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**Abstract.** A kinetic model describing physisorption and chemisorption of gas particles on a crystal surface is introduced. A single kinetic equation is used to model gas and physisorbed particles interacting with an average potential and colliding with phonons. This equation is coupled to a kinetic equation describing localized chemisorbed species. A modified kinetic entropy is introduced for the coupled system and the H theorem is established. Using a fluid scaling and the Chapman–Enskog asymptotic method, fluid boundary conditions for the physisorbed and chemisorbed species are derived from the kinetic model.

## INTRODUCTION

The interaction of gases with solid surfaces is of paramount importance in science and engineering applications like hypersonic reentry [1, 2, 3], combustion [4], ablation phenomena [5], condensation and evaporation [6, 7], or chemical deposition reactors [8]. This is a strong motivation for investigating kinetic models of adsorption processes—at a scale intermediate between molecular simulation [9] and fluid models [10]—and deriving rigorously kinetic as well as fluid surface boundary conditions using the Chapman–Enskog method.

Kinetic models assuming chemical equilibrium at the solid boundary only differ from Maxwell boundary conditions by the values of equilibrium partial densities. More detailed kinetic models involve Boltzmann equations taking into account the interaction of gas particles with an average surface potential as well as phonons near the surface boundary [11, 12, 13, 14, 15, 16, 17]. These models have led to important advances in the knowledge of condensation and evaporation, particle trapping, phonon drag, surface homogenization, or scattering kernels [11, 12, 13, 14, 15, 16, 17]. Only gas particles have been considered in such studies, in other words, only physisorption phenomena [11]. However, chemical bonds may also be formed between gas species and the surface and it is necessary to consider these chemisorbed species as *other chemical species* compared to their parent gas phase. A kinetic model describing both physisorption and chemisorption is presented in this study for a single monatomic gas, the situation of multicomponent mixtures or polyatomic gases lying out of the scope of the present work.

A single kinetic equation is used to describe both gas particles and physisorbed particles interacting with the surface. Using a single equation is natural since gas particles contacting with a surface should continuously transform into a layer of physisorbed particles. A kinetic equation describing localized *chemisorbed* species in a potential field interacting with phonons is coupled to the gas/physisorbate kinetic equation. The transition between gas/physisorbed particles and chemisorbed particles is described by surface chemistry terms in the kinetic equations. The solid phase is assumed to be a single species crystal and the surface reaction is written in the form



where  $A(p)$  denotes the gas/physisorbate particle,  $A(c)$  the chemisorbed particle on the surface,  $B(s)$  the crystal molecules on the surface, and  $B(b)$  the bulk crystal molecule, that is, a crystal molecule below the gas-surface interface. The crystal species are assumed to be at physical equilibrium—not necessarily chemical equilibrium, and,

consistently, the phonons are assumed to be at equilibrium. A modified kinetic entropy is introduced for the coupled gas/physisorbate and chemisorbate system and the H theorem is established.

A multiscale asymptotic analysis is performed in the gas and the adsorbate. The inner structure of the physisorbate and the chemisorbate are analyzed and closely related to interaction potentials. The traditional species fluid boundary conditions for adsorption [18, 10] are recovered at the interface. The Stefan gas flux from the adsorbate layer then results from the gas/physisorbate particle production by adsorption/desorption of the chemisorbate.

## KINETIC MODEL

### Kinetic equations

The gas/physisorbate kinetic equation typically describes particles interacting with an average potential and colliding with phonons [11, 12, 13]. Adding the chemisorbate equation appears to be new to the best of the authors' knowledge. The gas/physisorbed particles are governed by the kinetic equation [11, 12, 13]

$$\partial_t f_p + \mathbf{c} \cdot \partial_{\mathbf{x}} f_p - \frac{1}{m} \partial_{\mathbf{x}} w_p \cdot \partial_{\mathbf{c}} f_p = \mathcal{J}_{p,p}(f_p, f_p) + \mathcal{J}_{p,ph}(f_p) + C_{p,c}(f_p, f_c) \quad (2)$$

where  $t$  denotes time,  $\partial_t$  the time derivative operator,  $\mathbf{x}$  the spatial coordinate,  $\partial_{\mathbf{x}}$  the space derivative operator,  $\mathbf{c}$  the particle velocity,  $\partial_{\mathbf{c}}$  the velocity derivative operator,  $f_p(t, \mathbf{x}, \mathbf{c})$  the physisorbate particle distribution function,  $w_p$  the interaction potential between the *fixed* crystal and the gas particles,  $m$  the mass of a particle,  $\mathcal{J}_{p,p}$  the gas-gas collision operator,  $\mathcal{J}_{p,ph}$  the gas-phonon collision operator,  $C_{p,c}$  the chemical operator between gas/physisorbed particles and chemisorbed particles and  $f_c(t, \mathbf{x}, \mathbf{c})$  the chemisorbed particle distribution function. The solid surface is assumed to be planar and located at  $z = 0$  with the spatial coordinates written  $\mathbf{x} = (x, y, z)^t$ , the tangential coordinates are denoted by  $\mathbf{x}_{\parallel} = (x, y)^t$  and the basis vector in the normal direction oriented towards the gas by  $\mathbf{e}_z$ . The gas-gas collision operator  $\mathcal{J}_{p,p}$  is in the traditional form and the operators  $\mathcal{J}_{p,ph}$  and  $C_{p,c}$  vanish far from the surface as well as the potential  $w_p$  in such a way that letting  $z \rightarrow \infty$  in (2) yields the usual kinetic equation in the gas phase. There is thus a single kinetic framework describing both gas and physisorbed particles, the gas equation being recovered far from the surface.

The distribution function of the chemisorbate is governed by the kinetic equation

$$\partial_t f_c + \mathbf{c} \cdot \partial_{\mathbf{x}} f_c - \frac{1}{m} \partial_{\mathbf{x}} w_c \cdot \partial_{\mathbf{c}} f_c = \mathcal{J}_{c,ph}(f_c) + C_{c,p}(f_c, f_p), \quad (3)$$

where  $w_c$  denotes the interaction potential between the *fixed* crystal and the chemisorbed particles,  $\mathcal{J}_{c,ph}$  the chemisorbate/phonon collision operator, and  $C_{c,p}(f_c, f_p)$  the reactive operator between chemisorbed and gas/physisorbate species. This equation is an analog to a kinetic equation introduced to describe lattice gases by Bogdanov et al. [13].

The potentials  $w_p$  and  $w_c$  only depend on the normal coordinate  $z/\delta$  where  $\delta$  is a characteristic range of the surface potential. These potential are such that  $\lim_{\zeta \rightarrow 0} w_p(\zeta) = +\infty$ ,  $\lim_{\zeta \rightarrow +\infty} w_p(\zeta) = 0$ ,  $\lim_{\zeta \rightarrow 0} w_c(\zeta) = +\infty$ ,  $\lim_{\zeta \rightarrow \zeta^\infty} w_c(\zeta) = +\infty$ , where  $0 < \zeta^\infty < \infty$  is the maximum location of chemisorbed species. These interaction potentials typically involves an attractive zone and a repulsing zone as a Lenard-Jones potential integrated over all crystal particles.

### Collision operators

The source term  $\mathcal{J}_{p,ph}$  arise from collision operators between gas particles and phonons typically in the form

$$\mathcal{J}_{p,ph}(f_p) = \int ((g_{ph}(\mathbf{q}) + 1)f_p(\mathbf{c}') - g_{ph}(\mathbf{q})f_p(\mathbf{c})) \overline{W}_{p,ph} d\mathbf{c} d\mathbf{q}, \quad (4)$$

where  $g_{ph}$  denotes the phonon distribution function,  $\mathbf{q}$  the phonon wave vector or quasi-momentum,  $\mathbf{c}$  and  $\mathbf{c}'$  the particle velocities before and after the interaction, and  $\overline{W}_{p,ph}$  a transition probability. The small density approximation  $f_p \ll 1$  has been used in order to simplify (4) and the appearing of the additional factor 1 in the gain term is a typical quantum effect [19, 20, 21]. The operator (4) corresponds to collisions such that  $m\mathbf{c}' = m\mathbf{c} + \mathbf{q} + \mathbf{b}$  where  $\mathbf{b}$  is a vector of the reciprocal crystal lattice and there is another operator associated with collisions such that  $m\mathbf{c}' + \mathbf{q} = m\mathbf{c} + \mathbf{b}$  that lead to the same type of source term  $\mathcal{J}_{p,ph}$  and the corresponding details are omitted. The equilibrium relation corresponding to (4) reads  $(g_{ph}^e(\mathbf{q}) + 1)f_p^e(\mathbf{c}') = g_{ph}^e(\mathbf{q})f_p^e(\mathbf{c})$ , where the superscript  $e$  stands for physical equilibrium. The equilibrium distribution  $f_p^e$  is given by  $f_p^e = n_p M_p$  where  $n_p$  denotes the number of gas/physisorbed particles per



unit volume,  $M_p$  the Maxwellian  $M_p(\mathbf{c}) = (m/2\pi k_B T_w)^{3/2} \exp(-m|\mathbf{c}|^2/2k_B T_w)$ ,  $T_w$  is the wall temperature, and  $k_B$  the Boltzmann constant. Dividing the integrands in (4) by  $(g_{\text{ph}}^e(\mathbf{q}) + 1)M_p(\mathbf{c}') = g_{\text{ph}}^e(\mathbf{q})M_p(\mathbf{c})$  and further *assuming that phonons are at equilibrium*  $g_{\text{ph}}^e = g_{\text{ph}}$  yields

$$\mathcal{J}_{p,\text{ph}}(f_p) = \int \left( \frac{f_p(\mathbf{c}')}{M_p(\mathbf{c}')} - \frac{f_p(\mathbf{c})}{M_p(\mathbf{c})} \right) W_{p,\text{ph}} d\mathbf{c}', \quad (5)$$

where  $W_{p,\text{ph}} = \int g_{\text{ph}}^e(\mathbf{q})M_p(\mathbf{c})\overline{W}_{p,\text{ph}}d\mathbf{q}$  is the resulting transition probability that satisfies the reciprocity relation  $W_{p,\text{ph}}(\mathbf{c}, \mathbf{c}') = W_{p,\text{ph}}(\mathbf{c}', \mathbf{c})$  and is nonzero only in the neighborhood of the surface [11, 12]. The phonon collision operator for chemisorbed particles  $\mathcal{J}_{c,\text{ph}}$  is written in a similar form and the details are omitted.

The surface chemical reaction (1) involves the species A(p), A(c), B(b), and B(s) that are denoted for short by the subscripts {p, c, b, s}. For any species  $i \in \{p, c, b, s\}$ ,  $f_i$  denotes the distribution function,  $n_i$  the number density,  $m_i$  the Maxwellian  $M_i(\mathbf{c}) = (m_i/2\pi k_B T_w)^{3/2} \exp(-m_i|\mathbf{c}|^2/2k_B T_w)$ ,  $m_i$  the particle mass ( $m_p = m_c = m$ ),  $w_i$  the interaction potential with fixed crystal particles,  $E_i$  the formation energy, and  $m_i = m_i \exp(-(w_i + E_i)/k_B T_w)$  the modified Maxwellian. The reactive collision term  $C_{p,c}$  associated with (1) may then be written

$$C_{p,c} = \int (f_c(\mathbf{c}')f_b(\tilde{\mathbf{c}}') - f_p(\mathbf{c})f_s(\tilde{\mathbf{c}}))\overline{W}_{p,c}d\tilde{\mathbf{c}}d\mathbf{c}', \quad (6)$$

where  $\overline{W}_{p,c}$  denotes a reactive transition probability. This term is similar to typical reactive terms associated with gas phase chemical reactions and naturally involves collisions between gas and crystal particles [18, 22, 23]. Moreover, during a reactive collision with the surface, the work done by the fixed surface on the particle is the difference  $w_p - w_c$  and thus the work received by the fixed surface reads  $w_c - w_p$ . The work received by this fixed surface must be equal to the difference of total energy of the *fixed* particles that have no kinetic energy so that during a reactive collision we must have  $w_c - w_p = E_b - E_s$ . Assuming that the potential difference  $w_c - w_p$  is strictly increasing from  $-\infty$  to  $+\infty$  when  $\zeta$  is varying from 0 to  $\zeta^\infty$ , then there exists a unique  $\zeta_r$  such that  $w_c(\zeta_r) - w_p(\zeta_r) = E_b - E_s$ . The Dirac delta function  $\delta(w_c - w_p - E_b + E_s)$  included in the reactive transition probability thus yields a Dirac delta function  $\delta(\zeta - \zeta_r)$  in the collision term. The solid is assumed to be in thermal equilibrium consistently with the assumption that phonons are at equilibrium.

In order to embed the surface collision term (6) into the simplified framework introduced by Borman et al. where phonons are at equilibrium, the distributions  $f_b$  and  $f_s$  of the crystal species should be eliminated. A standard procedure is that already used for the phonon distribution  $g_{\text{ph}}$  in order to simplify  $\mathcal{J}_{p,\text{ph}}$  and  $\mathcal{J}_{c,\text{ph}}$ . To this aim, we use the chemical equilibrium relation  $f_c^{\text{ce}}f_b^{\text{ce}} = f_p^{\text{ce}}f_s^{\text{ce}}$  where the superscript <sup>ce</sup> stands for chemical equilibrium. The chemical equilibrium distributions read  $f_i^{\text{ce}} = n_i^{\text{ce}}M_i$  where the chemical equilibrium densities  $n_i^{\text{ce}}$ ,  $i \in \{p, c, b, s\}$ , are related by the equilibrium constraint between chemical potentials  $\mu_c^{\text{ce}} + \mu_b^{\text{ce}} = \mu_p^{\text{ce}} + \mu_s^{\text{ce}}$ . The chemical potential of the  $i$ th species is given by  $\mu_i = \log(n_i/z_i)$  where  $z_i = \Lambda_i^3 \exp(-E_i/k_B T_w)$  is the partition function of the  $i$ th species per unit volume,  $\Lambda_i = (2\pi k_B m_i T_w)^{1/2}/h_p$  and  $h_p$  the Planck constant. We also assume that the solid remains *at physical equilibrium*, assuming that chemistry is sufficiently slow, so that  $f_b(\tilde{\mathbf{c}}') = f_b^e(\tilde{\mathbf{c}}') = n_{\text{sf}}M_b(\tilde{\mathbf{c}}')$  and  $f_s(\tilde{\mathbf{c}}) = f_s^e(\tilde{\mathbf{c}}) = n_{\text{sf}}(1 - \sigma)M_s(\tilde{\mathbf{c}})$  where  $1 - \sigma = n_s/n_{\text{sf}}$  and  $\sigma$  denotes the coverage, that is, the fraction of sites occupied by the particles A(c). The number of surface molecules per unit volume  $n_{\text{sf}}$  is a constant characteristic of the surface and the coverage  $\sigma$  is independent of  $\zeta$  under the natural assumption that the chemisorbate is a monolayer. Dividing the integrands in (6) by the factor  $f_b^{\text{ce}}f_c^{\text{ce}} = f_s^{\text{ce}}f_p^{\text{ce}}$ , combining the previous assumptions, the resulting collision term is found after some algebra in the form

$$C_{p,c} = \int \left( \frac{f_c(\mathbf{c}')}{M_c(\mathbf{c}')} - (1 - \sigma) \frac{f_p(\mathbf{c})}{M_p(\mathbf{c})} \right) W_{p,c} d\mathbf{c}', \quad (7)$$

where  $W_{p,c} = \int M_s(\tilde{\mathbf{c}})M_p(\mathbf{c})n_{\text{sf}} \exp(-(E_s + E_p)/k_B T_w)\overline{W}_{p,c}d\tilde{\mathbf{c}}d\mathbf{c}'$  is the resulting reactive transition probability. The source term in the chemisorbate equation is in a similar form and the details are omitted. We may then introduce naturally the number densities *per unit surface*  $\tilde{n}_s = \int n_s dz$  and  $\tilde{n}_{\text{sf}} = \int n_{\text{sf}} dz$  such that  $\tilde{n}_s = \tilde{n}_{\text{sf}}(1 - \sigma)$  and the factor  $1 - \sigma$  associated with coverage satisfies the ordinary differential equation

$$\partial_t \tilde{n}_s = \tilde{n}_{\text{sf}} \partial_t (1 - \sigma) = \int C_{p,c} d\mathbf{c} dz. \quad (8)$$

The factor  $1 - \sigma$  is the only nonequilibrium part that remains from the crystal species B(s).

The collisional invariants of the gas collision operator  $\mathcal{J}_{p,p}$  are classically associated with particle number  $\psi^1 = 1$ , momentum  $\psi^{1+\nu} = mc_\nu$ ,  $\nu \in \{1, 2, 3\}$ , and energy  $\psi^5 = \frac{1}{2}m|c|^2 + \epsilon_p$ . Contrarily to gas-gas collision, momentum and energy are not conserved by the collision operators  $\mathcal{J}_{p,ph}$  and  $\mathcal{J}_{c,ph}$  since it may be given to phonons. Both operators  $\mathcal{J}_{p,ph}$  and  $\mathcal{J}_{c,ph}$  only conserve the number of gas particles with the invariant  $\psi^1 = 1$  as well as the reactive collision operators  $C_{p,c}$  and  $C_{c,p}$ .

## Kinetic entropy

The total kinetic entropy associated with the gas and the adsorbate is defined by

$$\mathcal{S}^{\text{kin}} = -k_B \int f_p (\log(f_p/m_p) - 1) d\mathbf{c} dz - k_B \int f_c (\log(f_c/m_c) - 1) d\mathbf{c} dz - k_B \tilde{n}_{sf} (1 - \sigma) (\log(1 - \sigma) - 1). \quad (9)$$

Multiplying the Boltzmann equation (2) by  $\log(f_p/m_p)$ , integrating with respect to  $\mathbf{c}$  and  $z$ , proceeding similarly for  $f_c$ , multiplying the ordinary differential equation (8) by  $\log(1 - \sigma)$ , and adding the resulting equations, we obtain that  $\partial_t \mathcal{S}^{\text{kin}} = v^{\text{kin}}$  where  $v^{\text{kin}}$  is the integrated entropy source. Using standard argument from the kinetic theory, the entropy source  $v^{\text{kin}}$  may then be written  $v^{\text{kin}} = v_{p,p}^{\text{kin}} + v_{p,ph}^{\text{kin}} + v_{c,ph}^{\text{kin}} + v_{p,c}^{\text{kin}} + v_{c,p}^{\text{kin}} + v_s^{\text{kin}}$  with

$$\begin{aligned} v_{p,p}^{\text{kin}} &= \frac{k_B}{4} \int \Upsilon(f_p \tilde{f}_p, f_p' \tilde{f}_p') W_{p,p} d\mathbf{c} d\tilde{\mathbf{c}} d\mathbf{c}' d\tilde{\mathbf{c}}' dz, & v_{p,ph}^{\text{kin}} &= \frac{k_B}{2} \int \Upsilon(f_p/m_p, f_p'/m_p') W_{p,ph} d\mathbf{c} d\mathbf{c}' dz, \\ v_{c,ph}^{\text{kin}} &= \frac{k_B}{2} \int \Upsilon(f_c/m_c, f_c'/m_c') W_{c,ph} d\mathbf{c} d\mathbf{c}' dz, & v_{p,c}^{\text{kin}} + v_{c,p}^{\text{kin}} + v_s^{\text{kin}} &= k_B \int \Upsilon(f_p(1 - \sigma)/m_p, f_c'/m_c') W_{p,c} d\mathbf{c} d\mathbf{c}' dz, \end{aligned}$$

where  $\Upsilon(x, y) = (x - y)(\log x - \log y)$ . Since  $\Upsilon$  only takes nonnegative values, all quantities  $v_{p,p}^{\text{kin}}$ ,  $v_{p,ph}^{\text{kin}}$ ,  $v_{c,ph}^{\text{kin}}$ , and  $v_{p,c}^{\text{kin}} + v_{c,p}^{\text{kin}} + v_s^{\text{kin}}$  are nonnegative terms and the H theorem is established.

## MULTISCALE FRAMEWORK

### Fluid scaling

Let  $T^*$  denotes a characteristic temperature,  $n^*$  a number density,  $\tau_p^*$  a collision time,  $m$  a particle mass,  $v^* = (k_B T^*/m)^{1/2}$  a characteristic thermal velocity,  $f^* = n^*/v^{*3}$  a characteristic particle distribution and  $\lambda^* = \tau_p^* v^*$  the mean free path. Similarly, let  $\tau_f^*$  denotes a characteristic fluid time,  $l^* = \tau_f^* v^*$  the fluid length,  $\tau_{ph}^*$  a characteristic time for phonon interaction related to characteristic transition probabilities  $1/\tau_{ph}^* = W_{p,ph}^* v^{*3} = W_{c,ph}^* v^{*3}$ , and  $\delta^*$  a typical length characteristic of the range of surface potential. Dividing both kinetic equations (2)(3) by  $n^*/\tau_f^* (v^*)^3$ , the resulting rescaled equations involve the dimensionless parameters  $\epsilon_p = \tau_p^*/\tau_f^* = \lambda^*/l^*$ ,  $\epsilon_{ph} = \tau_{ph}^*/\tau_f^*$ , and  $\epsilon = \delta^*/l^*$ . The characteristic times and lengths at the solid/gas interface are generally such that  $\tau_{ph}^* \leq \tau_p^* \ll \tau_f^*$  and  $\delta^* \leq \lambda^* \ll l^*$  and  $\epsilon_p$  represents the Knudsen number [12]. Since our aim in this work is to derive *fluid* boundary conditions, it is assumed that the small parameters  $\epsilon_p$ ,  $\epsilon_{ph}$ , and  $\epsilon$  are of the same *asymptotic order* of magnitude

$$\epsilon_{ph} = \alpha_{ph} \epsilon, \quad \epsilon_p = \alpha_p \epsilon, \quad (10)$$

where  $\alpha_{ph}$  and  $\alpha_p$  are positive constants. From a physical point of view, this means that particle collisions and phonon interactions are considered to be fast in comparison with fluid time and that both the mean free path  $\lambda^*$  and the surface potential characteristic range  $\delta^*$  are considered to be small in comparison with the fluid length  $l^*$ . This scaling may be seen as the *simplest fluid* scaling of the adsorbate layer model. Of course, other scalings may also be introduced as for instance a *kinetic scaling* upon using  $\tau_p^*$  instead of  $\tau_f^*$  for rescaling the kinetic equations [16, 17].

Keeping the same notation for rescaled quantities, the resulting rescaled kinetic equations are in the form

$$\partial_t f_p + \mathbf{c}_\parallel \cdot \partial_\parallel f_p + c_z \cdot \partial_z f_p - \frac{1}{m} \partial_z w_p \partial_{c_z} f_p = \frac{1}{\alpha_p \epsilon} \mathcal{J}_{p,p} + \frac{1}{\alpha_{ph} \epsilon} \mathcal{J}_{p,ph} + C_{p,c}, \quad (11)$$

$$\partial_t f_c + \mathbf{c}_\parallel \cdot \partial_\parallel f_c + c_z \cdot \partial_z f_c - \frac{1}{m} \partial_z w_c \partial_{c_z} f_c = \frac{1}{\alpha_{ph} \epsilon} \mathcal{J}_{c,ph} + C_{c,p} \quad (12)$$

where  $\mathbf{c}_\parallel$  denotes the tangential component of the particle velocity and  $\partial_\parallel$  the tangential derivative operator. Use has been made that  $w_p$  and  $w_c$  only depend on  $z$  and the chemistry operators  $C_{p,c}$  and  $C_{c,p}$  are assumed to be slow.

## Expansion in the gas

The kinetic equation in the gas is obtained from (11) by letting  $w_p = 0$ ,  $\mathcal{J}_{p,ph} = 0$  and  $C_{p,c} = 0$  and reads

$$\partial_t f_g + \mathbf{c}_{\parallel} \cdot \partial_{\parallel} f_g + c_z \cdot \partial_z f_g = \frac{1}{\alpha_p \epsilon} \mathcal{J}_{p,p}(f_g, f_g), \quad (13)$$

where  $f_g$  is the gas distribution function. This equation coincides with the traditional scaling of the Chapman-Enskog method. Since we investigate a fluid interacting with a wall, it is also natural to assume that the gas velocity  $\mathbf{v}_g$  vanish at zeroth order near the surface. We may thus write  $\mathbf{v}_g = \epsilon \bar{\mathbf{v}}_g$  near the surface and the normal component  $v_{gz}(0) = \mathbf{v}_g(0) \cdot \mathbf{e}_z = \epsilon \bar{\mathbf{v}}_g(0) \cdot \mathbf{e}_z$  is the Stefan velocity associated with the production of gas species.

Since the fluid convection velocity is of first order near the surface, the classical Chapman-Enskog expansion must be corrected and the terms proportional to the velocity  $\mathbf{v}_g$  must be shifted by one order. The corrected expansion of  $f_g$  in the gas phase *near the surface* is thus in the form  $f_g(t, \mathbf{x}_{\parallel}, z, \mathbf{c}) = f_g^{(0)}(t, \mathbf{x}_{\parallel}, z, \mathbf{c}) + \alpha_p \epsilon f_g^{(1)}(t, \mathbf{x}_{\parallel}, z, \mathbf{c}) + \mathcal{O}(\epsilon^2)$  with  $f_g^{(0)}$  and  $f_g^{(1)}$  given by

$$f_g^{(0)} = n_g \left( \frac{m}{2\pi k_B T_g} \right)^{\frac{3}{2}} \exp\left(-\frac{m|\mathbf{c}|^2}{2k_B T_g}\right), \quad f_g^{(1)} = \left( \frac{m \mathbf{c} \cdot \bar{\mathbf{v}}_g}{k_B T_g} + \alpha_p \phi_g^{(1)} \right) f_g^{(0)}, \quad (14)$$

where  $T_g$  denotes the gas temperature and  $n_g$  the gas number density. The corrector  $\phi_g^{(1)}$  reads  $\phi_g^{(1)} = -\phi^{\lambda} \cdot \partial_{\mathbf{x}}(1/k_B T_g)$  where  $\phi^{\lambda}$  is a vector function solution of the integral equation  $\mathcal{I}_g(\phi^{\lambda}) = (\frac{5k_B T_g}{2} - \frac{1}{2}m|\mathbf{c}|^2)\mathbf{c}$  with the Enskog constraints  $\int f_g^{(0)} \phi^{\lambda} \psi^l d\mathbf{c} = 0$  for  $1 \leq l \leq 5$  and  $\mathcal{I}_g$  is the linearized collision operator around the Maxwellian  $f_g^{(0)}$ .

## Multiscale expansion

The kinetic model appears as multiscale since it involves the normal coordinate  $z$  as well as the inner layer coordinate  $\zeta = z/\epsilon$  associated with surface potentials. The gas/physisorbate distribution is expanded in the multiscale form

$$f_p = \sum_i \epsilon^i f_p^{(i)}(t, \mathbf{x}_{\parallel}, z, \mathbf{c}) + \sum_i \epsilon^i \varphi_p^{(i)}(t, \mathbf{x}_{\parallel}, \zeta, \mathbf{c}), \quad (15)$$

where the *outer* expansion is that of the gas and  $\sum_i \epsilon^i \varphi_p^{(i)}(t, \mathbf{x}_{\parallel}, \zeta, \mathbf{c})$  is the adsorbate layer *corrector* expansion with correctors  $\varphi_p^{(i)}(t, \mathbf{x}_{\parallel}, \zeta, \mathbf{c})$  converging to zero as  $\zeta \rightarrow \infty$ . Any function  $\mathcal{F}(z)$  of the normal coordinate  $z$  may also be expanded near  $z = 0$  as a function of  $\zeta$  as  $\mathcal{F}(z(\zeta)) = \mathcal{F}(0) + \epsilon \zeta \partial_z \mathcal{F}(0) + \mathcal{O}(\epsilon^2)$  so that the *inner expansion* of the distribution  $f_p$  in the physisorbate is obtained by expanding the outer expansion around  $z = 0$  with  $z = \epsilon \zeta$  and adding the corrector expansion. This inner expansion is obtained in the form

$$f_p = \sum_i \epsilon^i f_p^{(i)}(t, \mathbf{x}_{\parallel}, \zeta, \mathbf{c}), \quad f_p^{(0)} = f_g^{(0)}(0) + \varphi_p^{(0)}, \quad f_p^{(1)} = f_g^{(1)}(0) + \zeta \partial_z f_g^{(0)}(0) + \varphi_p^{(1)}. \quad (16)$$

The chemisorbate distribution is expanded in the simpler form

$$f_c = \sum_i \epsilon^i f_c^{(i)}(t, \mathbf{x}_{\parallel}, \zeta, \mathbf{c}), \quad (17)$$

since the chemisorbate is localized in the adsorption layer. Since  $\zeta$  is the proper normal coordinate of the adsorbate layer, the rescaled equations obtained from (11)(12) to be used for the inner expansions (16)(17), are finally

$$\partial_t f_p + \mathbf{c}_{\parallel} \cdot \partial_{\parallel} f_p + \frac{1}{\epsilon} c_z \partial_z f_p - \frac{1}{\epsilon} \frac{1}{m} \partial_z w_p \partial_{c_z} f_p = \frac{1}{\alpha_p \epsilon} \mathcal{J}_{p,p} + \frac{1}{\alpha_{ph} \epsilon} \mathcal{J}_{p,ph} + C_{p,c}, \quad (18)$$

$$\partial_t f_c + \mathbf{c}_{\parallel} \cdot \partial_{\parallel} f_c + \frac{1}{\epsilon} c_z \partial_z f_c - \frac{1}{\epsilon} \frac{1}{m} \partial_z w_c \partial_{c_z} f_c = \frac{1}{\alpha_{ph} \epsilon} \mathcal{J}_{c,ph} + C_{c,p}. \quad (19)$$

## ASYMPTOTIC ANALYSIS OF THE ADSORBATE

### Zeroth order expansion in the physisorbate

In the physisorbate, at zeroth order, it is found from (18) that

$$c_z \partial_\zeta f_p^{(0)} - \frac{1}{m} \partial_\zeta w_p \partial_{c_z} f_p^{(0)} = \frac{1}{\alpha_p} \mathcal{J}_{p,p}(f_p^{(0)}, f_p^{(0)}) + \frac{1}{\alpha_{ph}} \mathcal{J}_{p,ph}(f_p^{(0)}). \quad (20)$$

Multiplying equation (20) by  $\log(f_p^{(0)}/m_p)$ , integrating over  $\zeta \in (0, \infty)$  and  $\mathbf{c} \in \mathbb{R}^3$ , using that  $f_p^{(0)} \rightarrow 0$  as  $\zeta \rightarrow 0$ , and  $f_p^{(0)} \rightarrow f_g^{(0)}(0)$  as  $\zeta \rightarrow \infty$ , in such a way that  $\lim_{\zeta \rightarrow \infty} \int c_z f_p^{(0)} (\log(f_p^{(0)}/m_p) - 1) d\mathbf{c} = \int c_z f_g^{(0)} (\log(f_g^{(0)}/m_p) - 1) d\mathbf{c} = 0$ , and using standard argument from kinetic theory, we obtain that

$$\frac{k_B}{4\alpha_p} \int \Upsilon(f_p^{(0)}/m_p, f_p^{(0)'}/m_p') W_{p,p} d\mathbf{c} d\tilde{\mathbf{c}} d\mathbf{c}' d\tilde{\mathbf{c}}' d\zeta + \frac{k_B}{2\alpha_{ph}} \int \Upsilon(f_p^{(0)}/m_p, f_p^{(0)'}/m_p') W_{p,ph} d\mathbf{c} d\mathbf{c}' d\zeta = 0.$$

Therefore, since the integrands are nonnegative, they must vanish identically. This shows that  $f_p^{(0)}$  is Maxwellian and this Maxwellian is at temperature  $T_w$  and with zero average velocity since  $\mathcal{J}_{p,ph}(f_p^{(0)}) = 0$ . Writing this Maxwellian for convenience in the form  $f_p^{(0)} = \bar{n}_p \exp(-w_p/k_B T_w) M_p$  where  $M_p$  is the wall Maxwellian, and using (20), it is obtained that  $c_z \partial_\zeta \bar{n}_p M_p = 0$  so that  $\bar{n}_p$  is independent of  $\zeta$ . The constant  $\bar{n}_p$  is identified by letting  $\zeta \rightarrow \infty$  and this yields  $\bar{n}_p = n_g(0)$  and  $T_w = T_g(0)$  so that

$$f_p^{(0)} = n_p M_p, \quad n_p = n_g(0) \exp\left(-\frac{w_p}{k_B T_w}\right). \quad (21)$$

Incidentally it has been obtained that  $T_g(0) = T_w$ ,  $\mathbf{v}_g(0) \cdot \mathbf{e}_x = \mathbf{v}_g(0) \cdot \mathbf{e}_y = 0$  which is generally assumed to hold *a priori* in fluid mechanics and is a classical result from kinetic theory [6]. Moreover, the expression of  $f_p^{(0)}$  shows that the physisorbate is naturally distributed as the function  $\exp(-w_p/k_B T_w)$ , as was intuitively expected, and that the physisorbate is *at equilibrium* with the bath of gas particles with number density  $n_g(0)$ .

### Zeroth order expansion in the chemisorbate

In the chemisorbate, it is found from (19) that

$$c_z \partial_\zeta f_c^{(0)} - \frac{1}{m} \partial_\zeta w_c \partial_{c_z} f_c^{(0)} = \frac{1}{\alpha_{ph}} \mathcal{J}_{c,ph}(f_c^{(0)}). \quad (22)$$

Multiplying by  $\log(f_c^{(0)}/m_c)$ , integrating over  $\zeta \in (0, \zeta^\infty)$  and  $\mathbf{c} \in \mathbb{R}^3$ , and using that  $f_c^{(0)}$  goes to zero as  $\zeta \rightarrow 0$  or as  $\zeta \rightarrow \zeta^\infty$ , it is obtained that

$$\frac{k_B}{2\alpha_{ph}} \int \Upsilon(f_c^{(0)}/m_c, f_c^{(0)'}/m_c') W_{c,ph} d\mathbf{c} d\mathbf{c}' d\zeta = 0.$$

Therefore, since the integrand is nonnegative, it vanishes identically. This shows that  $f_c^{(0)}$  is Maxwellian at temperature  $T_w$  and with zero average velocity since  $\mathcal{J}_{c,ph}(f_c^{(0)}) = 0$ . Writing this Maxwellian for convenience in the form

$$f_c^{(0)} = n_c M_c, \quad n_c = \bar{n}_c \exp\left(-\frac{w_c}{k_B T_w}\right), \quad (23)$$

where  $M_c$  is the wall Maxwellian and substituting this identity in (22) it is obtained that  $\partial_\zeta \bar{n}_c = 0$  and  $\bar{n}_c$  is independent of  $\zeta$ . The chemisorbate is thus distributed as the function  $\exp(-w_c/k_B T_w)$  as was intuitively expected and is localized since  $w_c$  goes to infinity as  $\zeta \rightarrow 0$  as well as for  $\zeta \rightarrow \zeta^\infty$ . In addition,  $\bar{n}_c$  is independent of the gas phase value  $n_g(0)$  at variance with the physisorbate that is at equilibrium with the bath of gas.

## Species fluid boundary condition

The zeroth order species conservation equations are obtained by taking the scalar product of the kinetic equations (18) and (19) by  $\psi^1 = 1$ —which is equivalent to integrating with respect to the velocity variable—and *keeping only zeroth order terms*. In the physisorbate, it is obtained that

$$\partial_t \int \mathbf{f}_p^{(0)} d\mathbf{c} + \partial_\zeta \int c_z \mathbf{f}_p^{(1)} d\mathbf{c} = \int C_{p,c}(\mathbf{f}_p^{(0)}, \mathbf{f}_c^{(0)}) d\mathbf{c}, \quad (24)$$

where we have used that  $\int \mathbf{c}_n \mathbf{f}_p^{(0)} d\mathbf{c} = 0$  and that the collisional invariant  $\psi^1 = 1$  is orthogonal to  $\mathcal{J}_{p,p}$  and  $\mathcal{J}_{p,ph}$ . Letting  $\zeta \rightarrow \infty$  in equation (24) it is obtained that  $\partial_t \int \mathbf{f}_g^{(0)}(0) d\mathbf{c} = 0$ , using that the limit of the derivative  $\partial_\zeta \int c_z \mathbf{f}_p^{(1)} d\mathbf{c}$  can only be zero because  $\int c_z \mathbf{f}_p^{(1)} d\mathbf{c}$  has a finite limit as  $\zeta \rightarrow \infty$ . This yields that  $\partial_t n_g(0) = 0$  at zeroth order which is also a consequence of the gas species conservation equation  $\partial_t n_g + \partial_x \cdot (n_g \mathbf{v}_g) = 0$  since  $\mathbf{v}_g = \mathcal{O}(\epsilon)$  around  $z = 0$ . This zeroth order relation implies that  $\partial_\zeta \int c_z \mathbf{f}_p^{(1)} d\mathbf{c} = \int C_{p,c}(\mathbf{f}_p^{(0)}, \mathbf{f}_c^{(0)}) d\mathbf{c}$  at zeroth order. Keeping in mind that  $\mathbf{f}_p^{(1)} = \mathbf{f}_g^{(1)}(0) + \zeta \partial_z \mathbf{f}_g^{(0)}(0) + \varphi_p^{(1)}$  and noting that  $\int c_z (\partial_z \mathbf{f}_g^{(0)})(0) d\mathbf{c} = 0$  it is obtained by integrating over  $\zeta \in (0, \infty)$  and  $\mathbf{c} \in \mathbb{R}^3$ , using  $\mathbf{f}_g^{(1)}(0) + \varphi_p^{(1)} \rightarrow 0$  as  $\zeta \rightarrow 0$  and  $\varphi_p^{(1)} \rightarrow 0$  as  $\zeta \rightarrow \infty$ , and rescaling from  $\zeta$  to  $z$ , that

$$n_g(0) \mathbf{v}_{gz}(0) = \int C_{p,c}(\mathbf{f}_p^{(0)}, \mathbf{f}_c^{(0)}) d\mathbf{c} dz. \quad (25)$$

In particular, at zeroth order, the dynamic term of the physisorbate plays no role and the Stefan flux towards the gas phase  $n_g(0) \mathbf{v}_{gz}(0)$  is due to the production of gas/physisorbate by adsorption/desorption of the chemisorbate.

The overall species conservation equation in the chemisorbate is obtained similarly and reads

$$\partial_t \tilde{n}_c = \partial_t \bar{n}_c \int \exp\left(-\frac{w_c}{k_b T_w}\right) dz = \int C_{c,p}(\mathbf{f}_c^{(0)}, \mathbf{f}_p^{(0)}) d\mathbf{c} dz, \quad (26)$$

where  $\tilde{n}_c = \bar{n}_c \int \exp(-w_c/k_b T_w) dz$  represents the total amount of chemisorbate available in the layer and may be interpreted as the overall *surface number density* of the chemisorbate. Therefore, we have recovered the traditional gas and chemisorbate fluid boundary conditions (25)(26) at a surface with adsorption [10, 18].

## Surface chemical reaction

The surface chemistry production may next be written by using the chemical potentials as well as *surface species* quantities. The reaction rate is first rewritten in the form

$$\int C_{p,c}(\mathbf{f}_p^{(0)}, \mathbf{f}_c^{(0)}) d\mathbf{c} dz = \mathcal{K}_{p,c} \left( \frac{\bar{n}_c}{z_c} - (1 - \sigma) \frac{n_g(0)}{z_g} \right),$$

where  $\mathcal{K}_{p,c} = \int W_{p,c} d\mathbf{c} d\mathbf{c}' dz$  is the overall surface reaction constant. It is then natural to rewrite the adsorption source term using the surface number density  $\tilde{n}_c = \bar{n}_c \int \exp(-w_c/k_b T_w) dz$  with the corresponding partition function [24]

$$\tilde{z}_c = z_c \int \exp\left(-\frac{w_c}{k_b T_w}\right) dz.$$

Keeping in mind that  $\tilde{n}_c = \sigma \tilde{n}_{sf}$ , we may further use the  $1 - \sigma$  factor coming from the free surface site concentration in order to form the chemical potential of the chemisorbed species per unit surface

$$\tilde{\mu}_c = \log\left(\frac{\tilde{n}_c}{\tilde{z}_c} \frac{1}{1 - \sigma}\right) = \log\left(\frac{\tilde{n}_{sf}}{\tilde{z}_c} \frac{\sigma}{1 - \sigma}\right).$$

The factor  $\sigma/(1 - \sigma)$  has then been recovered in the chemical potential of the chemisorbed species  $\tilde{\mu}_c$  as given by statistical mechanics. Keeping in mind that the chemical potential in the gas is  $\mu_g = \log(n_g/z_g)$ , the surface source term may further be rewritten as

$$\int C_{p,c}(\mathbf{f}_p^{(0)}, \mathbf{f}_c^{(0)}) d\mathbf{c} dz = \mathcal{K}'_{p,c} \left( \frac{\tilde{n}_{sf}}{\tilde{z}_c} \frac{\sigma}{1 - \sigma} - \frac{n_g(0)}{z_g} \right) = \mathcal{K}'_{p,c} \left( \exp(\tilde{\mu}_c) - \exp(\mu_g(0)) \right),$$

where  $\mathcal{K}'_{p,c} = (1 - \sigma) \mathcal{K}_{p,c}$ . Finally, at surface chemical equilibrium, we have  $\tilde{\mu}_c = \mu_g(0)$  so that  $\sigma/(1 - \sigma)$  is proportional to  $n_g(0)$  and the Langmuir isotherm [10] has been recovered.



## CONCLUSION

A kinetic model describing physisorption and chemisorption of gas particles on a crystal surface has been introduced, at a scale intermediate between molecular and macroscopic. The phonon and surface collision terms have simplified by assuming that the phonons and the crystal species are at equilibrium and the coupled system of gas/physisorbate and chemisorbate kinetic equations satisfies the H theorem. Using a fluid scaling and a multiscale framework, the structure of the adsorbate layer has been analyzed in terms of interaction potentials and the traditional fluid species boundary conditions have been recovered.

Many extension of this work may be considered like the situation of polyatomic gases or that of mixtures of gases involving complex surface reactions networks. First order accurate expansions with surface diffusion and rough surfaces are also of high scientific interest. Finally, multitemperature flows as well as state to state models also involve gas surface interactions of paramount importance for reentry and may also be investigated with similar models.

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