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Kinetic Theory of Chemical Reactions on Crystal Surfaces

Kazuo Aoki[†] and Vincent Giovangigli[⋆*]

[†]Mathematical Fluid Mechanics, Kyoto University, Kyoto, JAPAN

[⋆]CMAP–CNRS, École Polytechnique, Palaiseau, FRANCE

Abstract

A kinetic theory describing chemical reactions on crystal surfaces is introduced. Kinetic equations are used to model physisorbed-gas particles and chemisorbed particles interacting with fixed potentials and colliding with phonons. The phonons are assumed to be at equilibrium and the physisorbed-gas and chemisorbed species equations are coupled to similar kinetic equations describing crystal atoms on the surface. An arbitrary number of surface species and heterogeneous chemical reactions are considered, covering Langmuir-Hinshelwood as well as Eley-Rideal mechanisms and the species may be polyatomic. A kinetic entropy is introduced for the coupled system and the H theorem is established. Using a fluid scaling and a Chapman-Enskog method, fluid boundary conditions are derived from the kinetic model and involve complex surface chemistry as well as surface tangential multicomponent diffusion.

Keywords : Kinetic theory; Gas-surface interaction; Surface reactions; Chapman-Enskog; Fluid boundary conditions.

1 Introduction

Chemical reactions often occur at solid or liquid surfaces like in hypersonic reentry [1, 2, 3, 4, 5, 6], engine combustion [7], condensation and evaporation [8, 9, 10], or chemical vapor deposition [11, 12]. Although the description of reactive surfaces using molecular simulations [13, 14, 15] or macroscopic fluid models [16, 17, 18] has been highly successful, there is still a need to develop kinetic models at the mesoscopic scale. These models may be used in particular to derive fluid boundary conditions at reactive interfaces using the Chapman-Enskog method.

Kinetic gas-surface models involving chemical reactions have traditionally been investigated by using Maxwell type boundary conditions with boundary partial densities typically given by chemical equilibrium conditions, avoiding the complexities of gas surface interactions. More refined models of gas-solid interfaces based on physical grounds involve kinetic equations for gas particles interacting with a potential field and colliding with phonons that describe the fluctuating part of the surface [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31]. These models have been used to study condensation and evaporation, particle trapping, phonon drag, surface homogenization, or scattering kernels [19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31]. Such physical models have recently been extended to cover the situation of a single-species chemisorption [32, 33]. In this work, a kinetic model for complex chemical reaction networks on crystal surfaces—also

*Corresponding author : vincent.giovangigli@polytechnique.fr

involving polyatomic species—is investigated expanding previous work [32, 33] as well as preliminary results [34].

An arbitrary number of heterogeneous chemical reactions, physisorbed-gas species or chemisorbed species—that may be monatomic or polyatomic—are considered. The crystal is assumed to be monatomic for the sake of simplicity and the surface atoms may either be free sites or else bonded to chemisorbed species. The kinetic Boltzmann equations take into account the interaction of gas particles with average surface potentials as well as with phonons [20, 23, 27, 29, 30]. The potential fields are generated by fixed crystal particles and the phonons describe the fluctuating part of the surface. The phonons are assumed to be at equilibrium in this work for the sake of simplicity [20, 22, 24, 25] although a kinetic equation for phonons could also be considered [19, 35, 36, 37]. The physisorbed-gas, chemisorbed and crystal species kinetic equations are all coupled by chemistry source terms. The surface chemistry will be assumed to be slow enough so that the crystal surface essentially remains at physical equilibrium and only its chemical composition is out of equilibrium.

Using the *atomic site formalism* of heterogeneous chemistry, the chemical reactions are written in the form

$$\sum_{j\in\mathcal{F}^r} \mathfrak{M}_j \rightleftarrows \sum_{k\in\mathcal{B}^r} \mathfrak{M}_k, \qquad r \in \mathfrak{R}, \tag{1.1}$$

where $\mathfrak{M}_i$ is the symbol of the ith species that may either be a physisorbed-gas particle, a chemisorbed particle, a crystal free site particle or a bonded crystal particle, r denotes the reaction index and $\mathfrak{R}$ the reaction indexing set. The sets $\mathcal{F}^r$ and $\mathcal{B}^r$ denote respectively the indices of reactants and products of the rth reaction. The chemical reactions are described by using the atom site formalism that takes into account the crystal atoms, even though *macroscopically* it may also be described by using the open site formalism that formally hides the crystal atoms [17, 33]. The surface chemical reaction mechanism is arbitrarily complex and covers adsorption, desorption, Langmuir-Hinshelwood as well as Eley-Rideal reaction types. We first assume for the sake of simplicity that the chemisorbed molecules only occupy one crystal site on the surface, that is, that adsorption processes are monosite. The extension to the situation of multisite adsorption is then addressed separately in an extra section. The system is assumed to be isothermal and the phonon are consistently assumed to be at physical equilibrium as well as surface crystal atoms. A modified kinetic entropy is introduced for the coupled system of kinetic equations and an H theorem is established.

A Chapman-Enskog type expansion is introduced with a fluid scaling of the kinetic equations. A multiscale asymptotic analysis is performed and the Stefan convection velocity associated with overall mass production at the surface is naturally assumed to be small. The inner structure of the physisorbate, the chemisorbate, and the crystal layers are analyzed at zeroth order and closely related to interaction potentials. The gas species diffusive fluxes and the Stefan gas flow at the surface then results from the physisorbed-gas particles production by surface chemistry. The chemisorbed particles are also governed at zeroth order by differential equations with surface chemistry source terms. The traditional species fluid boundary conditions for reactive surfaces are recovered and involve heterogeneous chemistry production rates [16, 17, 18]. The dynamic boundary conditions associated with the pressure tensor and the heat flux at the interface are also addressed. We also establish the validity of the simpler *open site formalism* in order to describe the macroscopic equations. With this formalism the crystal free site atoms as well as the crystal atoms bonded to chemisorbed particles are removed and replaced by an open site symbol that is massless and atomless.

The inner structure of the physisorbate, the chemisorbate, and the free site layers are further analyzed at first order. The linearized systems of differential-integral equations that govern the perturbed distribution functions are found to differ from traditional half space problems. The corresponding first order species fluid boundary conditions also include extra terms associated with multicomponent tangential surface diffusion fluxes that are investigated in the physisorbate and the chemisorbate. Finally, the extension to multisite adsorption processes is investigated and the corresponding modified surface equations and multicomponent diffusion fluxes are presented.

The kinetic model is presented in Section 2 and the asymptotic framework in Section 3. Zeroth order expansions and species boundary conditions are investigated in Section 4 and the momentum and energy boundary conditions in Section 5. First order expansions are considered in Section 6 and the extension to the situation of multisite adsorption is addressed in Section 7.

2 A kinetic model

A kinetic model describing multicomponent gases nearby reactive crystal surfaces is presented. The kinetic equations involve monatomic or polyatomic particles interacting with surface potential fields and colliding with phonons, [19, 20, 21, 22, 23, 32, 33, 34]. This complex chemistry collisional formalism for surface reactions is new to the best of the authors' knowledge.

2.1 Kinetic equations for physisorbed-gas species

We consider a mixture of monatomic or polyatomic species indexed by $S_{\mathrm{g}} = \{1, \dots, \mathrm{N_g}\}$ where $\mathrm{N_g}$ denotes the number of physisorbed-gas species. The particules may approach the surface and be physisorbed but may also be chemisorbed by forming chemical bonds with the crystal atoms. The chemisorbed species are different chemical species and are indexed by $S_{\mathrm{c}} = \{\mathrm{N_g}+1, \dots, \mathrm{N_g}+\mathrm{N_c}\}$ where $\mathrm{N_c}$ denotes the number of chemisorbed species. We also consider the free sites crystal particles on the surface indexed by $S_{\mathrm{s}} = \{\mathrm{N_g}+\mathrm{N_c}+\mathrm{N_s}\}$, where $\mathrm{N_s} = 1$ is the number of free site species, and the index of the free sites $\mathrm{N_g}+\mathrm{N_c}+\mathrm{N_s}$ will sometimes be denoted by 's' for the sake of simplicity. Moreover, the crystal particles bonded to the chemisorbed particles are indexed by $S_{\mathrm{b}} = \{\mathrm{N_g}+\mathrm{N_c}+\mathrm{N_s}+1, \dots, \mathrm{N_g}+\mathrm{N_c}+\mathrm{N_s}+\mathrm{N_b}\}$ where $\mathrm{N_b}$ denotes the number of bulk species. It is first assumed in this work that the chemisorbed species only occupy one atom site on the crystal surface so that there are as many bulk species as chemisorbed species $\mathrm{N_b} = \mathrm{N_c}$. The more complex situation of multisite adsorption, where a chemisorbed species may be bonded to multiple crystal atoms, is addressed separately in Section 7. The resulting species indexing set S for heterogeneous chemistry is finally denoted by

$$S = S_{\mathrm{g}} \cup S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}} = \{1, \dots, \mathrm{N}\}, \tag{2.1}$$

where $\mathrm{N} = \mathrm{N_g}+\mathrm{N_c}+\mathrm{N_s}+\mathrm{N_b}$ is the total number of reactive species at the surface.

The Boltzmann equations governing physisorbed-gas species are in the form [19, 20, 21, 22, 23, 32, 33, 34]

$$\partial_t f_i + \boldsymbol{c}_i \cdot \boldsymbol{\partial_x} f_i - \frac{1}{m_i} \boldsymbol{\partial_x} \mathrm{W}_i \cdot \boldsymbol{\partial}_{\boldsymbol{c}_i} f_i = \sum_{j \in S_{\mathrm{g}}} J_{ij}(f_i, f_j) + J_{i,\mathrm{ph}}(f_i) + \mathcal{C}_i, \qquad i \in S_{\mathrm{g}}, \tag{2.2}$$

where ∂_t denotes the time derivative operator, $i \in S_{\mathrm{g}}$ the species index, $f_i(t, \boldsymbol{x}, \boldsymbol{c}_i, \mathrm{I})$ the ith species distribution function, $\boldsymbol{c}_i$ the ith species particle velocity, I the energy quantum state of the ith species, $\boldsymbol{\partial_x}$ the space derivative operator, m_i the particle mass, W_i the interaction potential between *fixed* crystal particles and the particles of the ith species, $\boldsymbol{\partial}_{\boldsymbol{c}_i}$ the velocity derivative operator, J_{ij} the collision operator between the ith and the jth physisorbed-gas species, $J_{i,\mathrm{ph}}$ the particle-phonon collision operator, and $\mathcal{C}_i$ the chemistry source term. The solid surface is denoted by Σ and assumed to be planar 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 coordinate vector $\boldsymbol{x}$ is also written $\boldsymbol{x} = (\boldsymbol{x}_{\shortparallel}, z)^t$ where $\boldsymbol{x}_{\shortparallel} = (x, y)^t$ is the two dimensional vector of tangential coordinates. Similarly the particle velocity $\boldsymbol{c}_i$ is written $\boldsymbol{c}_i = (\boldsymbol{c}_{i\shortparallel}, c_{iz})^t$ where $\boldsymbol{c}_{i\shortparallel}$ denotes the tangential two-dimentional velocity vector and c_{iz} the normal velocity.

The particle collision operator J_{ij} is in the traditional form [38, 39, 40, 41, 42, 43, 44]

$$J_{ij}(f_i, f_j) = \sum_{\substack{\mathrm{I}' \in \mathfrak{Q}_i \\ \mathrm{J},\mathrm{J}' \in \mathfrak{Q}_j}} \int \Big(f_i' f_j' \frac{a_{i\mathrm{I}} a_{j\mathrm{J}}}{a_{i\mathrm{I}'} a_{j\mathrm{J}'}} - f_i f_j \Big) \mathsf{W}_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\boldsymbol{c}_j \mathrm{d}\boldsymbol{c}_i' \mathrm{d}\boldsymbol{c}_j', \qquad i, j \in S_{\mathrm{g}}, \tag{2.3}$$

where, in a direct collision, $\boldsymbol{c}_j$ denotes the velocity of the collision partner, I and J the energy quantum state before collision, $\boldsymbol{c}_i'$ and $\boldsymbol{c}_j'$ the velocities after collision, I′ and J′ the energy states after collision, $a_{i\mathrm{I}}$ the degeneracy of the Ith quantum state, $\mathfrak{Q}_i$ the indexing set of the quantum energy states of the ith species, $\mathsf{W}_{ij}^{\mathrm{IJI'J'}}$ the transition probability of nonreactive collisions averaged over degeneracies and $f_i' = f_i(t, \boldsymbol{x}, \boldsymbol{c}_i', \mathrm{I}')$. Only collision operators J_{ij} between physisorbed-gas species $i, j \in S_{\mathrm{g}}$, are taken into account. The following reciprocity relations are satisfied by the transition probabilities [38, 39, 40, 41, 42, 43, 44]

$$a_{i\mathrm{I}} a_{j\mathrm{J}} \mathsf{W}_{ij}^{\mathrm{IJI'J'}} = a_{i\mathrm{I}'} a_{j\mathrm{J}'} \mathsf{W}_{ij}^{\mathrm{I'J'IJ}}. \tag{2.4}$$

The collision terms J_{ij} may be written equivalently in terms of collision cross sections [38, 39, 40, 41, 42, 43, 44].

The phonon collision operator $J_{i,\mathrm{ph}}$ will be investigated in Section 2.5 and the reactive operator $\mathcal{C}_i$ in Section 2.6. These collision operators $J_{i,\mathrm{ph}}$ and $\mathcal{C}_i$ for $i \in S_{\mathrm{g}}$ both vanish far from the surface as well as the potentials W_i in such a way that letting $z \to \infty$ in equation (2.2) yields the kinetic equations in the gas phase

$$\partial_t f_{\mathrm{g}i} + \boldsymbol{c}_i \cdot \boldsymbol{\partial_x} f_{\mathrm{g}i} = \sum_{j \in S_{\mathrm{g}}} J_{ij}(f_{\mathrm{g}i}, f_{\mathrm{g}j}), \qquad i \in S_{\mathrm{g}}, \tag{2.5}$$

where $f_{\mathrm{g}i}(t, \boldsymbol{x}, \boldsymbol{c}_i, \mathrm{I})$ denotes the *gas* distribution function of the ith species. The kinetic equation (2.5) is the standard Boltzmann equation for a mixture of monatomic or polyatomic gases and there is thus a single kinetic framework describing both gas and physisorbed mixtures, the gas equations being recovered far from the surface. No chemical reactions are considered in the gas phase for the sake of simplicity although they may be included in the model.

2.2 Kinetic equations for chemisorbed and crystal species

The distribution functions for the chemisorbed, the free sites and the bulk species are assumed to be governed by the kinetic equations [32, 33, 34].

$$\partial_t f_i + \boldsymbol{c}_i \cdot \boldsymbol{\partial_x} f_i - \frac{1}{m_i} \boldsymbol{\partial_x} \mathrm{W}_i \cdot \boldsymbol{\partial}_{\boldsymbol{c}_{\mathrm{s}}} f_i = J_{i,\mathrm{ph}}(f_i) + \mathcal{C}_i \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}, \tag{2.6}$$

where $f_i(t, \boldsymbol{x}, \boldsymbol{c}_i, \mathrm{I})$ denotes the ith species distribution function, $\boldsymbol{c}_i$ the particle velocity, I the energy quantum state, W_i the interaction potential with *fixed* crystal particles (interior crystal particles for the crystal surface species), m_i the particle mass, $J_{i,\mathrm{ph}}$ the particle-phonon collision operator and $\mathcal{C}_i$ the reactive source term. Since the crystal is monatomic, the crystal free site species as well as the bulk species—the crystal species that are bonded to chemisorbed species—are monatomic. The phonon collision operator $J_{i,\mathrm{ph}}$ will be investigated in Section 2.5 and the reactive operator $\mathcal{C}_i$ in Section 2.6. For the chemisorbed species, Equations (2.6) are analogous to that used for physisorbed species—using the corresponding chemisorption potential—and have a similar physical interpretation. They are also in the form derived by Bogoliubov and Bogoliubov [45] as well as in the form of a one-particle equation of the BBGKY hierarchy, as discussed in a quasi steady framework by Cercignani [46], and analogous to kinetic equations describing lattice gases introduced by Bogdanov et al. [23]. For the crystal species, the kinetic equations are further similar to that of the chemisorbed species equation since for crystal growth phenomena the chemisorbed layers are crystal layers. The equilibrium distributions associated with (2.6) are the appropriate Maxwellian distributions constrained by the crystal potentials w_i in agreement with statistical physics at equilibrium [47, 48, 49, 50, 51]. For the bulk species, the phonon collision term may also be interpreted as an overall relaxation operator encompassing phenomena of different origins.

The surface layer Σ is the last layer of crystal atoms located around $z = 0$ and is constituted by free site particles as well as bulk crystal particles bonded to chemisorbed species with distribution $f_\sigma = f_\mathrm{s} + \sum_{i \in S_\mathrm{b}} f_i$. We introduce for convenience the *standard or unperturbed* surface layer distribution function f_σ^e that is solution of the kinetic equation

$$\partial_t f_\sigma^\mathrm{e} + \boldsymbol{c}_\sigma \boldsymbol{\cdot} \boldsymbol{\partial_x} f_\sigma^\mathrm{e} - \frac{1}{m_\sigma} \boldsymbol{\partial_x} \mathrm{w}_\sigma \boldsymbol{\cdot} \boldsymbol{\partial}_{\boldsymbol{c}_\sigma} f_\sigma^\mathrm{e} = J_{\sigma,\mathrm{ph}}(f_\sigma^\mathrm{e}), \tag{2.7}$$

where $\mathrm{w}_\sigma = \mathrm{w}_i$ for any $i \in S_\mathrm{s} \cup S_\mathrm{b}$ denotes the interaction potential between fixed internal crystal particles and crystal surface particles, m_σ the particles mass, and $J_{\sigma,\mathrm{ph}}$ the crystal particle-phonon collision operator. The standard surface distribution function f_σ^e is that of an unperturbed crystal surface layer. The probability $1 - \theta$ to find an open site on the surface layer Σ is defined as the ratio

$$1 - \theta = \frac{f_\mathrm{s}}{f_\sigma^\mathrm{e}}. \tag{2.8}$$

The quantity θ is usually termed the coverage and represents the probability that a site is occupied by a chemisorbed particle in the monolayer chemisorbate. The probability of free sites $1 - \theta$ is defined here as a kinetic variable and will be shown to only depend on time t and tangential coordinate $\boldsymbol{x}_\shortparallel$ at zeroth order.

2.3 Summed potentials

The interaction potentials summed over *fixed* crystal particles w_i, $i \in S$, *are assumed to only depend on the normal coordinate* z for the sake of simplicity. These potentials are written in the form $\mathrm{w}_i = \mathrm{w}_i(z/\delta)$, where δ is a characteristic range of the surface potential also characteristic of the range of gas-phonon interaction and $\zeta = z/\delta$ is the corresponding rescaled normal coordinate. The potentials for the physisorbed-gas species are such that

$$\lim_{\zeta \to 0} \mathrm{w}_i(\zeta) = +\infty, \qquad \lim_{\zeta \to +\infty} \mathrm{w}_i(\zeta) = 0, \qquad i \in S_\mathrm{g}. \tag{2.9}$$

These potentials go to zero in the gas phase and explode at $\zeta = 0$, repelling all particles from the crystal surface. On the other hand, the potentials for the surface species are such that

$$\lim_{\zeta \to \zeta_i^-} \mathrm{w}_i(\zeta) = +\infty, \qquad \lim_{\zeta \to \zeta_i^+} \mathrm{w}_i(\zeta) = +\infty, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}, \tag{2.10}$$

where ζ_i^- and ζ_i^+ are fixed ζ coordinates, so that for any $i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}$ the ith species is localized over (ζ_i^-, ζ_i^+). For the sake of simplicity, the crystal surface particles are assumed to have the same potential $\mathrm{w}_j = \mathrm{w}_\sigma$ with $j \in S_{\mathrm{s}} \cup S_{\mathrm{b}}$, and are thus localized over the same interval $(\zeta_j^-, \zeta_j^+) = (\zeta_\sigma^-, \zeta_\sigma^+)$. We also assume that for any chemisorbed species $i \in S_{\mathrm{c}}$ we have $\zeta_\sigma^- < \zeta_i^- \leq 0 < \zeta_\sigma^+ < \zeta_i^+$. 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. The potentials of physisorbed-gas particles and the corresponding chemisorbed particles may also be interpreted as slices of potential energy surfaces [33].

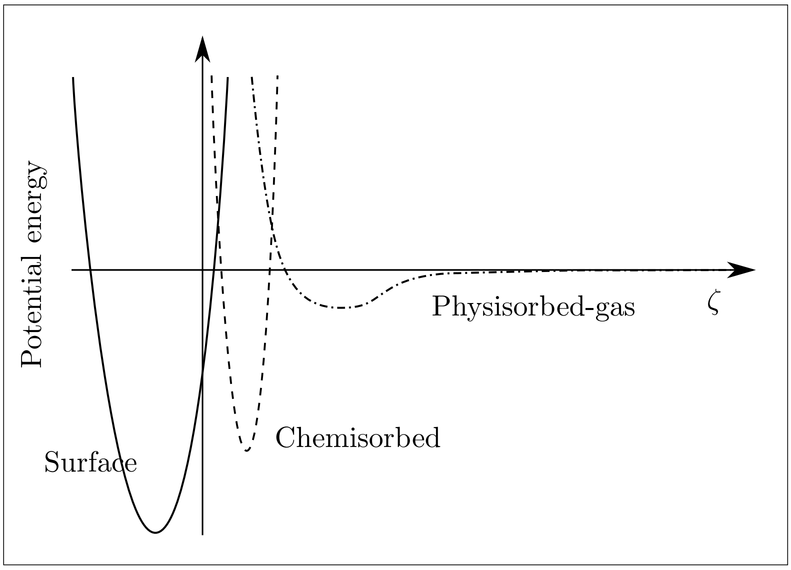

Figure 1: Typical surface interaction potentials as function of the distance from surface in arbitrary units.

Since the summed potentials only depend on z, periodic potential variations parallel to the surface are neither taken into account for chemisorbed species nor for crystal species. Similarly, lateral interactions between chemisorbed species, usually of van de Waals type, are not taken into account. The surface potential w_i, $i \in S$, are also assumed to be independent of the presence of chemisorbed species for the sake of simplicity—and thus independent of the coverage θ—so that in particular $\mathrm{w}_\sigma = \mathrm{w}_i$ for $i \in S_{\mathrm{s}} \cup S_{\mathrm{b}}$. In the same vein, dense gas effects between physisorbed species [52] are not considered in the kinetic model as well as sublimation or deposition reactions of crystal atoms [11, 12]. These simplifications are notably feasible when the chemisorbed species are of relatively small size, and the surface mole fractions are small so that the coverage of the surface θ is low.

Physisorption interaction potentials may be evaluated from standard potentials summed over lattices whereas chemisorption potentials are generally associated with quantum chemistry models [15, 53]. Experimental methods may be used to evaluate such adsorption potentials but quantum mechanical simulations using the density functional theory is the most reliable tool for a detailed description of adsorption and surface reaction [15, 54, 55, 56, 57, 58, 59, 60]. An alternative procedure may be the semi-empirical Reaxff method that has already been used in order to describe surface chemical reactions [61, 62]. Physisorption and chemisorption potentials may then be extracted from quantum simulations of adsorption phenomena.

2.4 Maxwellians

The species distribution functions at physical equilibrium are given by $f_i^{\mathrm{e}} = n_i \mathrm{M}_i$ where n_i denotes the number of particle per unit volume, M_i the wall Maxwellian of the ith species and the superscript $^{\mathrm{e}}$ stands for physical equilibrium. The wall Maxwellian distribution is in the form

$$\mathrm{M}_i = \Big(\frac{m_i}{2\pi k_{\mathrm{B}} T_{\mathrm{w}}}\Big)^{3/2} \frac{a_{i\mathrm{I}}}{\mathrm{Z}_i^{\mathrm{int}}} \exp\Big(-\frac{m_i|\boldsymbol{c}_i|^2}{2k_{\mathrm{B}}T_{\mathrm{w}}} - \frac{\mathrm{E}_{i\mathrm{I}}}{k_{\mathrm{B}}T_{\mathrm{w}}}\Big), \qquad i \in S, \tag{2.11}$$

where m_i denotes the mass of the ith species, k_{B} the Boltzmann constant, T_{w} the wall temperature, $a_{i\mathrm{I}}$ the degeneracy of the Ith state, $\mathrm{Z}_i^{\mathrm{int}}$ the internal partition function of the ith species, and $\mathrm{E}_{i\mathrm{I}}$ the energy of the ith species in the Ith state. The internal partition function $\mathrm{Z}_i^{\mathrm{int}}$ of the ith species is given by

$$\mathrm{Z}_i^{\mathrm{int}} = \sum_{\mathrm{I}\in\mathfrak{Q}_i} a_{i\mathrm{I}} \exp\Big(-\frac{\mathrm{E}_{i\mathrm{I}}}{k_{\mathrm{B}}T_{\mathrm{w}}}\Big). \tag{2.12}$$

We introduce for convenience the modified Maxwellian distributions

$$\mathsf{m}_i = \mathrm{M}_i \exp(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}}), \qquad i \in S, \tag{2.13}$$

that may be written

$$\mathsf{m}_i = \Big(\frac{m_i}{2\pi k_{\mathrm{B}} T_{\mathrm{w}}}\Big)^{3/2} \frac{a_{i\mathrm{I}}}{\mathrm{Z}_i^{\mathrm{int}}} \exp\Big(-\frac{m_i|\boldsymbol{c}_i|^2}{2k_{\mathrm{B}}T_{\mathrm{w}}} - \frac{\mathrm{E}_{i\mathrm{I}}+\mathrm{W}_i}{k_{\mathrm{B}}T_{\mathrm{w}}}\Big). \tag{2.14}$$

These modified Maxwellian distributions m_i, $i \in S$, will play a role in the analysis of the reactive surface layer. With the inclusion of the interaction potential W_i, the distribution m_i is indeed such that

$$\partial_t \mathsf{m}_i = 0, \qquad \boldsymbol{c}_i\cdot\boldsymbol{\partial}_{\boldsymbol{x}}\mathsf{m}_i - \frac{1}{m_i}\boldsymbol{\partial}_{\boldsymbol{x}}\mathrm{W}_i\cdot\boldsymbol{\partial}_{\boldsymbol{c}_i}\mathsf{m}_i = 0, \qquad i \in S, \tag{2.15}$$

and it will also be later established that $J_{i,\mathrm{ph}}(\mathsf{m}_i) = 0$. These modified Maxwellian distributions m_i, $i \in S$, thus appear as *natural solutions* of thin layer kinetic equations in a potential field with phonon interactions or equivalently as natural solutions of the steady nonreactive kinetic equations. Decomposing between parallel and normal directions with respect to Σ we may further write

$$\partial_t \mathsf{m}_i = 0, \qquad \boldsymbol{\partial}_{\shortparallel}\mathsf{m}_i = 0, \qquad c_{iz}\,\partial_z\mathsf{m}_i - \frac{1}{m_i}\partial_z\mathrm{W}_i\,\partial_{c_{iz}}\mathsf{m}_i = 0, \qquad i \in S, \tag{2.16}$$

where $\boldsymbol{\partial}_{\shortparallel}$ denotes the tangential spatial derivative operator, c_{iz} the normal velocity of the ith species, ∂_z the normal spatial derivative, and $\partial_{c_{iz}}$ the differential operator with respect to c_{iz}. The modified Maxwellian distributions also play a key role in the expression of the reactive collision term $\mathcal{C}_i$ and in the kinetic entropy.

Considering further the unperturbed surface layer distribution f_σ^{e}, it will be established in the following that

$$f_\sigma^{\mathrm{e}} = n_\sigma \mathrm{M}_\sigma, \tag{2.17}$$

where n_σ denotes the number density of the surface layer and M_σ the Maxellian distribution defined as (2.11). The number of surface molecules par unit volume n_σ will be shown to be in the form

$$n_\sigma = \mathsf{n}_\sigma \exp\Big(-\frac{\mathrm{W}_\sigma}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big), \tag{2.18}$$

where n_σ is a constant *characteristic of the crystal and its orientation* so that $f_\sigma^{\mathrm{e}} = \mathsf{n}_\sigma \mathsf{m}_\sigma$ with m_σ defined as (2.13). From (2.17) and (2.18) the standard distribution f_σ^{e} is indeed solution of (2.7) and we have $\partial_t f_\sigma^{\mathrm{e}} = 0$, $\boldsymbol{c}_\sigma \boldsymbol{\cdot} \boldsymbol{\partial_x} f_\sigma^{\mathrm{e}} - \frac{1}{m_\sigma} \boldsymbol{\partial_x} \mathrm{W}_\sigma \boldsymbol{\cdot} \boldsymbol{\partial_c} f_\sigma^{\mathrm{e}} = 0$, and $J_{\sigma,\mathrm{ph}}(f_\sigma^{\mathrm{e}}) = 0$ as for the modified Maxwellian distributions. One may also define the number density per unit surface

$$\widetilde{n}_\sigma = \int n_\sigma \, \mathrm{d}z = \mathsf{n}_\sigma \int \exp\Big(-\frac{\mathrm{W}_\sigma}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big) \mathrm{d}z, \tag{2.19}$$

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

$$n_i = \int f_i \, \mathrm{d}\boldsymbol{c}_i, \qquad \widetilde{n}_i = \int n_i \, \mathrm{d}z, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}, \tag{2.20}$$

so that $\widetilde{n}_i$ represents the number of particles of species i *per unit surface*, keeping in mind that chemisorbed species and surface crystal species are localized in space.

2.5 Phonon collision operators

The operator $J_{i,\mathrm{ph}}$ describing collisions between particles of species i and phonons is in the general form [19, 35, 36, 37]

$$J_{i,\mathrm{ph}} = \sum_{\mathrm{I}' \in \mathfrak{Q}_i} \int \Big(\big(f_{\mathrm{ph}}(\boldsymbol{q}) + 1\big) f_i(\boldsymbol{c}_i', \mathrm{I}') \frac{a_{i\mathrm{I}}}{a_{i\mathrm{I}'}} - f_{\mathrm{ph}}(\boldsymbol{q}) f_i(\boldsymbol{c}_i, \mathrm{I}) \Big) \overline{\mathsf{W}}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'} \, \mathrm{d}\boldsymbol{c}_i' \mathrm{d}\boldsymbol{q}, \tag{2.21}$$

where $f_{\mathrm{ph}}(\boldsymbol{q})$ denotes the phonon distribution function, $i \in S$ 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, I and I' the quantum energy states before and after the interaction, and $\overline{\mathsf{W}}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'}$ a transition probability average over degeneracies. Note that the dependence on t and $\boldsymbol{x}$ of the distribution functions has been left implicit to simplify notation and that the phonon collision operator is presented in more details in Appendix A. The dilute approximation has been used for f_i in order to simplify (2.21) and the appearing of the additional factor 1 in the gain term is a typical quantum effect [19, 35, 36, 37]. The transition probabilities satisfy reciprocity relations $a_{i\mathrm{I}} \overline{\mathsf{W}}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'} = a_{i\mathrm{I}'} \overline{\mathsf{W}}_{i,\mathrm{ph}}^{\mathrm{I}',\mathrm{I}}$ similar to that of nonreactive collision terms. The operator (2.21) 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 and 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 $J_{i,\mathrm{ph}}$ and the corresponding details are omitted.

The equilibrium relation between distribution functions corresponding to (2.21) reads

$$\big(f_{\mathrm{ph}}^{\mathrm{e}}(\boldsymbol{q}) + 1\big) f_i^{\mathrm{e}}(\boldsymbol{c}_i', \mathrm{I}') \frac{a_{i\mathrm{I}}}{a_{i\mathrm{I}'}} = f_{\mathrm{ph}}^{\mathrm{e}}(\boldsymbol{q}) f_i^{\mathrm{e}}(\boldsymbol{c}_i, \mathrm{I}), \tag{2.22}$$

where the superscript $^{\mathrm{e}}$ stands for *physical equilibrium.* The equilibrium distribution for the phonons $f_{\mathrm{ph}}^{\mathrm{e}}$ is the Bose-Einstein distribution and the equilibrium distribution for the

ith species f_i^{e} is given by $f_i^{\mathrm{e}} = n_i \mathrm{M}_i$ where n_i denotes the number of particles per unit volume, and M_i the wall Maxwellian distribution for any $i \in S$, [35, 36, 37]. Dividing then the integrand in the collision term (2.21) by the factor $\big(f_{\mathrm{ph}}^{\mathrm{e}}(\boldsymbol{q})+1\big)\mathsf{m}_i(\boldsymbol{c}_i', \mathrm{I}')a_{i\mathrm{I}}/a_{i\mathrm{I}'} = f_{\mathrm{ph}}^{\mathrm{e}}(\boldsymbol{q})\mathsf{m}_i(\boldsymbol{c}_i, \mathrm{I})$ and further *assuming that phonons are at equilibrium* $f_{\mathrm{ph}}^{\mathrm{e}} = f_{\mathrm{ph}}$, it is obtained that

$$J_{i,\mathrm{ph}}(f_i) = \sum_{\mathrm{I}' \in \mathfrak{Q}_i} \int \Big(\frac{f_i(\boldsymbol{c}_i', \mathrm{I}')}{\mathsf{m}_i(\boldsymbol{c}_i', \mathrm{I}')} - \frac{f_i(\boldsymbol{c}_i, \mathrm{I})}{\mathsf{m}_i(\boldsymbol{c}_i, \mathrm{I})} \Big) \mathsf{W}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'} \mathrm{d}\boldsymbol{c}_i', \tag{2.23}$$

where $\mathsf{W}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'} = \mathsf{m}_i(\boldsymbol{c}_i, \mathrm{I}) \int f_{\mathrm{ph}}^{\mathrm{e}}(\boldsymbol{q}) \overline{\mathsf{W}}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'} \mathrm{d}\boldsymbol{q}$ denotes the resulting transition probability. The assumption that phonons are at equilibrium is often used in the literature [20, 22, 24, 25] and the Boltzmann equilibrium distribution for internal energies is also due to the interaction with phonons. The transition probability $\mathsf{W}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'}$ satisfies the reciprocity relation $\mathsf{W}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'} = \mathsf{W}_{i,\mathrm{ph}}^{\mathrm{I}',\mathrm{I}}$ and is nonzero only in the neighborhood of the surface [19, 20]. The operators $J_{i,\mathrm{ph}}$ are sometimes simplified as $J_{i,\mathrm{ph}}(f_i) = -(f_i - n_i \mathrm{M}_i)/\tau_i$ where the relaxation time τ_i only depends on the reduced normal coordinate ζ [20, 22, 24, 25].

2.6 Reactive collision operators

The rth surface chemical reaction is written in the form (1.1) where $\mathcal{F}^r$ and $\mathcal{B}^r$ denote the indices for the reactants and products counted with their order of multiplicity and $\mathfrak{R}$ is the set of reaction indices. The letters $\mathcal{F}^r$ and $\mathcal{B}^r$ are mnemonics for forward and backward directions and we denote by F^r and B^r the indices of the quantum energy states of the reactants and products. We also denote by ν_{ir}^{fw} and ν_{ir}^{bk} the stoichiometric coefficients of the ith species in the rth reaction in the forward and backward directions, that is, the multiplicity of species i in $\mathcal{F}^r$ and $\mathcal{B}^r$, respectively, and by $\nu_{ir} = \nu_{ir}^{\mathrm{bk}} - \nu_{ir}^{\mathrm{fw}}$ the overall stoichiometric coefficient of the ith species in the rth reaction. With the atomic site convention, the reacting species are the physisorbed-gas species indexed by S_{g}, the chemisorbed species indexed by S_{c}, the crystal free site species indexed by S_{s} and the bulk species indexed by S_{b}, that is, the crystal molecules are included in the reaction mechanism. All particles involved in reactive collisions are thus properly taken into account in the symbolic description of the chemical reaction (1.1) so that it may be used in a kinetic framework [32, 33, 34].

The surface reactions (1.1) conserve the atoms associated with gaseous species, the number of sites as well as the crystal atoms [42, 17, 63, 64]. More specifically, denoting by $\mathfrak{A}_{\mathrm{g}}$ the sets of atoms associated with physisorbed-gas or chemisorbed particles and by $\mathfrak{a}_{il}$ the number of lth atoms in the ith species, then the stoichiometric coefficients satisfy

$$\sum_{i \in S} \mathfrak{a}_{il} \nu_{ir} = 0, \qquad r \in \mathfrak{R}, \quad l \in \mathfrak{A}_{\mathrm{g}}, \tag{2.24}$$

where we have set $\mathfrak{a}_{il} = 0$ for $i \in S_{\mathrm{s}} \cup S_{\mathrm{b}}$ and $l \in \mathfrak{A}_{\mathrm{g}}$. In addition, the conservation of crystal atoms reads

$$\sum_{i \in S_{\mathrm{b}}} \nu_{ir} + \nu_{\mathrm{s}r} = 0, \qquad r \in \mathfrak{R}, \tag{2.25}$$

and that of surface sites

$$\sum_{i \in S_{\mathrm{c}}} \nu_{ir} + \nu_{\mathrm{s}r} = 0, \qquad r \in \mathfrak{R}. \tag{2.26}$$

It is then convenient to extend the gas atom indexing set $\mathfrak{A}_{\mathrm{g}}$ into $\mathfrak{A} = \mathfrak{A}_{\mathrm{g}} \cup \{\mathcal{S}, \mathcal{C}\}$ where $\mathcal{C}$ denotes the crystal atom, $\mathcal{S}$ is a symbol for the site atom, and to define $\mathfrak{a}_{i\mathcal{S}} = 1$ if $i \in S_{\mathrm{c}} \cup S_{\mathrm{s}}$, $\mathfrak{a}_{i\mathcal{S}} = 0$ if $i \in S_{\mathrm{g}} \cup S_{\mathrm{b}}$, and $\mathfrak{a}_{i\mathcal{C}} = 1$ if $i \in S_{\mathrm{s}} \cup S_{\mathrm{b}}$, $\mathfrak{a}_{i\mathcal{C}} = 0$ if $i \in S_{\mathrm{g}} \cup S_{\mathrm{c}}$, so that the conservation of all atoms (2.24)–(2.26) reads $\sum_{i\in S}\mathfrak{a}_{il}\nu_{ir}=0$ for any $r\in\mathfrak{R}$ and any $l\in\mathfrak{A}$ and includes site conservation.

There is another symbolic way of describing heterogeneous chemical reactions where all the crystal molecules $\mathfrak{M}_i$ for $i\in S_{\mathrm{s}}\cup S_{\mathrm{b}}$ are *removed* and where the free sites species $\mathfrak{M}_{\mathrm{N_g+N_c}+1}$ is replaced by an open site symbol $\mathcal{O}$ that is massless and atomless [16, 17]. These two symbolic descriptions of surface chemical reactions are equally valid for a *macroscopic* description of surface chemistry but only the atomic site convention is useful in order to describe reactive collisions.

The reactive collision term for the ith species may be decomposed into

$$\mathcal{C}_i(f)=\sum_{r\in\mathfrak{R}}\mathcal{C}_i^r(f), \tag{2.27}$$

where $\mathcal{C}_i^r(f)$ represents the contribution of the rth reaction. The reactive collision term $\mathcal{C}_i^r(f)$ associated with (1.1) is written as for gas phase reactions [65, 66, 63, 42, 43]

$$\begin{aligned}\mathcal{C}_i^r(f)=\nu_{ir}^{\mathrm{fw}}&\sum_{\mathrm{F}_{\mathrm{I}}^r,\,\mathrm{B}^r}\int\Big(\mathcal{W}_{\mathcal{B}^r\mathcal{F}^r}^{\mathrm{B}^r\mathrm{F}^r}\prod_{k\in\mathcal{B}^r}\mathfrak{f}_k-\mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r}\prod_{j\in\mathcal{F}^r}\mathfrak{f}_j\Big)\prod_{j\in\mathcal{F}_i^r}\mathrm{d}\boldsymbol{c}_j\prod_{k\in\mathcal{B}^r}\mathrm{d}\boldsymbol{c}_k\\ -\nu_{ir}^{\mathrm{bk}}&\sum_{\mathrm{F}^r,\,\mathrm{B}_{\mathrm{I}}^r}\int\Big(\mathcal{W}_{\mathcal{B}^r\mathcal{F}^r}^{\mathrm{B}^r\mathrm{F}^r}\prod_{k\in\mathcal{B}^r}\mathfrak{f}_k-\mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r}\prod_{j\in\mathcal{F}^r}\mathfrak{f}_j\Big)\prod_{j\in\mathcal{F}^r}\mathrm{d}\boldsymbol{c}_j\prod_{k\in\mathcal{B}_i^r}\mathrm{d}\boldsymbol{c}_k,\end{aligned} \tag{2.28}$$

where $\mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r}$ denotes the transition probability that a collision between the reactants $\mathcal{F}^r$ with energies F^r lead to the products $\mathcal{B}^r$ with energies B^r, $\mathcal{F}_i^r$ the subset of $\mathcal{F}^r$ where the index i has been removed once with similar notation for $\mathcal{B}_i^r$, $\mathrm{F}_{\mathrm{I}}^r$ and $\mathrm{B}_{\mathrm{I}}^r$. The summation over F^r in (2.28) represents the sum over all quantum indices J for all $j\in\mathcal{F}^r$ with similar conventions for $\mathrm{F}_{\mathrm{I}}^r$, B^r, and $\mathrm{B}_{\mathrm{I}}^r$. The distributions $\mathfrak{f}_k$ are given by $\mathfrak{f}_k=f_k$ when $k\in S_{\mathrm{g}}\cup S_{\mathrm{s}}\cup S_{\mathrm{c}}$ and $\mathfrak{f}_k=f_\sigma$ when $k\in S_{\mathrm{b}}$. The surface distribution f_σ need to be used for bulk species since the chemisorbed molecules may collide with any atom of the crystal surface [33]. The following reciprocity relations hold between transition probabilities [65, 66, 63, 42, 43]

$$\mathcal{W}_{\mathcal{B}^r\mathcal{F}^r}^{\mathrm{B}^r\mathrm{F}^r}\prod_{j\in\mathcal{F}^r}\beta_{j\mathrm{J}}=\mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r}\prod_{k\in\mathcal{B}^r}\beta_{k\mathrm{K}}, \tag{2.29}$$

where $\beta_{i\mathrm{I}}=\mathrm{h}_{\mathrm{P}}^3/(a_{i\mathrm{I}}\mathfrak{m}_i^3)$ and h_{P} is the Planck constant, and generalize the relation (2.4) between nonreactive transition probabilities. The collision term (2.28) is similar to typical reactive terms associated with gas phase chemical reactions [63, 42, 43] and naturally involves collisions between physisorbed-gas particles, chemisorbed particles, crystal free sites particles and crystal bulk particles. The operator $\mathcal{C}_i$ is local in space as typical collision operators and the distribution functions are three dimensional in space. Reactive transition probabilities for surface reactions may generally be extracted from quantum mechanical simulations using the density functional theory [15, 55, 56, 57, 58, 59, 60, 61, 62].

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

$$\mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r}\prod_{j\in\mathcal{F}^r}\mathfrak{f}_j^{\mathrm{ce}}=\mathcal{W}_{\mathcal{B}^r\mathcal{F}^r}^{\mathrm{B}^r\mathrm{F}^r}\prod_{k\in\mathcal{B}^r}\mathfrak{f}_k^{\mathrm{ce}}, \tag{2.30}$$

where the chemical equilibrium distributions $\mathfrak{f}_i^{\mathrm{ce}}$, $i\in S$, are given by $\mathfrak{f}_i^{\mathrm{ce}}=n_i^{\mathrm{ce}}\mathrm{M}_i$, when $i\in S_{\mathrm{g}}\cup S_{\mathrm{s}}\cup S_{\mathrm{c}}$ with n_i^{ce} denoting the chemical equilibrium value of n_i, and by $\mathfrak{f}_i^{\mathrm{ce}}=\mathfrak{f}_i^{\mathrm{e}}=$

$f_\sigma^{\mathrm{e}} = n_\sigma \mathrm{M}_\sigma$ for $i \in S_{\mathrm{b}}$ since $n_\sigma^{\mathrm{ce}} = n_\sigma^{\mathrm{e}} = n_\sigma$ remains constant in time. The superscript $^{\mathrm{ce}}$ denotes chemical equilibrium whereas the superscript $^{\mathrm{e}}$ denotes physical equilibrium.

Using then the equilibrium relation (2.30), we may write the reactive source term as

$$\begin{aligned} \mathcal{C}_i^r(f) = \nu_{ir}^{\mathrm{fw}} \sum_{\mathrm{F}_\mathrm{I}^r,\,\mathrm{B}^r} \int \Big(\prod_{k\in\mathcal{B}^r} \frac{\mathfrak{f}_k}{\mathfrak{f}_k^{\mathrm{ce}}} - \prod_{j\in\mathcal{F}^r} \frac{\mathfrak{f}_j}{\mathfrak{f}_j^{\mathrm{ce}}} \Big) \mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} \prod_{j\in\mathcal{F}^r} \mathfrak{f}_j^{\mathrm{ce}} \prod_{j\in\mathcal{F}_i^r} \mathrm{d}\boldsymbol{c}_j \prod_{k\in\mathcal{B}^r} \mathrm{d}\boldsymbol{c}_k \\ - \nu_{ir}^{\mathrm{bk}} \sum_{\mathrm{F}^r,\,\mathrm{B}_\mathrm{I}^r} \int \Big(\prod_{k\in\mathcal{B}^r} \frac{\mathfrak{f}_k}{\mathfrak{f}_k^{\mathrm{ce}}} - \prod_{j\in\mathcal{F}^r} \frac{\mathfrak{f}_j}{\mathfrak{f}_j^{\mathrm{ce}}} \Big) \mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} \prod_{j\in\mathcal{F}^r} \mathfrak{f}_j^{\mathrm{ce}} \prod_{j\in\mathcal{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{k\in\mathcal{B}_i^r} \mathrm{d}\boldsymbol{c}_k. \end{aligned} \tag{2.31}$$

In order to simplify the reaction collision terms, we now assume that the surface distribution $\mathfrak{f}_k = f_\sigma$ involved for the bulk species $k \in S_{\mathrm{b}}$ *remains at physical equilibrium* $f_\sigma = f_\sigma^{\mathrm{e}}$. However, the surface distribution at physical equilibrium coincide with that at chemical equilibrium $f_\sigma^{\mathrm{e}} = f_\sigma^{\mathrm{ce}}$. The chemical production rates are then in the form

$$\begin{aligned} \mathcal{C}_i^r(f) = \nu_{ir}^{\mathrm{fw}} \sum_{\mathrm{F}_\mathrm{I}^r,\,\mathrm{B}^r} \int \Big(\prod_{k\in\overline{\mathcal{B}}^r} \frac{f_k}{f_k^{\mathrm{ce}}} - \prod_{j\in\overline{\mathcal{F}}^r} \frac{f_j}{f_j^{\mathrm{ce}}} \Big) \mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} \prod_{j\in\mathcal{F}^r} \mathfrak{f}_j^{\mathrm{ce}} \prod_{j\in\mathcal{F}_i^r} \mathrm{d}\boldsymbol{c}_j \prod_{k\in\mathcal{B}^r} \mathrm{d}\boldsymbol{c}_k \\ - \nu_{ir}^{\mathrm{bk}} \sum_{\mathrm{F}^r,\,\mathrm{B}_\mathrm{I}^r} \int \Big(\prod_{k\in\overline{\mathcal{B}}^r} \frac{f_k}{f_k^{\mathrm{ce}}} - \prod_{j\in\overline{\mathcal{F}}^r} \frac{f_j}{f_j^{\mathrm{ce}}} \Big) \mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} \prod_{j\in\mathcal{F}^r} \mathfrak{f}_j^{\mathrm{ce}} \prod_{j\in\mathcal{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{k\in\mathcal{B}_i^r} \mathrm{d}\boldsymbol{c}_k, \end{aligned} \tag{2.32}$$

where the overbar indexing sets $\overline{\mathcal{F}}^r$ and $\overline{\mathcal{B}}^r$ are obtained by removing any occurence of the bulk species in $\mathcal{F}^r$ and $\mathcal{B}^r$.

On the other hand, at chemical equilibrium, we have equality of the chemical potentials according to the chemical reaction (1.1)

$$\sum_{j\in\mathcal{F}^r} \mu_j^{\mathrm{ce}} = \sum_{k\in\mathcal{B}^r} \mu_k^{\mathrm{ce}}, \qquad r \in \mathfrak{R}, \tag{2.33}$$

where μ_i^{ce} denotes the chemical potential of the ith species at chemical equilibrium. This relation may also be written

$$\sum_{i\in S} \nu_{ir}^{\mathrm{fw}} \mu_i^{\mathrm{ce}} = \sum_{i\in S} \nu_{ir}^{\mathrm{bk}} \mu_i^{\mathrm{ce}}, \qquad r \in \mathfrak{R}. \tag{2.34}$$

The chemical potentials, that take into account the interaction potentials W_i, are in the form

$$\mu_i = \mu_i^{\mathrm{in}} + \frac{\mathrm{W}_i}{k_{\mathrm{B}} T_{\mathrm{w}}}, \tag{2.35}$$

where μ_i^{in} is the *intrinsic* species chemical potential [48, 49, 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 ith species, z_i the partition function per unit volume and n_i is the local number density with the influence of the force field [48, 49, 50]. For the bulk species $i \in S_{\mathrm{b}}$ we also have the chemical potential $\mu_i^{\mathrm{in}} = \log(n_\sigma/\mathrm{z}_i)$ since collision may occur with any crystal particle on the surface. These effective chemical potentials μ_i for $i \in S_{\mathrm{b}}$ yields activity coefficients for bulk species that are constants in agreement with heterogeneous surface chemistry [16]. 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 ith species par unit volume and $\mathrm{z}_i^{\mathrm{int}}$ the internal energy partition function. The translational partition functions are given by $\mathrm{z}_i^{\mathrm{tr}} = \Lambda_i^{-3}$ where $\Lambda_i = \mathrm{h}_{\mathrm{P}}/(2\pi k_{\mathrm{B}} \mathfrak{m}_i T_{\mathrm{w}})^{1/2}$ denotes the thermal de Broglie wavelength of the ith species and h_{P} the Planck constant.

After some algebra, using the equilibrium condition (2.33), the atom conservation relations (2.25)(2.26) as well as

$$\frac{f_k}{f_k^{\mathrm{ce}}} = \frac{1}{\exp(\mu_k^{\mathrm{ce}})} \frac{f_k}{\mathsf{m}_k \mathrm{Z}_k}, \qquad k \in S_{\mathrm{g}} \cup S_{\mathrm{c}} \cup S_{\mathrm{s}} = S \backslash S_{\mathrm{b}}, \tag{2.36}$$

the source term is obtained in the form

$$\begin{aligned} \mathcal{C}_i^r(f) = {}& \nu_{ir}^{\mathrm{fw}} \sum_{\mathrm{F}_{\mathrm{I}}^r,\, \mathrm{B}^r} \int \Big(\prod_{k\in\mathcal{B}^r} \frac{\gamma_k}{\mathrm{Z}_k} - \prod_{j\in\mathcal{F}^r} \frac{\gamma_j}{\mathrm{Z}_j} \Big) \widehat{\mathcal{W}}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} \prod_{j\in\mathcal{F}_i^r} \mathrm{d}\boldsymbol{c}_j \prod_{k\in\mathcal{B}^r} \mathrm{d}\boldsymbol{c}_k \\ & - \nu_{ir}^{\mathrm{bk}} \sum_{\mathrm{F}^r,\mathrm{B}_{\mathrm{I}}^r} \int \Big(\prod_{k\in\mathcal{B}^r} \frac{\gamma_k}{\mathrm{Z}_k} - \prod_{j\in\mathcal{F}^r} \frac{\gamma_j}{\mathrm{Z}_j} \Big) \widehat{\mathcal{W}}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} \prod_{j\in\mathcal{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{k\in\mathcal{B}_i^r} \mathrm{d}\boldsymbol{c}_k, \end{aligned} \tag{2.37}$$

where

$$\gamma_k = \frac{f_k}{\mathsf{m}_k} \qquad k \in S_{\mathrm{g}} \cup S_{\mathrm{c}} \cup S_{\mathrm{s}} = S \backslash S_{\mathrm{b}}, \qquad\qquad \gamma_k = \mathsf{n}_\sigma, \qquad k \in S_{\mathrm{b}}, \tag{2.38}$$

and

$$\widehat{\mathcal{W}}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} = \mathcal{W}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} \prod_{j\in\mathcal{F}^r} \frac{1}{\beta_{j\mathrm{J}}} \exp\Big(-\frac{m_j |\boldsymbol{c}_j|^2}{2k_{\mathrm{B}}T_{\mathrm{w}}} - \frac{\mathrm{E}_{j\mathrm{J}} + \mathrm{W}_j}{k_{\mathrm{B}}T_{\mathrm{w}}} \Big), \tag{2.39}$$

are rescaled transition probabilities such that $\widehat{\mathcal{W}}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} = \widehat{\mathcal{W}}_{\mathcal{B}^r\mathcal{F}^r}^{\mathrm{B}^r\mathrm{F}^r}$.

2.7 Collisional invariants

Collision invariants in kinetic models are closely related with macroscopic conservation laws. Since the model involves different types of collisions, represented by different collision integral operators, as well as different type of particles, several collisional invariants may be introduced. We generally define the functions ψ^l associated with particle numbers $\psi^l = (\delta_{il})_{i\in S}$, $l \in S$, where δ_{il} denotes the Kronecker symbol, momentum in three dimensions $\psi^{\mathrm{N}+\nu} = (m_i c_{i\nu})_{i\in S}$, $\nu \in \{1,2,3\}$, as well as total energy $\psi^{\mathrm{N}+4} = (\frac{1}{2} m_i |\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}} + \mathrm{W}_i)_{i\in S}$.

Mass, momentum, and energy is conserved in binary collisions between physisorbed-gas particles, associated with the collision operators J_{ij}, $i,j \in S_{\mathrm{g}}$, so that ψ^l for $l \in S_{\mathrm{g}}$, and $l = \mathrm{N}+1, \mathrm{N}+2, \mathrm{N}+3, \mathrm{N}+4$ are collisional invariants of the physisorbed-gas mixture. Moreover, for the physisorbed-gas species, only the first N_{g} components of these invariants are relevant and we may define $\psi_{\mathrm{g}}^l = (\delta_{il})_{i\in S_{\mathrm{g}}}$, $l \in S_{\mathrm{g}}$, $\psi_{\mathrm{g}}^{\mathrm{N}+\nu} = (m_i c_{i\nu})_{i\in S_{\mathrm{g}}}$, $\nu \in \{1,2,3\}$, as well as $\psi_{\mathrm{g}}^{\mathrm{N}+4} = (\frac{1}{2} m_i |\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}} + \mathrm{W}_i)_{i\in S_{\mathrm{g}}}$. The fluid governing equations in the physisorbate-gas are then obtained by taking moments of Boltzmann equations (2.2) using the physisorbed-gas scalar product

$$\langle\!\langle \xi, \zeta \rangle\!\rangle = \sum_{\substack{i\in S_{\mathrm{g}} \\ \mathrm{I}\in\mathfrak{Q}_i}} \int \xi_i \odot \zeta_i \, \mathrm{d}\boldsymbol{c}_i, \tag{2.40}$$

where $\xi = (\xi_i)_{i\in S_{\mathrm{g}}}$, $\zeta = (\zeta_i)_{i\in S_{\mathrm{g}}}$ and $\xi_i \odot \zeta_i$ is the maximum contracted product between tensors ξ_i and ζ_i.

We further define the atoms invariants as $\widetilde{\psi}^l = (\mathfrak{a}_{il})_{i\in S}$, $l \in \mathfrak{A}$, where $\mathfrak{a}_{il}$ denotes the number of atoms of type l in the molecule of type i for $i \in S$ and $l \in \mathfrak{A}$, and $\mathfrak{A}$ the set of all atoms associated with gas particles, crystal atoms and surface site [63]. Since atoms, momentum, and energy are conserved in reactive collisions, the invariants of the chemical operators $\mathcal{C}_i$, $i \in S$, are then $\widetilde{\psi}^l$, $l \in \mathfrak{A}$, and ψ^l for $l = \mathrm{N}+1, \mathrm{N}+2, \mathrm{N}+3, \mathrm{N}+4$.

On the other hand, contrarily to particle-particle collision operators, momentum and energy are not conserved by the collision operators with phonons $J_{i,\mathrm{ph}}$, since it may be given to phonons that are assumed to be at equilibrium. The operators $J_{i,\mathrm{ph}}$ only conserve the number of particles with the invariant $\psi^l = (\delta_{il})_{i\in S}$ for $l \in S$. Incidentally, when a kinetic equation is used to describe the phonons, energy is conserved during collisions between phonons and particles but not necessarily momentum because of the umklapp process [35].

2.8 Kinetic entropy

The kinetic entropies compatible with the phonon collision operators $J_{i,\mathrm{ph}}$ are slightly different from the traditional expressions. The origin of this modification is that phonons are assumed to be at equilibrium and the collision terms $J_{i,\mathrm{ph}}$ for $i \in S$ 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 being 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 [67, 68]. The modified entropies are generally not anymore required when phonons kinetic equations are taken into account [36, 37]. These modified entropies are further enriched in this work in order to take into account the species interaction potentials W_i, $i \in S$, as well as the entropy associated with chemisorbed and crystal species.

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

$$\mathcal{S}_i^{\mathrm{kin}} = -k_{\mathrm{B}} \sum_{\mathrm{I}\in\mathfrak{Q}_i} \int f_i\big(\log(f_i/\mathsf{m}_i\mathrm{Z}_i) - 1\big)\,\mathrm{d}\boldsymbol{c}_i, \qquad i \in S_{\mathrm{g}} \cup S_{\mathrm{c}} \cup S_{\mathrm{s}} = S\backslash S_{\mathrm{b}}, \tag{2.41}$$

the entropies associated with the bulk species by

$$\mathcal{S}_i^{\mathrm{kin}} = -k_{\mathrm{B}} \int f_i \log(\mathsf{n}_\sigma/\mathrm{Z}_i)\,\mathrm{d}\boldsymbol{c}_i, \qquad i \in S_{\mathrm{b}}, \tag{2.42}$$

and the total entropy by

$$\mathcal{S}^{\mathrm{kin}} = \sum_{i\in S} \mathcal{S}_i^{\mathrm{kin}}. \tag{2.43}$$

Multiplying the Boltzmann equation (2.2) by $\log(f_i/\mathsf{m}_i\mathrm{Z}_i)$, integrating with respect to $\mathrm{d}\boldsymbol{c}_i$, and summing over $\mathrm{I} \in \mathfrak{Q}_i$ for $i \in S_{\mathrm{g}} \cup S_{\mathrm{c}} \cup S_{\mathrm{s}} = S\backslash S_{\mathrm{b}}$, multiplying the kinetic equation (2.6) by $\log(\mathsf{n}_\sigma/\mathrm{Z}_i)$, integrating with respect to $\mathrm{d}\boldsymbol{c}_i$, for $i \in S_{\mathrm{b}}$, and adding the resulting balance laws, and using (2.15), we obtain a balance equation for $\mathcal{S}^{\mathrm{kin}}$ in the form

$$\partial_t \mathcal{S}^{\mathrm{kin}} + \boldsymbol{\partial_x}\cdot\boldsymbol{\mathcal{F}}^{\mathrm{kin}} = \mathfrak{v}^{\mathrm{kin}}, \tag{2.44}$$

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

$$\boldsymbol{\mathcal{F}}^{\mathrm{kin}} = -k_{\mathrm{B}} \sum_{\substack{i\in S\backslash S_{\mathrm{b}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \boldsymbol{c}_i f_i\big(\log(f_i/\mathsf{m}_i\mathrm{Z}_i) - 1\big)\,\mathrm{d}\boldsymbol{c}_i - k_{\mathrm{B}} \sum_{i\in S_{\mathrm{b}}} \int \boldsymbol{c}_i f_i \log(\mathsf{n}_\sigma/\mathrm{Z}_i)\,\mathrm{d}\boldsymbol{c}_i, \tag{2.45}$$

and $\mathfrak{v}^{\mathrm{kin}}$ denotes the kinetic entropy source term. This entropy source term $\mathfrak{v}^{\mathrm{kin}}$ may be split as $\mathfrak{v}^{\mathrm{kin}} = \mathfrak{v}_J + \mathfrak{v}_{\mathrm{ph}} + \mathfrak{v}_{\mathcal{C}}$ where

$$\mathfrak{v}_J = -\, k_{\mathrm{B}} \sum_{\substack{i,j\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int J_{ij}(f_i,f_j) \log(f_i/\mathsf{m}_i \mathrm{z}_i)\, \mathrm{d}\boldsymbol{c}_i, \tag{2.46}$$

$$\mathfrak{v}_{\mathrm{ph}} = -\, k_{\mathrm{B}} \sum_{\substack{i\in S\setminus S_{\mathrm{b}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int J_{i,\mathrm{ph}}(f_i) \log(f_i/\mathsf{m}_i \mathrm{z}_i)\, \mathrm{d}\boldsymbol{c}_i - k_{\mathrm{B}} \sum_{i\in S_{\mathrm{b}}} \int J_{i,\mathrm{ph}}(f_i) \log(\mathsf{n}_\sigma/\mathrm{z}_i)\, \mathrm{d}\boldsymbol{c}_i, \tag{2.47}$$

and

$$\mathfrak{v}_{\mathcal{C}} = -k_{\mathrm{B}} \sum_{\substack{i\in S\setminus S_{\mathrm{b}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \mathcal{C}_i \log(f_i/\mathsf{m}_i \mathrm{z}_i)\, \mathrm{d}\boldsymbol{c}_i - k_{\mathrm{B}} \sum_{i\in S_{\mathrm{b}}} \int \mathcal{C}_i \log(\mathsf{n}_\sigma/\mathrm{z}_i)\, \mathrm{d}\boldsymbol{c}_i. \tag{2.48}$$

We now investigate the sign of entropy production terms and first consider the production $\mathfrak{v}_J$ arising from the non reactive operators J_{ij}, $i,j \in S_{\mathrm{g}}$ associated with physisorbed-gas particles. We note that the factors $\log(f_i/\mathsf{m}_i\mathrm{z}_i)$ may be simplified as $\log f_i$ since $\big(\log(\mathsf{m}_i\mathrm{z}_i)\big)_{i\in S_{\mathrm{g}}}$ is a collisional invariant. The resulting entropy production $\mathfrak{v}_J$ thus coincides with the traditional expression and using standard arguments from kinetic theory, it is obtained that

$$\mathfrak{v}_J = \frac{k_{\mathrm{B}}}{4} \sum_{i,j\in S_{\mathrm{g}}} \sum_{\substack{\mathrm{I},\mathrm{I}'\in\mathfrak{Q}_i\\ \mathrm{J},\mathrm{J}'\in\mathfrak{Q}_j}} \int \Upsilon\big(f_i f_j, f_i' f_j' \frac{a_{i\mathrm{I}} a_{j\mathrm{J}}}{a_{i\mathrm{I}'} a_{j\mathrm{J}'}}\big)\, \mathsf{W}_{ij}^{\mathrm{IJI'J'}} \mathrm{d}\boldsymbol{c}_i \mathrm{d}\boldsymbol{c}_j \mathrm{d}\boldsymbol{c}_i' \mathrm{d}\boldsymbol{c}_j', \tag{2.49}$$

where Υ denotes the nonnegative function $\Upsilon(x,y) = (x-y)(\log x - \log y)$. Considering next the entropy production $\mathfrak{v}_{\mathrm{ph}}$ due to the interaction with phonons, we note that the factors $\log(f_i/\mathsf{m}_i\mathrm{z}_i)$ may be simplified into $\log(f_i/\mathsf{m}_i)$ since $\log \mathrm{z}_i$ is independent of $\boldsymbol{c}_i$ whereas the factors $\log(\mathsf{n}_\sigma/\mathrm{z}_{\mathrm{s}})$ yields zero contributions since they are independent of the species velocities. Using standard arguments from kinetic theory, it is then obtained after some algebra that

$$\mathfrak{v}_{\mathrm{ph}} = \frac{k_{\mathrm{B}}}{2} \sum_{i\in S\setminus S_{\mathrm{b}}} \sum_{\mathrm{I},\mathrm{I}'\in\mathfrak{Q}_i} \int \Upsilon\big(f_i/\mathsf{m}_i, f_i'/\mathsf{m}_i'\big)\, \mathsf{W}_{i,\mathrm{ph}}\, \mathrm{d}\boldsymbol{c}_i\, \mathrm{d}\boldsymbol{c}_i'. \tag{2.50}$$

Note that the bulk species contributions in the above sum vanish since the surface is assumed to be at physical equilibrium. Considering finally entropy production $\mathfrak{v}_{\mathcal{C}}$ associated with reactive collisions, it is obtained after some algebra that

$$\mathfrak{v}_{\mathcal{C}} = k_{\mathrm{B}} \sum_{r\in\mathfrak{R}} \sum_{\mathrm{F}^r,\mathrm{B}^r} \int \Upsilon\Big(\prod_{j\in\mathcal{F}^r} \frac{\gamma_j}{\mathrm{z}_j}, \prod_{k\in\mathcal{B}^r} \frac{\gamma_k}{\mathrm{z}_k}, \Big) \widehat{\mathcal{W}}_{\mathcal{F}^r\mathcal{B}^r}^{\mathrm{F}^r\mathrm{B}^r} \prod_{j\in\mathcal{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{k\in\mathcal{B}^r} \mathrm{d}\boldsymbol{c}_k, \tag{2.51}$$

where the reduced distributions γ_k are given in (2.38). Since the function Υ only takes nonnegative values, we conclude that all quantities $\mathfrak{v}_J$, $\mathfrak{v}_{\mathrm{ph}}$, and $\mathfrak{v}_{\mathcal{C}}$ are nonnegative terms. All collisions, nonreactive or reactive, thus lead to nonnegative entropy production. The Boltzmann equations (2.2) and (2.6) are thus compatible with the Boltzmann H theorem and lead to a dissipative structure of the reactive surface at the molecular level.

3 Multiscale framework

In order to investigate reactive *fluid* boundary conditions, a fluid scaling of the kinetic equations (2.2) 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.

3.1 Fluid scaling

We denote by $T^\star$ a characteristic temperature, $n^\star$ a characteristic number density, $m^\star$ a characteristic particle mass, and $\tau^\star$ a characteristic collision time. We write $v^\star = (k_{\mathrm{B}} T^\star/m^\star)^{1/2}$ the characteristic thermal velocity, $f^\star = n^\star/v^{\star 3}$ the characteristic particle distribution, $\lambda^\star = \tau^\star v^\star$ the characteristic mean free path, $\mathsf{W}^\star = 1/(n^\star \tau^\star v^{\star 6})$ the characteristic transition probability for inert collisions. We also denote by $\tau_{\mathrm{f}}^\star$ 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 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 $i \in S$, 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 W_i and $\mathsf{W}_{i,\mathrm{ph}}$, 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

$$\epsilon_\kappa = \frac{\tau^\star}{\tau_{\mathrm{f}}^\star} = \frac{\lambda^\star}{l^\star}, \qquad \epsilon_{\mathrm{ph}} = \frac{\tau_{\mathrm{ph}}^\star}{\tau_{\mathrm{f}}^\star}, \qquad \epsilon = \frac{\delta^\star}{l^\star}. \tag{3.1}$$

The characteristic times and lengths at the solid/gas interface are generally such that $\tau_{\mathrm{ph}}^\star \leq \tau^\star \ll \tau_{\mathrm{f}}^\star$ and $\delta^\star \leq \lambda^\star \ll l^\star$ and ϵ_κ represents the species Knudsen number [20]. Since our aim is to derive *fluid* boundary conditions, it is assumed in this work that the small parameters ϵ_κ, ϵ_{ph}, and ϵ are of the same *asymptotic* order of magnitude in the sense

$$\epsilon_\kappa = \alpha_\kappa\, \epsilon \qquad \epsilon_{\mathrm{ph}} = \alpha_{\mathrm{ph}}\, \epsilon, \tag{3.2}$$

where α_{ph} and α_κ 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 $l^\star$. Note that it is incidentally assumed that all species have comparable masses, collision frequencies and phonon interaction frequencies. This scaling may be seen as the *simplest fluid scaling* for the reactive surface layer model and it is a natural choice since we want to study fluid boundary conditions at a reactive interface.

Keeping in mind that the potential W_i only depends on z, the kinetic equation governing f_i is obtained in the form

$$\begin{aligned}\partial_t f_i + \boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel} f_i + c_{iz}\, \partial_z f_i - \frac{1}{m_i} \partial_z \mathrm{W}_i\, \partial_{c_{iz}} f_i &= \frac{1}{\alpha_\kappa \epsilon} \sum_{j \in S_{\mathrm{g}}} J_{ij}(f_i, f_j) \\ &+ \frac{1}{\alpha_{\mathrm{ph}} \epsilon} J_{i,\mathrm{ph}}(f_i) + \mathcal{C}_i, \qquad i \in S,\end{aligned} \tag{3.3}$$

where f_i denotes the distribution function, $\boldsymbol{c}_{i\shortparallel}$ the tangential velocity of the ith species with $\boldsymbol{c}_i = (\boldsymbol{c}_{i\shortparallel}, c_{iz})^t$, $\boldsymbol{\partial}_{\shortparallel}$ the tangential spatial derivative operator, c_{iz} the normal velocity of the ith species, ∂_z the normal spatial derivative, $\partial_{c_{iz}}$ the differential operator with respect to c_{iz}, J_{ij} the particles collision operator that are only nonzero for $i, j \in S_{\mathrm{g}}$, $J_{i,\mathrm{ph}}$

the phonon collision operator and $\mathcal{C}_i$ the chemistry source term. The chemistry operators $\mathcal{C}_i$, $i \in S$, are therefore assumed to be slow in comparison with the inert collision operators J_{ij}, $i,j \in S_{\rm g}$, and $J_{i,\rm ph}$, $i \in S$. These equations may be interpreted either as rescaled equations with rescaled quantities denoted as unscaled quantities, or, equivalently, as original unscaled equations where ϵ is a formal expansion parameter numerically equal to unity [39, 40].

3.2 Standard expansion in the gas

The kinetic equations in the gas, obtained from (3.3) by letting $i \in S_{\rm g}$, $\mathrm{W}_i = 0$, $J_{i,\rm ph} = 0$, $\mathcal{C}_i = 0$, read

$$\partial_t f_{{\rm g}i} + \boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel} f_{{\rm g}i} + c_{iz}\, \partial_z f_{{\rm g}i} = \frac{1}{\alpha_\kappa \epsilon} \sum_{j \in S_{\rm g}} J_{ij}(f_{{\rm g}i}, f_{{\rm g}j}), \qquad i \in S_{\rm g}. \tag{3.4}$$

These equations coincide with the traditional scaling of the Chapman-Enskog method using the formal expansion parameter $\alpha_\kappa\epsilon$. The standard Enskog expansion of the distribution functions $f_{{\rm g}i}$, $i \in S_{\rm g}$, valid in the gas is thus in the form

$$f_{{\rm g}i}(t, \boldsymbol{x}_{\shortparallel}, z, \boldsymbol{c}_i, \mathrm{I}) = \widehat{f}^{(0)}_{{\rm g}i}(t, \boldsymbol{x}_{\shortparallel}, z, \boldsymbol{c}_i, \mathrm{I}) + \alpha_\kappa \epsilon\, \widehat{f}^{(1)}_{{\rm g}i}(t, \boldsymbol{x}_{\shortparallel}, z, \boldsymbol{c}_i, \mathrm{I}) + \mathcal{O}(\epsilon^2). \tag{3.5}$$

At zeroth order, it is obtained that

$$\sum_{j \in S_{\rm g}} J_{ij}(\widehat{f}^{(0)}_{{\rm g}i}, \widehat{f}^{(0)}_{{\rm g}j}) = 0, \tag{3.6}$$

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

$$\widehat{f}^{(0)}_{{\rm g}i} = n_{{\rm g}i} \Big(\frac{\mathfrak{m}_i}{2\pi k_{\rm B} T_{\rm g}} \Big)^{3/2} \frac{a_{i\rm I}}{\mathrm{Z}^{\rm int}_i} \exp\Big(-\frac{\mathfrak{m}_i |\boldsymbol{c}_i - \boldsymbol{v}_{\rm g}|^2}{2 k_{\rm B} T_{\rm g}} - \frac{\mathrm{E}_{i\rm I}}{k_{\rm B} T_{\rm g}} \Big), \tag{3.7}$$

where $n_{{\rm g}i}$ is the local gas number density, $\mathfrak{m}_i$ the particle mass, $\boldsymbol{v}_{\rm g}$ the local gas velocity, and $T_{\rm g}$ the local gas temperature with

$$n_{{\rm g}i} = \sum_{\mathrm{I} \in \mathfrak{Q}_i} \int f_{{\rm g}i}\, {\rm d}\boldsymbol{c}_i, \qquad \rho_{\rm g} \boldsymbol{v}_{\rm g} = \sum_{\substack{i \in S_{\rm g} \\ \mathrm{I} \in \mathfrak{Q}_i}} \int \mathfrak{m}_i \boldsymbol{c}_i f_{{\rm g}i}\, {\rm d}\boldsymbol{c}_i, \tag{3.8}$$

$$\mathcal{E}_{\rm g}(T_{\rm g}) = \sum_{\substack{i \in S_{\rm g} \\ \mathrm{I} \in \mathfrak{Q}_i}} \int \big(\tfrac{1}{2} \mathfrak{m}_i |\boldsymbol{c}_i - \boldsymbol{v}_{\rm g}|^2 + \mathrm{E}_{i\rm I} \big) f_{{\rm g}i}\, {\rm d}\boldsymbol{c}_i. \tag{3.9}$$

The internal partition function $\mathrm{Z}^{\rm int}_i$ of the ith species in the gas is given by

$$\mathrm{Z}^{\rm int}_i(T_{\rm g}) = \sum_{\mathrm{I} \in \mathfrak{Q}_i} a_{i\rm I} \exp\Big(-\frac{\mathrm{E}_{i\rm I}}{k_{\rm B} T_{\rm g}} \Big). \tag{3.10}$$

We have denoted by $\rho_{\rm g} = \sum_{i \in S_{\rm g}} \mathfrak{m}_i n_{{\rm g}i}$ the gas mixture mass density, $n_{\rm g} = \sum_{i \in S_{\rm g}} n_{{\rm g}i}$ the gas mixture number density, $\mathcal{E}_{\rm g} = \frac{3}{2} n_{\rm g} k_{\rm B} T_{\rm g} + \sum_{i \in S_{\rm g}} n_{{\rm g}i} \mathfrak{e}_i$ the internal energy of the gas mixture per unit volume, and

$$\mathfrak{e}_i = \sum_{\mathrm{I} \in \mathfrak{Q}_i} \frac{a_{i\rm I}}{\mathrm{Z}^{\rm int}_i} \mathrm{E}_{i\rm I} \exp\Big(-\frac{\mathrm{E}_{i\rm I}}{k_{\rm B} T_{\rm g}} \Big), \tag{3.11}$$

the average energy of the ith species. The standard expansion (3.5) of the distribution function $f_{\mathrm{g}i}$ then yields the *outer expansion* of the ith physisorbed-gas distribution f_i.

At first order, the distribution $\widehat{f}_{\mathrm{g}}^{(1)} = (\widehat{f}_{\mathrm{g}i}^{(1)})_{i\in S_{\mathrm{g}}}$ is written in the form

$$\widehat{f}_{\mathrm{g}i}^{(1)} = \widehat{\phi}_{\mathrm{g}i}^{(1)} \widehat{f}_{\mathrm{g}i}^{(0)}, \tag{3.12}$$

and the first order perturbation $\widehat{\phi}_{\mathrm{g}}^{(1)} = (\widehat{\phi}_{\mathrm{g}i}^{(1)})_{i\in S_{\mathrm{g}}}$ is solution of the system of Boltzmann linearized integral equation [38, 39, 40, 41, 42, 43, 44]

$$\widehat{\mathcal{I}}_{\mathrm{g}i}(\widehat{\phi}_{\mathrm{g}}^{(1)}) = -\big(\partial_t \log \widehat{f}_{\mathrm{g}i}^{(0)} + \boldsymbol{c}_i\boldsymbol{\cdot}\boldsymbol{\partial_x} \log \widehat{f}_{\mathrm{g}i}^{(0)}\big), \qquad i \in S_{\mathrm{g}}, \tag{3.13}$$

completed by the Enskog constraints $\langle\!\langle \widehat{f}_{\mathrm{g}}^{(1)}, \psi_{\mathrm{g}}^{l} \rangle\!\rangle = 0$ for $1 \leq l \leq \mathrm{N_g} + 4$. The gas collision invariants ψ_{g}^{l} are associated with species number $\psi_{\mathrm{g}}^{l} = (\delta_{li})_{i\in S_{\mathrm{g}}}$, $l \in S_{\mathrm{g}}$, momentum $\psi_{\mathrm{g}}^{\mathrm{N_g}+\nu} = (\mathfrak{m}_i c_{i\nu})_{i\in S_{\mathrm{g}}}$, $\nu \in \{1, 2, 3\}$, and total energy $\psi_{\mathrm{g}}^{\mathrm{N_g}+4} = (\frac{1}{2}\mathfrak{m}_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}})_{i\in S_{\mathrm{g}}}$. The integral operator $\widehat{\mathcal{I}}_{\mathrm{g}} = (\widehat{\mathcal{I}}_{\mathrm{g}i})_{i\in S_{\mathrm{g}}}$ denotes the traditional linearized collision operator acting on $\varphi = (\varphi_i)_{i\in S_{\mathrm{g}}}$ with components

$$\widehat{\mathcal{I}}_{\mathrm{g}i}(\varphi) = -\frac{1}{\widehat{f}_{\mathrm{g}i}^{(0)}} \sum_{j\in S_{\mathrm{g}}} \big(J_{ij}(\widehat{f}_{\mathrm{g}i}^{(0)}, \widehat{f}_{\mathrm{g}j}^{(0)}\varphi_j) + J_{ij}(\widehat{f}_{\mathrm{g}i}^{(0)}\varphi_i, \widehat{f}_{\mathrm{g}j}^{(0)}) \big), \tag{3.14}$$

and the time derivative terms $\partial_t \widehat{f}_{\mathrm{g}i}^{(0)}$ in the integral equations (3.13) are evaluated from Euler equations [38, 39, 40, 41, 42, 43, 44].

After lengthy algebra, $\widehat{\phi}_{\mathrm{g}i}^{(1)}$ is found in the form [38, 39, 40, 41, 42, 43, 44]

$$\widehat{\phi}_{\mathrm{g}i}^{(1)} = -\widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{\eta}\boldsymbol{:}\boldsymbol{\partial_x}\boldsymbol{v}_{\mathrm{g}} - \tfrac{1}{3}\widehat{\phi}_{\mathrm{g}i}^{\kappa}\boldsymbol{\partial_x}\boldsymbol{\cdot}\boldsymbol{v}_{\mathrm{g}} - \sum_{j\in S_{\mathrm{g}}} \widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{D_j}\boldsymbol{\cdot}\boldsymbol{\partial_x} p_{\mathrm{g}j} - \widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{\widehat{\lambda}}\boldsymbol{\cdot}\boldsymbol{\partial_x}(1/k_{\mathrm{B}}T_{\mathrm{g}}), \tag{3.15}$$

where $p_{\mathrm{g}j}$ denotes the partial pressure of the jth species in the gas, $\widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{\eta}$, $i \in S_{\mathrm{g}}$, are traceless symmetric matrices, $\widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{\widehat{\lambda}}$, $i \in S_{\mathrm{g}}$, are vectors, $\widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{D_j}$, $i, j \in S_{\mathrm{g}}$, are vectors and $\widehat{\phi}_{\mathrm{g}i}^{\kappa}$, $i \in S_{\mathrm{g}}$, are scalars. The coefficients $\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{\eta} = (\widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{\eta})_{i\in S_{\mathrm{g}}}$, $\widehat{\phi}_{\mathrm{g}}^{\kappa} = (\widehat{\phi}_{\mathrm{g}i}^{\kappa})_{i\in S_{\mathrm{g}}}$, $\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{\widehat{\lambda}} = (\widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{\widehat{\lambda}})_{i\in S_{\mathrm{g}}}$, and $\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{D_j} = (\widehat{\boldsymbol{\phi}}_{\mathrm{g}i}^{D_j})_{i\in S_{\mathrm{g}}}$, for $j \in S_{\mathrm{g}}$, are solutions of systems of tensorial integral equations in the form [38, 39, 40, 41, 42, 43, 44]

$$\widehat{\mathcal{I}}_{\mathrm{g}i}(\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{\eta}) = \frac{\mathfrak{m}_i}{k_{\mathrm{B}}T_{\mathrm{g}}}\big((\boldsymbol{c}_i - \boldsymbol{v}_{\mathrm{g}})\otimes(\boldsymbol{c}_i - \boldsymbol{v}_{\mathrm{g}}) - \tfrac{1}{3}|\boldsymbol{c}_i - \boldsymbol{v}_{\mathrm{g}}|^2\boldsymbol{I}\big), \qquad i \in S_{\mathrm{g}}, \tag{3.16}$$

$$\widehat{\mathcal{I}}_{\mathrm{g}i}(\widehat{\phi}_{\mathrm{g}}^{\kappa}) = \frac{2\mathfrak{c}^{\mathrm{int}}}{\mathfrak{c}_{\mathrm{v}}k_{\mathrm{B}}T_{\mathrm{g}}}\big(\tfrac{1}{2}\mathfrak{m}_i|\boldsymbol{c}_i - \boldsymbol{v}_{\mathrm{g}}|^2 - \frac{3k_{\mathrm{B}}T_{\mathrm{g}}}{2}\big) + \frac{2\mathfrak{c}_{\mathrm{v}}^{\mathrm{tr}}}{\mathfrak{c}_{\mathrm{v}}k_{\mathrm{B}}T_{\mathrm{g}}}\big(\mathfrak{e}_i - \mathrm{E}_{i\mathrm{I}}\big), \qquad i \in S_{\mathrm{g}}, \tag{3.17}$$

$$\widehat{\mathcal{I}}_{\mathrm{g}i}(\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{\widehat{\lambda}}) = \Big(\frac{5k_{\mathrm{B}}T_{\mathrm{g}}}{2} - \tfrac{1}{2}\mathfrak{m}_i|\boldsymbol{c}_i - \boldsymbol{v}_{\mathrm{g}}|^2 + \mathfrak{e}_i - \mathrm{E}_{i\mathrm{I}}\Big)(\boldsymbol{c}_i - \boldsymbol{v}_{\mathrm{g}}), \qquad i \in S_{\mathrm{g}}, \tag{3.18}$$

$$\widehat{\mathcal{I}}_{\mathrm{g}i}(\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{D_j}) = \frac{1}{p_{\mathrm{g}i}}(\delta_{ij} - \mathrm{y}_{\mathrm{g}i})(\boldsymbol{c}_i - \boldsymbol{v}_{\mathrm{g}}), \qquad i, j \in S_{\mathrm{g}}, \tag{3.19}$$

with the Enskog constraints $\langle\!\langle \widehat{f}_{\mathrm{g}}^{(0)}\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{\eta}, \psi_{\mathrm{g}}^{l} \rangle\!\rangle = 0$, $\langle\!\langle \widehat{f}_{\mathrm{g}}^{(0)}\widehat{\phi}_{\mathrm{g}}^{\kappa}, \psi_{\mathrm{g}}^{l} \rangle\!\rangle = 0$, $\langle\!\langle \widehat{f}_{\mathrm{g}}^{(0)}\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{\widehat{\lambda}}, \psi_{\mathrm{g}}^{l} \rangle\!\rangle = 0$, and $\langle\!\langle \widehat{f}_{\mathrm{g}}^{(0)}\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{D_j}, \psi_{\mathrm{g}}^{l} \rangle\!\rangle = 0$, for $j \in S_{\mathrm{g}}$ and $1 \leq l \leq \mathrm{N_g} + 4$. In these equations, $\boldsymbol{I}$ denotes the three dimensional identity tensor, $\mathfrak{c}_{\mathrm{v}}^{\mathrm{tr}} = \frac{3}{2}k_{\mathrm{B}}$ the translational constant-volume specific heat per molecule, $\mathfrak{c}^{\mathrm{int}} = \sum_{i\in S_{\mathrm{g}}} \mathrm{x}_{\mathrm{g}i}\mathfrak{c}_i^{\mathrm{int}}$ the mixture internal heat capacity per molecule, $\mathfrak{c}_i^{\mathrm{int}} = \mathrm{d}\mathfrak{e}_i/\mathrm{d}T_{\mathrm{g}}$ the internal heat capacity of the ith species, $\mathfrak{c}_{\mathrm{v}} = \mathfrak{c}_{\mathrm{v}}^{\mathrm{tr}} + \mathfrak{c}^{\mathrm{int}}$ the mixture heat capacity at constant-volume per molecule, $\mathfrak{e}_i$ the average internal energy of the ith gaseous species, $\mathsf{x}_{\mathrm{g}i} = n_{\mathrm{g}i}/n_{\mathrm{g}}$ the mole fraction of the ith species in the gas and $\mathsf{y}_{\mathrm{g}i} = \rho_{\mathrm{g}i}/\rho_{\mathrm{g}}$ the mass fraction of the ith species in the gas with $\rho_{\mathrm{g}i} = \mathfrak{m}_i n_{\mathrm{g}i}$. The fluid shear viscosity η, volume viscosity κ, partial thermal conductivity $\widehat{\lambda}$, multicomponent diffusion coefficients D_{ij}, $i, j \in S_{\mathrm{g}}$, and the Soret coefficients θ_i^{th}, $i \in S_{\mathrm{g}}$, may then be expressed in terms of the perturbed distributions $\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{\eta}$, $\widehat{\phi}_{\mathrm{g}}^{\kappa}$, $\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{\widehat{\lambda}}$, and $\widehat{\boldsymbol{\phi}}_{\mathrm{g}}^{D_j}$, $j \in S_{\mathrm{g}}$ [38, 39, 40, 41, 42, 43, 44]

3.3 Corrected expansion near the surface

Since we investigate a fluid interacting with a solid surface, it is natural to assume that the fluid velocity is of first order $\boldsymbol{v}_{\mathrm{g}}(t, \boldsymbol{x}_{\shortparallel}, z) = \mathcal{O}(\epsilon)$ in the neighborhood of the surface. In addition, for the sake of simplicity, we also assume that the tangential gas velocity $\boldsymbol{v}_{\mathrm{g}\shortparallel} = \boldsymbol{v}_{\mathrm{g}} - v_{\mathrm{g}z}\boldsymbol{e}_z$ vanishes at the surface $z = 0$. The gas velocity at the solid-gas interface $z = 0$ is thus in the form

$$\boldsymbol{v}_{\mathrm{g}}(t, \boldsymbol{x}_{\shortparallel}, 0) = \epsilon \mathfrak{v}_{\mathrm{g}z}(t, \boldsymbol{x}_{\shortparallel})\boldsymbol{e}_z, \tag{3.20}$$

where $\mathfrak{v}_{\mathrm{g}z}(t, \boldsymbol{x}_{\shortparallel})$ denotes the normal component of the rescaled velocity $\boldsymbol{v}_{\mathrm{g}}/\epsilon$ at $z = 0$. The normal velocity at the wall $\boldsymbol{v}_{\mathrm{g}} = \epsilon \mathfrak{v}_{\mathrm{g}z}\boldsymbol{e}_z$ represents the Stefan flow. When a surface exchanges mass with a fluid, there is indeed an induced normal convection velocity—termed the Stefan velocity—that compensates for mass fluid production. Assuming that this velocity is small near the solid interface is natural and assuming that $\boldsymbol{v}_{\mathrm{g}\shortparallel} = \boldsymbol{v}_{\mathrm{g}} - v_{\mathrm{g}z}\boldsymbol{e}_z$ vanishes at the interface is the classical adherence condition [69, 70]. The model could be generalized in order to take into account a first order slip velocity $\boldsymbol{v}_{\mathrm{g}\shortparallel}(t, \boldsymbol{x}_{\shortparallel}, 0) = \mathcal{O}(\epsilon)$ at the surface $z = 0$ but such an extension lays beyond the scope of the present work.

The fluid convection velocity near the planar surface $\boldsymbol{v}_{\mathrm{g}}$ being of first order in ϵ, the outer expansion (3.5) need to be corrected near the surface. All terms proportional to the velocity $\boldsymbol{v}_{\mathrm{g}}$ must be shifted by one order in the outer expansion near $z = 0$. The corrected expansion of the species distribution functions $f_{\mathrm{g}i}$ valid in the gas phase near the surface are denoted in the form

$$f_{\mathrm{g}i} = f_{\mathrm{g}i}^{(0)} + \epsilon f_{\mathrm{g}i}^{(1)} + \epsilon^2 f_{\mathrm{g}i}^{(2)} + \mathcal{O}(\epsilon^3). \tag{3.21}$$

The second order term $f_{\mathrm{g}i}^{(2)}$ will play no role but need to be taken into account formally in some of the expansions.

After some algebra, it is obtained from (3.5)–(3.19) that $f_{\mathrm{g}i}^{(0)}$ is the zero velocity Maxwellian distribution

$$f_{\mathrm{g}i}^{(0)} = n_{\mathrm{g}i}\Big(\frac{\mathfrak{m}_i}{2\pi k_{\mathrm{B}} T_{\mathrm{g}}}\Big)^{3/2} \frac{\mathfrak{a}_{i\mathrm{I}}}{\mathrm{Z}_i^{\mathrm{int}}} \exp\Big(-\frac{\mathfrak{m}_i |\boldsymbol{c}_i|^2}{2k_{\mathrm{B}} T_{\mathrm{g}}} - \frac{\mathrm{E}_{i\mathrm{I}}}{k_{\mathrm{B}} T_{\mathrm{g}}}\Big), \tag{3.22}$$

where all quantities like $\mathrm{Z}^{\mathrm{int}}$ or T_{g} are evaluated at $z = 0$. The modified integral operator $\mathcal{I}_{\mathrm{g}} = (\mathcal{I}_{\mathrm{g}i})_{i \in S_{\mathrm{g}}}$ operating on $\varphi = (\varphi)_{i \in S_{\mathrm{g}}}$ is found to be the linearized collision operator around the zero velocity Maxwellians $f_{\mathrm{g}i}^{(0)}$

$$\mathcal{I}_{\mathrm{g}i}(\varphi) = -\sum_{j \in S_{\mathrm{g}}} \frac{1}{f_{\mathrm{g}i}^{(0)}} \big(J_{ij}(f_{\mathrm{g}i}^{(0)}, f_{\mathrm{g}j}^{(0)}\varphi_j) + J_{ij}(f_{\mathrm{g}i}^{(0)}\varphi_i, f_{\mathrm{g}j}^{(0)}) \big). \tag{3.23}$$

The modified first order term $f_{\mathrm{g}i}^{(1)}$ is also in the form

$$f_{\mathrm{g}i}^{(1)} = \Big(\frac{\mathfrak{m}_i c_{iz} \mathfrak{v}_{\mathrm{g}z}}{k_{\mathrm{B}} T_{\mathrm{g}}} + \alpha_\kappa \phi_{\mathrm{g}i}^{(1)}\Big) f_{\mathrm{g}i}^{(0)}, \tag{3.24}$$

with $v_{gz}(t,\boldsymbol{x}_{\shortparallel},0)=\epsilon v_{gz}(t,\boldsymbol{x}_{\shortparallel})$ and $\phi_{gi}^{(1)}$ given by

$$\phi_{gi}^{(1)}=-\boldsymbol{\phi}_{gi}^{\eta}\boldsymbol{:}\boldsymbol{\partial_x}\boldsymbol{v}_{g}-\tfrac{1}{3}\phi_{gi}^{\kappa}\boldsymbol{\partial_x}\boldsymbol{\cdot}\boldsymbol{v}_{g}-\sum_{j\in S_g}\boldsymbol{\phi}_{gi}^{D_j}\boldsymbol{\cdot}\boldsymbol{\partial_x}p_{gj}-\boldsymbol{\phi}_{gi}^{\widehat{\lambda}}\boldsymbol{\cdot}\boldsymbol{\partial_x}(1/k_B T_g). \tag{3.25}$$

The tensor function $\boldsymbol{\phi}_{g}^{\eta}=(\boldsymbol{\phi}_{gi}^{\eta})_{i\in S_g}$ is solution of the equation system

$$\mathcal{I}_{gi}(\boldsymbol{\phi}_{g}^{\eta})=\frac{m_i}{k_B T_g}\big(\boldsymbol{c}_i\otimes\boldsymbol{c}_i-\tfrac{1}{3}|\boldsymbol{c}_i|^2\boldsymbol{I}\big),\qquad i\in S_g,$$

with $\langle\!\langle f_g^{(0)}\boldsymbol{\phi}_g^{\eta},\psi_g^l\rangle\!\rangle=0$, $1\leq l\leq \mathrm{N_g}+4$, and the scalar type function $\phi_g^{\kappa}=(\phi_{gi}^{\kappa})_{i\in S_g}$ is solution of the equation system

$$\mathcal{I}_{gi}(\phi_{g}^{\kappa})=\frac{2\mathfrak{c}^{\mathrm{int}}}{\mathfrak{c}_{\mathrm{v}}k_B T_g}\big(\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2-\frac{3k_B T_g}{2}\big)+\frac{2\mathfrak{c}_{\mathrm{v}}^{\mathrm{tr}}}{\mathfrak{c}_{\mathrm{v}}k_B T_g}\big(e_i-\mathrm{E}_{i\mathrm{I}}\big),\qquad i\in S_g,$$

with $\langle\!\langle f_g^{(0)}\phi_g^{\kappa},\psi_g^l\rangle\!\rangle=0$, $1\leq l\leq \mathrm{N_g}+4$. The vector function $\boldsymbol{\phi}_g^{D_j}=(\boldsymbol{\phi}_{gi}^{D_j})_{i\in S_g}$, $j\in S_g$, are the solutions of the integral equation systems

$$\mathcal{I}_{gi}(\boldsymbol{\phi}_{g}^{D_j})=\frac{1}{p_{gi}}(\delta_{ij}-\mathsf{y}_{gi})\boldsymbol{c}_i,\qquad i,j\in S_g, \tag{3.26}$$

with the Enskog constraints $\langle\!\langle f_g^{(0)}\boldsymbol{\phi}_g^{D_j},\psi_g^l\rangle\!\rangle=0$ for $j\in S_g$ and $1\leq l\leq \mathrm{N_g}+4$. Finally, the vector function $\boldsymbol{\phi}_g^{\widehat{\lambda}}=(\boldsymbol{\phi}_{gi}^{\widehat{\lambda}})_{i\in S_g}$ is the solution of the integral equation system

$$\mathcal{I}_{gi}(\boldsymbol{\phi}_{g}^{\widehat{\lambda}})=\Big(\frac{5k_B T_g}{2}-\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2+e_i-\mathrm{E}_{i\mathrm{I}}\Big)\boldsymbol{c}_i,\qquad i\in S_g, \tag{3.27}$$

with the Enskog constraints $\langle\!\langle f_g^{(0)}\boldsymbol{\phi}_g^{\widehat{\lambda}},\psi_g^l\rangle\!\rangle=0$, $1\leq l\leq \mathrm{N_g}+4$.

Since $\boldsymbol{v}_g=\mathcal{O}(\epsilon)$ near the interface we further deduce that $\boldsymbol{\partial_x}\boldsymbol{v}_g=\mathcal{O}(\epsilon)$ at zeroth order, and from the isothermal assumption we also have $\boldsymbol{\partial_x}T_g=\mathcal{O}(\epsilon)$ so that the main terms in (3.25) are the diffusion terms. More specifically, at zeroth order, $\phi_{gi}^{(1)}$ is reduced to $\phi_{gi}^{(1)}=-\sum_{j\in S_g}\boldsymbol{\phi}_{gi}^{D_j}\boldsymbol{\cdot}\boldsymbol{\partial_x}p_{gj}$. Moreover, from the species mass conservation equation of the ith species [42]

$$\partial_t n_{gi}+\boldsymbol{\partial_x}\boldsymbol{\cdot}(n_{gi}\boldsymbol{v}_g)+\boldsymbol{\partial_x}\boldsymbol{\cdot}\boldsymbol{\mathcal{F}}_i=0,$$

where $\boldsymbol{\mathcal{F}}_i=\epsilon\sum_{\mathrm{I}\in\mathfrak{Q}_i}\int(\boldsymbol{c}_i-\boldsymbol{v}_g)\phi_{gi}^{(1)}f_{gi}^{(0)}\,\mathrm{d}\boldsymbol{c}_i$ is the particle diffusion flux of the ith species in the gas, we also note that

$$\partial_t n_{gi}(t,\boldsymbol{x}_{\shortparallel},0)=\mathcal{O}(\epsilon), \tag{3.28}$$

in such a way that n_{gi} is slowly varying in time near the surface.

3.4 Multiscale expansion

The surface potentials W_i, $i\in S$, depend on the reactive surface layer coordinate denoted by

$$\zeta=\frac{z}{\epsilon}. \tag{3.29}$$

The problem thus appears to be multiscale since it involves the normal coordinate z as well as the inner layer coordinate $\zeta=z/\epsilon$. The physisorbed-gas distributions f_i, $i\in S_g$, are expanded in the multiscale form

$$f_i=\sum_j\epsilon^j f_{gi}^{(j)}(t,\boldsymbol{x}_{\shortparallel},z,\boldsymbol{c}_i,\mathrm{I})+\sum_j\epsilon^j \mathsf{f}_{\mathrm{l}ci}^{(j)}(t,\boldsymbol{x}_{\shortparallel},\zeta,\boldsymbol{c}_i,\mathrm{I}),\qquad i\in S_g, \tag{3.30}$$

where $\sum_j \epsilon^j f_{\mathrm{g}i}^{(j)}(t, \boldsymbol{x}_{\shortparallel}, z, \boldsymbol{c}_i, \mathrm{I})$ is the *outer* expansion and $\sum_j \epsilon^j \mathsf{f}_{\mathrm{lc}i}^{(j)}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I})$ the surface *layer corrector* expansion. The surface layer correctors $\mathsf{f}_{\mathrm{lc}i}^{(j)}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I})$, $j \geq 0$, must converge to zero as $\zeta \to \infty$ in such a way that the outer gas expansion (3.21), evaluated in Section 3.2, is recovered in the gas phase.

The *inner expansions* f_i, $i \in S_{\mathrm{g}}$, of the distributions f_i, $i \in S_{\mathrm{g}}$, in the physisorbate are next obtained by first expanding in terms of ζ the outer expansions $\sum_j \epsilon^j f_{\mathrm{g}i}^{(j)}(t, \boldsymbol{x}_{\shortparallel}, z, \boldsymbol{c}_i, \mathrm{I})$ using $z = \epsilon\zeta$ and then adding the layer corrector expansions. The inner expansion $\mathsf{f}_{\mathrm{g}i} = \mathsf{f}_{\mathrm{g}i}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I}) = f_{\mathrm{g}i}(t, \boldsymbol{x}_{\shortparallel}, \epsilon\zeta, \boldsymbol{c}_i, \mathrm{I})$ of $f_{\mathrm{g}i}$ is written in the form

$$\mathsf{f}_{\mathrm{g}i}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I}) = \sum_j \epsilon^j \mathsf{f}_{\mathrm{g}i}^{(j)}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I}), \tag{3.31}$$

and it is found notably that $\mathsf{f}_{\mathrm{g}i}^{(0)}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I}) = f_{\mathrm{g}i}^{(0)}(t, \boldsymbol{x}_{\shortparallel}, 0, \boldsymbol{c}_i, \mathrm{I})$ and $\mathsf{f}_{\mathrm{g}i}^{(1)}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I}) = f_{\mathrm{g}i}^{(1)}(t, \boldsymbol{x}_{\shortparallel}, 0, \boldsymbol{c}_i, \mathrm{I}) + \zeta(\partial_z f_{\mathrm{g}i}^{(0)})(t, \boldsymbol{x}_{\shortparallel}, 0, \boldsymbol{c}_i, \mathrm{I})$. These relations may we written

$$\mathsf{f}_{\mathrm{g}i}^{(0)} = \overline{f}_{\mathrm{g}i}^{(0)}, \qquad \mathsf{f}_{\mathrm{g}i}^{(1)} = \overline{f}_{\mathrm{g}i}^{(1)} + \zeta\overline{\partial_z f}_{\mathrm{g}i}^{(0)}, \qquad i \in S_{\mathrm{g}}, \tag{3.32}$$

where for any function $\mathcal{A} = \mathcal{A}(t, \boldsymbol{x}_{\shortparallel}, z, \boldsymbol{c}_i, \mathrm{I})$ we write $\overline{\mathcal{A}}(t, \boldsymbol{x}_{\shortparallel}, \boldsymbol{c}_i, \mathrm{I}) = \mathcal{A}(t, \boldsymbol{x}_{\shortparallel}, 0, \boldsymbol{c}_i, \mathrm{I})$ its restriction for $z = 0$. The *inner expansion* of the distribution of the ith species f_i in the physisorbate then reads

$$\mathsf{f}_i = \sum_j \epsilon^j \mathsf{f}_i^{(j)}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I}), \tag{3.33}$$

where

$$\mathsf{f}_i^{(j)} = \mathsf{f}_{\mathrm{g}i}^{(j)} + \mathsf{f}_{\mathrm{lc}i}^{(j)}, \qquad j \geq 0. \tag{3.34}$$

The inner distribution coefficient $\mathsf{f}_i^{(j)}$ thus involve a polynomial $\mathsf{f}_{\mathrm{g}i}^{(j)}$ in terms of ζ arising from the Taylor expansion of the $f_{\mathrm{g}i}^{(k)}$, $k \geq 1$, and a thin layer corrector $\mathsf{f}_{\mathrm{lc}i}^{(j)}$.

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

$$f_i = \sum_j \epsilon^j \mathsf{f}_i^{(j)}(t, \boldsymbol{x}_{\shortparallel}, \zeta, \boldsymbol{c}_i, \mathrm{I}), \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}} \cup \{\sigma\}, \tag{3.35}$$

since such distributions are localized in the adsorption layer and only involve the inner layer coordinate ζ.

3.5 Inner layer kinetic equations

Since ζ is the proper normal coordinate of the reactive surface layer, the rescaled equations governing the physisorbed inner distributions f_i and involving ζ derivatives, obtained from (3.3), are in the form

$$\begin{aligned} \partial_t \mathsf{f}_i + \boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel} \mathsf{f}_i + \frac{1}{\epsilon} c_{iz}\, \partial_\zeta \mathsf{f}_i - \frac{1}{\epsilon}\frac{1}{m_i} \partial_\zeta \mathrm{W}_i\, \partial_{c_{iz}} \mathsf{f}_i &= \frac{1}{\alpha_\kappa \epsilon} \sum_{j \in S_{\mathrm{g}}} J_{ij}(\mathsf{f}_i, \mathsf{f}_j) \\ &+ \frac{1}{\alpha_{\mathrm{ph}}\epsilon} J_{i,\mathrm{ph}}(\mathsf{f}_i) + \mathcal{C}_i, \qquad i \in S_{\mathrm{g}}. \end{aligned} \tag{3.36}$$

Similarly, since $f_{\mathrm{g}i}$ satisfies the Boltzmann equation (2.5), we may perform the change of variable from z to ζ so that the inner expansion $\mathsf{f}_{\mathrm{g}i}$ of $f_{\mathrm{g}i}$ satisfies the kinetic equation

$$\partial_t \mathsf{f}_{\mathrm{g}i} + \boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel} \mathsf{f}_{\mathrm{g}i} + \frac{1}{\epsilon} c_{iz}\, \partial_\zeta \mathsf{f}_{\mathrm{g}i} = \frac{1}{\alpha_\kappa \epsilon} \sum_{j \in S_{\mathrm{g}}} J_{ij}(\mathsf{f}_{\mathrm{g}i}, \mathsf{f}_{\mathrm{g}j}), \qquad i \in S_{\mathrm{g}}. \tag{3.37}$$

Substituting the inner expansion f_{gi} of f_{gi} into (3.37) and equating the powers of ϵ, we also obtain kinetic equations satisfied by the expansion coefficients $\mathsf{f}_{gi}^{(j)}$ for $j \geq 0$. At the order ϵ^{-1}, we obtain that

$$c_{iz}\,\partial_\zeta \mathsf{f}_{gi}^{(0)} = \frac{1}{\alpha_\kappa}\sum_{j\in S_g} J_{ij}(\mathsf{f}_{gi}^{(0)},\mathsf{f}_{gj}^{(0)}), \qquad i\in S_g,$$

and each of these terms vanish since $\mathsf{f}_{gi}^{(0)} = \overline{f}_{gi}^{(0)} = f_{gi}^{(0)}(t,\boldsymbol{x}_{\shortparallel},0,\boldsymbol{c}_i,\mathrm{I})$ is independent of ζ and $\mathsf{f}_{gi}^{(0)}$ is Maxwellian so that $J_{ij}\big(\mathsf{f}_{gi}^{(0)},\mathsf{f}_{gj}^{(0)}\big) = 0$ for any $i,j\in S_g$.

At the next order ϵ^0, letting $\Xi_g^{(1)} = (\Xi_{gi}^{(1)})_{i\in S_g}$, with $\Xi_{gi}^{(1)} = \mathsf{f}_{gi}^{(1)}/\mathsf{f}_{gi}^{(0)}$, we obtain that

$$c_{iz}\,\partial_\zeta \Xi_{gi}^{(1)} + \mathcal{I}_{gi}(\Xi_g^{(1)})/\alpha_\kappa = -\big(\partial_t \log \mathsf{f}_{gi}^{(0)} + \boldsymbol{c}_{i\shortparallel}\boldsymbol{\cdot}\boldsymbol{\partial}_{\shortparallel}\log \mathsf{f}_{gi}^{(0)}\big), \tag{3.38}$$

and

$$\Xi_{gi}^{(1)} = \frac{m_i c_{iz} v_{gz}}{k_B \overline{T}_g} + \alpha_\kappa \overline{\phi}_{gi}^{(1)} + \zeta\,\overline{\partial_z \log f_{gi}^{(0)}}, \qquad i\in S_g,$$

since $\mathsf{f}_{gi}^{(1)} = \overline{f}_{gi}^{(1)} + \zeta\overline{\partial_z f_{gi}^{(0)}}$, $\overline{f}_{gi}^{(1)} = \Big(\frac{m_i c_{iz} v_{gz}}{k_B\overline{T}_g} + \alpha_\kappa\overline{\phi}_{gi}^{(1)}\Big)\overline{f}_{gi}^{(0)}$ and $\mathsf{f}_{gi}^{(0)} = \overline{f}_{gi}^{(0)}$. Using now that both $(m_i c_{iz})_{i\in S_g}$ and $\big(\overline{\partial_z \log f_{gi}^{(0)}}\big)_{i\in S_g}$ are collisional invariants and are in the nullspace of the operator $\mathcal{I}_g$, we deduce that $\mathcal{I}_g(\Xi_g^{(1)})/\alpha_\kappa = \mathcal{I}_g\big(\overline{\phi}_g^{(1)}\big)$, and since $\partial_\zeta \Xi_g^{(1)} = \overline{\partial_z \log f_{gi}^{(0)}}$ we obtain that (3.38) coincides with

$$\mathcal{I}_{gi}(\overline{\phi}_g^{(1)}) = -\big(\partial_t \log \overline{f}_{gi}^{(0)} + \boldsymbol{c}_{i\shortparallel}\boldsymbol{\cdot}\boldsymbol{\partial}_{\shortparallel}\log \overline{f}_{gi}^{(0)} + c_{iz}\,\overline{\partial_z \log f_{gi}^{(0)}}\big),$$

that is simply the linearized Boltzmann equation written at $z=0$.

Subtracting equation (3.37) from (3.36) for $i\in S_g$, we also obtain the equation

$$\begin{aligned}\partial_t(\mathsf{f}_i - \mathsf{f}_{gi}) + \boldsymbol{c}_{i\shortparallel}\boldsymbol{\cdot}\boldsymbol{\partial}_{\shortparallel}(\mathsf{f}_i - \mathsf{f}_{gi}) + \frac{1}{\epsilon}c_{iz}\,\partial_\zeta(\mathsf{f}_i - \mathsf{f}_{gi}) - \frac{1}{\epsilon}\frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\mathsf{f}_i = \\ \frac{1}{\alpha_\kappa\epsilon}\sum_{j\in S_g}\Big\{J_{ij}(\mathsf{f}_i,\mathsf{f}_j) - J_{ij}(\mathsf{f}_{gi},\mathsf{f}_{gj})\Big\} + \frac{1}{\alpha_{ph}\epsilon}J_{i,ph}(\mathsf{f}_i) + \mathcal{C}_i, \qquad i\in S_g,\end{aligned} \tag{3.39}$$

that will be convenient in order to investigate the inner structure of the reactive surface layer. The advantage of (3.39) is that all terms go to zero when ζ goes to infinity, avoiding all integrability technicalities.

Finally, for the localized surface species, we obtain a similar rescaled equation using the proper normal coordinate ζ

$$\begin{aligned}\partial_t f_i + \boldsymbol{c}_{i\shortparallel}\boldsymbol{\cdot}\boldsymbol{\partial}_{\shortparallel} f_i + \frac{1}{\epsilon}c_{iz}\,\partial_\zeta f_i - \frac{1}{\epsilon}\frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}} f_i = \\ \frac{1}{\alpha_{ph}\epsilon}J_{i,ph}(f_i) + \mathcal{C}_i, \qquad i\in S_c\cup S_s\cup S_b.\end{aligned} \tag{3.40}$$

4 Zeroth order expansions in the adsorbate

Zeroth order expansions are investigated in the reactive surface layer and next the corresponding fluid boundary conditions.

4.1 Zeroth order expansion for physisorbed-gas species

In the physisorbate, using (3.36), the ith species equation is found in the form

$$c_{iz}\,\partial_\zeta \mathsf{f}_i^{(0)} - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\mathsf{f}_i^{(0)} = \frac{1}{\alpha_\kappa}\sum_{j\in S_{\mathrm{g}}} J_{ij}(\mathsf{f}_i^{(0)},\mathsf{f}_i^{(0)}) + \frac{1}{\alpha_{\mathrm{ph}}} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}), \qquad i\in S_{\mathrm{g}}. \tag{4.1}$$

Using (2.15) we may rewrite (4.1) in the form

$$\mathsf{m}_i\Big(c_{iz}\,\partial_\zeta(\mathsf{f}_i^{(0)}/\mathsf{m}_i) - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}(\mathsf{f}_i^{(0)}/\mathsf{m}_i)\Big) = \frac{1}{\alpha_\kappa}\sum_{j\in S_{\mathrm{g}}} J_{ij}(\mathsf{f}_i^{(0)},\mathsf{f}_j^{(0)}) + \frac{1}{\alpha_{\mathrm{ph}}} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}), \tag{4.2}$$

We multiply (4.2) by $\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)$, make use of $\partial_{\mathcal{A}}\big(\mathcal{A}(\log\mathcal{A}-1)\big) = \log\mathcal{A}$, reintegrate the m_i factor inside the spatial and velocity derivatives using (2.15), integrate over $\zeta\in(0,\infty)$, $\boldsymbol{c}_i\in\mathbb{R}^3$, and then sum over $i\in S_{\mathrm{g}}$ and $\mathrm{I}\in \mathfrak{Q}_i$. Using that $\mathsf{f}_i^{(0)}\to \overline{f}_{\mathrm{g}i}^{(0)}$ as $\zeta\to\infty$, since the corrector $\mathsf{f}_{\mathrm{lc}i}^{(0)}$ goes to zero as $\zeta\to\infty$, we note that the first term in the left of (4.2) yields after integration a null contribution for any $i\in S_{\mathrm{g}}$ or $\mathrm{I}\in\mathfrak{Q}_i$ at the gas boundary since

$$\lim_{\zeta\to\infty}\int c_{iz}\mathsf{f}_i^{(0)}\big(\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)-1\big)\,\mathrm{d}\boldsymbol{c}_i = \int c_{iz}\overline{f}_{\mathrm{g}i}^{(0)}\big(\log(\overline{f}_{\mathrm{g}i}^{(0)}/\mathrm{M}_i)-1\big)\,\mathrm{d}\boldsymbol{c}_i = 0,$$

keeping in mind that $\overline{f}_{\mathrm{g}i}^{(0)}$ and M_i are even in the normal velocity. Similarly, keeping in mind that $\mathsf{f}_i^{(0)}\to 0$ as $\zeta\to 0$ since the surface repulsive potential repel all physisorbed-gas particles, we also obtain a zero contribution of the first term at the surface boundary since

$$\lim_{\zeta\to 0}\int c_{iz}\mathsf{f}_i^{(0)}\big(\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)-1\big)\,\mathrm{d}\boldsymbol{c}_i = 0.$$

The second terms of the left of (4.2) also yields a null contribution for any $i\in S_{\mathrm{g}}$ or $\mathrm{I}\in\mathfrak{Q}_i$ after integration since it is in divergence form

$$-\partial_{c_{iz}}\Big(\frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\mathsf{f}_i^{(0)}\big(\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)-1\big)\Big),$$

and $\mathsf{f}_i^{(0)}\big(\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)-1\big)$ goes to zero as $|\boldsymbol{c}_i|\to\infty$. We have thus established that

$$\frac{1}{\alpha_\kappa}\sum_{\substack{i,j\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}}\int J_{ij}(\mathsf{f}_i^{(0)},\mathsf{f}_j^{(0)})\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \frac{1}{\alpha_{\mathrm{ph}}}\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}}\int J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)})\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta = 0. \tag{4.3}$$

Such entropy production type terms have been investigated up to the scaling factor $-k_{\mathrm{B}}$ in (2.46)(2.47) and have nonpositive integrands. Such integrands thus vanish so that $\mathsf{f}_i^{(0)}$ is a Maxwellian from $J_{ij}(\mathsf{f}_i^{(0)},\mathsf{f}_j^{(0)})=0$ and is at temperature T_{w} with zero average velocity since $J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)})=0$. Writting this Maxwellian for convenience as

$$\mathsf{f}_i^{(0)} = \mathsf{n}_i\exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}}T_{\mathrm{w}}}\Big)\mathrm{M}_i, \tag{4.4}$$

where M_i is given by (2.11), and substituting this identity in (4.1) yields that $\partial_\zeta \mathsf{n}_i = 0$ so that n_i is independent of ζ. The constant n_i is identified by letting $\zeta \to \infty$ in (4.4) and it is obtained that $\mathsf{n}_i(t, \boldsymbol{x}_{\shortparallel}) = n_{\mathrm{g}i}(t, \boldsymbol{x}_{\shortparallel}, 0)$ so that

$$\mathsf{n}_i = \overline{n}_{\mathrm{g}i}, \tag{4.5}$$

where for any quantity $\mathcal{A} = \mathcal{A}(t, \boldsymbol{x}_{\shortparallel}, z, \boldsymbol{c}_i, \mathrm{I})$ we denote by $\overline{\mathcal{A}}(t, \boldsymbol{x}_{\shortparallel}, \boldsymbol{c}_i, \mathrm{I}) = \mathcal{A}(t, \boldsymbol{x}_{\shortparallel}, 0, \boldsymbol{c}_i, \mathrm{I})$ its restriction for $z = 0$. It has thus been established that

$$\mathsf{f}_i^{(0)} = \mathsf{n}_i \mathsf{m}_i = \overline{n}_{\mathrm{g}i} \mathsf{m}_i = n_i \mathrm{M}_i, \qquad i \in S_{\mathrm{g}}. \tag{4.6}$$

and the number of physisorbed-gas particles of the ith species per unit volume n_i can be written

$$n_i(t, \boldsymbol{x}_{\shortparallel}, \zeta) = \overline{n}_{\mathrm{g}i}(t, \boldsymbol{x}_{\shortparallel}) \exp\Big(-\frac{\mathrm{W}_i(\zeta)}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big), \qquad i \in S_{\mathrm{g}}. \tag{4.7}$$

This expression establishes that, in the physisorbate, the ith species is naturally distributed like $\exp\big(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}}\big)$ as was expected based of physical grounds [20, 48]. Moreover the ith species in the physisorbate is *at equilibrium* with the bath of the ith gas particles having number density $\overline{n}_{\mathrm{g}i}(t, \boldsymbol{x}_{\shortparallel}) = n_{\mathrm{g}i}(t, \boldsymbol{x}_{\shortparallel}, 0)$ and arising from the gas phase. Since $\mathsf{f}_{\mathrm{lc}i}^{(0)} = \mathsf{f}_i^{(0)} - \overline{f}_{\mathrm{g}i}^{(0)}$ we also obtain that for any $i \in S_{\mathrm{g}}$

$$\mathsf{f}_{\mathrm{lc}i}^{(0)} = \overline{n}_{\mathrm{g}i} \Big(\frac{m_i}{2\pi k_{\mathrm{B}} T_{\mathrm{w}}}\Big)^{3/2} \frac{a_{i\mathrm{I}}}{\mathrm{Z}_i^{\mathrm{int}}} \exp\Big(-\frac{m_i|\boldsymbol{c}_i|^2}{k_{\mathrm{B}} T_{\mathrm{w}}} - \frac{\mathrm{E}_{i\mathrm{I}}}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big) \Big\{\exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big) - 1\Big\}. \tag{4.8}$$

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

As a final remark, we note that the *kinematic* boundary condition [69, 70]

$$T_{\mathrm{g}}(t, \boldsymbol{x}_{\shortparallel}, 0) = T_{\mathrm{w}}, \tag{4.9}$$

has been established by writting that the gas Maxwellian distribution is at equilibrium with phonons, using $J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}) = 0$. We also recover the relations $\boldsymbol{v}_{\mathrm{g}}(t, \boldsymbol{x}_{\shortparallel}, 0)\cdot\boldsymbol{e}_x = 0$ and $\boldsymbol{v}_{\mathrm{g}}(t, \boldsymbol{x}_{\shortparallel}, 0)\cdot\boldsymbol{e}_y = 0$. In contrast, the *dynamic* boundary conditions for mass, momentum or energy will be obtained as moments of the kinetic equations. The model could also be generalized by taking into account a first order temperature difference $T_{\mathrm{g}} - T_{\mathrm{w}} = \mathcal{O}(\epsilon)$ but such an extension lays beyond the scope of the present work.

4.2 Zeroth order expansion for chemisorbed and crystal species

For the chemisorbed species as well as the crystal species, the kinetic equation (3.40) yields that

$$c_{iz}\, \partial_\zeta \mathsf{f}_i^{(0)} - \frac{1}{m_i} \partial_\zeta \mathrm{W}_i \partial_{c_{iz}} \mathsf{f}_i^{(0)} = \frac{1}{\alpha_{\mathrm{ph}}} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}), \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}, \tag{4.10}$$

Multiplying by $\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)$, and proceeding as for the physisorbate it is obtained that

$$c_{iz}\, \partial_\zeta \Big(\mathsf{f}_i^{(0)} \big(\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i) - 1\big)\Big) - \frac{1}{m_i} \partial_\zeta \mathrm{W}_i\, \partial_{c_{iz}} \Big(\mathsf{f}_i^{(0)} \big(\log(\mathsf{f}_i^{(0)}/\mathsf{m}_i) - 1\big)\Big) = \frac{1}{\alpha_{\mathrm{ph}}} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}) \log(\mathsf{f}_i^{(0)}/\mathsf{m}_i).$$

Integrating over $\zeta \in (\zeta_i^-, \zeta_i^+)$ and $\boldsymbol{c}_i \in \mathbb{R}^3$, summing over $\mathrm{I} \in \mathfrak{Q}_i$, using that $\mathsf{f}_i^{(0)}$ goes to zero as $\zeta \to \zeta_i^-$ and as $\zeta \to \zeta_i^+$, the particles being repelled by the potential, and that $\mathsf{f}_i^{(0)}$ goes to zero as $|\boldsymbol{c}_i|$ goes to infinity, it is obtained that

$$\frac{1}{\alpha_{\mathrm{ph}}} \sum_{\mathrm{I} \in \mathfrak{Q}_i} \int J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}) \log(\mathsf{f}_i^{(0)}/\mathsf{m}_i)\, \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta = 0.$$

From the expression of the entropy source (2.47) established for the H theorem, it is deduced that $\mathsf{f}_i^{(0)}$ is a Maxwellian at temperature T_{w} and with zero average velocity. Writting this Maxwellian for convenience in the form

$$\mathsf{f}_i^{(0)} = \mathsf{n}_i \exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big) \mathrm{M}_i, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}, \tag{4.11}$$

where M_i is given by equation (2.11), and substituting this identity in (4.10), it is obtained that $\partial_\zeta \mathsf{n}_i = 0$ and n_i is independent of ζ.

The number densities in the chemisorbate and crystal last layer are thus in the form

$$n_i(t, \boldsymbol{x}_{\shortparallel}, \zeta) = \mathsf{n}_i(t, \boldsymbol{x}_{\shortparallel}) \exp\Big(-\frac{\mathrm{W}_i(\zeta)}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big), \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}, \tag{4.12}$$

and the ith species is distributed as the function $\exp\big(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}}\big)$, as was expected based on physical grounds, so that it is localized since W_i goes to infinity as $\zeta \to \zeta_i^-$ or $\zeta \to \zeta_i^+$. We may also introduce the number of chemisorbed particles *per unit surface*

$$\widetilde{n}_i(t, \boldsymbol{x}_{\shortparallel}) = \int n_i \, \mathrm{d}z, \qquad i \in S_{\mathrm{c}},$$

that is related to $\mathsf{n}_i(t, \boldsymbol{x}_{\shortparallel})$ via a configuration integral

$$\widetilde{n}_i = \mathsf{n}_i \int \exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big)\, \mathrm{d}z, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}.$$

We have thus established that $\mathsf{f}_i^{(0)}$ may be written

$$\mathsf{f}_i^{(0)} = \mathsf{n}_i \mathsf{m}_i = \widetilde{n}_i \widetilde{\mathsf{m}}_i, \tag{4.13}$$

where the rescaled maxwellian $\widetilde{\mathsf{m}}_i$ is given by $\widetilde{\mathsf{m}}_i = \mathsf{m}_i / \int \exp\big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}}T_{\mathrm{w}}}\big)\, \mathrm{d}z$. Finally, both n_i and $\widetilde{n}_i$ are independent of the gas phase values $\overline{n}_{\mathrm{g}j}(t, \boldsymbol{x}_{\shortparallel})$, $j \in S_{\mathrm{g}}$, at variance with the physisorbate species that is *at equilibrium* with the bath of gas. Note also incidentally that, with the exponential dependence of n_i on the potential $-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}}$, all terms in the general form $\partial_\zeta \mathrm{W}_i\, \mathsf{f}_i^{(0)}$ involved in the kinetic equations (4.10) go to zero as $\zeta \to \zeta_i^-$ or as $\zeta \to \zeta_i^+$.

Proceeding similarly for the standard surface distribution that is solution of (2.7) it is recovered that $f_\sigma^{\mathrm{e}} = \mathsf{f}_\sigma^{\mathrm{e}}$ is given by (2.17) with a number density of the surface layer n_σ in the form (2.18), so that the surface atoms are spatially distributed as the function $\exp\big(-\mathrm{W}_\sigma/k_{\mathrm{B}}T_{\mathrm{w}}\big)$. The quantities $n_\sigma(t, \boldsymbol{x}_{\shortparallel}, \zeta)$ and $\mathsf{n}_\sigma(t, \boldsymbol{x}_{\shortparallel})$ are characteristic of the crystal surface and its orientation and related to the number of surface atoms per unit surface $\widetilde{n}_\sigma(t, \boldsymbol{x}_{\shortparallel}) = \int n_\sigma \, \mathrm{d}z$, defined as in (2.19), that also depends on the crystal and its orientation. We may thus write that $f_\sigma^{\mathrm{e}} = \mathsf{f}_\sigma^{\mathrm{e}} = \mathsf{n}_\sigma \mathsf{m}_\sigma = \widetilde{n}_\sigma \widetilde{\mathsf{m}}_\sigma$ where $\widetilde{\mathsf{m}}_\sigma = \mathsf{m}_\sigma / \int \exp\big(-\frac{\mathrm{W}_\sigma}{k_{\mathrm{B}}T_{\mathrm{w}}}\big)\, \mathrm{d}z$.

From the structure of the free site distribution $\mathsf{f}_\mathrm{s}^{(0)}$ and that of the equilibrium crystal layer standard distribution $f_\sigma^\mathrm{e} = \mathsf{f}_\sigma^\mathrm{e}$ given by (2.17), and since $\mathrm{W}_\mathrm{s} = \mathrm{W}_\sigma$, we deduce that *at zeroth order* the probability of free site $\mathsf{f}_\mathrm{s}^{(0)}/\mathsf{f}_\sigma^\mathrm{e}$ simplifies into

$$\frac{\mathsf{f}_\mathrm{s}^{(0)}}{\mathsf{f}_\sigma^\mathrm{e}} = \frac{\mathsf{n}_\mathrm{s}}{\mathsf{n}_\sigma} = \frac{\widetilde{n}_\mathrm{s}}{\widetilde{n}_\sigma}, \tag{4.14}$$

and therefore *only depends on time and tangential coordinate.* The zeroth order coverage $\widetilde{\theta}(t, \boldsymbol{x}_\shortparallel)$ is then obtained as

$$\widetilde{\theta}(t, \boldsymbol{x}_\shortparallel) = 1 - \frac{\mathsf{n}_\mathrm{s}}{\mathsf{n}_\sigma} = 1 - \frac{\widetilde{n}_\mathrm{s}}{\widetilde{n}_\sigma},$$

and is thus independent of ζ. Since the chemisorbate is assumed to be monolayer and the adsorption process is monosite, we have the natural constraints

$$\sum_{i\in S_\mathrm{c}} \widetilde{n}_i + \widetilde{n}_\mathrm{s} = \widetilde{n}_\sigma, \qquad \sum_{i\in S_\mathrm{b}} \widetilde{n}_i + \widetilde{n}_\mathrm{s} = \widetilde{n}_\sigma. \tag{4.15}$$

Defining $\widetilde{n}_\mathrm{c} = \sum_{i\in S_\mathrm{c}} \widetilde{n}_i$ and $\widetilde{n}_\mathrm{b} = \sum_{i\in S_\mathrm{b}} \widetilde{n}_i$ as the number of chemisorbed species per unit surface or bulk species per unit surface we thus have $\widetilde{n}_\mathrm{c} + \widetilde{n}_\mathrm{s} = \widetilde{n}_\mathrm{b} + \widetilde{n}_\mathrm{s} = \widetilde{n}_\sigma$ in such a way that $\widetilde{n}_\mathrm{c} = \widetilde{n}_\mathrm{b} = \widetilde{\theta}\,\widetilde{n}_\sigma$ and $\widetilde{n}_\mathrm{s} = (1-\widetilde{\theta})\widetilde{n}_\sigma$. Moreover, for each chemisorbed species $i \in S_\mathrm{c}$, there exists a unique bulk species $\mathrm{b}(i) \in S_\mathrm{b}$, to form a chemical pair, and then $\widetilde{n}_i = \widetilde{n}_{\mathrm{b}(i)}$.

4.3 Species mass boundary conditions

The zeroth order mass conservation equations are obtained by taking the scalar product of kinetic equations by the mass collisional invariants and keeping only zeroth order terms. Taking the scalar product of Boltzmann equations with the mass invariants is equivalent to integrating each Boltzmann equation with respect to the velocity variable and summing over the quantum energy states.

In the physisorbate, using the difference equation (3.39) for convenience, it is obtained that

$$\sum_{\mathrm{I}\in\mathfrak{Q}_i} \partial_t \int (\mathsf{f}_i^{(0)} - \mathsf{f}_{\mathrm{g}i}^{(0)})\,\mathrm{d}\boldsymbol{c}_i + \sum_{\mathrm{I}\in\mathfrak{Q}_i} \partial_\zeta \int c_{iz}(\mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(1)})\mathrm{d}\boldsymbol{c}_i = \sum_{\mathrm{I}\in\mathfrak{Q}_i} \int \mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i, \tag{4.16}$$

where $\mathcal{C}_i^{(0)}$ denotes the chemical production terms evaluated with the Maxwellian distributions $\mathsf{f}_i^{(0)}$, $i \in S$. We have used here that $\int \boldsymbol{c}_{i\shortparallel}\mathsf{f}_i^{(0)}\mathrm{d}\boldsymbol{c}_i = \int \boldsymbol{c}_{i\shortparallel}\mathsf{f}_{\mathrm{g}i}^{(0)}\mathrm{d}\boldsymbol{c}_i = 0$ and that the mass collisional invariants ψ_g^l, $1 \le l \le \mathrm{N}_\mathrm{g}$, are orthogonal to the collision operators J_{ij} and $J_{i,\mathrm{ph}}$. Moreover, since $\partial_t n_{\mathrm{g}i}(0) = \mathcal{O}(\epsilon)$ from (3.28), the first term vanishes at zeroth order and we obtain that

$$\sum_{\mathrm{I}\in\mathfrak{Q}_i} \partial_\zeta \int c_{iz}(\mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(1)})\mathrm{d}\boldsymbol{c}_i = \sum_{\mathrm{I}\in\mathfrak{Q}_i} \int \mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i.$$

In order to integrate over $\zeta \in (0, \infty)$, we need to determine the limits of $\mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(1)}$ at both ends of the interval. Noting that $\mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(1)} = \mathsf{f}_{\mathrm{lc}i}^{(1)}$, we first obtain that $\mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(1)}$ goes to zero as $\zeta \to \infty$. Moreover, $\mathsf{f}_i^{(1)}$ goes to zero as $\zeta \to 0$, since there are not anymore physisorbed-gas particles at the surface, and using $\mathsf{f}_{\mathrm{g}i}^{(1)} = \overline{f}_{\mathrm{g}i}^{(1)} + \zeta\overline{\partial_z \log f_{\mathrm{g}i}^{(0)}}$, we next obtain that $\mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(1)}$ goes to $-\overline{f}_{\mathrm{g}i}^{(1)}$ as $\zeta \to 0$. Integrating with respect to ζ over $(0,\infty)$ thus yields

$$\sum_{\mathrm{I}\in\mathfrak{Q}_i} \int c_{iz} \overline{f}_{\mathrm{g}i}^{(1)} \mathrm{d}\boldsymbol{c}_i = \sum_{\mathrm{I}\in\mathfrak{Q}_i} \int \mathcal{C}_i^{(0)} \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta. \tag{4.17}$$

Using next the relation $\overline{f}_{\mathrm{g}i}^{(1)} = \Big(\frac{m_i c_{iz} v_{\mathrm{g}z}}{k_{\mathrm{B}} \overline{T}_{\mathrm{g}}} + \alpha_\kappa \overline{\phi}_{\mathrm{g}i}^{(1)} \Big) \overline{f}_{\mathrm{g}i}^{(0)}$ the total particle flux of the ith species in the gas may be written

$$\sum_{\mathrm{I}\in\mathfrak{Q}_i} \epsilon \int c_{iz} \overline{f}_{\mathrm{g}i}^{(1)} \mathrm{d}\boldsymbol{c}_i = \overline{n}_{\mathrm{g}i} \overline{v}_{\mathrm{g}z} + \overline{\mathcal{F}}_{zi},$$

where $\overline{v}_{\mathrm{g}z} = \epsilon v_{\mathrm{g}z}$ and $\overline{\mathcal{F}}_{zi} = \epsilon \int c_{iz} \alpha_\kappa \overline{\phi}_{\mathrm{g}i}^{(1)} \overline{f}_{\mathrm{g}i}^{(0)} \mathrm{d}\boldsymbol{c}_i$ denotes the normal diffusion flux of the ith species, and the overbar symbol means that it is evaluated at $z = 0$. Denoting for short by $\mathfrak{w}_i^{(0)}$ the zeroth order number of particles of the ith species produced by unit surface and unit time by surface chemistry

$$\mathfrak{w}_i^{(0)} = \sum_{\mathrm{I}\in\mathfrak{Q}_i} \int \mathcal{C}_i^{(0)} \mathrm{d}\boldsymbol{c}_i \mathrm{d}z, \tag{4.18}$$

where the integral of the production terms is performed over z, the boundary condition for the ith gaseous species finally reads

$$\overline{n}_{\mathrm{g}i} \overline{v}_{\mathrm{g}z} + \overline{\mathcal{F}}_{zi} = \mathfrak{w}_i^{(0)}. \tag{4.19}$$

The species diffusion flux may also be expressed as $\boldsymbol{\mathcal{F}}_i = n_{\mathrm{g}i} \boldsymbol{V}_i$ where $\boldsymbol{V}_i$ denotes the mass based species diffusion velocity that is in the form

$$\boldsymbol{V}_i = -\sum_{j\in S_{\mathrm{g}}} D_{ij} \boldsymbol{d}_j - \theta_i^{\mathrm{th}} \boldsymbol{\partial_x} \log T_{\mathrm{g}}, \qquad i \in S_{\mathrm{g}}, \tag{4.20}$$

and where $\boldsymbol{d}_j = \boldsymbol{\partial_x} \mathsf{x}_{\mathrm{g}j}$ denotes the diffusion driving force of the jth species in the gas and $\mathsf{x}_{\mathrm{g}j} = n_{\mathrm{g}j}/n_{\mathrm{g}}$ the mole fraction of the jth species [38, 39, 40, 41, 42, 43, 44]. These boundary conditions (4.19) exactly correspond to that used at a reactive surface in multicomponent flow models [16, 17, 18, 42].

We may further multiply (4.19) by m_i and sum *over the gas species* and use the mass constraint between the particle fluxes $\sum_{i\in S_{\mathrm{g}}} m_i \boldsymbol{\mathcal{F}}_i = 0$ to get that

$$\overline{\rho}_{\mathrm{g}} \overline{v}_{\mathrm{g}z} = \sum_{i\in S_{\mathrm{g}}} m_i \mathfrak{w}_i^{(0)}, \tag{4.21}$$

where $\overline{\rho}_{\mathrm{g}} = \sum_{i\in S_{\mathrm{g}}} m_i \overline{n}_{\mathrm{g}i}$ is the gas mass density at the solid boundary $z = 0$. In particular, the Stefan mass flux towards the gas phase $\overline{\rho}_{\mathrm{g}} \overline{v}_{\mathrm{g}z}$ is due to the overall mass production of physisorbed-gas species by the surface chemistry $\sum_{i\in S_{\mathrm{g}}} m_i \mathfrak{w}_i^{(0)}$. Using the total mass conservation in chemical reactions $\sum_{i\in S} m_i \mathfrak{w}_i^{(0)} = 0$ and the conservation of the number of sites $m_{\mathrm{s}} \mathfrak{w}_{\mathrm{s}}^{(0)} + \sum_{i\in S_{\mathrm{b}}} m_i \mathfrak{w}_i^{(0)} = 0$, we obtain that $\sum_{i\in S_{\mathrm{g}}} m_i \mathfrak{w}_i^{(0)} = -\sum_{i\in S_{\mathrm{c}}} m_i \mathfrak{w}_i^{(0)}$ is the rate of total mass exchange between the gas and the surface due to chemisorption processes.

The integrated mass conservation equation (3.40) in the chemisorbate may be obtained with a similar procedure and yields that

$$\partial_t \mathsf{n}_i \int \exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}} T_{\mathrm{w}}}\Big) \mathrm{d}\zeta = \sum_{\mathrm{I} \in \mathfrak{Q}_i} \int \mathcal{C}_i^{(0)} \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta, \tag{4.22}$$

where $\mathcal{C}_i^{(0)}$ denotes—as for physisorbed species—the zeroth order chemical production rate. Defining the molecular production rate $\mathfrak{w}_i^{(0)}$ for any species as in (4.18), and using the z variable instead of ζ, the equation (4.22) may be rewritten

$$\partial_t \widetilde{n}_i = \mathfrak{w}_i^{(0)}, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}, \tag{4.23}$$

where $\widetilde{n}_i = \mathsf{n}_i \int \exp\big(-\mathrm{W}_i / k_{\mathrm{B}} T_{\mathrm{w}}\big) \mathrm{d}z$ 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.

In summary, it has been established that

$$\overline{n}_{\mathrm{g}i} \overline{v}_{\mathrm{g}z} + \overline{\mathcal{F}}_{zi} = \mathfrak{w}_i^{(0)}, \qquad i \in S_{\mathrm{g}}, \qquad\qquad \overline{\rho}_{\mathrm{g}} \overline{v}_{\mathrm{g}z} = \sum_{i \in S_{\mathrm{g}}} m_i \mathfrak{w}_i^{(0)},$$

$$\partial_t \widetilde{n}_i = \mathfrak{w}_i^{(0)}, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}.$$

We have therefore recovered the species *fluid* boundary conditions at a reactive surface including chemisorbed species and crystal species [16, 17, 18, 42].

4.4 Surface chemical production rates

The integrated surface chemistry term $\mathfrak{w}_i^{(0)} = \sum_{\mathrm{I} \in \mathfrak{Q}_i} \int \mathcal{C}_i^{(0)} \mathrm{d}\boldsymbol{c}_i \mathrm{d}z$ evaluated with the layer distributions $\mathsf{f}_i^{(0)}$, $i \in S$, is obtained in the form

$$\mathfrak{w}_i^{(0)} = \sum_{r \in \mathfrak{R}} (\nu_{ir}^{\mathrm{bk}} - \nu_{ir}^{\mathrm{fw}}) \chi_r, \tag{4.24}$$

where χ_r denotes the rate of progress of the rth surface reaction. Letting then for short $\mathfrak{n}_k = \mathsf{n}_k$ when $k \in S \backslash S_{\mathrm{b}}$ and $\mathfrak{n}_k = \mathsf{n}_\sigma$ when $k \in S_{\mathrm{b}}$, we have at zeroth order $\gamma_k^{(0)} = \mathfrak{n}_k$ for any $k \in S$, where $\gamma_k^{(0)} = \mathsf{f}_k^{(0)} / \mathsf{m}_k$ and γ_k has been introduced in (2.38). Using the kinetic expression (2.37), the macroscopic rate χ_r is found in the form

$$\chi_r = \mathcal{K}_r \Big(\prod_{j \in \mathcal{F}^r} \frac{\mathfrak{n}_j}{\mathrm{Z}_j} - \prod_{k \in \mathcal{B}^r} \frac{\mathfrak{n}_k}{\mathrm{Z}_k} \Big), \tag{4.25}$$

where $\mathcal{K}_r$ is the overall reaction constant of the rth reaction through the layer

$$\mathcal{K}_r = \sum_{\mathrm{F}^r, \mathrm{B}^r} \int \widehat{\mathcal{W}}_{\mathcal{F}^r \mathcal{B}^r}^{\mathrm{F}^r \mathrm{B}^r} \prod_{j \in \mathcal{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{k \in \mathcal{B}^r} \mathrm{d}\boldsymbol{c}_k \; \mathrm{d}z. \tag{4.26}$$

The rate of progress χ_r may also be rewritten

$$\chi_r = \mathcal{K}_r \Big(\prod_{i \in S} \Big(\frac{\mathfrak{n}_i}{\mathrm{Z}_i}\Big)^{\nu_{ir}^{\mathrm{fw}}} - \prod_{i \in S} \Big(\frac{\mathfrak{n}_i}{\mathrm{Z}_i}\Big)^{\nu_{ir}^{\mathrm{bk}}} \Big),$$

making use of the reaction stoichiometric coefficients.

The surface chemistry rate χ_r may also be naturally rewritten by using the surface species number densities (4.12). To this aim, the partition function of any surface species $\widetilde{\mathrm{z}}_i$ is defined with a configuration integral [53]

$$\widetilde{\mathrm{z}}_i = \mathrm{z}_i \int \exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}}T_{\mathrm{w}}}\Big)\mathrm{d}z, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}. \tag{4.27}$$

We then note that for any chemisorbed or free site species

$$\frac{\mathcal{n}_i}{\mathrm{z}_i} = \frac{\mathsf{n}_i}{\mathrm{z}_i} = \frac{\widetilde{n}_i}{\widetilde{\mathrm{z}}_i}, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}}. \tag{4.28}$$

Letting then for the gaseous species $\widetilde{\mathcal{n}}_i = \mathcal{n}_i = \overline{n}_{gi}$ and $\widetilde{\mathrm{z}}_i = \mathrm{z}_i$, $i \in S_{\mathrm{g}}$, for the chemisorbed and free sites $\widetilde{\mathcal{n}}_i = \widetilde{n}_i$, $i \in S_{\mathrm{c}} \cup S_{\mathrm{s}}$, and for the bulk species $\widetilde{\mathcal{n}}_i = \widetilde{n}_\sigma$, $i \in S_{\mathrm{b}}$, then the rate of progress may then be evaluated in the form

$$\chi_r = \mathcal{K}_r \left(\prod_{i\in S} \Big(\frac{\widetilde{\mathcal{n}}_i}{\widetilde{\mathrm{z}}_i}\Big)^{\nu_{ir}^{\mathrm{fw}}} - \prod_{i\in S} \Big(\frac{\widetilde{\mathcal{n}}_i}{\widetilde{\mathrm{z}}_i}\Big)^{\nu_{ir}^{\mathrm{bk}}} \right). \tag{4.29}$$

These expresssions are fully compatible with the atomic site formalism of heterogeneous chemistry. The traditional mass conservation equations as well as surface chemical production rates have thus been recovered from the kinetic model. From the expression of the rates of progress, we also recover the Langmuir-Hinshelwood and Eley-Rideal kinetics as well as the Langmuir isotherms at equilibrium [17, 32, 33, 34].

It is also possible to write the rate of progress in a form compatible with the open site convention by excluding the crystal species. To this aim, the rates of progress is rewritten as

$$\chi_r = \mathcal{K}_r' \Big(\prod_{k\in S_{\mathrm{g}}\cup S_{\mathrm{c}}} \widetilde{\mathcal{n}}_k^{\nu_{kr}^{\mathrm{fw}}} (1-\widetilde{\theta})^{\nu_{\mathrm{s}r}^{\mathrm{fw}}} - \frac{1}{\mathcal{K}_r^{\mathrm{e}}} \prod_{k\in S_{\mathrm{g}}\cup S_{\mathrm{c}}} \widetilde{\mathcal{n}}_k^{\nu_{kr}^{\mathrm{bk}}} (1-\widetilde{\theta})^{\nu_{\mathrm{s}r}^{\mathrm{bk}}} \Big), \tag{4.30}$$

where $\mathcal{K}_r'$ and $\mathcal{K}_r^{\mathrm{e}}$ are the proper direct and equilibrium constants

$$\mathcal{K}_r' = \mathcal{K}_r \widetilde{n}_\sigma^{\bar{\nu}} \prod_{i\in S} \widetilde{\mathrm{z}}_i^{-\nu_{ir}^{\mathrm{fw}}}, \qquad \mathcal{K}_r^{\mathrm{e}} = \prod_{i\in S} \widetilde{\mathrm{z}}_i^{-\nu_{ir}},$$

and

$$\bar{\nu} = \sum_{i\in S_{\mathrm{b}}} \nu_{ir}^{\mathrm{fw}} + \nu_{\mathrm{s}r}^{\mathrm{fw}} = \sum_{i\in S_{\mathrm{b}}} \nu_{ir}^{\mathrm{bk}} + \nu_{\mathrm{s}r}^{\mathrm{bk}}.$$

These expresssions are fully compatible with the open site formalism with the elimination of the crystal species and with the free atom species, formally replaced by an open site symbol $\mathcal{O}$, is taken into account with a simple coverage probability $\widetilde{\theta}$.

We may further factorize the product $(1-\widetilde{\theta})^{\bar{\nu}}$ in the rates of progress (4.30), using that $\bar{\nu} = \sum_{i\in S_{\mathrm{b}}} \nu_{ir}^{\mathrm{fw}} + \nu_{\mathrm{s}r}^{\mathrm{fw}} = \sum_{i\in S_{\mathrm{b}}} \nu_{ir}^{\mathrm{bk}} + \nu_{\mathrm{s}r}^{\mathrm{bk}}$. The factors $(1-\widetilde{\theta})^{\nu_{\mathrm{s}r}^{\mathrm{fw}}}$ and $(1-\widetilde{\theta})^{\nu_{\mathrm{s}r}^{\mathrm{bk}}}$ are then incorporated in the corresponding products over the chemisorbed species using the modified number densities $\widetilde{n}_i/(1-\widetilde{\theta})$ for $i \in S_{\mathrm{c}}$. Further assuming that the formation energies of bulk species are equal, keeping in mind that they correspond to a typical bond energy with the crystal, we obtain that the bulk species partition functions are equal $\widetilde{\mathrm{z}}_i = \widetilde{\mathrm{z}}_{\mathrm{b}}$, for $i \in S_{\mathrm{b}}$, where $\widetilde{\mathrm{z}}_{\mathrm{b}}$ denotes their common value. It is then possible to rewrite the rates of progress in a form that *fully eliminates all crystal species*, including the open site. To this aim, we introduce the following modified chemical potential of chemisorbed species

$$\widetilde{\mu}_i = \log\Big(\frac{\widetilde{n}_i}{\widetilde{\mathrm{Z}}_i'(1-\widetilde{\theta})}\Big), \qquad i \in S_{\mathrm{c}}, \tag{4.31}$$

where $\widetilde{\mathrm{Z}}_i' = \widetilde{\mathrm{Z}}_i\widetilde{\mathrm{Z}}_{\mathrm{b}}/\widetilde{\mathrm{Z}}_{\mathrm{s}}$ is a partition function of the ith chemisorbed species taking into account the crystal bond energy. This modified potential includes the $1-\widetilde{\theta}$ factor associated with the free site density in agreement with statistical mechanics for low coverage *that exclude crystal species* [53, 49]. Letting also naturally for the gas species

$$\widetilde{\mu}_i = \log\Big(\frac{\widetilde{n}_i}{\widetilde{\mathrm{Z}}_i}\Big) = \log\Big(\frac{\overline{n}_{gi}}{\mathrm{Z}_i}\Big), \qquad i \in S_{\mathrm{g}}, \tag{4.32}$$

the rate of progress is then obtained in a general form associated with statistical mechanics [71, 72, 42]

$$\chi_r = \mathcal{K}_r''\Big(\exp\Big(\sum_{k\in S_{\mathrm{g}}\cup S_{\mathrm{c}}} \nu_{kr}^{\mathrm{fw}}\widetilde{\mu}_k\Big) - \exp\Big(\sum_{k\in S_{\mathrm{g}}\cup S_{\mathrm{c}}} \nu_{kr}^{\mathrm{bk}}\widetilde{\mu}_k\Big)\Big), \tag{4.33}$$

where $\mathcal{K}_r''$ is positive. The various expressions of the production rate derived with the atomic site formalism (4.29), the open site formalism (4.30), and the mechanistic formalism using the modified potentials (4.31) thus gradually eliminate the crystal surface species. However, even though the saturation factor $1-\widetilde{\theta}$ is sometimes integrated into the chemical potential of the chemisorbed species $\tilde{\mu}_i$, it still originates from the surface free crystal atom species.

5 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 mass dynamic 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 have been obtained by identifying Maxwellian distributions.

5.1 Normal momentum boundary conditions

We multiply by $m_i c_{iz}$ and ϵ the difference equation (3.39), integrate with respect to the particle velocity $\boldsymbol{c}_i$, sum over $i \in S_{\mathrm{g}}$ and $\mathrm{I} \in \mathfrak{Q}_i$, and keep all terms of order ϵ^0 or ϵ^1. Keeping in mind that both $\mathsf{f}_i^{(0)}$ and $\mathsf{f}_{\mathrm{g}i}^{(0)}$ are even with respect to c_{iz}, as well as with respect to $\boldsymbol{c}_{i\shortparallel}$, the resulting equation is in the form

$$\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \partial_\zeta \int m_i c_{iz}^2(\mathsf{f}_i^{(0)} + \epsilon\mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(0)} - \epsilon\mathsf{f}_{\mathrm{g}i}^{(1)})\,\mathrm{d}\boldsymbol{c}_i - \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \partial_\zeta \mathrm{W}_i\, c_{iz}\partial_{c_{iz}}(\mathsf{f}_i^{(0)} + \epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i$$
$$- \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{1}{\alpha_{\mathrm{ph}}} \int m_i c_{iz} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)} + \epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i = \epsilon \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int m_i c_{iz}\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i.$$

Integrating with respect to ζ, keeping in mind that $\mathsf{f}_{\mathrm{lc}i}^{(0)} = \mathsf{f}_i^{(0)} - \mathsf{f}_{\mathrm{g}i}^{(0)}$ and $\mathsf{f}_{\mathrm{lc}i}^{(1)} = \mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(1)}$ go to zero as $\zeta \to \infty$, that $\mathsf{f}_i^{(0)}$ and $\mathsf{f}_i^{(1)}$ go to zero as $\zeta \to 0$, and that $\mathsf{f}_{\mathrm{g}i}^{(0)}$ and $\mathsf{f}_{\mathrm{g}i}^{(1)}$ go respectively to $\overline{f}^{(0)}_{\mathrm{g}i}$ and $\overline{f}^{(1)}_{\mathrm{g}i}$ as $\zeta \to 0$, yields a normal momentum balance associated with the physorbate-gas species

$$\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \mathfrak{m}_i c_{iz}^2 (\overline{f}^{(0)}_{\mathrm{g}i} + \epsilon \overline{f}^{(1)}_{\mathrm{g}i})\,\mathrm{d}\boldsymbol{c}_i - \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \partial_\zeta \mathrm{W}_i\, c_{iz} \partial_{c_{iz}} (\mathsf{f}^{(0)}_i + \epsilon \mathsf{f}^{(1)}_i)\,\mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta$$

$$= \frac{1}{\alpha_{\mathrm{ph}}} \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \mathfrak{m}_i c_{iz} J_{i,\mathrm{ph}} (\mathsf{f}^{(0)}_i + \epsilon \mathsf{f}^{(1)}_i)\,\mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta + \epsilon \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \mathfrak{m}_i c_{iz} \mathcal{C}^{(0)}_i \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta. \qquad (5.1)$$

A direct calculation yields

$$\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \mathfrak{m}_i c_{iz}^2 \overline{f}^{(0)}_{\mathrm{g}i}\,\mathrm{d}\boldsymbol{c}_i = \sum_{i\in S_{\mathrm{g}}} \overline{p}_{\mathrm{g}i} = \overline{p}_{\mathrm{g}},$$

where $p_{\mathrm{g}i} = n_{\mathrm{g}i} k_{\mathrm{B}} T_{\mathrm{g}}$ denotes the gas pressure of the ith species, $p_{\mathrm{g}} = \sum_{i\in S_{\mathrm{g}}} p_{\mathrm{g}i}$ the gas pressure and $\overline{p}_{\mathrm{g}}$ the gas pressure at $z=0$. Using the definition of the viscous tensor $\boldsymbol{\Pi}_{\mathrm{g}}$ in the gas and the properties of the Navier-Stokes correctors $\phi_{\mathrm{g}i}$, $i \in S_{\mathrm{g}}$, it is established [38, 39, 40, 41, 42, 43, 44] that

$$\epsilon \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \mathfrak{m}_i \int \boldsymbol{c}_i \otimes \boldsymbol{c}_i \overline{f}^{(1)}_{\mathrm{g}i}\,\mathrm{d}\boldsymbol{c}_i = \overline{\boldsymbol{\Pi}}_{\mathrm{g}}, \qquad (5.2)$$

where $\overline{\boldsymbol{\Pi}}_{\mathrm{g}}$ is the viscous tensor at $z=0$. The viscous tensor may also be expanded in terms of the macroscopic variable gradients and shown to be in the form

$$\boldsymbol{\Pi}_{\mathrm{g}} = -\epsilon\kappa \boldsymbol{\partial_x}\cdot\boldsymbol{v}_{\mathrm{g}} \boldsymbol{I} - \epsilon\eta \big(\boldsymbol{\partial_x} \boldsymbol{v}_{\mathrm{g}} + (\boldsymbol{\partial_x} \boldsymbol{v}_{\mathrm{g}})^t - \tfrac{2}{3} \boldsymbol{\partial_x}\cdot\boldsymbol{v}_{\mathrm{g}} \boldsymbol{I}\big), \qquad (5.3)$$

where κ denotes the volume viscosity and η the shear viscosity. Use has been made that the term proportional to $\mathfrak{m}_i c_{iz} \overline{f}^{(0)}_{\mathrm{g}i}$ as well as that associated with $\boldsymbol{\phi}^{\widehat{\lambda}}_{\mathrm{g}i}\cdot\boldsymbol{\partial_x}(1/k_{\mathrm{B}}T_{\mathrm{g}})$ and $\boldsymbol{\phi}^{D_j}_{\mathrm{g}i}\cdot\boldsymbol{\partial_x} p_{\mathrm{g}j}$ in $\overline{f}^{(1)}_{\mathrm{g}i}$ yield null contributions in $\mathfrak{m}_i \int \boldsymbol{c}_i\otimes\boldsymbol{c}_i \overline{f}^{(1)}_{\mathrm{g}i}\,\mathrm{d}\boldsymbol{c}_i$. Defining naturally the pressure tensor in the gas by

$$\boldsymbol{\mathcal{P}}^{\mathrm{g}} = p_{\mathrm{g}} \boldsymbol{I} + \boldsymbol{\Pi}_{\mathrm{g}}, \qquad (5.4)$$

and considering the zz components of (5.2), we thus have

$$\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \mathfrak{m}_i c_{iz}^2 (\overline{f}^{(0)}_{\mathrm{g}i} + \epsilon \overline{f}^{(1)}_{\mathrm{g}i})\,\mathrm{d}\boldsymbol{c}_i = \overline{p}_{\mathrm{g}} + \overline{\Pi}_{\mathrm{g}zz} = \overline{\mathcal{P}}^{\mathrm{g}}_{zz},$$

where $\Pi_{\mathrm{g}zz}$ is the zz component of $\boldsymbol{\Pi}_{\mathrm{g}}$.

In order to eliminate the reactive source term in the right hand side of (5.1), we form the normal momentum balance of the surface species for $i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}$ that are similar except for the absence of a flux coming from the gas. Denoting for short by S_Σ the surface species indexing set

$$S_\Sigma = S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}},$$

the resulting momentum balance associated with surface species is in the form

$$
\begin{aligned}
&-\sum_{\substack{i\in S_\Sigma\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \partial_\zeta \mathrm{W}_i\, c_{iz}\partial_{c_{iz}}(\mathsf{f}_i^{(0)}+\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta = \\
&\qquad \sum_{\substack{i\in S_\Sigma\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{1}{\alpha_{\mathrm{ph}}}\int \mathfrak{m}_i c_{iz} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}+\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \epsilon\sum_{\substack{i\in S_\Sigma\\ \mathrm{I}\in\mathfrak{Q}_i}}\int \mathfrak{m}_i c_{iz}\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.
\end{aligned}
\tag{5.5}
$$

Adding the momentum balance equations (5.1) and (5.5), using momentum conservation in chemical reactions

$$
\sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}}\int \mathfrak{m}_i c_{iz}\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta = 0,
$$

and integrating by part with respect to the normal velocity variable the potential terms

$$
-\sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \partial_\zeta \mathrm{W}_i\, c_{iz}\partial_{c_{iz}}(\mathsf{f}_i^{(0)}+\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta = \sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \partial_\zeta \mathrm{W}_i\,(\mathsf{f}_i^{(0)}+\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta,
$$

it is obtained that

$$
\overline{p}_{\mathrm{g}} + \overline{\Pi}_{\mathrm{g}zz} = -\sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \partial_\zeta \mathrm{W}_i\,(\mathsf{f}_i^{(0)}+\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{1}{\alpha_{\mathrm{ph}}}\int \mathfrak{m}_i c_{iz} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}+\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.
$$

The solid crystal pressure tensor—opposite of the crystal Cauchy tensor—at the surface is then naturally defined as

$$
\mathcal{P}_{zz}^{\mathrm{so}} = -\sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \partial_\zeta \mathrm{W}_i\,(\mathsf{f}_i^{(0)}+\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{1}{\alpha_{\mathrm{ph}}}\int \mathfrak{m}_i c_{iz} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(0)}+\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.
$$

This expression may be simplified by using

$$
(\partial_\zeta \mathrm{W}_i)\, n_i(\zeta) = -\overline{p}_{\mathrm{g}i}\partial_\zeta\big(\exp(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}})\big), \qquad i\in S_{\mathrm{g}},
$$

where n_i are the zeroth order number densities, and

$$
(\partial_\zeta \mathrm{W}_i)\, n_i(\zeta) = -\mathsf{n}_i k_{\mathrm{B}}T_{\mathrm{w}}\partial_\zeta\big(\exp(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}})\big), \qquad i\in S_\Sigma = S_{\mathrm{c}}\cup S_{\mathrm{s}}\cup S_{\mathrm{b}},
$$

and integrating with respect to ζ, in such a way that

$$
\mathcal{P}_{zz}^{\mathrm{so}} = p_{\mathrm{g}} - \sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \epsilon\int \partial_\zeta \mathrm{W}_i\mathsf{f}_i^{(1)}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{\epsilon}{\alpha_{\mathrm{ph}}}\int \mathfrak{m}_i c_{iz} J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.
$$

The first two terms of the right hand side represent the total force per unit surface acting on the physisorbate, chemisorbate, and surface layer, whereas the third term 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 the pressure term acting on the physisorbate, it appears that it is dominant term. We may finally write the resulting boundary condition in the form

$$
\overline{\mathcal{P}}_{zz}^{\mathrm{g}} = \mathcal{P}_{zz}^{\mathrm{so}},
\tag{5.6}
$$

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

5.2 Tangential momentum boundary conditions

We multiply by $m_i\boldsymbol{c}_{i\shortparallel}$ and ϵ the difference equation (3.39), integrate with respect to the particle velocity $\boldsymbol{c}_i$, sum with respect to $i \in S_{\mathrm{g}}$ and $\mathrm{I} \in \mathfrak{Q}_i$, and keep all terms of order ϵ^0 and ϵ^1. Keeping in mind that both $\mathsf{f}_i^{(0)}$ and $\mathsf{f}_{\mathrm{g}i}^{(0)}$ are even with respect to c_{iz} and $\boldsymbol{c}_{i\shortparallel}$ and that the phonon interaction operators vanish for Maxwellians, the resulting equation is in the form

$$\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \epsilon\,\boldsymbol{\partial}_{\shortparallel}\boldsymbol{\cdot}\int m_i\boldsymbol{c}_{i\shortparallel}\otimes\boldsymbol{c}_{i\shortparallel}(\mathsf{f}_i^{(0)}-\mathsf{f}_{\mathrm{g}i}^{(0)})\mathrm{d}\boldsymbol{c}_i + \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \epsilon\,\partial_\zeta\int m_i c_{iz}\boldsymbol{c}_{i\shortparallel}(\mathsf{f}_i^{(1)}-\mathsf{f}_{\mathrm{g}i}^{(1)})\,\mathrm{d}\boldsymbol{c}_i =$$

$$\frac{\epsilon}{\alpha_{\mathrm{ph}}}\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}}\int m_i\boldsymbol{c}_{i\shortparallel}J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i + \epsilon\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}}\int m_i\boldsymbol{c}_{i\shortparallel}\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i.$$

We may then integrate with respect to ζ and use that $\mathsf{f}_i^{(0)}$ and $\mathsf{f}_i^{(1)}$ go to zero as $\zeta\to 0$, $\mathsf{f}_i^{(0)}-\mathsf{f}_{\mathrm{g}i}^{(0)}$ and $\mathsf{f}_i^{(1)}-\mathsf{f}_{\mathrm{g}i}^{(1)}$ go to zero as $\zeta\to\infty$, $\mathsf{f}_{\mathrm{g}i}^{(0)}\to\overline{f}_{\mathrm{g}i}^{(0)}$ and $\mathsf{f}_{\mathrm{g}i}^{(1)}\to\overline{f}_{\mathrm{g}i}^{(1)}$ as $\zeta\to 0$ to get that

$$\sum_{i\in S_{\mathrm{g}}}\epsilon\,\boldsymbol{\partial}_{\shortparallel}\overline{p}_{\mathrm{g}i}\int\Big\{\exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}}T_{\mathrm{w}}}\Big)-1\Big\}\mathrm{d}\zeta + \epsilon\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}}\int m_i c_{iz}\boldsymbol{c}_{i\shortparallel}\overline{f}_{\mathrm{g}i}^{(1)}\,\mathrm{d}\boldsymbol{c}_i =$$

$$\frac{\epsilon}{\alpha_{\mathrm{ph}}}\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}}\int m_i\boldsymbol{c}_{i\shortparallel}J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}}\epsilon\int m_i\boldsymbol{c}_{i\shortparallel}\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

The second term may be evaluated as $\overline{\boldsymbol{\Pi}}_{\mathrm{g}\shortparallel z}$ by using (5.2) in the $\shortparallel z$ directions, where $\boldsymbol{\Pi}_{\mathrm{g}\shortparallel z}$ denotes the tangential components of $\boldsymbol{\Pi}_{\mathrm{g}}\boldsymbol{\cdot}\boldsymbol{e}_z$. In order to eliminate the reactive source term, we may again form the overall layer tangential momentum balance of the surface species. The resulting equations are obtained in the form

$$0=\frac{\epsilon}{\alpha_{\mathrm{ph}}}\sum_{\substack{i\in S_\Sigma\\ \mathrm{I}\in\mathfrak{Q}_i}}\int m_i\boldsymbol{c}_{i\shortparallel}J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{\substack{i\in S_\Sigma\\ \mathrm{I}\in\mathfrak{Q}_i}}\epsilon\int m_i\boldsymbol{c}_{i\shortparallel}\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

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

$$\overline{\boldsymbol{\Pi}}_{\mathrm{g}\shortparallel z}=\sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}}\frac{\epsilon}{\alpha_{\mathrm{ph}}}\int m_i\boldsymbol{c}_{i\shortparallel}J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{i\in S_{\mathrm{g}}}\epsilon\,\boldsymbol{\partial}_{\shortparallel}\overline{p}_{\mathrm{g}i}\int\Big\{1-\exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}}T_{\mathrm{w}}}\Big)\Big\}\mathrm{d}\zeta.$$

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

$$\boldsymbol{\mathcal{P}}^{\mathrm{so}}_{\shortparallel z}=\sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}}\frac{\epsilon}{\alpha_{\mathrm{ph}}}\int m_i\boldsymbol{c}_{i\shortparallel}J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \sum_{i\in S_{\mathrm{g}}}\epsilon\,\boldsymbol{\partial}_{\shortparallel}\overline{p}_{\mathrm{g}i}\int\Big\{1-\exp\Big(-\frac{\mathrm{W}_i}{k_{\mathrm{B}}T_{\mathrm{w}}}\Big)\Big\}\mathrm{d}\zeta,$$

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

$$\boldsymbol{\mathcal{P}}^{\mathrm{g}}_{\shortparallel z}=\overline{\boldsymbol{\Pi}}_{\mathrm{g}\shortparallel z}=\boldsymbol{\mathcal{P}}^{\mathrm{so}}_{\shortparallel z}, \tag{5.7}$$

and only first order terms remain. Note that when there is one single species, then the second term of $\boldsymbol{\mathcal{P}}^{\mathrm{so}}_{\shortparallel z}$ is $\mathcal{O}(\epsilon^2)$ and may be discarded since $\boldsymbol{\partial}_{\shortparallel}\overline{p}_{\mathrm{g}} = \mathcal{O}(\epsilon)$ from the momentum conservation equation.

5.3 Thermal boundary condition

We multiply by $\frac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}} + \mathrm{W}_i$ and ϵ the kinetic equation (3.36) for $i \in S_{\mathrm{g}}$, multiply by $\frac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}}$ and ϵ the gas kinetic equation (3.37), and form the difference equation. Integrating then with respect to the particle velocity, summing over $i \in S_{\mathrm{g}}$ and $\mathrm{I} \in \mathfrak{Q}_i$, and keeping all terms of order ϵ^0 and ϵ^1, it is obtained that

$$\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \partial_\zeta \int c_{iz}\Big\{(\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}} + \mathrm{W}_i)(\mathsf{f}_i^{(0)} + \epsilon\mathsf{f}_i^{(1)}) - (\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}})(\mathsf{f}_{\mathrm{g}i}^{(0)} + \epsilon\mathsf{f}_{\mathrm{g}i}^{(1)})\Big\}\mathrm{d}\boldsymbol{c}_i =$$

$$\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{1}{\alpha_{\mathrm{ph}}} \int (\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}} + \mathrm{W}_i) J_{i,\mathrm{ph}}(\epsilon\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i$$

$$+ \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \epsilon \int (\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}} + \mathrm{W}_i)\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i.$$

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

$$\sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \epsilon \int c_{iz}(\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}})\overline{f}_{\mathrm{g}i}^{(1)}\,\mathrm{d}\boldsymbol{c}_i = \frac{\epsilon}{\alpha_{\mathrm{ph}}} \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \tfrac{1}{2}m_i|\boldsymbol{c}_i|^2 J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta$$
$$+ \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \epsilon \int (\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}} + \mathrm{W}_i)\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta. \quad (5.8)$$

Using the definition of the heat flux in the gas, specialized in the normal direction, the moment associated with $f_{\mathrm{g}i}^{(1)}$ is evaluated in the form

$$\epsilon \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int c_{iz}(\tfrac{1}{2}m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_{i\mathrm{I}})\overline{f}_{\mathrm{g}i}^{(1)}\,\mathrm{d}\boldsymbol{c}_i = \sum_{i\in S_{\mathrm{g}}} \big(\tfrac{5}{2}k_{\mathrm{B}}\overline{T}_{\mathrm{g}} + e_i\big)n_{\mathrm{g}i}v_{\mathrm{g}z} + \overline{\boldsymbol{Q}}_z.$$

The heat flux may also be written

$$\boldsymbol{Q} = -\epsilon\widehat{\lambda}\boldsymbol{\partial_x}T_{\mathrm{g}} - p\sum_{i\in S}\epsilon\theta_i^{\mathrm{th}}\boldsymbol{d}_i + \sum_{i\in S_{\mathrm{g}}}\big(\tfrac{5}{2}k_{\mathrm{B}}T_{\mathrm{g}} + e_i\big)\boldsymbol{\mathcal{F}}_i,$$

where $\widehat{\lambda}$ is the partial thermal conductivity, θ_i the ith species thermal diffusion coefficient and $\boldsymbol{d}_i = (\boldsymbol{\partial_x}p_{\mathrm{g}i})/p_{\mathrm{g}}$ the diffusion driving force of the ith species.

In order to eliminate the reactive source term in the right hand side of (5.8), proceeding as for the momentum balance equations, we may use the thermal balance of the surface species. The resulting equations are in the form

$$\sum_{\substack{i\in S_\Sigma\\ \mathrm{I}\in\mathfrak{Q}_i}} \epsilon\,\partial_t \int (\tfrac12 m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_i + \mathrm{W}_i)\mathsf{f}_i^{(0)}\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta = \sum_{\substack{i\in S_\Sigma\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{\epsilon}{\alpha_{\mathrm{ph}}} \int \tfrac12 m_i|\boldsymbol{c}_i|^2 J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta$$
$$+ \sum_{\substack{i\in S_\Sigma\\ \mathrm{I}\in\mathfrak{Q}_i}} \epsilon \int (\tfrac12 m_i|\boldsymbol{c}_i|^2 + \mathrm{E}_i + \mathrm{W}_i)\mathcal{C}_i^{(0)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

Letting then for $i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}$

$$\widetilde{\mathrm{E}}_i = \mathrm{E}_i + \int \mathrm{W}_i \exp\big(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}}\big)\mathrm{d}\zeta \;\Big/\; \int \exp\big(-\mathrm{W}_i/k_{\mathrm{B}}T_{\mathrm{w}}\big)\mathrm{d}\zeta, \tag{5.9}$$

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

$$\sum_{i\in S_{\mathrm{g}}} \big(\tfrac52 k_{\mathrm{B}}\overline{T}_{\mathrm{g}} + e_i\big)\overline{n}_{\mathrm{g}i}\overline{v}_{\mathrm{g}z} + \overline{\boldsymbol{Q}}_z + \sum_{i\in S_\Sigma} \partial_t\big((\tfrac32 k_{\mathrm{B}}\overline{T}_{\mathrm{g}} + \widetilde{\mathrm{E}}_i)\tilde{n}_i\big) =$$
$$\sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{\epsilon}{\alpha_{\mathrm{ph}}} \int \tfrac12 m_i|\boldsymbol{c}_i|^2 J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta.$$

The solid heat flux at the surface is defined as

$$\boldsymbol{Q}_z^{\mathrm{so}} = \sum_{\substack{i\in S\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{\epsilon}{\alpha_{\mathrm{ph}}} \int \tfrac12 m_i|\boldsymbol{c}_i|^2 J_{i,\mathrm{ph}}(\mathsf{f}_i^{(1)})\,\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta,$$

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. We have thus established that

$$\sum_{i\in S_{\mathrm{g}}} \big(\tfrac52 k_{\mathrm{B}}\overline{T}_{\mathrm{g}} + e_i\big)\overline{n}_{\mathrm{g}i}\overline{v}_{\mathrm{g}z} + \overline{\boldsymbol{Q}}_z + \sum_{i\in S_\Sigma} \partial_t\big((\tfrac32 k_{\mathrm{B}}T_{\mathrm{w}} + \widetilde{\mathrm{E}}_i)\tilde{n}_i\big) = \boldsymbol{Q}_z^{\mathrm{so}}, \tag{5.10}$$

and we may also use that $\partial_t\tilde{n}_i$ is directly expressed in terms of the surface reaction rate. This relation corresponds to that generally used for thermal balances at reactive surfaces [17, 42]. Incidentally, the heat flux in the solid cannot be expressed in terms of the temperature gradient in the solid because phonon kinetic equations are not taken into account [35].

6 First order expansions and multicomponent diffusion

First order expansions are investigated as well as multicomponent diffusion in the physisorbate and the chemisorbate layers.

6.1 Simplified phonon interaction operator

In order to simplify the analysis of first order equations in the reactive surface layer it is assumed that the phonon collision operators are in the relaxation form

$$\frac{1}{\alpha_{\mathrm{ph}}} J_{i,\mathrm{ph}}(\varphi_i) = -\frac{1}{\tau_{i,\mathrm{ph}}}\big(\varphi_i - \langle\varphi_i\rangle_{\mathrm{M}_i}\big), \qquad i \in S, \tag{6.1}$$

where the relaxation times $\tau_{i,\mathrm{ph}} = \tau_{i,\mathrm{ph}}(\zeta)$ are independent of the velocity $\boldsymbol{c}_i$ and where $\langle \varphi_i \rangle$ denotes for short the integral over the velocity and the sum over the quantum numbers

$$\langle \varphi_i \rangle = \sum_{\mathrm{I} \in \mathfrak{Q}_i} \int \varphi_i \, \mathrm{d}\boldsymbol{c}_i, \qquad i \in S.$$

Such an assumption introduced by Borman et al. [19, 20] simplifies the analysis at first order as well as the derivation of the corresponding species fluid equations. Since there is no interaction with phonons far from the surface Σ, we also have for the physisorbate species

$$\lim_{\zeta \to \infty} \tau_{i,\mathrm{ph}}(\zeta) = +\infty, \qquad i \in S_{\mathrm{g}}. \tag{6.2}$$

A natural further simplifying assumption, concerning the chemisorbed, free site and bulk species, is that the corresponding relaxation times are constants independent of ζ, keeping in mind that the surface and chemisorbed layers are thin layers

$$\tau_{i,\mathrm{ph}} = \text{constant}, \qquad i \in S_{\mathrm{c}} \cup S_{\mathrm{s}} \cup S_{\mathrm{b}}. \tag{6.3}$$

We then have $\tau_{i,\mathrm{ph}}(\zeta) = \tau_{i,\mathrm{ph}} = \text{constant}$ for $\zeta \in (\zeta_i^-, \zeta_i^+)$ whereas $\tau_{i,\mathrm{ph}}(\zeta) = +\infty$ outside of this interval. The dynamics associated with phonon interactions has thus been simplified in the form of simple relaxation operators.

6.2 First order expansion in the gas as a thin layer

A prerequisite to the study of physisorbate diffusive processes is to investigate first order gas kinetic equations in the thin layer form (3.38). We indeed *already know the correct first order integral equations* that must be recovered. More specifically, at zeroth order, we have $\overline{\phi}_{\mathrm{g}i}^{(1)} = -\sum_{j \in S_{\mathrm{g}}} \overline{\phi}_{\mathrm{g}i}^{D_j} \cdot \overline{\boldsymbol{\partial_x} p_{\mathrm{g}j}}$ and from (3.26) we also have

$$\mathcal{I}_{\mathrm{g}i}(\overline{\phi}_{\mathrm{g}}^{(1)}) = -\sum_{j \in S_{\mathrm{g}}} \frac{1}{\overline{p}_{\mathrm{g}i}} (\delta_{ij} - \mathsf{y}_{\mathrm{g}i}) \boldsymbol{c}_i \cdot \overline{\boldsymbol{\partial_x} p}_{\mathrm{g}j}. \tag{6.4}$$

These equations are exactly the integral equations obtained by letting $\boldsymbol{v}_{\mathrm{g}} = 0$ in the traditional first order integral equations for diffusion processes in the gas.

Keeping in mind that $\Xi_{\mathrm{g}i}^{(1)} = \mathsf{f}_{\mathrm{g}i}^{(1)} / \mathsf{f}_{\mathrm{g}i}^{(0)}$ and $\Xi_{\mathrm{g}}^{(1)} = (\Xi_{\mathrm{g}i}^{(1)})_{i \in S_{\mathrm{g}}}$, the first order equations in the thin layer form (3.38) are

$$c_{iz} \, \partial_\zeta \Xi_{\mathrm{g}i}^{(1)} + \mathcal{I}_{\mathrm{g}i}(\Xi_{\mathrm{g}}^{(1)}) / \alpha_\kappa = -\big(\partial_t \log \mathsf{f}_{\mathrm{g}i}^{(0)} + \boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_\shortparallel \log \mathsf{f}_{\mathrm{g}i}^{(0)} \big), \qquad i \in S_{\mathrm{g}}, \tag{6.5}$$

where $\mathsf{f}_{\mathrm{g}i}^{(0)} = \overline{f}_{\mathrm{g}i}^{(0)}$ and

$$\Xi_{\mathrm{g}i}^{(1)} = \frac{m_i c_{iz} v_{\mathrm{g}z}}{k_{\mathrm{B}} \overline{T}_{\mathrm{g}}} + \alpha_\kappa \overline{\phi}_{\mathrm{g}i}^{(1)} + \zeta \overline{\partial_z \log f}_{\mathrm{g}i}^{(0)}, \qquad i \in S_{\mathrm{g}}.$$

We first observe that the left hand side of (6.5) does contain the required ith gas species integral operator $\mathcal{I}_{\mathrm{g}i}$. Moreover, using $\boldsymbol{\partial_x} T_{\mathrm{g}} = \mathcal{O}(\epsilon)$ and $\boldsymbol{\partial_x} \boldsymbol{v}_{\mathrm{g}} = \mathcal{O}(\epsilon)$, the tangential gradient terms of the right hand side yields $-\boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_\shortparallel \log \mathsf{f}_{\mathrm{g}i}^{(0)} = -\boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_\shortparallel \log \overline{p}_{\mathrm{g}i}$ involving the pressure gradients in the tangential direction. However, the pressure normal derivatives present in (6.4) are missing in the right hand side of (6.5). We thus proceed as in Section 3.5 and transfer the term $c_{iz} \partial_\zeta \Xi_{\mathrm{g}i}^{(1)} = c_{iz} \overline{\partial_z \log f}_{\mathrm{g}i}^{(0)} = c_{iz} \overline{\partial_z \log p}_{\mathrm{g}i}$ from the left hand side to the right hand side. A full pressure gradient term $\boldsymbol{c}_i \cdot \overline{\boldsymbol{\partial_x} \log p}_{\mathrm{g}i}$ then appears with tangential derivative as well as normal derivatives in the right hand side. By subtracting $\zeta\overline{\partial_z \log f_{gi}^{(0)}}$ from $\Xi_{gi}^{(1)}$, the corresponding first order distribution $\mathsf{f}_{gi}^{(1)} - \zeta\overline{\partial_z f_{gi}^{(0)}}$ also has a finite limit as $\zeta \to \infty$.

In order to complete the right hand side, we also need the terms arising usually through the derivative $\partial_t \log \mathsf{f}_{gi}^{(0)}$ as in the gas phase. However, since $\partial_t \boldsymbol{v}_{\mathrm{g}} = \mathcal{O}(\epsilon)$, $\partial_t n_{\mathrm{g}i} = \mathcal{O}(\epsilon)$, and $\partial_t T_{\mathrm{g}} = \mathcal{O}(\epsilon)$, the derivative $\partial_t \log \mathsf{f}_{gi}^{(0)}$ is found to be $\mathcal{O}(\epsilon)$. Ignoring formally that $\partial_t \boldsymbol{v}_{\mathrm{g}} = \mathcal{O}(\epsilon)$, the velocity term $\partial_t \boldsymbol{v}_{\mathrm{g}}$ in $\partial_t \log \mathsf{f}_{gi}^{(0)}$ should yield contributions with the total pressure gradient term as in the gas phase. We would then evaluate $\partial_{\boldsymbol{v}_{\mathrm{g}}} \log f_{\mathrm{g}i}^{(0)} \cdot (\partial_t \boldsymbol{v}_{\mathrm{g}} + \boldsymbol{v}_{\mathrm{g}} \cdot \boldsymbol{\partial_x} \boldsymbol{v}_{\mathrm{g}})$ as $-\mathfrak{m}_i \boldsymbol{c}_i \cdot \boldsymbol{\partial_x} p_{\mathrm{g}} / \rho_{\mathrm{g}} k_{\mathrm{B}} T_{\mathrm{g}}$ using Euler momentum equation $\partial_t \boldsymbol{v}_{\mathrm{g}} + \boldsymbol{v}_{\mathrm{g}} \cdot \boldsymbol{\partial_x} \boldsymbol{v}_{\mathrm{g}} = -\boldsymbol{\partial_x} p_{\mathrm{g}} / \rho_{\mathrm{g}}$, and the proper right hand side (6.4) would then be recovered. In our situation, however, since the mixture velocity is absent from $\mathsf{f}_{gi}^{(0)} = \overline{f}_{gi}^{(0)}$, we have to proceed differently. Since $\partial_t \boldsymbol{v}_{\mathrm{g}} = \mathcal{O}(\epsilon)$ we observe that *the momentum equation is then an equilibrium relation at zeroth order*, without any time derivative term, in the form $-\boldsymbol{\partial_x} p_{\mathrm{g}} / \rho_{\mathrm{g}} = \mathcal{O}(\epsilon)$. We may thus subtract the equilibrium $\mathcal{O}(\epsilon)$ term $-\boldsymbol{\partial_x} p_{\mathrm{g}} / \rho_{\mathrm{g}}$ multiplied by the proper factor $\mathfrak{m}_i \boldsymbol{c}_i / k_{\mathrm{B}} T_{\mathrm{g}}$ to recover the exact right hand side of first order equations for diffusive processes (6.4). The resulting equations are then well posed with a right hand side in the range of the gas collision operator, that is, orthogonal to the collision invariants. The only difference with the traditional situation is that instead of using Euler unsteady equations, we have used here Euler equilibrium relations in order to form the proper right hand side

$$-\frac{1}{p_{\mathrm{g}i}} \boldsymbol{c}_i \cdot \overline{\boldsymbol{\partial_x} p_{\mathrm{g}i}} + \frac{\mathfrak{m}_i \boldsymbol{c}_i}{k_{\mathrm{B}} T_{\mathrm{g}}} \cdot \frac{\overline{\boldsymbol{\partial_x} p_{\mathrm{g}}}}{\rho_{\mathrm{g}}}, \qquad i \in S_{\mathrm{g}}.$$

Collecting previous results, we introduce the modified first order unknowns

$$\Phi_{\mathrm{g}i}^{(1)} = \frac{\mathfrak{m}_i c_{iz} v_{\mathrm{g}z}}{k_{\mathrm{B}} \overline{T}_{\mathrm{g}}} + \alpha_\kappa \overline{\phi}_{\mathrm{g}i}^{(1)} = \Xi_{\mathrm{g}i}^{(1)} - \zeta \overline{\partial_z \log f_{\mathrm{g}i}^{(0)}}, \qquad i \in S_{\mathrm{g}}, \tag{6.6}$$

the correct right hand sides

$$\Psi_{\mathrm{g}i}^{(1)} = -\sum_{l \in S_{\mathrm{g}}} \frac{1}{p_{\mathrm{g}i}} (\delta_{il} - \mathsf{y}_{\mathrm{g}i}) \big(\boldsymbol{\partial}_{\shortparallel} \overline{p}_{\mathrm{g}l} \cdot \boldsymbol{c}_{i\shortparallel} + \overline{\partial_z p_{\mathrm{g}l}} c_{iz} \big), \qquad i \in S_{\mathrm{g}}, \tag{6.7}$$

and defining the operator $\mathcal{H}_{\mathrm{g}} = (\mathcal{H}_{\mathrm{g}i})_{i \in S_{\mathrm{g}}}$ by

$$\mathcal{H}_{\mathrm{g}i}(\varphi) = c_{iz}\, \partial_\zeta \varphi + \frac{1}{\alpha_\kappa} \mathcal{I}_{\mathrm{g}i}(\varphi), \qquad i \in S_{\mathrm{g}}, \tag{6.8}$$

the correct first order linearized equations written in the thin layer form read

$$\mathcal{H}_{\mathrm{g}i}(\Phi_{\mathrm{g}}^{(1)}) = \Psi_{\mathrm{g}i}^{(1)}, \qquad i \in S_{\mathrm{g}}. \tag{6.9}$$

We have thus recovered with (6.7) the full three dimensional pressure gradient evaluated at $z = 0$. The solution must also ensure the Enskog constraints $\langle\!\langle f_{\mathrm{g}}^{(0)} \Phi_{\mathrm{g}}^{(1)}, \psi_{\mathrm{g}}^l \rangle\!\rangle = 0$ for $1 \le l \le \mathrm{N}_{\mathrm{g}} + 4$ that reduces to the single constraint $\langle\!\langle f_{\mathrm{g}}^{(0)} \Phi_{\mathrm{g}}^{(1)}, (\mathfrak{m}_i \boldsymbol{c}_i)_{i \in S_{\mathrm{g}}} \rangle\!\rangle = 0$ for vector systems. It is further natural to write the coupled equations in vector form by letting

$$\mathcal{H}_{\mathrm{g}} = (\mathcal{H}_{\mathrm{g}i})_{i \in S_{\mathrm{g}}}, \qquad \Phi_{\mathrm{g}}^{(1)} = (\Phi_{\mathrm{g}i}^{(1)})_{i \in S_{\mathrm{g}}}, \qquad \Psi_{\mathrm{g}}^{(1)} = (\Psi_{\mathrm{g}i}^{(1)})_{i \in S_{\mathrm{g}}},$$

in such a way that

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

with the Enskog constraints $\langle\!\langle f_{\rm g}^{(0)}\Phi_{\rm g}^{(1)},\psi_{\rm g}^{l}\rangle\!\rangle = 0$ for $1 \le l \le \mathrm{N_g}+4$.

Since $(m_i c_{iz})_{i\in S_{\rm g}}$ is a collisional invariant, it is in the nullspace of the linearized operator $\mathcal{I}_{\rm g} = (\mathcal{I}_{{\rm g}i})_{i\in S_{\rm g}}$ and moreover $\Phi_{\rm g}^{(1)}$ is independent of ζ so that $\mathcal{H}_{{\rm g}i}(\Phi_{\rm g}^{(1)}) = \mathcal{I}_{{\rm g}i}(\Phi_{\rm g}^{(1)})/\alpha_\kappa = \mathcal{I}_{{\rm g}i}(\phi_{\rm g}^{(1)})$. We thus have recovered the classical linearized gas integral equations for diffusion processes (6.4).

In summary, we have first obtained a pressure normal gradient term by transferring the term $c_{iz}\partial_\zeta(\zeta\overline{\partial_z \log f_{{\rm g}i}^{(0)}}) = c_{iz}\overline{\partial_z \log f_{{\rm g}i}^{(0)}}$ from the left to the right hand side. We then have obtained the total pressure gradient—usually arising through the time derivative $\partial_t \boldsymbol{v}_{\rm g}$ of the velocity—by adding the proper linear combinations of the momentum equilibrium condition—the fluid mechanical equilibrium equation—in order to finally obtain the proper integral equations. It is interesting then to establish a short cut that allows to derive the proper diffusion integral equations. To this aim, we note that the contribution of the momentum equilibrium condition may be obtained by adding an extra term simply proportional to the momentum collisional invariant $(m_i\boldsymbol{c}_i)_{i\in S_{\rm g}}$ to the right hand side and by taking the scalar product with $(m_i\boldsymbol{c}_i \mathsf{f}_{{\rm g}i}^{(0)})_{i\in S_{\rm g}}$. We may thus simply write as a shortcut that

$$\mathcal{I}_{{\rm g}i}(\Phi_{\rm g}^{(1)}) = -\boldsymbol{c}_i\cdot\overline{\boldsymbol{\partial_x}\log p_{{\rm g}i}} + m_i\boldsymbol{c}_i\cdot\mathcal{L},$$

and take the scalar product of the equation with $(m_j\boldsymbol{c}_j\mathsf{f}_{{\rm g}j}^{(0)})_{j\in S_{\rm g}}$ to get that

$$\mathcal{L} = \frac{\overline{\boldsymbol{\partial_x} p_{\rm g}}}{\overline{\rho}_{\rm g} k_{\rm B}\overline{T}_{\rm g}},$$

in order to recover the proper right hand side for a well posed system of integral equations (6.7). This is the convenient method that will be used to investigate the physisorbate layer's diffusion processes. Finally, the distribution function at zeroth order may further be decomposed along the species partial pressure gradients [38, 39, 40, 41, 42, 43, 44] as also summarized in Appendix B.

6.3 First order expansion in the physisorbate

From equation (3.36) and the inner expansion (3.33), the first order equation in the physisorbate is obtained in the form

$$\partial_t \mathsf{f}_i^{(0)} + \boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel}\mathsf{f}_i^{(0)} + c_{iz}\,\partial_\zeta \mathsf{f}_i^{(1)} - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\mathsf{f}_i^{(1)} - \frac{1}{\alpha_\kappa}\sum_{j\in S_{\rm g}}\big(J_{ij}(\mathsf{f}_i^{(0)},\mathsf{f}_j^{(1)}) + J_{ij}(\mathsf{f}_i^{(1)},\mathsf{f}_j^{(0)})\big)$$
$$+\frac{1}{\tau_{i,\mathrm{ph}}}\big(\mathsf{f}_i^{(1)} - \langle \mathsf{f}_i^{(1)}\rangle \mathrm{M}_i\big) = \mathcal{C}_i^{(0)}, \qquad i\in S_{\rm g}. \tag{6.10}$$

Following the procedure already used in Section 6.2 for first order gas equations written in the thin layer form, we first have to subtract the ζ component of $\mathsf{f}_i^{(1)}$. We thus consider $\mathsf{f}_i^{(1)} - \zeta\overline{\partial_z f_{{\rm g}i}^{(0)}}$ and the corresponding reduced unknown

$$\Phi_i^{(1)} = \frac{\mathsf{f}_i^{(1)}}{\mathsf{f}_i^{(0)}} - \zeta\frac{\overline{\partial_z f_{{\rm g}i}^{(0)}}}{\mathsf{f}_i^{(0)}} = \Big(\frac{m_i c_{iz} v_{{\rm g}z}}{k_{\rm B}T_{\rm g}} + \alpha_\kappa\overline{\phi}_{{\rm g}i}^{(1)}\Big)\frac{\overline{f}_{{\rm g}i}^{(0)}}{\mathsf{f}_i^{(0)}} + \frac{\mathsf{f}_{{\rm l}ci}^{(1)}}{\mathsf{f}_i^{(0)}}. \tag{6.11}$$

Defining then the linearized collision operator $\mathcal{I} = (\mathcal{I}_i)_{i\in S_{\rm g}}$ operating on $\varphi = (\varphi_i)_{i\in S_{\rm g}}$ around the zeroth order inner distribution $\mathsf{f}_i^{(0)}$ by

$$\mathcal{I}_i(\varphi) = -\frac{1}{\mathsf{f}_i^{(0)}}\sum_{j\in S_{\rm g}}\big(J_{ij}(\mathsf{f}_i^{(0)},\mathsf{f}_j^{(0)}\varphi_j) + J_{ij}(\mathsf{f}_i^{(0)}\varphi_i,\mathsf{f}_j^{(0)})\big), \tag{6.12}$$

where $\mathsf{f}_i^{(0)}$ is given by (4.4), and the operator $\mathcal{H} = (\mathcal{H}_i)_{i\in S_{\rm g}}$ by

$$\mathcal{H}_i(\varphi) = c_{iz}\,\partial_\zeta \varphi_i - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\varphi_i + \frac{1}{\alpha_\kappa}\mathcal{I}_i(\varphi) + \frac{1}{\tau_{i,\mathrm{ph}}}\big(\varphi_i - \langle \varphi_i \mathrm{M}_i\rangle\big), \tag{6.13}$$

the ith first order linearized system reads $\mathcal{H}_i(\Phi_i^{(1)}) = \widehat{\Psi}_i^{(1)}$ with the right hand side first in the form

$$\widehat{\Psi}_i^{(1)} = \frac{\mathcal{C}_i^{(0)}}{\mathsf{f}_i^{(0)}} - \partial_t \log \mathsf{f}_i^{(0)} - \boldsymbol{c}_{i\parallel}\boldsymbol{\cdot}\boldsymbol{\partial}_\parallel \log \mathsf{f}_i^{(0)} - c_{iz}\,\frac{\overline{\partial_z f_{\mathrm{g}i}^{(0)}}}{\mathsf{f}_i^{(0)}}, \qquad i\in S_{\rm g}.$$

However, the chemistry is assumed to be slow so that $\mathcal{C}_i^{(0)} = \mathcal{O}(\epsilon)$, the tangential derivative term reduces to $\boldsymbol{c}_{i\parallel}\boldsymbol{\cdot}\boldsymbol{\partial}_\parallel \log \mathsf{f}_i^{(0)} = \boldsymbol{c}_{i\parallel}\boldsymbol{\cdot}\boldsymbol{\partial}_\parallel \log p_i$ where $p_i = n_i k_{\rm B} T_{\rm w}$, the normal derivative term also simplifies with $\overline{\partial_z f_{\mathrm{g}i}^{(0)}}/\mathsf{f}_i^{(0)} = (\overline{\partial_z p_{\mathrm{g}i}})/p_i$, and we also need to add the proper linear combination of the momentum equilibrium relation $m_i\boldsymbol{c}_i\boldsymbol{\cdot}\boldsymbol{\mathcal{L}}$ replacing of the time derivative $\partial_t \log \mathsf{f}_i^{(0)} = \mathcal{O}(\epsilon)$. The corrected right hand side is thus in the form

$$\Psi_i^{(1)} = -\frac{\boldsymbol{c}_{i\parallel}\boldsymbol{\cdot}\boldsymbol{\partial}_\parallel p_i + c_{iz}\overline{\partial_z p}_{\mathrm{g}i}}{p_i} + m_i\boldsymbol{c}_i\boldsymbol{\cdot}\boldsymbol{\mathcal{L}}, \tag{6.14}$$

and the first order system for diffusive processes read

$$\mathcal{H}_i(\Phi^{(1)}) = \Psi_i^{(1)}. \tag{6.15}$$

The factor $\boldsymbol{\mathcal{L}}$ may then be obtained by taking the scalar product (2.40) with $(m_i\boldsymbol{c}_i\mathsf{f}_i^{(0)})_{i\in S_{\rm g}}$. It is important to note that the tangential driving gradients involve p_i but the normal driving gradients involve $p_{\mathrm{g}i}$ and arise form the multiscale expansion. The boundary conditions further read

$$\lim_{\zeta\to 0}\mathsf{f}_i^{(1)} = 0, \qquad \lim_{\zeta\to\infty}(\mathsf{f}_i^{(1)} - \mathsf{f}_{\mathrm{g}i}^{(1)}) = 0, \tag{6.16}$$

since the corrector $\mathsf{f}_{\mathrm{lc}i}^{(1)}$ goes to zero as $\zeta\to\infty$ and there are not anymore particles as $\zeta\to 0$.

We may then split the right hand side in the form

$$\Psi_i^{(1)} = \Psi_{i,\mathrm{ev}}^{(1)} + \Psi_{i,\mathrm{od}}^{(1)}, \qquad i\in S_{\rm g},$$

where $\Psi_{i,\mathrm{ev}}^{(1)}$ and $\Psi_{i,\mathrm{od}}^{(1)}$ are respectively even and odd functions of the tangential velocity $\boldsymbol{c}_{i\parallel}$. The solution $\Phi_i^{(1)}$ is correspondingly decomposed in the form

$$\Phi_i^{(1)} = \Phi_{i,\mathrm{ev}}^{(1)} + \Phi_{i,\mathrm{od}}^{(1)}, \qquad i\in S_{\rm g}, \tag{6.17}$$

where $\Phi_{i,\mathrm{ev}}^{(1)}$ and $\Phi_{i,\mathrm{od}}^{(1)}$ are respectively even and odd functions of the tangential velocity $\boldsymbol{c}_{i\parallel}$ and thus $\mathsf{f}_{i,\mathrm{ev}}^{(1)} = \mathsf{f}_i^{(0)}\Phi_{i,\mathrm{ev}}^{(1)}$ and $\mathsf{f}_{i,\mathrm{od}}^{(1)} = \mathsf{f}_i^{(0)}\Phi_{i,\mathrm{od}}^{(1)}$ are respectively even and odd in the tangential velocity $\boldsymbol{c}_{i\parallel}$. Letting then $\Phi_{\mathrm{ev}}^{(1)} = (\Phi_{i,\mathrm{ev}}^{(1)})_{i\in S_{\rm g}}$ and $\Phi_{\mathrm{od}}^{(1)} = (\Phi_{i,\mathrm{od}}^{(1)})_{i\in S_{\rm g}}$ we obtain the systems of equations

$$\mathcal{H}_i(\Phi_{\mathrm{ev}}^{(1)}) = \Psi_{i,\mathrm{ev}}^{(1)}, \qquad \mathcal{H}_i(\Phi_{\mathrm{od}}^{(1)}) = \Psi_{i,\mathrm{od}}^{(1)}, \qquad i\in S_{\rm g}, \tag{6.18}$$

with

$$\Psi^{(1)}_{i,\mathrm{ev}} = -\frac{c_{iz}\,\overline{\partial_z p_{\mathrm{g}i}}}{p_i} + m_i c_{iz}\mathcal{L}_{\mathrm{ev}}, \qquad \Psi^{(1)}_{i,\mathrm{od}} = -\frac{\boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel} p_i}{p_i} + m_i\boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\mathcal{L}}_{\mathrm{od}},$$

where $\mathcal{L}_{\mathrm{ev}}$ and $\boldsymbol{\mathcal{L}}_{\mathrm{od}}$ are respectively the tangential and normal momentum equilibrium relations. The scalar $\mathcal{L}_{\mathrm{ev}}$ and vector $\boldsymbol{\mathcal{L}}_{\mathrm{od}}$ are easily identified by taking the moments of the corresponding equations with $(m_i\boldsymbol{c}_{i\shortparallel}\mathsf{f}_i^{(0)})_{i\in S_{\mathrm{g}}}$ and $(m_i c_{iz}\mathsf{f}_i^{(0)})_{i\in S_{\mathrm{g}}}$ respectively and found in the form

$$\boldsymbol{\mathcal{L}}_{\mathrm{od}} = \frac{1}{\rho k_{\mathrm{B}}T_{\mathrm{w}}}\Big(\boldsymbol{\partial}_{\shortparallel} p + \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \partial_\zeta \int m_i c_{iz}\boldsymbol{c}_{i\shortparallel}\mathsf{f}_i^{(0)}\Phi^{(1)}_{i,\mathrm{od}}\mathrm{d}\boldsymbol{c}_i + \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{1}{\tau_{i,\mathrm{ph}}}\int m_i\boldsymbol{c}_{i\shortparallel}\mathsf{f}_i^{(0)}\Phi^{(1)}_{i,\mathrm{od}}\mathrm{d}\boldsymbol{c}_i\Big),$$

$$\begin{aligned}\mathcal{L}_{\mathrm{ev}} = \frac{1}{\rho k_{\mathrm{B}}T_{\mathrm{w}}}\Big(&\overline{\partial_z p}_{\mathrm{g}} + \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \partial_\zeta \int m_i c_{iz}^2\mathsf{f}_i^{(0)}\Phi^{(1)}_{i,\mathrm{ev}}\mathrm{d}c_i \\ &+ \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \partial_\zeta \mathrm{W}_i\mathsf{f}_i^{(0)}\Phi^{(1)}_{i,\mathrm{ev}}\mathrm{d}\boldsymbol{c}_i + \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \frac{1}{\tau_{i,\mathrm{ph}}}\int m_i c_{iz}\mathsf{f}_i^{(0)}\Phi^{(1)}_{i,\mathrm{ev}}\mathrm{d}\boldsymbol{c}_i\Big).\end{aligned}$$

We again observe that the tangential momentum equilibrium condition of the physisorbate $\boldsymbol{\mathcal{L}}_{\mathrm{od}} = \mathcal{O}(\epsilon)$ involves $\boldsymbol{\partial}_{\shortparallel} p$ whereas normal momentum equilibrium condition $\mathcal{L}_{\mathrm{ev}} = \mathcal{O}(\epsilon)$ involves the gas normal driving pressure $\overline{\partial_z p}_{\mathrm{g}}$. The resulting equations for the odd components of (6.18) are then in the form

$$\begin{aligned} c_{iz}\partial_\zeta\Phi^{(1)}_{i,\mathrm{od}} &- \frac{m_i\boldsymbol{c}_{i\shortparallel}}{\rho k_{\mathrm{B}}T_{\mathrm{w}}}\cdot\sum_{\substack{j\in S_{\mathrm{g}}\\ \mathrm{J}\in\mathfrak{Q}_j}} \partial_\zeta\int m_j c_{jz}\boldsymbol{c}_{j\shortparallel}\mathsf{f}_j^{(0)}\Phi^{(1)}_{j,\mathrm{od}}\mathrm{d}\boldsymbol{c}_j - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\Phi^{(1)}_{i,\mathrm{od}} \\ &+ \frac{1}{\alpha_\kappa}\mathcal{I}_i(\Phi^{(1)}_{\mathrm{od}}) + \frac{\Phi^{(1)}_{i,\mathrm{od}}}{\tau_{i,\mathrm{ph}}} - \frac{m_i\boldsymbol{c}_{i\shortparallel}}{\rho k_{\mathrm{B}}T_{\mathrm{w}}}\cdot\sum_{\substack{j\in S_{\mathrm{g}}\\ \mathrm{J}\in\mathfrak{Q}_j}}\frac{1}{\tau_{j,\mathrm{ph}}}\int m_j\boldsymbol{c}_{j\shortparallel}\mathsf{f}_j^{(0)}\Phi^{(1)}_{j,\mathrm{od}}\mathrm{d}\boldsymbol{c}_j \\ &= -\sum_{l\in S_{\mathrm{g}}}\frac{1}{p_i}(\delta_{il}-\mathsf{y}_i)\boldsymbol{c}_{i\shortparallel}\cdot\boldsymbol{\partial}_{\shortparallel} p_l, \qquad i\in S_{\mathrm{g}}. \end{aligned} \tag{6.19}$$

In these equations we are naturally using the thermodynamic state of the physisorbate layer with $p_i = n_i k_{\mathrm{B}}T_{\mathrm{w}}$, $n = \sum_{i\in S_{\mathrm{g}}} n_i$ and $\mathsf{x}_i = n_i/n$, for $i\in S_{\mathrm{g}}$, and the mass fractions are correspondingly $\mathsf{y}_i = \rho_i/\rho$ with $\rho_i = n_i m_i$, for $i\in S_{\mathrm{g}}$, where $\rho = \sum_{i\in S_{\mathrm{g}}}\rho_i$. The equations for the even component are finally addressed in Appendix C.

6.4 Multicomponent tangential diffusion in the physisorbate

Considering tangential diffusion in the physisorbate, taking into account the similar gas phase problem solution [38, 39, 40, 41, 42, 43, 44] summarized in Appendix B, it is natural to seek a solution to (6.19) in the form

$$\Phi^{(1)}_{i,\mathrm{od}} = -\sum_{l\in S_{\mathrm{g}}}\boldsymbol{\Phi}^{(1),l}_{i,\mathrm{od}}\cdot\boldsymbol{\partial}_{\shortparallel} p_l. \tag{6.20}$$

The corresponding system of integro-differential equations for $\Phi_{i,\mathrm{od}}^{(1),l}$ is similar to that for the gas and found in the form

$$c_{iz}\partial_\zeta \Phi_{i,\mathrm{od}}^{(1),l} - \frac{\mathfrak{m}_i \boldsymbol{c}_{i\shortparallel}}{\rho k_{\mathrm{B}} T_{\mathrm{w}}} \cdot \sum_{\substack{j\in S_{\mathrm{g}}\\ \mathrm{J}\in\mathfrak{Q}_j}} \partial_\zeta \int \mathfrak{m}_j c_{jz} \boldsymbol{c}_{j\shortparallel} \otimes \mathsf{f}_j^{(0)} \Phi_{j,\mathrm{od}}^{(1),l} \mathrm{d}\boldsymbol{c}_j - \frac{1}{\mathfrak{m}_i} \partial_\zeta \mathrm{W}_i \partial_{c_{iz}} \Phi_{i,\mathrm{od}}^{(1),l} + \frac{1}{\alpha_\kappa} \mathcal{I}_i(\Phi_{\mathrm{od}}^{(1),l})$$

$$+ \frac{\Phi_{i,\mathrm{od}}^{(1),l}}{\tau_{i,\mathrm{ph}}} - \frac{\mathfrak{m}_i \boldsymbol{c}_{i\shortparallel}}{\rho k_{\mathrm{B}} T_{\mathrm{w}}} \cdot \sum_{\substack{j\in S_{\mathrm{g}}\\ \mathrm{J}\in\mathfrak{Q}_j}} \frac{1}{\tau_{j,\mathrm{ph}}} \int \mathfrak{m}_j \boldsymbol{c}_{j\shortparallel} \otimes \mathsf{f}_j^{(0)} \Phi_{j,\mathrm{od}}^{(1),l} \mathrm{d}\boldsymbol{c}_j = \frac{1}{p_i}(\delta_{il} - \mathsf{y}_i)\boldsymbol{c}_{i\shortparallel}, \tag{6.21}$$

with the right hand side

$$\Psi_{i,\mathrm{od}}^{(1),l} = \frac{1}{p_i}(\delta_{il} - \mathsf{y}_i)\boldsymbol{c}_{i\shortparallel}, \tag{6.22}$$

and the natural Enskog constraint reads $\langle\!\langle \mathsf{f}_{\mathrm{od}}^{(1)}, (\mathfrak{m}_i \boldsymbol{c}_{i\shortparallel})_{i\in S_{\mathrm{g}}} \rangle\!\rangle = 0$.

We will use a Galerkin method with the approximation space

$$\mathrm{Span}\{\ \phi^{1000k\shortparallel};\ k \in S_{\mathrm{g}}\ \}, \tag{6.23}$$

where

$$\phi^{1000k\shortparallel} = (\boldsymbol{w}_{i\shortparallel}\delta_{ki})_{i\in S_{\mathrm{g}}}, \qquad \boldsymbol{w}_{i\shortparallel} = \Big(\frac{\mathfrak{m}_i}{2k_{\mathrm{B}}T_{\mathrm{w}}}\Big)^{1/2} \boldsymbol{c}_{i\shortparallel}. \tag{6.24}$$

These basis functions are natural two-dimensional versions of the traditional three dimensional basis functions that are detailed in [42] on page 87. In the notation ϕ^{abcdk}, the first index a refers to the tensorial rank with respect to $\mathbb{R}^3$, the second index $b = 0$ to the absence of polarization effects, the third index c to the degree of the Laguerre and Sonine polynomial, the fourth index d to the degree of the Wang Chang and Uhlenbeck polynomial in terms of reduced internal energies and the last index k refers to the species. We have added the $\shortparallel$ symbol to indicate that the vector basis functions $\phi^{1000k\shortparallel}$ are projected onto the tangential plane.

We are using here the simplest approximation space associated with diffusive processes [38, 39, 40, 41, 42, 43, 44]. The right hand side of (6.21) is expressed as

$$\Psi_{\mathrm{od}}^{(1),l} = \sum_{k\in S_{\mathrm{g}}} \frac{\sqrt{2}}{\sqrt{\mathfrak{m}_k k_{\mathrm{B}} T_{\mathrm{w}}}} \frac{1}{n_k} (\delta_{kl} - \mathsf{y}_k) \phi^{1000k\shortparallel},$$

and the solution is expanded in the form [38, 39, 40, 41, 42, 43, 44]

$$\Phi_{\mathrm{od}}^{(1),l} = \sum_{k\in S_{\mathrm{g}}} \frac{\sqrt{2\mathfrak{m}_k}}{p\sqrt{k_{\mathrm{B}}T_{\mathrm{w}}}} \alpha_k^l \phi^{1000k\shortparallel}.$$

The resulting equations are obtained by using Galerkin method, i.e., by taking the scalar product of equations (6.21) by the basis functions $\phi^{1000k\shortparallel}$ for $k \in S_{\mathrm{g}}$. It is then remarkable that all differential operators vanishes in such a way that the equations reduce to a linear system instead of linear differential equations in ζ. We have thus recovered a traditional transport linear system in such a way that the Galerkin method then reduces to the standard variational method of multicomponent transport. The resulting linear system involve the L matrix given by

$$L_{kl} = \frac{\sqrt{\mathfrak{m}_k \mathfrak{m}_l}}{\alpha_\kappa p} [\phi^{1000k\shortparallel}, \phi^{1000l\shortparallel}], \qquad k, l \in S_{\mathrm{g}}, \tag{6.25}$$

where for any $f = (f_i)_{i\in S_{\mathrm{g}}}$ and $g = (g_i)_{i\in S_{\mathrm{g}}}$ with f_i and g_i functions of $\boldsymbol{c}_i$ and I, the bracket product $[f,g]$ denotes

$$[f,g] = \sum_{\substack{i\in S_{\mathrm{g}}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int f_i \odot \mathcal{I}_i(g)\, \mathrm{d}\boldsymbol{c}_i,$$

and $\odot$ is the maximum contracted product between two tensors. The matrix $L = (L_{kl})_{k,l\in S_{\mathrm{g}}}$ is symmetric positive semi-definite with nullspace spanned by $\mathbb{1} \in \mathbb{R}^{\mathrm{N_g}}$ with $\mathbb{1} = (1)_{i\in S_{\mathrm{g}}}$. In other words $L = L^t$, $L \geq 0$, and $N(L) = \mathbb{R}\mathbb{1}$. The components of L are given by

$$L_{kk} = \sum_{\substack{l\in S_{\mathrm{g}}\\ l\neq k}} \frac{\mathsf{x}_k\mathsf{x}_l}{\mathcal{D}_{kl}}, \qquad L_{kl} = -\frac{\mathsf{x}_k\mathsf{x}_l}{\mathcal{D}_{kl}}, \quad l\neq k, \qquad k,l\in S_{\mathrm{g}},$$

where $\mathcal{D}_{kl}$ is the binary diffusion coefficient of the physisorbate pairs of species [38, 39, 40, 41, 42, 43, 44]. Further introducing the diagonal matrix

$$\mathsf{D} = \mathrm{diag}\Big(\frac{m_k n_k}{p\tau_{k,\mathrm{ph}}}\Big)_{k\in S_{\mathrm{g}}}, \tag{6.26}$$

and letting $\mathsf{y} = (\mathsf{y}_i)_{i\in S_{\mathrm{g}}}$, the resulting transport linear system is found after some algebra to be in the form

$$L\alpha^l + \mathsf{D}\alpha^l - \mathsf{y}\langle \mathsf{D}\alpha^l, \mathbb{1}\rangle = \beta^l, \tag{6.27}$$

where $\langle\, ,\rangle$ denotes the scalar product in $\mathbb{R}^{\mathrm{N_g}}$, $\alpha^l = (\alpha_k^l)_{k\in S_{\mathrm{g}}}$, $\beta^l = (\beta_k^l)_{k\in S_{\mathrm{g}}}$, $\beta_k^l = \delta_{kl} - \mathsf{y}_k$, $\langle \mathbb{1}, \beta^l\rangle = 0$, and the solution α^l must satisfy the constraint $\langle \mathsf{y}, \alpha^l\rangle = 0$. The transport linear system is then rewritten in the convenient form

$$\Big(L + (\mathbb{I} - \mathsf{y}\otimes\mathbb{1})\mathsf{D}(\mathbb{I} - \mathbb{1}\otimes\mathsf{y})\Big)\alpha^l = \beta^l. \tag{6.28}$$

Letting $\widetilde{L} = L + (\mathbb{I} - \mathsf{y}\otimes\mathbb{1})\mathsf{D}(\mathbb{I} - \mathbb{1}\otimes\mathsf{y})$, the matrix $\widetilde{L}$ then has properties similar to that of L, in such a way that $\widetilde{L} = \widetilde{L}^t$, $\widetilde{L} \geq 0$, and $N(\widetilde{L}) = \mathbb{R}\mathbb{1}$. Then for any positive coefficient $\nu > 0$ the solution α^l is given by [41, 42]

$$\alpha^l = \Big(L + (\mathbb{I} - \mathsf{y}\otimes\mathbb{1})\mathsf{D}(\mathbb{I} - \mathbb{1}\otimes\mathsf{y}) + \nu\mathsf{y}\otimes\mathsf{y}\Big)^{-1}\beta^l, \tag{6.29}$$

and thus depends smoothly on the diagonal D. In particular, as $\mathsf{D} \to 0$ when $\zeta \to \infty$, we exactly recover the tangential diffusion process of the gas mixture and $\lim_{\zeta\to\infty} \alpha^l = \alpha_{\mathrm{g}}^l$ where α_{g}^l is the corresponding solution of the gas phase transport linear system presented more specifically in Appendix B.

Finally, the tangential fluxes in the physisorbate are naturally defined as

$$\boldsymbol{F}_{i\shortparallel} = \epsilon \sum_{\mathrm{I}\in\mathfrak{Q}_i} \int \boldsymbol{c}_{i\shortparallel} \mathsf{f}_i^{(0)} \Phi_{i,\mathrm{od}}^{(1)} \mathrm{d}\boldsymbol{c}_i,$$

and taking into account the decomposition of $\Phi_{i,\mathrm{od}}^{(1)}$, these fluxes are given by

$$\boldsymbol{F}_{i\shortparallel} = -\epsilon \sum_{l\in S_{\mathrm{g}}} n_i \alpha_i^l \frac{\boldsymbol{\partial}_{\shortparallel} p_l}{p}.$$

Further assuming that the crystal is free of tangential stress in such a way that $\boldsymbol{\partial}_{\shortparallel} p = \mathcal{O}(\epsilon)$, the tangential flux is then in the form $\boldsymbol{F}_{i\shortparallel} = -\epsilon \sum_{l\in S_{\mathrm{g}}} n_i \alpha_i^l \boldsymbol{\partial}_{\shortparallel} \mathsf{x}_l$ where the mole fraction of the lth species is given by $\mathsf{x}_l = n_l/n$, whereas in the gas the tangential flux reads $\boldsymbol{F}_{\mathrm{g}i\shortparallel} = -\epsilon \sum_{l\in S_{\mathrm{g}}} \overline{n}_{\mathrm{g}i} \alpha_{\mathrm{g}i}^l \boldsymbol{\partial}_{\shortparallel} \overline{\mathsf{x}}_{\mathrm{g}l}$.

6.5 First order expansion in the chemisorbate

Proceeding similarly as for the physisorbate and using (3.40), the first order equations for the chemisorbate species and the crystal species read

$$\partial_t \mathsf{f}_i^{(0)} + \boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_{\shortparallel} \mathsf{f}_i^{(0)} + c_{iz}\,\partial_\zeta \mathsf{f}_i^{(1)} - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}} \mathsf{f}_i^{(1)} + \frac{1}{\tau_{i,\mathrm{ph}}}\big(\mathsf{f}_i^{(1)} - \langle \mathsf{f}_i^{(1)} \rangle \mathrm{M}_i\big)$$
$$= \mathcal{C}_i^{(0)} \qquad i \in S_\mathrm{c} \cup S_\mathrm{s} \cup S_\mathrm{b}, \tag{6.30}$$

Letting then

$$\Phi_i^{(1)} = \mathsf{f}_i^{(1)} / \mathsf{f}_i^{(0)} \tag{6.31}$$

and defining the operator $\mathcal{H}_i$ acting on φ_i by by

$$\mathcal{H}_i(\varphi_i) = c_{iz}\,\partial_\zeta \varphi_i - \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\,\partial_{c_{iz}}\varphi_i + \frac{1}{\tau_{i,\mathrm{ph}}}\big(\varphi_i - \langle \varphi_i \mathrm{M}_i \rangle\big), \tag{6.32}$$

the linearized equations may be written

$$\mathcal{H}_i(\Phi_i^{(1)}) = \Psi_i^{(1)}, \tag{6.33}$$

where

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

An important difference with the physisorbate is the absence of any normal gradient of the species partial pressures. Normal gradients indeed arise for physisorbed species through inner expansions of the gas distribution functions and are thus absent for chemisorbed species. The boundary conditions are

$$\lim_{\zeta \to \zeta_i^-} \mathsf{f}_i^{(1)} = 0, \qquad \lim_{\zeta \to \zeta_i^+} \mathsf{f}_i^{(1)} = 0, \tag{6.34}$$

and it is natural to impose an Enskog type constraint for the first order corrector $\mathsf{f}_i^{(1)}$ in the form

$$\int \mathsf{f}_i^{(1)}\, \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta = 0, \qquad i \in S_\mathrm{c} \cup S_\mathrm{s} \cup S_\mathrm{b}, \tag{6.35}$$

since the average value of $\mathsf{f}_i^{(1)}$ is otherwise undetermined because $\mathcal{H}_i(\mathbb{1}) = 0$ and any term proportional to $\mathsf{f}_i^{(0)}$ could be added to $\mathsf{f}_i^{(1)}$, keeping in mind that $\lim_{\zeta \to \zeta_i^-} \mathsf{f}_i^{(0)} = \lim_{\zeta \to \zeta_i^+} \mathsf{f}_i^{(0)} = 0$. It is further possible to introduce *layer averaged kinetic equations* as discussed in Appendix D. The surface diffusion fluxes may then be elegantly and equivalently obtained from the layer averaged equations. The layer averaged equations present many similarities with standard three dimensional kinetic equations.

The right hand side may be decomposed in the form

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

where

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

are respectively even and odd functions of the tangential velocity $\boldsymbol{c}_{i\shortparallel}$. The solution $\Phi_i^{(1)}$ is then decomposed in the form

$$\Phi_i^{(1)} = \Phi_{i,\mathrm{ev}}^{(1)} + \Phi_{i,\mathrm{od}}^{(1)}, \qquad i \in S_\mathrm{c} \cup S_\mathrm{s} \cup S_\mathrm{b}, \tag{6.36}$$

with $\Phi_\mathrm{ev}^{(1)} = (\Phi_{i,\mathrm{ev}}^{(1)})_{i\in S_\mathrm{c}}$, $\Phi_\mathrm{od}^{(1)} = (\Phi_{i,\mathrm{od}}^{(1)})_{i\in S_\mathrm{c}}$ so that

$$\mathcal{H}_i(\Phi_{i,\mathrm{ev}}^{(1)}) = \Psi_{i,\mathrm{ev}}^{(1)}, \qquad \mathcal{H}_i(\Phi_{i,\mathrm{od}}^{(1)}) = \Psi_{i,\mathrm{od}}^{(1)}, \qquad i \in S_\mathrm{c} \cup S_\mathrm{s} \cup S_\mathrm{b}, \tag{6.37}$$

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

6.6 Tangential multicomponent diffusion in the chemisorbate

A remarkable point of crystal surfaces is that the total species number per unit surface is constant $\sum_{i\in S_\mathrm{c}} \widetilde{n}_i + \widetilde{n}_\mathrm{s} = \widetilde{n}_\sigma$ or equivalently $\sum_{i\in S_\mathrm{b}} \widetilde{n}_i + \widetilde{n}_\mathrm{s} = \widetilde{n}_\sigma$ and the molar based mixture velocity vanishes also in a reference frame attached to the crystal because of the interaction with phonons. There is a corresponding contraint stating that the total tangential molar flux must vanish [74, 75]

$$\sum_{\substack{i\in S_\mathrm{c}\\ \mathrm{I}\in\mathfrak{Q}_i}} \int \boldsymbol{c}_{i\shortparallel}\, \mathsf{f}_i^{(0)}\Phi_{i,\mathrm{od}}^{(1)}\, \mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta + \int \boldsymbol{c}_{\mathrm{s}\shortparallel}\mathsf{f}_\mathrm{s}^{(0)}\Phi_{\mathrm{s,od}}^{(1)}\, \mathrm{d}\boldsymbol{c}_\mathrm{s}\mathrm{d}\zeta = 0,$$

since diffusion processes are naturally measured with respect to the cristal. This constraint is analogous to the usual mass conservation constraint between mass fluxes in a multicomponent mixture. It is then natural to define surface diffusion velocities on a crystal with respect to the molar average velocity.

It is also natural to consider the coupled system of equations constituted by the chemisorbate and the free sites and we denote by $S_\mathcal{T}$ the corresponding species indexing set

$$S_\mathcal{T} = S_\mathrm{c} \cup S_\mathrm{s}.$$

The bulk species—constrained to follow the chemisorbed species—are uncoupled and will be examined later. A main task is to determine the integrated tangential fluxes that will be needed when investigating the chemisorbed species macroscopic equations

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

Following the formalism developped by Waldmann for molar based diffusion detailed in [73, 33], the proper fluxes are in the form $\widetilde{\boldsymbol{F}}_{i\shortparallel} = \widetilde{n}_i\widetilde{\boldsymbol{W}}_{i\shortparallel}$ with a molar tangential layer diffusion velocity $\widetilde{\boldsymbol{W}}_{i\shortparallel}$ given by

$$\widetilde{\boldsymbol{W}}_{i\shortparallel} = \frac{\epsilon}{\widetilde{n}_i} \sum_{\mathrm{I}\in\mathfrak{Q}_i} \int \boldsymbol{c}_{i\shortparallel}\mathsf{f}_i^{(0)}\Phi_{i,\mathrm{od}}^{(1)}\mathrm{d}\boldsymbol{c}_i\mathrm{d}\zeta - \frac{\epsilon}{\widetilde{n}_\sigma} \sum_{\substack{j\in S_\mathcal{T}\\ \mathrm{J}\in\mathfrak{Q}_j}} \int \boldsymbol{c}_{j\shortparallel}\mathsf{f}_j^{(0)}\Phi_{j,\mathrm{od}}^{(1)}\mathrm{d}\boldsymbol{c}_j\mathrm{d}\zeta. \tag{6.38}$$

The kinetic equations for the chemisorbed and free site species are written by using the vector operator

$$\mathcal{H} = (\mathcal{H}_i)_{i\in S_\mathcal{T}}, \tag{6.39}$$

acting on families of perturbed distribution functions $\Phi^{(1)}_{\rm od} = (\Phi^{(1)}_{i,\rm od})_{i\in S_\mathcal{T}}$ where $\mathcal{H}_i$ is the differential-integral operator (6.32). The coupled first order equation for the odd part of the distribution functions is then in the form

$$\mathcal{H}(\Phi^{(1)}_{\rm od}) = \Psi^{(1)}_{\rm od}, \tag{6.40}$$

where $\Psi^{(1)}_{\rm od} = (\Psi^{(1)}_{i,\rm od})_{i\in S_\mathcal{T}}$ or equivalently $\mathcal{H}_i(\Phi^{(1)}_{i,\rm od}) = \Psi^{(1)}_{i,\rm od}$ for $i \in S_\mathcal{T}$. The right hand side is in the form $\Psi^{(1)}_{i,\rm od} = -\boldsymbol{c}_{i\shortparallel}\boldsymbol{\cdot}\boldsymbol{\partial}_{\shortparallel} \log \mathsf{f}^{(0)}_i$ and using $\mathsf{f}^{(0)}_i = \mathsf{n}_i\mathsf{m}_i$ and $\widetilde{n}_i = \mathsf{n}_i \int \exp\big(-\mathrm{W}_i/k_{\rm B}T_{\rm w}\big){\rm d}z$, where $\widetilde{n}_i$ is the surface concentration of the ith surface species, we obtain

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

where $\widetilde{p}_i = \widetilde{n}_i k_{\rm B}T_{\rm w}$ denotes the surface partial pressure of the ith species. Denoting by $\widetilde{p} = \sum_{l\in S_\mathcal{T}} \widetilde{p}_l = \sum_{l\in S_{\rm c}} \widetilde{p}_l + \widetilde{p}_{\rm s} = \widetilde{n}_\sigma k_{\rm B}T_{\rm w}$ the total surface pressure, which remains constant, and $\widetilde{\mathrm{x}}_i = \widetilde{p}_i/\widetilde{p}$ the surface mole fraction of the ith species, we may then write that

$$\Psi^{(1)}_{i,\rm od} = -\sum_{l\in S_\mathcal{T}} \frac{1}{\widetilde{\mathrm{x}}_i}\boldsymbol{c}_{i\shortparallel}\boldsymbol{\cdot}\widetilde{\boldsymbol{d}}_l\,\delta_{il},$$

where

$$\widetilde{\boldsymbol{d}}_i = \boldsymbol{\partial}_{\shortparallel}\widetilde{\mathrm{x}}_i, \tag{6.41}$$

denotes the surface diffusion driving force of the ith species. These diffusion driving forces are constrained by the relation

$$\sum_{l\in S_\mathcal{T}} \widetilde{\boldsymbol{d}}_l = \sum_{l\in S_{\rm c}} \widetilde{\boldsymbol{d}}_l + \widetilde{\boldsymbol{d}}_{\rm s} = 0.$$

Multicomponent diffusion fluxes and coefficients defined with respect to the molar averaged velocity have been investigated by Waldmann [73] and summarized in Appendix C of [33]. Waldmann's analysis must then be adapted to the situation of tangential surface diffusion. To this aim, the right hand side is rewritten in the form

$$\Psi^{(1)}_{\rm od} = -\widetilde{p}\sum_{l\in S_\mathcal{T}} \Psi^{(1),l}\boldsymbol{\cdot}\widetilde{\boldsymbol{d}}_l,$$

where $\Psi^{(1),l} = (\Psi^{(1),l}_i)_{i\in S_\mathcal{T}}$ and

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

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

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

with boundary conditions similar to (6.34), and taking into account the simple structure of $\mathcal{H}$ and of $\Psi^{(1),l}$, the solution $\Phi^{(1),l}$ is found in the form $\Phi^{(1),l} = (\Phi^{(1),l}_i)_{i\in S_\mathcal{T}}$ with

$$\Phi^{(1),l}_i = \frac{\tau_{i,\rm ph}}{\widetilde{p}_i}(\delta_{il} - \widetilde{\mathrm{x}}_i)\boldsymbol{c}_{i\shortparallel},$$

where we have used that $\partial_\zeta \Phi^{(1),l}_i = 0$ and $\partial_{c_{iz}}\Phi^{(1),l}_i = 0$. The molar diffusion velocities are then given by

$$\widetilde{\widetilde{\boldsymbol{W}}}_{i\shortparallel} = -\epsilon\sum_{l\in S_\mathcal{T}} \widetilde{D}_{il}\widetilde{\boldsymbol{d}}_l, \tag{6.42}$$

where the multicomponent diffusion coefficients $\widetilde{D}_{il}$, $i, l \in S_{\mathcal{T}}$, read [33]

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

All calculations done, it is found that

$$\widetilde{D}_{il} = \delta_{il} \frac{D_i^{\shortparallel}}{\widetilde{\mathsf{x}}_i} - (D_i^{\shortparallel} + D_l^{\shortparallel}) + \sum_{j \in S_{\mathcal{T}}} \widetilde{\mathsf{x}}_j D_j^{\shortparallel}, \qquad i, j \in S_{\mathcal{T}}, \tag{6.43}$$

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

$$D_i^{\shortparallel} = \frac{k_{\mathrm{B}} T_{\mathrm{w}}}{m_i} \tau_{i,\mathrm{ph}}, \qquad i \in S_{\mathcal{T}}, \tag{6.44}$$

that is directly proportional to the relaxation time $\tau_{i,\mathrm{ph}}$ for interaction with phonons. The matrix $\widetilde{D}$ is symmetric $\widetilde{D} = \widetilde{D}^t$ with $\widetilde{D}\widetilde{\mathsf{x}} = 0$ where $\widetilde{\mathsf{x}} = (\widetilde{\mathsf{x}}_i)_{i \in S_{\mathcal{T}}}$ is the surface mole fraction vector. The matrix $\widetilde{D}$ is positive semi-definite with nullspace given by $N(\widetilde{D}) = \mathbb{R}\,\widetilde{\mathsf{x}}$ and for any vector $\mathfrak{y} = (\mathfrak{y}_i)_{i \in S_{\mathcal{T}}}$ we have

$$\langle \widetilde{D}\, \mathfrak{y}, \mathfrak{y} \rangle = \sum_{i \in S_{\mathcal{T}}} \frac{1}{\widetilde{\mathsf{x}}_i} D_i^{\shortparallel} \Big(\mathfrak{y}_i - \widetilde{\mathsf{x}}_i \sum_{l \in S_{\mathcal{T}}} \mathfrak{y}_l \Big)^2.$$

Since $\widetilde{D}\widetilde{\mathsf{x}} = 0$ we also obtain that $\sum_{i \in S_{\mathcal{T}}} \widetilde{\mathsf{x}}_i \widetilde{\boldsymbol{W}}_{i\shortparallel} = 0$ and the diffusion process is compatible with the molecular structure of the crystal, that is, it is guaranteed that $\widetilde{n}_\sigma$ remains constant. Incidentally, the analysis may equivalently be conducted using the layer averaged equation, since only the integrated fluxes are required, as presented in Appendix D.

The relations (6.43) and (6.44) expressing the surface diffusion coefficients further 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 [76, 77] and thermal agitation is represented by the interaction with phonons in the model.

6.7 Chemisorbed and free site first order equations

In the chemisorbate, it is obtained at first order that

$$\partial_t \int (\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)}) \mathrm{d}\boldsymbol{c}_i + \boldsymbol{\partial}_{\shortparallel} \boldsymbol{\cdot} \int \boldsymbol{c}_{i\shortparallel} (\mathsf{f}_i^{(0)} + \epsilon \mathsf{f}_i^{(1)})) \mathrm{d}\boldsymbol{c}_i + \partial_\zeta \int c_{iz} (\mathsf{f}_i^{(1)} + \epsilon \mathsf{f}_i^{(2)}) \mathrm{d}\boldsymbol{c}_i = \int \mathcal{C}_i^{(0)} \mathrm{d}\boldsymbol{c}_i. \tag{6.45}$$

The first time derivative term yields the contribution

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

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 ζ from the natural Enskog type constraint $\int \mathsf{f}_i^{(1)} \, \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta = 0$.

For the tangential derivative terms, we first note that $\int \boldsymbol{c}_{i\shortparallel} \mathsf{f}_i^{(0)} \mathrm{d}\boldsymbol{c}_i = 0$. For the next tangential term involving $\mathsf{f}_i^{(1)} = \mathsf{f}_i^{(0)} \Phi_i^{(1)}$, we may use the decomposition $\Phi_i^{(1)} = \Phi_{i,\mathrm{ev}}^{(1)} + \Phi_{i,\mathrm{od}}^{(1)}$

where $\mathcal{H}_i(\Phi^{(1)}_{i,\mathrm{ev}}) = \Psi^{(1)}_{i,\mathrm{ev}}$ and $\mathcal{H}_i(\Phi^{(1)}_{i,\mathrm{od}}) = \Psi^{(1)}_{i,\mathrm{od}}$ and the results of previous Section 6.6. The tangential fluxes have indeed been shown to be in the form

$$\widetilde{\boldsymbol{F}}_{i\shortparallel} = \widetilde{n}_i \widetilde{\boldsymbol{W}}_{i\shortparallel} = \epsilon \int \boldsymbol{c}_{i\shortparallel} \mathrm{f}^{(1)}_i \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta = \epsilon \int \boldsymbol{c}_{i\shortparallel} \mathrm{f}^{(1)}_{i,\mathrm{od}} \mathrm{d}\boldsymbol{c}_i \mathrm{d}\zeta = -\epsilon \widetilde{n}_i \sum_{l\in S_{\mathcal{T}}} \widetilde{D}_{il} \widetilde{\boldsymbol{d}}_l,$$

where $\widetilde{\boldsymbol{d}}_i = \boldsymbol{\partial}_{\shortparallel} \widetilde{\mathrm{x}}_i = \boldsymbol{\partial}_{\shortparallel} \widetilde{n}_i / \widetilde{n}_\sigma$. In addition, integrating over ζ and summing over $\mathrm{I} \in \mathfrak{Q}_i$, the normal derivatives terms in (6.45) do not contribute since there are no particles at the limits $\zeta \to 0$ and $\zeta \to \zeta_i^+$.

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

$$\partial_t \widetilde{n}_i - \epsilon \sum_{l\in S_{\mathcal{T}}} \boldsymbol{\partial}_{\shortparallel} \boldsymbol{\cdot} \Big(\widetilde{n}_i \widetilde{D}_{il} \boldsymbol{\partial}_{\shortparallel} \widetilde{n}_l / \widetilde{n}_\sigma \Big) = \mathfrak{w}^{(0)}_i. \tag{6.46}$$

It is then observed that the kinetic model yields a surface diffusion term that is directly due to the interaction with phonons.

Since $\sum_{i\in S_{\mathcal{T}}} \widetilde{\boldsymbol{F}}_{i\shortparallel} = 0$ or equivalently $\widetilde{D}\widetilde{\mathrm{x}} = 0$, we also recover that $\sum_{i\in S_{\mathcal{T}}} \widetilde{n}_i = \sum_{i\in S_{\mathrm{c}}} \widetilde{n}_i + \widetilde{n}_{\mathrm{s}}$ is governed by the equation $\partial_t \Big(\sum_{i\in S_{\mathcal{T}}} \widetilde{n}_i \Big) = 0$ keeping in mind that $\sum_{i\in S_{\mathrm{c}}} \int \mathcal{C}^{(0)}_i \mathrm{d}\boldsymbol{c}_i \mathrm{d}z + \int \mathcal{C}^{(0)}_{\mathrm{s}} \mathrm{d}\boldsymbol{c}_{\mathrm{s}} \mathrm{d}z = 0$ from the conservation of sites by chemical reactions. It is therefore recovered that $\sum_{i\in S_{\mathcal{T}}} \widetilde{n}_i = \widetilde{n}_\sigma$ remains constant in time.

7 Extension to multisite adsorption

We investigate in this section the situation where chemisorbed species may occupy several atom sites on the crystal surface.

7.1 Multisite adsorption

The reactive surface model presented in the previous sections has been obtained with the simplifying assumption that chemisorbed species are adsorbed on single site atoms of the crystal surface. However, chemisorbed species on a flat surface may sometimes occupy several atoms sites. We thus assume now that the ith chemisorbed species requires $\mathscr{s}_i \geq 1$ sites to be chemisorbed on the crystal surface. To each chemisorbed species, say of index $i \in S_{\mathrm{c}}$, we may then associate $\mathscr{s}_i$ bulk species with indices denoted by $\mathrm{b}(i,1), \dots, \mathrm{b}(i,\mathscr{s}_i)$ that are all in S_{b}. The $\mathscr{s}_i$ sites associated with $i \in S_{\mathrm{c}}$ are thus $\mathrm{b}(i,1), \dots, \mathrm{b}(i,\mathscr{s}_i) \in S_{\mathrm{b}}$. The number of bulk species is then $\mathrm{N_b} = \sum_{i\in S_{\mathrm{c}}} \mathscr{s}_i$. The simplified monosite adsorption case investigated in previous sections then corresponds to $\mathscr{s}_i = 1$ for any $i \in S_{\mathrm{c}}$.

The kinetic equations are similar when multisite adsorption occur but collisions are naturally more complex. The chemisorption of the ith particle involves a collision with $\mathscr{s}_i$ free site crystal atoms and similarly the desorption process involve the collision with $\mathscr{s}_i$ crystal atoms of the solid surface. Whenever a chemisorbed species $\mathfrak{M}_i$ for $i \in S_{\mathrm{c}}$ is involved in a reaction, all its attached $\mathscr{s}_i$ bulk species are thus automatically involved. Assuming for illustration that the ith chemisorbed species has a direct gas-phase parent with index $\mathrm{g}(i) \in S_{\mathrm{g}}$, noting for short by s the free site index, and assuming that there is no dissociation during adsorption, then the direct multisite adsorption of $\mathfrak{M}_{g(i)}$ into $\mathfrak{M}_i$ may be written with the atomic site convention

$$\mathfrak{M}_{\mathrm{g}(i)} + \mathscr{s}_i \, \mathfrak{M}_{\mathrm{s}} \;\rightleftarrows\; \mathfrak{M}_i + \sum_{1\leq j\leq \mathscr{s}_i} \mathfrak{M}_{\mathrm{b}(i,j)}. \tag{7.1}$$

The same adsorption reaction would be written in the form

$$\mathfrak{M}_{\mathrm{g}(i)} + \mathfrak{s}_i \mathcal{O}(\mathrm{s}) \rightleftarrows \mathfrak{M}_i, \tag{7.2}$$

with the open site formalism. As a typical example, using the open site formalism, the reaction of adsorption of Propene C_3H_6 on platinum Pt requires two free sites and may be written [78]

$$C_3H_6 + 2\mathrm{Pt}(\mathrm{s}) \rightleftarrows C_3H_6(\mathrm{s}),$$

where C_3H_6 denotes the Propene gaseous molecule, Pt(s) the open site symbol of a platinum crystal surface and C_3H_6(s) the adsorbed molecule, whereas the adsorption of water vapor H_2O on the same surface reads

$$H_2O + \mathrm{Pt}(\mathrm{s}) \rightleftarrows H_2O(\mathrm{s}),$$

the adsorbed water molecule H_2O(s) only occupying a single platinum atom site [78].

The number density of chemisorbed species per unit surface $\widetilde{n}_i$, $i \in S_{\mathrm{c}}$, then corresponds to $\mathfrak{s}_i \widetilde{n}_i = \sum_{1 \leq j \leq \mathfrak{s}_i} \widetilde{n}_{\mathrm{b}(i,j)}$ moles of bulk species per unit surface with $\widetilde{n}_{\mathrm{b}(i,1)} = \cdots = \widetilde{n}_{\mathrm{b}(i,\mathfrak{s}_i)} = \widetilde{n}_i$. The monolayer constraints between species numbers then reads

$$\sum_{i \in S_{\mathrm{c}}} \mathfrak{s}_i \widetilde{n}_i + \widetilde{n}_{\mathrm{s}} = \widetilde{n}_\sigma.$$

We introduce for convenience the notation $\mathfrak{s}_{\mathrm{s}} = 1$ so that $\sum_{i \in S_{\mathcal{T}}} \mathfrak{s}_i \widetilde{n}_i = \widetilde{n}_\sigma$ with $S_{\mathcal{T}} = S_{\mathrm{c}} \cup S_{\mathrm{s}}$. In this situation of multisite adsorption, it is natural to define *the site mole fractions*

$$\widetilde{\mathrm{x}}_i^{\mathfrak{s}} = \frac{\mathfrak{s}_i \widetilde{n}_i}{\widetilde{n}_\sigma}, \qquad i \in S_{\mathcal{T}} = S_{\mathrm{c}} \cup S_{\mathrm{s}}, \tag{7.3}$$

that sum up to unity, keeping in mind that $\widetilde{n}_\sigma = \sum_{i \in S_{\mathcal{T}}} \mathfrak{s}_i \widetilde{n}_i$ remains constant from the structure of the crystal surface. These fractions represent site mole fractions, that is, the local ratio of the number of sites occupied by the ith chemisorbed or free site species per unit surface divided by the total number of sites per unit surface.

In the situation of a single species being adsorbed of several sites, the modified potentials (4.31) are then typically in the form

$$\widetilde{\mu}_i = \log\Big(\frac{\widetilde{n}_i}{\widetilde{\mathrm{z}}_i' (1 - \widetilde{\theta})^{\mathfrak{s}_i}} \Big),$$

involving the traditional factor $(1 - \widetilde{\theta})^{\mathfrak{s}_i}$ in the denominator [79, 80].

7.2 Surface tangential diffusion with multisite adsorption

In order to investigate the tangential mass fluxes of chemisorbed species in the multisite situation, a similar analysis to that of Section 6.6 may be conducted. Incidentally, diffusion processes in the physisorbate are naturally unchanged by multisite chemisorption. Considering again the indexing set $S_{\mathcal{T}} = S_{\mathrm{c}} \cup S_{\mathrm{s}}$, the kinetic equations are found in the form $\mathcal{H}(\Phi_{\mathrm{od}}^{(1)}) = \Psi_{\mathrm{od}}^{(1)}$ where $\Psi_{\mathrm{od}}^{(1)} = (\Psi_{i,\mathrm{od}}^{(1)})_{i \in S_{\mathcal{T}}}$ and $\Psi_{i,\mathrm{od}}^{(1)} = -\boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_\shortparallel \log \mathrm{f}_i^{(0)}$. It is then natural to use the site molar fractions and to write that

$$\Psi_{i,\mathrm{od}}^{(1)} = -\boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_\shortparallel \log \mathrm{f}_i^{(0)} = -\boldsymbol{c}_{i\shortparallel} \cdot \boldsymbol{\partial}_\shortparallel \log(\mathfrak{s}_i \widetilde{n}_i), \qquad i \in S_{\mathcal{T}}.$$

Applying the Waldman formalism, the new diffusion driving forces are

$$\widetilde{\boldsymbol{d}}_i = \boldsymbol{\partial}_\shortparallel \widetilde{\mathrm{x}}_i^{\mathfrak{s}}, \qquad i \in S_{\mathcal{T}}. \tag{7.4}$$

and are constrained by the relation $\sum_{l\in S_{\mathcal{T}}} \widetilde{\boldsymbol{d}}_l = 0$. The right hand side is rewritten in the form

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

where $\Psi^{(1),l} = (\Psi^{(1),l}_i)_{i\in S_{\mathcal{T}}}$ and

$$\Psi^{(1),l}_i = \frac{1}{\widetilde{p}\widetilde{\mathsf{x}}^s_i}(\delta_{il} - \widetilde{\mathsf{x}}^s_i)\boldsymbol{c}_{i\shortparallel}, \qquad i, l \in S_{\mathcal{T}}.$$

The tangential diffusion velocities are then obtained in the form

$$\widetilde{\boldsymbol{W}}_{i\shortparallel} = -\epsilon \sum_{l\in S_{\mathcal{T}}} \widetilde{D}_{il}\widetilde{\boldsymbol{d}}_l, \qquad i \in S_{\mathcal{T}}, \tag{7.5}$$

with the fluxes $\widetilde{\boldsymbol{F}}_{i\shortparallel}$ given by $\widetilde{\boldsymbol{F}}_{i\shortparallel} = \widetilde{n}_i \widetilde{\boldsymbol{W}}_{i\shortparallel}$.

The analysis is similar to that conducted in Section 6.6 *provided that the site mole fractions per unit surface are used instead of the ordinary mole fractions* per unit surface. The multicomponent diffusion coefficients are then found in the form

$$\widetilde{D}_{il} = \delta_{il}\frac{D^{\shortparallel}_i}{\widetilde{\mathsf{x}}^s_i} - (D^{\shortparallel}_i + D^{\shortparallel}_l) + \sum_{j\in S_{\mathcal{T}}} D^{\shortparallel}_j \widetilde{\mathsf{x}}^s_j, \qquad i, l \in S_{\mathcal{T}}.$$

where $D^{\shortparallel}_i = k_{\mathrm{B}} T_{\mathrm{w}} \tau_{i,\mathrm{ph}}/m_i$, $i \in S_{\mathcal{T}}$, denotes the surface diffusion coefficient of the ith species associated with phonon interactions. In the situation of single site adsorption where $s_i = 1$, for $i \in S_{\mathcal{T}}$, we naturally recover the result of the previous section. The matrix $\widetilde{D} = (\widetilde{D})_{i,l\in S_{\mathcal{T}}}$ is symmetric $\widetilde{D} = \widetilde{D}^t$ and $N(\widetilde{D}) = \mathbb{R}\widetilde{\mathsf{x}}^s$ where $\widetilde{\mathsf{x}}^s = (\widetilde{\mathsf{x}}^s_i)_{i\in S_{\mathcal{T}}}$. In particular, since $\widetilde{D}\widetilde{\mathsf{x}}^s = 0$, we have $\sum_{l\in S_{\mathcal{T}}} \widetilde{D}_{il} s_l \widetilde{\mathsf{x}}_l = 0$ so that $\sum_{i\in S_{\mathcal{T}}} s_i \widetilde{n}_i \widetilde{\boldsymbol{W}}_{i\shortparallel} = 0$. In other words, we obtain the natural site number diffusion constraint

$$\sum_{i\in S_{\mathcal{T}}} s_i \widetilde{\boldsymbol{F}}_{i\shortparallel} = 0, \tag{7.6}$$

generalizing the monosite constraint. Although this constraint is physically natural, *it appears to have been overlooked in the literature in the multisite situation.* Finally, the various macroscopic boundary conditions for the gas and the surface species are found to be unchanged.

8 Conclusion

The kinetic model describing complex chemical reactions 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 temperature variations in the crystal as well as the situations where $T_{\mathrm{g}} \neq T_{\mathrm{w}}$. The linearized first order equations associated with the physisorbate and the chemisorbate also lead to new half space integro-differential equations that have never been investigated. Finally, multitemperature flows as well as state to state models involving gas surface interactions, which are of paramount importance for reentry, may also be investigated with similar models.

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A Collision operators with phonons

We denote in this section the species quantum indices in the form $(\mathrm{I},\widetilde{\mathrm{I}})$ where $\widetilde{\mathrm{I}}$ is an index for the degeneracies of the energy state I, ranging in an indexing set denoted by $\widetilde{\mathfrak{Q}}_{i\mathrm{I}}$. These degeneracies may typically be magnetic quantum numbers [73, 41].

The detailed operator $\mathcal{J}_{i,\mathrm{ph}}$ describing collisions between particles of species i and phonons taking into account the detailed quantum states $(\mathrm{I},\widetilde{\mathrm{I}})$ are in the general form [19, 35, 36, 37]

$$\mathcal{J}_{i,\mathrm{ph}} = \sum_{\substack{\mathrm{I}'\in\mathfrak{Q}_i \\ \widetilde{\mathrm{I}}'\in\widetilde{\mathfrak{Q}}_{i\mathrm{I}}}} \int \Big(\big(f_{\mathrm{ph}}(\boldsymbol{q})+1\big)\mathfrak{f}_i(\boldsymbol{c}_i',\mathrm{I}',\widetilde{\mathrm{I}}') - f_{\mathrm{ph}}(\boldsymbol{q})\mathfrak{f}_i(\boldsymbol{c}_i,\mathrm{I},\widetilde{\mathrm{I}})\Big) \mathcal{W}_{i,\mathrm{ph}}^{\mathrm{I},\widetilde{\mathrm{I}},\mathrm{I}',\widetilde{\mathrm{I}}'} \,\mathrm{d}\boldsymbol{c}_i'\mathrm{d}\boldsymbol{q}, \tag{A.1}$$

where $f_{\mathrm{ph}}(\boldsymbol{q})$ denotes the phonon distribution function, $i \in S$ 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 $\mathcal{W}_{i,\mathrm{ph}}^{\mathrm{I},\widetilde{\mathrm{I}},\mathrm{I}',\widetilde{\mathrm{I}}'}$ a transition probability. The dilute approximation has been used for f_i in order to simplify (A.1) and the appearing of the additional factor 1 in the gain term is a typical quantum effect [19, 35, 36, 37].

Proceeding as in Waldmann [73] and Oxenius [81], and assuming that the distributions are isotropic in such a way that $\mathfrak{f}_i(\boldsymbol{c}_i,\mathrm{I},\widetilde{\mathrm{I}}) = \mathfrak{f}_i(\boldsymbol{c}_i,\mathrm{I})$ is independent of $\widetilde{\mathrm{I}}$, we may set

$$f_i(\boldsymbol{c}_i,\mathrm{I}) = \sum_{\widetilde{\mathrm{I}}\in\widetilde{\mathfrak{Q}}_{i\mathrm{I}}} \mathfrak{f}_i(\boldsymbol{c}_i,\mathrm{I},\widetilde{\mathrm{I}}) = a_{i\mathrm{I}}\mathfrak{f}_i(\boldsymbol{c}_i,\mathrm{I}). \tag{A.2}$$

The operator (A.1) is then obtained in the form (2.21) with the degeneracy averaged transition probabilities

$$\overline{\mathsf{W}}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'} = \frac{1}{a_{i\mathrm{I}}} \sum_{\widetilde{\mathrm{I}},\widetilde{\mathrm{I}}'\in\widetilde{\mathfrak{Q}}_{i\mathrm{I}}} \mathcal{W}_{i,\mathrm{ph}}^{\mathrm{I},\widetilde{\mathrm{I}},\mathrm{I}',\widetilde{\mathrm{I}}'},$$

and these transition probabilities are such that $a_{i\mathrm{I}}\overline{\mathsf{W}}_{i,\mathrm{ph}}^{\mathrm{I},\mathrm{I}'} = a_{i\mathrm{I}'}\overline{\mathsf{W}}_{i,\mathrm{ph}}^{\mathrm{I}',\mathrm{I}}$, [73, 81]. The operator (A.1) corresponds to collisions such that $\mathfrak{m}_i\boldsymbol{c}_i = \mathfrak{m}_i\boldsymbol{c}_i' + \boldsymbol{q} + \boldsymbol{b}$ where $\boldsymbol{b}$ is a vector of the reciprocal crystal lattice and there is another operator associated with collisions such that $\mathfrak{m}_i\boldsymbol{c}_i + \boldsymbol{q} = \mathfrak{m}_i\boldsymbol{c}_i' + \boldsymbol{b}$ that leads to the same type of simplified source term $J_{i,\mathrm{ph}}$ and the corresponding details are omitted.

B Diffusion transport linear system in the gas

The transport linear systems associated with diffusion in the gas phase are well documented [38, 39, 40, 41, 42, 43, 44] and we summarize the results used in the paper. The integral equations (6.4) are solved with $\phi_{\mathrm{g}}^{(1)}$ written in the form

$$\phi_{\mathrm{g}i}^{(1)} = -\sum_{l\in S_{\mathrm{g}}} \boldsymbol{\phi}_{\mathrm{g}i}^{(1),l} \boldsymbol{\cdot} \boldsymbol{\partial_x} p_{\mathrm{g}l}, \tag{B.1}$$

and the right hand sides are found in the form

$$\boldsymbol{\psi}_{\mathrm{g}i}^{(1),l} = \frac{1}{p_{\mathrm{g}i}}(\delta_{il} - \mathsf{y}_{\mathrm{g}i})\boldsymbol{c}_i. \tag{B.2}$$

The Enskog constraints reduce to $\langle\!\langle (f_{\mathrm{g}i}^{(0)}\boldsymbol{\phi}_{i,\mathrm{g}}^{(1),l})_{i\in S_\mathrm{g}}, (m_i\boldsymbol{c}_i)_{i\in S_\mathrm{g}}\rangle\!\rangle = 0$ and the system is then solved by using a variational method.

We use the variational approximation space spanned by

$$\mathrm{Span}\{\ \phi^{1000k};\ k\in S_\mathrm{g}\ \}, \tag{B.3}$$

where

$$\phi^{1000k} = (\boldsymbol{w}_i\delta_{ki})_{i\in S_\mathrm{g}}, \qquad \boldsymbol{w}_i = \Big(\frac{m_i}{2k_\mathrm{B}T_\mathrm{w}}\Big)^{1/2}\boldsymbol{c}_i. \tag{B.4}$$

The right hand side may be expressed in the form

$$\boldsymbol{\psi}_{\mathrm{g}}^{(1),l} = \sum_{k\in S_\mathrm{g}} \frac{\sqrt{2}}{\sqrt{m_k k_\mathrm{B}T_\mathrm{w}}}\frac{1}{n_k}(\delta_{kl} - \mathsf{y}_k)\phi^{1000k},$$

and the solution is expanded as

$$\boldsymbol{\phi}_{\mathrm{g}}^{(1),l} = \sum_{k\in S_\mathrm{g}} \frac{\sqrt{2m_k}}{p\sqrt{k_\mathrm{B}T_\mathrm{w}}}\,\alpha_k^l\phi^{1000k}.$$

The transport linear system is obtained by taking the scalar product of the gas integral equations by the basis functions ϕ^{1000k} for $k\in S_\mathrm{g}$, and the resulting matrix L_g is

$$L_{\mathrm{g},\,kl} = \tfrac{2}{3}\frac{\sqrt{m_k m_l}}{\alpha_\kappa p}[\phi^{1000k},\phi^{1000l}]_\mathrm{g}, \qquad k,l\in S_\mathrm{g}, \tag{B.5}$$

where for any $f = (f_i)_{i\in S_\mathrm{g}}$ and $g = (g_i)_{i\in S_\mathrm{g}}$ with f_i and g_i functions of $\boldsymbol{c}_i$ and I, the bracket product $[f,g]_\mathrm{g}$ denotes $[f,g]_\mathrm{g} = \sum_{i\in S_\mathrm{g}}\sum_{\mathrm{I}\in\mathfrak{Q}_i}\int f_i\odot\mathcal{I}_{\mathrm{g}i}(g)\,\mathrm{d}\boldsymbol{c}_i$. The matrix $L_\mathrm{g} = (L_{\mathrm{g},\,kl})_{k,l\in S_\mathrm{g}}$ is symmetric positive semi-definite with nullspace spanned by $\mathbb{I}\in\mathbb{R}^\mathrm{N}$, that is, $L_\mathrm{g} = L_\mathrm{g}^t$, $L_\mathrm{g}\geq 0$, and $N(L_\mathrm{g}) = \mathbb{R}\mathbb{I}$, and its components are given by

$$L_{\mathrm{g}\,kk} = \sum_{\substack{l\in S_\mathrm{g}\\ l\neq k}} \frac{\mathsf{x}_{\mathrm{g}k}\mathsf{x}_{\mathrm{g}l}}{\mathcal{D}_{kl}}, \qquad L_{\mathrm{g}\,kl} = -\frac{\mathsf{x}_{\mathrm{g}k}\mathsf{x}_{\mathrm{g}l}}{\mathcal{D}_{kl}}, \quad k\neq l, \qquad k,l\in S_\mathrm{g},$$

where $\mathsf{x}_{\mathrm{g}k} = n_{\mathrm{g}k}/n_\mathrm{g}$ denotes the mole fraction of the kth species in the gas and $\mathcal{D}_{kl}$ the binary diffusion coefficient for the (k,l) species pair [39, 40, 41, 42, 43, 44]. The resulting transport linear system is found after some algebra in the form

$$L_\mathrm{g}\alpha_\mathrm{g}^l = \beta_\mathrm{g}^l, \qquad l\in S_\mathrm{g}, \tag{B.6}$$

where $\alpha_\mathrm{g}^l = (\alpha_{\mathrm{g}\,k}^l)_{k\in S_\mathrm{g}}$, $\beta_\mathrm{g}^l = (\beta_{\mathrm{g}\,k}^l)_{k\in S_\mathrm{g}}$, $\beta_{\mathrm{g}\,k}^l = \delta_{kl} - \mathsf{y}_{\mathrm{g}k}$, $\langle\mathbb{I},\beta_\mathrm{g}^l\rangle = 0$, and the mass constraint yields that the solution α_g^l must satisfy $\langle\mathsf{y},\alpha_\mathrm{g}^l\rangle = 0$. Then for any positive coefficient $\nu > 0$ the solution α_g^l is given by

$$\alpha_\mathrm{g}^l = \Big(L_\mathrm{g} + \nu\mathsf{y}_\mathrm{g}\otimes\mathsf{y}_\mathrm{g}\Big)^{-1}\beta_\mathrm{g}^l, \qquad l\in S_\mathrm{g}. \tag{B.7}$$

The molar diffusion flux of the ith species is then given by

$$\boldsymbol{F}_{\mathrm{g}i} = -\epsilon\sum_{l\in S_\mathrm{g}} n_{\mathrm{g}i}\alpha_{\mathrm{g}i}^l\frac{\boldsymbol{\partial_x}p_{\mathrm{g}l}}{p_\mathrm{g}}, \tag{B.8}$$

and its projection on the tangential plane yields the flux used in Section 6.4. Since $\boldsymbol{\partial_x}p_\mathrm{g} = \mathcal{O}(\epsilon)$, these diffusion fluxes may also be written $\boldsymbol{F}_{\mathrm{g}i} = -\epsilon\sum_{l\in S_\mathrm{g}} n_{\mathrm{g}i}\alpha_{\mathrm{g}i}^l\boldsymbol{\partial_x}\mathsf{x}_{\mathrm{g}l}$.

C Normal multicomponent diffusion in the physisorbate

Condidering normal diffusion in the physisorbate, the equations governing even components of perturbed distribution functions $\Phi^{(1)}_{i,\mathrm{ev}}$ resulting from (6.18) are in the form

$$\begin{aligned}
c_{iz}\partial_\zeta \Phi^{(1)}_{i,\mathrm{ev}} &- \frac{m_i c_{iz}}{\rho k_{\mathrm{B}} T_{\mathrm{w}}} \sum_{\substack{j\in S_{\mathrm{g}}\\ \mathrm{J}\in\mathfrak{Q}_j}} \partial_\zeta \int m_j c_{jz}^2 \mathsf{f}^{(0)}_j \Phi^{(1)}_{j,\mathrm{ev}} \mathrm{d}\boldsymbol{c}_j + \frac{1}{\alpha_\kappa}\mathcal{I}_i(\Phi^{(1)}_{\mathrm{ev}}) \\
&- \frac{1}{m_i}\partial_\zeta \mathrm{W}_i\, \partial_{c_{iz}} \Phi^{(1)}_{i,\mathrm{ev}} - \frac{m_i c_{iz}}{\rho k_{\mathrm{B}} T_{\mathrm{w}}} \sum_{\substack{j\in S_{\mathrm{g}}\\ \mathrm{J}\in\mathfrak{Q}_j}} \int \partial_\zeta \mathrm{W}_j\, \mathsf{f}^{(0)}_j \Phi^{(1)}_{j,\mathrm{ev}} \mathrm{d}\boldsymbol{c}_j \\
&+ \frac{\Phi^{(1)}_{i,\mathrm{ev}} - \langle \Phi^{(1)}_{i,\mathrm{ev}} \mathrm{M}_i\rangle}{\tau_{i,\mathrm{ph}}} - \frac{m_i c_{iz}}{\rho k_{\mathrm{B}} T_{\mathrm{w}}} \sum_{\substack{j\in S_{\mathrm{g}}\\ \mathrm{J}\in\mathfrak{Q}_j}} \frac{1}{\tau_{j,\mathrm{ph}}} \int m_j c_{jz} \mathsf{f}^{(0)}_j \Phi^{(1)}_{j,\mathrm{ev}} \mathrm{d}\boldsymbol{c}_j \\
&= \frac{\mathcal{C}^{(0)}_i}{\mathsf{f}^{(0)}_i} - \sum_{l\in S_{\mathrm{g}}} \frac{1}{p_i}(\delta_{il} - \mathsf{y}_i) c_{iz}\partial_z p_{\mathrm{g}l}, \qquad i\in S_{\mathrm{g}}.
\end{aligned} \tag{C.1}$$

Taking into account the similar gas phase problem solution, it is natural to seek a solution of (C.1) in the form

$$\Phi^{(1)}_{i,\mathrm{ev}} = -\sum_{l\in S_{\mathrm{g}}} \Phi^{(1),l}_{i,\mathrm{ev}} \partial_z p_{\mathrm{g}l} + \Phi^{(1),v_{\mathrm{g}}}_{i,\mathrm{ev}}, \qquad i\in S_{\mathrm{g}}, \tag{C.2}$$

with a diffusional part $-\sum_{l\in S_{\mathrm{g}}} \Phi^{(1),l}_{i,\mathrm{ev}} \partial_z p_{\mathrm{g}l}$ and a remaining term $\Phi^{(1),v_{\mathrm{g}}}_{i,\mathrm{ev}}$ that will involve chemistry, diffusion and convection. The diffusional part is naturally assumed to obey the mass conservation Enskog constraint $\langle\!\langle \mathsf{f}^{(0)}\Phi^{(1),l}_{\mathrm{ev}}, (m_i c_{iz})_{i\in S_{\mathrm{g}}} \rangle\!\rangle = 0$ where $\mathsf{f}^{(0)}\Phi^{(1),l}_{\mathrm{ev}} = \big(\mathsf{f}^{(0)}_i \Phi^{(1),l}_{i,\mathrm{ev}}\big)_{i\in S_{\mathrm{g}}}$.

The differential-integral equations (C.1) are then solved using a Galerkin procedure with the convenient approximation space

$$\mathrm{Span}\{\ \phi^{0000k};\ k\in S_{\mathrm{g}};\ \ \phi^{1000kz};\ k\in S_{\mathrm{g}}\ \}, \tag{C.3}$$

where

$$\phi^{0000k} = (\delta_{ki})_{i\in S_{\mathrm{g}}}, \qquad \phi^{1000kz} = (w_{iz}\delta_{ki})_{i\in S_{\mathrm{g}}}, \qquad w_{iz} = \Big(\frac{m_k}{2k_{\mathrm{B}}T_{\mathrm{w}}}\Big)^{1/2} c_{iz}. \tag{C.4}$$

The basis functions ϕ^{1000kz} are the natural one-dimensional versions of the traditional corresponding three dimensional basis functions whereas the ϕ^{0000k} are the natural scalar basis functions. The solutions are expanded in the form

$$\Phi^{(1),l}_{\mathrm{ev}} = \sum_{k\in S_{\mathrm{g}}} \frac{\sqrt{2m_k}}{p\sqrt{k_{\mathrm{B}}T_{\mathrm{w}}}}\, \widetilde{\alpha}^l_k \phi^{1000kz}, \tag{C.5}$$

$$\Phi^{(1),v_{\mathrm{g}}}_{\mathrm{ev}} = \sum_{k\in S_{\mathrm{g}}} \frac{\sqrt{2m_k}}{\sqrt{k_{\mathrm{B}}T_{\mathrm{w}}}}\, \widehat{\alpha}_k \phi^{1000kz} + \sum_{k\in S_{\mathrm{g}}} \widehat{\alpha}'_k \phi^{0000k}. \tag{C.6}$$

It is indeed natural that $\Phi^{(1),l}_{\mathrm{ev}}$, $l\in S_{\mathrm{g}}$, are odd with respect to the normal species velocities.

We next use a superposition method, first solving a partial system for the simpler diffusional component of the solution $-\sum_{l\in S_{\rm g}} \Phi^{(1),l}_{i,\rm ev}\partial_z p_{{\rm g}l}$ and then solving a full system for more complex remaining part of the solution $\Phi^{(1),v_{\rm g}}_{i,\rm ev}$. Considering first the system (C.1) without the chemistry source terms $\mathcal{C}^{(0)}_i/\mathsf{f}^{(0)}_i$, for the diffusional part of the solution, and taking the product with the test functions $\mathsf{f}^{(0)}\phi^{1000kz} = (\mathsf{f}^{(0)}_i\phi^{1000kz}_i)_{i\in S_{\rm g}}$, $k\in S_{\rm g}$, using (2.40), we obtain simple linear systems for the $\widetilde{\alpha}^l = (\widetilde{\alpha}^l_k)_{k\in S_{\rm g}}$. After some algebra, it is naturally found that the governing equations reduce to the same transport linear systems with the same mass constraint as for tangential diffusion so that

$$\widetilde{\alpha}^l = \alpha^l, \qquad l\in S_{\rm g}, \tag{C.7}$$

and diffusion is recovered to be isotropic. Therefore, the solution $\widetilde{\alpha}^l$ converges towards that of the gas $\widetilde{\alpha}^l \to \alpha^l_{\rm g}$ as $\zeta\to\infty$ as we have already established for α^l. The diffusive flux of the ith species F_{iz} in the normal direction may thus be written

$$F_{iz} = -\epsilon \sum_{l\in S_{\rm g}} n_i\alpha^l_i \frac{\overline{\partial_z p_{{\rm g}l}}}{p}, \qquad i\in S_{\rm g}, \tag{C.8}$$

or equivalently $F_{iz} = -\epsilon\sum_{l\in S_{\rm g}} \overline{n}_{\rm g}\mathsf{x}_i\alpha^l_i\overline{\partial_z \mathsf{x}_{{\rm g}l}}$, and converges towards the corresponding gas flux $F_{{\rm g}iz} = -\epsilon\sum_{l\in S_{\rm g}} \overline{n}_{\rm g}\overline{\mathsf{x}}_{i,\rm g}\alpha^l_{{\rm g}i}\overline{\partial_z \mathsf{x}_{{\rm g}l}}$,

Once the diffusive component of the solution $\Phi^{(1),l}_{\rm ev}$, $l\in S_{\rm g}$, are known, we may use the decomposition (C.2) and obtain a variational formulation for the remaining part of the solution $\Phi^{(1),v_{\rm g}}_{i,\rm ev}$. Important simplifications are then obtained from the simple structure of ϕ^{1000kz} and ϕ^{0000k}. In particular, the multiplication by $\mathsf{f}^{(0)}\phi^{0000k}$, $k\in S_{\rm g}$, using the scalar product (2.40), yields

$$n_k\partial_\zeta\widehat{\alpha}_k - \frac{n_k}{k_{\rm B}T_{\rm w}}\partial_\zeta \mathrm{w}_k\,\widehat{\alpha}_k + \partial_\zeta F_{kz} = \mathfrak{C}^{(0)}_k, \tag{C.9}$$

where

$$\mathfrak{C}^{(0)}_k = \sum_{\mathrm{K}\in\mathfrak{Q}_k}\int \mathcal{C}^{(0)}_k \mathrm{d}\boldsymbol{c}_k.$$

Using then $\partial_\zeta \log n_k = -\partial_\zeta \mathrm{w}_k/k_{\rm B}T_{\rm w}$, we may rewrite (C.9) in the form $\partial_\zeta(n_k\widehat{\alpha}_k + F_{kz}) = \mathfrak{C}^{(0)}_k$, and by integration, we obtain that

$$n_k\widehat{\alpha}_k = \int_0^\zeta \mathfrak{C}^{(0)}_k \mathrm{d}\hat{\zeta} - F_{kz}. \tag{C.10}$$

From the compatibility with the gases for $\zeta\to\infty$, and using (C.6), we also deduce that

$$\lim_{\zeta\to\infty}\widehat{\alpha}_k = v_{\rm g}, \qquad \lim_{\zeta\to\infty}\widehat{\alpha}'_k = 0,$$

and we may alternatively write that $n_k\widehat{\alpha}_k = n_{{\rm g}k}v_{\rm g} + F_{{\rm g}kz} - \int_\zeta^\infty \mathfrak{C}^{(0)}_k\mathrm{d}\hat{\zeta} - F_{kz}$. By integrating (C.9) over $(0,\infty)$, we also recover the fluid boundary condition (4.19) since $\mathfrak{w}^{(0)}_k = \int \mathfrak{C}^{(0)}_k \mathrm{d}z$. On the other hand, taking the scalar product with $\mathsf{f}^{(0)}\phi^{1000kz}$, $k\in S_{\rm g}$, using (2.40), it is found that

$$n_k\partial_\zeta\widehat{\alpha}'_k - \mathsf{y}_k\sum_{j\in S_{\rm g}} n_j\partial_\zeta\widehat{\alpha}'_j = \mathsf{b}_k,$$

where $\mathsf{b}_k = \frac{p}{k_{\mathrm{B}} T_{\mathrm{w}}} \big(\sum_{l \in S_{\mathrm{g}}} L_{kl} \widehat{\alpha}_l + \mathsf{D}_{kk} \widehat{\alpha}_k - \mathsf{y}_k \langle \mathsf{D} \widehat{\alpha}, \mathbb{I} \rangle \big)$. We may then impose the constraint $\sum_{j \in S_{\mathrm{g}}} n_j \partial_\zeta \widehat{\alpha}'_j = 0$ to finally get that $\widehat{\alpha}'_k = - \int_\zeta^\infty \frac{\mathsf{b}_k}{n_k} \mathrm{d}\zeta$.

In conclusion, diffusive processes are isotropic in the physisorbate and converge towards that of the gas associated with $\overline{\phi}^{(1)}_{\mathrm{g}i}$. The physisorbate perturbed distribution functions also have components $\Phi^{(1),v_{\mathrm{g}}}_{i,\mathrm{ev}}$ converging towards the remaining parts $m_i c_{iz} v_{\mathrm{g}z} / k_{\mathrm{B}} \overline{T}_{\mathrm{g}}$ of the gas corrected perturbed distribution functions.

D Layer-averaged kinetic equation

We investigate in this section *layer-averaged* or *partially integrated* kinetic equations for the surface species $S_{\mathcal{T}} = S_{\mathrm{c}} \cup S_{\mathrm{s}}$. The layer-averaged zeroth order densities are defined by

$$\widetilde{\mathsf{f}}^{(0)}_i = \int \mathsf{f}^{(0)}_i \mathrm{d}c_{iz} \mathrm{d}\zeta, \qquad i \in S_{\mathcal{T}},$$

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

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

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

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

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

$$\widetilde{\mathcal{H}}_i(\widetilde{\Phi}^{(1)}_{i,\mathrm{od}}) = \widetilde{\Psi}^{(1)}_{i,\mathrm{od}}, \qquad i \in S_{\mathcal{T}}, \tag{D.1}$$

where $\widetilde{\Psi}^{(1)}_{i,\mathrm{od}} = -\boldsymbol{c}_{i\parallel} \cdot \boldsymbol{\partial}_\parallel \log \widetilde{\mathsf{f}}^{(0)}_i$, $i \in S_{\mathcal{T}}$. These equations are directly obtained by multiplying $\mathcal{H}_i(\Phi^{(1)}_{i,\mathrm{od}}) = \Psi^{(1)}_{i,\mathrm{od}}$ by $\mathsf{f}^{(0)}_i$, partially integrating the resulting kinetic equations with $\mathrm{d}c_{iz}\mathrm{d}\zeta$, and then dividing by $\widetilde{\mathsf{f}}^{(0)}_i$. Letting then $\widetilde{\Phi}^{(1)}_{\mathrm{od}} = (\widetilde{\Phi}^{(1)}_{i,\mathrm{od}})_{i \in S_{\mathcal{T}}}$, $\widetilde{\mathcal{H}} = (\widetilde{\mathcal{H}}_i)_{i \in S_{\mathcal{T}}}$, and $\widetilde{\Psi}^{(1)}_{\mathrm{od}} = (\widetilde{\Psi}^{(1)}_{i,\mathrm{od}})_{i \in S_{\mathcal{T}}}$, we obtain $\widetilde{\mathcal{H}}(\widetilde{\Phi}^{(1)}_{\mathrm{od}}) = \widetilde{\Psi}^{(1)}_{\mathrm{od}}$.

It is further possible to introduce a *surface bracket operator* acting on pairs $\widetilde{\Phi} = (\widetilde{\Phi}_i)_{i \in S_{\mathcal{T}}}$ and $\widetilde{\Phi}' = (\widetilde{\Phi}'_i)_{i \in S_{\mathcal{T}}}$, where $\widetilde{\Phi}_i$ and $\widetilde{\Phi}'_i$ are functions of $\boldsymbol{c}_{i\parallel}$, in the form

$$[\![\widetilde{\Phi}, \widetilde{\Phi}']\!] = \sum_{i \in S_{\mathcal{T}}} \int \widetilde{\mathsf{f}}^{(0)}_i \widetilde{\mathcal{H}}_i(\widetilde{\Phi}_i) \odot \widetilde{\Phi}'_i \mathrm{d}\boldsymbol{c}_{i\parallel}. \tag{D.2}$$

This 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.

The layer-averaged kinetic equation (D.1) may be used whenever one wants to obtain the layer-averaged distribution $\widetilde{\Phi}^{(1)}_{i,\mathrm{od}}$ or any of its moment with respect to the tangential velocity $\boldsymbol{c}_{i\parallel}$. These equations are natural since only the integrated quantities are physically interesting and all the results of Section 6.6 may be recovered. The tangential diffusion fluxes in particular may be expressed as

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

The Waldmann formalism for the surface kinetic equation also leads to

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

where $\widetilde{\Psi}^{(1),l}_{\mathrm{od}} = (\widetilde{\Psi}^{(1),l}_{i,\mathrm{od}})_{i\in S_{\mathcal{T}}}$ and $\widetilde{\Psi}^{(1),l}_{i,\mathrm{od}} = \frac{1}{\widetilde{p}_i}(\delta_{il} - \widetilde{\mathrm{x}}_i)\boldsymbol{c}_{i\shortparallel}$, for $i,l \in S_{\mathcal{T}}$. The solutions $\widetilde{\Phi}^{(1),l}_{\mathrm{od}}$ to the integral equations $\widetilde{\mathcal{H}}(\widetilde{\Phi}^{(1),l}_{\mathrm{od}}) = \widetilde{\Psi}^{(1),l}_{\mathrm{od}}$ for $l \in S_{\mathcal{T}}$ are found in the explicit form

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

The tangential velocities may also be written

$$\widetilde{\boldsymbol{W}}_{i\shortparallel} = \frac{\epsilon}{\widetilde{n}_i} \int \widetilde{\mathrm{f}}^{(0)}_i \widetilde{\Phi}^{(1)}_{i,\mathrm{od}} \boldsymbol{c}_{i\shortparallel} \mathrm{d}\boldsymbol{c}_{i\shortparallel} - \frac{\epsilon}{\widetilde{n}_\sigma} \sum_{j\in S_{\mathcal{T}}} \int \widetilde{\mathrm{f}}^{(0)}_j \widetilde{\Phi}^{(1)}_{j,\mathrm{od}} \boldsymbol{c}_{j\shortparallel} \mathrm{d}\boldsymbol{c}_{j\shortparallel}, \tag{D.3}$$

and from the isotropy of the layer-averaged operator, we recover the molar diffusion velocities from (6.42) and the diffusion coefficients

$$\widetilde{D}_{il} = \frac{\widetilde{p}}{2\widetilde{n}_i} \int \widetilde{\mathrm{f}}^{(0)}_i \widetilde{\Phi}^{(1),l}_{i,\mathrm{od}} \cdot \boldsymbol{c}_{i\shortparallel}\, \mathrm{d}\boldsymbol{c}_{i\shortparallel} - \frac{\widetilde{p}}{2\widetilde{n}_\sigma} \sum_{j\in S_{\mathcal{T}}} \int \widetilde{\mathrm{f}}^{(0)}_j \widetilde{\Phi}^{(1),l}_{j,\mathrm{od}} \cdot \boldsymbol{c}_{j\shortparallel}\, \mathrm{d}\boldsymbol{c}_{j\shortparallel}.$$

The diffusion coefficient may also be written as $\widetilde{D}_{il} = \frac{k_{\mathrm{B}} T_{\mathrm{w}} \widetilde{p}}{2} [\![\widetilde{\Phi}^{(1),i}_{\mathrm{od}}, \widetilde{\Phi}^{(1),l}_{\mathrm{od}}]\!]$, for $i,l \in S_{\mathcal{T}}$ and so that the two-dimensional surface formalism for layer averaged quantities is similar to that of gas mixtures in three dimensions mutatis mutandis.

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