# A Kinetic Model of Adsorption on Crystal Surfaces

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A kinetic theory 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 a crystal potential and colliding with phonons. The phonons are assumed to be at equilibrium and the physisorbate/gas equation is coupled to similar kinetic equations describing chemisorbed particles and crystal atoms on the surface. A kinetic entropy is introduced for the coupled system and the H theorem is established. Using the Chapman-Enskog method with a fluid scaling, the asymptotic structure of the adsorbate is investigated and fluid boundary conditions are derived from the kinetic model.

## I. INTRODUCTION

The interaction of gases with solid surfaces is of paramount importance in science and engineering with applications in hypersonic reentry [1–6], combustion [7], ablation [8], condensation and evaporation [9–11], chemical deposition [12], catalysis [13], or corrosion [14]. This is a strong motivation for investigating kinetic models of adsorption processes, at a scale intermediate between molecular simulation [15–17] and fluid models [18–20], as well as deriving fluid boundary conditions at reactive surfaces by using the Chapman-Enskog method.

The interaction of gas particles with solid walls has been the object of various studies in a kinetic framework. Models assuming chemical equilibrium at the boundary may be investigated by using Maxwell type boundary conditions with boundary partial densities obtained from equilibrium conditions, avoiding the complexities of gas surface interaction. More refined models of gas-solid interfaces involve kinetic equations for gas particles interacting with a crystal potential and colliding with phonons that describe the fluctuating part of the surface potential [21–33]. These models have led to important advances in the knowledge of condensation and evaporation, particle trapping, phonon drag, surface homogenization, or scattering kernels [21–33]. Only gas particles have been considered in such studies, in other words, only physisorption phenomena [21]. However, chemical bonds may also be formed between particles and the surface and these chemisorbed species have to be considered as *other chemical species* compared to their parents gas phase. Such chemisorbed species play a fundamental role in surface chemistry, notably as active intermediate species in heterogeneous reaction mechanisms [1–14].

A kinetic theory model describing physisorption and chemisorption of gas particles on a solid surface is presented in this work. Such a *kinetic* model was not previously available to the best of the authors' knowledge and is an attempt to fill the gap between molecular dynamics [15–17] and macroscopic fluid models of reactive surfaces [18–20]. A single monatomic gas interacting with a monatomic crystal is considered, the situation of polyatomic gases or that of multicomponent mixtures with heterogenous chemical reactions other than adsorption laying beyond the scope of the present work.

A unique kinetic equation is used to describe 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. These particles interact with a potential field generated by fixed crystal particles and collide with phonons describing the fluctuating part of the surface potential. A kinetic equation for volume or surface phonons could also be introduced [21, 34–36] but it is assumed in this work for the sake of simplicity that phonons are at equilibrium [22, 24, 26, 27].

Using classical heterogeneous reaction formalism [18–20], the adsorption surface reaction may be written in the form

$$\mathrm{A} + \mathcal{C}(\mathrm{s}) \rightleftarrows \mathrm{A}(\mathrm{s}) + \mathcal{C}(\mathrm{b}), \tag{1}$$

where A denotes the monatomic physisorbed/gas particle, A(s) the chemisorbed particle on the surface, $\mathcal{C}$ the crystal atom, $\mathcal{C}$(s) the crystal molecule on the surface that is a free site, and $\mathcal{C}$(b) the bulk crystal molecule, that is, a crystal molecule bonded to a chemisorbed molecule. New kinetic equations for the chemisorbed species A(s) and the crystal surface species $\mathcal{C}$(s) and $\mathcal{C}$(b) are introduced and coupled to the physisorbed/gas kinetic equation. The transition between physisorbed/gas particles A and chemisorbed particles A(s) is described by surface chemistry terms in the kinetic equations and it is assumed that surface chemistry is slow in such a way that the crystal surface essentially remains at physical equilibrium [37]. A modified kinetic entropy is introduced for the coupled system and the H theorem is established.

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A Chapman-Enskog type expansion is next investigated with a fluid scaling of the kinetic equations. A multiscale asymptotic analysis is performed and the fluid Stefan velocity associated with adsorption is naturally assumed to be small. The inner structure of the physisorbate, the chemisorbate, and the free atom layer are analyzed at zeroth order and closely related to interaction potentials. The zeroth order species boundary conditions are obtained and the Stefan gas flow issuing from the adsorbate layer results from the physisorbed/gas particle production by adsorption/desorption of the chemisorbate. The dynamic boundary conditions associated with the pressure tensor and the heat flux at the interface are also addressed.

The inner structure of the physisorbate, the chemisorbate, and the free site layer are next analyzed at first order. The linearized equations governing the perturbed distribution functions are differential-integral equations involving interaction potentials and phonon collision operators that differ from traditional Knudsen layer equations as well as the corresponding boundary conditions. The resulting first order surface species boundary conditions also involve tangential diffusion—due to the interaction with phonons—that is investigated in a molar framework. The first order gas Stefan flow issuing from the adsorbate finally involves a robin type boundary condition with mixed derivatives.

The kinetic model is presented in Section II and the asymptotic framework in Section III. Zeroth order expansions and mass boundary conditions are investigated in Section IV, momentum and thermal boundary conditions in Section V and first order expansions in Section VI.

## II. A KINETIC MODEL

The kinetic equations modeling gas adsorption on a solid surface are presented in this section. These equations typically describe particles interacting with a potential field and colliding with phonons [21, 22, 25]. The chemisorbate equation as well as the kinetic description of the crystal species appear to be new to the authors' knowledge [37].

### A. Kinetic equations for the adsorbate

We consider a single monatomic gas governed by the Boltzmann equation [21, 22, 25]

$$\partial_t f_{\rm p} + \boldsymbol{c}_{\rm p}\cdot\boldsymbol{\partial}_{\boldsymbol{x}} f_{\rm p} - \frac{1}{m_{\rm p}}\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{w}_{\rm p}\cdot\boldsymbol{\partial}_{\boldsymbol{c}_{\rm p}} f_{\rm p} = J_{\rm p,p}(f_{\rm p},f_{\rm p}) + \mathcal{J}_{\rm p,ph}(f_{\rm p}) + \mathcal{C}_{\rm p}, \qquad (2)$$

where $\partial_t$ stands for the time derivative operator, $\boldsymbol{\partial}_{\boldsymbol{x}}$ the space derivative operator, $f_{\rm p}(t,\boldsymbol{x},\boldsymbol{c}_{\rm p})$ the physisorbate/gas particle distribution function, $\boldsymbol{c}_{\rm p}$ the physisorbed/gas particle velocity, $m_{\rm p}$ the particle mass that is the mass $m_{\rm A}$ of atom A, $\mathrm{w}_{\rm p}$ the interaction potential between *fixed* crystal particles and physisorbed/gas particles, $\boldsymbol{\partial}_{\boldsymbol{c}_{\rm p}}$ the velocity derivative operator, $J_{\rm p,p}$ the gas-gas collision operator, $\mathcal{J}_{\rm p,ph}$ the gas-phonon collision operator, and $\mathcal{C}_{\rm p}$ the chemistry source term. The solid surface is assumed to be planar and located at $z=0$ with the spatial coordinates written $\boldsymbol{x}=(x,y,z)^t$ and $\boldsymbol{e}_z$ denotes the base vector in the normal direction oriented towards the gas.

The gas-gas collision operator $J_{\rm p,p}$ is in the traditional form [38–41]

$$J_{\rm p,p}(f_{\rm p},\widetilde{f}_{\rm p}) = \int\!\!\big(f_{\rm p}(\boldsymbol{c}'_{\rm p})f_{\rm p}(\widetilde{\boldsymbol{c}}'_{\rm p}) - f_{\rm p}(\boldsymbol{c}_{\rm p})f_{\rm p}(\widetilde{\boldsymbol{c}}_{\rm p})\big)\mathsf{W}_{\rm p,p}\mathrm{d}\widetilde{\boldsymbol{c}}_{\rm p}\,\mathrm{d}\boldsymbol{c}'_{\rm p}\mathrm{d}\widetilde{\boldsymbol{c}}'_{\rm p}, \quad (3)$$

where in a direct collision $\widetilde{\boldsymbol{c}}_{\rm p}$ denotes the velocity of the collision partner, $\boldsymbol{c}'_{\rm p}$ and $\widetilde{\boldsymbol{c}}'_{\rm p}$ the velocities after collision, and $\mathsf{W}_{\rm p,p}$ the transition probability for gas-gas collisions. Only binary collisions are considered and the transition probability $\mathsf{W}_{\rm p,p}$ satisfies the reciprocity relation $\mathsf{W}_{\rm p,p}(\boldsymbol{c}_{\rm p},\widetilde{\boldsymbol{c}}_{\rm p},\boldsymbol{c}'_{\rm p},\widetilde{\boldsymbol{c}}'_{\rm p}) = \mathsf{W}_{\rm p,p}(\boldsymbol{c}'_{\rm p},\widetilde{\boldsymbol{c}}'_{\rm p},\boldsymbol{c}_{\rm p},\widetilde{\boldsymbol{c}}_{\rm p})$ associated with microreversibility. The collision term $J_{\rm p,p}$ may equivalently be written in terms of collision cross sections [38–41].

The phonon collision operators will be investigated in Section II E and the reactive operators in Section II F. These collision operators $\mathcal{J}_{\rm p,ph}$ and $\mathcal{C}_{\rm p}$ both vanish far from the surface as well as the potential $\mathrm{w}_{\rm p}$ in such a way that letting $z\to\infty$ in equation (2) yields the kinetic equation in the gas phase

$$\partial_t f_{\rm g} + \boldsymbol{c}_{\rm p}\cdot\boldsymbol{\partial}_{\boldsymbol{x}} f_{\rm g} = J_{\rm p,p}(f_{\rm g},f_{\rm g}), \qquad (4)$$

where $f_{\rm g}(t,\boldsymbol{x},\boldsymbol{c}_{\rm p})$ denotes the gas particle distribution function and the gas particle velocity $\boldsymbol{c}_{\rm p}$ may equivalently be denoted by $\boldsymbol{c}_{\rm g}$. The kinetic equation (4) is the standard Boltzmann equation for a single monatomic gas and there is thus a single kinetic framework describing both gas and physisorbed particles, the gas equation being recovered far from the surface.

Chemisorption involves the formation of a chemical bond between the adsorbate and the adsorbent [17]. The particles of the chemisorbate A(s) are localized on the solid surface $\Sigma$ and have to be considered as different chemical species. The distribution function of the chemisorbate is governed by the kinetic equation

$$\partial_t f_{\rm c} + \boldsymbol{c}_{\rm c}\cdot\boldsymbol{\partial}_{\boldsymbol{x}} f_{\rm c} - \frac{1}{m_{\rm c}}\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{w}_{\rm c}\cdot\boldsymbol{\partial}_{\boldsymbol{c}_{\rm c}} f_{\rm c} = \mathcal{J}_{\rm c,ph}(f_{\rm c}) + \mathcal{C}_{\rm c}, \quad (5)$$

where $f_{\rm c}(t,\boldsymbol{x},\boldsymbol{c}_{\rm c})$ denotes the chemisorbed particle distribution function, $\boldsymbol{c}_{\rm c}$ the particle velocity, $\mathrm{w}_{\rm c}$ the interaction potential between *fixed* crystal particles and chemisorbed particles, $m_{\rm c}=m_{\rm A}$ the particle mass, $\mathcal{J}_{\rm c,ph}$ the chemisorbed particles/phonon collision term and $\mathcal{C}_{\rm c}$ the reactive source term. This equation is analogous to

that used for the physisorbed species—with the physisorbate potential $\mathrm{w_p}$ replaced by the chemisorbate potential $\mathrm{w_c}$—with a similar physical interpretation. It is also in the form derived by Bogoliubov and Bogoliubov [42] and similar to kinetic equations describing lattice gases introduced by Bogdanov et al. [25].

### B. Kinetic equations for the surface layer

The distribution function for the free sites $\mathcal{C}(\mathrm{s})$ on the surface $\Sigma$ is assumed to be governed by the kinetic equation

$$\partial_t f_\mathrm{s} + \boldsymbol{c}_\mathrm{s}\cdot\boldsymbol{\partial}_{\boldsymbol{x}} f_\mathrm{s} - \frac{1}{m_\mathrm{s}}\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{w_s}\cdot\boldsymbol{\partial}_{\boldsymbol{c}_\mathrm{s}} f_\mathrm{s} = \mathcal{J}_{\mathrm{s,ph}}(f_\mathrm{s}) + \mathcal{C}_\mathrm{s}, \quad (6)$$

where $f_\mathrm{s}(t,\boldsymbol{x},\boldsymbol{c}_\mathrm{s})$ denotes the free site particle distribution function, $\boldsymbol{c}_\mathrm{s}$ the particle velocity, $\mathrm{w_s}$ the interaction potential between *fixed* interior crystal particles (not on the surface layer) and free site crystal surface particles, $m_\mathrm{s}$ the particle mass that is the mass $m_\mathcal{C}$ of atom $\mathcal{C}$, $\mathcal{J}_{\mathrm{s,ph}}$ the crystal particle/phonon collision operator and $\mathcal{C}_\mathrm{s}$ the reactive source term. The phonon collision operators will be investigated in Section II E and the reactive operators in Section II F. Equation (6) is naturally similar to the chemisorbate kinetic equation since for crystal growth phenomena the chemisorbed layer is also a crystal layer. Equation (6) is also in the general form derived by Bogoliubov and Bogoliubov [42] as well as in the form of a one-particle equation obtained form the BBGKY hierarchy. The equilibrium distribution associated with (6) is a Maxwellian distribution constrained by the crystal potential $\mathrm{w_s}$ in agreement with statistical physics at equilibrium [43–46]. In other words, the free site particles are moving at velocity $\boldsymbol{c}_\mathrm{s}$ but trapped by the crystal potential $\mathrm{w_s}$. In previous work, it was assumed that the crystal species distributions remain Maxwellian [37] but this simplifying assumption—valid at zeroth order—is not anymore feasible at first order since surface diffusion of chemisorbed species naturally involves surface diffusion of free sites.

A similar kinetic equation may be written to describe the distribution $f_\mathrm{b}$ of the bulk species $\mathcal{C}(\mathrm{b})$ located on the surface $\Sigma$ in the form

$$\partial_t f_\mathrm{b} + \boldsymbol{c}_\mathrm{b}\cdot\boldsymbol{\partial}_{\boldsymbol{x}} f_\mathrm{b} - \frac{1}{m_\mathrm{b}}\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{w_b}\cdot\boldsymbol{\partial}_{\boldsymbol{c}_\mathrm{b}} f_\mathrm{b} = \mathcal{J}_{\mathrm{b,ph}}(f_\mathrm{b}) + \mathcal{C}_\mathrm{b}, \quad (7)$$

where $f_\mathrm{b}(t,\boldsymbol{x},\boldsymbol{c}_\mathrm{b})$ denotes the bulk particle—of the crystal surface—distribution function, $\boldsymbol{c}_\mathrm{b}$ the particle velocity, $\mathrm{w_b} = \mathrm{w_s}$ the interaction potential between fixed inner crystal particles and crystal surface particles, $m_\mathrm{b} = m_\mathcal{C}$ the particle mass, $\mathcal{J}_{\mathrm{b,ph}}$ the bulk crystal particle/phonon collision operator and $\mathcal{C}_\mathrm{b}$ the reactive source term. Essentially macroscopic moments of this equation will be used, in order notably to establish links with traditional fluid boundary conditions. This equation is analogous to the free site equation with a similar physical interpretation. The phonon collision term may also be interpreted as an overall relaxation operator encompassing phenomena of different origins.

The surface layer $\Sigma$ is the last layer of atoms of the crystal located around $z = 0$ and constituted by free site particles $\mathcal{C}(\mathrm{s})$ as well as bulk crystal particles $\mathcal{C}(\mathrm{b})$. The *unperturbed or standard* surface layer distribution function $f^\mathrm{e}_\sigma$ is solution of the kinetic equation

$$\partial_t f^\mathrm{e}_\sigma + \boldsymbol{c}_\sigma\cdot\boldsymbol{\partial}_{\boldsymbol{x}} f^\mathrm{e}_\sigma - \frac{1}{m_\sigma}\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{w}_\sigma\cdot\boldsymbol{\partial}_{\boldsymbol{c}_\sigma} f^\mathrm{e}_\sigma = \mathcal{J}_{\sigma,\mathrm{ph}}(f^\mathrm{e}_\sigma), \quad (8)$$

where $\mathrm{w}_\sigma = \mathrm{w_s}$ denotes the interaction potential between fixed interior crystal particles and crystal surface particles, $m_\sigma = m_\mathcal{C}$, and $\mathcal{J}_{\mathrm{s,ph}} = \mathcal{J}_{\sigma,\mathrm{ph}}$ the crystal particle/phonon collision operator. The standard surface distribution function $f^\mathrm{e}_\sigma$ may be seen as that of a physically unperturbed crystal surface. The probability $1-\theta$ to find an open site $\mathcal{C}(\mathrm{s})$ on the surface layer $\Sigma$ is then defined as the ratio

$$1-\theta = \frac{f_\mathrm{s}}{f^\mathrm{e}_\sigma}, \quad (9)$$

so that $f_\mathrm{s}(\boldsymbol{c}_\mathrm{s}) = \big(1-\theta(\boldsymbol{c}_\mathrm{s})\big) f^\mathrm{e}_\sigma(\boldsymbol{c}_\mathrm{s})$. The quantity $\theta$ is usually termed the coverage and represents the probability that a crystal site is occupied by a particle A(s) in the monolayer chemisorbate whereas $1-\theta$ is the probability that a crystal site is free. A kinetic equation governing the probability $1-\theta$ is easily obtained from (6) and (8) but will not be needed in the following. The probability of free sites $1-\theta$ is obtained here as a kinetic variable and will be shown to only depend on time $t$ and tangential coordinate $\boldsymbol{x}_\shortparallel$ at zeroth order as was assumed in previous work [37].

### C. Summed potentials

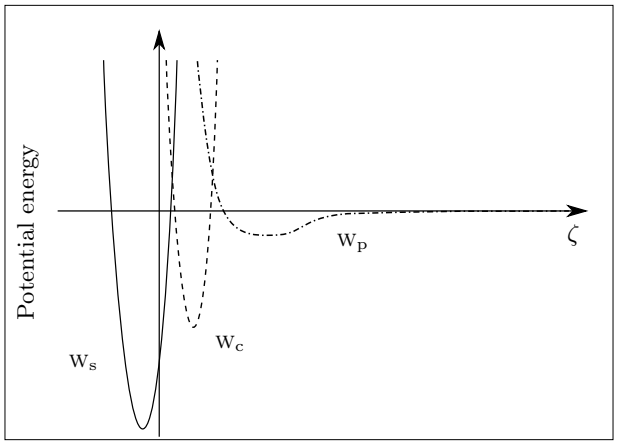


FIG. 1. Typical surface interaction potentials as function of the distance from surface in arbitrary units; —— $\mathrm{w_s} = \mathrm{w}_\sigma$; - - - $\mathrm{w_p}$; – – – $\mathrm{w_c}$.

The interaction potentials—summed over fixed crystal particles—$\mathrm{w_p}$, $\mathrm{w_c}$, and $\mathrm{w_s} = \mathrm{w_b} = \mathrm{w}_\sigma$ are assumed to only depend on the normal coordinate $z$ in order to simplify the algebra involved in the solution of the kinetic equations. These potentials are written in the form $\mathrm{w_p} = \mathrm{w_p}(z/\delta)$, $\mathrm{w_c} = \mathrm{w_c}(z/\delta)$, and $\mathrm{w}_\sigma = \mathrm{w}_\sigma(z/\delta)$, where $\delta$ is a characteristic range of the surface potential also characteristic of the range of gas-phonons interaction and $\zeta = z/\delta$ is the corresponding rescaled normal coordinate. The potentials are such that

$$\lim_{\zeta\to 0} \mathrm{w_p}(\zeta) = +\infty, \qquad \lim_{\zeta\to+\infty} \mathrm{w_p}(\zeta) = 0, \tag{10}$$

$$\lim_{\zeta\to\zeta_c^-} \mathrm{w_c}(\zeta) = +\infty, \qquad \lim_{\zeta\to\zeta_c^+} \mathrm{w_c}(\zeta) = +\infty, \tag{11}$$

$$\lim_{\zeta\to\zeta_\sigma^-} \mathrm{w_s}(\zeta) = +\infty, \qquad \lim_{\zeta\to\zeta_\sigma^+} \mathrm{w_s}(\zeta) = +\infty, \tag{12}$$

where chemisorbed particles are localized over $(\zeta_c^-, \zeta_c^+)$ and the crystal surface layer over $(\zeta_\sigma^-, \zeta_\sigma^+)$ with typically $\zeta_\sigma^- < \zeta_c^- = 0 < \zeta_\sigma^+ < \zeta_c^+$. These interaction potentials usually involve an attractive zone and a repulsing zone as Lennard-Jones potentials integrated over all crystal particles as illustrated in Figure 1.

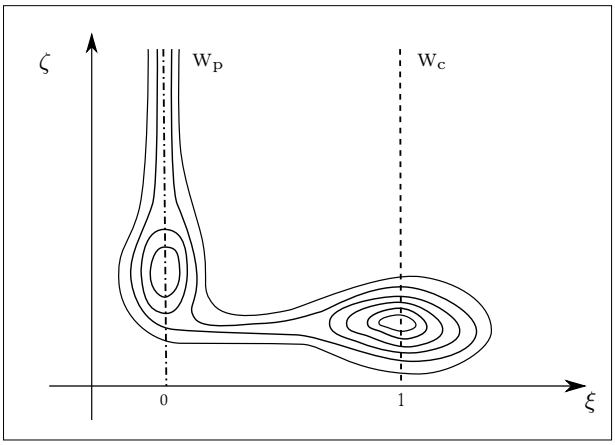


FIG. 2. Contour plots of a potential energy surface as function of the distance from surface $\zeta$ and the reaction coordinate $\xi$ in arbitrary units. The slice $\xi = 0$ corresponds to the physisorbed/gas particles potential $\mathrm{w_p}$ and the slice $\xi = 1$ to the chemisorbed particles potential $\mathrm{w_c}$.

The potentials $\mathrm{w_p}$ and $\mathrm{w_c}$ may also be interpreted as slices $\mathrm{w_p} = \mathcal{W}(0,\zeta)$ and $\mathrm{w_c} = \mathcal{W}(1,\zeta)$ of a potential energy surface $\mathcal{W}(\xi,\zeta)$ where $\xi$ denotes a reaction coordinate. The potential $\mathrm{w_p}$ then corresponds to the gas/physisorbed slice $\xi = 0$ and $\mathrm{w_c}$ to the chemisorbed slice $\xi = 1$ as illustrated in Figure 2.

The summed potentials being functions of $z$, periodic potential variations parallel to $\Sigma$ are not taken into account for surface species neither lateral interactions between chemisorbed species. The surface potential $\mathrm{w_p}$, $\mathrm{w_c}$, and $\mathrm{w}_\sigma$ are also assumed to be independent of the coverage $\theta$. These simplifications are notably feasible when the chemisorbed species are of relatively small size and the coverage of the surface $\theta$ is low. In the same vein, dense gas effects between physisorbed species are not considered in the kinetic model as well as sublimation of $\mathcal{C}$ atoms in the physisorbate.

### D. Maxwellians

We denote by $m_i$ the mass of the $i$th species, $\mathrm{E}_i$ the formation energy of the $i$th species and $n_i$ the number of particles per unit volume of the $i$th species. The wall Maxwellian distribution of the $i$th species is given by

$$\mathrm{M}_i(\boldsymbol{c}_i) = \Big(\frac{m_i}{2\pi k_\mathrm{B} T_\mathrm{w}}\Big)^{3/2} \exp\Big(-\frac{m_i|\boldsymbol{c}_i|^2}{2k_\mathrm{B}T_\mathrm{w}}\Big), \tag{13}$$

where $T_\mathrm{w}$ denotes the wall temperature, $k_\mathrm{B}$ the Boltzmann constant, and $i \in \{\mathrm{p},\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}$. It will later be established that the equilibrium distributions $f_i^\mathrm{e}$, $i \in \{\mathrm{p},\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}$, are Maxwellian $f_i^\mathrm{e} = n_i \mathrm{M}_i$ in agreement with statistical physics [35, 36, 43–46].

We introduce for convenience the modified Maxwellian distributions

$$\mathrm{m}_i = \mathrm{M}_i \exp(-\mathrm{w}_i/k_\mathrm{B}T_\mathrm{w}), \qquad i \in \{\mathrm{p},\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}, \tag{14}$$

that may be written

$$\mathrm{m}_i = \Big(\frac{m_i}{2\pi k_\mathrm{B} T_\mathrm{w}}\Big)^{3/2} \exp\Big(-\frac{m_i|\boldsymbol{c}_i|^2}{2k_\mathrm{B}T_\mathrm{w}} - \frac{\mathrm{w}_i}{k_\mathrm{B}T_\mathrm{w}}\Big). \tag{15}$$

These modified Maxwellian distributions will play an important role in the analysis of the adsorbate layer. With the inclusion of the interaction potential $\mathrm{w}_i$ in the distribution $\mathrm{m}_i$, $i \in \{\mathrm{p},\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}$, it is indeed obtained that

$$\boldsymbol{c}_i\cdot\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{m}_i - \frac{1}{m_i}\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{w}_i\cdot\boldsymbol{\partial}_{\boldsymbol{c}_i}\mathrm{m}_i = 0, \tag{16}$$

as well as

$$\partial_t \mathrm{m}_i = 0, \qquad \mathcal{J}_{i,\mathrm{ph}}(\mathrm{m}_i) = 0. \tag{17}$$

The relations $\partial_t \mathrm{m}_i = 0$ and $\boldsymbol{c}_i\cdot\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{m}_i - \frac{1}{m_i}\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{w}_i\cdot\boldsymbol{\partial}_{\boldsymbol{c}_i}\mathrm{m}_i = 0$ are direct consequences of (15) keeping in mind that the system is isothermal whereas the relation $\mathcal{J}_{i,\mathrm{ph}}(\mathrm{m}_i) = 0$ will be established in the next section. The modified Maxwellian distributions $\mathrm{m}_i$, $i \in \{\mathrm{p},\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}$, thus appear as *natural solutions* of isothermal thin layer kinetic equations in a potential field with phonon interactions or equivalently as natural steady solutions of the corresponding kinetic equations. Decomposing between parallel and normal directions with respect to $\Sigma$, we may further write

$$\boldsymbol{\partial}_\shortparallel \mathrm{m}_i = 0, \qquad c_{iz}\,\partial_z \mathrm{m}_i - \frac{1}{m_i}\partial_z \mathrm{w}_i\,\partial_{c_{iz}}\mathrm{m}_i = 0, \tag{18}$$

where $\boldsymbol{\partial}_\shortparallel$ denotes the tangential spatial derivative operator, $c_{iz}$ the normal velocity of the $i$th species, $\partial_z$ the

normal spatial derivative, and $\partial_{c_{iz}}$ the differential operator with respect to $c_{iz}$. The modified distributions will also play a key role in the expression of the reactive collision term and in the kinetic entropy as investigated in the following sections.

Considering further the standard or unperturbed surface layer distribution $f_\sigma^{\rm e}$, we have

$$f_\sigma^{\rm e} = n_\sigma {\rm M}_\sigma, \tag{19}$$

where $n_\sigma$ denotes the—standard—number density of the surface layer and ${\rm M}_\sigma$ the Maxellian distribution (13). The number density $n_\sigma$ is given by

$$n_\sigma = \overline{n}_\sigma \exp\Big(-\frac{{\rm W}_\sigma}{k_{\rm B}T_{\rm w}}\Big), \tag{20}$$

where $\overline{n}_\sigma$ is a constant *characteristic of the crystal and its orientation*. The distribution $f_\sigma^{\rm e}$ defined by the relations (19)(20) is indeed an exact solution of (8) since we have $f_\sigma^{\rm e} = \overline{n}_\sigma {\rm m}_\sigma$. We will later recover (20) when investigating the structure of the adsorbate at zeroth order. One may further define

$$\widetilde{n}_\sigma = \int n_\sigma \, {\rm d}z, \tag{21}$$

that represents the number of surface atoms *per unit surface* and is also characteristic of the surface. A similar notation is also introduced for all surface species

$$n_i = \int f_i \, {\rm d}\boldsymbol{c}_i, \qquad \widetilde{n}_i = \int n_i \, {\rm d}z, \qquad i \in \{{\rm c}, {\rm s}, {\rm b}\}, \tag{22}$$

where $\widetilde{n}_i$ represents the number of particules of species $i$ *per unit surface*.

### E. Phonon collision operators

The collision term $\mathcal{J}_{i,{\rm ph}}$ between particles of species $i \in \{{\rm p}, {\rm c}, {\rm s}, {\rm b}, \sigma\}$ and phonons involve operators in the general form [21, 34–36]

$$\mathcal{J}_{i,{\rm ph}} = \int\Big(\big(f_{\rm ph}(\boldsymbol{q})+1\big) f_i(\boldsymbol{c}_i') - f_{\rm ph}(\boldsymbol{q}) f_i(\boldsymbol{c}_i)\Big)\overline{\mathsf{W}}_{i,{\rm ph}} \, {\rm d}\boldsymbol{c}_i' {\rm d}\boldsymbol{q}, \tag{23}$$

where $f_{\rm ph}(\boldsymbol{q})$ denotes the phonon distribution function, $i \in \{{\rm p}, {\rm c}, {\rm s}, {\rm b}, \sigma\}$ the species index, $\boldsymbol{q}$ the phonon wave vector or quasi-momentum, $\boldsymbol{c}_i$ and $\boldsymbol{c}_i'$ the particle velocities before and after the interaction, and $\overline{\mathsf{W}}_{i,{\rm ph}}$ a transition probability. The dilute approximation has been used for $f_i$ in order to simplify (23) and the appearing of the additional factor 1 in the gain term is a typical quantum effect [21, 34–36]. The operator (23) corresponds to collisions such that $m_i \boldsymbol{c}_i = m_i \boldsymbol{c}_i' + \boldsymbol{q} + \boldsymbol{b}$ where $\boldsymbol{b}$ is a vector of the reciprocal crystal lattice. There is another operator associated with collisions such that $m_i \boldsymbol{c}_i + \boldsymbol{q} = m_i \boldsymbol{c}_i' + \boldsymbol{b}$ that leads to the same type of simplified source term and the corresponding details are omitted.

The equilibrium relation between distribution functions corresponding to (23) reads $\big(f_{\rm ph}^{\rm e}(\boldsymbol{q})+1\big) f_i^{\rm e}(\boldsymbol{c}_i') = f_{\rm ph}^{\rm e}(\boldsymbol{q}) f_i^{\rm e}(\boldsymbol{c}_i)$ where the superscript $^{\rm e}$ stands for *physical equilibrium*. The equilibrium distribution for the phonons $f_{\rm ph}^{\rm e}$ is the Bose-Einstein distribution, $f_i^{\rm e}$ is the wall Maxwellian of the $i$th species, and the equilibrium relation may be rewritten for convenience in the form $\big(f_{\rm ph}^{\rm e}(\boldsymbol{q})+1\big){\rm m}_i(\boldsymbol{c}_i') = f_{\rm ph}^{\rm e}(\boldsymbol{q}){\rm m}_i(\boldsymbol{c}_i)$. Dividing then the integrands in the collision term (23) by the factor $\big(f_{\rm ph}^{\rm e}(\boldsymbol{q})+1\big){\rm m}_i(\boldsymbol{c}_i') = f_{\rm ph}^{\rm e}(\boldsymbol{q}){\rm m}_i(\boldsymbol{c}_i)$ and further *assuming that phonons are at equilibrium* $f_{\rm ph}^{\rm e} = f_{\rm ph}$, it is obtained that

$$\mathcal{J}_{i,{\rm ph}}(f_i) = \int\Big(\frac{f_i(\boldsymbol{c}_i')}{{\rm m}_i(\boldsymbol{c}_i')} - \frac{f_i(\boldsymbol{c}_i)}{{\rm m}_i(\boldsymbol{c}_i)}\Big)\mathsf{W}_{i,{\rm ph}} {\rm d}\boldsymbol{c}_i', \tag{24}$$

where $\mathsf{W}_{i,{\rm ph}} = {\rm m}_i(\boldsymbol{c}_i)\int f_{\rm ph}^{\rm e}(\boldsymbol{q})\overline{\mathsf{W}}_{i,{\rm ph}} {\rm d}\boldsymbol{q}$ denotes the resulting transition probability. This assumption of phonons at equilibrium is frequently introduced in the literature and eliminates the phonon distribution function $f_{\rm ph}$ that is governed by kinetic equations [22, 24, 26, 27]. The transition probability $\mathsf{W}_{i,{\rm ph}}$ satisfies the reciprocity relation $\mathsf{W}_{i,{\rm ph}}(\boldsymbol{c}_i, \boldsymbol{c}_i') = \mathsf{W}_{i,{\rm ph}}(\boldsymbol{c}_i', \boldsymbol{c}_i)$ and is nonzero only in the neighborhood of the surface [21, 22]. This term $\mathcal{J}_{i,{\rm ph}}$ may further be simplified as $-(f_i - n_i {\rm M}_i)/\tau_{i,{\rm ph}}$ where $\tau_{i,{\rm ph}}$ denotes a relaxation time [22] as will be assumed in Section VI.

### F. Reactive collision operators

The typical geometry of gas/crystal interactions is depicted in Figure 3 where a physisorbed/gas particle denoted by A is approaching the surface $\Sigma$ and may collide with a free site crystal species $\mathcal{C}$(s). The particle A may then be transformed into a chemisorbed particle A(s) and the crystal species into $\mathcal{C}$(b), that is, into a surface layer particle bonded with a chemisorbed particle. The chemisorbed species A(s) may move on the surface and is not bonded to a fixed crystal particle $\mathcal{C}$(b) because of surface diffusion [47, 48]. The chemisorbed particles A(s) may also collide with the surface layer $\Sigma$ of the crystal and desorb. In order to keep notation short, in the following, the subscript p is associated with physisorbed/gas particles A, the subscript c to chemisorbed particles A(s), the subscript s to free site crystal species $\mathcal{C}$(s), the subscript b to bulk crystal species $\mathcal{C}$(b) that are on the surface layer $\Sigma$ and the subscript $\sigma$ to the surface layer particles. In summary, the subscripts $\{{\rm p}, {\rm c}, {\rm s}, {\rm b}, \sigma\}$ correspond respectively to A, A(s), $\mathcal{C}$(s), $\mathcal{C}$(b), and $\Sigma$.

The adsorption chemical reaction may be written as (1) when using the 'atomic site convention' of heterogeneous chemistry [18–20]. With the *atomic site convention*, the crystal molecules $\mathcal{C}$(s) and $\mathcal{C}$(b) are included in the reaction description and the number of active site 's' as well as both atomic elements A and $\mathcal{C}$ are conserved in (1). The atomic site convention is more complete than the *open site convention* that would corresponds to the

adsorption reaction written in the variant form [18, 19]

$$\mathrm{A} + \mathcal{O}(\mathrm{s}) \rightleftarrows \mathrm{A}(\mathrm{s}), \tag{25}$$

where $\mathcal{O}(\mathrm{s})$ is the symbol of an *open site*—a free site—on the surface $\Sigma$. The open site symbolic species $\mathcal{O}(\mathrm{s})$ *is massless and contains no elements* and only the number of active sites 's' and the number of element A are concerned and conserved in (25). The properties of the open site $\mathcal{O}(\mathrm{s})$ symbol in (25) may generally be determined by using the atomic site convention, so that for instance the formation energy of $\mathcal{O}(\mathrm{s})$ is $\mathrm{E_s} - \mathrm{E_b}$ [19]. These two symbolic descriptions are equally valid in order to describe *macroscopically* heterogeneous chemical reaction mechanisms but the atomic site convention is more convenient in order to describe *molecular reactive collisions*.

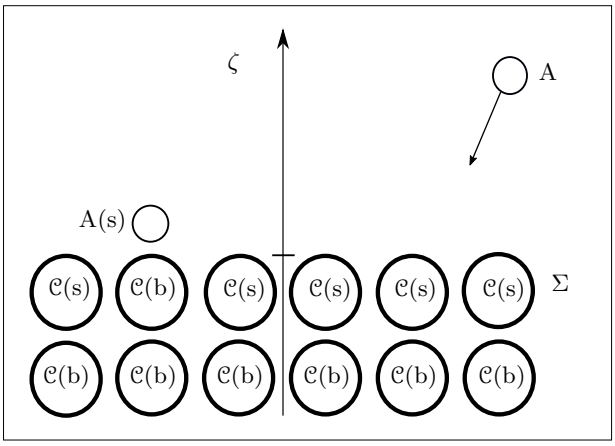


FIG. 3. Geometry of the particle-solid interaction.

The reactive collision term $\mathcal{C}_\mathrm{p}$ associated with (1) may be written

$$\mathcal{C}_\mathrm{p} = \int \big(f_\sigma(\boldsymbol{c}_\mathrm{b}) f_\mathrm{c}(\boldsymbol{c}_\mathrm{c}) - f_\mathrm{s}(\boldsymbol{c}_\mathrm{s}) f_\mathrm{p}(\boldsymbol{c}_\mathrm{p})\big)\overline{\mathsf{W}}^{+}\mathrm{d}\boldsymbol{c}_\mathrm{b}\,\mathrm{d}\boldsymbol{c}_\mathrm{c}\mathrm{d}\boldsymbol{c}_\mathrm{s}, \tag{26}$$

where $\overline{\mathsf{W}}^{+}$ denotes a reactive transition probability. The collision term (26) is typical of reactive terms associated with gas phase chemical reactions [40, 41, 49] and naturally involves collisions between particles A and free surface sites $\mathcal{C}(\mathrm{s})$ in the forward direction and collisions between the particles A(s) and surface crystal atoms in the backward direction. The operator $\mathcal{C}_\mathrm{p}$ is local in space as typical collision operators and the distribution functions are considered to be three dimensional in space. The surface distribution $f_\sigma$ is used in the desorbing backward direction since the chemisorbed molecule A(s) may collide with any particle of the crystal surface that then becomes a bulk species. The desorption rate depends only *linearly* in particular on the surface concentration of the chemisorbed species $\widetilde{n}_\mathrm{c}$, with a crystal surface having a constant surface number density $\widetilde{n}_\sigma$. The activity coefficient of single bulk species $\mathcal{C}(\mathrm{b})$ is consistently taken to be unity in heterogeneous chemistry models [18].

In order to simplify the reactive source term, we further observe that, *at chemical equilibrium*, the statistical equilibrium relation holds

$$f_\sigma^{\mathrm{ce}} f_\mathrm{c}^{\mathrm{ce}} = f_\mathrm{s}^{\mathrm{ce}} f_\mathrm{p}^{\mathrm{ce}}, \tag{27}$$

with equilibrium distributions given by $f_i^{\mathrm{ce}} = n_i^{\mathrm{ce}} \mathrm{M}_i$, where the superscript $^{\mathrm{ce}}$ denotes chemical equilibrium, the superscript $^{\mathrm{e}}$ denotes physical equilibrium, $n_i^{\mathrm{ce}}$ the chemical equilibrium value of $n_i$ for $i \in \{\mathrm{p}, \mathrm{c}, \mathrm{s}\}$ and $f_\sigma^{\mathrm{ce}} = f_\sigma^{\mathrm{e}} = n_\sigma \mathrm{M}_\sigma$ since $n_\sigma^{\mathrm{ce}} = n_\sigma^{\mathrm{e}} = n_\sigma$ remains constant in time.

In order to simplify the reactive source term, using the equilibrium relation (27), one may write

$$\mathcal{C}_\mathrm{p} = \int \Big( \frac{f_\sigma}{f_\sigma^{\mathrm{ce}}} \frac{f_\mathrm{c}}{f_\mathrm{c}^{\mathrm{ce}}} - \frac{f_\mathrm{s}}{f_\mathrm{s}^{\mathrm{ce}}} \frac{f_\mathrm{p}}{f_\mathrm{p}^{\mathrm{ce}}} \Big) f_\mathrm{s}^{\mathrm{ce}} f_\mathrm{p}^{\mathrm{ce}} \overline{\mathsf{W}}^{+} \mathrm{d}\boldsymbol{c}_\mathrm{b} \mathrm{d}\boldsymbol{c}_\mathrm{c} \mathrm{d}\boldsymbol{c}_\mathrm{s}, \tag{28}$$

and assuming that the surface *remains at physical equilibrium* $f_\sigma = f_\sigma^{\mathrm{e}}$ the chemical production rate is found in the form

$$\mathcal{C}_\mathrm{p} = \int \Big( \frac{f_\mathrm{c}}{f_\mathrm{c}^{\mathrm{ce}}} - \frac{f_\mathrm{s}}{f_\mathrm{s}^{\mathrm{ce}}} \frac{f_\mathrm{p}}{f_\mathrm{p}^{\mathrm{ce}}} \Big) f_\mathrm{s}^{\mathrm{ce}} f_\mathrm{p}^{\mathrm{ce}} \overline{\mathsf{W}}^{+} \mathrm{d}\boldsymbol{c}_\mathrm{b} \mathrm{d}\boldsymbol{c}_\mathrm{c} \mathrm{d}\boldsymbol{c}_\mathrm{s}. \tag{29}$$

The assumption that $f_\sigma = f_\sigma^{\mathrm{e}}$ means that surface chemistry is slow and that the surface is essentially not modified by chemistry. It is also consistent with the assumption that the phonons are at equilibrium.

On the other hand, at chemical equilibrium, we have equality of the chemical potentials $\mu_\mathrm{b}^{\mathrm{ce}} + \mu_\mathrm{c}^{\mathrm{ce}} = \mu_\mathrm{s}^{\mathrm{ce}} + \mu_\mathrm{p}^{\mathrm{ce}}$ according to the chemical reaction (1). These chemical potentials, that must take into account the interaction potentials $\mathrm{W}_i$, are in the form

$$\mu_i = \mu_i^{\mathrm{in}} + \frac{\mathrm{W}_i}{k_\mathrm{B} T_\mathrm{w}}, \tag{30}$$

where $\mu_i^{\mathrm{in}}$ is the *intrinsic* chemical potential of the $i$th species [44, 45, 50]. The intrinsic chemical potential is given by the usual formula $\mu_i^{\mathrm{in}} = g_i / k_\mathrm{B} T = \log(n_i / \mathrm{z}_i)$ where $g_i$ denotes the Gibbs function of the $i$th species, $\mathrm{z}_i$ the partition function per unit volume and $n_i$ the local value with the influence of the force field for $i \in \{\mathrm{c}, \mathrm{s}, \mathrm{p}\}$ [44, 45, 50]. For the bulk species we also have the chemical potential $\mu_\mathrm{b}^{\mathrm{in}} = \log(n_\sigma / \mathrm{z}_\mathrm{b})$ since collision may occur with any crystal particle on the surface. This chemical potential $\mu_\mathrm{b}$ yields an activity coefficient for the bulk species $\mathcal{C}(\mathrm{b})$ equal to unity in agreement with heterogeneous surface chemistry [18]. The partition functions are in the form $\mathrm{z}_i = \mathrm{z}_i^{\mathrm{tr}} \mathrm{z}_i^{\mathrm{int}}$ where $\mathrm{z}_i^{\mathrm{tr}}$ is the translational partition function of the $i$th species par unit volume and $\mathrm{z}_i^{\mathrm{int}}$ the internal energy partition function. The translational partition functions are given by $\mathrm{z}_\mathrm{b}^{\mathrm{tr}} = \mathrm{z}_\mathrm{s}^{\mathrm{tr}} = \Lambda_{\mathcal{C}}^{-3}$ and $\mathrm{z}_\mathrm{p}^{\mathrm{tr}} = \mathrm{z}_\mathrm{c}^{\mathrm{tr}} = \Lambda_\mathrm{A}^{-3}$ where $\Lambda_\mathrm{A} = \mathrm{h_P} / (2\pi k_\mathrm{B} m_\mathrm{A} T_\mathrm{w})^{1/2}$ and $\Lambda_{\mathcal{C}} = \mathrm{h_P} / (2\pi k_\mathrm{B} m_{\mathcal{C}} T_\mathrm{w})^{1/2}$ are the species thermal de Broglie wavelengths and $\mathrm{h_P}$ the Planck constant. On the other hand, the internal partition function of the $i$th species is given by $\mathrm{z}_i^{\mathrm{int}} = \exp(-\mathrm{E}_i / k_\mathrm{B} T_\mathrm{w})$.

The equilibrium relation between chemical potentials $\mu_{\rm b}^{\rm ce}+\mu_{\rm c}^{\rm ce}=\mu_{\rm s}^{\rm ce}+\mu_{\rm p}^{\rm ce}$ implies that

$$\frac{n_\sigma}{\mathrm{z_b}\exp\!\big(-\frac{\mathrm{w}_\sigma}{k_{\rm B}T_{\rm w}}\big)}\,\frac{n_{\rm c}^{\rm ce}}{\mathrm{z_c}\exp\!\big(-\frac{\mathrm{w_c}}{k_{\rm B}T_{\rm w}}\big)}=\frac{n_{\rm s}^{\rm ce}}{\mathrm{z_s}\exp\!\big(-\frac{\mathrm{w_s}}{k_{\rm B}T_{\rm w}}\big)}\,\frac{n_{\rm p}^{\rm ce}}{\mathrm{z_p}\exp\!\big(-\frac{\mathrm{w_p}}{k_{\rm B}T_{\rm w}}\big)}. \quad (31)$$

Combining (29) with (31), letting $\mathsf{W}^+=\overline{\mathsf{W}}^+\mathrm{z_p z_s m_p m_s}$, and noting that $n_\sigma/\exp\!\big(-\frac{\mathrm{w}_\sigma}{k_{\rm B}T_{\rm w}}\big)=\overline{n}_\sigma$ we obtain that

$$\mathcal{C}_{\rm p}=\int\Big(\frac{\overline{n}_\sigma}{\mathrm{z_b}}\frac{f_{\rm c}(\boldsymbol{c}_{\rm c})}{\mathrm{z_c m_c}(\boldsymbol{c}_{\rm c})}-\frac{f_{\rm s}(\boldsymbol{c}_{\rm s})}{\mathrm{z_s m_s}(\boldsymbol{c}_{\rm s})}\frac{f_{\rm p}(\boldsymbol{c})}{\mathrm{z_p m_p}(\boldsymbol{c})}\Big)\mathrm{d}\boldsymbol{c}_{\rm b}\mathrm{d}\boldsymbol{c}_{\rm c}\mathrm{d}\boldsymbol{c}_{\rm s}. \quad (32)$$

Since we have

$$\frac{f_{\rm s}(\boldsymbol{c}_{\rm s})}{\mathrm{z_s m_s}(\boldsymbol{c}_{\rm s})}=\frac{(1-\theta)\overline{n}_\sigma}{\mathrm{z_s}},$$

the fraction of available sites $1-\theta=f_{\rm s}/f_\sigma^{\rm e}$ is the only nonequilibrium part remaining from the crystal species distributions in the production rate. Further letting for the sake of notational simplicity

$$\gamma_k=\frac{f_k}{\mathrm{m}_k\mathrm{z}_k},\quad k\in\{\mathrm{p,c,s}\},\qquad \gamma_{\rm b}=\frac{\overline{n}_\sigma}{\mathrm{z_b}}, \quad (33)$$

the following simplified expression is obtained for the source term

$$\mathcal{C}_{\rm p}=\int\big(\gamma_{\rm b}\gamma_{\rm c}-\gamma_{\rm s}\gamma_{\rm p}\big)\mathsf{W}^+\mathrm{d}\boldsymbol{c}_{\rm b}\mathrm{d}\boldsymbol{c}_{\rm c}\mathrm{d}\boldsymbol{c}_{\rm s}. \quad (34)$$

The source terms for the other species are then obtained in a similar form

$$\mathcal{C}_{\rm c}=\int\big(\gamma_{\rm s}\gamma_{\rm p}-\gamma_{\rm b}\gamma_{\rm c}\big)\mathsf{W}^+\mathrm{d}\boldsymbol{c}_{\rm b}\mathrm{d}\boldsymbol{c}_{\rm s}\mathrm{d}\boldsymbol{c}_{\rm p}, \quad (35)$$

$$\mathcal{C}_{\rm s}=\int\big(\gamma_{\rm b}\gamma_{\rm c}-\gamma_{\rm s}\gamma_{\rm p}\big)\mathsf{W}^+\mathrm{d}\boldsymbol{c}_{\rm b}\mathrm{d}\boldsymbol{c}_{\rm c}\mathrm{d}\boldsymbol{c}_{\rm p}, \quad (36)$$

$$\mathcal{C}_{\rm b}=\int\big(\gamma_{\rm b}\gamma_{\rm c}-\gamma_{\rm s}\gamma_{\rm p}\big)\mathsf{W}^+\mathrm{d}\boldsymbol{c}_{\rm c}\mathrm{d}\boldsymbol{c}_{\rm s}\mathrm{d}\boldsymbol{c}_{\rm p}, \quad (37)$$

and may be used in the corresponding species kinetic equations.

Incidentally, during a reactive collision with the surface, the work done by the *fixed crystal* on the particles is the difference $\mathrm{w_p}-\mathrm{w_c}$ and thus the work received by the fixed crystal reads $\mathrm{w_c}-\mathrm{w_p}$. The work received by the fixed crystal must be equal to the difference of total energy of *fixed* crystal particles that have no kinetic energy so that during a reactive collision we must have $\mathrm{w_c}-\mathrm{w_p}=\mathrm{e_b}-\mathrm{e_s}$ which represents the energy of the chemical bond.

### G. Collisional invariants

Collision invariants of integral operators in kinetic equations are closely related with macroscopic conservation laws. The collisional invariants of the gas collision operator $J_{\rm p,p}$ are classically associated with particle number $\psi_{\rm p}^1=1$, momentum $\psi_{\rm p}^{1+\nu}=m_{\rm p}c_{{\rm p}\nu}$, $\nu\in\{1,2,3\}$, as well as energy $\psi_{\rm p}^5=\frac{1}{2}m_{\rm p}|\boldsymbol{c}_{\rm p}|^2+\mathrm{e_p}$. The macroscopic governing equations are then obtained by taking moments of (2) using the scalar product

$$\langle\!\langle\xi,\zeta\rangle\!\rangle=\int\xi\odot\zeta\,\mathrm{d}\boldsymbol{c}_{\rm p},$$

where $\xi\odot\zeta$ is the contracted product between tensors $\xi$ and $\zeta$. The macroscopic properties naturally associated with the gas read $\langle\!\langle f_{\rm g},\psi_{\rm p}^1\rangle\!\rangle=n_{\rm g}$, $\langle\!\langle f_{\rm g},\psi_{\rm g}^{1+\nu}\rangle\!\rangle=\rho_{\rm g}v_{{\rm g}\,\nu}$, $\langle\!\langle f_{\rm g},\psi_{\rm p}^5\rangle\!\rangle=\frac{1}{2}\rho_{\rm g}|\boldsymbol{v}_{\rm g}|^2+\mathcal{E}_{\rm g}$ where $\mathcal{E}_{\rm g}=n_{\rm g}(\frac{3}{2}k_{\rm B}T_{\rm g}+\mathrm{e_p})$ denotes the internal energy per unit volume and $v_{{\rm g}\,\nu}$ the component in direction $\nu$ of the mass average gas velocity $\boldsymbol{v}_{\rm g}$. Considering the surface species, analogous scalar products may be introduced as well as the corresponding collisional invariants. The reactive collision operators $\mathcal{C}_i$, for $i\in\{\mathrm{p,c,s,b}\}$, that are *collision operators between particles*, also conserve mass, momentum and total energy including the potential energy.

Contrarily to particle-particle collision operators, momentum and energy are not conserved by the collision operators with phonons $\mathcal{J}_{i,\rm ph}$ since they may be given to phonons that are assumed to be at equilibrium. The operators $\mathcal{J}_{i,\rm ph}$ only conserve the number of particles with the invariant $\psi_i^1=1$ for $i\in\{\mathrm{p,c,s,b},\sigma\}$. When kinetic equations are used to describe the phonons, energy is conserved during collisions between phonons and particles but not necessarily momentum because of the umklapp process [34].

### H. Kinetic entropy

The kinetic entropies compatible with the phonon collision operators $\mathcal{J}_{i,\rm ph}$ are slightly different from the traditional expressions. The origin of this modification is that phonons are supposed to be at equilibrium and the collision terms $\mathcal{J}_{i,\rm ph}$ for $i\in\{\mathrm{p,c,s,b},\sigma\}$ have been simplified accordingly. However, since phonons are interacting with gas particles as well as chemisorbed particles, there should be a phonon entropy increase associated with this interaction. Such an increase of phonon entropy having been discarded, it is natural that the corresponding terms are missing in the total entropy production. In order to solve this technical difficulty, modified entropies have to be introduced [51, 52]. The modified entropies are generally not anymore required when phonons kinetic equations are taken into account [35, 36]. These entropies are further modified in this work in order to take into account the interaction potentials as well as the entropy associated with the surface species.

The kinetic entropies per unit volume associated with the physisorbed/gas particles, chemisorbed particles, and free sites are defined by

$$\mathcal{S}_i^{\rm kin}=-k_{\rm B}\int f_i\big(\log(f_i/\mathrm{z}_i\mathrm{m}_i)-1\big)\,\mathrm{d}\boldsymbol{c}_i,\quad i\in\{\mathrm{p,c,s}\}. \quad (38)$$

On the other hand, taking into account the simplifications associated with the source terms, the entropy associated with the bulk species is defined as

$$\mathcal{S}_{\mathrm{b}}^{\mathrm{kin}} = -k_{\mathrm{B}} \int f_{\mathrm{b}} \log(\overline{n}_\sigma/\mathrm{z_b})\, \mathrm{d}\boldsymbol{c}_{\mathrm{b}}, \tag{39}$$

and the total entropy by

$$\mathcal{S}^{\mathrm{kin}} = \mathcal{S}_{\mathrm{p}}^{\mathrm{kin}} + \mathcal{S}_{\mathrm{c}}^{\mathrm{kin}} + \mathcal{S}_{\mathrm{s}}^{\mathrm{kin}} + \mathcal{S}_{\mathrm{b}}^{\mathrm{kin}}. \tag{40}$$

Similarly, we define the entropy fluxes by

$$\boldsymbol{\mathcal{F}}_i^{\mathrm{kin}} = -k_{\mathrm{B}} \int \boldsymbol{c}_i f_i \big(\log(f_i/\mathrm{z}_i\mathrm{m}_i) - 1\big)\, \mathrm{d}\boldsymbol{c}_i, \quad i \in \{\mathrm{p},\mathrm{c},\mathrm{s}\}, \tag{41}$$

and for the bulk species

$$\boldsymbol{\mathcal{F}}_{\mathrm{b}}^{\mathrm{kin}} = -k_{\mathrm{B}} \int \boldsymbol{c}_{\mathrm{b}} f_{\mathrm{b}} \log(\overline{n}_\sigma/\mathrm{z_b})\, \mathrm{d}\boldsymbol{c}_{\mathrm{b}}. \tag{42}$$

Multiplying the Boltzmann equation (2) by $\log(f_{\mathrm{p}}/\mathrm{z_p m_p})$, using (16) and (17), integrating with respect to $\mathrm{d}\boldsymbol{c}_{\mathrm{p}}$, proceeding similarly for $f_{\mathrm{c}}$ and $f_{\mathrm{s}}$, multipying the equation (7) by $\log(\overline{n}_\sigma/\mathrm{z_b})$ and integrating with respect to $\mathrm{d}\boldsymbol{c}_{\mathrm{b}}$, and adding the resulting balance laws, we obtain a balance equation for $\mathcal{S}^{\mathrm{kin}}$ in the form

$$\partial_t \mathcal{S}^{\mathrm{kin}} + \boldsymbol{\partial}_{\boldsymbol{x}} \cdot \boldsymbol{\mathcal{F}}^{\mathrm{kin}} = \mathfrak{v}^{\mathrm{kin}}, \tag{43}$$

where $\boldsymbol{\mathcal{F}}^{\mathrm{kin}}$ is the kinetic entropy flux

$$\boldsymbol{\mathcal{F}}^{\mathrm{kin}} = \boldsymbol{\mathcal{F}}_{\mathrm{p}}^{\mathrm{kin}} + \boldsymbol{\mathcal{F}}_{\mathrm{c}}^{\mathrm{kin}} + \boldsymbol{\mathcal{F}}_{\mathrm{s}}^{\mathrm{kin}} + \boldsymbol{\mathcal{F}}_{\mathrm{b}}^{\mathrm{kin}},$$

and $\mathfrak{v}^{\mathrm{kin}}$ the kinetic entropy source term. The entropy source term $\mathfrak{v}^{\mathrm{kin}}$ may be split as $\mathfrak{v}^{\mathrm{kin}} = \mathfrak{v}_{\mathrm{p,p}} + \mathfrak{v}_{\mathrm{p,ph}} + \mathfrak{v}_{\mathrm{c,ph}} + \mathfrak{v}_{\mathrm{s,ph}} + \mathfrak{v}_{\mathrm{p}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{c}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{s}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{b}}^{\mathrm{r}}$, where

$$\mathfrak{v}_{\mathrm{p,p}} = -k_{\mathrm{B}} \int J_{\mathrm{p,p}}(f_{\mathrm{p}}, f_{\mathrm{p}}) \log(f_{\mathrm{p}}/\mathrm{z_p m_p})\, \mathrm{d}\boldsymbol{c}_{\mathrm{p}}, \tag{44}$$

$$\mathfrak{v}_{i,\mathrm{ph}} = -k_{\mathrm{B}} \int J_{i,\mathrm{ph}}(f_i) \log(f_i/\mathrm{z}_i\mathrm{m}_i)\, \mathrm{d}\boldsymbol{c}_i, \quad i \in \{\mathrm{p},\mathrm{c},\mathrm{s}\}, \tag{45}$$

$$\mathfrak{v}_i^{\mathrm{r}} = -k_{\mathrm{B}} \int \mathcal{C}_i \log(f_i/\mathrm{z}_i\mathrm{m}_i)\, \mathrm{d}\boldsymbol{c}_i, \quad i \in \{\mathrm{p},\mathrm{c},\mathrm{s}\}, \tag{46}$$

and

$$\mathfrak{v}_{\mathrm{b}}^{\mathrm{r}} = -k_{\mathrm{B}} \int \mathcal{C}_{\mathrm{b}} \log(\overline{n}_\sigma/\mathrm{z_b})\, \mathrm{d}\boldsymbol{c}_{\mathrm{b}}. \tag{47}$$

Noting that $\log(\mathrm{z_p m_p})$ is a collisional invariant and may be eliminated from (44) and using standard arguments from kinetic theory, it is obtained after some algebra that

$$\mathfrak{v}_{\mathrm{p,p}} = \frac{k_{\mathrm{B}}}{4} \int \Upsilon\big(f_{\mathrm{p}}\widetilde{f}_{\mathrm{p}}, f'_{\mathrm{p}}\widetilde{f}'_{\mathrm{p}}\big)\, \mathsf{W}_{\mathrm{p,p}}\, \mathrm{d}\boldsymbol{c}_{\mathrm{p}}\, \mathrm{d}\widetilde{\boldsymbol{c}}_{\mathrm{p}}\, \mathrm{d}\boldsymbol{c}'_{\mathrm{p}} \mathrm{d}\widetilde{\boldsymbol{c}}'_{\mathrm{p}}, \tag{48}$$

where $\Upsilon$ denotes the nonnegative function $\Upsilon(x,y) = (x-y)(\log x - \log y)$. Similarly, noting that $\log(\mathrm{z}_i)$ is independent of $\boldsymbol{c}_i$ and may be eliminated from (45), it is obtained for $i \in \{\mathrm{p},\mathrm{c},\mathrm{s}\}$ that

$$\mathfrak{v}_{i,\mathrm{ph}} = \frac{k_{\mathrm{B}}}{2} \int \Upsilon\big(f_i/\mathrm{m}_i, f'_i/\mathrm{m}'_i\big)\, \mathsf{W}_{i,\mathrm{ph}}\, \mathrm{d}\boldsymbol{c}_i\, \mathrm{d}\boldsymbol{c}'_i. \tag{49}$$

The bulk species contribution $\mathfrak{v}_{\mathrm{b,ph}}$ vanishes because the surface is assumed to be at physical equilibrium. Finally, using analogous arguments for reactive collisions, and keeping the notation of (33), it is also obtained that

$$\mathfrak{v}_{\mathrm{p}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{c}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{s}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{b}}^{\mathrm{r}} = k_{\mathrm{B}} \int \Upsilon\big(\gamma_{\mathrm{p}}\gamma_{\mathrm{s}}, \gamma_{\mathrm{b}}\gamma_{\mathrm{c}}\big)\, \mathsf{W}^{+} \mathrm{d}\boldsymbol{c}_\sigma \mathrm{d}\boldsymbol{c}_{\mathrm{c}} \mathrm{d}\boldsymbol{c}_{\mathrm{s}} \mathrm{d}\boldsymbol{c}_{\mathrm{p}}. \tag{50}$$

Since the function $\Upsilon$ only takes nonnegative values, we conclude that all quantities $\mathfrak{v}_{\mathrm{p,p}}$, $\mathfrak{v}_{i,\mathrm{ph}}$, $i \in \{\mathrm{p},\mathrm{c},\mathrm{s}\}$, and $\mathfrak{v}_{\mathrm{p}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{c}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{s}}^{\mathrm{r}} + \mathfrak{v}_{\mathrm{b}}^{\mathrm{r}}$ appearing in $\mathfrak{v}^{\mathrm{kin}}$ are nonnegative. All collisions, nonreactive or reactive, thus lead to nonnegative entropy production. The Boltzmann equations (2) and (5) are thus compatible with Boltzmann H-theorem and lead to a dissipative structure at the molecular level.

## III. MULTISCALE FRAMEWORK

In order to investigate reactive *fluid* boundary conditions, a fluid scaling of the kinetic equations is introduced along with a multiscale framework. Introducing a *kinetic* scaling would be of high scientific interest but lay beyond the scope of the present work.

### A. Fluid scaling

We introduce characteristic quantities that are marked with the $^\star$ superscript. We denote by $T^\star$ a characteristic temperature, $n^\star$ a characteristic number density, $m^\star$ a particle mass, and $\tau_{\mathrm{p}}^\star$ a characteristic collision time. We write $v^\star = (k_{\mathrm{B}}T^\star/m^\star)^{1/2}$ the corresponding characteristic thermal velocity, $f^\star = n^\star/v^{\star 3}$ the characteristic particle distribution, $\lambda^\star = \tau_{\mathrm{p}}^\star v^\star$ the mean free path, $\mathsf{W}_{\mathrm{p,p}}^\star = 1/(n^\star \tau_{\mathrm{p}}^\star v^{\star 6})$ a characteristic transition probability, $\mathrm{w}^\star = m^\star v^{\star 2}$ a characteristic potential and $\tau_{\mathrm{f}}^\star$ a characteristic fluid time with $l^\star = \tau_{\mathrm{f}}^\star v^\star$ the corresponding fluid length. We also introduce a characteristic time for phonon interaction $\tau_{\mathrm{ph}}^\star$ that is easily related to the characteristic transition probabilities $\mathsf{W}_{i,\mathrm{ph}}^\star$ with $1/\tau_{\mathrm{ph}}^\star = \mathsf{W}_{i,\mathrm{ph}}^\star v^{\star 6}$ for $i \in \{\mathrm{p},\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}$, as well as a typical length $\delta^\star$ characteristic of the range of the surface potential, that is, the distance normal to the surface where the quantities $\mathrm{w}_{\mathrm{p}}$, $\mathrm{w}_{\mathrm{c}}$, $\mathsf{W}_{\mathrm{p,ph}}$, and $\mathsf{W}_{\mathrm{c,ph}}$, are significant.

Dividing the kinetic equations by $n^\star/\tau_{\mathrm{f}}^\star v^{\star 3}$, the resulting rescaled kinetic equations involve—after some algebra—the dimensionless parameters

$$\epsilon_{\mathrm{p}} = \frac{\tau_{\mathrm{p}}^\star}{\tau_{\mathrm{f}}^\star} = \frac{\lambda^\star}{l^\star}, \qquad \epsilon_{\mathrm{ph}} = \frac{\tau_{\mathrm{ph}}^\star}{\tau_{\mathrm{f}}^\star}, \qquad \epsilon = \frac{\delta^\star}{l^\star}. \tag{51}$$

The characteristic times and lengths at the solid/gas interface are generally such that $\tau^\star_{\rm ph} \le \tau^\star_{\rm p} \ll \tau^\star_{\rm f}$ and $\delta^\star \le \lambda^\star \ll l^\star$ and $\epsilon_{\rm p}$ represents the Knudsen number [22]. Since our aim is to derive *fluid* boundary conditions, it is assumed in this work that the small parameters $\epsilon_{\rm p}$, $\epsilon_{\rm ph}$, and $\epsilon$ are of the same *asymptotic* order of magnitude in the sense

$$\epsilon_{\rm p} = \alpha_{\rm p}\,\epsilon \qquad \epsilon_{\rm ph} = \alpha_{\rm ph}\,\epsilon, \tag{52}$$

where $\alpha_{\rm ph}$ and $\alpha_{\rm p}$ are positive constants. From a physical point of view, it means that particle collisions and phonons interactions are considered to be fast in comparison with fluid time and that both the mean free path $\lambda^\star$ and the surface potential characteristic range $\delta^\star$ are considered to be small in comparison with the fluid length $l^\star$. This scaling may be seen as the *simplest fluid scaling* of the adsorbate layer model. Of course, other scaling may further be introduced as for instance a kinetic scaling upon using $\tau^\star_{\rm p}$ instead of $\tau^\star_{\rm f}$ for rescaling the kinetic equations [31, 32].

Keeping in mind that the potential $\mathrm{w}_i$ only depends on $z$, the kinetic equation governing $f_i$ is obtained in the form

$$\partial_t f_i + \boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel} f_i + c_{iz}\,\partial_z f_i - \frac{1}{m_i}\partial_z \mathrm{w}_i\,\partial_{c_{iz}} f_i = \frac{\delta_{i\rm p}}{\alpha_{\rm p}\epsilon} J_{\rm p,p}(f_{\rm p},f_{\rm p}) + \frac{1}{\alpha_{\rm ph}\epsilon}\mathcal{J}_{i,\rm ph}(f_i) + \mathcal{C}_i, \tag{53}$$

where $i \in \{\mathrm{p},\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}$ denotes the species index, $f_i$ the distribution function, $\boldsymbol{c}_{i\shortparallel}$ the tangential velocity of the $i$th species, $\boldsymbol{\partial}_{\shortparallel}$ the tangential spatial derivative operator, $c_{iz}$ the normal velocity of the $i$th species, $\partial_z$ the normal spatial derivative, $\partial_{c_{iz}}$ the differential operator with respect to $c_{iz}$, $\delta_{ij}$ the Kronecker symbol, $J_{\rm p,p}$ the gas-gas collision operator, $\mathcal{J}_{i,\rm ph}$ the phonon collision operator and $\mathcal{C}_i$ the chemistry source term. The tangential velocity $\boldsymbol{c}_{i\shortparallel}$ is a two-dimentional vector and the particle velocity reads $\boldsymbol{c}_i = (\boldsymbol{c}_{i\shortparallel}, c_{iz})^t$. In this kinetic equation, the chemistry operator $\mathcal{C}_i$ is assumed to be slow in comparison with the inert collision operators $J_{\rm p,p}$ and $\mathcal{J}_{i,\rm ph}$. These equations may be interpreted either as rescaled equations with rescaled quantities denoted as unscaled quantities, or, equivalently, as original unscaled equations where $\epsilon$ is a formal expansion parameter numerically equal to unity [38, 39]. These two asymptotic procedures are equivalent and the second interpretation, used in particular by Ferziger and Kaper [39], is often more convenient.

### B. Standard expansion in the gas

The kinetic equation in the gas, obtained from (53) by letting $i = \mathrm{p}$, $\mathrm{w}_{\rm p} = 0$, $\mathcal{J}_{\rm p,ph} = 0$, and $\mathcal{C}_{\rm p} = 0$, reads

$$\partial_t f_{\rm g} + \boldsymbol{c}_{\rm g\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel} f_{\rm g} + c_{\rm gz}\,\partial_z f_{\rm g} = \frac{1}{\alpha_{\rm p}\epsilon} J_{\rm p,p}(f_{\rm g},f_{\rm g}), \tag{54}$$

where the gas particle velocity is denoted by $\boldsymbol{c}_{\rm g} = \boldsymbol{c}_{\rm p}$. This equation coincides with the traditional scaling of the Chapman-Enskog method with the formal expansion parameter $\alpha_{\rm p}\epsilon$. The standard Enskog expansion of the distribution function valid in the gas is then in the form

$$\begin{aligned} f_{\rm g}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm g}) =& \widehat{f}^{(0)}_{\rm g}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm g}) \\ &+ \alpha_{\rm p}\epsilon\,\widehat{f}^{(1)}_{\rm g}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm g}) + \mathcal{O}(\epsilon^2). \end{aligned} \tag{55}$$

The expansion (55) of the distribution function $f_{\rm g}$ then yields the *outer expansion* of the physisorbate distribution $f_{\rm p}$. At zeroth order, it is obtained that

$$J_{\rm p,p}(\widehat{f}^{(0)}_{\rm g},\widehat{f}^{(0)}_{\rm g}) = 0, \tag{56}$$

and from the H theorem, it is found that $\log \widehat{f}^{(0)}_{\rm g}$ is a collisional invariant so that $\widehat{f}^{(0)}_{\rm g}$ is a Maxwellian distribution. The Maxwellian distribution in the gas phase is in the form

$$\widehat{f}^{(0)}_{\rm g} = n_{\rm g}\Big(\frac{m_{\rm g}}{2\pi k_{\rm B} T_{\rm g}}\Big)^{\frac{3}{2}} \exp\Big(-\frac{m_{\rm g}|\boldsymbol{c}_{\rm g}-\boldsymbol{v}_{\rm g}|^2}{2k_{\rm B}T_{\rm g}}\Big), \tag{57}$$

where $n_{\rm g}$ is the local gas number density, $m_{\rm g}$ the particle mass equal to $m_{\rm A}$, $\boldsymbol{v}_{\rm g}$ the local gas velocity, and $T_{\rm g}$ the local gas temperature with

$$n_{\rm g} = \int f_{\rm g}\,\mathrm{d}\boldsymbol{c}_{\rm g}, \qquad n_{\rm g}\boldsymbol{v}_{\rm g} = \int \boldsymbol{c}_{\rm g} f_{\rm g}\,\mathrm{d}\boldsymbol{c}_{\rm g}, \tag{58}$$

$$n_{\rm g}\tfrac{3}{2}k_{\rm B}T_{\rm g} = \int \tfrac{1}{2}m_{\rm g}|\boldsymbol{c}_{\rm g}-\boldsymbol{v}_{\rm g}|^2 f_{\rm g}\,\mathrm{d}\boldsymbol{c}_{\rm g}. \tag{59}$$

At first order, it is obtained that $\widehat{\phi}^{(1)}_{\rm g} = \widehat{f}^{(1)}_{\rm g}/\widehat{f}^{(0)}_{\rm g}$ is the solution of the Boltzmann linearized integral equation [38–40]

$$\widehat{\mathcal{I}}_{\rm g}(\widehat{\phi}^{(1)}_{\rm g}) = -\big(\partial_t \log \widehat{f}^{(0)}_{\rm g} + \boldsymbol{c}_{\rm g}\cdot\boldsymbol{\partial}_{\boldsymbol{x}} \log \widehat{f}^{(0)}_{\rm g}\big), \tag{60}$$

completed by the Enskog constraints $\langle\!\langle \widehat{f}^{(0)}_{\rm g}\widehat{\phi}^{(1)}_{\rm g}, \psi^l_{\rm p}\rangle\!\rangle = 0$ for $1 \le l \le 5$. Here $\widehat{\mathcal{I}}_{\rm g}$ denotes the linearized collision operator

$$\widehat{\mathcal{I}}_{\rm g}(\psi) = -\frac{1}{\widehat{f}^{(0)}_{\rm g}}\big(J_{\rm p,p}(\widehat{f}^{(0)}_{\rm g},\widehat{f}^{(0)}_{\rm g}\psi) + J_{\rm p,p}(\widehat{f}^{(0)}_{\rm g}\psi,\widehat{f}^{(0)}_{\rm g})\big), \tag{61}$$

and the time derivative term $\partial_t \widehat{f}^{(0)}_{\rm g}$ in (60) is evaluated with Euler equations [38–40].

After lengthy algebra, $\widehat{\phi}_{\rm g}^{(1)}$ is found in the form

$$\widehat{\phi}_{\rm g}^{(1)} = -\widehat{\boldsymbol{\phi}}^{\eta}\!:\!\boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{v}_{\rm g} - \widehat{\boldsymbol{\phi}}^{\lambda}\cdot\boldsymbol{\partial}_{\boldsymbol{x}}(1/k_{\rm B}T_{\rm g}), \tag{62}$$

where $\widehat{\boldsymbol{\phi}}^{\eta}$ is a traceless symmetric matrix and $\widehat{\boldsymbol{\phi}}^{\lambda}$ a vector. The coefficients $\widehat{\boldsymbol{\phi}}^{\eta}$ and $\widehat{\boldsymbol{\phi}}^{\lambda}$ are solutions of the tensorial integral equations

$$\widehat{\mathcal{I}}_{\rm g}(\widehat{\boldsymbol{\phi}}^{\eta}) = \frac{m_{\rm g}}{k_{\rm B}T_{\rm g}}\big((\boldsymbol{c}_{\rm g}-\boldsymbol{v}_{\rm g})\otimes(\boldsymbol{c}_{\rm g}-\boldsymbol{v}_{\rm g})-\tfrac{1}{3}|\boldsymbol{c}_{\rm g}-\boldsymbol{v}_{\rm g}|^2\boldsymbol{I}\big), \tag{63}$$

$$\widehat{\mathcal{I}}_{\rm g}(\widehat{\boldsymbol{\phi}}^{\lambda}) = \Big(\frac{5k_{\rm B}T_{\rm g}}{2} - \tfrac{1}{2}m_{\rm g}|\boldsymbol{c}_{\rm g}-\boldsymbol{v}_{\rm g}|^2\Big)(\boldsymbol{c}_{\rm g}-\boldsymbol{v}_{\rm g}), \tag{64}$$

with the Enskog constraints $\langle\!\langle \widehat{f}_{\rm g}^{(0)}\widehat{\boldsymbol{\phi}}^{\eta}, \psi_{\rm p}^{l}\rangle\!\rangle = 0$ and $\langle\!\langle \widehat{f}_{\rm g}^{(0)}\widehat{\boldsymbol{\phi}}^{\lambda}, \psi_{\rm p}^{l}\rangle\!\rangle = 0$ for $1 \le l \le 5$, where $\boldsymbol{I}$ denotes the three dimensional identity tensor. The fluid shear viscosity $\eta$ and the thermal conductivity $\lambda$ may then be expressed in terms of the perturbed distributions $\widehat{\boldsymbol{\phi}}^{\eta}$ and $\widehat{\boldsymbol{\phi}}^{\lambda}$ [38–40].

### C. Corrected expansion near the surface

Since we investigate a fluid interacting with a solid surface, it is natural to assume for the sake of simplicity that the gas tangential velocity vanishes at the interface $\boldsymbol{v}_{\rm g\shortparallel} = \boldsymbol{v}_{\rm g} - v_{{\rm g}z}\boldsymbol{e}_z = 0$ and that the normal fluid velocity $v_{{\rm g}z}$ is of first order in $\epsilon$ near the interface. The gas velocity due to the Stefan flow is thus in the form

$$\boldsymbol{v}_{\rm g} = \epsilon\overline{\boldsymbol{v}}_{\rm g} = \epsilon\overline{v}_{{\rm g}z}\boldsymbol{e}_z, \tag{65}$$

where $\overline{v}_{{\rm g}z}$ denotes the normal component of the rescaled velocity $\overline{\boldsymbol{v}}_{\rm g}$. When a surface exchanges mass with a fluid, there exits indeed an induced normal velocity—termed the Stefan velocity—generated in order to compensate for fluid production. Assuming that such a velocity $\boldsymbol{v}_{\rm g} = v_{{\rm g}z}\boldsymbol{e}_z$ is small near a solid interface is natural and assuming that $\boldsymbol{v}_{\rm g\shortparallel} = \boldsymbol{v}_{\rm g} - v_{{\rm g}z}\boldsymbol{e}_z$ vanishes at the interface is the classical adherence condition [53, 54]. The model could be generalized by taking into account a first order slip $\boldsymbol{v}_{\rm g\shortparallel} = \mathcal{O}(\epsilon)$ but such an extension is beyond the scope of the present work.

The fluid convection velocity near the planar surface $\boldsymbol{v}_{\rm g}$ being of first order in $\epsilon$, the outer expansion (55) need to be corrected near the surface. All terms proportional to the velocity $\boldsymbol{v}_{\rm g}$ must be shifted by one order in the outer expansion near $z = 0$. The corrected expansion of the distribution function $f_{\rm g}$ valid in the gas phase near the surface is denoted in the form

$$\begin{aligned} f_{\rm g}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm g}) =& f_{\rm g}^{(0)}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm g}) + \epsilon f_{\rm g}^{(1)}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm g}) \\ &+ \epsilon^2 f_{\rm g}^{(2)}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm g}) + \mathcal{O}(\epsilon^3). \end{aligned} \tag{66}$$

The corrected expansion (66) of the distribution function $f_{\rm g}$ then yields the proper *outer expansion* of the physisorbate distribution $f_{\rm p}$.

After some algebra, it is obtained from (55)–(64) that $f_{\rm g}^{(0)}$ is the zero velocity Maxwellian distribution

$$f_{\rm g}^{(0)} = n_{\rm g}\Big(\frac{m_{\rm g}}{2\pi k_{\rm B}T_{\rm g}}\Big)^{\frac{3}{2}}\exp\Big(-\frac{m_{\rm g}|\boldsymbol{c}_{\rm g}|^2}{2k_{\rm B}T_{\rm g}}\Big), \tag{67}$$

and the first order term $f_{\rm g}^{(1)}$ is in the form

$$f_{\rm g}^{(1)} = \Big(\frac{m_{\rm g}c_{{\rm g}z}\overline{v}_{{\rm g}z}}{k_{\rm B}T_{\rm g}} + \alpha_{\rm p}\phi_{\rm g}^{(1)}\Big)f_{\rm g}^{(0)}, \tag{68}$$

with $\phi_{\rm g}^{(1)}$ given by

$$\phi_{\rm g}^{(1)} = -\boldsymbol{\phi}^{\eta}\!:\!\boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{v}_{\rm g} - \boldsymbol{\phi}^{\lambda}\cdot\boldsymbol{\partial}_{\boldsymbol{x}}(1/k_{\rm B}T_{\rm g}). \tag{69}$$

The vector function $\boldsymbol{\phi}^{\lambda}$ is the solution of the integral equation

$$\mathcal{I}_{\rm g}(\boldsymbol{\phi}^{\lambda}) = \Big(\frac{5k_{\rm B}T_{\rm g}}{2} - \tfrac{1}{2}m_{\rm g}|\boldsymbol{c}_{\rm g}|^2\Big)\boldsymbol{c}_{\rm g}, \tag{70}$$

with the Enskog constraints $\langle\!\langle f_{\rm g}^{(0)}\boldsymbol{\phi}^{\lambda}, \psi_{\rm p}^{l}\rangle\!\rangle = 0$, $1 \le l \le 5$, whereas the tensor function $\boldsymbol{\phi}^{\eta}$ is solution of the equation

$$\mathcal{I}_{\rm g}(\boldsymbol{\phi}^{\eta}) = \frac{m_{\rm g}}{k_{\rm B}T_{\rm g}}\big(\boldsymbol{c}_{\rm g}\otimes\boldsymbol{c}_{\rm g} - \tfrac{1}{3}|\boldsymbol{c}_{\rm g}|^2\boldsymbol{I}\big),$$

with the constraints $\langle\!\langle f_{\rm g}^{(0)}\boldsymbol{\phi}^{\eta}, \psi_{\rm p}^{l}\rangle\!\rangle = 0$, $1 \le l \le 5$. The modified integral operator $\mathcal{I}_{\rm g}$ is also the linearized collision operator

$$\mathcal{I}_{\rm g}(\psi) = -\frac{1}{f_{\rm g}^{(0)}}\big(J_{\rm p,p}(f_{\rm g}^{(0)}, f_{\rm g}^{(0)}\psi) + J_{\rm p,p}(f_{\rm g}^{(0)}\psi, f_{\rm g}^{(0)})\big), \tag{71}$$

around the zero velocity Maxwellian $f_{\rm g}^{(0)}$. Using Enskog constraint $\langle\!\langle f_{\rm g}^{(0)}\phi_{\rm g}^{(1)}, m_{\rm g}c_{{\rm g}z}\rangle\!\rangle = 0$, we note in particular the useful relation $\int \boldsymbol{c}_{\rm g}f_{\rm g}^{(1)}{\rm d}\boldsymbol{c}_{\rm g} = n_{\rm g}\overline{v}_{{\rm g}z}\boldsymbol{e}_z = n_{\rm g}\overline{\boldsymbol{v}}_{\rm g}$. The second order term $f_{\rm g}^{(2)}$ will play no role but need to be taken into account formally in some of the expansions.

Since the tangential component vanishes $\boldsymbol{v}_{\rm g\shortparallel} = 0$ we also have $\boldsymbol{\partial}_{\shortparallel}\boldsymbol{v}_{\rm g\shortparallel} = 0$ and similarly since $v_{{\rm g}z} = \mathcal{O}(\epsilon)$ near the interface we deduce that $\partial_z v_{{\rm g}z} = \mathcal{O}(\epsilon)$ as well as $\boldsymbol{\partial}_{\shortparallel}v_{{\rm g}z} = \mathcal{O}(\epsilon)$. Therefore, only possibly $\partial_z\boldsymbol{v}_{\rm g\shortparallel}$ remain in the gradient $\boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{v}_{\rm g}$ at zeroth order. From the gas mass conservation equation

$$\partial_t n_{\rm g} + \boldsymbol{\partial}_{\boldsymbol{x}}\cdot(n_{\rm g}\boldsymbol{v}_{\rm g}) = \partial_t n_{\rm g} + \partial_z(n_{\rm g}v_{{\rm g}z}) = 0,$$

we also deduce that

$$\partial_t n_{\rm g}(0) = \mathcal{O}(\epsilon), \tag{72}$$

so that $n_{\rm g}(0)$ is slowly varying in time.

### D. Multiscale expansion

The surface interaction potentials $\mathrm{W_p}$, $\mathrm{W_c}$ and $\mathrm{W_s}$ depend on the adsorbate layer coordinate denoted by

$$\zeta = \frac{z}{\epsilon}. \tag{73}$$

The problem thus appears as multiscale since it involves the normal coordinate $z$ as well as the inner layer coordinate $\zeta = z/\epsilon$. The physisorbed/gas distribution is thus expanded in the multiscale form

$$f_{\rm p}(t,\boldsymbol{x}_{\shortparallel},z,\zeta,\boldsymbol{c}_{\rm p}) = \sum_j \epsilon^j f_{\rm g}^{(j)}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm p}) + \sum_j \epsilon^j \mathsf{f}_{\rm lc}^{(j)}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_{\rm p}), \qquad (74)$$

where $\sum_j \epsilon^j f_{\rm g}^{(j)}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm p})$ is the *outer* expansion and $\sum_j \epsilon^j \mathsf{f}_{\rm lc}^{(j)}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_{\rm p})$ the *layer corrector* expansion. The adsorbate layer correctors $\mathsf{f}_{\rm lc}^{(j)}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_{\rm p})$, $j \geq 0$, have to converge to zero as $\zeta \to \infty$ in such a way that the gas expansion is recovered in the gas phase. The proper *outer expansion* of the distribution function in the gas phase (66) has been evaluated independently in Section III C.

The *inner expansion* $\mathsf{f}_{\rm g}$ of $f_{\rm g} = \sum_j \epsilon^j f_{\rm g}^{(j)}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_{\rm p})$ is next deduced by expanding $f_{\rm g}$ around $z = 0$ with $z = \epsilon\zeta$. The inner expansion $\mathsf{f}_{\rm g}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_{\rm p}) = f_{\rm g}(t,\boldsymbol{x}_{\shortparallel},\epsilon\zeta,\boldsymbol{c}_{\rm p})$ of $f_{\rm g}$ is a function $\zeta$ and is obtained in the form

$$\mathsf{f}_{\rm g}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_{\rm p}) = \sum_j \epsilon^j \mathsf{f}_{\rm g}^{(j)}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_{\rm p}), \qquad (75)$$

with notably

$$\mathsf{f}_{\rm g}^{(0)} = f_{\rm g}^{(0)}(0), \qquad \mathsf{f}_{\rm g}^{(1)} = f_{\rm g}^{(1)}(0) + \zeta\partial_z f_{\rm g}^{(0)}(0), \qquad (76)$$

$$\mathsf{f}_{\rm g}^{(2)} = f_{\rm g}^{(2)}(0) + \zeta\partial_z f_{\rm g}^{(1)}(0) + \tfrac{1}{2}\zeta^2\partial_z^2 f_{\rm g}^{(0)}(0). \qquad (77)$$

The *inner expansion* $\mathsf{f}_{\rm p}$ of the distribution $f_{\rm p}$ is then given by

$$\mathsf{f}_{\rm p}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_{\rm p}) = \sum_j \epsilon^j \mathsf{f}_{\rm p}^{(j)}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_{\rm p}), \qquad (78)$$

with

$$\mathsf{f}_{\rm p}^{(j)} = \mathsf{f}_{\rm g}^{(j)} + \mathsf{f}_{\rm lc}^{(j)}, \qquad j \geq 0. \qquad (79)$$

The term $\mathsf{f}_{\rm g}^{(j)}$ is a polynomial in $\zeta$ of the $j$th degree resulting from the inner expansion $\mathsf{f}_{\rm g}$ of $f_{\rm g}$ and $\mathsf{f}_{\rm lc}^{(j)}$ is the $j$th layer corrector that goes to zero as $\zeta \to \infty$.

The chemisorbate, free site, bulk and surface distributions are expanded in the simpler form

$$f_i = \mathsf{f}_i = \sum_j \epsilon^j \mathsf{f}_i^{(j)}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_i), \qquad i \in \{\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}, \quad (80)$$

since such distributions are localized in the adsorption layer and only involve the inner layer coordinate $\zeta$.

### E. Inner layer kinetic equations

Since $\zeta$ is the proper normal coordinate of the adsorbate layer, the rescaled equations governing the inner expansions $\mathsf{f}_i$, $i \in \{\mathrm{p},\mathrm{c},\mathrm{s},\mathrm{b},\sigma\}$, and obtained from (53), are in the form

$$\partial_t \mathsf{f}_i + \boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\mathsf{f}_i + \frac{1}{\epsilon}c_{iz}\,\partial_\zeta \mathsf{f}_i - \frac{1}{\epsilon}\frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\mathsf{f}_i = \frac{\delta_{i\mathrm{p}}}{\alpha_{\rm p}\epsilon}J_{\mathrm{p,p}}(\mathsf{f}_{\rm p},\mathsf{f}_{\rm p}) + \frac{1}{\alpha_{\rm ph}\epsilon}\mathcal{J}_{i,\mathrm{ph}}(\mathsf{f}_i) + \mathcal{C}_i. \qquad (81)$$

On the other hand, since $f_{\rm g}$ satisfies the Boltzmann equation (4), we may perform the change of variable from $z$ to $\zeta$ in (4) so that the inner expansion $\mathsf{f}_{\rm g}$ of $f_{\rm g}$ satisfies the rescaled kinetic equation

$$\partial_t \mathsf{f}_{\rm g} + \boldsymbol{c}_{\rm p\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\mathsf{f}_{\rm g} + \frac{1}{\epsilon}c_{\rm pz}\,\partial_\zeta \mathsf{f}_{\rm g} = \frac{1}{\alpha_{\rm p}\epsilon}J_{\mathrm{p,p}}(\mathsf{f}_{\rm g},\mathsf{f}_{\rm g}), \qquad (82)$$

that naturally contains no force term, phonon collision term or reactive term. Substituting the inner expansion $\mathsf{f}_{\rm g}$ of $f_{\rm g}$ into (82) and equating the powers of $\epsilon$ yields the kinetic equations satisfied by the expansion coefficients $\mathsf{f}_{\rm g}^{(j)}$ for $j \geq 0$. At the order $\epsilon^{-1}$, we obtain that

$$c_{\rm pz}\,\partial_\zeta \mathsf{f}_{\rm g}^{(0)} = \frac{1}{\alpha_{\rm p}}J_{\mathrm{p,p}}(\mathsf{f}_{\rm g}^{(0)},\mathsf{f}_{\rm g}^{(0)}), \qquad (83)$$

and each term of (83) indeed vanishes since $\mathsf{f}_{\rm g}^{(0)} = f_{\rm g}^{(0)}(0)$, $J_{\mathrm{p,p}}\big(f_{\rm g}^{(0)}(0), f_{\rm g}^{(0)}(0)\big) = 0$ and $\partial_\zeta\big(f_{\rm g}^{(0)}(0)\big) = 0$. At the order $\epsilon^0$, letting $\Phi_{\rm g}^{(1)} = \mathsf{f}_{\rm g}^{(1)}/\mathsf{f}_{\rm g}^{(0)}$ we obtain that

$$\partial_t \mathsf{f}_{\rm g}^{(0)} + \boldsymbol{c}_{\rm p\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\mathsf{f}_{\rm g}^{(0)} + c_{\rm pz}\,\mathsf{f}_{\rm g}^{(0)}\partial_\zeta\Phi_{\rm g}^{(1)} + \mathsf{f}_{\rm g}^{(0)}\mathcal{I}_{\rm g}(\Phi_{\rm g}^{(1)})/\alpha_{\rm p} = 0, \qquad (84)$$

and using $\mathsf{f}_{\rm g}^{(1)} = f_{\rm g}^{(1)}(0) + \zeta\partial_z f_{\rm g}^{(0)}(0)$ where $f_{\rm g}^{(1)} = \Big(\frac{m_{\rm g}c_{\rm gz}\overline{v}_{\rm gz}}{k_{\rm B}T_{\rm g}} + \alpha_{\rm p}\phi_{\rm g}^{(1)}\Big)f_{\rm g}^{(0)}$ yields

$$\Phi_{\rm g}^{(1)} = \zeta\partial_z \log f_{\rm g}^{(0)}(0) + \frac{m_{\rm g}c_{\rm gz}\overline{v}_{\rm gz}}{k_{\rm B}T_{\rm g}} + \alpha_{\rm p}\phi_{\rm g}^{(1)}. \qquad (85)$$

Defining the operator

$$\mathcal{H}_{\rm g}(\varphi) = c_{\rm pz}\,\partial_\zeta\varphi + \frac{1}{\alpha_{\rm p}}\mathcal{I}_{\rm g}(\varphi),$$

the first order linearized system (84) then reads

$$\mathcal{H}_{\rm g}(\Phi_{\rm g}^{(1)}) = \Psi_{\rm g}^{(1)}, \qquad (86)$$

where

$$\Psi_{\rm g}^{(1)} = -\partial_t \log \mathsf{f}_{\rm g}^{(0)} - \boldsymbol{c}_{\rm p\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel} \log \mathsf{f}_{\rm g}^{(0)}. \tag{87}$$

Since $\mathcal{I}_{\rm g}$ vanishes for collision invariants, we observe that

$$\mathcal{I}_{\rm g}\big(m_{\rm g} c_{{\rm g}z}\big) = 0, \qquad \mathcal{I}_{\rm g}\big(\partial_z \log f_{\rm g}^{(0)}(0)\big) = 0,$$

so that $\mathcal{I}_{\rm g}(\Phi_{\rm g}^{(1)})/\alpha_{\rm p} = \mathcal{I}_{\rm g}\big(\phi_{\rm g}^{(1)}\big)$. Moreover, using $\partial_\zeta \Phi_{\rm g}^{(1)} = \partial_z \log f_{\rm g}^{(0)}$ we obtain that $c_{{\rm p}z}\, \partial_\zeta \Phi_{\rm g}^{(1)} = c_{{\rm p}z}\, \partial_z \log f_{\rm g}^{(0)}$ in such a way that (86) exactly coincides with the linearized Boltzmann equation

$$\mathcal{I}_{\rm g}\big(\phi_{\rm g}^{(1)}\big) = -\partial_t \log f_{\rm g}^{(0)} - \boldsymbol{c}_{\rm p\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel} \log f_{\rm g}^{(0)} - c_{{\rm p}z}\, \partial_z \log f_{\rm g}^{(0)},$$

written at the origin $z = 0$.

Subtracting finally equation (82) from that governing the inner expansion of the physisorbate (81) with $i = {\rm p}$, we obtain a kinetic equation for the difference $\mathsf{f}_{\rm p} - \mathsf{f}_{\rm g}$

$$\partial_t(\mathsf{f}_{\rm p} - \mathsf{f}_{\rm g}) + \boldsymbol{c}_{\rm p\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel}(\mathsf{f}_{\rm p} - \mathsf{f}_{\rm g}) + \frac{1}{\epsilon} c_{{\rm p}z}\, \partial_\zeta(\mathsf{f}_{\rm p} - \mathsf{f}_{\rm g}) - \frac{1}{\epsilon}\frac{1}{m_{\rm p}} \partial_\zeta {\rm W}_{\rm p}\, \partial_{c_{{\rm p}z}} \mathsf{f}_{\rm p} =$$
$$\frac{1}{\alpha_{\rm p}\epsilon}\Big\{ J_{\rm p,p}(\mathsf{f}_{\rm p}, \mathsf{f}_{\rm p}) - J_{\rm p,p}(\mathsf{f}_{\rm g}, \mathsf{f}_{\rm g}) \Big\} + \frac{1}{\alpha_{\rm ph}\epsilon} \mathcal{J}_{\rm p,ph}(\mathsf{f}_{\rm p}) + \mathcal{C}_{\rm p}. \tag{88}$$

This equation as well as (81) will be convenient in the following in order to investigate the inner structure of the adsorbate. The advantage of (88) is that all terms go to zero when $\zeta$ goes to infinity.

## IV. ZEROTH ORDER EXPANSIONS IN THE ADSORBATE

Zeroth order expansions are investigated in the adsorbate layer and next the corresponding species mass fluid boundary conditions.

### A. Zeroth order expansion in the physisorbate

In the physisorbate, using the kinetic equation (81) with $i = {\rm p}$, it is found that

$$c_{{\rm p}z}\, \partial_\zeta \mathsf{f}_{\rm p}^{(0)} - \frac{1}{m_{\rm p}} \partial_\zeta {\rm W}_{\rm p}\, \partial_{c_{{\rm p}z}} \mathsf{f}_{\rm p}^{(0)} = \frac{1}{\alpha_{\rm p}} J_{\rm p,p}(\mathsf{f}_{\rm p}^{(0)}, \mathsf{f}_{\rm p}^{(0)}) + \frac{1}{\alpha_{\rm ph}} \mathcal{J}_{\rm p,ph}(\mathsf{f}_{\rm p}^{(0)}). \tag{89}$$

Multiplying (89) by $\log(\mathsf{f}_{\rm p}^{(0)}/{\rm m}_{\rm p})$, making use of (16) and $\partial_{\mathcal{A}}\big(\mathcal{A}(\log \mathcal{A} - 1)\big) = \log \mathcal{A}$, letting for short $\mathfrak{s}_{\rm p} = \mathsf{f}_{\rm p}^{(0)}\big(\log(\mathsf{f}_{\rm p}^{(0)}/{\rm m}_{\rm p}) - 1\big)$ it is obtained that

$$\partial_\zeta(c_{{\rm p}z}\mathfrak{s}_{\rm p}) - \partial_{c_{{\rm p}z}}\Big(\frac{\partial_\zeta {\rm W}_{\rm p}}{m_{\rm p}}\mathfrak{s}_{\rm p}\Big) = \frac{1}{\alpha_{\rm p}} J_{\rm p,p}(\mathsf{f}_{\rm p}^{(0)}, \mathsf{f}_{\rm p}^{(0)}) \log\Big(\frac{\mathsf{f}_{\rm p}^{(0)}}{{\rm m}_{\rm p}}\Big) + \frac{1}{\alpha_{\rm ph}} \mathcal{J}_{\rm p,ph}(\mathsf{f}_{\rm p}^{(0)}) \log\Big(\frac{\mathsf{f}_{\rm p}^{(0)}}{{\rm m}_{\rm p}}\Big). \tag{90}$$

We integrate this equation over $\zeta \in (0, \infty)$ and $\boldsymbol{c}_{\rm p} \in \mathbb{R}^3$ and use that $\mathsf{f}_{\rm p}^{(0)} \to 0$ as $\zeta \to 0$ since the surface repulsive potential repels all physisorbed/gas particles, and $\mathsf{f}_{\rm p}^{(0)} \to f_{\rm g}^{(0)}(0)$ as $\zeta \to \infty$ since the corrector $\mathsf{f}_{\rm lc}^{(0)}$ goes to zero as $\zeta \to \infty$. The first term in the left hand side of (90) yields after integration a null contribution since

$$\lim_{\zeta\to\infty} \int c_{{\rm p}z} \mathsf{f}_{\rm p}^{(0)} \big(\log(\mathsf{f}_{\rm p}^{(0)}/{\rm m}_{\rm p}) - 1\big)\, {\rm d}\boldsymbol{c}_{\rm p} = \int c_{{\rm p}z} f_{\rm g}^{(0)} \big(\log(f_{\rm g}^{(0)}/{\rm m}_{\rm p}) - 1\big)\, {\rm d}\boldsymbol{c}_{\rm g} = 0,$$

keeping in mind that $f_{\rm g}^{(0)}$ is even in the normal velocity, and moreover

$$\lim_{\zeta\to 0} \int c_{{\rm p}z} \mathsf{f}_{\rm p}^{(0)} \big(\log(\mathsf{f}_{\rm p}^{(0)}/{\rm m}_{\rm p}) - 1\big)\, {\rm d}\boldsymbol{c}_{\rm p} = 0,$$

because $f_{\rm p}^{(0)} = 0$ for $\zeta = 0$. The second term in the left hand side of (90) also yields a null contribution after integration since it is in divergence form and $\mathfrak{s}_{\rm p} = \mathsf{f}_{\rm p}^{(0)}\big(\log(\mathsf{f}_{\rm p}^{(0)}/{\rm m}_{\rm p}) - 1\big)$ goes to zero as $|\boldsymbol{c}_{\rm p}| \to \infty$. We have thus established that

$$\frac{1}{\alpha_{\rm p}} \int J_{\rm p,p}(\mathsf{f}_{\rm p}^{(0)}, \mathsf{f}_{\rm p}^{(0)}) \log(\mathsf{f}_{\rm p}^{(0)}/{\rm m}_{\rm p})\, {\rm d}\boldsymbol{c}_{\rm p}{\rm d}\zeta + \frac{1}{\alpha_{\rm ph}} \int \mathcal{J}_{\rm p,ph}(\mathsf{f}_{\rm p}^{(0)}) \log(\mathsf{f}_{\rm p}^{(0)}/{\rm m}_{\rm p})\, {\rm d}\boldsymbol{c}_{\rm p}{\rm d}\zeta = 0.$$

Such terms have been investigated up to the scaling factor $-k_{\rm B}$ when investigating entropy production in (48)(49) and are nonpositive. Using $J_{\rm p,p}(\mathsf{f}_{\rm p}^{(0)}, \mathsf{f}_{\rm p}^{(0)}) = 0$, we first deduce that $\mathsf{f}_{\rm p}^{(0)}$ is locally Maxwellian with a local temperature and average velocity. Using $\mathcal{J}_{\rm p,ph}(\mathsf{f}_{\rm p}^{(0)}) = 0$, we further obtain that the local temperature is the wall temperature $T_{\rm w}$ and the average velocity vanishes. Writting this Maxwellian for convenience as

$$\mathsf{f}_{\rm p}^{(0)} = \overline{n}_{\rm p} \exp\Big(-\frac{{\rm W}_{\rm p}}{k_{\rm B} T_{\rm w}}\Big) {\rm M}_{\rm p}, \tag{91}$$

where $\mathrm{M}_\mathrm{p}$ is given by (13), and substituting this identity in (89), it is next obtained that $c_{\mathrm{p}z}\partial_\zeta \overline{n}_\mathrm{p}\,\mathrm{M}_\mathrm{p}=0$ so that $\partial_\zeta\overline{n}_\mathrm{p}=0$ and $\overline{n}_\mathrm{p}$ is independent of $\zeta$. This constant $\overline{n}_\mathrm{p}$ is identified by letting $\zeta\to\infty$ in (91) and it is obtained that

$$\overline{n}_\mathrm{p}=n_\mathrm{g}(0), \tag{92}$$

where $n_\mathrm{g}(0)$ denotes the gas number density along the surface $n_\mathrm{g}(t,\boldsymbol{x}_{\shortparallel},0)$. It has thus been established that

$$\mathsf{f}_\mathrm{p}^{(0)}=n_\mathrm{p}\mathrm{M}_\mathrm{p}, \tag{93}$$

where the number of physisorbed/gas particles per unit volume $n_\mathrm{p}$ reads

$$n_\mathrm{p}(\zeta)=n_\mathrm{g}(0)\exp\Big(-\frac{\mathrm{W}_\mathrm{p}}{k_\mathrm{B}T_\mathrm{w}}\Big). \tag{94}$$

This expression of $n_\mathrm{p}(\zeta)$ establishes that the physisorbate is naturally distributed like $\exp\big(-\mathrm{W}_\mathrm{p}/k_\mathrm{B}T_\mathrm{w}\big)$ as was expected based on physical grounds [22, 45]. Moreover the physisorbate is *at equilibrium* with the bath of gas particles having number density $n_\mathrm{g}(0)$ coming from the gas phase. Since $\mathsf{f}_\mathrm{lc}^{(0)}=\mathsf{f}_\mathrm{p}^{(0)}-f_\mathrm{g}^{(0)}(0)$ where

$$f_\mathrm{g}^{(0)}(0)=n_\mathrm{g}(0)\Big(\frac{m_\mathrm{p}}{2\pi k_\mathrm{B}T_\mathrm{w}}\Big)^{3/2}\exp\Big(-\frac{m_\mathrm{p}|\boldsymbol{c}_\mathrm{p}|^2}{k_\mathrm{B}T_\mathrm{w}}\Big)$$

it is also obtained that

$$\mathsf{f}_\mathrm{lc}^{(0)}=f_\mathrm{g}^{(0)}(0)\Big\{\exp\Big(-\frac{\mathrm{W}_\mathrm{p}}{k_\mathrm{B}T_\mathrm{w}}\Big)-1\Big\}. \tag{95}$$

The layer corrector $\mathsf{f}_\mathrm{lc}^{(0)}$ thus converges to zero as $\zeta\to\infty$ as the potential $\mathrm{W}_\mathrm{p}$, and the excess molecular density in the physisorbate $n_\mathrm{p}-n_\mathrm{g}(0)$ is naturally distributed as the positive values of the function $\exp\big(-\mathrm{W}_\mathrm{p}/k_\mathrm{B}T_\mathrm{w}\big)-1$.

By identifying the Maxwellian distributions, we have recovered that

$$T_\mathrm{g}(0)=T_\mathrm{w},\qquad \boldsymbol{v}_\mathrm{g}(0)\cdot\boldsymbol{e}_x=\boldsymbol{v}_\mathrm{g}(0)\cdot\boldsymbol{e}_y=0, \tag{96}$$

and these *kinematic* boundary conditions [53, 54] have been established by writting that the gas Maxwellian distribution is at equilibrium with phonons. In contrast, the *dynamic* boundary conditions for mass, momentum or energy will be obtained as moments of the kinetic equations. The model could incidentally be generalized by taking into account a first order slip temperature difference $T_\mathrm{g}-T_\mathrm{w}=\mathcal{O}(\epsilon)$ but such an extension is beyond the scope of the present work.

### B. Zeroth order expansion in the chemisorbate

In the chemisorbed layer, using the kinetic equation (81) with $i=\mathrm{c}$, it is found that

$$c_{\mathrm{c}z}\,\partial_\zeta\mathsf{f}_\mathrm{c}^{(0)}-\frac{1}{m_\mathrm{c}}\partial_\zeta\mathrm{W}_\mathrm{c}\partial_{c_{\mathrm{c}z}}\mathsf{f}_\mathrm{c}^{(0)}=\frac{1}{\alpha_\mathrm{ph}}\mathcal{J}_{\mathrm{c,ph}}(\mathsf{f}_\mathrm{c}^{(0)}). \tag{97}$$

Multiplying by $\log(\mathsf{f}_\mathrm{c}^{(0)}/\mathrm{m}_\mathrm{c})$, letting for short $\mathfrak{s}_\mathrm{c}=\mathsf{f}_\mathrm{c}^{(0)}\big(\log(\mathsf{f}_\mathrm{c}^{(0)}/\mathrm{m}_\mathrm{c})-1\big)$, and proceeding as for the physisorbate, it is obtained that

$$\partial_\zeta\big(c_{\mathrm{c}z}\mathfrak{s}_\mathrm{c}\big)-\partial_{c_{\mathrm{c}z}}\Big(\frac{\partial_\zeta\mathrm{W}_\mathrm{c}}{m_\mathrm{c}}\mathfrak{s}_\mathrm{c}\Big)=\frac{1}{\alpha_\mathrm{ph}}\mathcal{J}_{\mathrm{c,ph}}(\mathsf{f}_\mathrm{p}^{(0)})\log(\mathsf{f}_\mathrm{c}^{(0)}/\mathrm{m}_\mathrm{c}).$$

Integrating over $\zeta\in(\zeta_\mathrm{c}^-,\zeta_\mathrm{c}^+)$ and $\boldsymbol{c}_\mathrm{c}\in\mathbb{R}^3$, and since $\mathsf{f}_\mathrm{c}^{(0)}$ goes to zero as $\zeta\to\zeta_\mathrm{c}^-$ and as $\zeta\to\zeta_\mathrm{c}^+$, it is obtained that

$$\frac{1}{\alpha_\mathrm{ph}}\int\mathcal{J}_{\mathrm{c,ph}}(\mathsf{f}_\mathrm{c}^{(0)})\log(\mathsf{f}_\mathrm{c}^{(0)}/\mathrm{m}_\mathrm{c})\,\mathrm{d}\boldsymbol{c}_\mathrm{c}\mathrm{d}\zeta=0.$$

From $\mathcal{J}_{\mathrm{c,ph}}(\mathsf{f}_\mathrm{c}^{(0)})=0$ and the expression of the entropy source (49) established for the H theorem, it is deduced that $\mathsf{f}_\mathrm{c}^{(0)}$ is a Maxwellian at temperature $T_\mathrm{w}$ and with zero average velocity. Writting this Maxwellian for convenience in the form

$$\mathsf{f}_\mathrm{c}^{(0)}=\overline{n}_\mathrm{c}\exp\Big(-\frac{\mathrm{W}_\mathrm{c}}{k_\mathrm{B}T_\mathrm{w}}\Big)\mathrm{M}_\mathrm{c}, \tag{98}$$

where $\mathrm{M}_\mathrm{c}$ is given by equation (13), and substituting this identity in (97), it is obtained that $c_z\partial_\zeta\overline{n}_\mathrm{c}\,\mathrm{M}_\mathrm{c}=0$ so that $\partial_\zeta\overline{n}_\mathrm{c}=0$ and $\overline{n}_\mathrm{c}$ is independent of $\zeta$.

The number density in the chemisorbate is thus in the form

$$n_\mathrm{c}=\overline{n}_\mathrm{c}\exp\Big(-\frac{\mathrm{W}_\mathrm{c}}{k_\mathrm{B}T_\mathrm{w}}\Big), \tag{99}$$

where $\overline{n}_\mathrm{c}=\overline{n}_\mathrm{c}(t,\boldsymbol{x}_{\shortparallel})$ so that the chemisorbate is distributed as $\exp\big(-\mathrm{W}_\mathrm{c}/k_\mathrm{B}T_\mathrm{w}\big)$ as was expected based on physical grounds and is localized since $\mathrm{W}_\mathrm{c}$ goes to infinity as $\zeta\to\zeta_\mathrm{c}^-$ as well as $\zeta\to\zeta_\mathrm{c}^+$. We may next introduce the number of chemisorbed particles *per unit surface* $\widetilde{n}_\mathrm{c}(t,\boldsymbol{x}_{\shortparallel})=\int n_\mathrm{c}\,\mathrm{d}z$ that is related to $\overline{n}_\mathrm{c}$ via a configuration integral

$$\widetilde{n}_\mathrm{c}=\overline{n}_\mathrm{c}\int\exp\Big(-\frac{\mathrm{W}_\mathrm{c}}{k_\mathrm{B}T_\mathrm{w}}\Big)\,\mathrm{d}z.$$

The number density of the chemisorbate per unit surface $\widetilde{n}_\mathrm{c}(t,\boldsymbol{x}_{\shortparallel})$ thus arises naturally from the kinetic framework and is often used in macroscopic fluid models. Finally, both $\overline{n}_\mathrm{c}$ and $\widetilde{n}_\mathrm{c}$ are independent of the gas phase value $n_\mathrm{g}(0)$ at variance with the physisorbate that is *at equilibrium* with the bath of gas.

### C. Zeroth order expansion at the surface

Using the kinetic equation (81) with $i=\mathrm{s}$, the zeroth order distribution of free site $\mathsf{f}_\mathrm{s}^{(0)}$ is governed by the kinetic equation

$$c_{\mathrm{s}z}\,\partial_\zeta\mathsf{f}_\mathrm{s}^{(0)}-\frac{1}{m_\mathrm{s}}\partial_\zeta\mathrm{W}_\mathrm{s}\partial_{c_{\mathrm{s}z}}\mathsf{f}_\mathrm{s}^{(0)}=\frac{1}{\alpha_\mathrm{ph}}\mathcal{J}_{\mathrm{s,ph}}(\mathsf{f}_\mathrm{s}^{(0)}). \tag{100}$$

Proceeding as for the chemisorbate, it is found that

$$\mathsf{f}_{\rm s}^{(0)} = n_{\rm s}\mathrm{M}_{\rm s}, \qquad n_{\rm s} = \overline{n}_{\rm s}\exp\Big(-\frac{\mathrm{W}_{\rm s}}{k_{\rm B}T_{\rm w}}\Big), \tag{101}$$

where $\overline{n}_{\rm s} = \overline{n}_{\rm s}(t, \boldsymbol{x}_{\shortparallel})$ and $\mathrm{M}_{\rm s}$ is given by equation (13). The quantity $\overline{n}_{\rm s}$ is also directly related to the number of free site per unit surface $\widetilde{n}_{\rm s}(t, \boldsymbol{x}_{\shortparallel}) = \int n_{\rm s}\,\mathrm{d}z$. The free site atoms are spatially distributed as the function $\exp\big(-\mathrm{W}_{\rm s}/k_{\rm B}T_{\rm w}\big)$ as was expected based on physical grounds and are of course localized since $\mathrm{W}_{\rm s}$ goes to infinity as $\zeta \to \zeta_\sigma^-$ or as $\zeta \to \zeta_\sigma^+$. This Maxwellian structure that was assumed to hold in [37] is established here from the governing kinetic equation. Such a Maxwellian structure (100) constrained by the localized potential $\mathrm{W}_{\rm s}$ is exactly that given by statistical mechanics at equilibrium [43–46].

Proceeding similarly for the standard surface distribution, it is also recovered that $\mathsf{f}_\sigma^{(0)} = f_\sigma^{\rm e}$ is given by (19) with a number density of the surface layer $n_\sigma$ in the form (20) and the surface atoms are spatially distributed as $\exp\big(-\mathrm{W}_\sigma/k_{\rm B}T_{\rm w}\big)$. The zeroth order solution $\mathsf{f}_\sigma^{(0)} = f_\sigma^{\rm e}$ is furthermore the exact solution $f_\sigma^{\rm e} = n_\sigma \mathrm{M}_\sigma$ of the thin layer equation since it is an exact solution of the full kinetic equation (8). The quantities $n_\sigma$ and $\overline{n}_\sigma$ are characteristic of the crystal surface and its orientation and are related to the number of surface atoms per unit surface $\widetilde{n}_\sigma = \int n_\sigma\,\mathrm{d}z$.

From the structure of the free site distribution $\mathsf{f}_{\rm s}^{(0)}$ and that of the crystal layer standard distribution $\mathsf{f}_\sigma^{(0)} = f_\sigma^{\rm e}$ given by (19), we deduce that *at zeroth order* the probability of free site $1 - \overline{\theta} = \mathsf{f}_{\rm s}^{(0)}/\mathsf{f}_\sigma^{(0)}$ simplifies into

$$1 - \overline{\theta} = \frac{\mathsf{f}_{\rm s}^{(0)}}{\mathsf{f}_\sigma^{(0)}} = \frac{\overline{n}_{\rm s}}{\overline{n}_\sigma} = \frac{\widetilde{n}_{\rm s}}{\widetilde{n}_\sigma}, \tag{102}$$

and therefore *only depends on time and tangential coordinate* $\overline{\theta} = \overline{\theta}(t, \boldsymbol{x}_{\shortparallel})$. This structural property $\overline{\theta} = \overline{\theta}(t, \boldsymbol{x}_{\shortparallel})$ was assumed to hold in previous work [37] and is established here from the asymptotic analysis of the kinetic equations. The number of free site per unit surface $\widetilde{n}_{\rm s}$ may also be written $\widetilde{n}_{\rm s} = (1 - \overline{\theta})\widetilde{n}_\sigma$ and since the chemisorbate is assumed to be monolayer we have $\widetilde{n}_{\rm s} + \widetilde{n}_{\rm c} = \widetilde{n}_\sigma$ and

$$\widetilde{n}_{\rm c} = \overline{\theta}\,\widetilde{n}_\sigma, \qquad \widetilde{n}_{\rm s} = (1 - \overline{\theta})\,\widetilde{n}_\sigma. \tag{103}$$

The monolayer relation $\widetilde{n}_{\rm s} + \widetilde{n}_{\rm c} = \widetilde{n}_\sigma$ is naturally associated with surface densities whereas the volume distributions of $\mathcal{C}$(s) and A(s) are not located at the same reduced normal coordinate $\zeta$.

### D. Species mass boundary conditions

The zeroth order mass conservation equations are obtained by taking the scalar product of the kinetic equations (81) or (88) by the mass collisional invariants—which is equivalent to integrating with respect to the velocity variable—and keeping only zeroth order terms.

In the physisorbate, using the difference equation (88) for convenience, it is obtained that

$$\partial_t \int (\mathsf{f}_{\rm p}^{(0)} - \mathsf{f}_{\rm g}^{(0)})\,\mathrm{d}\boldsymbol{c}_{\rm p} + \partial_\zeta \int c_{{\rm p}z}(\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)})\mathrm{d}\boldsymbol{c}_{\rm p} = \int \mathcal{C}_{\rm p}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm p}, \tag{104}$$

where $\mathcal{C}_{\rm p}^{(0)}$ denotes the chemical production term evaluated with the zeroth order adsorbate layer distributions $\mathsf{f}_i^{(0)}$, $i \in \{\mathrm{p}, \mathrm{c}, \mathrm{s}\}$. We have used here that $\int \boldsymbol{c}_{\rm p\shortparallel}\mathsf{f}_{\rm p}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm p} = \int \boldsymbol{c}_{\rm p\shortparallel}\mathsf{f}_{\rm g}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm g} = 0$ and that the collisional invariant $\psi_{\rm p}^1 = 1$ is orthogonal to $J_{\rm p,p}$ and $\mathcal{J}_{\rm p,ph}$. Moreover, since $\partial_t n_{\rm g}(0) = \mathcal{O}(\epsilon)$ from (72), the first term $\partial_t \int (\mathsf{f}_{\rm p}^{(0)} - \mathsf{f}_{\rm g}^{(0)})\,\mathrm{d}\boldsymbol{c}_{\rm p}$ vanishes at zeroth order and we obtain that

$$\partial_\zeta \int c_{{\rm p}z}(\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)})\mathrm{d}\boldsymbol{c}_{\rm p} = \int \mathcal{C}_{\rm p}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm p}. \tag{105}$$

Using that $\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)} = \mathsf{f}_{\rm lc}^{(1)}$ goes to zero as $\zeta \to \infty$, that $\mathsf{f}_{\rm p}^{(1)}$ goes to zero as $\zeta \to 0$, since there are not anymore particles when $\zeta \to 0$, that $\mathsf{f}_{\rm g}^{(1)} = f_{\rm g}^{(1)}(0) + \zeta\partial_z f_{\rm g}^{(0)}(0)$, that $\zeta\partial_z f_{\rm g}^{(0)}(0)$ go to zero as $\zeta \to 0$, and that $\int c_z f_{\rm g}^{(1)}(0)\mathrm{d}\boldsymbol{c}_{\rm g} = n_{\rm g}(0)\overline{v}_{{\rm g}z}(0)$, we obtain by integrating (105) over $\zeta \in (0, \infty)$ the relation

$$n_{\rm g}(0)\overline{v}_{{\rm g}z}(0) = \int \mathcal{C}_{\rm p}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm p}\mathrm{d}\zeta. \tag{106}$$

The Stefan flux $n_{\rm g}(0)\overline{v}_{{\rm g}z}(0)$ is thus expressed in terms of the zeroth order physisorbate/gas production rate by chemistry in the layer. This relation may be rewritten in the form

$$n_{\rm g}(0)v_{{\rm g}z}(0) = \int \mathcal{C}_{\rm p}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm p}\mathrm{d}z, \tag{107}$$

where the integral of the production term $\mathcal{C}_{\rm p}^{(0)}$ is now performed over $z$ rather than $\zeta$. In particular, the dynamics of the physisorbate does not play a role and the mass flux towards the gas phase $n_{\rm p}(0)v_{{\rm p}z}(0)$ is entirely due to the production of physisorbed/gas species by adsorption/desorption of the chemisorbate.

On the other hand, the integrated mass conservation equation in the chemisorbate may be obtained with a similar procedure and yields that

$$\partial_t \overline{n}_{\rm c} \int \exp\Big(-\frac{\mathrm{W}_{\rm c}}{k_{\rm B}T_{\rm w}}\Big)\mathrm{d}\zeta = \int \mathcal{C}_{\rm c}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm c}\mathrm{d}\zeta, \tag{108}$$

where $\mathcal{C}_{\rm c}^{(0)}$ denotes the production of chemisorbed species by the surface chemistry in the layer and evaluated with zeroth order distributions. This equation may be rewritten

$$\partial_t \widetilde{n}_{\rm c} = \int \mathcal{C}_{\rm c}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm c}\mathrm{d}z, \tag{109}$$

where $\widetilde{n}_{\rm c}(t,\boldsymbol{x}_{\shortparallel}) = \overline{n}_{\rm c}\int\exp\bigl(-{\rm w}_{\rm c}/k_{\rm B}T_{\rm w}\bigr){\rm d}z$ represents the total amount of chemisorbate available in the layer *per unit surface* and may be interpreted as the natural *surface number density* of the chemisorbate.

Proceeding similarly for the free sites and bulk species we obtain finally that

$$n_{\rm g}(0)v_{{\rm g}z}(0) = \int\mathcal{C}_{\rm p}^{(0)}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z, \quad \partial_t\widetilde{n}_{\rm c} = \int\mathcal{C}_{\rm c}^{(0)}{\rm d}\boldsymbol{c}_{\rm c}{\rm d}z, \tag{110}$$

$$\partial_t\widetilde{n}_{\rm s} = \int\mathcal{C}_{\rm s}^{(0)}{\rm d}\boldsymbol{c}_{\rm s}{\rm d}z \qquad \partial_t\widetilde{n}_{\rm b} = \int\mathcal{C}_{\rm b}^{(0)}{\rm d}\boldsymbol{c}_{\rm b}{\rm d}z, \tag{111}$$

with $\widetilde{n}_{\rm c} = \widetilde{n}_{\rm b} = \overline{\theta}\,\widetilde{n}_\sigma$ and $\widetilde{n}_{\rm s} = (1-\overline{\theta})\widetilde{n}_\sigma$ and it is easily checked that

$$\int\mathcal{C}_{\rm p}^{(0)}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z = \int\mathcal{C}_{\rm s}^{(0)}{\rm d}\boldsymbol{c}_{\rm s}{\rm d}z = -\int\mathcal{C}_{\rm c}^{(0)}{\rm d}\boldsymbol{c}_{\rm c}{\rm d}z = -\int\mathcal{C}_{\rm b}^{(0)}{\rm d}\boldsymbol{c}_{\rm b}{\rm d}z.$$

We have thus recovered the traditional mass fluid boundary conditions at a surface with adsorption including the equation for the gas, the chemisorbed species and the coverage [18–20, 40].

### E. Surface chemical reaction

The integrated surface chemistry term $\int\mathcal{C}_{\rm p}^{(0)}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z$ evaluated with the zeroth order adsorbate layer distributions $\mathfrak{f}_i^{(0)}$, $i\in\{{\rm p},{\rm c},{\rm s}\}$, is found in the form

$$\int\mathcal{C}_{\rm p}^{(0)}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z = \mathcal{K}\Bigl(\frac{\overline{n}_\sigma}{{\rm z}_{\rm b}}\frac{\overline{n}_{\rm c}}{{\rm z}_{\rm c}} - \frac{\overline{n}_{\rm s}}{{\rm z}_{\rm s}}\frac{n_{\rm g}(0)}{{\rm z}_{\rm p}}\Bigr), \tag{112}$$

where $\mathcal{K}$ is the surface reaction overall constant

$$\mathcal{K} = \int\mathsf{W}^+{\rm d}\boldsymbol{c}_\sigma{\rm d}\boldsymbol{c}_{\rm s}{\rm d}\boldsymbol{c}_{\rm c}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z. \tag{113}$$

This rate (112) may then be rewritten using number densities per unit surface. Defining the partition function of the surface species with a configuration integral [55]

$$\widetilde{\rm z}_i = {\rm z}_i\int\exp\Bigl(-\frac{{\rm w}_i}{k_{\rm B}T_{\rm w}}\Bigr){\rm d}z, \qquad i\in\{{\rm c},{\rm s},{\rm b}\}, \tag{114}$$

letting ${\rm z}_{\rm g} = {\rm z}_{\rm p}$ and noting that

$$\frac{\overline{n}_i}{{\rm z}_i} = \frac{\widetilde{n}_i}{\widetilde{\rm z}_i}, \qquad i\in\{{\rm c},{\rm s},{\rm b}\}, \tag{115}$$

it is indeed obtained that

$$\int\mathcal{C}_{\rm p}^{(0)}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z = \mathcal{K}\Bigl(\frac{\widetilde{n}_\sigma}{\widetilde{\rm z}_{\rm b}}\frac{\widetilde{n}_{\rm c}}{\widetilde{\rm z}_{\rm c}} - \frac{\widetilde{n}_{\rm s}}{\widetilde{\rm z}_{\rm s}}\frac{n_{\rm g}(0)}{{\rm z}_{\rm g}}\Bigr). \tag{116}$$

This expression of the chemical production rate is compatible with *the atomic site* description of the surface adsorption reaction since it involves the same species as well as the surface number densities and the gas density at the interface $z=0$.

Another expression of the surface reaction rate consists in eliminating the bulk crystal species and reducing the site species to a simple coverage probability $1-\overline{\theta}$. To this aim, letting

$$\widetilde{\rm z}'_{\rm c} = \frac{\widetilde{\rm z}_{\rm c}\widetilde{\rm z}_{\rm b}}{\widetilde{\rm z}_{\rm s}} = \widetilde{\rm z}_{\rm c}\exp\Bigl(-\frac{{\rm E}_{\rm b}-{\rm E}_{\rm s}}{k_{\rm B}T_{\rm w}}\Bigr),$$

that is a partition function for the chemisorbed surface species taking into account the crystal bonding energy ${\rm E}_{\rm b}-{\rm E}_{\rm s}$, and letting $\mathcal{K}' = \mathcal{K}\widetilde{n}_\sigma/\widetilde{\rm z}_{\rm s}$, we obtain

$$\int\mathcal{C}_{\rm p}^{(0)}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z = \mathcal{K}'\Bigl(\frac{\widetilde{n}_{\rm c}}{\widetilde{\rm z}'_{\rm c}} - (1-\overline{\theta})\frac{n_{\rm g}(0)}{{\rm z}_{\rm g}}\Bigr). \tag{117}$$

This rate is compatible with *the open site* description of the surface adsorption reaction, with the opensite $\mathcal{O}({\rm s})$ simply taken into account with a probability factor $1-\overline{\theta}$ and the bonding energy taken into account in the modified surface partition function $\widetilde{\rm z}'_{\rm c}$. The traditional macroscopic species balances as well as the surface chemical production rates for both the atomic and open site conventions *have thus been recovered from the kinetic model*.

The surface production rate may also be rewritten by *completely eliminating all surface crystal species*. To this aim, we may define a new chemical potential

$$\widetilde{\mu}_{\rm c} = \log\Bigl(\frac{\widetilde{n}_{\rm c}}{\widetilde{\rm z}'_{\rm c}}\frac{1}{1-\overline{\theta}}\Bigr) = \log\Bigl(\frac{\widetilde{n}_\sigma}{\widetilde{\rm z}'_{\rm c}}\frac{\overline{\theta}}{1-\overline{\theta}}\Bigr),$$

that involves the $1-\overline{\theta}$ factor coming from the free site density, in agreement with the statistical mechanics of adsorption at low coverage *that excludes crystal species* [44, 55]. Keeping in mind that the chemical potential in the gas is $\mu_{\rm g} = \log(n_{\rm g}/{\rm z}_{\rm g})$, the surface source term is then obtained in the general form associated with statistical mechanics [40, 56, 57]

$$\int\mathcal{C}_{\rm p}^{(0)}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z = \mathcal{K}''\Bigl(\exp(\widetilde{\mu}_{\rm c}) - \exp\bigl(\mu_{\rm g}(0)\bigr)\Bigr), \tag{118}$$

where $\mathcal{K}'' = \mathcal{K}'(1-\overline{\theta})$. At chemical equilibrium, we finally have $\widetilde{\mu}_{\rm c} = \mu_{\rm g}(0)$ in such a way that $\overline{\theta}/(1-\overline{\theta})$ is proportional to $n_{\rm g}(0)$ and the Langmuir isotherm [19] is recovered.

The various expressions of the production rate $\int\mathcal{C}_{\rm p}^{(0)}{\rm d}\boldsymbol{c}_{\rm p}{\rm d}z$ derived with the atomic site formalism (116), the open site formalism (117), and the adsorption mechanistic formalism (118) thus gradually eliminate the crystal surface species. The atomic site formalism still seems to be the relevant one in order to describe reactive collisions. In addition, even though the saturation factor $1-\overline{\theta}$ may be integrated into a chemical potential for the chemisorbed species $\widetilde{\mu}_{\rm c}$, it still originates from the surface crystal species $\mathcal{C}({\rm s})$.

## V. MOMENTUM AND THERMAL BOUNDARY CONDITIONS

We investigate in this section the normal momentum, tangential momentum, and energy dynamic boundary conditions at zeroth order, completing the dynamic mass boundary conditions obtained in previous sections. These dynamic boundary conditions are obtained by taking appropriate moments of the kinetic equations whereas the kinematic boundary conditions are generally obtained by identifying Maxwellian distributions.

### A. Normal momentum boundary conditions

We multiply by $m_{\rm p}c_{{\rm p}z}$ and $\epsilon$ the difference equation (88), integrate with respect to the particle velocity and keep all terms of order $\epsilon^0$ or $\epsilon^1$. Keeping in mind that both $\mathsf{f}_{\rm p}^{(0)}$ and $\mathsf{f}_{\rm g}^{(0)}$ are even with respect to $c_{{\rm p}z}$, as well as with respect to $\boldsymbol{c}_{{\rm p}\shortparallel}$, the resulting equation is in the form

$$\partial_\zeta \int m_{\rm p} c_{{\rm p}z}^2 (\mathsf{f}_{\rm p}^{(0)} + \epsilon \mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(0)} - \epsilon \mathsf{f}_{\rm g}^{(1)})\, {\rm d}\boldsymbol{c}_{\rm p} - \int \partial_\zeta {\rm W}_{\rm p}\, c_{{\rm p}z} \partial_{c_{{\rm p}z}} (\mathsf{f}_{\rm p}^{(0)} + \epsilon \mathsf{f}_{\rm p}^{(1)})\, {\rm d}\boldsymbol{c}_{\rm p}$$
$$- \frac{1}{\alpha_{\rm ph}} \int m_{\rm p} c_{{\rm p}z} \mathcal{J}_{\rm p,ph} (\mathsf{f}_{\rm p}^{(0)} + \epsilon \mathsf{f}_{\rm p}^{(1)})\, {\rm d}\boldsymbol{c}_{\rm p} = \epsilon \int m_{\rm p} c_{{\rm p}z} \mathcal{C}_{\rm p}^{(0)} {\rm d}\boldsymbol{c}_{\rm p}.$$

Integrating with respect to $\zeta$, keeping in mind that $\mathsf{f}_{\rm lc}^{(0)} = \mathsf{f}_{\rm p}^{(0)} - \mathsf{f}_{\rm g}^{(0)}$ and $\mathsf{f}_{\rm lc}^{(1)} = \mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}$ go to zero as $\zeta \to \infty$, that $\mathsf{f}_{\rm p}^{(0)} \to 0$ and $\mathsf{f}_{\rm p}^{(1)} \to 0$ as $\zeta \to 0$, and that $\mathsf{f}_{\rm g}^{(0)}$ and $\mathsf{f}_{\rm g}^{(1)}$ go respectively to $f_{\rm g}^{(0)}$ and $f_{\rm g}^{(1)}$ as $\zeta \to 0$, yields that

$$\int m_{\rm p} c_{{\rm p}z}^2 (f_{\rm g}^{(0)} + \epsilon f_{\rm g}^{(1)})\, {\rm d}\boldsymbol{c}_{\rm p} - \int \partial_\zeta {\rm W}_{\rm p}\, c_{{\rm p}z} \partial_{c_{{\rm p}z}} (\mathsf{f}_{\rm p}^{(0)} + \epsilon \mathsf{f}_{\rm p}^{(1)})\, {\rm d}\boldsymbol{c}_{\rm p} {\rm d}\zeta$$
$$- \frac{1}{\alpha_{\rm ph}} \int m_{\rm p} c_{{\rm p}z} \mathcal{J}_{\rm p,ph} (\mathsf{f}_{\rm p}^{(0)} + \epsilon \mathsf{f}_{\rm p}^{(1)})\, {\rm d}\boldsymbol{c}_{\rm p} {\rm d}\zeta = \epsilon \int m_{\rm p} c_{{\rm p}z} \mathcal{C}_{\rm p}^{(0)} {\rm d}\boldsymbol{c}_{\rm p} {\rm d}\zeta. \tag{119}$$

A direct calculation yields

$$\int m_{\rm p} c_{{\rm p}z}^2 f_{\rm g}^{(0)}\, {\rm d}\boldsymbol{c}_{\rm p} = n_{\rm g} k_{\rm B} T_{\rm g} = p_{\rm g},$$

where $p_{\rm g} = n_{\rm g} k_{\rm B} T_{\rm g}$ denotes the pressure is the gas. Using the definition of the viscosity coefficient $\eta$ and the isotropy of $J_{\rm p,p}$, it is established that

$$\epsilon m_{\rm p} \int \boldsymbol{c}_{\rm p} \otimes \boldsymbol{c}_{\rm p} f_{\rm g}^{(1)}\, {\rm d}\boldsymbol{c}_{\rm p} = -\epsilon m_{\rm p} \int \boldsymbol{c}_{\rm p} \otimes \boldsymbol{c}_{\rm p} \alpha_{\rm p} \boldsymbol{\phi}^\eta\, {\rm d}\boldsymbol{c}_{\rm p}$$
$$= -\epsilon \eta\, \mathbf{S} = \boldsymbol{\Pi}, \tag{120}$$

where

$$\mathbf{S} = \boldsymbol{\partial}_{\boldsymbol{x}} \boldsymbol{v}_{\rm g} + (\boldsymbol{\partial}_{\boldsymbol{x}} \boldsymbol{v}_{\rm g})^t - \tfrac{2}{3} \boldsymbol{\partial}_{\boldsymbol{x}} \cdot \boldsymbol{v}_{\rm g} \boldsymbol{I},$$

denotes the symmetric traceless strain rate tensor and $\boldsymbol{\Pi} = -\epsilon\eta\mathbf{S}$ the viscous tensor in the gas. Use has been made that the term proportional to $c_{{\rm p}z} f_{\rm g}^{(0)}$ as well as that associated with $\boldsymbol{\phi}^\lambda f_{\rm g}^{(0)}$ in $f_{\rm g}^{(1)}$ yield null contributions in $m_{\rm p} \int \boldsymbol{c}_{\rm p} \otimes \boldsymbol{c}_{\rm p} f_{\rm g}^{(1)}\, {\rm d}\boldsymbol{c}_{\rm p}$. Defining the pressure tensor in the gas by

$$\boldsymbol{\mathcal{P}}^{\rm g} = p_{\rm g} \boldsymbol{I} + \boldsymbol{\Pi}, \tag{121}$$

and considering in particular the $zz$ components of (120), we obtain that

$$\int m_{\rm p} c_{{\rm p}z}^2 (f_{\rm g}^{(0)} + \epsilon f_{\rm g}^{(1)})\, {\rm d}\boldsymbol{c}_{\rm p} = p_{\rm g} + \Pi_{zz} = \mathcal{P}_{zz}^{\rm g},$$

where $\Pi_{zz}$ is the $zz$ component of $\boldsymbol{\Pi}$ and $\mathcal{P}_{zz}^{\rm g}$ the $zz$ component of $\boldsymbol{\mathcal{P}}^{\rm g}$.

In order to eliminate the reactive source term in the right hand side of (119), we form the normal momentum balance of surface species that are similar except for the absence of flux coming from the gas. The resulting equations are obtained in the form

$$- \int \partial_\zeta {\rm W}_i\, c_{iz} \partial_{c_{iz}} (\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)})\, {\rm d}\boldsymbol{c}_i {\rm d}\zeta$$
$$- \frac{1}{\alpha_{\rm ph}} \int m_i c_{iz} \mathcal{J}_{i,{\rm ph}} (\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)})\, {\rm d}\boldsymbol{c}_i {\rm d}\zeta =$$
$$\epsilon \int m_i c_{iz} \mathcal{C}_i^{(0)} {\rm d}\boldsymbol{c}_i {\rm d}\zeta.$$

Adding the momentum equations of all species, using momentum conservation in chemical reactions, and integrating by parts with respect to the normal velocity variable the potential term, it is obtained that

$$p_{\rm g} + \Pi_{zz} = -\sum_{\rm p,c,s,b} \int \partial_\zeta {\rm W}_i\, (\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)})\, {\rm d}\boldsymbol{c}_i {\rm d}\zeta$$
$$+ \sum_{\rm p,c,s,b} \frac{1}{\alpha_{\rm ph}} \int m_i c_{iz} \mathcal{J}_{i,{\rm ph}} (\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)})\, {\rm d}\boldsymbol{c}_i {\rm d}\zeta.$$

The solid crystal pressure tensor—opposite of the crystal

Cauchy tensor—at the surface is then defined as

$$\boldsymbol{\mathcal{P}}^{\rm so}_{zz} = -\,\boldsymbol{\sigma}^{\rm so}_{zz} = -\sum_{\rm p,c,s,b}\int \partial_\zeta \mathrm{w}_i\,(\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{\rm p,c,s,b}\frac{1}{\alpha_{\rm ph}}\int m_i c_{iz}\mathcal{J}_{i,\rm ph}(\mathsf{f}_i^{(0)} + \epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta,$$

and may be simplified—using that the zeroth order potential terms of surface species are eliminated after integration with respect to $\zeta$—in the form

$$\boldsymbol{\mathcal{P}}^{\rm so}_{zz} = -\int \partial_\zeta \mathrm{w}_{\rm p}\mathsf{f}_{\rm p}^{(0)}\,\mathrm{d}\boldsymbol{c}_{\rm p}\mathrm{d}\zeta - \sum_{\rm p,c,s,b}\epsilon\int \partial_\zeta \mathrm{w}_i\mathsf{f}_i^{(1)}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{\rm p,c,s,b}\frac{\epsilon}{\alpha_{\rm ph}}\int m_i c_{iz}\mathcal{J}_{i,\rm ph}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

The first two terms represent the total force per unit surface acting on the physisorbate, chemisorbate, and surface layer, whereas the second sum represents the gain in momentum by the species due to the interaction with phonons per unit surface and time and also represents a force per unit surface. Since all zeroth order terms vanish except that acting on the physisorbate, it appears that the dominant term represents the action of the solid on the physisorbate. We may finally write the resulting boundary condition in the form

$$\boldsymbol{\mathcal{P}}^{\rm g}_{zz} = \boldsymbol{\mathcal{P}}^{\rm so}_{zz} = -\boldsymbol{\sigma}^{\rm so}_{zz}, \tag{122}$$

that is the traditional momentum boundary condition, the contribution of the normal velocity term being of higher order.

### B. Tangential momentum boundary conditions

We multiply by $m_{\rm p}\boldsymbol{c}_{\rm p\shortparallel}$ and $\epsilon$ the difference equation (88), integrate with respect to the particle velocity and keep all term of order $\epsilon^{-1}$ and $\epsilon^0$. On the other hand, it will be established in Section VI B that $\boldsymbol{\partial}_\shortparallel n_{\rm g} = \mathcal{O}(\epsilon)$ in such a way that $\boldsymbol{\partial}_\shortparallel \mathsf{f}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$ and $\boldsymbol{\partial}_\shortparallel \mathsf{f}_{\rm g}^{(0)} = \mathcal{O}(\epsilon)$. Keeping in mind that both $\mathsf{f}_{\rm p}^{(0)}$ and $\mathsf{f}_{\rm g}^{(0)}$ are even with respect to $c_{\rm pz}$ and $\boldsymbol{c}_{\rm p\shortparallel}$, and since $\boldsymbol{\partial}_\shortparallel \mathsf{f}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$ and $\boldsymbol{\partial}_\shortparallel \mathsf{f}_{\rm g}^{(0)} = \mathcal{O}(\epsilon)$, the resulting equation is in the form

$$\partial_\zeta \int m_{\rm p} c_{\rm pz}\boldsymbol{c}_{\rm p\shortparallel}(\mathsf{f}_{\rm p}^{(0)} + \epsilon\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(0)} - \epsilon\mathsf{f}_{\rm g}^{(1)})\,\mathrm{d}\boldsymbol{c}_{\rm p} - \frac{1}{\alpha_{\rm ph}}\int m_{\rm p}\boldsymbol{c}_{\rm p\shortparallel}\mathcal{J}_{\rm p,ph}(\mathsf{f}_{\rm p}^{(0)} + \epsilon\mathsf{f}_{\rm p}^{(1)})\,\mathrm{d}\boldsymbol{c}_{\rm p} = \epsilon\int m_{\rm p}\boldsymbol{c}_{\rm p\shortparallel}\mathcal{C}_{\rm p}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm p}.$$

Integrating with respect to $\zeta$ yields that

$$\epsilon\int m_{\rm p} c_{\rm pz}\boldsymbol{c}_{\rm p\shortparallel} f_{\rm g}^{(1)}\,\mathrm{d}\boldsymbol{c}_{\rm p} - \frac{\epsilon}{\alpha_{\rm ph}}\int m_{\rm p}\boldsymbol{c}_{\rm p\shortparallel}\mathcal{J}_{\rm p,ph}(\mathsf{f}_{\rm p}^{(1)})\,\mathrm{d}\boldsymbol{c}_{\rm p}\mathrm{d}\zeta = \epsilon\int m_{\rm p}\boldsymbol{c}_{\rm p\shortparallel}\mathcal{C}_{\rm p}^{(0)}\mathrm{d}\boldsymbol{c}_{\rm p}\mathrm{d}\zeta.$$

The first term may be evaluated as $\varPi_{\shortparallel z}$ by using (120) in the $\shortparallel z$ directions. Moreover, in order to eliminate the reactive source term, we may form the overall layer tangential momentum balance of the surface species. The resulting equations are obtained in the form

$$0 = \frac{\epsilon}{\alpha_{\rm ph}}\int m_i\boldsymbol{c}_{i\shortparallel}\mathcal{J}_{i,\rm ph}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \epsilon\int m_i c_{iz}\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

Adding all the species tangential momentum balance and using the conservation of momentum in the chemical collision operators yields

$$\varPi_{\shortparallel z} = \sum_{\rm p,c,s,b}\frac{\epsilon}{\alpha_{\rm ph}}\int m_i\boldsymbol{c}_{i\shortparallel}\mathcal{J}_{i,\rm ph}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

It is then natural to define the tangential component of the normal stress in the solid as

$$\boldsymbol{\mathcal{P}}^{\rm so}_{\shortparallel z} = -\boldsymbol{\sigma}^{\rm so}_{\shortparallel z} = \sum_{\rm p,c,s,b}\frac{\epsilon}{\alpha_{\rm ph}}\int m_i\boldsymbol{c}_{i\shortparallel}\mathcal{J}_{i,\rm ph}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta,$$

since it represents the gain in tangential momentum by the surface species due to interaction with phonon per unit surface and time and thus represents a tangential force per unit surface. We thus finally obtain the equality of the tangential component of the normall stress or pressure tensor

$$\boldsymbol{\mathcal{P}}^{\rm g}_{\shortparallel z} = \varPi_{\shortparallel z} = \boldsymbol{\mathcal{P}}^{\rm so}_{\shortparallel z} = -\boldsymbol{\sigma}^{\rm so}_{\shortparallel z}, \tag{123}$$

and only first order term remain.

### C. Thermal boundary condition

We multiply by $\frac{1}{2}m_{\rm p}|\boldsymbol{c}_{\rm p}|^2 + \mathrm{E}_{\rm p} + \mathrm{w}_{\rm p}$ and $\epsilon$ the kinetic equation (81) for $i = \mathrm{p}$, multiply by $\frac{1}{2}m_{\rm p}|\boldsymbol{c}_{\rm p}|^2 + \mathrm{E}_{\rm p}$ and $\epsilon$ the gas kinetic equation (82), and form the difference equation. Integrating then with respect to the particle velocity, and keeping all term of order $\epsilon^0$ and $\epsilon^1$, it is obtained that

$$\partial_\zeta \int c_{\mathrm{p}z}\Big\{(\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2+\mathrm{E}_{\mathrm{p}}+\mathrm{W}_{\mathrm{p}})(\mathsf{f}_{\mathrm{p}}^{(0)}+\epsilon\mathsf{f}_{\mathrm{p}}^{(1)})-(\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2+\mathrm{E}_{\mathrm{p}})(\mathsf{f}_{\mathrm{g}}^{(0)}+\epsilon\mathsf{f}_{\mathrm{g}}^{(1)})\Big\}\mathrm{d}\boldsymbol{c}_{\mathrm{p}}=$$
$$\frac{1}{\alpha_{\mathrm{ph}}}\int(\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2+\mathrm{E}_{\mathrm{p}}+\mathrm{W}_{\mathrm{p}})\mathcal{J}_{\mathrm{p,ph}}(\epsilon\mathsf{f}_{\mathrm{p}}^{(1)})\,\mathrm{d}\boldsymbol{c}_{\mathrm{p}}+\epsilon\int(\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2+\mathrm{E}_{\mathrm{p}}+\mathrm{W}_{\mathrm{p}})\mathcal{C}_{\mathrm{p}}^{(0)}\mathrm{d}\boldsymbol{c}_{\mathrm{p}}.$$

Use has been made that $\partial_t n_{\mathrm{g}}=\mathcal{O}(\epsilon)$, in order to suppress the time derivative term. In addition, since $\mathsf{f}_{\mathrm{p}}^{(0)}$ and $\mathsf{f}_{\mathrm{g}}^{(0)}$ are even in $\boldsymbol{c}_{\mathrm{p}\shortparallel}$, the integrals containing $\mathsf{f}_{\mathrm{p}}^{(0)}$ and $\mathsf{f}_{\mathrm{g}}^{(0)}$ on the left hand side vanish, and since constants are orthogonal to the collision operators, the term containing $\mathrm{E}_{\mathrm{p}}+\mathrm{W}_{\mathrm{p}}$ in the first integral on the right-hand side has vanishing contribution. Then, integrating this equation with respect to $\zeta$, it is obtained that

$$\epsilon\int c_{\mathrm{p}z}(\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2+\mathrm{E}_{\mathrm{p}})\mathsf{f}_{\mathrm{g}}^{(1)}\,\mathrm{d}\boldsymbol{c}_{\mathrm{p}}=$$
$$\frac{\epsilon}{\alpha_{\mathrm{ph}}}\int\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2\mathcal{J}_{\mathrm{p,ph}}(\mathsf{f}_{\mathrm{p}}^{(1)})\,\mathrm{d}\boldsymbol{c}_{\mathrm{p}}\mathrm{d}\zeta$$
$$+\epsilon\int(\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2+\mathrm{E}_{\mathrm{p}}+\mathrm{W}_{\mathrm{p}})\mathcal{C}_{\mathrm{p}}^{(0)}\mathrm{d}\boldsymbol{c}_{\mathrm{p}}\mathrm{d}\zeta. \tag{124}$$

Using the definition of the thermal conductivity coefficient $\lambda$ and the isotropy of $J_{\mathrm{p,p}}$, it is established that

$$\epsilon\int c_{\mathrm{p}z}\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2\alpha_{\mathrm{p}}\boldsymbol{\phi}^{\lambda}f_{\mathrm{g}}^{(0)}\,\mathrm{d}\boldsymbol{c}_{\mathrm{p}}=-\epsilon\lambda\,\partial_z T_{\mathrm{g}}=Q_z,$$

where $\boldsymbol{Q}=-\epsilon\lambda\boldsymbol{\partial}_{\boldsymbol{x}}T_{\mathrm{g}}$ denotes the heat flux in the gas. The moment associated with $f_{\mathrm{g}}^{(1)}$ is then evaluated as

$$\epsilon\int c_{\mathrm{p}z}(\tfrac{1}{2}m_{\mathrm{p}}|\boldsymbol{c}_{\mathrm{p}}|^2+\mathrm{E}_{\mathrm{p}})f_{\mathrm{g}}^{(1)}\,\mathrm{d}\boldsymbol{c}_{\mathrm{p}}=\big(\tfrac{5}{2}k_{\mathrm{B}}T_{\mathrm{g}}+\mathrm{E}_{\mathrm{p}}\big)n_{\mathrm{g}}v_{\mathrm{g}z}+Q_z.$$

In order to eliminate the reactive source term in the right hand side of (124), proceeding as for the momentum balance equations, we may use the thermal balance of the surface species. The resulting equations are in the form

$$\epsilon\partial_t\int(\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2+\mathrm{E}_i+\mathrm{W}_i)\mathsf{f}_i^{(0)}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta=$$
$$\frac{\epsilon}{\alpha_{\mathrm{ph}}}\int\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2\mathcal{J}_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta$$
$$+\epsilon\int(\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2+\mathrm{E}_i+\mathrm{W}_i)\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

Letting then

$$\widetilde{\mathrm{W}}_i=\int\mathrm{W}_i\exp\big(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}}\big)\mathrm{d}\zeta\,\Big/\int\exp\big(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}}\big)\mathrm{d}\zeta,$$

and

$$\widetilde{\mathrm{E}}_i=\mathrm{E}_i+\widetilde{\mathrm{W}}_i, \tag{125}$$

adding the energy balance of all the species and using the conservation of energy in chemical reactions yields

$$\big(\tfrac{5}{2}k_{\mathrm{B}}T_{\mathrm{g}}+\mathrm{E}_{\mathrm{p}}\big)n_{\mathrm{g}}v_{\mathrm{g}z}+Q_z+\sum_{\mathrm{c,s,b}}\partial_t\big((\tfrac{3}{2}k_{\mathrm{B}}T_{\mathrm{g}}+\widetilde{\mathrm{E}}_i)\widetilde{n}_i\big)=$$
$$\sum_{\mathrm{p,c,s,b}}\frac{\epsilon}{\alpha_{\mathrm{ph}}}\int\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2\mathcal{J}_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

The solid heat flux at the surface is defined as

$$Q_z^{\mathrm{so}}=\sum_{\mathrm{p,c,s,b}}\frac{\epsilon}{\alpha_{\mathrm{ph}}}\int\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2\mathcal{J}_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta,$$

since it represents the gain in kinetic energy of the species due to interaction with phonons per unit surface and time and represents a heat flux. Using then the governing equations for the surface species, we have established that

$$\big(\tfrac{5}{2}k_{\mathrm{B}}T_{\mathrm{g}}+\mathrm{E}_{\mathrm{p}}\big)n_{\mathrm{g}}v_{\mathrm{g}z}+Q_z+\sum_{\mathrm{c,s,b}}(\tfrac{3}{2}k_{\mathrm{B}}T_{\mathrm{g}}+\widetilde{\mathrm{E}}_i)\int\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}z$$
$$=Q_z^{\mathrm{so}}. \tag{126}$$

Finally letting $\mathrm{H}_i=\frac{3}{2}k_{\mathrm{B}}T_{\mathrm{g}}+\widetilde{\mathrm{E}}_i$ for $i\in\{\mathrm{c,s,b}\}$ and $\mathrm{H}_{\mathrm{p}}=\frac{5}{2}k_{\mathrm{B}}T_{\mathrm{g}}+\mathrm{E}_{\mathrm{p}}$, we may write (126) in the form

$$Q_z+\sum_{\mathrm{p,c,s,b}}\mathrm{H}_i\int\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}z=Q_z^{\mathrm{so}}. \tag{127}$$

This relation corresponds to the usual thermal flux balance at a reactive surface where the temperature is fixed [19, 40].

The resulting dynamics boundary conditions (122)(123) and (127) completes the species mass boundary conditions obtained in Section IV. There are nevertheless limitations for such boundary conditions that originate from various assumptions used in the model. The system is first isothermal so that the surface and bulk temperature gradients cannot properly be taken into account. The surface is also constrained to have the same temperature as the gas and the solid body and thus has no thermal degrees of freedom. The phonons are also assumed to be at equilibrium and the heat flux in the solid cannot be expressed in terms of the temperature gradient in the solid.

## VI. FIRST ORDER EXPANSIONS IN THE ADSORBATE

First order expansions are investigated in the adsorbate layer as well as the corresponding species fluid boundary conditions.

### A. Simplified phonon interaction operator

It is assumed in the following that the phonon collision operators are in the relaxation form

$$\frac{1}{\alpha_{\rm ph}}\mathcal{J}_{i,\rm ph}(\varphi_i) = -\frac{1}{\tau_{i,\rm ph}}\big(\varphi_i - \langle\varphi_i\rangle_{\rm M_i}\big), \tag{128}$$

for $i \in \{\rm p, c, s, b, \sigma\}$, where the relaxation times $\tau_{i,\rm ph}$ are independent of the velocity $\boldsymbol{c}_i$ and $\langle\varphi_i\rangle$ denotes for short the integral over the corresponding velocity space

$$\langle\varphi_i\rangle = \int \varphi_i \,\mathrm{d}\boldsymbol{c}_i, \qquad i \in \{\rm p, c, s, b, \sigma\}.$$

This assumption introduced by Borman et al. simplifies the analysis of the adsorbate layer [21–24, 31]. For the physisorbate species, keeping in mind that there is no interaction with phonons far from the surface, we must also have $\lim_{\zeta\to\infty}\tau_{\rm p,ph}(\zeta) = +\infty$.

A further simplifying assumption concerning the chemisorbed and surface species is that the relaxation times $\tau_{\rm c,ph}$, $\tau_{\rm s,ph}$ and $\tau_{\rm b,ph}$ are also independent of $\zeta$

$$\tau_{\rm c,ph} = \text{Cte}, \qquad \tau_{\rm s,ph} = \text{Cte} \qquad \tau_{\rm b,ph} = \text{Cte}. \tag{129}$$

This assumption seems natural since the surface and chemisorbed layers are *thin layers*. The relaxation times are then given by $\tau_{i,\rm ph}$ in the relevant zones $(\zeta_i^-, \zeta_i^+)$, $i \in \{\rm c, s, b\}$, and are $+\infty$ outside of these zones. Diffusion processes on surfaces or in solids being due to thermal agitation, we will naturally find that collisions with phonons lead to surface diffusion and in particular to diffusion of the chemisorbed species. Since the bulk species denote crystal atoms bonded with chemisorbed particles A(s), they must naturally have *the same macroscopic surface diffusion velocity* and this will yield a constraint expressing $\tau_{\rm b,ph}$ in terms of $\tau_{\rm c,ph}$ established in the following.

### B. Orders of magnitude

Prior to investigating higher order equations, we need to estimate the asymptotic order of various quantities. The gas momentum equation at the origin $z = 0$ is first in the form

$$m_{\rm g} n_{\rm g}\partial_t \boldsymbol{v}_{\rm g} + m_{\rm g} n_{\rm g}\boldsymbol{v}_{\rm g}\cdot\boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{v}_{\rm g} + \boldsymbol{\partial}_{\boldsymbol{x}}(k_{\rm B} n_{\rm g} T_{\rm g}) + \boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{\Pi}_{\rm g} = 0,$$

where $\boldsymbol{\Pi}_{\rm g} = -\epsilon\eta\mathsf{S}$ denotes the viscous tensor. Since the velocity $\boldsymbol{v}_{\rm g}$ is $\mathcal{O}(\epsilon)$ near the surface and also necessarily its time derivative $\partial_t\boldsymbol{v}_{\rm g} = \epsilon\partial_t\overline{v}_{\rm g}$, this equation implies that the pressure gradient is $\boldsymbol{\partial}_{\boldsymbol{x}}(n_{\rm g}T_{\rm g})(0) = \mathcal{O}(\epsilon)$. Using this relation in the tangential direction, and since $T_{\rm g}(0) = T_{\rm w}$ is constant along the surface, we obtain that

$$\boldsymbol{\partial}_{\shortparallel} n_{\rm g}(0) = \mathcal{O}(\epsilon). \tag{130}$$

This estimate (130), deduced $\boldsymbol{\partial}_{\boldsymbol{x}}(n_{\rm g}T_{\rm g}) = \mathcal{O}(\epsilon)$, will eliminate surface diffusion effects *in the physisorbate*. This is natural since the physisorbate is a *single species fluid* and there is no term proportional to the number density gradient in such a single species fluid perturbed distribution function. The integral equation for the perturbed distribution function $\widehat{\phi}_{\rm g}^{(1)}$ indeed reads $\widehat{\mathcal{I}}_{\rm g}(\widehat{\phi}_{\rm g}^{(1)}) = -(\partial_t\log\widehat{f}_{\rm g}^{(0)} + \boldsymbol{c}_{\rm g}\cdot\boldsymbol{\partial}_{\boldsymbol{x}}\log\widehat{f}_{\rm g}^{(0)})$ and in the expression of the right hand side, the $\boldsymbol{\partial}_{\boldsymbol{x}}n_{\rm g}$ term coming from $\boldsymbol{c}_{\rm g}\cdot\boldsymbol{\partial}_{\boldsymbol{x}}\log\widehat{f}_{\rm g}^{(0)}$ is exactly compensated by the $\boldsymbol{\partial}_{\boldsymbol{x}}n_{\rm g}$ term arising from the pressure gradient term of the momentum equation obtained from $(\partial_{\boldsymbol{v}_{\rm g}}\log\widehat{f}_{\rm g}^{(0)})\partial_t\boldsymbol{v}_{\rm g}$ through $\partial_t\log\widehat{f}_{\rm g}^{(0)}$.

We have already seen in Section III C that $\boldsymbol{\partial}_{\shortparallel}\boldsymbol{v}_{\rm g\shortparallel} = 0$ and $\boldsymbol{\partial}_{\boldsymbol{x}}v_{{\rm g}z} = \mathcal{O}(\epsilon)$ so that only $\partial_z\boldsymbol{v}_{\rm g\shortparallel}$ may remain in the gradient $\boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{v}_{\rm g}$ at zeroth order. However, assuming that the crystal is free of tangential stress $\boldsymbol{\sigma}_{\shortparallel z} = 0$, we obtain from the zeroth order dynamic boundary condition (123) at the interface that $\partial_z\boldsymbol{v}_{\rm g\shortparallel} = \mathcal{O}(\epsilon)$. Using previous velocity gradient estimates we thus have $\boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{v} = \mathcal{O}(\epsilon)$ and of course $\boldsymbol{\partial}_{\boldsymbol{x}}T = \mathcal{O}(\epsilon)$ since the system is isothermal. The number densities $n_{\rm s}$, $n_{\rm c}$, $n_\sigma$, and $\mathsf{W}_{\rm p,c}$ are also naturally assumed to be $\mathcal{O}(1)$ and by integrating through the adsorbate layer it is obtained that $\widetilde{n}_{\rm s}$, $\widetilde{n}_{\rm c}$, and $\widetilde{n}_\sigma$, are $\mathcal{O}(\epsilon)$. One thus observes a reduction of the asymptotic order of surface concentrations due to *the lower surface dimension* since the adsorbate layer has thickness $\mathcal{O}(\epsilon)$.

In the following sections, we will further assume that *the surface chemistry is slow* in such a way that

$$\overline{\mathsf{W}}^+ = \mathcal{O}(\epsilon^{\mathsf{a}}), \tag{131}$$

where $\mathsf{a} = 1$. This is a feasible assumption since surface chemistry is generally slow in comparison with homogeneous chemistry and we have also seen that $\partial_t n_{\rm g}(0) = \mathcal{O}(\epsilon)$ and $\boldsymbol{v}_{\rm g} = \mathcal{O}(\epsilon)$ so that the main adsorption reactant is slowly transported to the surface. This assumption (131) with $\mathsf{a} = 1$ corresponds in the case of homogeneous reactions to that of Maxwellian chemistry [40].

The assumption (131) implies that $\mathcal{C}_i^{(0)} = \mathcal{O}(\epsilon^{\mathsf{a}})$, for $i \in \{\rm p, c, s, b\}$ and that the reaction constant $\mathcal{K}$ defined in (113) is $\mathcal{O}(\epsilon^{1+\mathsf{a}})$ since $\overline{\mathsf{W}}^+ = \mathcal{O}(\epsilon^{\mathsf{a}})$ and the integration variable is $z$. This notably implies that $\int\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}z = \mathcal{O}(\epsilon^{1+\mathsf{a}})$ as well as $\partial_t\int\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}z = \mathcal{O}(\epsilon^{1+\mathsf{a}})$ for $i \in \{\rm p, c, s, b\}$. It is then obtained from (109) that $\partial_t\widetilde{n}_{\rm c} = \mathcal{O}(\epsilon^{1+\mathsf{a}})$ and from $\widetilde{n}_{\rm c} = \overline{\theta}\widetilde{n}_\sigma$ that $\partial_t\overline{\theta} = \mathcal{O}(\epsilon^{\mathsf{a}})$. We also obtain from the expression of the Stefan flux that $v_{{\rm g}z}(0) = \mathcal{O}(\epsilon^{1+\mathsf{a}})$ and using the mass conservation equation that $\partial_z v_{{\rm g}z}(0) = \mathcal{O}(\epsilon^{1+\mathsf{a}})$. In this situation, both expansion coefficients $\phi_{\rm g}^{(1)}$ and $\phi_{\rm g}^{(2)}$ are $\mathcal{O}(\epsilon)$ as well as

$f_{\rm g}^{(1)}$ and $f_{\rm g}^{(2)}$ and these orders of magnitude will be used in the next sections.

### C. First order expansion in the physisorbate

From equation (81) and the inner expansion (78), the first order equation in the physisorbate is obtained in the form

$$\partial_t \mathsf{f}_{\rm p}^{(0)} + \boldsymbol{c}_{\rm p\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\mathsf{f}_{\rm p}^{(0)} + c_{\rm pz}\,\partial_\zeta \mathsf{f}_{\rm p}^{(1)} - \frac{1}{m_{\rm p}}\partial_\zeta \mathrm{W}_{\rm p}\,\partial_{c_{\rm pz}}\mathsf{f}_{\rm p}^{(1)} + \frac{1}{\alpha_{\rm p}}\mathsf{f}_{\rm p}^{(0)}\mathcal{I}_{\rm p}(\mathsf{f}_{\rm p}^{(1)}/\mathsf{f}_{\rm p}^{(0)}) + \frac{1}{\tau_{\rm p,ph}}\big(\mathsf{f}_{\rm p}^{(1)} - \langle \mathsf{f}_{\rm p}^{(1)}\rangle_{\mathrm{M_p}}\big) = \mathcal{C}_{\rm p}^{(0)}, \tag{132}$$

where $\mathcal{I}_{\rm p}$ denotes the linearized collision operator around the zeroth order inner distribution $\mathsf{f}_{\rm p}^{(0)}$

$$\mathcal{I}_{\rm p}(\psi) = -\frac{1}{\mathsf{f}_{\rm p}^{(0)}}\big(J_{\rm p,p}(\mathsf{f}_{\rm p}^{(0)},\mathsf{f}_{\rm p}^{(0)}\psi) + J_{\rm p,p}(\mathsf{f}_{\rm p}^{(0)}\psi,\mathsf{f}_{\rm p}^{(0)})\big). \tag{133}$$

We introduce $\Phi_{\rm p}^{(1)} = \mathsf{f}_{\rm p}^{(1)}/\mathsf{f}_{\rm p}^{(0)}$ as well as the operator

$$\mathcal{H}_{\rm p}(\varphi) = c_{\rm pz}\,\partial_\zeta\varphi - \frac{1}{m_{\rm p}}\partial_\zeta \mathrm{W}_{\rm p}\,\partial_{c_{\rm pz}}\varphi + \frac{1}{\alpha_{\rm p}}\mathcal{I}_{\rm p}(\varphi) + \frac{1}{\tau_{\rm p,ph}}\big(\varphi - \langle\varphi_{\mathrm{M_p}}\rangle\big),$$

and we note that $\langle\Phi_{\rm p}^{(1)}\mathsf{f}_{\rm p}^{(0)}\rangle_{\mathrm{M_p}} = \langle\Phi_{\rm p}^{(1)}{}_{\mathrm{M_p}}\rangle\mathsf{f}_{\rm p}^{(0)}$. The first order linearized system then reads

$$\mathcal{H}_{\rm p}(\Phi_{\rm p}^{(1)}) = \Psi_{\rm p}^{(1)}, \tag{134}$$

where

$$\Psi_{\rm p}^{(1)} = \frac{\mathcal{C}_{\rm p}^{(0)}}{\mathsf{f}_{\rm p}^{(0)}} - \partial_t \log \mathsf{f}_{\rm p}^{(0)} - \boldsymbol{c}_{\rm p\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\log \mathsf{f}_{\rm p}^{(0)}.$$

Moreover, keeping in mind that $\mathcal{C}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$ with $\mathsf{a}=1$, that $\partial_t \mathsf{f}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$ and $\boldsymbol{\partial}_{\shortparallel}\mathsf{f}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$, it is then found that $\Psi_{\rm p}^{(1)}$ vanishes at zeroth order. On the other hand, with $\mathsf{f}_{\rm p}^{(1)}$ decomposed into $\mathsf{f}_{\rm p}^{(1)} = \mathsf{f}_{\rm g}^{(1)} + \mathsf{f}_{\rm lc}^{(1)}$ the boundary conditions for $\mathsf{f}_{\rm p}^{(1)}$ are

$$\lim_{\zeta\to 0}\mathsf{f}_{\rm p}^{(1)} = 0, \qquad \lim_{\zeta\to\infty}(\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}) = 0, \tag{135}$$

since there are no physisorbed particles as $\zeta\to 0$ and the corrector $\mathsf{f}_{\rm lc}^{(1)}$ goes to zero as $\zeta\to\infty$.

### D. First order expansion of surface species

Proceeding similarly for the chemisorbate and surface species, the first order equations obtained form (81) are in the form

$$\partial_t \mathsf{f}_i^{(0)} + \boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\mathsf{f}_i^{(0)} + c_{iz}\,\partial_\zeta \mathsf{f}_i^{(1)} - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\mathsf{f}_i^{(1)} + \frac{1}{\tau_{i,\rm ph}}\big(\mathsf{f}_i^{(1)} - \langle \mathsf{f}_i^{(1)}\rangle_{\mathrm{M}_i}\big) = \mathcal{C}_i^{(0)}, \tag{136}$$

where $i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}$. We Introduce $\Phi_i^{(1)} = \mathsf{f}_i^{(1)}/\mathsf{f}_i^{(0)}$ for the surface species $i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}$ as well as the operator $\mathcal{H}_i$ naturally associated with (136)

$$\mathcal{H}_i(\varphi) = c_{iz}\,\partial_\zeta\varphi - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\varphi + \frac{1}{\tau_{i,\rm ph}}\big(\varphi - \langle\varphi_{\mathrm{M}_i}\rangle\big),$$

and we note that $\langle\Phi_i^{(1)}\mathsf{f}_i^{(0)}\rangle_{\mathrm{M}_i} = \langle\Phi_i^{(1)}{}_{\mathrm{M}_i}\rangle\mathsf{f}_i^{(0)}$. The integral equation for the $i$th species is then in the form

$$\mathcal{H}_i(\Phi_i^{(1)}) = \Psi_i^{(1)}, \qquad i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}, \tag{137}$$

where

$$\Psi_i^{(1)} = \frac{\mathcal{C}_i^{(0)}}{\mathsf{f}_i^{(0)}} - \partial_t \log \mathsf{f}_i^{(0)} - \boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\log \mathsf{f}_i^{(0)}, \qquad i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}. \tag{138}$$

Moreover, the boundary conditions read

$$\lim_{\zeta\to\zeta_i^-}\mathsf{f}_i^{(1)} = 0, \qquad \lim_{\zeta\to\zeta_i^+}\mathsf{f}_i^{(1)} = 0. \tag{139}$$

It is further natural to impose an Enskog type constraint for the perturbed distribution $\Phi_i^{(1)}$ in the form

$$\int \mathsf{f}_i^{(0)}\Phi_i^{(1)}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta = 0, \qquad i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}, \tag{140}$$

in order to determine the average value of $\Phi_i^{(1)}$. Denoting by $\mathbb{1}$ the function equal to unity, we indeed have $\mathcal{H}_i(\mathbb{1}) = 0$ with $\lim_{\zeta\to\zeta_i^-}\mathsf{f}_i^{(0)} = 0$ and $\lim_{\zeta\to\zeta_i^+}\mathsf{f}_i^{(0)} = 0$ so that any constant could otherwise be added to $\Phi_i^{(1)}$. This contrasts with the physisorbate where the only function $\phi_{\rm p}$ such that $\mathcal{H}_{\rm p}(\phi_{\rm p}) = 0$ with $\lim_{\zeta\to 0}\mathsf{f}_{\rm p}^{(0)}\phi_{\rm p} = 0$ and

$\lim_{\zeta\to+\infty}\mathsf{f}_{\rm p}^{(0)}\phi_{\rm p}=0$ is the zero function. Indeed, it is found—as in the study of the zeroth order physisorbate layer—that $\mathsf{f}_{\rm p}^{(0)}\phi_{\rm p}$ is then proportional to $\mathsf{f}_{\rm p}^{(0)}$ so that $\phi_{\rm p}$ must be a constant. But this constant *must then be zero* since $\lim_{\zeta\to+\infty}\mathsf{f}_{\rm p}^{(0)}=f_{\rm g}^{(0)}$, keeping in mind that $\mathrm{w}_{\rm p}$ goes to zero as $\zeta\to\infty$ and that $f_{\rm g}^{(0)}$ is nonzero.

The right hand side of (138) may then be decomposed in the form

$$\Psi_i^{(1)}=\Psi_{i,\rm ev}^{(1)}+\Psi_{i,\rm od}^{(1)},\qquad i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}.$$

where

$$\Psi_{i,\rm ev}^{(1)}=\frac{\mathcal{C}_i^{(0)}}{\mathsf{f}_i^{(0)}}-\partial_t\log\mathsf{f}_i^{(0)},\qquad \Psi_{i,\rm od}^{(1)}=-\boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\log\mathsf{f}_i^{(0)},$$

are respectively even and odd functions of the tangential velocity $\boldsymbol{c}_{i\shortparallel}$. The solution $\Phi_i^{(1)}$ may thus be written

$$\Phi_i^{(1)}=\Phi_{i,\rm ev}^{(1)}+\Phi_{i,\rm od}^{(1)},\qquad i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}.\tag{141}$$

where

$$\mathcal{H}_i(\Phi_{i,\rm ev}^{(1)})=\Psi_{i,\rm ev}^{(1)},\qquad \mathcal{H}_i(\Phi_{i,\rm od}^{(1)})=\Psi_{i,\rm od}^{(1)}.\tag{142}$$

The distributions $\mathsf{f}_{i,\rm ev}^{(1)}=\mathsf{f}_i^{(0)}\Phi_{i,\rm ev}^{(1)}$ and $\mathsf{f}_{i,\rm od}^{(1)}=\mathsf{f}_i^{(0)}\Phi_{i,\rm od}^{(1)}$ are respectively even and odd in the tangential velocity $\boldsymbol{c}_{i\shortparallel}$ and the Enskog constraint reduces to $\int\mathsf{f}_i^{(0)}\Phi_{i,\rm ev}^{(1)}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta=0$ since that for $\Phi_{i,\rm od}^{(1)}$ is automatically satisfied. Moreover, at both sides $\zeta=\zeta_i^-$ and $\zeta=\zeta_i^+$ the distributions $\mathsf{f}_{i,\rm ev}^{(1)}$ and $\mathsf{f}_{i,\rm od}^{(1)}$ must go to zero.

### E. Tangential surface diffusion

We investigate in this section the species molar fluxes associated with surface tangential diffusion

$$\widetilde{\boldsymbol{F}}_{i\shortparallel}=\epsilon\int\mathsf{f}_i^{(1)}\boldsymbol{c}_{i\shortparallel}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta=\epsilon\int\mathsf{f}_i^{(0)}\Phi_{i,\rm od}^{(1)}\,\boldsymbol{c}_{i\shortparallel}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta,$$

where $i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}$. These fluxes are required prior to investigating surface species fluid boundary conditions. We consider the coupled system of equations associated with the chemisorbate and free site species and denote by $\mathfrak{S}$ the corresponding indexing set $\mathfrak{S}=\{\mathrm{c},\mathrm{s}\}$. The bulk species—constrained to follow the chemisorbed species—uncouples and will be examined separately later.

A remarkable point of monolayer crystal surfaces is that the total species number per unit surface is constant $\sum_{i\in\mathfrak{S}}\widetilde{n}_i=\widetilde{n}_\sigma$ from the lattice structure of the crystal. There is then a corresponding constraint stating that the total surface molar flux vanish [59, 60]

$$\sum_{i\in\mathfrak{S}}\widetilde{\boldsymbol{F}}_{i\shortparallel}=\epsilon\sum_{i\in\mathfrak{S}}\int\mathsf{f}_i^{(0)}\Phi_{i,\rm od}^{(1)}\,\boldsymbol{c}_{i\shortparallel}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta=0.\tag{143}$$

This constraint is analogous to the usual mass conservation constraint between mass fluxes in a multicomponent mixture and is naturally associated here to the fixed total number of crystal atom on the surface. It is thus natural to define diffusion velocities $\widetilde{\boldsymbol{W}}_{i\shortparallel}$ with respect to the molar velocity

$$\widetilde{\boldsymbol{W}}_{i\shortparallel}=\frac{\epsilon}{\widetilde{n}_i}\int\mathsf{f}_i^{(0)}\Phi_{i,\rm od}^{(1)}\boldsymbol{c}_{i\shortparallel}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta-\frac{\epsilon}{\widetilde{n}}\sum_{j\in\mathfrak{S}}\int\mathsf{f}_j^{(0)}\Phi_{j,\rm od}^{(1)}\boldsymbol{c}_{j\shortparallel}\mathrm{d}\boldsymbol{c}_j\mathrm{d}\zeta,\tag{144}$$

and the diffusion fluxes as $\widetilde{\boldsymbol{F}}_{i\shortparallel}=\widetilde{n}_i\widetilde{\boldsymbol{W}}_{i\shortparallel}$. We may then use the formalism developped by Waldmann for molar based diffusion transport presented in Appendix A and adapted to the situation of thin layers *mutatis mutandis*.

The kinetic equations are written using the vector operator

$$\mathcal{H}=(\mathcal{H}_{\rm c},\mathcal{H}_{\rm s})^t,\tag{145}$$

acting on pairs of perturbed distribution functions $\Phi_{\rm od}^{(1)}=(\Phi_{\rm c,od}^{(1)},\Phi_{\rm s,od}^{(1)})^t$. The right hand side is in the form $\Psi_{\rm od}^{(1)}=(\Psi_{\rm c,od}^{(1)},\Psi_{\rm s,od}^{(1)})^t$ and from $\mathsf{f}_i^{(0)}=\widetilde{n}_i\,\widetilde{\mathrm{m}}_i$ where $\widetilde{n}_i$ is the surface concentration of the $i$th species, we obtain that

$$\Psi_{i,\rm od}^{(1)}=-\boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\log\mathsf{f}_i^{(0)}=-\boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\log\widetilde{n}_i=-\boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\log\widetilde{p}_i,$$

where $\widetilde{p}_i=\widetilde{n}_i k_{\rm B}T_{\rm w}$ denotes the surface partial pressure of the $i$th species. Denoting by $\widetilde{p}=\sum_{l\in\mathfrak{S}}\widetilde{p}_l$ the total surface pressure—that remains constant—and $\widetilde{\mathsf{x}}_i=\widetilde{p}_i/\widetilde{p}$ the surface mole fraction of the $i$th species, we may then write that

$$\Psi_{i,\rm od}^{(1)}=-\widetilde{p}\sum_{l\in\mathfrak{S}}\frac{1}{\widetilde{p}_i}\boldsymbol{c}_{i\shortparallel}\cdot\widetilde{\boldsymbol{d}}_l\,\delta_{il},$$

where the species surface diffusion driving forces are given by

$$\widetilde{\boldsymbol{d}}_i=\boldsymbol{\partial}_{\shortparallel}\widetilde{\mathsf{x}}_i,\qquad i\in\mathfrak{S},\tag{146}$$

and are constrained by the relation

$$\sum_{l\in\mathfrak{S}}\widetilde{\boldsymbol{d}}_l=0.$$

Adapting the formalism of Waldmann, the right hand side is rewritten in the form

$$\Psi_{\rm od}^{(1)}=-\widetilde{p}\sum_{l\in\mathfrak{S}}\Psi^{(1),l}\cdot\widetilde{\boldsymbol{d}}_l,$$

where $\Psi^{(1),l}=(\Psi_i^{(1),l})_{i\in\mathfrak{S}}$ and

$$\Psi_i^{(1),l}=\frac{1}{\widetilde{p}_i}(\delta_{il}-\widetilde{\mathsf{x}}_i)\boldsymbol{c}_{i\shortparallel}.$$

Denoting by $\Phi^{(1),l}$ the solution to the integral equations

$$\mathcal{H}(\Phi^{(1),l}) = \Psi^{(1),l},$$

with the boundary conditions $\lim_{\zeta\to\zeta_i^-} \mathsf{f}_i^{(0)}\Phi_i^{(1),l} = 0$ and $\lim_{\zeta\to\zeta_i^+} \mathsf{f}_i^{(0)}\Phi_i^{(1),l} = 0$, the molar diffusion velocities are then obtained in the form

$$\widetilde{\boldsymbol{W}}_{i\shortparallel} = -\sum_{l\in\mathfrak{S}}\Big\{\frac{\epsilon\widetilde{p}}{\widetilde{n}_i}\int \mathsf{f}_i^{(0)}\boldsymbol{c}_{i\shortparallel}\otimes\Phi_i^{(1),l}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta - \sum_{j\in\mathfrak{S}}\frac{\epsilon\widetilde{p}}{\widetilde{n}}\int \boldsymbol{c}_{j\shortparallel}\mathsf{f}_j^{(0)}\otimes\Phi_j^{(1),l}\,\mathrm{d}\boldsymbol{c}_j\mathrm{d}\zeta\Big\}\widetilde{\boldsymbol{d}}_l. \tag{147}$$

The particle tangential velocities $\boldsymbol{c}_{i\shortparallel}$ being two-dimensional vectors, the right hand sides $\Psi_i^{(1),l}$, the perturbed distributions $\Phi_i^{(1),l}$, the tangential fluxes $\widetilde{\boldsymbol{F}}_{i\shortparallel}$ and velocities $\widetilde{\boldsymbol{W}}_{i\shortparallel}$ are also two-dimensional vectors. We may now use the tangential isotropy of the operator $\mathcal{H}$ to deduce that the vector $\Phi_i^{(1),l}$ is necessarily proportional to the vector $\boldsymbol{c}_{i\shortparallel}$ with a coefficient that is scalar function of the scalar invariant $|\boldsymbol{c}_{i\shortparallel}|^2$ and this implies the isotropy relation

$$\int \mathsf{f}_i^{(0)}\boldsymbol{c}_{i\shortparallel}\otimes\Phi_i^{(1),l}\mathrm{d}\boldsymbol{c}_i = \frac{1}{2}\int \mathsf{f}_i^{(0)}\boldsymbol{c}_{i\shortparallel}\cdot\Phi_i^{(1),l}\mathrm{d}\boldsymbol{c}_i\widetilde{\boldsymbol{I}},$$

where $\widetilde{\boldsymbol{I}}$ is the identity tensor in the two-dimensional tangential plane. This relation is analogous to that traditionally obtained for isotropic gas mixtures in three dimensional velocity spaces [9, 38, 39]. We thus obtain the diffusion velocities in the form

$$\widetilde{\boldsymbol{W}}_{i\shortparallel} = -\sum_{l\in\mathfrak{S}}\epsilon\widetilde{D}_{il}\widetilde{\boldsymbol{d}}_l, \tag{148}$$

where the surface multicomponent diffusion coefficients are given by

$$\widetilde{D}_{il} = \frac{\widetilde{p}}{2\widetilde{n}_i}\int \mathsf{f}_i^{(0)}\Phi_i^{(1),l}\cdot\boldsymbol{c}_{i\shortparallel}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta - \frac{\widetilde{p}}{2\widetilde{n}}\sum_{j\in\mathfrak{S}}\int \mathsf{f}_j^{(0)}\Phi_j^{(1),l}\cdot\boldsymbol{c}_{j\shortparallel}\,\mathrm{d}\boldsymbol{c}_j\mathrm{d}\zeta, \qquad i,l\in\mathfrak{S}.$$

Since the relaxation times $\tau_{i,\mathrm{ph}}$ are independent of $\zeta$ and of $c_{iz}$, the solutions $\Phi^{(1),l}$, $l\in\mathfrak{S}$, are further found in the explicit form

$$\Phi_i^{(1),l} = \tau_{i,\mathrm{ph}}\frac{1}{\widetilde{p}_i}(\delta_{il}-\widetilde{\mathsf{x}}_i)\boldsymbol{c}_{i\shortparallel}, \qquad i,l\in\mathfrak{S}. \tag{149}$$

After some algebra, the surface tangential diffusion matrix $\widetilde{D} = (\widetilde{D}_{il})_{i,l\in\mathfrak{S}}$ is found to be

$$\widetilde{D} = D^{\shortparallel}\begin{pmatrix} \widetilde{\mathsf{x}}_{\mathrm{s}}/\widetilde{\mathsf{x}}_{\mathrm{c}} & -1 \\ -1 & \widetilde{\mathsf{x}}_{\mathrm{c}}/\widetilde{\mathsf{x}}_{\mathrm{s}}\end{pmatrix}, \tag{150}$$

with an effective molar diffusion coefficient $D^{\shortparallel}$ of the surface binary mixture $D^{\shortparallel}$ given by

$$D^{\shortparallel} = \widetilde{\mathsf{x}}_{\mathrm{c}}D_{\mathrm{s}}^{\shortparallel} + \widetilde{\mathsf{x}}_{\mathrm{s}}D_{\mathrm{c}}^{\shortparallel}, \tag{151}$$

where $D_i^{\shortparallel}$ denotes the surface diffusion coefficient of the $i$th species associated with phonon interactions

$$D_i^{\shortparallel} = \frac{k_{\mathrm{B}}T_{\mathrm{w}}}{m_i}\tau_{i,\mathrm{ph}}, \qquad i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}, \tag{152}$$

that is directly proportional to the relaxation time $\tau_{i,\mathrm{ph}}$. The matrix $\widetilde{D}$ is symmetric $\widetilde{D} = \widetilde{D}^t$ and such that $\widetilde{D}\widetilde{\mathsf{x}} = 0$ where $\widetilde{\mathsf{x}} = (\widetilde{\mathsf{x}}_{\mathrm{c}},\widetilde{\mathsf{x}}_{\mathrm{s}})^t$ denotes the mole fraction vector, in agreement with the theory. The relation $\widetilde{D}\widetilde{\mathsf{x}} = 0$ implies in particular the natural constraint (143) between the tangential fluxes $\sum_{i\in\mathfrak{S}}\widetilde{\boldsymbol{F}}_{i\shortparallel} = \sum_{i\in\mathfrak{S}}\widetilde{n}_i\widetilde{\boldsymbol{W}}_{i\shortparallel} = 0$.

In addition, since the bulk species $\mathcal{C}(\mathrm{b})$ is by definition following the chemisorbed species, we must also have $D_{\mathrm{c}}^{\shortparallel} = D_{\mathrm{b}}^{\shortparallel}$ and this yields the natural constraint $\tau_{\mathrm{b,ph}}/m_{\mathrm{b}} = \tau_{\mathrm{c,ph}}/m_{\mathrm{c}}$. Considering the system constituted by the chemisorbed species and the bulk species also yields that the bulk species is diffusing exactly like the chemisorbed species with $\widetilde{\mathsf{x}}_{\mathrm{b}} = \widetilde{\mathsf{x}}_{\mathrm{c}}$ and $\widetilde{\boldsymbol{W}}_{\mathrm{b}\shortparallel} = \widetilde{\boldsymbol{W}}_{\mathrm{c}\shortparallel}$.

The advantage of the preceeding formalism is that it fully applies to multicomponent mixtures. However, since we are considering a binary mixture, the diffusion fluxed may be further simplified by using $\boldsymbol{\partial}_{\shortparallel}\widetilde{\mathsf{x}}_{\mathrm{c}} = -\boldsymbol{\partial}_{\shortparallel}\widetilde{\mathsf{x}}_{\mathrm{s}}$ and $\boldsymbol{\partial}_{\shortparallel}\widetilde{\mathsf{x}}_{\mathrm{b}} = -\boldsymbol{\partial}_{\shortparallel}\widetilde{\mathsf{x}}_{\mathrm{s}}$. From (148) and (150), the resulting effective tangential mass fluxes $\widetilde{\boldsymbol{F}}_{i\shortparallel} = \widetilde{n}_i\widetilde{\boldsymbol{W}}_{i\shortparallel}$ are finally in the form

$$\widetilde{\boldsymbol{F}}_{i\shortparallel} = \epsilon\int \boldsymbol{c}_{i\shortparallel}\mathsf{f}_i^{(1)}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta = -\epsilon D^{\shortparallel}\partial_{\shortparallel}\widetilde{n}_i, \qquad i\in\{\mathrm{c},\mathrm{s},\mathrm{b}\}, \tag{153}$$

with $D^{\shortparallel}$ given by (151). Incidentally, the diffusion velocity of the chemisorbate may also be expressed in terms of the gradient of the modified surface chemical potential $\widetilde{\mu}_{\mathrm{c}}$ since $\boldsymbol{\partial}_{\shortparallel}\widetilde{\mu}_{\mathrm{c}}$ is proportional to $\boldsymbol{\partial}_{\shortparallel}\widetilde{\mathsf{x}}_{\mathrm{c}}$.

The relations (153), (151), and (152) expressing the diffusion fluxes and the surface diffusion coefficients show that surface diffusion is due to the interaction with phonons. This is a natural results since surface diffusion and volume diffusion in solids are consequences of thermal agitation [47, 48] and thermal agitation is represented by the interaction with phonons in the model.

### F. Layer-averaged kinetic equation

We investigate in this section *layer-averaged* or *partially integrated* kinetic equations for the surface species.

The layer-averaged zeroth order densities are defined by

$$\widetilde{\mathsf{f}}_i^{(0)} = \int \mathsf{f}_i^{(0)} \mathrm{d}c_{iz}\mathrm{d}\zeta, \qquad i \in \{\mathrm{c},\mathrm{s},\mathrm{b}\},$$

and the layer-averaged odd perturbed distributions $\Phi_{i,\mathrm{od}}^{(1)}$ as

$$\widetilde{\Phi}_{i,\mathrm{od}}^{(1)} = \frac{1}{\widetilde{\mathsf{f}}_i^{(0)}} \int \mathsf{f}_i^{(0)} \Phi_{i,\mathrm{od}}^{(1)} \mathrm{d}c_{iz}\mathrm{d}\zeta, \qquad i \in \{\mathrm{c},\mathrm{s},\mathrm{b}\}.$$

Since the relaxation times for the surface species are independent of $c_{iz}$ and $\zeta$, we may then define the $i$th layer-averaged kinetic operator $\widetilde{\mathcal{H}}_i$ as

$$\widetilde{\mathcal{H}}_i(\widetilde{\varphi}) = \frac{1}{\tau_{i,\mathrm{ph}}}\Big(\widetilde{\varphi} - \int \widetilde{\varphi}\, \widetilde{\mathrm{M}}_i \mathrm{d}\boldsymbol{c}_{i\shortparallel}\Big), \qquad i \in \{\mathrm{c},\mathrm{s},\mathrm{b}\},$$

where $\widetilde{\mathrm{M}}_i$ is the tangential two-dimentional Maxwellian of the $i$th species, and the layer-averaged perturbed distributions $\widetilde{\Phi}_{i,\mathrm{od}}^{(1)}$ then satisfy the kinetic equations

$$\widetilde{\mathcal{H}}_i(\widetilde{\Phi}_{i,\mathrm{od}}^{(1)}) = \widetilde{\Psi}_{i,\mathrm{od}}^{(1)}, \qquad i \in \{\mathrm{c},\mathrm{s},\mathrm{b}\}, \tag{154}$$

where

$$\widetilde{\Psi}_{i,\mathrm{od}}^{(1)} = -\boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel} \log \widetilde{\mathsf{f}}_i^{(0)}, \qquad i \in \{\mathrm{c},\mathrm{s},\mathrm{b}\}.$$

These equations are directly obtained by multiplying $\mathcal{H}_i(\Phi_{i,\mathrm{od}}^{(1)}) = \Psi_{i,\mathrm{od}}^{(1)}$ by $\mathsf{f}_i^{(0)}$, partially integrating the resulting kinetic equations with $\mathrm{d}c_{iz}\mathrm{d}\zeta$, and then dividing by $\widetilde{\mathsf{f}}_i^{(0)}$. Letting then $\widetilde{\Phi}_{\mathrm{od}}^{(1)} = (\widetilde{\Phi}_{i,\mathrm{od}}^{(1)})_{i\in\mathfrak{S}}$, $\widetilde{\mathcal{H}} = (\widetilde{\mathcal{H}}_i)_{i\in\mathfrak{S}}$, and $\widetilde{\Psi}_{\mathrm{od}}^{(1)} = (\widetilde{\Psi}_{i,\mathrm{od}}^{(1)})_{i\in\mathfrak{S}}$, we obtain $\widetilde{\mathcal{H}}(\widetilde{\Phi}_{\mathrm{od}}^{(1)}) = \widetilde{\Psi}_{\mathrm{od}}^{(1)}$.

These layer-averaged kinetic equation (154) may be used whenever one wants to obtain the layer-averaged distribution $\widetilde{\Phi}_{i,\mathrm{od}}^{(1)}$ or any of its moment with respect to the tangential velocity $\boldsymbol{c}_{i\shortparallel}$. The tangential diffusion fluxes in particular may be expressed as

$$\widetilde{\boldsymbol{F}}_{i\shortparallel} = \epsilon \int \widetilde{\mathsf{f}}_i^{(0)} \widetilde{\Phi}_{i,\mathrm{od}}^{(1)}\, \boldsymbol{c}_{i\shortparallel} \mathrm{d}\boldsymbol{c}_{i\shortparallel}, \qquad i \in \{\mathrm{c},\mathrm{s},\mathrm{b}\}.$$

The Waldmann formalism for the surface kinetic equation also leads to

$$\widetilde{\Psi}_{\mathrm{od}}^{(1)} = -\widetilde{p} \sum_{l\in\mathfrak{S}} \widetilde{\Psi}_{\mathrm{od}}^{(1),l} \cdot \widetilde{\boldsymbol{d}}_l,$$

where $\widetilde{\Psi}_{\mathrm{od}}^{(1),l} = (\widetilde{\Psi}_{i,\mathrm{od}}^{(1),l})_{i\in\mathfrak{S}}$ and

$$\widetilde{\Psi}_{i,\mathrm{od}}^{(1),l} = \frac{1}{\widetilde{p}_i}(\delta_{il} - \widetilde{\mathsf{x}}_i)\boldsymbol{c}_{i\shortparallel}.$$

The solutions $\widetilde{\Phi}_{\mathrm{od}}^{(1),l}$ to the integral equations

$$\widetilde{\mathcal{H}}(\widetilde{\Phi}_{\mathrm{od}}^{(1),l}) = \widetilde{\Psi}_{\mathrm{od}}^{(1),l},$$

are found in the explicit form

$$\widetilde{\Phi}_{i,\mathrm{od}}^{(1),l} = \tau_{i,\mathrm{ph}} \frac{1}{\widetilde{p}_i}(\delta_{il} - \widetilde{\mathsf{x}}_i)\boldsymbol{c}_{i\shortparallel}, \qquad i,l \in \mathfrak{S}.$$

The tangential velocities may also be written

$$\widetilde{\boldsymbol{W}}_{i\shortparallel} = \frac{\epsilon}{\widetilde{n}_i} \int \widetilde{\mathsf{f}}_i^{(0)} \widetilde{\Phi}_{i,\mathrm{od}}^{(1)} \boldsymbol{c}_{i\shortparallel} \mathrm{d}\boldsymbol{c}_{i\shortparallel} - \frac{\epsilon}{\widetilde{n}} \sum_{j\in\mathfrak{S}} \int \widetilde{\mathsf{f}}_j^{(0)} \widetilde{\Phi}_{j,\mathrm{od}}^{(1)} \boldsymbol{c}_{j\shortparallel} \mathrm{d}\boldsymbol{c}_{j\shortparallel}, \tag{155}$$

and from the isotropy of the layer-averaged operator, we recover the molar diffusion velocities from (148) and the diffusion coefficients

$$\begin{aligned}\widetilde{D}_{il} =& \frac{\widetilde{p}}{2\widetilde{n}_i} \int \widetilde{\mathsf{f}}_i^{(0)} \widetilde{\Phi}_{i,\mathrm{od}}^{(1),l} \cdot \boldsymbol{c}_{i\shortparallel}\, \mathrm{d}\boldsymbol{c}_{i\shortparallel} \\ &- \frac{\widetilde{p}}{2\widetilde{n}} \sum_{j\in\mathfrak{S}} \int \widetilde{\mathsf{f}}_j^{(0)} \widetilde{\Phi}_{j,\mathrm{od}}^{(1),l} \cdot \boldsymbol{c}_{j\shortparallel}\, \mathrm{d}\boldsymbol{c}_{j\shortparallel},\end{aligned}$$

and all the results of the previous section are elegantly recovered with the layer-averaged kinetic equations.

It is then possible to introduce a *surface bracket operator* acting on pairs $\widetilde{\Phi} = (\widetilde{\Phi}_i)_{i\in\mathfrak{S}}$ and $\widetilde{\Phi}' = (\widetilde{\Phi}'_i)_{i\in\mathfrak{S}}$, where $\widetilde{\Phi}_i$ and $\widetilde{\Phi}'_i$ are functions of $\boldsymbol{c}_{i\shortparallel}$, in the form

$$[\![\widetilde{\Phi}, \widetilde{\Phi}']\!] = \sum_{i\in\mathfrak{S}} \int \widetilde{\mathsf{f}}_i^{(0)} \widetilde{\mathcal{H}}_i(\widetilde{\Phi}_i) \odot \widetilde{\Phi}'_i \mathrm{d}\boldsymbol{c}_{i\shortparallel}. \tag{156}$$

The surface bracket operator is also symmetric $[\![\widetilde{\Phi}, \widetilde{\Phi}']\!] = [\![\widetilde{\Phi}', \widetilde{\Phi}]\!]$, positive semi-definite $[\![\widetilde{\Phi}, \widetilde{\Phi}]\!] \geq 0$, and its kernel is spanned by constants. It is then obtained after some algebra that

$$\widetilde{D}_{il} = \frac{k_{\mathrm{B}} T_{\mathrm{w}} \widetilde{p}}{2} [\![\widetilde{\Phi}_{\mathrm{od}}^{(1),i}, \widetilde{\Phi}_{\mathrm{od}}^{(1),l}]\!],$$

so that the two-dimensional surface formalism for layer averaged quantities is entirely similar to that of gas mixtures in three dimensions mutatis mutandis.

### G. Physisorbate mass boundary condition

The first order accurate mass conservation equation, obtained by taking the scalar product of the difference kinetic equation (88) with the mass collisional invariant $\psi_{\mathrm{p}}^1 = 1$ and keeping zeroth *and* first order terms, is in the form

$$\partial_t \int (\mathsf{f}_{\rm p}^{(0)} - \mathsf{f}_{\rm g}^{(0)}) {\rm d}\boldsymbol{c}_{\rm p} + \partial_t \int \epsilon (\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}) {\rm d}\boldsymbol{c}_{\rm p} + \boldsymbol{\partial}_{\shortparallel} \cdot \int \epsilon \boldsymbol{c}_{{\rm p}\shortparallel} (\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}) {\rm d}\boldsymbol{c}_{\rm p} + \partial_\zeta \int c_{{\rm p}z} (\mathsf{f}_{\rm p}^{(1)} + \epsilon \mathsf{f}_{\rm p}^{(2)} - \mathsf{f}_{\rm g}^{(1)} - \epsilon \mathsf{f}_{\rm g}^{(2)}) {\rm d}\boldsymbol{c}_{\rm p} = \int \mathcal{C}_{\rm p}^{(0)} {\rm d}\boldsymbol{c}_{\rm p}.$$

Use has been made of $\int \boldsymbol{c}_{\rm p}\, \mathsf{f}_{\rm p}^{(0)}\, {\rm d}\boldsymbol{c}_{\rm p} = \int \boldsymbol{c}_{\rm p}\, \mathsf{f}_{\rm g}^{(0)} {\rm d}\boldsymbol{c}_{\rm p} = 0$ and that the chemical term $\mathcal{C}_{\rm p}^{(0)}$ is already of first order since $\mathsf{a} = 1$. The order of magnitude of the contributions in the above equation must be investigated in order to obtain the effective boundary condition.

The zeroth time derivative term is in the form

$$\partial_t \int (\mathsf{f}_{\rm p}^{(0)} - \mathsf{f}_{\rm g}^{(0)}) {\rm d}\boldsymbol{c}_{\rm p} = \partial_t n_{\rm g}(0) \Big\{ \exp\Big( - \frac{{\rm W}_{\rm p}}{k_{\rm B} T_{\rm w}} \Big) - 1 \Big\},$$

and may be rewritten using the total mass conservation equation in the gas. Since it has been established that $\partial_t n_{\rm g}(0)$ is $\mathcal{O}(\epsilon)$ this term is already of first order in $\epsilon$. Concerning the other time derivative term $\epsilon \partial_t \int (\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}) {\rm d}\boldsymbol{c}_{\rm p}$ we note that

$$\partial_t (\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}) = \mathsf{f}_{\rm p}^{(0)} \partial_t (\Phi_{\rm p}^{(1)} - \Phi_{\rm g}^{(1)}) + (\mathsf{f}_{\rm p}^{(0)} - \mathsf{f}_{\rm g}^{(0)}) \partial_t \Phi_{\rm g}^{(1)} + \partial_t \log n_{\rm g}^{(0)} (\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}),$$

where $\mathsf{f}_{\rm g}^{(1)}$ and $\Phi_{\rm g}^{(1)}$ are associated with the gas distribution inner expansion $\mathsf{f}_{\rm g}$ and have been defined in Section III E. Moreover, we have $\partial_t \log n_{\rm g}^{(0)} = \mathcal{O}(\epsilon)$, and since $\mathsf{a} = 1$ we also have $\overline{v}_{{\rm g}z} = \mathcal{O}(\epsilon)$, $\phi_{\rm g}^{(1)} = \mathcal{O}(\epsilon)$ so that $\partial_t \overline{v}_{{\rm g}z} = \mathcal{O}(\epsilon)$, $\partial_t \phi_{\rm g}^{(1)} = \mathcal{O}(\epsilon)$, and $\partial_t \Phi_{\rm g}^{(1)} = \mathcal{O}(\epsilon)$. In order to establish that $\partial_t (\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}) = \mathcal{O}(\epsilon)$, it is thus sufficient to establish that $\partial_t \Phi_{\rm p}^{(1)} - \partial_t \Phi_{\rm g}^{(1)} = \mathcal{O}(\epsilon)$. To this aim, we first note that

$$\mathcal{H}_{\rm p} (\Phi_{\rm p}^{(1)} - \Phi_{\rm g}^{(1)}) = \Psi_{\rm p}^{(1)} - \Psi_{\rm g}^{(1)} - (\mathcal{H}_{\rm p} - \mathcal{H}_{\rm g})(\Phi_{\rm g}^{(1)}),$$

where $\Psi_{\rm g}^{(1)}$ and $\mathcal{H}_{\rm g}$ have been defined in Section III E. Differentiating this relation with respect to time, we obtain that

$$\mathcal{H}_{\rm p} (\partial_t \Phi_{\rm p}^{(1)} - \partial_t \Phi_{\rm g}^{(1)}) = \partial_t \Psi_{\rm p}^{(1)} - \partial_t \Psi_{\rm g}^{(1)} - (\mathcal{H}_{\rm p} - \mathcal{H}_{\rm g})(\partial_t \Phi_{\rm g}^{(1)}), \tag{157}$$

keeping in mind that the adsorbate is isotherm. However we have $\partial_t \Psi_{\rm p}^{(1)} = \mathcal{O}(\epsilon)$ and $\partial_t \Psi_{\rm g}^{(1)} = \mathcal{O}(\epsilon)$ since $\partial_t \mathcal{C}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$, $\partial_t \mathsf{f}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$, $\boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$, $\partial_t^2 \mathsf{f}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$ and $\partial_t \boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$. Moreover, $\partial_t \Phi_{\rm p}^{(1)} - \partial_t \Phi_{\rm g}^{(1)}$ goes to zero as $\zeta \to \infty$ and its limit as $\zeta \to 0$ is $-\partial_t \Phi_{\rm g}^{(1)}$ that is also $\mathcal{O}(\epsilon)$. Therefore, as the solution of (157), the difference $\partial_t \Phi_{\rm p}^{(1)} - \partial_t \Phi_{\rm g}^{(1)}$ is also $\mathcal{O}(\epsilon)$ and $\epsilon \partial_t \int (\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}) {\rm d}\boldsymbol{c}_{\rm p}$ is thus of second order.

The zeroth order tangential flux vanish

$$\int \boldsymbol{c}_{{\rm p}\shortparallel} (\boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\rm p}^{(0)} - \boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\rm g}^{(0)}) {\rm d}\boldsymbol{c}_{\rm p} = 0,$$

and concerning the first order tangential flux $\epsilon \boldsymbol{c}_{{\rm p}\shortparallel} (\boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\rm p}^{(1)} - \boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\rm g}^{(1)}) {\rm d}\boldsymbol{c}_{\rm p}$ we note that

$$\mathcal{H}_{\rm p} (\boldsymbol{\partial}_{\shortparallel} \Phi_{\rm p}^{(1)} - \boldsymbol{\partial}_{\shortparallel} \Phi_{\rm g}^{(1)}) = \boldsymbol{\partial}_{\shortparallel} \Psi_{\rm p}^{(1)} - \boldsymbol{\partial}_{\shortparallel} \Psi_{\rm g}^{(1)} - (\mathcal{H}_{\rm p} - \mathcal{H}_{\rm g})(\boldsymbol{\partial}_{\shortparallel} \Phi_{\rm g}^{(1)}),$$

and we may argue in a similar way as for time derivative terms, using that $\boldsymbol{\partial}_{\shortparallel} \Psi_{\rm p}^{(1)} = \mathcal{O}(\epsilon)$, $\boldsymbol{\partial}_{\shortparallel} \Psi_{\rm g}^{(1)} = \mathcal{O}(\epsilon)$, and $\boldsymbol{\partial}_{\shortparallel} \Phi_{\rm g}^{(1)} = \mathcal{O}(\epsilon)$ from $\boldsymbol{\partial}_{\shortparallel} \mathcal{C}_{\rm p}^{(0)} = \mathcal{O}(\epsilon)$, $\boldsymbol{\partial}_{\shortparallel} \overline{v}_{{\rm g}z} = \mathcal{O}(\epsilon)$, and $\boldsymbol{\partial}_{\shortparallel} T_{\rm g} = \boldsymbol{\partial}_{\shortparallel} T_{\rm w} = \mathcal{O}(\epsilon)$, in order to establish that $\boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\rm p}^{(1)} - \boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\rm g}^{(1)} = \mathcal{O}(\epsilon)$ so that the term $\epsilon \boldsymbol{\partial}_{\shortparallel} \int \boldsymbol{c}_{{\rm p}\shortparallel} (\mathsf{f}_{\rm p}^{(1)} - \mathsf{f}_{\rm g}^{(1)}) {\rm d}\boldsymbol{c}_{\rm p}$ is of second order.

We next have to investigate the contributions arising from the normal derivative terms $\partial_\zeta \int c_{{\rm p}z} (\mathsf{f}_{\rm p}^{(1)} + \epsilon \mathsf{f}_{\rm p}^{(2)} - \mathsf{f}_{\rm g}^{(1)} - \epsilon \mathsf{f}_{\rm g}^{(2)}) {\rm d}\boldsymbol{c}_{\rm p}$ that may directly be integrated over $(0, \infty)$ and yields the integral

$$\int c_{{\rm p}z} \big( f_{\rm g}^{(1)}(0) + \epsilon f_{\rm g}^{(2)}(0) \big) {\rm d}\boldsymbol{c}_{\rm p},$$

since the integrand goes to zero as $\zeta \to +\infty$, goes to $-\big( f_{\rm g}^{(1)}(0) + \epsilon f_{\rm g}^{(2)}(0) \big)$ as $\zeta \to 0$. We then note that $\epsilon f_{\rm g}^{(2)}$ is of higher order and that so that only $f_{\rm g}^{(1)}$ contributes as for the zeroth order situation.

Collecting previous results, and integrating over ${\rm d}z = \epsilon {\rm d}\zeta$, the first order accurate fluid boundary condition for the physisorbate is finally obtained in the form

$$\partial_z \big( n_{\rm g} v_{{\rm g}z} \big)(0) \int \Big\{ 1 - \exp\Big( - \frac{{\rm W}_{\rm p}}{k_{\rm B} T_{\rm w}} \Big) \Big\} {\rm d}z + \big( n_{\rm g} v_{{\rm g}z} \big)(0) = \int \mathcal{C}_{\rm p}^{(0)} {\rm d}\boldsymbol{c}_{\rm p} {\rm d}z. \tag{158}$$

The difference with the less accurate version (110) is thus in the normal derivative term of the Stefan flux. We have therefore obtained a robin—mixed derivative—law for the Stefan normal flux $n_{\rm g} v_{{\rm g}z}$ at $z = 0$ that is new to the best of the authors' knowledge. This law may be termed Navier-Stefan law since it uses a Navier type relation in order to express the Stefan flux.

### H. Surface species mass boundary conditions

For the surface species, it is obtained at first order accuracy that

$$\partial_t \int (\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)}) \mathrm{d}\boldsymbol{c}_i + \boldsymbol{\partial}_{\shortparallel} \cdot \int \boldsymbol{c}_{i\shortparallel} \, (\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)})\big) \mathrm{d}\boldsymbol{c}_i + \partial_\zeta \int c_{iz} (\mathsf{f}_i^{(1)} + \epsilon \mathsf{f}_i^{(2)}) \mathrm{d}\boldsymbol{c}_i = \int \mathcal{C}_i^{(0)} \mathrm{d}\boldsymbol{c}_i,$$

where $i \in \{\mathrm{c}, \mathrm{s}\}$. The first time derivative term yields the contribution

$$\partial_t \int \mathsf{f}_i^{(0)} \mathrm{d}\boldsymbol{c}_i = \partial_t \overline{n}_i \, \exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big), \qquad i \in \{\mathrm{c}, \mathrm{s}, \mathrm{b}\},$$

and the other time derivative term $\partial_t \int \mathsf{f}_i^{(1)} \mathrm{d}\boldsymbol{c}_i$ yields a zero contribution when integrated over $\zeta$ from the natural Enskog constraint $\int \mathsf{f}_i^{(1)} \, \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta = 0$.

For the tangential derivative terms, we first note that $\int \boldsymbol{c}_{i\shortparallel} \mathsf{f}_i^{(0)} \mathrm{d}\boldsymbol{c}_i = 0$ whereas at first order, we may use (153) to get that $\epsilon \int \boldsymbol{c}_{i\shortparallel} \mathsf{f}_i^{(1)} \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta = -\epsilon D^{\shortparallel} \boldsymbol{\partial}_{\shortparallel} \widetilde{n}_i$ where $D^{\shortparallel} = \widetilde{\mathsf{x}}_{\mathrm{s}} D_{\mathrm{c}}^{\shortparallel} + \widetilde{\mathsf{x}}_{\mathrm{c}} D_{\mathrm{s}}^{\shortparallel}$ is the effective binary tangential surface diffusion coefficient. On the other hand, the normal derivatives terms do not contribute to the integral over $\zeta$ since there are no particles at the limits $\zeta \to \zeta_\sigma^-$ and $\zeta \to \zeta_\sigma^+$.

The overall mass conservation equation in the chemisorbate is obtained in the form

$$\partial_t \widetilde{n}_i - \epsilon \boldsymbol{\partial}_{\shortparallel} \cdot \big(D^{\shortparallel} \boldsymbol{\partial}_{\shortparallel} \widetilde{n}_i\big) = \int \mathcal{C}_i^{(0)} \mathrm{d}\boldsymbol{c}_i \mathrm{d}z, \qquad i \in \{\mathrm{c}, \mathrm{s}, \mathrm{b}\}, \tag{159}$$

and is the first order accurate version of (111). We have thus obtained a surface diffusion term due to the interaction with phonons. This is in agreement with statistical mechanics of surface diffusion or surface diffusion in solids that can be directly related to atom fluctuations and atom jumps of the crystal lattice [47, 48].

The overall mass conservation equation summed over the chemisorbed and the free sites then yields

$$\partial_t (\widetilde{n}_{\mathrm{c}} + \widetilde{n}_{\mathrm{s}}) - \epsilon \boldsymbol{\partial}_{\shortparallel} \cdot \big(D^{\shortparallel} \boldsymbol{\partial}_{\shortparallel} (\widetilde{n}_{\mathrm{c}} + \widetilde{n}_{\mathrm{s}})\big) = 0, \tag{160}$$

since $\int \mathcal{C}_{\mathrm{c}}^{(0)} \mathrm{d}\boldsymbol{c}_{\mathrm{c}} \mathrm{d}z + \int \mathcal{C}_{\mathrm{s}}^{(0)} \mathrm{d}\boldsymbol{c}_{\mathrm{s}} \mathrm{d}z = 0$. We thus recover that the local number of surface particles is the constant solution $\widetilde{n}_{\mathrm{c}} + \widetilde{n}_{\mathrm{s}} = \widetilde{n}_\sigma$.

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## VII. CONCLUSION

The kinetic model describing physisorption and chemisorption of gas particles on a solid surface introduced in this work may be extended is various directions. Adding bulk and surface phonon kinetic equations would allow to take into account variations of temperature in the crystal. Using a different scaling would also allow the surface to have its own temperature. The situation of polyatomic gases or mixtures of gases with complex surface reactions mechanisms that are commonly used in practical applications is also of high scientific interest.

The linearized first order equations associated with the physisorbate and the chemisorbate also lead to new half space integro-differential equations that have not been investigated. Multitemperature flows as well as state to state models also involve gas surface interactions of paramount importance for reentry and may be investigated using similar models and techniques. Finally, using a kinetic scaling instead of the fluid scaling used in this paper is also of high scientific interest.

### Appendix A: Molar multicomponent diffusion

Multicomponent diffusion fluxes and coefficients defined with respect to the molar averaged velocity have been investigated by Waldmann [58]. We summarize in this Appendix Waldmann's analysis and adapt it to the situation of tangential surface diffusion.

We consider a gas mixture constituted by N species and denote by $\boldsymbol{w}$ the molar average velocity

$$\boldsymbol{w} = \frac{1}{n} \sum_{i \in \mathfrak{S}} \int f_i \boldsymbol{c}_i \mathrm{d}\boldsymbol{c}_i, \tag{A1}$$

where $\mathfrak{S} = \{1, \ldots, \mathrm{N}\}$ denotes the species indexing set, N the number of species, $n_i$ the number density of the $i$th species, $n = \sum_{i \in \mathfrak{S}} n_i$ the mixture number density, $\boldsymbol{C}_i = \boldsymbol{c}_i - \boldsymbol{v}$ the reduced velocity, and $\boldsymbol{v}$ the usual mass average mixture velocity. The species diffusion velocities with respect to the mass average velocity $\boldsymbol{v}$ are defined as

$$\boldsymbol{V}_i = \frac{1}{n_i} \int f_i \boldsymbol{c}_i \mathrm{d}\boldsymbol{c}_i - \boldsymbol{v} = \frac{1}{n_i} \int f_i \boldsymbol{C}_i \mathrm{d}\boldsymbol{c}_i, \qquad i \in \mathfrak{S}, \tag{A2}$$

and those with respect to the mole average velocity $\boldsymbol{w}$ as

$$\boldsymbol{W}_i = \frac{1}{n_i} \int f_i \boldsymbol{c}_i \mathrm{d}\boldsymbol{c}_i - \boldsymbol{w}, \qquad i \in \mathfrak{S}. \tag{A3}$$

Denoting by $\mathsf{x}_i = n_i/n$ the mole fraction of the $i$th species, $\mathfrak{m}_i$ the particle mass of the $i$th species, $\rho_i = \mathfrak{m}_i n_i$ the partial density of the $i$th species, $\rho = \sum_{i \in \mathfrak{S}} \rho_i$ the total density of the mixture, $\mathsf{y}_i = \rho_i/\rho$ the mass fraction of the $i$th species, the following relations are easily established [58]

$$\boldsymbol{w} = \boldsymbol{v} + \sum_{i \in \mathfrak{S}} \mathsf{x}_i \boldsymbol{V}_i = \boldsymbol{v} + \frac{1}{n} \sum_{i \in \mathfrak{S}} \int f_i \boldsymbol{C}_i \mathrm{d}\boldsymbol{c}_i, \tag{A4}$$

$$\boldsymbol{W}_i = \boldsymbol{V}_i - \sum_{l\in\mathfrak{S}} \mathsf{x}_l \boldsymbol{V}_l$$
$$= \frac{1}{n_i}\int f_i \boldsymbol{C}_i \mathrm{d}\boldsymbol{c}_i - \frac{1}{n}\sum_{l\in\mathfrak{S}}\int f_l \boldsymbol{C}_l \mathrm{d}\boldsymbol{c}_l, \qquad \text{(A5)}$$

$$\boldsymbol{V}_i = \boldsymbol{W}_i - \sum_{l\in\mathfrak{S}} \mathsf{y}_l \boldsymbol{W}_l. \qquad \text{(A6)}$$

On the other hand, the system of integral equations associated with multicomponent diffusion may be written in the vector form [58]

$$\mathcal{I}(\phi^{(1)}) = \Psi^{(1)}, \qquad \text{(A7)}$$

where $\mathcal{I} = (\mathcal{I}_i)_{i\in\mathfrak{S}}$ denotes the linearized collision vector operator, $\mathcal{I}_i$ the linearized collision operator of the $i$th species, $\phi = (\phi_i^{(1)})_{i\in\mathfrak{S}}$ the family of perturbed distribution functions, $\phi_i^{(1)}$ the perturbed distribution function of the $i$th species, $\Psi^{(1)} = (\Psi_i^{(1)})_{i\in\mathfrak{S}}$ the right hand side with

$$\Psi_i^{(1)} = -\frac{1}{\mathsf{x}_i}\boldsymbol{C}_i\cdot\boldsymbol{d}_i, = -\sum_{l\in\mathfrak{S}}\frac{1}{\mathsf{x}_i}\boldsymbol{C}_i\cdot\boldsymbol{d}_l\delta_{il}, \qquad \text{(A8)}$$

and $\boldsymbol{d}_i$ the diffusion driving force of the $i$th species

$$\boldsymbol{d}_i = \boldsymbol{\partial}_{\boldsymbol{x}}\mathsf{x}_i + (\mathsf{x}_i - \mathsf{y}_i)\boldsymbol{\partial}_{\boldsymbol{x}}\log p. \qquad \text{(A9)}$$

The solution $\phi = (\phi_i^{(1)})_{i\in\mathfrak{S}}$ must also be orthogonal to the collision invariants of the multicomponent gas $\langle\!\langle f^{(0)}\phi, \psi^l\rangle\!\rangle = 0$ for $1 \le l \le \mathrm{N}+4$ where $\langle\!\langle f^{(0)}\xi,\zeta\rangle\!\rangle$ denotes the natural scalar product $\langle\!\langle f^{(0)}\xi,\zeta\rangle\!\rangle = \sum_{i\in\mathfrak{S}}\int f_i^{(0)}\xi_i\odot\zeta_i\,\mathrm{d}\boldsymbol{c}_i$, $f_i^{(0)}$ the Maxwellian distribution of the $i$th species, $\psi^l = (\delta_{il})_{i\in\mathfrak{S}}$ for $l\in\mathfrak{S}$, $\psi^{\mathrm{N}+\nu} = (m_i c_{\nu i})_{i\in\mathfrak{S}}$ for $1\le\nu\le 3$, $\psi^{\mathrm{N}+4} = (\frac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_i)_{i\in\mathfrak{S}}$ where $\mathrm{E}_i$ is the formation energy of the $i$th species.

The diffusion driving forces $(\boldsymbol{d}_l)_{l\in\mathfrak{S}}$ are linearly dependent with $\sum_{l\in\mathfrak{S}}\boldsymbol{d}_l = 0$ and are decomposed in the form

$$\boldsymbol{d}_l = \mathrm{d}\!\!\!^{-}_l - \mathsf{x}_l\sum_{k\in\mathfrak{S}}\mathrm{d}\!\!\!^{-}_k, \qquad l\in\mathfrak{S}, \qquad \text{(A10)}$$

where $(\mathrm{d}\!\!\!^{-}_l)_{l\in\mathfrak{S}}$ are *unconstrained* diffusion driving forces. A typical choice may be for instance $\mathrm{d}\!\!\!^{-}_l = \boldsymbol{\partial}_{\boldsymbol{x}}\mathsf{x}_l - \mathsf{y}_l\boldsymbol{\partial}_{\boldsymbol{x}}\log p$ and $\sum_{k\in\mathfrak{S}}\mathrm{d}\!\!\!^{-}_k = -\boldsymbol{\partial}_{\boldsymbol{x}}\log p$. The right hand side is then decomposed in the form

$$\Psi^{(1)} = -p\sum_{l\in\mathfrak{S}}\Psi^{(1),l}\cdot\mathrm{d}\!\!\!^{-}_l, \qquad \text{(A11)}$$

where

$$\Psi^{(1),l} = (\Psi_i^{(1),l})_{i\in\mathfrak{S}}, \qquad \Psi_i^{(1),l} = \frac{1}{p_i}(\delta_{il} - \mathsf{x}_i)\boldsymbol{C}_i.$$

We may then write

$$\phi_i^{(1)} = -p\sum_{l\in\mathfrak{S}}\phi_i^{(1),l}\cdot\mathrm{d}\!\!\!^{-}_l,$$

where $\phi^{(1),l} = (\phi_i^{(1),l})_{i\in\mathfrak{S}}$ is the solution of the integral equation system

$$\mathcal{I}(\phi^{(1),l}) = \Psi^{(1),l}, \qquad \text{(A12)}$$

with the Enskog constraints $\langle\!\langle f^{(0)}\phi^{(1),l}, \psi^{l'}\rangle\!\rangle = 0$ for $1\le l'\le \mathrm{N}+4$. The molar diffusion velocities are then obtained in the form

$$\boldsymbol{W}_i = -\sum_{l\in\mathfrak{S}} D_{il}^{\mathrm{mol}}\mathrm{d}\!\!\!^{-}_l = -\sum_{l\in\mathfrak{S}} D_{il}^{\mathrm{mol}}\boldsymbol{d}_l, \qquad \text{(A13)}$$

where

$$D_{il}^{\mathrm{mol}} = \frac{p}{3n_i}\int f_i^{(0)}\phi_i^{(1),l}\cdot\boldsymbol{c}_i\mathrm{d}\boldsymbol{c}_i - \frac{p}{3n}\sum_{j\in\mathfrak{S}}\int f_j^{(0)}\phi_j^{(1),l}\cdot\boldsymbol{c}_j\mathrm{d}\boldsymbol{c}_j,$$

where we have used the isotropy of the Boltzmann linearized collision operator [9, 38–40, 58]. Letting $D^{\mathrm{mol}} = (D_{ij}^{\mathrm{mol}})_{i,j\in\mathfrak{S}}$ and $\mathsf{x} = (\mathsf{x}_1,\dots,\mathsf{x}_{\mathrm{N}})^t$ we then have the relations [58]

$$D^{\mathrm{mol}} = (D^{\mathrm{mol}})^t, \qquad D^{\mathrm{mol}}\mathsf{x} = 0, \qquad \text{(A14)}$$

that are analogous to that obtained with the mass based diffusion coefficients $D = D^t$ and $D\mathsf{y} = 0$ *mutatis mutandis*.

Adapting the molar diffusion formalism of Waldmann developped for multicomponent gases in three dimensions to the situation of two-dimensional tangential surface diffusion, the tangential diffusion velocities with respect to the molar average mixture velocity are obtained in the form

$$\widetilde{\boldsymbol{W}}_{i\shortparallel} = \frac{1}{\widetilde{n}_i}\int f_i\boldsymbol{c}_{i\shortparallel}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta - \frac{1}{\widetilde{n}}\sum_{j\in\mathfrak{S}}\int f_j\boldsymbol{c}_{j\shortparallel}\mathrm{d}\boldsymbol{c}_j\mathrm{d}\zeta. \qquad \text{(A15)}$$

These velocities may then be used in order to investigate the surface tangential fluxes. Finally, for multicomponent gases, the mole average velocity $\boldsymbol{w}$ is generally nonzero—although it is often neglected for practical applications—but it is exactly zero on a crystal surface.

[1] I. Armenise, M. Capitelli, C. Gorse, M. Cacciatore, and M. Rutigliano, Nonequilibrium vibrational kinetics of an $O_2/O$ mixture hitting a catalytic surface, J. Space. Rockets, **37**, (2000), pp. 318–323.

[2] D. Bruno, M. Cacciatore, S. Longo, and M. Rutigliano, Gas-surface scattering models for particle fluid dynamics: a comparison between analytical approximate models and molecular dynamics calculations, Chem. Phys. Letters, **320**, (2000), pp. 245–254.

[3] E. Kustova, Z. Nagnibeda, I. Armenise, and M. Capitelli, Nonequilibrium kinetics and heat transfer in $O_2/O$ mixtures near catalytic surfaces, J. Thermo. Heat Transfer, **16**, (2002), pp. 238–244.

[4] E. Kustova, Z. Nagnibeda, Y. Shevelev and N. Syzranova, Comparison of different models for non-equilibrium CO2 flows in a shock layer near a blunt body, Shock Wave, **21**, (2011), pp. 273–285.

[5] O. Deutschmann, U. Riedel, and J. Warnatz, Modeling of nitrogen and oxygen recombination on partial catalytic surfaces, ASME. J. Heat Transfer **117**, (1995), pp. 495-501.

[6] A. Turchi, P. Congedo, and T.E. Magin, Thermochemical ablation modeling forward uncertainty analysis—Part I: Numerical methods and effect of model parameters, Int. J. Therm. Sciences, **118**, (2017) pp. 497–509.

[7] V. Giovangigli and S. Candel, Extinction limits of catalyzed stagnation point flow flames, Comb. Sci. and Tech., **48**, (1986), pp. 1–30.

[8] S. Poovathingal, T.E. Schwartzentruber, V.J. Murray, and T.K. Minton, Molecular simulations of carbone ablation using beam experiments and resolved microstructure, AIAA J., **54**, (2016), pp. 999-1010.

[9] Y. Sone, *Molecular Gas Dynamics, Theory, Techniques, and Applications*, Birkhaüser, Boston, (2007).

[10] K. Aoki, Y. Sone, and T. Yamada, Numerical analysis of gas flows condensing on its plane condensed phase on the basis of kinetic theory, Phys. Fluids A, **2**, (1990), pp. 1867–1878.

[11] A. Frezzotti, Boundary conditions at the vapor-liquid interface, Phys. Fluids, **23**, (2011), 030609.

[12] A. Ern, V. Giovangigli and M. Smooke, Numerical study of a three-dimensional chemical vapor deposition reactor with detailed chemistry, J. Comp. Phys., **126**, (1996), pp. 21–39.

[13] M.E. Davis and R.J. Davis, *Fundamentals of Chemical Reaction Engineering*, McGraw-Hill, New-York, (2003).

[14] P. Marcus, *Corrosion Mechanisms in Theory and Practice*, CRC Press, Taylor and Francis, (2012).

[15] S. Succi, G. Smith, and E. Kaxiras, Lattice Boltzmann simulation of reactive microflows over catalytic surfaces, J. Stat. Phys., **107**, (2002), pp. 343–366.

[16] K. Reuter and M. Scheffler, First-principles kinetic Monte Carlo simulations for heterogeneous catalysis: Application to the CO oxidation at $RuO_2(110)$, Phys. Rev. B, **73**, (2006), 045433.

[17] A. Groß, *Theoretical Surface Science, A microscopic Perspective*, Springer Verlag, Berlin (2009).

[18] M.E. Coltrin, R.J. Kee, and F.M. Rupley, Surface chemkin: A general formalism and software for analyzing heterogeneous chemical kinetic at a gas-surface interface, Chem. Kin., **23**, (1991), pp. 1111–1128.

[19] R.J. Kee, M.E. Coltrin, and P. Glarborg, *Chemically Reacting Flow*, Wiley, Hoboken (2003).

[20] O. Deutschmann, Modeling the interaction between catalytic surfaces and gas-phase, Catal. Lett., **145**, (2015), pp. 272–289.

[21] V.D. Borman, S.Yu. Krylov, A.V. Prosyanov, and A.M. Kharitonov, Theory of transport processes in a nonequilibrium gas-solid system, Sov. Phys. JETP, **63**, (1986), pp. 43–56.

[22] V.D. Borman, S.Yu. Krylov, and A.V. Prosyanov, Theory of nonequilibrium phenomena at a gas-solid interface, Sov. Phys. JETP, **67**, (1988), pp. 2110–2121.

[23] A.V. Prosyanov, V.D. Borman, S.Yu. Krylov, and B.I. Nikolaev, New mechanism of mass transfer in a gas-adsorbate-solid system, Phys. Letters A, **140**, (1989), pp. 55–58.

[24] J.J.M. Beenakker, V.D. Borman, and S.Yu Krylov, Molecular transport in the nanometer regime, Phys. Rev. Lett., **72**, (1994), pp. 514.

[25] A.V. Bogdanov, G.V. Dubrovskiy, M.P. Krutikov, D.V. Kulginov, and V.M. Strelchenya, *Interaction of gases with surfaces*, Springer Verlag, Berlin, (1995).

[26] J.J.M. Beenakker and S.Yu. Krylov, One-dimensional surface diffusion : Density dependence in a smooth potential, J. Chem. Phys., **107**, (1997), pp. 4015–4023.

[27] S.Yu. Krylov, A.V. Prosyanov, and J.J.M. Beenakker, One-dimensional surface diffusion II: Density dependence in a corrugated potential, J. Chem. Phys., **107**, (1997), pp. 6970–6979.

[28] A.Yu. Pankov, V.D. Borman, and S.Yu. Krylov, Kinetic theory of rotating molecules interacting with a solid surface, J. Exp. Theor. Phys., **86**, (1998), pp. 737–744.

[29] A. Frezzotti and L. Gibelli, A kinetic model for fluid-wall interaction, Proc. IMechE, **22**, (2007), pp. 787–795.

[30] A. Frezzotti, S.V. Nedea, A.J. Spijker, and L. Gibelli, Comparison of molecular dynamics and kinetic modeling of gas-surface interactions, Rarefied Gas Dynamics Conference, AIP Conference Proceedings 1084, 635–640 (2008).

[31] K. Aoki, P. Charrier and P. Degond, A hierarchy of models related to nanoflows and surface diffusion, Kin. Rel. Models, **4**, (2011), pp. 53-85.

[32] S. Brull, P. Charrier, L. Mieussens, Gas-surface interaction and boundary conditions for the Boltzmann equation, Kin. Rel. Models, **7**, (2014), pp. 219-251.

[33] S. Brull, P. Charrier, L. Mieussens, Nanoscale roughness effect on Maxwell-like boundary conditions for the Boltzmann equation, Physics of Fluids, **28**, (2016) 082004.

[34] E.M. Lifshitz and L.P. Pitaevskii, *Physical Kinetics*, Landau and Lifshitz course on theoretical physics, Volume 10, Elsevier, (1981).

[35] A. Rossani, Generalized kinetic theory of electrons and phonons, Physica A, **305**, (2002), pp. 323–329.

[36] M. Galler, *Multigroup Equations for the Description of the Particle Transport in Semiconductors*, World Scientific, Singapore, (2005).

[37] K. Aoki, V. Giovangigli and M. Hattori, A kinetic model of adsorption on solid surfaces, Rarefied Gas Dynamics Conference, AIP Conference Proceedings 1786, 100005 (2016).

[38] S. Chapman and T.G. Cowling, *The Mathematical The-*

*ory of Non-Uniform Gases*, Cambridge University Press, (1970).

[39] J.H. Ferziger, H.G. Kaper, *Mathematical theory of transport processes in gases*, North Holland, Amsterdam, (1972).

[40] V. Giovangigli, *Multicomponent Flow Modeling*, Birkhaüser, Boston, (1999).

[41] E. Nagnibeda and E. Kustova, *Non-Equilibrium Reacting Gas Flows*, Springer Verlag, Berlin, (2009).

[42] N.N. Bogoliubov and N.N. Bogoliubov (Jr), Generalized kinetic equations for a dynamical system interacting with a phonon field, Teoret. Mat. Fiz., **43**, (1980) pp. 3-17.

[43] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, Landau and Lifshitz course on theoretical physics, Volume 5, Elsevier, (1980).

[44] Diu, B., C. Guthmann, D. Lederer, and B. Roulet, *Éléments de Physique Statistique*, Hermann, Paris, (1989).

[45] J.S. Rowlinson and B. Widom, *Molecular Theory of Capillarity*, Dover publications, Mineola, 1989 and 2002.

[46] J.H. Weiner, *Statistical Mechanics of Elasticity*, Dover publications, Mineola, 2002.

[47] H. Mehrer, *Diffusion in Solids*, Springer series in solid state physics 155, Springer Verlag, New York (2007).

[48] G. Antczak and G. Ehrlich, *Surface Diffusion*, Cambridge University press, (2010).

[49] A. Ern and V. Giovangigli, The Kinetic equilibrium regime, Physica-A, **260**, (1998), pp. 49–72.

[50] J.G. Powles, S.E. Baker, and W.A.B. Evans, The chemical potential in atomically inhomogeneous fluids in external force fields by computer simulations, J. Chem. Phys., **101**, (1994) pp. 4098–4102.

[51] N. Masmoudi, Diffusion limit of a semiconductor Boltzmann-Poisson system, SIAM J. Math. Anal., **38**, (2007), pp. 1788-1807

[52] A. Majorana and C. Milazzo Space homogeneous solutions of the linear semiconductor Boltzmann equation, J. Math. Anal. and Appl., **259**, (2001), pp. 609–629.

[53] G.K. Batchelor, *An Introduction to Fluid dynamics*, Cambridge University Press, Cambridge, 1967.

[54] R. Scardovelli and S. Zaleski, Direct numerical simulation of free-surface and interfacial flow, Ann. Rev. Fluid Mech., **31**, (1999), pp. 567–603.

[55] D.M. Ruthven, *Principles of Adsorption & Adsorption Processes*, John Wiley & Sons, New York, (1984).

[56] M.R. Marcelin, Sur la mécanique des phénomènes irréversibles, Comptes Rendus de l'Académie des Sciences de Paris, Séance du 5 décembre 1910, (1910), pp. 1052–1055.

[57] J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes*, Springer Verlag, New York (1987)

[58] L. Waldmann, Transporterscheinungen in gasen von mittlerem druck. *Handbuch der Physik*, S. Flügge ed., **12**, Springer Verlag, Berlin 295–514, (1958).

[59] R. Krishna, Multicomponent surface diffusion of adsorbed species: A description based on the generalized Maxwell-Stefan equations, Chem. Eng. Science **45**, (1990), pp. 1779–1791.

[60] V.M. Janardhanan and O. Deutschmann, Modeling diffusion limitation in solid-oxide fuel cells, Electrochimica Acta **56**, (2011), pp. 9775–9782.