and hence cannot satisfy the inflow boundary condition (51). Thus we have to introduce in the expansion of ϕ a Knudsen-layer corrector

$$\phi(t,x,z,v_x,e_z) = \phi^0(t,x,z,v_x,e_z) + \psi^0(t,x,\frac{z}{\varepsilon},v_x,e_z) + \varepsilon\phi^1(t,x,z,v_x,e_z) + ...,$$

where ϕ^0 is still defined by (54) and satisfies (50, 52, 53), and $\psi^0(t,x,y,v_x,e_z)$ is given by

$$\begin{aligned}
v_z(0,e_z)\partial_y\psi^0 &= Q[\psi^0], \text{ for } |e_z| \geq \sqrt{W_m},\ 0 < y < +\infty, && (55)\\
\psi^0(t,x,0,v_x,e_z)_{|e_z>0} &= f^0(t,x,0,v_x,v_z(0,e_z)) - \phi^0(t,x,0,v_x,e_z), && (56)
\end{aligned}$$

and should rapidly decrease to 0 for large y. It is useful to introduce $\chi(t,x,y,v_x,e_z)$ defined by

$$\chi(t,x,y,v_x,e_z) = \psi^0(t,x,y,v_x,e_z) + \phi^0(t,x,0,v_x,e_z). \tag{57}$$

Thus χ is the unique bounded solution of the following linear half-space problem

$$\begin{aligned}
v_z(0,e_z)\partial_y\chi &= Q_0[\chi] && (58)\\
\chi(t,x,0,v_x,e_z)_{|e_z>0} &= f^0(t,x,0,v_x,v_z(0,e_z)), && (59)
\end{aligned}$$

where

$$Q_0[\chi] = \int_{\mathcal{E}(0)} K(0,e,e')\,(G(e)\chi(e') - G(e')\chi(e))\,J(0,e')\;de'.$$

Then using the result given in [21] and [23] on the linear half-space problem we get the approximation

$$\chi(t,x,y,v_x,e_z)_{|e_z<0} \approx \chi^{(1)}(t,x,y,v_x,e_z)_{|e_z<0} = \kappa(t,x)G \tag{60}$$

for every $y \geq 0$, where κ can be determined as follows. A standard result on the linear half-space problem (58–59) shows that χ necessarily satisfies $\int_{\mathcal{E}(z)} e_z\chi(t,x,y,v_x,e_z)\,de = 0$ for every y. Then, writing this relation at $y = 0$ and using the boundary condition (59) and the approximation (60) give the definition

$$\begin{aligned}
\kappa(t,x) &= -\frac{\int_{e_z>0 \text{ in } \mathcal{E}(0)} e_z f^0(t,x,0,v_x,v_z(0,e_z))\,de}{\int_{e_z<0 \text{ in } \mathcal{E}(0)} e_z G(e)\,de}\\
&= \frac{\int_{v_z>0}\int v_z f^0(t,x,0,v_x,v_z)\,dv_x dv_z}{\int_{v_z>0}\int v_z M(v_x,v_z)\,dv_x dv_z},
\end{aligned} \tag{61}$$

where $M(v_x, v_z) = G(v_x, e_z(0, v_z)) = \exp(-(v_x^2 + v_z^2)/2)$.

Now, note that (44) has to be modified according to the Knudsen layer correction to get

$$\begin{aligned} f^0(t, x, 0, v_x, v_z)_{v_z<0} &= \phi^0(t, x, 0, v_x, e_z(0, v_z)) + \psi^0(t, x, 0, v_x, e_z(0, v_z)) \\ &= \chi(t, x, 0, v_x, e_z(0, v_z)). \end{aligned}$$

Consequently, the definition (57) of χ and the approximation (60) give the following approximation of the outgoing distribution

$$f^0(t, x, 0, v_x, v_z)_{v_z<0} \approx \kappa(t, x) M(v_x, v_z), \tag{62}$$

which gives in dimensional variables the classical perfect accommodation boundary condition (41) (sometimes called the diffuse reflexion boundary condition), provided that the coefficient κ is such that the corresponding approximation of the mass flux of f^0 at the boundary $z = 0$ is zero. Indeed, the definition (61) of κ implies that this property holds.

(3) Finally, we assume $\eta = O(1)$, which corresponds to $\tau^*_{ms} \approx \tau^*_z \ll t^*_B$. The LKSL problem satisfied by ϕ^0 is

$$\begin{aligned} v_z(z, e_z)\partial_z \phi^0 &= Q[\phi^0], \quad \text{for } z_+(e_z) < z < z_-(e_z), & (63)\\ \phi^0(t, x, 0, v_x, e_z)_{e_z>\sqrt{W_m}} &= f^0(t, x, 0, v_x, v_z(0, e_z)), & (64)\\ \phi^0(t, x, z_-(e_z), v_x, e_z) &= \phi^0(t, x, z_-(e_z), v_x, -e_z), & (65)\\ \phi^0(t, x, z_+(e_z), v_x, e_z) &= \phi^0(t, x, z_+(e_z), v_x, -e_z), \text{ for } |e_z| < \sqrt{W_m}. & (66) \end{aligned}$$

We can claim that this linear kinetic surface layer (LKSL) problem has a unique solution and that this solution has a zero mass flux through the surface $z = 0$ (see lemma 1 in the following):

$$\int_{|e_z|>\sqrt{W_m}} \int e_z \phi^0(t, x, 0, v_x, e_z)\, dv_x de_z = 0. \tag{67}$$

Now if we solve the LKSL problem (63-66), then $\phi^0(t, x, 0, v_x, e_z)$, which is the value of the solution at $z = 0$ for $e_z < 0$, gives a boundary value for (44). This value linearily depends on the inflow data: $\phi^0(t, x, 0, v_x, e_z(0, v_z)) = \mathcal{A}\ (f^0(t, x, 0, v_x, .)_{|v_z>0})$, where $\mathcal{A}$ is called the "albedo" operator $\mathcal{A}$. Consequently, the boundary condition (44) of (43) reads

$$f^0(t, x, 0, v_x, v_z < 0) = \mathcal{A}\ (f^0(t, x, 0, v_x, .)_{|v_z>0}). \tag{68}$$

This relation can be interpreted as an exact boundary condition. However, the operator $\mathcal{A}$ is implicitely defined: we must solve the LKSL problem (63-66) to get $\phi^0(t, x, 0, v_x, e_z)_{e_z<0}$, which could be done approximately by a numerical computation. Nevertheless, it is possible to get an approximation of the operator $\mathcal{A}$ that explicitely gives $\phi^0(t, x, 0, v_x, e_z)_{e_z<0}$ as a function of $f^0(t, x, 0, v_x, v_z(0, e_z))_{|e_z>0}$: using again Lemma 1 we conclude that

$$\begin{aligned} \phi^0(t, x, 0, v_x, e_z)_{e_z<0} &\approx \phi^{0,1}(t, x, 0, v_x, e_z)_{e_z<0}, \\ &\approx (1 - a(e_z)) f^0(t, x, 0, v_x, -v_z(0, e_z)) + a(e_z)\alpha(t, x) G(v_x, e_z). \end{aligned}$$

From (44), we get

$$\begin{aligned} f^0(t, x, 0, v_x, v_z)_{v_z<0} &\approx \phi^{0,1}(t, x, 0, v_x, e_z(0, v_z)) \\ &\approx (1 - a(v_z)) f^0(t, x, 0, v_x, -v_z) + a(v_z)\beta(t, x) M(v_x, v_z). \end{aligned}$$

Moreover, for the same reason as for the previous regime, the approximation of mass flux of f^0 through the boundary $z = 0$, and hence the coefficient β can be uniquely determined. Coming back

in dimensional variables, we get (3). From this relation we can easily check that the associated scattering kernel satisfies the properties of non-negativeness, normalization and since $a(v) = a(-v)$, the property of reciprocity.

□

Lemma 1. *Let us consider the linear kinetic surface layer problem (LKSL)*

$$\begin{aligned} v_z(z,e_z)\partial_z\phi^0 &= Q[\phi^0], \quad \textit{for } z_+(e_z) < z < z_-(e_z), && (69)\\ \phi^0(0,v_x,e_z)_{e_z>\sqrt{W_m}} &= f^*(v_x, v_z(0,e_z)), && (70)\\ \phi^0(z_-(e_z),v_x,e_z) &= \phi^0(z_-(e_z),v_x,-e_z), && (71)\\ \phi^0(z_+(e_z),v_x,e_z) &= \phi^0(z_+(e_z),v_x,-e_z), \ \textit{for } |e_z| < \sqrt{W_m}. && (72) \end{aligned}$$

This problem has a unique solution and this solution has a zero mass flux through the surface $z = 0$:

$$\int_{|e_z|>\sqrt{W_m}} \int e_z\phi^0(0,v_x,e_z)\ dv_x de_z = 0. \tag{73}$$

Moreover in a first approximation we have

$$\phi^0(0,v_x,e_z)_{|e_z<-\sqrt{W_m}} \approx (1-a(e_z))f^*(v_x,-v_z(0,e_z)) + a(e_z)\alpha_1 G(v_x,e_z),$$

where the coefficient a is given by

$$a(e) = 1 - \exp\left(-\frac{2\tau_z(e_z)}{\bar{\tau}_{ms}(e)}\right). \tag{74}$$

Proof :
(i) Existence and uniqueness: Existence and uniqueness of a solution of the LKSL problem (69-72) can be proved by using standard techniques in linear transport problems. The reader can refer, for instance, to [20].

(ii) Mass flux at $z = 0$: Multiplying (69) by $|e_z|\sigma(z,e_z)$ and using (13), we get

$$e_z\partial_z\phi^0 = Q[\phi^0]|e_z|\sigma(z,e_z).$$

Now we integrate this relation with respect to z. It comes

$$\int_{z_+(e_z)}^{z_-(e_z)} e_z\partial_z\phi^0\ dz = \int_{z_+(e_z)}^{z_-(e_z)} Q[\phi^0]|e_z|\sigma(z,e_z)\ dz,$$

or,

$$e_z\phi^0(z_-(e_z),v_x,e_z) - e_z\phi^0(z_+(e_z),v_x,e_z) = \int_{z_+(e_z)}^{z_-(e_z)} Q[\phi^0]|e_z|\sigma(z,e_z)\ dz,$$

where $z_+(e_z) = 0$ for $|e_z| > \sqrt{W_m}$. Now integrating with respect to v_x and e_z, we find

$$\begin{aligned} \int\int e_z\phi^0(z_-(e_z),v_x,e_z)\ dv_x de_z - \int\int e_z\phi^0(z_+(e_z),v_x,e_z)\ dv_x de_z \\ = \int\int\int_{z_+(e_z)}^{z_-(e_z)} Q[\phi^0]|e_z|\sigma(z,e_z)\ dz dv_x de_z. \end{aligned} \tag{75}$$

But since $e_z\phi^0(z_\pm(e_z),v_x,e_z)\ dv_xde_z$ is an odd function of e_z (see (71) and (72)), the first term of the left-hand side of this relation vanishes and the second one gives

$$\begin{aligned}\int\int e_z\phi^0(z_+(e_z),v_x,e_z)\ dv_xde_z &= \int\int_{|e_z|<\sqrt{W_m}} e_z\phi^0(z_+(e_z),v_x,e_z)\ de_zdv_x\\ &+ \int\int_{|e_z|>\sqrt{W_m}} e_z\phi^0(0,v_x,e_z)\ de_zdv_x,\\ &= \int\int_{|e_z|>\sqrt{W_m}} e_z\phi^0(0,v_x,e_z)\ de_zdv_x.\end{aligned}$$

Consequently, (75) now reads

$$-\int\int_{|e_z|>\sqrt{W_m}} e_z\phi^0(0,v_x,e_z)\ de_zdv_x = \int\int\int_{z_+(e_z)}^{z_-(e_z)} Q[\phi^0]|e_z|\sigma(z,e_z)\ dzdv_xde_z.$$

Finally, inverting the integration with respect to z and the integration with respect to v_x and e_z in the right-hand side (see (16)), we get

$$\begin{aligned}-\int\int_{|e_z|>\sqrt{W_m}} e_z\phi^0(0,v_x,e_z)\ dv_xde_z &= \int_0^L\int_{\mathcal{E}(z)} Q[\phi^0]|e_z|\sigma(z,e_z)\,dedz,\\ &= 0,\end{aligned}$$

due to the mass conservation (see (25)).

(iii) Approximate solution of the LKSL problem

First, we multiply (69) by $\sigma(z,e_z)$, and we use the decomposition of the collision operator into gain and loss terms to rewrite (69) as

$$sign(e_z)\partial_z\phi^0 = \sigma(z,e_z)Q^+[\phi^0] - \frac{\sigma(z,e_z)}{\tau_{ms}(z,e_z)}\phi^0,\ \text{for } z_+(e_z)<z<z_-(e_z) \tag{76}$$

Now we proceed by looking for an approximate solution of the boundary value problem (76,70–72) in the form $\phi^0=\phi^{0,(1)}+\phi^{0,(2)}+....$, and we detail below how we construct the first approximation $\phi^{0,(1)}$.

Let us remark that if f^* is a Maxwellian, then $\alpha G(v_x,e_z)$ is a solution of the LKSL problem for any constant α. Therefore, we propose to construct a first approximation $\phi^{0,(1)}$ of ϕ^0 as follows. We replace ϕ^0 in the gain term of (76) by the Maxwellian $\phi^{0,(0)}=\alpha_1\,G(v_x,e_z)$ (where the constant α_1 is undetermined for the moment) to get the following problem that defines $\phi^{0,(1)}$:

$$sign(e_z)\partial_z\phi^{0,(1)} = \frac{\sigma(z,e_z)}{\tau_{ms}(z,e_z)}\left(\alpha_1\frac{G(e)}{\tau_{ms}(z,e)}-\phi^{0,(1)}\right),\quad z_+(e_z)<z<z_-(e_z), \tag{77}$$

$$\phi^{0,(1)}(0,v_x,e_z)_{e_z>\sqrt{W_m}} = f^*(v_x,v_z(0,e_z)), \tag{78}$$

$$\phi^{0,(1)}(z_-(e_z),v_x,e_z) = \phi^{0,(1)}(z_-(e_z),v_x,-e_z), \tag{79}$$

$$\phi^{0,(1)}(z_+(e_z),v_x,e_z) = \phi^{0,(1)}(z_+(e_z),v_x,-e_z),\ \text{for } |e_z|<\sqrt{W_m}. \tag{80}$$

Then the solution $\phi^{0,(1)}$ can be explicitely constructed by integrating (77) along trajectories of free and trapped molecules. This approach guarantees that the corresponding approximated boundary condition (3) is exact is f is a Maxwellian.

free molecules with $e_z>0$ ($e_z>\sqrt{W_m}$):

in that case, particles go from $z_+(e_z) = 0$ to $z_-(e_z)$, and we can integrate (77) between 0 and some $z \in [0, z_-(e_z)]$ to get

$$\begin{aligned}\phi^{0,(1)}(z, v_x, e_z) &= \exp\left(-\int_0^z \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta\right) f^*(v_x, v_z(0, e_z)) \\ &+ \exp\left(-\int_0^z \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta\right) \int_0^z \exp\left(\int_0^\zeta \frac{\sigma(\eta, e_z)}{\tau_{ms}(\eta, e)} d\eta\right) \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta \ \alpha_1 G.\end{aligned} \tag{81}$$

We write this relation at $z = z_-(e_z)$, we use the definition of $\overline{\tau}_{ms}$ (see (23)), and then exact computations of the integral of the exponential gives

$$\phi^{0,(1)}(z_-(e_z), v_x, e_z)_{|e_z>0} = \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right) f^*(v_x, v_z(0, e_z)) + \left(1 - \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right)\right) \alpha_1 G. \tag{82}$$

free molecules with $e_z < 0$ ($e_z < -\sqrt{W_m}$):

in that case, particles go from $z_-(e_z)$ to $z_+(e_z) = 0$. First, we use (79), (82), the even parity of $\bar{\tau}_{ms}$, τ_z and G and the odd parity of $v_z(0, e_z)$ with respect to e_z to obtain the distribution of outgoing particles at $z = z_-(e_z)$:

$$\phi^{0,(1)}(z_-(e_z), v_x, e_z)_{|e_z<0} = \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right) f^*(v_x, -v_z(0, e_z)) + \left(1 - \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right)\right) \alpha_1 G.$$

Then we can integrate (77) between $z_-(e_z)$ and some $z \in [0, z_-(e_z)]$ to get

$$\begin{aligned}&\phi^{0,(1)}(z, v_x, e_z) = \\ &\exp\left(-\int_z^{z_-} \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta\right) \left(\exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right) f^*(v_x, -v_z(0, e_z)) + (1 - \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right))\alpha_1 G\right) \\ &- \left(\exp\left(-\int_z^{z_-} \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta\right) - 1\right) \alpha_1 G,\end{aligned}$$

and hence the distribution of outgoing particles at $z = 0$:

$$\phi^{0,(1)}(0, v_x, e_z)_{|e_z<0} = \exp\left(-\frac{2\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right) f^*(v_x, -v_z(0, e_z)) + \left(1 - \exp\left(-\frac{2\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right)\right) \alpha_1 G.$$

This shows that we can construct the first approximation $\phi^{0,(1)}$ for free particles, and that this approximation satisfies a Maxwell boundary condition at $z = 0$ with the accomodation coefficient $a(e) = 1 - \exp\left(-\frac{2\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right)$, provided that the coefficient α_1 can be defined such that the corresponding mass flux is zero. Indeed, using (78) and (83), it is sufficient to set

$$\alpha_1 = \left(\int\int_{e_z>\sqrt{W_m}} e_z a(e) f^*(v_x, -v_z(0, e_z)) de_z dv_x\right) / \left(\int\int_{e_z>\sqrt{W_m}} e_z a(e) G(v_x, e_z) de_z dv_x\right).$$

Now, $\phi^{0,(1)}$ must also be constructed for trapped particles in order to have a complete approximation of ϕ^0. In the following, we follow the same approach as that used for free particles.

trapped molecules with $e_z > 0$ ($e_z < \sqrt{W_m}$):

in that case, particles go from $z_+(e_z)$ to $z_-(e_z)$, and we can integrate (77) between $z_+(e_z)$ and some $z \in [z_+(e_z), z_-(e_z)]$ to get

$$\begin{aligned}\phi^{0,(1)}(z, v_x, e_z) &= \exp\left(-\int_{z_+(e_z)}^{z} \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta\right) \phi^{0,(1)}(z_+(e_z), v_x, e_z) \\ &+ \exp\left(-\int_{z_+(e_z)}^{z} \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta\right) \int_{z_+(e_z)}^{z} \exp\left(\int_{z_+(e_z)}^{\zeta} \frac{\sigma(\eta, e_z)}{\tau_{ms}(\eta, e)} d\eta\right) \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta \ \alpha_1 G,\end{aligned} \tag{83}$$

and thus

$$\phi^{0,(1)}(z_-(e_z), v_x, e_z)_{|e_z>0} = \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right) \phi^{0,(1)}(z_+(e_z), v_x, e_z) + \left(1 - \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right)\right) \alpha_1 G. \tag{84}$$

trapped molecules with $e_z < 0$ ($e_z > -\sqrt{W_m}$):

in that case, particles go from $z_-(e_z)$ to $z_+(e_z)$. Consequently, we use (79), (84), the even parity of $\bar{\tau}_{ms}$, τ_z and G and the odd parity of $v_z(0, e_z)$ with respect to e_z to obtain the distribution of outgoing particles at $z = z_-(e_z)$:

$$\phi^{0,(1)}(z_-(e_z), v_x, e_z)_{|e_z<0} = \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right) \phi^{0,(1)}(z_+(e_z), v_x, -e_z) + \left(1 - \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right)\right) \alpha_1 G.$$

Then we can integrate (77) between $z_-(e_z)$ and some $z \in [z_+(e_z), z_-(e_z)]$ to get

$$\begin{aligned}\phi^{0,(1)}(z, v_x, e_z) = \exp\left(-\int_{z}^{z_-} \frac{\sigma(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta\right) &\left(\exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right) \phi^{0,(1)}(z_+(e_z), v_x, -e_z)\right. \\ &\left. +(1 - \exp\left(-\frac{\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right))\alpha_1 G\right) \\ - \left(\exp\left(-\int_{z}^{z_-} \frac{\tilde{\sigma}(\zeta, e_z)}{\tau_{ms}(\zeta, e)} d\zeta\right) - 1\right) &\alpha_1 G,\end{aligned} \tag{85}$$

and thus

$$\phi^{0,(1)}(z_+(e_z), v_x, e_z)_{|e_z<0} = \exp\left(-\frac{2\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right) \phi^{0,(1)}(z_+(e_z), v_x, -e_z) + \left(1 - \exp\left(-\frac{2\tau_z(e_z)}{\overline{\tau}_{ms}(e)}\right)\right) \alpha_1 G.$$

Then we can use (80) in the previous relation to deduce that $\phi^{0,(1)}(z_+(e_z), v_x, e_z) = \alpha_1 G$ for every trapped particles. Finally, using (83) and (85) we obtain

$$\phi^{0,(1)}(z, v_x, -e_z) = \alpha_1 G, \quad \text{for } z_+(e_z) \leq z \leq z_-(e_z),$$

that is to say that trapped molecules are in equilibrium in $[z_+(e_z), z_-(e_z)]$. The first approximation $\phi^{0,(1)}$ of ϕ^0 now is completely defined.

□

4 Derivation of boundary conditions: wall with nanoscale roughness

We assumed so far that the surface of the solid wall is flat and that the potential has the simplified form (8). Following the same approach, but with notations and algebra a bit more tricky,

we could obtain similar results for a more general attractive-repulsive surface potential $\mathcal{V}(x,z)$, corresponding to a smooth wall, i.e. such that $\mathcal{V}(x,z) = +\infty$ at $z = L$. Moreover we can extend the approach to the case of a wall with nanoscale roughness (a wall on which there are a great number of minute asperities and which may induce multiple scattering as indicated in [26]). More precisely, let us consider the following configuration for the wall : we assume that the surface layer is included in $[0, L]$ and that the potential $\mathcal{V}(x,z)$ is such that

$$\mathcal{V}(x,z) = \mathcal{V}_{\#}(\frac{x}{L_*}, z), \tag{86}$$

where $L_* = \beta_* L$ and β_* is a positive constant that characterizes the roughness of the wall, and $\mathcal{V}_{\#}(y,z)$ is a periodic function of the nanoscopic variable y with period 1. This nanoscopic variable y allows us to describe how a molecule impiging the surface layer at microscopic coordinate x sees the nanoscopic roughness of the wall. Moreover we assume that there exist $z = \zeta_\infty(y)$ a 1-periodic function with $0 \leq \zeta_\infty(y) < L$ and $z = \zeta_0(y)$ a 1-periodic function with $0 \leq \zeta_0(y) < \zeta_\infty(y)$ such that (see figure 4)

$$\lim_{z' < \zeta_\infty(y), z' \to \zeta_\infty(y)} \mathcal{V}_{\#}(y,z') = +\infty, \tag{87}$$

$$\mathcal{V}_{\#}(y, \zeta_0(y)) = 0. \tag{88}$$

Finally, we assume that the potential is attractive-repulsive, i.e.

$$\text{for } \zeta_0(y) < z < \zeta_\infty(y),\ \partial_z \mathcal{V}_{\#}(y,z) > 0, \quad \text{for } 0 < z < \zeta_0(y),\ \partial_z \mathcal{V}_{\#}(y,z) < 0, \tag{89}$$

and that

$$\mathcal{V}_{\#}(y,z) = \mathcal{V}_m, \quad \text{for } z \leq 0. \tag{90}$$

The total energy of a molecule is

$$E(x,z,v_x,v_z) = \frac{m}{2}|v|^2 + \mathcal{V}(x,z),$$

and this total energy remains constant as long as the molecule does not collide with a phonon. Note that in this section, we do not use the change of velocity variables $v \mapsto e(v,z)$. Indeed, since the potential is not assumed to be separable into $U(x) + W(z)$ here, there is no obvious change of variable that would simplify the equations.

With these assumptions, the flow of molecules is described by the following system of kinetic equations

$$\begin{aligned} &\partial_t f + v_x \partial_x f + v_z \partial_z f = 0, \quad z < 0, \\ &\partial_t f + v_x \partial_x f + v_z \partial_z f - \frac{1}{m}\partial_x \mathcal{V}(x,z)\partial_{v_x} f - \frac{1}{m}\partial_z \mathcal{V}(x,z)\partial_{v_z} f = Q[f], \quad 0 < z < L, \end{aligned} \tag{91}$$

where the molecule-phonon collision term writes

$$Q[f] = \int K(v,v')(M(v)f(v') - M(v')f(v))dv', \tag{92}$$

and satisfies the properties recalled in proposition 1. Moreover the distribution function f is continuous through the interface $z = 0$.

In the following, we compute the scattering kernel of asymptotic boundary conditions corresponding to various regimes. However, we find it more convenient to use the following form of the scattering kernel:

$$k(v' \to v) = R(v' \to v)\frac{|v'_z|}{|v_z|},$$

where R is the standard form (as used in (4)). With this new kernel, properties of normalization (6) and reciprocity (7) now read:

$$\int_{v_z<0} k(v' \to v) v_z \, dv = -v'_z, \tag{93}$$

$$|v_z| k(v' \to v) M(v') = |v'_z| k(-v \to -v') M(v). \tag{94}$$

Proposition 3. *Under the hypothesis (86–90), in the limit $\varepsilon = \frac{\tau^*_{ms}}{t^*_B} \to 0$, the gas-surface interaction depends on the order of magnitude of $\eta = \frac{\tau^*_{ms}}{\tau^*_{fl}}$ (where τ^*_{fl} is the characteristic time of flight of a molecule through the surface layer), and can be described by the following boundary conditions at $z = 0$:*

1. *for $\eta = O(\frac{1}{\varepsilon})$, the boundary condition is the "specular" boundary condition which writes for a rough wall*

$$f(t, x, 0, v_x, v_z)_{|v_z<0} = \int_{v'_z>0} k(v' \to v) f(t, x, 0, v') \, dv', \tag{95}$$

   where the scattering kernel k, given by (111), is a probability density that is non-negative and satisfies the normalization and reciprocity properties (93–94).

2. *for $\eta = O(1)$, the boundary condition writes, in a first approximation, as*

$$f(t, x, 0, v) = \int_{v'_z>0} k_1(v' \to v) f(t, x, 0, v') \, dv' + a^{\#}(v) \, \sigma(t, x) M(v), \tag{96}$$

   where $k_1(v' \to v)$ can be viewed as a scattering kernel of non thermalized molecules, and is defined by (121), $a^{\#}(v)$ is the fraction of incident molecules that are re-emitted with the velocity v after a collision with a phonon (see (122)), and σ is such that the mass flux at $z = 0$ is zero (defined in (131)). This boundary condition satisfies the properties of non negativeness, normalization, and reciprocity.

Proof: We denote by $\phi = f_{|0<z<L}$, and we write f and ϕ as functions of $(t, x, y = \frac{x}{L_*}, z, v_x, v_z)$, periodic in y, with period 1. We use the same reference quantities and nondimensional variables as in the previous sections. With these new functions, the dimensionless form of system (91) is

$$\partial_t f + v_x \partial_x f + \frac{\eta}{\beta_* \varepsilon} v_x \partial_y f + v_z \partial_z f = 0, \quad \text{for } z < 0, \tag{97}$$

$$\partial_t \phi + v_x \partial_x \phi + \frac{\eta}{\beta_* \varepsilon} v_x \partial_y \phi + \frac{\eta}{\varepsilon} v_z \partial_z \phi - \frac{1}{2\beta_*} \frac{\eta}{\varepsilon} \partial_y \mathcal{V}_{\#}(y, z) \partial_{v_x} \phi - \frac{1}{2} \frac{\eta}{\varepsilon} \partial_z \mathcal{V}_{\#}(y, z) \partial_{v_z} \phi = \frac{1}{\varepsilon} Q[\phi], \tag{98}$$

for $0 < z < 1$, with interface conditions

$$\phi(t, x, y, 0, v_x, v_z)_{v_z>0} = f(t, x, y, 0, v_x, v_z), \tag{99}$$

$$f(t, x, y, 0, v_x, v_z)_{|v_z<0} = \phi(t, x, y, 0, v_x, v_z) \tag{100}$$

for every $y \in [0, 1]$.

We define the average of f over a period:

$$F(t, x, z, v_x, v_z) = \int_0^1 f(t, x, y, z, v_x, v_z) \, dy.$$

Integrating (97) with respect to y and taking into account the 1-periodicity , we obtain

$$\partial_t F + v_x \partial_x F + v_z \partial_z F = 0, \tag{101}$$

for $z < 0$, and the boundary condition (100) leads to

$$F(t,x,0,v_x,v_z)_{|v_z<0} = \int_0^1 \phi(t,x,y,0,v_x,v_z)dy. \tag{102}$$

Now, we use an expansion of f, F, and ϕ in terms of powers of ε, and we identify the terms of same order of magnitude.

(1) We consider the case $\eta = O(\frac{1}{\varepsilon})$, which implies that $\tau_{fl}^* \ll \tau_{ms}^* \ll t_B^*$ (i.e. a weak molecule-phonon interaction). We find at zeroth order $\partial_y f^0 = 0$ for $z < 0$, which means that f^0 does not depend on y, and hence $F^0(t,x,z,v_x,v_z) = f^0(t,x,z,v_x,v_z)$. Consequently, equations (101) and (102) give

$$\partial_t F^0 + v_x\partial_x F^0 + v_z\partial_z F^0 = 0, \quad z<0, \tag{103}$$

$$F^0(t,x,0,v_x,v_z)_{v_z<0} = \int_0^1 \phi^0(t,x,y,0,v_x,v_z)dy. \tag{104}$$

However, ϕ^0 stil depends on y and we get

$$\frac{1}{\beta_*}v_x\partial_y\phi^0 + v_z\partial_z\phi^0 - \frac{1}{2\beta_*}\partial_y\mathcal{V}_\#(y,z)\partial_{v_x}\phi^0 - \frac{1}{2}\partial_z\mathcal{V}_\#(y,z)\partial_{v_z}\phi^0 = 0, \tag{105}$$

with a boundary condition coming from (99) which is

$$\phi^0(t,x,y,0,v_x,v_z)_{v_z>0} = F^0(t,x,0,v_x,v_z),\ \forall y\in[0,1]. \tag{106}$$

Note that the zeroth-order system (103–106) in (F^0,ϕ^0) is closed, contrary to the original system (97), (99), (101), (100) in (F,ϕ).

Relation (106) means that the molecules impinging the surface layer with velocity $v=(v_x,v_z)$ see the roughness of the wall from any nanoscopic variable y with the same probabiliy. Relation (104) means that the number of molecules going out of the surface layer at microscopic point x with velocity v is the sum over y of molecules going out with velocity v at the nanoscopic points $y,\ y\in[0,1]$.

The characteristic curves of the LKSL problem (105), defined by $\dot{y}(t) = v_x(t)/\beta_*$, $\dot{z}(t) = v_z(t)$, $\dot{v}_x(t) = -\partial_y\mathcal{V}_\#(y(t),z(t))/2\beta_*$, and $\dot{v}_z(t) = -\partial_z\mathcal{V}_\#(y(t),z(t))/2$, are the trajectories of the molecules in the surface potential field. We denote by $(y,v) = (y(y',v'),v(y',v')) = \Lambda(y',v')$ the mapping that gives the position and the velocity (y,v) of a molecule leaving the surface layer (i. e. with $v_z<0$ at $z=0$) as a function of its position and velocity (y',v') when entering the surface layer (i.e. with $v_z'>0$ at $z=0$), see figure 4. Note that due to the time reversibility of these trajectories, we have the important property

$$(y,v) = \Lambda(y',v') \quad\Leftrightarrow\quad (y',-v') = \Lambda(y,-v), \tag{107}$$

and hence $v' = -\Lambda_2(y,-v)$ for every (y,v,y',v') related by a characteristic curve. Another important property is that the Jacobian of the transformation $(y,v)=\Lambda(y',v')$ can be computed so that we have:

$$|v_z'|dy'dv' = |v_z|dydv, \tag{108}$$

see a proof in appendix A. The last property is that the total energy is conserved along the characteristic and the potential energy has the same value $\mathcal{V}_m$ at the head $(y,0)$ and the foot $(y',0)$ of this characteristic, which yields

$$|\Lambda_2(y',v')| = |\Lambda_2(y,-v)| = |v| = |v'|. \tag{109}$$

These relations are essential to derive a collision kernel for problem (103-104) and to prove some of its properties.

Let y in $[0,1]$ and v such that $v_z < 0$. Then using the fact that ϕ^0 is constant along the characteristics, we get $\phi^0(t,x,y,0,v) = \phi^0(t,x,y',0,v')$, where (y',v') are such that $(y,v) = \Lambda(y',v')$. Then using (106) and the previous relation $v' = -\Lambda_2(y,-v)$, we get

$$\phi^0(t,x,y,0,v) = F^0(t,x,0,-\Lambda_2(y,-v)).$$

Finally, we inject this relation into (104) to get

$$F^0(t,x,0,v_x,v_z)_{v_z<0} = \int_0^1 F^0(t,x,0,-\Lambda_2(y,-v))\,dy,$$

which can be rewritten

$$F^0(t,x,0,v_x,v_z)_{v_z<0} = \int_{v'_z>0} k(v'\to v)F^0(t,x,0,v')\,dv', \tag{110}$$

where the collision kernel k is defined by

$$k(v'\to v) = \int_0^1 \delta(v' + \Lambda_2(y,-v))\,dy. \tag{111}$$

This kernel is obviously non-negative, and it satisfies

$$\int_{v'_z>0} k(v'\to v)\ dv' = 1,$$

and hence is a probability density. Indeed, note that a direct integration of (111) with respect to v' and the use of variables v, y give this result.

The normalization property (93) is obtained as follows: first, we use (111) to get

$$\int_{v_z<0} k(v'\to v)v_z\,dv = -\int_{v_z<0}\int_0^1 \delta(v'+\Lambda_2(y,-v))|v_z|\,dydv.$$

Then, we use the change variables $(y,v) = \Lambda(y',w')$ and its properties (107) and (108) to get

$$\begin{aligned}\int_{v_z<0} k(v'\to v)v_z\ &= -\int_{w'_z>0}\int_0^1 \delta(v'-w')|w'_z|\,dy'dw' \\ &= -\int_0^1 |v'_z|\,dy' = -v'_z.\end{aligned}$$

Finally, the reciprocity property (94) is obtained as follows. First, we consider a given velocity v (with $v_z<0$) and a test function θ, and we use (93) to get

$$\begin{aligned}\int_{v'_z>0} |v_z|k(v'\to v)M(v')\theta(v')\,dv' &= \int_{v'_z>0}\int_0^1 |v_z|\delta(v'+\Lambda_2(y,-v))M(v')\theta(v')\,dydv' \\ &= \int_0^1 |v_z|M(\Lambda_2(y,-v))\theta(-\Lambda_2(y,-v))\,dy \\ &= \int_0^1 \theta(-\Lambda_2(y,-v))\,dy\,|v_z|M(v)\end{aligned} \tag{112}$$

from (109). Moreover, (93) also gives

$$\int_{v'_z>0} |v'_z|k(-v\to -v')M(v)\theta(v')\,dv' = \int_{v'_z>0}\int_0^1 |v'_z|\delta(-v+\Lambda_2(y,v'))M(v)\theta(v')\,dydv'.$$

Then, we write y' instead of y, and we use the change of variables $(y,w) = \Lambda(y',v')$ and its properties (107) and (108) to get

$$\begin{aligned}\int_{v_z'>0} |v_z'| k(-v \to -v') M(v) \theta(v')\, dv' &= \int_{w_z<0} \int_0^1 |w_z| \delta(-v+w) M(v) \theta(-\Lambda_2(y,-w))\, dy dw \\ &= \int_0^1 \theta(-\Lambda_2(y,-v))\, dy\, |v_z| M(v).\end{aligned} \tag{113}$$

Then, we compare (112) and (113) to find that the two left-hand sides are equal for every test function θ. The reciprocity property $|v_z| k(v' \to v) M(v') = |v_z'| k(-v \to -v') M(v)$ follows.

(2) Now we consider the case $\eta = O(1)$, which means that τ_{fl}^* (the characteristic time of flight of a molecule across the surface layer) is comparable with τ_{ms}^* (the characteristic time of molecule-phonon relaxation). The zeroth order terms of the expansion are still denoted by F^0 and ϕ^0, where F^0 satisfies the same equation:

$$\partial_t F^0 + v_x \partial_x F^0 + v_z \partial_z F^0 = 0, \quad z < 0, \tag{114}$$

$$F^0(t,x,0,v_x,v_z)_{v_z<0} = \int_0^1 \phi^0(t,x,y,0,v_x,v_z) dy, \tag{115}$$

and ϕ^0 now is the periodic solution of

$$\frac{1}{\beta_*} v_x \partial_y \phi^0 + v_z \partial_z \phi^0 - \frac{1}{2\beta_*} \partial_y \mathcal{V}_\#(y,z) \partial_{v_x} \phi^0 - \frac{1}{2} \partial_z \mathcal{V}_\#(y,z) \partial_{v_z} \phi^0 = Q[\phi^0], \tag{116}$$

$$\phi^0(t,x,y,0,v_x,v_z)_{v_z>0} = F^0(t,x,0,v_x,v_z), \ \forall y \in [0,1]. \tag{117}$$

As in section 3.1, the right-hand-side of this equation is approximated by $Q_+[\alpha(t,x)\mathcal{M}] - \frac{\phi^0}{\tau_{ms}}$, where $\tau_{ms}(v) = (\int K(v,v') M(v')\, dv')^{-1}$ is the molecule-phonon relaxation time, and where $\mathcal{M}(y,z,v_x,v_z) = \exp(-|v|^2/2 - \mathcal{V}_\#(y,z))$ which is constant along the characteristics, and α is a free parameter that will be determined later. To integrate (116), it is useful to define the mean molecule-phonon relaxation time $\bar{\tau}_{ms}(y',v')$ along the characteristic curve passing by $(y',0,v')$ by $\bar{\tau}_{ms}(y',v') = (\frac{1}{\tau_{fl}(y',v')} \int_0^{\tau_{fl}(y',v')} \frac{1}{\tau_{ms}(v(s))}\, ds)^{-1}$. Then the solutions of (116) with boundary condition (117) satisfy

$$\begin{aligned}\phi^0(t,x,y,0,v) = &\exp(-r(y',v')) F^0(t,x,0,v') \\ &+ (1 - \exp(-r(y',v'))) \sigma(t,x) M(v),\end{aligned} \tag{118}$$

where $r(y',v') = \tau_{fl}(y',v')/\bar{\tau}_{ms}(y',v')$, $\tau_{fl}(y',v')$ is the free time of flight of a molecule across the surface layer in which it enters at $(y', z=0, v')$), and $\sigma(t,x) = \alpha(t,x)\exp(-\mathcal{V}_m)$ is still to be determined. First, note that $r(y',v') = r(y,-v)$: indeed it is defined as the ratio of the free time of flight of a molecule along the trajectory that starts at (y',v') and ends at (y,v) and the mean relaxation time along this trajectory. Since this trajectory is the same as the one that starts at $(y,-v)$ and ends at $(y',-v')$ (see (107)), these two times are the same at (y',v') and $(y,-v)$. Then (118) can be rewritten as

$$\begin{aligned}\phi^0(t,x,y,0,v) = &\exp(-r(y,-v)) F^0(t,x,0,-\Lambda_2(y,-v)) \\ &+ (1 - \exp(-r(y,-v)))\, \sigma(t,x) M(v),\end{aligned} \tag{119}$$

where v' has been replaced by $-\Lambda_2(y,-v)$ due to (107).

Now, we use (115), and the outgoing distribution $F^0(t,x,0,v)$ is found to be

$$\begin{aligned} F^0(t,x,0,v) &= \int_0^1 \left(\exp(-r(y,-v))F^0(t,x,0,-\Lambda_2(y,-v)) + (1-\exp(-r(y,-v)))\,\sigma(t,x)M(v)\right)\,dy \\ &= \int_0^1 \int_{v_z'>0} (\exp(-r(y,-v))F^0(t,x,0,v')\delta(v'+\Lambda_2(y,-v))\,dv'dy \\ &\quad + \int_0^1 (1-\exp(-r(y,-v)))\,\sigma(t,x)M(v))\,dy \\ &= \int_{v_z'>0} k_1(v'\to v)F^0(t,x,0,v')\,dv' + \left(1-\int_0^1 \exp(-r(y,-v))\,dy\right)\,\sigma(t,x)M(v), \end{aligned} \tag{120}$$

where $k_1(v'\to v)$ can be viewed as a scattering kernel of non thermalized molecules, and is defined by

$$k_1(v'\to v) = \int_0^1 \exp(-r(y,-v))\delta(v'+\Lambda_2(y,-v))\,dy. \tag{121}$$

Moreover, the coefficient $a^{\#}(v)$ of (96) is found to be

$$a^{\#}(v) = 1 - \int_0^1 \exp(-r(y,-v))\,dy. \tag{122}$$

The computation of σ and the reciprocity of this boundary condition are proved in appendix B.

5 Comments and concluding remarks

1- In this approach, the boundary for the Boltzmann equation is considered to be located at $z=0$ which is the outer limit of the surface layer. The surface layer is considered as belonging to the solid phase. This is a two-phase description in opposition to the nanoscale models which are three-phase models (gas, surface layer, solid).

2- The boundary condition (3) is a Maxwell-like condition but the "accommodation coefficient" $a = a(v)$ depends on the velocity. More precisely the coefficient $a(v)$ must be interpreted as the fraction of diffusively evaporated molecules. A Maxwell-like condition with a coefficient depending on the velocity has been previously given in [9]. Nevertheless the authors propose a different expression : $\hat{a}(v) = \frac{1}{1+(\tau_{ms}/(2\tau_z))}$. Let us remark that $\hat{a}(v)$ can be interpreted as a Pade approximant of $a(v)$ given in (42), which can be explained since the boundary condition is derived in [9] from a nanoscale kinetic model obtained by averaging (29-34) over the surface layer.

3- It is classical in the litterature (see for instance [11]) to introduce the so-called accommodation coefficients $\alpha(\varphi)$ to describe the the interaction of a gas with a surface

$$\alpha(\varphi) = \frac{\int_{v_z>0}\int |v_z|\varphi(v)\phi(v)dv_xdv_z - \int_{v_z<0}\int |v_z|\varphi(v)\phi(v)dv_xdv_z}{\int_{v_z>0}\int |v_z|\varphi(v)\phi(v)dv_xdv_z - J_0\int_{v_z<0}\int |v_z|\varphi(v)M(v)dv_xdv_z},$$

where $J_0 = \int_{v_z>0}\int v_z a(v_z)\phi(0,v_x,v_z)dv_xdv_z / \int_{v_z>0}\int v_z a(v_z)M(v_x,v_z)dv_xdv_z$, and $\varphi(v) = v_x$ or v_z, or $|v|^2/2$ (accommodation coefficient for tangential or normal momentum or for energy). A drawback of the Maxwell's boundary condition noted in [11] is that those various accommodation coefficients are equal, and equal to the factor a (which explains why this coefficient is often called the accommodation coefficient), which is not realistic since it is well-known that momentum and energy accommodate differently in physical interactions. In contrast, the boundary condition (3)

derived in the present paper gives different accommodation coefficients for energy and momentum.

4- We notice that the boundary conditions obtained by this approach do not contain any free parameter to be adjusted. All the information comes from the smaller scale (nanoscale). In particular the coefficient a in the Maxwell-like condition is given provided the interaction potential is known (and thus, τ_z and τ_{ms}). It is interesting to look at the influence of the velocity on the fraction of diffusively evaporated molecules $a(v)$. Since we assumed that the scattering kernel of the molecule-phonon collision term is bounded below and above (19), then so is τ_{ms}. Thus the behavior of a for large $|v|$ depends essentially on τ_z. Since $\lim_{|v_z|\to+\infty} \tau_z(v_z) = 0$, it appears that the fraction of diffusively evaporated molecules tends to decrease for high velocities. Finally we remark also that a perfect accommodation boundary condition can be obtained even if the interaction potential is purely repulsive. This is in contradiction with the idea that a diffusive departure of molecules from a surface is due to desorption of trapped molecules (see [9]).

5- We considered in section 4 rough walls with a periodicity assumption. This assumption allows to take into account the roughness of a surface in a simple way. Such a technique is commonly used for molecular dynamics simulations in gas-surface interaction or in related applications such as porous media. It can be relevant for instance when the solid is a crystal or a composite material. Of course, for a wall with nanoscale roughness, even the "specular" reflexion condition depends on the description of the surface potential. The smooth wall can be seen as a particular case of a rough wall by taking $k(v' \to v) = \delta_{v-(v'_x,-v'_z)}$. Of course, taking advantage of such models for practical numerical simulations requires accurate experiments to characterize the various parameters for a given material. For computational purposes, an approximation of the scattering kernel $k(v_p \to v_q)$ (for (v_p, v_q) in a discrete velocity grid) can be obtained by numerical solutions of the characteristic curves in a unit cell of the surface layer.

6- In any boundary condition, the population of trapped molecules is not taken into account. This is justified when we consider a bulk flow in a domain whose size is much greater than the thickness L of the boundary layer. But when the size of the domain becomes smaller (for instance in a channel with diameter comparable with L), then this might not be correct. In such a configuration the number of molecules trapped in the surface layer cannot be neglected. Indeed if we assume that the flow is stationary, then the distribution function writes

$$\frac{m\ n_0}{2k\pi T} e^{-\mathcal{V}(x,z)/kT} e^{-m(v_x^2+v_z^2)/2kT}.$$

Thus, the ratio of the number density of gas molecules at the outer boundary of the surface layer (and in the channel, i.e at $z \leq 0$) over the number density of gas molecules at the bottom of the well potential (i.e at $z = z_*$) is equal to

$$\frac{n(x,0)}{n(x,z_*)} = e^{-\mathcal{V}_m/kT},$$

so that the number density of gas molecules inside the surface layer is much larger that the number density of gas molecules in the channel when $kT \ll \mathcal{V}_m$ (see for instance [22] for numerical results by means of molecular dynamics simulations). Thus in the vicinity of the wall we have to take into account the molecules inside the surface layer, for instance to estimate the mass flux parallel to the wall.

To conclude this paper we recall how the gas-surface interaction is described by the proposed kinetic approach (for a smooth wall) at different scales and for various regimes.

- At the smaller scale (the nanoscale, i.e. on a domain $[0, x^*] \times [0, z^*]$ with x^* and $z^* \approx 1$ nanometer), the gas interaction is described by the two-dimensionnal kinetic model for the

flow inside the surface layer (29–34), suggested in [9] and [1] (coupled with the Boltzmann equation for the bulk flow). Then the gas-solid interaction at larger scales is derived from this model by formal systematic asymptotic analysis with various convenient scalings.

- If we consider a gas flow in a domain $[0, x^{**}] \times [0, z^{**}]$ with $x^{**} \approx z^{**} \gg 1$ nanometer, but where x^{**} is the characteristic length of evolution of the flow in the x-direction inside the surface layer, then the gas-surface interaction can be described by the Boltzmann equation coupled with a one-dimensional kinetic or diffusion model describing the flow inside the surface layer of adsorbed molecules (mobile adsorption) which can be interpreted as non local boundary conditions for the Boltzmann equation in the bulk flow (see [1]).
- At a larger scale, we consider a gas flow on a domain $[0, x^{***}] \times [0, z^{***}]$ where $x^{***} \approx z^{***}$ is the characteristic length of evolution of the Boltzmann equation in the bulk flow. Then the gas-surface interaction can be described by the Boltzmann equation coupled with a local boundary condition that depends on the ratio τ^*_{ms}/τ^*_z:
  - If τ^*_{ms}, the characteristic time of relaxation of the molecules by the phonons, and τ^*_z, the characteristic time for a molecule to cross the surface layer are comparable, then this boundary condition is implicitly given through the solution of a one-dimensional boundary value problem for a linear transport equation. This boundary condition can be approximated by the numerical solution of the boundary value problem but it can also be approximated at first order by a Maxwell-like condition with a factor (the fraction of diffusively evaporated molecules) that depends on the velocity of the molecules. This fraction also depends on the temperature of the wall (through M, $\bar{\tau}_{ms}$, and $\bar{r}$) and of the morphology of the surface (through Λ).
  - If $\tau^*_z \ll \tau^*_{ms}$, then the local boundary condition obtained is the well-known specular reflexion.
  - If when $\tau^*_{ms} \ll \tau^*_z$, then the local boundary condition obtained is the classical perfect accommodation boundary condition.

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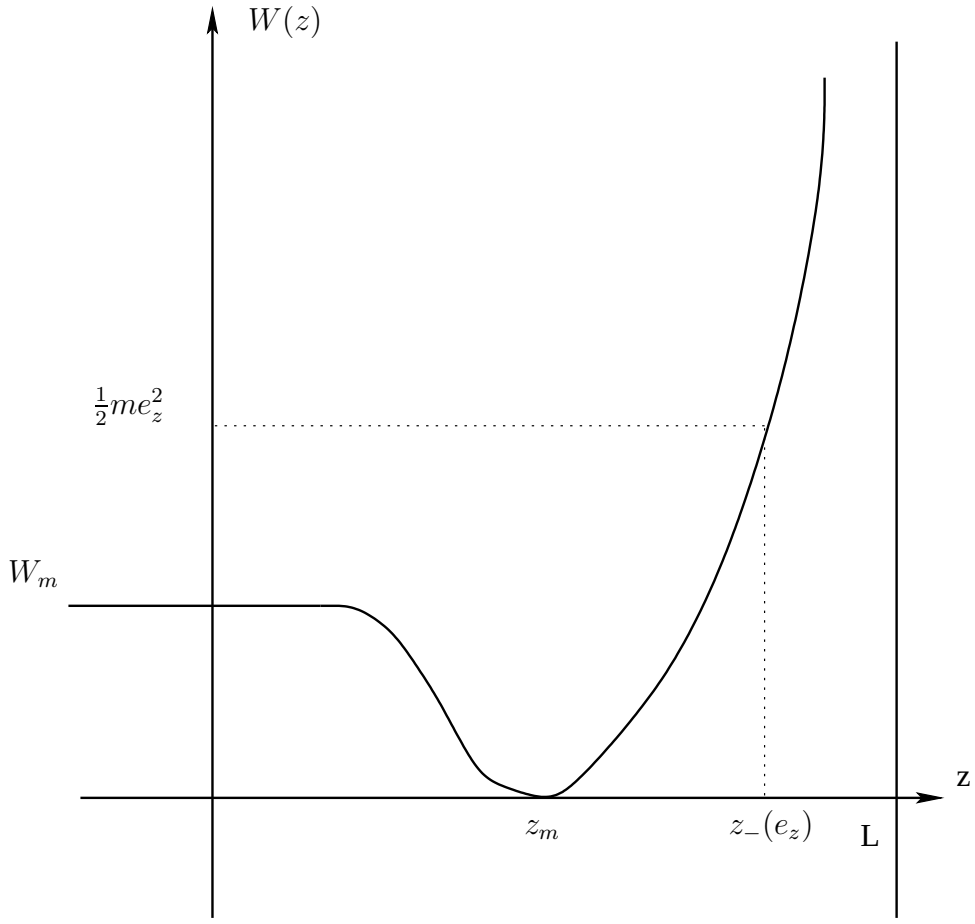

Figure 1: Free particles: $|e_z| > \sqrt{\frac{2}{m}W_m}$ and $z < z_(e_z)$.

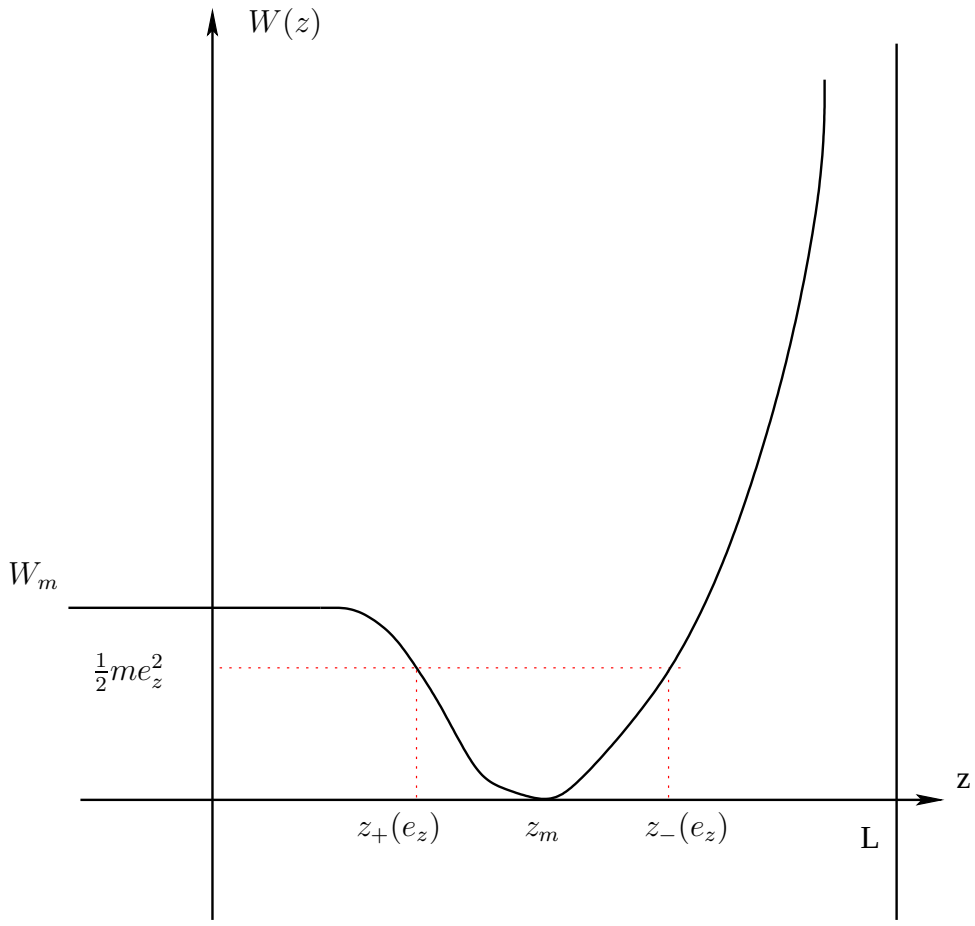

Figure 2: Trapped particles: $|e_z| < \sqrt{\frac{2}{m}W_m}$ and $z_+(e_z) < z < z_-(e_z)$

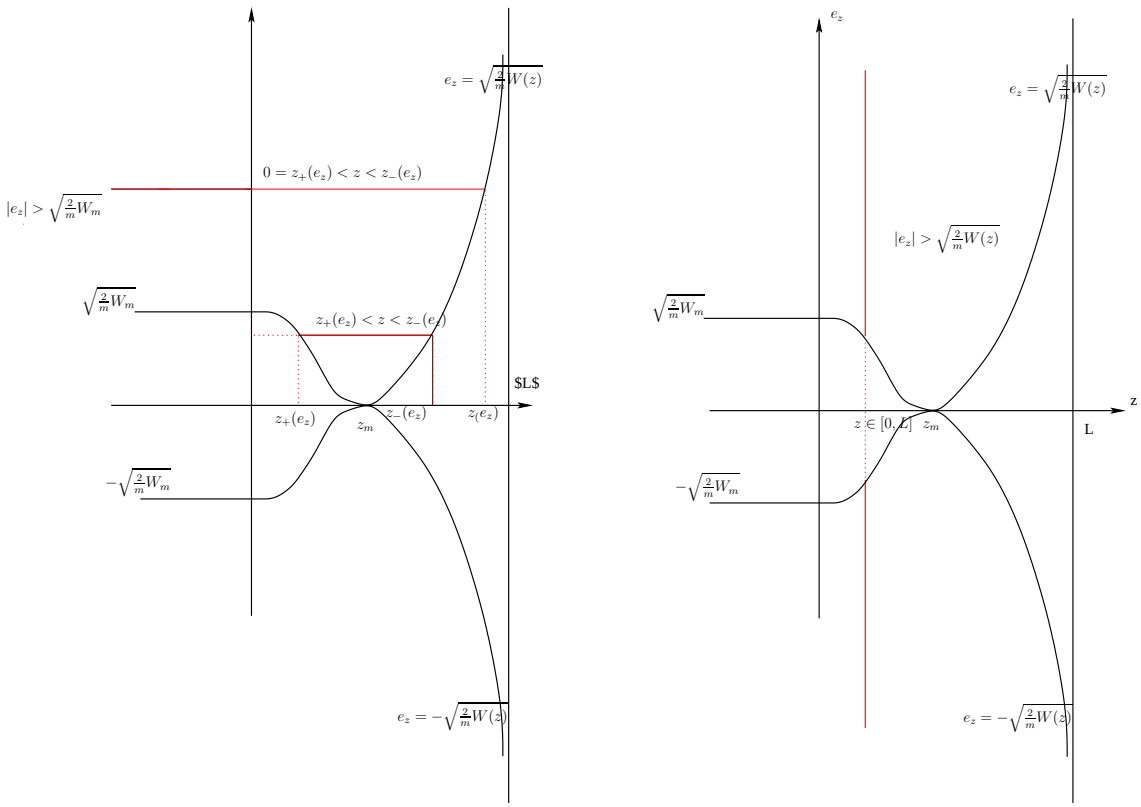

Figure 3: Domain of integration with respect to e_z at a fixed z (left), with respect to z at a fixed e_z (right)

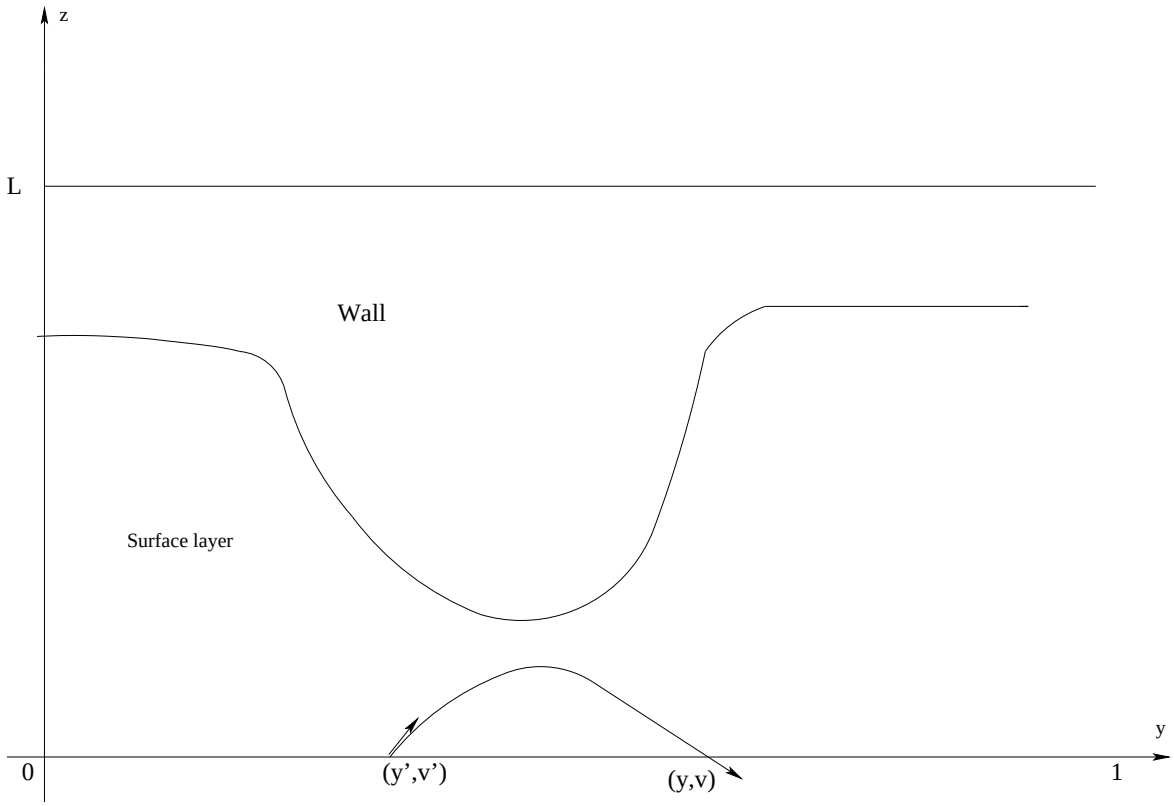

Figure 4: surface layer for a wall with nanoscale roughness and trajectory of a particle

A Computation of the Jacobian of the transformation $(y, v) = \Lambda(y', v')$

Let $\varphi_{in}(y', v')$ be a function defined for $y' \in [0, 1]$ and v' such that $v'_z > 0$. Let $\varphi_{out}(y, v)$ be the outgoing value (at $z = 0$, for $v_z < 0$) of the solution $\varphi(y, z, v)$ of (105), with $\varphi_{in}(y', v')_{|v'_z>0}$ as an inflow boundary data (at $z = 0$), that is to say, φ is a y-periodic function solution of:

$$\begin{aligned} &\frac{1}{\beta_*} v_x \partial_y \varphi + v_z \partial_z \varphi - \frac{1}{2\beta_*} \partial_y \mathcal{V}_\#(y, z) \partial_{v_x} \varphi - \frac{1}{2} \partial_z \mathcal{V}_\#(y, z) \partial_{v_z} \varphi = 0, \\ &\varphi(y', 0, v')_{v'_z>0} = \varphi_{in}(y', v'), \ \forall y' \in [0, 1]. \end{aligned} \tag{123}$$

Since this solution is constant along the characteristics, we have:

$$\varphi_{out}(y, v) = \varphi_{in}(y', v'), \tag{124}$$

where $(y, v) = \Lambda(y', v')$ has been introduced before (107).

Denote by J the Jacobian of the change of variables $(y, v) = \Lambda(y', v')$, then, using (124), we can write the average outgoing mass flux as:

$$\int_0^1 \int_{v_z<0} \varphi_{out}(y, v)|v_z| \, dydv = \int_0^1 \int_{v'_z>0} \varphi_{in}(y', v')|\Lambda_2(y', v')|J \, dy'dv', \tag{125}$$

Moreover, it can easily been obtained that the average mass flux is zero, which reads

$$\int_0^1 \int_{v_z<0} \varphi_{out}(y, v)|v_z| \, dydv = \int_0^1 \int_{v'_z>0} \varphi_{in}(y', v')|v'_z| \, dy'dv'. \tag{126}$$

Indeed, integrating equation (123) with respect to (y, z) on the cell $\{y \in [0, 1], 0 < z < \zeta_\infty(y)\}$, using the y-periodicity of φ, and then taking into account that φ is zero at $z = \zeta_\infty(y)$, we get

$$\int_0^1 \varphi(y, 0, v)v_z dy = -\frac{1}{2} \int \begin{pmatrix} \frac{1}{\beta_*} \partial_y \mathcal{V}_\# \\ \partial_z \mathcal{V}_\# \end{pmatrix} . \nabla_v \varphi(y, 0, v) \ dydz.$$

Then, we can integrate the previous relation with respect to v: the right-hand side vanishes, and we get:

$$\int \int_0^1 \varphi(y, 0, v)v_z \, dydv = 0,$$

which gives (126).

Now, we compare (125) and (126) to get

$$\int_0^1 \int_{v'_z>0} \varphi_{in}(y', v')|\Lambda_2(y', v')|J \, dy'dv' = \int_0^1 \int_{v'_z>0} \varphi_{in}(y', v')|v'_z| \, dy'dv', \tag{127}$$

which is true for every function φ_{in}. Consequently, we deduce that the Jacobian J satisfies

$$J = \frac{|v'_z|}{|\Lambda_2(y', v')|} = \frac{|v'_z|}{|v_z|}, \tag{128}$$

which reads in the following more symmetric way

$$|v'_z|dy'dv' = |v_z|dydv. \tag{129}$$

B Reciprocity property for the Maxwell like boundary condition (96)

Computation of σ. This parameter can be determined with the constraint of zero mass flux of F^0 through the boundary $z = 0$, that is to say

$$\int_{v_z<0} v_z F^0(t,x,0,v)\,dv + \int_{v'_z>0} v'_z F^0(t,x,0,v')\,dv' = 0.$$

Indeed, integrating equation (116) with respect to (y,z) on the cell $\{y \in [0,1], 0 < z < \zeta_\infty(y)\}$, using the y-periodicity of ϕ^0, and then taking into account that ϕ^0 is zero at $z = \zeta_\infty(y)$, we get

$$\int_0^1 \phi^0 v_z dy = -\frac{1}{2}\int \begin{pmatrix} \frac{1}{\beta_*}\partial_y \mathcal{V}_\# \\ \partial_z \mathcal{V}_\# \end{pmatrix} . \nabla_v \phi^0 \; dydz.$$

But (117) and (115) imply $\int_0^1 \phi^0 v_z dy = v_z F^0(t,x,0,v_x,v_z)$, so that after integration in v we obtain

$$\int F^0 v_z dv = -\int \begin{pmatrix} \frac{1}{\beta_*}\partial_y \mathcal{V}_\# \\ \partial_z \mathcal{V}_\# \end{pmatrix} . \left(\int \nabla_v \phi^0 \; dv \right) dydz = 0, \tag{130}$$

which means that the mass flux of F^0 through the boundary $z = 0$ vanishes.

Then using (120), we rapidly find

$$\sigma(t,x) = -\frac{\int_{v'_z>0} \left(v'_z + \int_{v_z<0} v_z k_1(v' \to v)\,dv \right) F^0(t,x,0,v')\,dv'}{\int_{v_z<0} v_z \left(1 - \int_0^1 \exp(-r(y,-v))\,dy \right) M(v)\,dv}.$$

Note that the integral with k_1 can be computed: by using (121), the change of variables $(y,v) = \Lambda(y',w')$ and the property of $r(y',v')$ mentioned above, we find

$$\begin{aligned}
\int_{v_z<0} v_z k_1(v' \to v)\,dv &= -\int_{v_z<0}\int_0^1 |v_z| \exp(-r(y,-v))\delta(v' + \Lambda_2(y,-v))\,dydv \\
&= -\int_{w'_z>0}\int_0^1 |w'_z| \exp(-r(y',w'))\delta(v' - w')\,dy'dw' \\
&= -v'_z \int_0^1 \exp(-r(y',v'))\,dy'.
\end{aligned}$$

Consequently, the final form of σ is:

$$\sigma(t,x) = \frac{\int_{v'_z>0} v'_z \left(1 - \int_0^1 \exp(-r(y',v'))\,dy' \right) F^0(t,x,0,v')\,dv'}{-\int_{v_z<0} v_z \left(1 - \int_0^1 \exp(-r(y,-v))\,dy \right) M(v)\,dv}, \tag{131}$$

where the denominator is a constant denoted by C in the following.

Scattering kernel for the boundary condition (120). Using (131) in (120), we find

$$\begin{aligned}
F^0(t,x,0,v) &= \int_{v'_z>0} k_1(v' \to v) F^0(t,x,0,v')\,dv' \\
&\quad + \left(1 - \int_0^1 \exp(-r(y,-v))\,dy \right) \frac{1}{C} \int_{v'_z>0} v'_z \left(1 - \int_0^1 \exp(-r(y',v'))\,dy' \right) F^0(t,x,0,v')\,dv' M(v) \\
&= \int_{v'_z>0} k^\#(v' \to v) F^0(t,x,0,v')\,dv',
\end{aligned}$$

with the scattering kernel $k^{\#}(v' \to v) = k_1(v' \to v) + k_2(v' \to v)$, where

$$k_2(v' \to v) = \left(1 - \int_0^1 \exp(-r(y,-v))\,dy\right) \frac{1}{C}\, v'_z \left(1 - \int_0^1 \exp(-r(y',v'))\,dy'\right) M(v).$$

This kernel can be written

$$k_2(v' \to v) = \frac{1}{C}\psi(-v)\psi(v')|v'_z|M(v), \tag{132}$$

where $\psi(w) = 1 - \int_0^1 \exp(-r(y,w))\,dy$.

Consequently, the reciprocity of $k^{\#}$ can be deduced from the reciprocity of the kernels k_1 and k_2.

Reciprocity of k_1. Using the definition of k_1 ((121)), we have

$$|v_z|k_1(v' \to v)M(v') = \int_0^1 \exp(-r(y,-v))\delta(v' + \Lambda_2(y,-v))|v_z|M(v')\,dy. \tag{133}$$

Then for a given v and some test function θ, we have

$$\begin{aligned}\int_{v'_z>0} |v_z|k_1(v' \to v)M(v')\theta(v')\,dv' &= \int_{v'_z>0}\int_0^1 \exp(-r(y,-v))\delta(v' + \Lambda_2(y,-v))|v_z|M(v')\theta(v')\,dydv' \\ &= \int_0^1 \exp(-r(y,-v))|v_z|M(-\Lambda_2(y,-v))\theta(-\Lambda_2(y,-v))\,dy \\ &= \int_0^1 \exp(-r(y,-v))\theta(-\Lambda_2(y,-v))\,dy\,|v_z|M(v),\end{aligned} \tag{134}$$

where we used (109).

Moreover, we can use (133) to write

$$|v'_z|k_1(-v \to -v')M(v) = \int_0^1 \exp(-r(y',v'))\delta(-v + \Lambda_2(y',v'))|v'_z|M(v)\,dy'.$$

Then, with the same v and test function θ as above, we have

$$\begin{aligned}\int_{v'_z>0} |v'_z|k_1(-v \to -v')M(v)\theta(v')\,dv' &= \int_{v'_z>0}\int_0^1 \exp(-r(y',v'))\delta(-v + \Lambda_2(y',v'))|v'_z|M(v)\theta(v')\,dy'dv' \\ &= \int_{w_z<0}\int_0^1 \exp(-r(y,-w))\delta(-v+w)|w_z|M(v)\theta(-\Lambda_2(y,-w))\,dydw \\ &= \int_0^1 \exp(-r(y,-v))\theta(-\Lambda_2(y,-v))\,dy\,|v_z|M(v).\end{aligned} \tag{135}$$

Comparing (134) and (135), we find that the two left-hand sides are equal for every v and every test function θ, and then we have

$$|v_z|k_1(v' \to v)M(v') = |v'_z|k_1(-v \to -v')M(v),$$

which is the reciprocity relation for k_1.

Reciprocity of k_2. This property is straightforward: using (132), we have

$$\begin{aligned}|v_z|k_2(v' \to v)M(v') &= \frac{1}{C}\psi(-v)\psi(v')|v_z||v'_z|M(v)M(v') \\ &= \frac{1}{C}\psi(v')\psi(-v)|v'_z||v_z|M(-v')M(-v) \\ &= |v'_z|k_2(-v \to -v')M(-v),\end{aligned}$$

since M depends only on the norm of v.

The reciprocity of $k^{\#}$ follows, which completes the proof.