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Abstract

A half-space problem of a linear kinetic equation for gas molecules physisorbed close to a solid surface, relevant to a kinetic model of gas-surface interactions and derived by Aoki *et al.* (K. Aoki *et al.*, in: Phys. Rev. E 106:035306, 2022), is considered. The equation contains a confinement potential in the vicinity of the solid surface and an interaction term between gas molecules and phonons. It is proved that a unique solution exists when the incoming molecular flux is specified at infinity. This validates the natural observation that the half-space problem serves as the boundary condition for the Boltzmann equation. It is also proved that the sequence of approximate solutions used for the existence proof converges exponentially fast. In addition, numerical results showing the details of the solution to the half-space problem are presented.

1 Introduction

The boundary condition for the Boltzmann equation results from complex gas-surface interactions and specifies scattering kernels relating the incident and reflected molecular fluxes at the surface. The most conventional boundary condition is the Maxwell-type condition, which is a linear combination of specular and diffuse reflection [17, 28]. In addition to it, more general boundary conditions have been proposed [19, 23, 18, 17, 25, 29]. However, most of these boundary conditions are of mathematical or empirical nature and are not directly related to physical properties, such as the characteristics of the gas and surface molecules and interaction potentials. A more physical approach would be to use molecular dynamics simulations to understand the relation between the incident and reflected molecular fluxes [31, 26, 33, 32, 16]. However, although useful for assessing the existing boundary conditions, this approach is in general not helpful in the construction of new models.

An alternative physical approach is the *kinetic* approach based on kinetic equations describing the behavior of gas molecules interacting with the surface molecules [13, 12, 9,

11, 20, 1, 14, 15, 5, 2, 3, 4, 30]. The typical kinetic equations include a potential generated by fixed crystal molecules and a collision term with phonons describing the fluctuating part of the potential of the crystal molecules.

In a recent paper [6], a kinetic model of gas-surface interactions, which follows the line of [13, 12, 9, 11, 20, 1, 14, 15, 5, 2, 3, 4], was proposed and was used to construct the boundary condition for the Boltzmann equation. The model contains a confinement potential in the vicinity of the solid surface, which produces a thin layer of physisorbed molecules (physisorbate layer), as well as the interaction term between gas molecules (the Boltzmann collision term) and that between gas molecules and phonons, where the term "gas molecules" is also used for physisorbed gas molecules. Under the assumptions that (i) the gas-phonon interaction is much more frequent than the gas-gas interaction inside the physisorbate layer; (ii) the thickness of the physisorbate layer is much smaller than the mean free path of the gas molecules; and (iii) the gas-phonon interaction is described by a simple collision model of relaxation type, an asymptotic analysis was performed, and a linear kinetic equation for the physisorbate layer was derived together with its boundary condition at infinity. The resulting kinetic equation and the boundary condition at infinity form a half-space problem, in which no boundary condition is imposed on the solid surface because the confinement potential prevents the gas molecules from reaching the surface.

Suppose that the half-space problem has a unique solution when the velocity distribution function of the gas molecule toward the surface is assigned at infinity. It is a natural assumption based on numerical computation as well as physical considerations [6]. This means that the outgoing velocity distribution of the gas molecules at infinity is determined by the incident distribution towards the surface there. Since the thickness of the physisorbate layer is much smaller than the mean free path, the infinity in the scale of the layer can be regarded as the surface of the solid wall in the scale of the mean free path. Therefore, the half-space problem plays the role of the boundary condition on the surface for the Boltzmann equation that is valid outside the physisorbate layer.

In our previous paper [6], the half-space problem for the physisorbate layer mentioned above was also solved numerically, and the results provided the numerical evidence of the existence and uniqueness of the solution. In addition, based on an iteration scheme and its first iteration, an analytic model of the boundary condition for the Boltzmann equation was constructed, and the numerical assessment of the model showed its effectiveness.

The first aim of the present study is to rigorously prove the existence and uniqueness of the solution to the half-space problem for the physisorbate layer studied numerically and approximately in [6]. In addition, the sequence of iterative approximate solutions, which is used for the existence proof, is shown to converge exponentially fast with respect to the number of iterations. The second aim is to investigate the behavior of the solution to the half-space problem numerically. Since special interest was put on the Boltzmann boundary condition in [6], attention was focused not on the behavior of the solution itself but on the relation between the incoming and outgoing molecular fluxes at infinity. In this paper, we put more attention to the details of the solution in the physisorbate layer and show some related numerical results.

The paper is organized as follows. The kinetic model for gas-surface interactions proposed in [6] and the resulting half-space problem for the physisorbate layer are summarized in Sec. 2. Section 3 is devoted to rigorous proof of mathematical properties, such as the existence and uniqueness of the solution, for the half-space problem. In Sec. 4, some numerical results showing the behavior of the solution to the half-space problem are presented. Concluding remarks are given in Sec. 5.

2 Kinetic equations and physisorbate layer

In this section, we summarize the kinetic model of gas-surface interactions proposed in [6] and the resulting half-space problem for the physisorbate layer.

2.1 Kinetic model

We consider a single monatomic gas in a half space ($z > 0$) interacting with a plane crystal surface located at $z = 0$, where $\boldsymbol{x} = (x, y, z)$ indicates the space coordinates. We assume that the gas molecules are subject to an interaction potential W generated by the *fixed* crystal molecules. The interaction potential W is assumed to depend only on the normal coordinate z for simplicity and is written in the form

$$W(z) = W_{\rm s}(z/\delta) = W_{\rm s}(\zeta), \tag{1}$$

where δ is a characteristic range of the surface potential and $\zeta = z/\delta$ denotes the rescaled normal coordinate, which is dimensionless. The rescaled potential $W_{\rm s}$ is such that

$$\lim_{\zeta\to 0} W_{\rm s}(\zeta) = +\infty, \qquad \lim_{\zeta\to+\infty} W_{\rm s}(\zeta) = 0, \tag{2}$$

and usually involves an attractive zone and a repulsing zone as Lennard-Jones potentials integrated over all crystal molecules, as illustrated in Fig. 1. To be more specific, we assume the following:

(i) the potential $W_{\rm s}(\zeta)$ is a smooth function of ζ and has a single minimum $W_{\rm min}(< 0)$ at $\zeta = \zeta_{\rm min}(> 0)$, i.e. $W_{\rm min} = W_{\rm s}(\zeta_{\rm min})$;

(ii) in the interval $(0, \zeta_{\rm min})$, $W_{\rm s}(\zeta)$ decreases from $+\infty$ to $W_{\rm min}$ monotonically, so that $(0, \zeta_{\rm min})$ is the repulsive zone;

(iii) in the interval $(\zeta_{\rm min}, \infty)$, $W_{\rm s}(\zeta)$ increases from $W_{\rm min}$ to 0 monotonically, so that $(\zeta_{\rm min}, \infty)$ is the attractive zone;

(iv) in the repulsive zone $(0, \zeta_{\rm min})$, $W_{\rm s}(\zeta)$ is convex downward.

The gas molecules that are trapped by the potential well are called the physisorbed molecules and the set of such molecules forms the physisorbate.

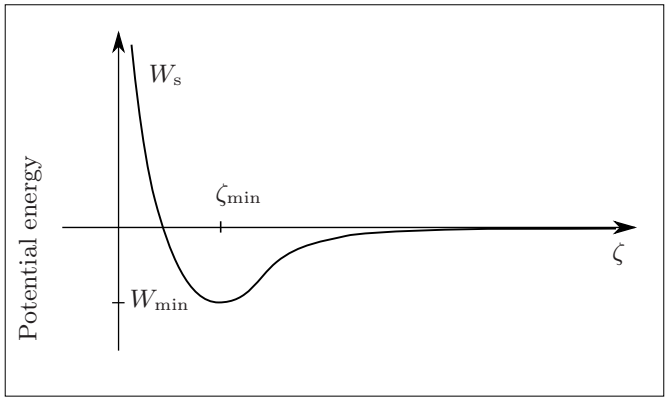


Figure 1: Typical surface interaction potential $W_{\rm s}$ as function of ζ.

The behavior of the gas is assumed to be governed by the following kinetic equation of Boltzmann type [13, 12, 11, 1, 2, 3, 4, 5, 6]:

$$\frac{\partial f}{\partial t} + \boldsymbol{c} \cdot \frac{\partial f}{\partial \boldsymbol{x}} - \frac{1}{m}\frac{\mathrm{d}W}{\mathrm{d}z}\frac{\partial f}{\partial c_z} = J(f,f) + J_{\mathrm{ph}}(f), \tag{3}$$

where m is the mass of a gas molecule, $f(t, \boldsymbol{x}, \boldsymbol{c})$ is the velocity distribution function for the gas molecules (including the physisorbed molecules), t is the time variable, $\boldsymbol{c} = (c_x, c_y, c_z)$ is the velocity of the gas molecules with c_x, c_y, and c_z being its x, y, and z components, $J(f,f)$ is the Boltzmann collision operator describing the gas-gas collision, and $J_{\mathrm{ph}}(f)$ is the gas-phonon collision operator.

Since the explicit form of the Boltzmann collision operator $J(f,f)$ is not relevant to the present paper, it is omitted here. In [6], under the assumption that the phonons are in equilibrium, the following simple model of relaxation type is used for the gas-phonon collision operator $J_{\mathrm{ph}}(f)$:

$$J_{\mathrm{ph}}(f) = \frac{1}{\tau_{\mathrm{ph}}}\big(nM - f\big). \tag{4}$$

Here, τ_{ph} is the relaxation time of gas-phonon interactions and n and M are, respectively, the molecular number density and the wall Maxwellian given by

$$n = \int_{\mathbf{R}^3} f \,\mathrm{d}\boldsymbol{c}, \tag{5a}$$

$$M = \left(\frac{m}{2\pi k_{\mathrm{B}} T_{\mathrm{w}}}\right)^{3/2} \exp\left(-\frac{m|\boldsymbol{c}|^2}{2k_{\mathrm{B}}T_{\mathrm{w}}}\right), \tag{5b}$$

where k_{B} is the Boltzmann constant, T_{w} is the temperature of the solid wall, and the domain of integration in (5a) is the whole space of $\boldsymbol{c}$. The model (4) was inspired by [13, 12] and was used in [1, 2, 3, 4, 5, 6]. We further assume that τ_{ph} has the same length scale of variation as the potential W and is a function of the scaled normal coordinate ζ, i.e.,

$$\tau_{\mathrm{ph}}(z) = \tau_{\mathrm{ph,s}}(z/\delta) = \tau_{\mathrm{ph,s}}(\zeta). \tag{6}$$

Since there is no interaction between molecules and phonons far from the surface, we naturally assume that [6]

$$\lim_{z\to\infty} \tau_{\mathrm{ph}}(z) = \lim_{\zeta\to\infty} \tau_{\mathrm{ph,s}}(\zeta) = \infty. \tag{7}$$

It is also natural to assume that

(v) $\tau_{\mathrm{ph,s}}(\zeta)$ is an increasing function of ζ in $[0, +\infty)$ with a finite positive $\tau_{\mathrm{ph,s}}(0)$;

(vi) $1/\tau_{\mathrm{ph,s}}(\zeta)$ is integrable over $[0, +\infty)$.

Since J_{ph} as well as the potential W vanishes far from the surface, we may let $z \to \infty$ (or $\zeta \to \infty$) in (3) to obtain the kinetic equation in the gas phase

$$\frac{\partial f_{\mathrm{g}}}{\partial t} + \boldsymbol{c} \cdot \frac{\partial f_{\mathrm{g}}}{\partial \boldsymbol{x}} = J(f_{\mathrm{g}}, f_{\mathrm{g}}), \tag{8}$$

where $f_{\mathrm{g}}(t, \boldsymbol{x}, \boldsymbol{c})$ denotes the velocity distribution function of gas molecules. Equation (8) is the standard Boltzmann equation for a monatomic gas, and the distribution f must converge to f_{g} far from the surface.

2.2 Normalization and parameter setting

In order to nondimensionalize the kinetic equation (3), we introduce characteristic quantities that are marked with the * superscript. We denote by $n^\star$ the characteristic number density, $c^\star = (k_\mathrm{B}T_\mathrm{w}/m)^{1/2}$ the characteristic thermal speed, $f^\star = n^\star/c^{\star 3}$ the characteristic molecular velocity distribution, $\tau_\mathrm{fr}^\star$ the characteristic mean free time, $\lambda^\star = \tau_\mathrm{fr}^\star c^\star$ the characteristic mean free path, $W^\star = mc^{\star 2} = k_\mathrm{B}T_\mathrm{w}$ the characteristic potential, and $\tau_\mathrm{ph}^\star$ the characteristic time for gas-phonon interaction. We recall that δ is the distance normal to the surface where the potential W is significant, so that $\tau_\mathrm{la}^\star = \delta/c^\star$ indicates the corresponding characteristic time of transit through the potential.

With these characteristic quantities, we introduce the dimensionless quantities $\hat{t}$, $\hat{\boldsymbol{x}}$, $\hat{\boldsymbol{c}}$, $\hat{n}$, $\hat{f}$, $\hat{f}_\mathrm{g}$, $\hat{M}$, $\hat{W}$, $\hat{\tau}_\mathrm{ph}$, and $\hat{W}_\mathrm{min}$, which correspond to t, $\boldsymbol{x}$, $\boldsymbol{c}$, n, f, f_g, M, W, τ_ph, and W_min, respectively, by the following relations:

$$\begin{aligned}
&\hat{t} = t/\tau_\mathrm{fr}^\star, \qquad \hat{\boldsymbol{x}} = \boldsymbol{x}/\lambda^\star, \qquad \hat{\boldsymbol{c}} = \boldsymbol{c}/c^\star, \qquad \hat{n} = n/n^\star,\\
&\hat{f} = f\,c^{\star 3}/n^\star, \qquad \hat{f}_\mathrm{g} = f_\mathrm{g}\,c^{\star 3}/n^\star, \qquad \hat{M} = Mc^{\star 3},\\
&\hat{W}(\zeta) = W(z)/W^\star = W_\mathrm{s}(\zeta)/k_\mathrm{B}T_\mathrm{w}, \quad \hat{\tau}_\mathrm{ph}(\zeta) = \tau_\mathrm{ph}(z)/\tau_\mathrm{ph}^\star = \tau_\mathrm{ph,s}(\zeta)/\tau_\mathrm{ph}^\star,\\
&\hat{W}_\mathrm{min} = W_\mathrm{min}/k_\mathrm{B}T_\mathrm{w}.
\end{aligned} \tag{9}$$

Correspondingly, the collision operators $J(f,f)$ and $J_\mathrm{ph}(f)$ are nondimensionalized as

$$J(f,f) = \frac{n^\star}{\tau_\mathrm{fr}^\star c^{\star 3}}\hat{J}(\hat{f},\hat{f}), \tag{10}$$

and

$$J_\mathrm{ph}(f) = \frac{n^\star}{\tau_\mathrm{ph}^\star c^{\star 3}}\hat{J}_\mathrm{ph}(\hat{f}), \qquad \hat{J}_\mathrm{ph}(\hat{f}) = \frac{1}{\hat{\tau}_\mathrm{ph}}(\hat{n}\hat{M} - \hat{f}), \tag{11}$$

where

$$\hat{n} = \int_{\mathbf{R}^3} \hat{f}\,\mathrm{d}\hat{\boldsymbol{c}}, \tag{12a}$$

$$\hat{M} = (2\pi)^{-3/2}\exp\bigl(-|\hat{\boldsymbol{c}}|^2/2\bigr), \tag{12b}$$

and the domain of integration is the whole space of $\hat{\boldsymbol{c}}$. The explicit form of $\hat{J}(\hat{f},\hat{f})$, which is not relevant in this paper, is omitted.

Substituting (9)–(12) into (3), we obtain the dimensionless version of (3), which is characterized by the following two dimensionless parameters:

$$\epsilon_\mathrm{ph} = \frac{\tau_\mathrm{ph}^\star}{\tau_\mathrm{fr}^\star}, \qquad \epsilon = \frac{\delta}{\lambda^\star} = \frac{\tau_\mathrm{la}^\star}{\tau_\mathrm{fr}^\star}. \tag{13}$$

The kinetic scaling introduced in [6] reads

$$\epsilon_\mathrm{ph} = \epsilon \ll 1. \tag{14}$$

This means that the effective range δ of the potential, which is also the effective range of the gas-phonon interactions, is much shorter than the characteristic mean free path $\lambda^\star$. Therefore, the molecules trapped by the potential and interacting with the phonons form a thin layer, which may be called the physisorbate layer, in the scale of the mean free path. Equation (14) also indicates that the characteristic time for gas-phonon interactions $\tau_\mathrm{ph}^\star$

is the same as the transit time across the layer $\tau_{\rm la}^\star$ and is much smaller than the mean free time $\tau_{\rm fr}^\star$. The parameter setting (14) may be the simplest *kinetic scaling* for the present model of the physisorbate layer. This differs from the *fluid scaling* used in the derivation of fluid-type boundary conditions [5, 2, 3, 4].

In summary, we obtain the dimensionless version of (3) in the following form:

$$\frac{\partial \hat{f}}{\partial \hat{t}} + \hat{\boldsymbol{c}}_\parallel \cdot \frac{\partial \hat{f}}{\partial \hat{\boldsymbol{x}}_\parallel} + \hat{c}_z \frac{\partial \hat{f}}{\partial \hat{z}} - \frac{1}{\epsilon} \frac{\mathrm{d}\hat{W}}{\mathrm{d}\zeta} \frac{\partial \hat{f}}{\partial \hat{c}_z} = \frac{1}{\epsilon} \hat{J}_{\rm ph}(\hat{f}) + \hat{J}(\hat{f}, \hat{f}), \tag{15}$$

where $\hat{\boldsymbol{c}}_\parallel = (\hat{c}_x, \hat{c}_y)$ and $\hat{\boldsymbol{x}}_\parallel = (\hat{x}, \hat{y})$. By taking the limit $\zeta \to \infty$ of (15), we recover the dimensionless version of the Boltzmann equation (8) in the gas phase, i.e.

$$\frac{\partial \hat{f}_{\rm g}}{\partial \hat{t}} + \hat{\boldsymbol{c}} \cdot \frac{\partial \hat{f}_{\rm g}}{\partial \hat{\boldsymbol{x}}} = \hat{J}(\hat{f}_{\rm g}, \hat{f}_{\rm g}). \tag{16}$$

2.3 Physisorbate layer and boundary condition for Boltzmann equation

In order to investigate the physisorbate layer, we assume

$$\hat{f} = \hat{f}(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \zeta, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z), \tag{17}$$

because $\zeta = z/\delta = \hat{z}/\epsilon$ is the appropriate normal coordinate for the layer. Then, (15) is recast as

$$\epsilon \left(\frac{\partial \hat{f}}{\partial \hat{t}} + \hat{\boldsymbol{c}}_\parallel \cdot \frac{\partial \hat{f}}{\partial \hat{\boldsymbol{x}}_\parallel} \right) + \hat{c}_z \frac{\partial \hat{f}}{\partial \zeta} - \frac{\mathrm{d}\hat{W}}{\mathrm{d}\zeta} \frac{\partial \hat{f}}{\partial \hat{c}_z} = \hat{J}_{\rm ph}(\hat{f}) + \epsilon \hat{J}(\hat{f}, \hat{f}). \tag{18}$$

This form suggests that $\hat{f}$ and thus $\hat{f}_{\rm g}$ be expanded as $\hat{f} = \hat{f}^{\langle 0 \rangle} + O(\epsilon)$ and $\hat{f}_{\rm g} = \hat{f}_{\rm g}^{\langle 0 \rangle} + O(\epsilon)$, respectively. It is obvious that $\hat{f}_{\rm g}^{\langle 0 \rangle}$ is also governed by the Boltzmann equation (16). In the following, we consider only the zeroth order terms in ϵ and identify $\hat{f}^{\langle 0 \rangle}$ and $\hat{f}_{\rm g}^{\langle 0 \rangle}$ with $\hat{f}$ and $\hat{f}_{\rm g}$, respectively (or equivalently, we omit the superscript $\langle 0 \rangle$). From (18), (11), and (12), the equation for the zeroth order is obtained as

$$\hat{c}_z \frac{\partial \hat{f}}{\partial \zeta} - \frac{\mathrm{d}\hat{W}(\zeta)}{\mathrm{d}\zeta} \frac{\partial \hat{f}}{\partial \hat{c}_z} = \frac{1}{\hat{\tau}_{\rm ph}(\zeta)} (\hat{n}\hat{M} - \hat{f}), \tag{19}$$

where $\hat{n}$ and $\hat{M}$ are given by (12a) and (12b), respectively. Note that $\hat{n}$ here is the zeroth-order number density in the physisorbate layer. Equation (19) is the kinetic equation governing the physisorbate layer that will be investigated in the following.

Integrating both sides of (19) with respect to $\hat{\boldsymbol{c}}$ over the whole space, we have $(\partial/\partial\zeta) \int_{\mathbf{R}^3} \hat{c}_z \hat{f} \mathrm{d}\hat{\boldsymbol{c}} = 0$, which leads to

$$\int_{\mathbf{R}^3} \hat{c}_z \hat{f} \mathrm{d}\hat{\boldsymbol{c}} = 0, \tag{20}$$

because $\hat{f} \to 0$ as $\zeta \to 0$. This indicates the particle conservation.

As discussed in [6], the connection condition between the inner physisorbate layer and the outer gas domain at the zeroth order is given by

$$\hat{f}(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \zeta \to \infty, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z) = \hat{f}_{\rm g}(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \hat{z} = 0, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z). \tag{21}$$

Note that $\hat{f}_{\rm g}$ and thus (16) have been extended to the crystal surface $\hat{z} = 0$. Condition (21) means physically that the outer edge of the inner physisorbate layer may be identified with the solid surface for the outer gas domain (see [6] for a more quantitative argument).

As pointed out in [6], (19) is likely to have a unique solution when $\hat{f}$ for the molecules toward the surface ($\hat{c}_z < 0$) is imposed at infinity, that is,

$$\hat{f}(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \zeta, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z) \to \hat{f}_\infty(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z), \quad \text{as} \quad \zeta \to \infty, \quad \text{for} \quad \hat{c}_z < 0, \tag{22}$$

where $\hat{f}_\infty$ is an arbitrary function of $\hat{t}$, $\hat{\boldsymbol{x}}_\parallel$, $\hat{\boldsymbol{c}}_\parallel$, and $\hat{c}_z$ consistent with $\hat{f}_{\rm g}$ at $\hat{z} = 0$. This property, which has been confirmed numerically in [6], will be established mathematically in Sec. 3.

Thus, the kinetic equation (19) with the boundary condition (22) determines the solution $\hat{f}$ and thus $\hat{f}$ for $\hat{c}_z > 0$ at infinity, and this constitutes the physisorbate-layer problem. This means that the solution defines the operator Λ that maps $\hat{f}$ for $\hat{c}_z < 0$ to $\hat{f}$ for $\hat{c}_z > 0$ at infinity, i.e.,

$$\hat{f}(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \zeta \to \infty, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z > 0) = \Lambda \hat{f}(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \zeta \to \infty, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z < 0), \tag{23}$$

or equivalently, because of (21),

$$\hat{f}_{\rm g}(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \hat{z} = 0, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z > 0) = \Lambda \hat{f}_{\rm g}(\hat{t}, \hat{\boldsymbol{x}}_\parallel, \hat{z} = 0, \hat{\boldsymbol{c}}_\parallel, \hat{c}_z < 0). \tag{24}$$

This relation indicates that the operator Λ provides the boundary condition for the Boltzmann equation on the surface $\hat{z} = 0$.

2.4 Half-space problem for the physisorbate layer

Equation (19) and boundary condition (22) form a boundary-value problem in the half space $\zeta > 0$. In this subsection, the problem will be transformed into some different forms for later convenience. Since the variables $\hat{t}$ and $\hat{\boldsymbol{x}}_\parallel$ are just the parameters, we will omit them hereafter.

Here, we simplify some notations for convenience in the mathematical arguments in Sec. 3. To be more specific, we omit the hat $\hat{}$ for the dimensionless variables and the subscript ph of $\hat{\tau}_{\rm ph}$, that is,

$$(\hat{f},\, \hat{\boldsymbol{c}}_\parallel,\, \hat{c}_z,\, \hat{W},\, \hat{\tau}_{\rm ph},\, \hat{n},\, \hat{M},\, \hat{f}_\infty,\, \hat{W}_{\rm min}) \Rightarrow (f,\, \boldsymbol{c}_\parallel,\, c_z,\, W,\, \tau,\, n,\, M,\, f_\infty,\, W_{\rm min}). \tag{25}$$

No confusion is expected with these changes. Then, the half-space problem (19) and (22) reads as follows:

$$c_z \frac{\partial f}{\partial \zeta} - \frac{{\rm d}W(\zeta)}{{\rm d}\zeta} \frac{\partial f}{\partial c_z} = \frac{1}{\tau(\zeta)}(nM - f), \tag{26a}$$

$$n = \int_{\mathbf{R}^3} f {\rm d}\boldsymbol{c}, \tag{26b}$$

$$M = (2\pi)^{-3/2} \exp\left(-|\boldsymbol{c}|^2/2\right), \tag{26c}$$

$$f \to f_\infty(\boldsymbol{c}_\parallel, c_z), \quad \text{for} \quad c_z < 0, \quad \text{as} \quad \zeta \to \infty. \tag{26d}$$

If we introduce the marginal

$$F(\zeta, c_z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\zeta, \boldsymbol{c}_\parallel, c_z) {\rm d}c_x {\rm d}c_y, \tag{27}$$

and integrate (26) with respect to c_x and c_y each from $-\infty$ to ∞, we obtain the following half-space problem for $F(\zeta, c_z)$:

$$c_z \frac{\partial F(\zeta, c_z)}{\partial \zeta} - \frac{\mathrm{d}W(\zeta)}{\mathrm{d}\zeta} \frac{\partial F(\zeta, c_z)}{\partial c_z} = \frac{1}{\tau(\zeta)}[n(\zeta)\mathcal{M}(c_z) - F(\zeta, c_z)], \tag{28a}$$

$$n(\zeta) = \int_{-\infty}^{\infty} F(\zeta, c_z)\mathrm{d}c_z, \tag{28b}$$

$$\mathcal{M}(c_z) = (2\pi)^{-1/2} \exp\left(-c_z^2/2\right), \tag{28c}$$

$$F(\zeta, c_z) \to F_\infty(c_z), \quad \text{for } c_z < 0, \quad \text{as } \zeta \to \infty, \tag{28d}$$

where $F_\infty(c_z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_\infty(\boldsymbol{c}_\parallel, c_z)\mathrm{d}c_x\mathrm{d}c_y$.

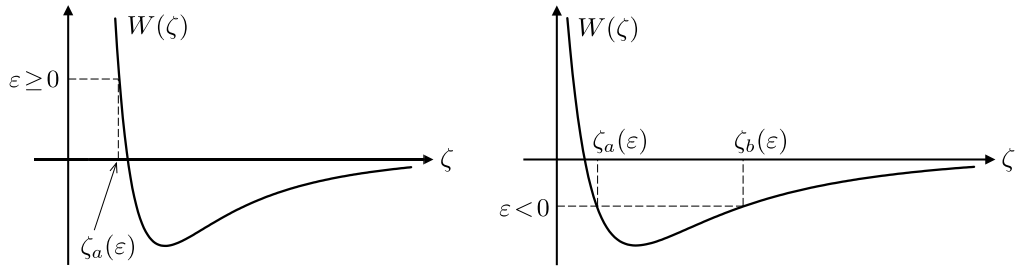
Now, let us put

$$\varepsilon = \frac{1}{2}c_z^2 + W(\zeta). \tag{29}$$

Then, for each $\varepsilon \in [W_{\min}, \infty)$, the range of ζ is as follows:

$$\begin{cases} [\zeta_a(\varepsilon),\ \infty) & \text{for } \varepsilon \geq 0, \\ [\zeta_a(\varepsilon),\ \zeta_b(\varepsilon)] & \text{for } W_{\min} \leq \varepsilon < 0, \end{cases} \tag{30}$$

where $\zeta_a(\varepsilon)$ is the solution of $\varepsilon = W(\zeta)$ for $\varepsilon \geq 0$, and $\zeta_a(\varepsilon)$ and $\zeta_b(\varepsilon)$ are the two solutions of the same equation satisfying $\zeta_a(\varepsilon) \leq \zeta_{\min} \leq \zeta_b(\varepsilon)$ for $W_{\min} \leq \varepsilon < 0$. The locations of $\zeta_a(\varepsilon)$ and $\zeta_b(\varepsilon)$ are shown schematically in Fig. 2.



(a) (b)

Figure 2: The locations of $\zeta_a(\varepsilon)$ and $\zeta_b(\varepsilon)$. (a) $\varepsilon \geq 0$, (b) $W_{\min} \leq \varepsilon < 0$.

Using (29), we transform the independent variables from (ζ, c_z) to (ζ, ε) and define

$$F_\pm(\zeta, \varepsilon) = F\left(\zeta, \pm\sqrt{2[\varepsilon - W(\zeta)]}\right). \tag{31}$$

Note that F_+ corresponds to $c_z > 0$, and F_- to $c_z < 0$. Then, the problem (28) is transformed to

$$\pm\sqrt{2[\varepsilon - W(\zeta)]} \frac{\partial F_\pm(\zeta, \varepsilon)}{\partial \zeta} = \frac{1}{\tau(\zeta)}\left[n(\zeta)\mathcal{M}(\zeta, \varepsilon) - F_\pm(\zeta, \varepsilon)\right], \tag{32a}$$

$$n(\zeta) = \int_{W(\zeta)}^{\infty} [F_-(\zeta, \varepsilon) + F_+(\zeta, \varepsilon)] \frac{\mathrm{d}\varepsilon}{\sqrt{2[\varepsilon - W(\zeta)]}}, \tag{32b}$$

$$\mathcal{M}(\zeta, \varepsilon) = (2\pi)^{-1/2} \exp\left(-\varepsilon + W(\zeta)\right), \tag{32c}$$

$$F_-(\zeta, \varepsilon) \to F_\infty(-\sqrt{2\varepsilon}), \quad \text{for } \varepsilon > 0, \quad \text{as } \zeta \to \infty, \tag{32d}$$

where $\mathcal{M}(\zeta,\varepsilon)$ is the expression of $\mathcal{M}(c_z)$ in (28c) in terms of ζ and ε. In addition, we need to assume the continuity condition

$$F_+\left(\zeta_a(\varepsilon),\varepsilon\right) = F_-\left(\zeta_a(\varepsilon),\varepsilon\right), \quad \text{for} \ \ \varepsilon > W_{\min}, \tag{33a}$$

$$F_-\left(\zeta_b(\varepsilon),\varepsilon\right) = F_+\left(\zeta_b(\varepsilon),\varepsilon\right), \quad \text{for} \ \ W_{\min} < \varepsilon < 0, \tag{33b}$$

at $\zeta = \zeta_a(\varepsilon)$ and $\zeta_b(\varepsilon)$ to complete the half-space problem in the new variables (ζ,ε). The conditions (33a) and (33b) are natural because the molecules with energy ε reaching the points $\zeta = \zeta_a(\varepsilon)$ and $\zeta_b(\varepsilon)$ stop ($c_z = 0$) there and then change the direction of motion.

In the problem (28) or (32), the dependence on c_x and c_y has been averaged out because of (27). However, once the solution $F(\zeta, c_z)$ or $F_\pm(\zeta,\varepsilon)$ is obtained, the density $n(\zeta)$ is also known. Therefore, (26a) reduces to a PDE, which can be solved in response to the boundary condition (26d). Therefore, the problem (26) and the problem (28) or (32) are equivalent. Here, we note that $[F_\pm(\zeta,\varepsilon),\, W(\zeta),\, n(\zeta),\, \mathcal{M}(\zeta,\varepsilon),\, F_\infty(-\sqrt{2\varepsilon}),\, \tau(\zeta)]$ in this subsection are equal to $[\phi_\pm(\zeta,\varepsilon),\, \hat{\mathrm{W}}(\zeta),\, \hat{\mathsf{n}}(\zeta),\, \hat{\mathrm{M}}_{\mathrm{m}}(\zeta,\varepsilon),\, \phi_\infty(-\sqrt{2\varepsilon}),\, \hat{\tau}_{\mathrm{ph}}(\zeta)]$ in Sec. VI A in [6].

2.5 Iteration scheme

On the basis of (32), the following iteration scheme is defined:

$$\pm\sqrt{2[\varepsilon - W(\zeta)]}\,\frac{\partial F_\pm^k(\zeta,\varepsilon)}{\partial\zeta} = \frac{1}{\tau(\zeta)}\left[n^{k-1}(\zeta)\mathcal{M}(\zeta,\varepsilon) - F_\pm^k(\zeta,\varepsilon)\right], \tag{34a}$$

$$n^k(\zeta) = \int_{W(\zeta)}^{\infty} [F_-^k(\zeta,\varepsilon) + F_+^k(\zeta,\varepsilon)]\frac{\mathrm{d}\varepsilon}{\sqrt{2[\varepsilon - W(\zeta)]}}, \tag{34b}$$

$$F_-^k(\zeta,\varepsilon) \to F_\infty(-\sqrt{2\varepsilon}), \quad \text{for} \ \ \varepsilon > 0, \quad \text{as} \ \ \zeta \to \infty, \tag{34c}$$

$$F_+^k\left(\zeta_a(\varepsilon),\varepsilon\right) = F_-^k\left(\zeta_a(\varepsilon),\varepsilon\right), \quad \text{for} \ \ \varepsilon > W_{\min}, \tag{34d}$$

$$F_-^k\left(\zeta_b(\varepsilon),\varepsilon\right) = F_+^k\left(\zeta_b(\varepsilon),\varepsilon\right), \quad \text{for} \ \ W_{\min} < \varepsilon < 0, \tag{34e}$$

where $F_\pm^k$ and n^k are the kth iteration corresponding to $F_\pm$ and n, respectively. This scheme, starting from the zero initial values, i.e.,

$$F_\pm^0 = n^0 = 0, \tag{35}$$

will be used in the proofs in Sec. 3. In [6], essentially the same scheme with different initial values has been used in the numerical analysis of the problem (32), as well as in the construction of a model of the boundary condition for the Boltzmann equation.

From (34), $F_\pm^k$ can be solved in terms of n^{k-1} as follows:

$$F_+^k(\zeta,\varepsilon) = \theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\Bigg(F_-^k(\zeta_a(\varepsilon),\varepsilon) + \int_{\zeta_a(\varepsilon)}^{\zeta} \theta(s,\zeta_a(\varepsilon);\varepsilon)\frac{n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\Bigg), \tag{36a}$$

$$\begin{aligned} F_-^k(\zeta,\varepsilon) = {} & \mathbf{1}_{\varepsilon>0}\,\theta(\zeta,\infty;\varepsilon)\Bigg(F_\infty(-\sqrt{2\varepsilon}) + \int_{\zeta}^{\infty} \theta(\infty,s;\varepsilon)\frac{n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\Bigg) \\ & + \mathbf{1}_{W_{\min}<\varepsilon<0}\,\theta(\zeta,\zeta_b(\varepsilon);\varepsilon)\Bigg(F_+^k(\zeta_b(\varepsilon),\varepsilon) + \int_{\zeta}^{\zeta_b(\varepsilon)} \theta(\zeta_b(\varepsilon),s;\varepsilon)\frac{n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\Bigg), \end{aligned} \tag{36b}$$

where

$$\theta(a,b;\varepsilon) = \exp\left(-\int_a^b \frac{\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\right), \tag{37}$$

and $\mathbf{1}_{\mathcal{S}}$ is the indicator function of the set $\mathcal{S}$, that is, $\mathbf{1}_{\mathcal{S}} = 1$ for $w \in \mathcal{S}$ and $\mathbf{1}_{\mathcal{S}} = 0$ for $w \notin \mathcal{S}$ with w being the relevant variable. It should be noted that $F_-^k(\zeta,\varepsilon)$ and thus $F_+^k(\zeta,\varepsilon)$ are generally discontinuous at $\varepsilon = 0$, i.e., $\lim_{\varepsilon\to 0^-} F_\pm^k(\zeta,\varepsilon) \neq \lim_{\varepsilon\to 0^+} F_\pm^k(\zeta,\varepsilon)$. If necessary, the value of $F_\pm(\zeta,\varepsilon)$ at $\varepsilon = 0$ may naturally be defined by $\lim_{\varepsilon\to 0^+} F_\pm(\zeta,\varepsilon)$. We should also note that $\mathbf{1}_{\varepsilon>0}$ and $\mathbf{1}_{W_{\min}<\varepsilon<0}$ in (36) implicitly mean $\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}$ and $\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}$, respectively, since the range of ζ is given by (30). This convention will be used unless confusion arises.

One easily checks that

$$\theta(a,b;\varepsilon)\,\theta(b,c;\varepsilon) = \theta(a,c;\varepsilon), \qquad \theta(b,a;\varepsilon) = \theta(a,b;\varepsilon)^{-1}, \tag{38a}$$

$$a < b \implies 0 < \theta(a,b;\varepsilon) < 1, \qquad a > b \implies \theta(a,b;\varepsilon) > 1. \tag{38b}$$

On the other hand, defining

$$\mu(s,\varepsilon) := \frac{1}{\tau(s)\sqrt{2[\varepsilon - W(s)]}} > 0, \tag{39}$$

one readily obtains

$$\partial_a\theta(a,b;\varepsilon) = \theta(a,b;\varepsilon)\mu(a,\varepsilon), \qquad \partial_b\theta(a,b;\varepsilon) = -\theta(a,b;\varepsilon)\mu(b,\varepsilon). \tag{40}$$

These properties of the function $\theta(a,b;\varepsilon)$ will be used repeatedly in Sec. 3.

3 Mathematical properties of half-space problem for the physisorbate layer

In this section, we prove some mathematical properties of the half-space problem (28) for the physisorbate layer. The structure of the problem differs from that of the traditional half-space problems of the linearized Boltzmann equation relevant to Knudsen layers [7, 21, 8] in the following points:

(a) the gas molecules are subject to an external attractive-repulsive potential;

(b) the gas molecules interact only with phonons;

(c) there are no gas molecules on the surface $\zeta = 0$ because of the infinite potential barrier there.

Before getting to the main points, we recall here that the potential $W(\zeta)$ and the relaxation time $\tau(\zeta)$ appearing in this section are, respectively, assumed to satisfy the dimensionless version of the conditions (2) and (i)–(iv) in Sec. 2.1 and that of the conditions (7), (v), and (vi) there. We note that the property (c), which has been used in deriving (20), is a physical consequence from the assumption (2) for the potential. In this section, we consider the class of solutions to the problem (28) satisfying the property (c) (cf. Theorem 1 below).

3.1 Main results

The main results are stated as follows:

Theorem 1. *Assume that* $0 \le F_\infty(c_z) \le (A/\sqrt{2\pi})\exp(-c_z^2/2)$ *for some positive constant* A. *Then, the problem* (28) *has the unique solution satisfying the inequality* $0 \le F(\zeta, c_z) \le C(1/\sqrt{2\pi})\exp\left(-c_z^2/2 - W(\zeta)\right)$ *for some constant* C. *Moreover, the limit* $\lim_{\zeta\to+\infty} F(\zeta, c_z)$ *exists for* $c_z > 0$.

In fact, the resulting inequality for $F(\zeta, c_z)$ indicates that $F(\zeta, c_z)$ enjoys the property (c) because $\lim_{\zeta\to 0^+}\exp\left(-c_z^2/2 - W(\zeta)\right) = 0$. The existence in Theorem 1 is proved for the transformed problem (32) and (33), rather than the problem (28), with the help of the iteration scheme in Sec. 2.5. It is shown that the sequences $\{n^k\}$ and $\{F_\pm^k\}$, based on (34) and (35), converge exponentially fast with respect to the number of iteration k. Let

$$\ell = \int_0^\infty \frac{\mathrm{d}s}{\tau(s)} < +\infty, \qquad K = \frac{\sqrt{2}\zeta_{\min}}{\tau(0)} + \frac{\ell}{\sqrt{2}}.$$

Then, we have the following:

Theorem 2. *Under the same conditions as in Theorem 1, i.e.,* $0 \le F_\infty(-\sqrt{2\varepsilon}) \le (A/\sqrt{2\pi})\exp(-\varepsilon)$, *the sequence* $\{n^k\}$ *is nonnegative, nondecreasing in* k, *and converges exponentially fast to its limit* $n\,(\ge 0)$ *as* $k \to \infty$ *in* $L^1\left(\mathbf{R}^+; \mathrm{d}\zeta/\tau(\zeta)\right)$:

$$\|n - n^k\|_{L^1(\mathbf{R}^+;\mathrm{d}\zeta/\tau(\zeta))} = \int_0^\infty |n(\zeta) - n^k(\zeta)|\frac{\mathrm{d}\zeta}{\tau(\zeta)} < A\ell e^{|W_{\min}|}\mathcal{L}^k,$$

where

$$0 \le \mathcal{L} \le 1 - \frac{e^{-K}}{\sqrt{\pi}}\int_{|W_{\min}|+1}^\infty \frac{e^{-u}}{\sqrt{u}}\mathrm{d}u < 1.$$

In addition, the sequence $\{F_\pm^k\}$ *is nonnegative, nondecreasing in* k, *and converges exponentially fast as* $k \to \infty$ *in* $L^1\left(\mathbf{R}^+ \times \mathbf{R}; \mathbf{1}_{\varepsilon > W(\zeta)}\mathrm{d}\varepsilon\mathrm{d}\zeta/\tau(\zeta)\sqrt{2[\varepsilon - W(\zeta)]}\right)$ *to their limits*

$F_\pm\,(\geq 0)$:

$$\begin{aligned}
&\|F_+ - F_+^k\|_{L^1\left(\mathbf{R}^+\times\mathbf{R};\mathbf{1}_{\varepsilon>W(\zeta)}\mathrm{d}\varepsilon\mathrm{d}\zeta/\tau(\zeta)\sqrt{2[\varepsilon-W(\zeta)]}\right)}\\
&\quad + \|F_- - F_-^k\|_{L^1\left(\mathbf{R}^+\times\mathbf{R};\mathbf{1}_{\varepsilon>W(\zeta)}\mathrm{d}\varepsilon\mathrm{d}\zeta/\tau(\zeta)\sqrt{2[\varepsilon-W(\zeta)]}\right)}\\
&= \int_0^\infty\int_{-\infty}^\infty \left[|F_+(\zeta,\varepsilon) - F_+^k(\zeta,\varepsilon)| + |F_-(\zeta,\varepsilon) - F_-^k(\zeta,\varepsilon)|\right]\frac{\mathbf{1}_{\varepsilon>W(\zeta)}\mathrm{d}\varepsilon\mathrm{d}\zeta}{\tau(\zeta)\sqrt{2[\varepsilon-W(\zeta)]}}\\
&< A\ell e^{|W_{\min}|}\mathcal{L}^k.
\end{aligned}$$

3.2 Proof of uniqueness

Here, we prove the uniqueness in Theorem 1.

Lemma 1. *If the problem* (28) *has a solution* $F(\zeta,c_z)$ *satisfying the inequality* $|F(\zeta,c_z)|\leq Ce^{-W(\zeta)}\mathcal{M}(c_z)$ *for some constant* C*, then the solution is unique.*

Proof. Let us denote $\partial_\zeta = \partial/\partial\zeta$, $\partial_{c_z} = \partial/\partial c_z$, $G'(\zeta) = \mathrm{d}G(\zeta)/\mathrm{d}\zeta$, where $G(\zeta)$ is an arbitrary function of ζ, and

$$E(\zeta,c_z) = e^{-W(\zeta)}\mathcal{M}(c_z).$$

This is indeed a modified Maxwellian that is a natural equilibrium solution to the layer equation (28a). By linearity of the problem (28), it suffices to consider the problem with $F_\infty(c_z)=0$ and to prove that the only possible solution satisfying the condition $|F(\zeta,c_z)|\leq CE(\zeta,c_z)$ is $F(\zeta,c_z)=0$.

If we multiply both sides of (28a) by $F(\zeta,c_z)/E(\zeta,c_z)$ and take account of the relations $\partial_\zeta[1/E(\zeta,c_z)] = W'(\zeta)/E(\zeta,c_z)$ and $\partial_{c_z}[1/E(\zeta,c_z)] = c_z/E(\zeta,c_z)$, we have

$$\begin{aligned}
&\partial_\zeta\left(\frac{1}{2}c_z\frac{F(\zeta,c_z)^2}{E(\zeta,c_z)}\right) - \partial_{c_z}\left(\frac{1}{2}W'(\zeta)\frac{F(\zeta,c_z)^2}{E(\zeta,c_z)}\right)\\
&\qquad = \frac{e^{W(\zeta)}}{\tau(\zeta)}\left(n(\zeta)F(\zeta,c_z) - \frac{F(\zeta,c_z)^2}{\mathcal{M}(c_z)}\right).
\end{aligned}\tag{41}$$

Integrating this equation with respect to ζ and c_z over $(0,+\infty)$ and $(-\infty,+\infty)$, respectively, leads to

$$\begin{aligned}
&\left[\int_{-\infty}^\infty \frac{1}{2}c_z\frac{F(\zeta,c_z)^2}{E(\zeta,c_z)}\mathrm{d}c_z\right]_{\zeta=0}^{\zeta=+\infty} - \left[\int_0^\infty \frac{1}{2}W'(\zeta)\frac{F(\zeta,c_z)^2}{E(\zeta,c_z)}\mathrm{d}\zeta\right]_{c_z=-\infty}^{c_z=+\infty}\\
&\qquad = \int_0^\infty \frac{e^{W(\zeta)}}{\tau(\zeta)}\left(n(\zeta)^2 - \int_{-\infty}^\infty \frac{F(\zeta,c_z)^2}{\mathcal{M}(c_z)}\mathrm{d}c_z\right)\mathrm{d}\zeta.
\end{aligned}\tag{42}$$

Because $0\leq F(\zeta,c_z)^2/E(\zeta,c_z) < C^2e^{-W(\zeta)}\mathcal{M}(c_z)$, we find

$$\left|\int_{-\infty}^\infty \frac{1}{2}c_z\frac{F(\zeta,c_z)^2}{E(\zeta,c_z)}\mathrm{d}c_z\right| \leq C^2e^{-W(\zeta)}\int_{-\infty}^\infty \frac{1}{2}|c_z|\mathcal{M}(c_z)\mathrm{d}c_z \to 0,$$

as $\zeta\to 0^+$ and

$$\left|\int_0^\infty \frac{1}{2}W'(\zeta)\frac{F(\zeta,c_z)^2}{E(\zeta,c_z)}\mathrm{d}\zeta\right| \leq C^2\mathcal{M}(c_z)\int_0^\infty \frac{1}{2}|W'(\zeta)|e^{-W(\zeta)}\mathrm{d}\zeta \to 0,$$

as $|c_z| \to +\infty$. In addition, since $F_\infty(c_z) = 0$, it follows that

$$\lim_{\zeta\to+\infty} \int_{-\infty}^{\infty} \frac{1}{2} c_z \frac{F(\zeta, c_z)^2}{E(\zeta, c_z)} \mathrm{d}c_z = \lim_{\zeta\to+\infty} \int_{0}^{\infty} \frac{1}{2} c_z \frac{F(\zeta, c_z)^2}{E(\zeta, c_z)} \mathrm{d}c_z \geq 0.$$

Therefore, with the help of (28b) and $\int_{-\infty}^{\infty} \mathcal{M}(c_z)\mathrm{d}c_z = 1$, (42) gives

$$\mathcal{I} := \int_0^\infty \frac{e^{W(\zeta)}}{\tau(\zeta)} \left[\Big(\int_{-\infty}^{\infty} F(\zeta, c_z)\mathrm{d}c_z \Big)^2 - \int_{-\infty}^{\infty} \mathcal{M}(c_z)\mathrm{d}c_z \int_{-\infty}^{\infty} \frac{F(\zeta, c_z)^2}{\mathcal{M}(c_z)} \mathrm{d}c_z \right] \mathrm{d}\zeta \geq 0.$$

On the other hand, it follows from the Cauchy–Schwarz inequality that

$$\mathcal{I} \leq 0.$$

This means that we are in the equality case in the Cauchy–Schwarz inequality for a.e. $\zeta > 0$, so that $F(\zeta, \cdot)$ must be proportional to $\mathcal{M}$:

$$F(\zeta, c_z) = c(\zeta)\mathcal{M}(c_z), \quad \text{so that} \quad c(\zeta) = n(\zeta) = \int_{-\infty}^{\infty} F(\zeta, c_z)\mathrm{d}c_z.$$

The substitution of this form into (28a) leads to

$$c_z \mathcal{M}(c_z)[n'(\zeta) + W'(\zeta)n(\zeta)] = 0,$$

which gives

$$n(\zeta) = Be^{-W(\zeta)},$$

for some constant B. Therefore, letting $\zeta \to +\infty$, one finds that

$$F(\zeta, c_z) = Be^{-W(\zeta)}\mathcal{M}(c_z) \to B\mathcal{M}(c_z), \quad \text{as } \zeta \to +\infty,$$

since $W(\zeta) \to 0$ as $\zeta \to +\infty$. Then, the boundary condition (28d) with $F_\infty(c_z) = 0$ implies that $B = 0$, so that we have $F(\zeta, c_z) = 0$. □

3.3 Proof of existence

In this section, we prove the existence of the solution and its limit as $\zeta \to \infty$ in Theorem 1. The existence proof is based on the approximating sequence $\{F_\pm^k\}$ constructed by (36) with (35).

3.3.1 Computing $F_\pm^k(\zeta_a(\varepsilon), \varepsilon)$ and $F_\pm^k(\zeta_b(\varepsilon), \varepsilon)$

In the case where $\varepsilon > 0$, one obtains from (36b) and (34d)

$$\begin{aligned}
&F_\pm^k(\zeta_a(\varepsilon), \varepsilon) \\
&\quad = \theta(\zeta_a(\varepsilon), \infty; \varepsilon) F_\infty(-\sqrt{2\varepsilon}) + \int_{\zeta_a(\varepsilon)}^{\infty} \theta(\zeta_a(\varepsilon), s; \varepsilon) \frac{n^{k-1}(s)\mathcal{M}(s, \varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}} \\
&\quad = \theta(\zeta_a(\varepsilon), \infty; \varepsilon) F_\infty(-\sqrt{2\varepsilon}) + \int_{\zeta_a(\varepsilon)}^{\infty} \theta(\zeta_a(\varepsilon), s; \varepsilon) \mu(s, \varepsilon) n^{k-1}(s)\mathcal{M}(s, \varepsilon)\mathrm{d}s \\
&\quad = \theta(\zeta_a(\varepsilon), \infty; \varepsilon) F_\infty\left(-\sqrt{2\varepsilon}\right) - \int_{\zeta_a(\varepsilon)}^{\infty} \partial_s \theta(\zeta_a(\varepsilon), s; \varepsilon) n^{k-1}(s)\mathcal{M}(s, \varepsilon)\mathrm{d}s. \qquad (43)
\end{aligned}$$

On the other hand, if $W_{\min} < \varepsilon < 0$, we first use (36b) to compute

$$F_-^k(\zeta_a(\varepsilon),\varepsilon) = \theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)\Bigg(F_+^k(\zeta_b(\varepsilon),\varepsilon) + \int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \theta(\zeta_b(\varepsilon),s;\varepsilon)\frac{n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\Bigg),$$

and then inject in the r.h.s. the following expression of $F_+^k(\zeta_b(\varepsilon),\varepsilon)$, obtained from (36a):

$$F_+^k(\zeta_b(\varepsilon),\varepsilon) = \theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)\Bigg(F_-^k(\zeta_a(\varepsilon),\varepsilon) + \int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \theta(s,\zeta_a(\varepsilon);\varepsilon)\frac{n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\Bigg).$$

This leads us to the equality

$$\begin{aligned} &F_\pm^k(\zeta_a(\varepsilon),\varepsilon)[1-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)^2] \\ &\quad = \theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \theta(\zeta_b(\varepsilon),s;\varepsilon)\mu(s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s \\ &\quad + \theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)^2\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \theta(s,\zeta_a(\varepsilon);\varepsilon)\mu(s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s, \end{aligned} \tag{44}$$

with the help of (34d) and (39). Likewise

$$\begin{aligned} &F_\pm^k(\zeta_b(\varepsilon),\varepsilon)[1-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)^2] \\ &\quad = \theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \theta(s,\zeta_a(\varepsilon);\varepsilon)\mu(s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s \\ &\quad + \theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)^2\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \theta(\zeta_b(\varepsilon),s;\varepsilon)\mu(s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s, \end{aligned} \tag{45}$$

with the help of (34e) and (39).

Equation (44) can be recast as follows: for $W_{\min} < \varepsilon < 0$,

$$\begin{aligned} &F_\pm^k(\zeta_a(\varepsilon),\varepsilon)\,\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)\,[\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon) - \theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)] \\ &\quad = \theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} [-\partial_s\theta(\zeta_b(\varepsilon),s;\varepsilon) \\ &\qquad\qquad + \partial_s\theta(s,\zeta_b(\varepsilon);\varepsilon)]n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s, \end{aligned}$$

or, equivalently,

$$F_\pm^k(\zeta_a(\varepsilon),\varepsilon) = \int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \tfrac{\partial_s\theta(s,\zeta_b(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_b(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)} n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s. \tag{46}$$

Similarly, (45) leads to the following expression: for $W_{\min} < \varepsilon < 0$,

$$F_\pm^k(\zeta_b(\varepsilon),\varepsilon) = \int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \tfrac{\partial_s\theta(s,\zeta_a(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_a(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)} n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s. \tag{47}$$

One easily checks that

$$\frac{\partial_s\theta(s,\zeta_b(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_b(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)} \geq 0, \quad \frac{\partial_s\theta(s,\zeta_a(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_a(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)} \geq 0,$$

and

$$\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \frac{\partial_s\theta(s,\zeta_b(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_b(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}\mathrm{d}s = 1,$$
$$\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \frac{\partial_s\theta(s,\zeta_a(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_a(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}\mathrm{d}s = 1.$$

Thus $F_\pm^k(\zeta_a(\varepsilon),\varepsilon)$ and $F_\pm^k(\zeta_b(\varepsilon),\varepsilon)$ are averages of $n^{k-1}(s)\mathcal{M}(s,\varepsilon)$ for $s\in[\zeta_a(\varepsilon),\zeta_b(\varepsilon)]$.

3.3.2 Simplifying the formulas (36)

Next we plug (43), (46), and (47) in (36). Then, (36a) leads to

$$\begin{aligned}
F_+^k(\zeta,\varepsilon) &= \theta(\zeta_a(\varepsilon),\zeta;\varepsilon)F_-^k(\zeta_a(\varepsilon),\varepsilon) + \int_{\zeta_a(\varepsilon)}^{\zeta} \theta(s,\zeta;\varepsilon)\mu(s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s \\
&= \theta(\zeta_a(\varepsilon),\zeta;\varepsilon)F_-^k(\zeta_a(\varepsilon),\varepsilon) + \int_{\zeta_a(\varepsilon)}^{\zeta} \partial_s\theta(s,\zeta;\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s \\
&= \mathbf{1}_{\varepsilon>0}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon}) \\
&\quad - \mathbf{1}_{\varepsilon>0}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\int_{\zeta_a(\varepsilon)}^{\infty} \partial_s\theta(\zeta_a(\varepsilon),s;\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s \\
&\quad + \mathbf{1}_{W_{\min}<\varepsilon<0}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon) \\
&\qquad\qquad \times \int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} \frac{\partial_s\theta(s,\zeta_b(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_b(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)} n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s \\
&\quad + \mathbf{1}_{W(\zeta)<\varepsilon}\int_{\zeta_a(\varepsilon)}^{\zeta} \partial_s\theta(s,\zeta;\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s,
\end{aligned}$$

while (36b) is recast as

$$
\begin{aligned}
&F_-^k(\zeta,\varepsilon)\\
&\quad=\mathbf{1}_{\varepsilon>0}\,\theta(\zeta,\infty;\varepsilon)\left(F_\infty(-\sqrt{2\varepsilon})+\int_\zeta^\infty \theta(\infty,s;\varepsilon)\tfrac{n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon-W(s)]}}\right)\\
&\qquad+\mathbf{1}_{W_{\min}<\varepsilon<0}\,\theta(\zeta,\zeta_b(\varepsilon);\varepsilon)\left(F_+^k(\zeta_b(\varepsilon),\varepsilon)\right.\\
&\qquad\qquad\left.+\int_\zeta^{\zeta_b(\varepsilon)}\theta(\zeta_b(\varepsilon),s;\varepsilon)\tfrac{n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon-W(s)]}}\right)\\
&\quad=\mathbf{1}_{\varepsilon>0}\,\theta(\zeta,\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon})+\mathbf{1}_{\varepsilon>0}\int_\zeta^\infty\theta(\zeta,s;\varepsilon)\mu(s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s\\
&\qquad+\mathbf{1}_{W_{\min}<\varepsilon<0}\,\theta(\zeta,\zeta_b(\varepsilon);\varepsilon)\\
&\qquad\qquad\times\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)}\tfrac{\partial_s\theta(s,\zeta_a(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_a(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s\\
&\qquad+\mathbf{1}_{W_{\min}<\varepsilon<0}\int_\zeta^{\zeta_b(\varepsilon)}\theta(\zeta,s;\varepsilon)\mu(s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s\\
&\quad=\mathbf{1}_{\varepsilon>0}\,\theta(\zeta,\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon})-\mathbf{1}_{\varepsilon>0}\int_\zeta^\infty\partial_s\theta(\zeta,s;\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s\\
&\qquad+\mathbf{1}_{W_{\min}<\varepsilon<0}\,\theta(\zeta,\zeta_b(\varepsilon);\varepsilon)\\
&\qquad\qquad\times\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)}\tfrac{\partial_s\theta(s,\zeta_a(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_a(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s\\
&\qquad-\mathbf{1}_{W_{\min}<\varepsilon<0}\int_\zeta^{\zeta_b(\varepsilon)}\partial_s\theta(\zeta,s;\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s.
\end{aligned}
$$

Summarizing, we have proved that

$$
\begin{aligned}
F_+^k(\zeta,\varepsilon)&=\mathbf{1}_{\varepsilon>0}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon})\\
&\qquad+\int_0^\infty K_+(\zeta,s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s,
\end{aligned}\tag{48a}
$$

$$
\begin{aligned}
F_-^k(\zeta,\varepsilon)&=\mathbf{1}_{\varepsilon>0}\,\theta(\zeta,\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon})\\
&\qquad+\int_0^\infty K_-(\zeta,s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s,
\end{aligned}\tag{48b}
$$

where

$$
\begin{aligned}
K_+(\zeta,s,\varepsilon) := & -\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta_a(\varepsilon),\zeta,\varepsilon)\,\partial_s\theta(\zeta_a(\varepsilon),s,\varepsilon)\mathbf{1}_{s>\zeta_a(\varepsilon)} \\
& + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}\,\theta(\zeta_a(\varepsilon),\zeta,\varepsilon) \\
& \qquad \times \tfrac{\partial_s\theta(s,\zeta_b(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_b(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)} \\
& + \mathbf{1}_{\varepsilon>0}\partial_s\theta(s,\zeta,\varepsilon)\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta} \\
& + \mathbf{1}_{W_{\min}<\varepsilon<0}\partial_s\theta(s,\zeta,\varepsilon)\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta<\zeta_b(\varepsilon)}, \qquad (49a)
\end{aligned}
$$

$$
\begin{aligned}
K_-(\zeta,s,\varepsilon) := & -\mathbf{1}_{\varepsilon>0}\partial_s\theta(\zeta,s;\varepsilon)\mathbf{1}_{s>\zeta>\zeta_a(\varepsilon)} \\
& - \mathbf{1}_{W_{\min}<\varepsilon<0}\,\partial_s\theta(\zeta,s;\varepsilon)\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<s<\zeta_b(\varepsilon)} \\
& + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}\theta(\zeta,\zeta_b(\varepsilon);\varepsilon) \\
& \qquad \times \tfrac{\partial_s\theta(s,\zeta_a(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_a(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}. \qquad (49b)
\end{aligned}
$$

Since both position variables ζ and s appear in (49), the indicator functions for these variables, such as $\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}$, $\mathbf{1}_{s>\zeta_a(\varepsilon)}$, and $\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<s<\zeta_b(\varepsilon)}$, are shown explicitly to avoid confusion.

3.3.3 Properties of $K_\pm(\zeta,s,\varepsilon)$

Equations (39) and (40) show that $-\partial_s\theta(\zeta,s;\varepsilon)>0$ and $\partial_s\theta(s,\,\zeta;\varepsilon)>0$, so that

$$K_\pm(\zeta,s,\varepsilon)\geq 0.$$

On the other hand

$$
\begin{aligned}
&\int_0^\infty K_+(\zeta,s,\varepsilon)\mathrm{d}s \\
&\quad = \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)[1-\theta(\zeta_a(\varepsilon),\infty;\varepsilon)] \\
&\qquad + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon) \\
&\qquad + (\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}+\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)})[1-\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)],
\end{aligned}
$$

or, equivalently,

$$
\begin{aligned}
&\int_0^\infty K_+(\zeta,s,\varepsilon)\mathrm{d}s \\
&\quad = (\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}+\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)})\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon) \\
&\qquad + (\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}+\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)})[1-\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)] \\
&\qquad - \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon) \\
&\quad = \mathbf{1}_{W(\zeta)<\varepsilon} - \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon). \qquad (50)
\end{aligned}
$$

Likewise, one easily finds that

$$
\begin{aligned}
&\int_0^\infty K_-(\zeta,s,\varepsilon)\mathrm{d}s \\
&\quad = \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}[1-\theta(\zeta,\infty;\varepsilon)] \\
&\qquad + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}[1-\theta(\zeta,\zeta_b(\varepsilon);\varepsilon)] \\
&\qquad + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}\,\theta(\zeta,\zeta_b(\varepsilon);\varepsilon) \\
&\quad = \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)} + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)} - \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\theta(\zeta,\infty;\varepsilon) \\
&\quad = \mathbf{1}_{W(\zeta)<\varepsilon} - \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\theta(\zeta,\infty;\varepsilon). \qquad (51)
\end{aligned}
$$

3.3.4 Monotonicity of the approximating sequence

In this section, we seek to prove the following result for the approximating sequences $\{F_\pm^k\}$ and $\{n^k\}$ based on (34) and (35).

Lemma 2. *Assume that* $0 \le F_\infty(-\sqrt{2\varepsilon}) \le Ae^{-\varepsilon}/\sqrt{2\pi}$. *Then*

$$0 = F_\pm^0(\zeta,\varepsilon) \le F_\pm^1(\zeta,\varepsilon) \le F_\pm^2(\zeta,\varepsilon) \le \ldots \le F_\pm^k(\zeta,\varepsilon) \le \ldots \le Ae^{-\varepsilon}/\sqrt{2\pi}.$$

Therefore

$$0 = n^0(\zeta) \le n^1(\zeta) \le n^2(\zeta) \le \ldots \le n^k(\zeta) \le \ldots \le Ae^{-W(\zeta)}.$$

Proof. Since

$$\begin{aligned} F_+^{k+1}(\zeta,\varepsilon) - F_+^k(\zeta,\varepsilon) &= \int_0^\infty K_+(\zeta,s,\varepsilon)[n^k(s) - n^{k-1}(s)]\mathcal{M}(s,\varepsilon)\mathrm{d}s, \\ F_-^{k+1}(\zeta,\varepsilon) - F_-^k(\zeta,\varepsilon) &= \int_0^\infty K_-(\zeta,s,\varepsilon)[n^k(s) - n^{k-1}(s)]\mathcal{M}(s,\varepsilon)\mathrm{d}s, \end{aligned}$$

with $K_\pm(\zeta,s,\varepsilon) \ge 0$, one has

$$n^k \ge n^{k-1} \implies F_\pm^{k+1} \ge F_\pm^k.$$

On the other hand, by definition of $n^k(\zeta)$, one has

$$\begin{aligned} n^k(\zeta) - n^{k-1}(\zeta) = &\int_{W(\zeta)}^\infty [F_+^k(\zeta,\varepsilon) - F_+^{k-1}(\zeta,\varepsilon)]\frac{\mathrm{d}\varepsilon}{\sqrt{2[\varepsilon - W(\zeta)]}} \\ &+ \int_{W(\zeta)}^\infty [F_-^k(\zeta,\varepsilon) - F_-^{k-1}(\zeta,\varepsilon)]\frac{\mathrm{d}\varepsilon}{\sqrt{2[\varepsilon - W(\zeta)]}}, \end{aligned}$$

so that

$$F_\pm^k \ge F_\pm^{k-1} \implies n^k \ge n^{k-1} \implies F_\pm^{k+1} \ge F_\pm^k.$$

Besides

$$\begin{aligned} F_+^1(\zeta,\varepsilon) &= \mathbf{1}_{\varepsilon>0}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon}) \ge 0 = F_+^0(\zeta,\varepsilon), \\ F_-^1(\zeta,\varepsilon) &= \mathbf{1}_{\varepsilon>0}\,\theta(\zeta,\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon}) \ge 0 = F_-^0(\zeta,\varepsilon), \end{aligned}$$

so that, by induction, we conclude that

$$\begin{aligned} &0 = F_\pm^0(\zeta,\varepsilon) \le F_\pm^1(\zeta,\varepsilon) \le F_\pm^2(\zeta,\varepsilon) \le \ldots \le F_\pm^k(\zeta,\varepsilon) \le \ldots, \\ &0 = n^0(\zeta) \le n^1(\zeta) \le n^2(\zeta) \le \ldots \le n^k(\zeta) \le \ldots. \end{aligned}$$

It remains to prove the upper bound. Here again, we proceed by induction. Clearly

$$F_\pm^0 = 0 \implies n^0 = 0 \implies F_\pm^0 \le Ae^{-\varepsilon}/\sqrt{2\pi} \quad \text{and} \quad n^0\mathcal{M}(\zeta,\varepsilon) \le Ae^{-\varepsilon}/\sqrt{2\pi}.$$

Next we prove that

$$n^{k-1}(\zeta)\mathcal{M}(\zeta,\varepsilon) \le Ae^{-\varepsilon}/\sqrt{2\pi} \implies F_\pm^k \le Ae^{-\varepsilon}/\sqrt{2\pi}.$$

Indeed, by the use of (50) and (51), the following inequalities follow from (48a) and (48b):

$$\begin{aligned}
F_+^k(\zeta,\varepsilon) &= \mathbf{1}_{\varepsilon>0}\,\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon}) \\
&\quad + \int_0^\infty K_+(\zeta,s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s \\
&\le \mathbf{1}_{\varepsilon>0}\,\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon)Ae^{-\varepsilon}/\sqrt{2\pi} \\
&\quad + \left[\int_0^\infty K_+(\zeta,s,\varepsilon)\mathrm{d}s\right] Ae^{-\varepsilon}/\sqrt{2\pi} \\
&\le \mathbf{1}_{\varepsilon>0}\,\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon)Ae^{-\varepsilon}/\sqrt{2\pi} \\
&\quad + [\mathbf{1}_{W(\zeta)<\varepsilon} - \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\,\theta(\zeta_a(\varepsilon),\infty;\varepsilon)]Ae^{-\varepsilon}/\sqrt{2\pi} \\
&= \mathbf{1}_{W(\zeta)<\varepsilon}Ae^{-\varepsilon}/\sqrt{2\pi} \\
&\le Ae^{-\varepsilon}/\sqrt{2\pi},
\end{aligned}$$

while

$$\begin{aligned}
F_-^k(\zeta,\varepsilon) &= \mathbf{1}_{\varepsilon>0}\,\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta,\infty;\varepsilon)F_\infty(-\sqrt{2\varepsilon}) + \int_0^\infty K_-(\zeta,s,\varepsilon)n^{k-1}(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s \\
&\le \mathbf{1}_{\varepsilon>0}\,\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta,\infty;\varepsilon)Ae^{-\varepsilon}/\sqrt{2\pi} + \left[\int_0^\infty K_-(\zeta,s,\varepsilon)\mathrm{d}s\right] Ae^{-\varepsilon}/\sqrt{2\pi} \\
&\le \mathbf{1}_{\varepsilon>0}\,\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\,\theta(\zeta,\infty;\varepsilon)Ae^{-\varepsilon}/\sqrt{2\pi} \\
&\quad + [\mathbf{1}_{W(\zeta)<\varepsilon} - \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\theta(\zeta,\infty,\varepsilon)]Ae^{-\varepsilon}/\sqrt{2\pi} \\
&= \mathbf{1}_{W(\zeta)<\varepsilon}Ae^{-\varepsilon}/\sqrt{2\pi} \\
&\le Ae^{-\varepsilon}/\sqrt{2\pi},
\end{aligned}$$

where $\mathbf{1}_{\varepsilon>0}$ in (48) has been replaced with the more explicit representation $\mathbf{1}_{\varepsilon>0}\,\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}$ in consistency with the expressions (50) and (51).

It remains to prove that

$$F_\pm^k \le Ae^{-\varepsilon}/\sqrt{2\pi} \implies n^k(\zeta)\mathcal{M}(\zeta,\varepsilon) \le Ae^{-\varepsilon}/\sqrt{2\pi}.$$

Observe that

$$\begin{aligned}
n^k(\zeta) &= \int_{W(\zeta)}^\infty [F_-^k(\zeta,\varepsilon) + F_+^k(\zeta,\varepsilon)]\frac{\mathrm{d}\varepsilon}{\sqrt{2[\varepsilon - W(\zeta)]}} \\
&\le \frac{2A}{\sqrt{2\pi}}\int_{W(\zeta)}^\infty \frac{e^{-\varepsilon}\mathrm{d}\varepsilon}{\sqrt{2[\varepsilon - W(\zeta)]}} = \frac{2Ae^{-W(\zeta)}}{\sqrt{2\pi}}\int_0^\infty \frac{e^{-u}\mathrm{d}u}{\sqrt{2u}} \\
&= \frac{Ae^{-W(\zeta)}}{\sqrt{\pi}}\Gamma\left(\frac{1}{2}\right) = Ae^{-W(\zeta)},
\end{aligned}$$

where $\Gamma(x) = \int_0^\infty s^{x-1}e^{-s}\mathrm{d}s$ is Euler's gamma function. Thus, it follows that

$$F_\pm^k \le Ae^{-\varepsilon}/\sqrt{2\pi} \implies n^k(\zeta) \le Ae^{-W(\zeta)} \implies n^k(\zeta)\mathcal{M}(\zeta,\varepsilon) \le Ae^{-\varepsilon}/\sqrt{2\pi}.$$

This completes the proof of monotonicity of the approximating sequence. □

3.3.5 Existence proof for problem (32)

Using Lemma 2 and applying the monotone convergence theorem, we find that $F_{\pm}^{k}(\zeta,\varepsilon) \to F_{\pm}(\zeta,\varepsilon)$ and $n^{k}(\zeta) \to n(\zeta)$ as $k \to \infty$. Then, we pass to the limit as $k \to \infty$ in the formulas (36) to obtain

$$
\begin{aligned}
F_{+}(\zeta,\varepsilon) &= \theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\Bigg(F_{-}(\zeta_a(\varepsilon),\varepsilon) \\
&\qquad + \int_{\zeta_a(\varepsilon)}^{\zeta} \theta(s,\zeta_a(\varepsilon);\varepsilon)\frac{n(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\Bigg), \\
F_{-}(\zeta,\varepsilon) &= \mathbf{1}_{\varepsilon>0}\,\theta(\zeta,\infty;\varepsilon)\Bigg(F_{\infty}(-\sqrt{2\varepsilon}) \\
&\qquad + \int_{\zeta}^{\infty} \theta(\infty,s;\varepsilon)\frac{n(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\Bigg) \\
&\quad + \mathbf{1}_{W_{\min}<\varepsilon<0}\,\theta(\zeta,\zeta_b(\varepsilon);\varepsilon)\Bigg(F_{+}(\zeta_b(\varepsilon),\varepsilon) \\
&\qquad + \int_{\zeta}^{\zeta_b(\varepsilon)} \theta(\zeta_b(\varepsilon),s;\varepsilon)\frac{n(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s}{\tau(s)\sqrt{2[\varepsilon - W(s)]}}\Bigg).
\end{aligned}
$$

It is readily seen that these equations are equivalent to (32) and (33). In other words, the nondecreasing sequence $\{F_{\pm}^{k}\}$ converges to a solution of the problem (32), which shows the existence of a solution $F_{\pm}$ of (32) satisfying the inequality

$$
0 \le F_{\pm}(\zeta,\varepsilon) \le Ae^{-\varepsilon}/\sqrt{2\pi}.
$$

As for the uniqueness of such a solution, it has already been proved in Lemma 1.

3.3.6 Convergence as $\zeta \to \infty$

We investigate the limit of $F_{\pm}(\zeta,\varepsilon)$ as $\zeta \to \infty$ on the basis of the expressions (48) and (49). Therefore, it is sufficient to consider the case of $\varepsilon > 0$. Let us recall the definition (37) of the function $\theta(a,b;\varepsilon)$ and its properties (38) and (40), as well as the definitions (32c) for $\mathcal{M}(s,\varepsilon)$ and (39) for $\mu(s,\varepsilon)$.

Choose $\varepsilon > 0$ to be kept fixed. Then, it follows from (49a) that

$$
\begin{aligned}
0 &\le K_{+}(\zeta,s,\varepsilon) \\
&= \mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta}\theta(s,\zeta;\varepsilon)\mu(s,\varepsilon) \\
&\quad + \mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\mathbf{1}_{s>\zeta_a(\varepsilon)}\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\theta(\zeta_a(\varepsilon),s;\varepsilon)\mu(s,\varepsilon) \\
&\le \mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\mathbf{1}_{s>\zeta_a(\varepsilon)}\,2\mu(s,\varepsilon),
\end{aligned}
$$

and

$$
\begin{aligned}
&\lim_{\zeta\to+\infty} K_{+}(\zeta,s,\varepsilon) \\
&\quad = \mathbf{1}_{s>\zeta_a(\varepsilon)}\mu(s,\varepsilon)[\theta(s,+\infty;\varepsilon) + \theta(\zeta_a(\varepsilon),+\infty;\varepsilon)\,\theta(\zeta_a(\varepsilon),s;\varepsilon)].
\end{aligned}
$$

Similarly, (49b) leads to

$$
0 \le K_{-}(\zeta,s,\varepsilon) = \mathbf{1}_{s>\zeta>\zeta_a(\varepsilon)}\theta(\zeta,s;\varepsilon)\mu(s,\varepsilon) \le \mathbf{1}_{s>\zeta>\zeta_a(\varepsilon)}\mu(s,\varepsilon),
$$

so that

$$\lim_{\zeta\to+\infty} K_-(\zeta,s,\varepsilon)=0.$$

Assume that

$$0\le F_\infty(-\sqrt{2\varepsilon})\le Ae^{-\varepsilon}/\sqrt{2\pi},$$

so that we know from Lemma 2 that

$$0\le F_\pm(\zeta,\varepsilon)\le Ae^{-\varepsilon}/\sqrt{2\pi}\quad\text{ and }\quad 0\le n(\zeta)\le Ae^{-W(\zeta)}.$$

Then

$$\begin{aligned}
0&\le K_+(\zeta,s,\varepsilon)n(s)\mathcal{M}(s,\varepsilon)\\
&\le 2\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\mathbf{1}_{s>\zeta_a(\varepsilon)}\mu(s,\varepsilon)Ae^{-W(s)}\tfrac{1}{\sqrt{2\pi}}e^{-\varepsilon+W(s)}\\
&= A\sqrt{\tfrac{2}{\pi}}e^{-\varepsilon}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\mathbf{1}_{s>\zeta_a(\varepsilon)}\mu(s,\varepsilon)\\
&\le A\sqrt{\tfrac{2}{\pi}}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\mathbf{1}_{s>\zeta_a(\varepsilon)}\mu(s,\varepsilon),
\end{aligned}$$

while

$$\begin{aligned}
0&\le K_-(\zeta,s,\varepsilon)n(s)\mathcal{M}(s,\varepsilon)\\
&\le \mathbf{1}_{s>\zeta>\zeta_a(\varepsilon)}\mu(s,\varepsilon)Ae^{-W(s)}\tfrac{1}{\sqrt{2\pi}}e^{-\varepsilon+W(s)}\\
&= \tfrac{A}{\sqrt{2\pi}}e^{-\varepsilon}\mathbf{1}_{s>\zeta>\zeta_a(\varepsilon)}\mu(s,\varepsilon)\\
&\le \tfrac{A}{\sqrt{2\pi}}\mathbf{1}_{s>\zeta>\zeta_a(\varepsilon)}\mu(s,\varepsilon).
\end{aligned}$$

Since

$$\int_0^\infty \mathbf{1}_{s>\zeta_a(\varepsilon)}\mu(s,\varepsilon)\mathrm{d}s<\infty,$$

we conclude by dominated convergence that, for each $\varepsilon>0$, one has

$$\begin{aligned}
&\lim_{\zeta\to+\infty}\int_0^\infty K_+(\zeta,s,\varepsilon)n(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s\\
&\quad=\int_0^\infty \mathbf{1}_{s>\zeta_a(\varepsilon)}\mu(s,\varepsilon)[\theta(s,+\infty,\varepsilon)\\
&\qquad\qquad+\theta(\zeta_a(\varepsilon),+\infty,\varepsilon)\theta(\zeta_a(\varepsilon),s,\varepsilon)]n(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s,\\
&\lim_{\zeta\to+\infty}\int_0^\infty K_-(\zeta,s,\varepsilon)n(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s=0.
\end{aligned}$$

Hence, for each $\varepsilon>0$,

$$\begin{aligned}
&\lim_{\zeta\to+\infty}F_+(\zeta,\varepsilon)\\
&\quad=\theta(\zeta_a(\varepsilon),\infty;\varepsilon)^2F_\infty(-\sqrt{2\varepsilon})\\
&\qquad+\int_{\zeta_a(\varepsilon)}^\infty \mu(s,\varepsilon)[\theta(s,+\infty,\varepsilon)\\
&\qquad\qquad+\theta(\zeta_a(\varepsilon),+\infty,\varepsilon)\theta(\zeta_a(\varepsilon),s,\varepsilon)]n(s)\mathcal{M}(s,\varepsilon)\mathrm{d}s, \qquad (52a)\\
&\lim_{\zeta\to+\infty}F_-(\zeta,\varepsilon)=F_\infty(-\sqrt{2\varepsilon}). \qquad (52b)
\end{aligned}$$

Equation (52b) confirms that the boundary condition (28d) in the problem (28) is satisfied, while (52a) shows that the limit of the solution $F(\zeta,c_z)$ to the problem (28) as $\zeta\to\infty$ exists for $c_z>0$.

3.4 Proof of exponential convergence of approximating sequence $\{F_\pm^k\}$

We finally prove Theorem 2. Let us return to the integral transformation (48). Multiplying each side of both equalities by $\mu(\zeta,\varepsilon)\tau(\zeta)$ and integrating in $\varepsilon > W(\zeta)$, one finds that

$$n^k(\zeta) = \int_0^\infty \mathcal{K}(\zeta,s)n^{k-1}(s)\mathrm{d}s + N(\zeta)\,, \qquad n^0 = 0, \tag{53}$$

where

$$\mathcal{K}(\zeta,s) := \tau(\zeta)\int_{W(\zeta)}^\infty [K_+(\zeta,s,\varepsilon) + K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathcal{M}(s,\varepsilon)\mathrm{d}\varepsilon, \tag{54}$$

and

$$N(\zeta) := \tau(\zeta)\int_{W(\zeta)}^\infty \mathbf{1}_{\varepsilon>0}\,[\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\theta(\zeta_a(\varepsilon),\infty;\varepsilon) + \theta(\zeta,\infty;\varepsilon)]F_\infty(-\sqrt{2\varepsilon})\mu(\zeta,\varepsilon)\mathrm{d}\varepsilon. \tag{55}$$

The following two things suggest considering the quantity

$$\int_0^\infty n^k(\zeta)\frac{\mathrm{d}\zeta}{\tau(\zeta)}\,:$$

- if $n^k(\zeta)$ converges to a limit $n_\infty^k > 0$ as $\zeta \to +\infty$, the weight $1/\tau(\zeta)$, known to be integrable on the half-line, will make the function $\zeta \mapsto n^k(\zeta)/\tau(\zeta)$ also integrable; and
- there is the prefactor $\tau(\zeta)$ in the definition (54) of $\mathcal{K}(\zeta,s)$ as well as in the definition (55) of $N(\zeta)$.

Thus, multiplying both sides of (53) by $1/\tau(\zeta)$, integrating in ζ over the half-line, and exchanging the order of integration in ζ and in s in the first integral on the right-hand side of (53), we arrive at the equality

$$\int_0^\infty n^k(\zeta)\frac{\mathrm{d}\zeta}{\tau(\zeta)} = \int_0^\infty \left(\int_0^\infty \mathcal{K}(\zeta,s)\frac{\tau(s)}{\tau(\zeta)}\mathrm{d}\zeta\right) n^{k-1}(s)\frac{\mathrm{d}s}{\tau(s)} + \int_0^\infty N(\zeta)\frac{\mathrm{d}\zeta}{\tau(\zeta)}. \tag{56}$$

Therefore, we are left with the task of computing

$$\begin{aligned}
&\int_0^\infty \mathcal{K}(\zeta,s)\frac{\mathrm{d}\zeta}{\tau(\zeta)} \\
&\quad= \int_0^\infty\int_{W(\zeta)}^\infty [K_+(\zeta,s,\varepsilon) + K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathcal{M}(s,\varepsilon)\mathrm{d}\varepsilon\mathrm{d}\zeta \\
&\quad= \int_0^\infty \mathcal{M}(s,\varepsilon)\left(\int_{\zeta_a(\varepsilon)}^\infty [K_+(\zeta,s,\varepsilon)+K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathrm{d}\zeta\right)\mathrm{d}\varepsilon \\
&\qquad+ \int_{W_{\min}}^0 \mathcal{M}(s,\varepsilon)\left(\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} [K_+(\zeta,s,\varepsilon)+K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathrm{d}\zeta\right)\mathrm{d}\varepsilon.
\end{aligned} \tag{57}$$

3.4.1 Computing the inner integrals in (57)

We recall from (49a) and (49b) that

$$\begin{aligned}
&\mu(\zeta,\varepsilon)K_+(\zeta,s,\varepsilon)\\
&\quad=\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta>\zeta_a(\varepsilon)}\mathbf{1}_{s>\zeta_a(\varepsilon)}[-\partial_\zeta\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)]\theta(\zeta_a(\varepsilon),s;\varepsilon)\mu(s,\varepsilon)\\
&\qquad+\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}[-\partial_\zeta\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)]\\
&\qquad\qquad\times\tfrac{[\theta(s,\zeta_b(\varepsilon);\varepsilon)+\theta(\zeta_b(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}\\
&\qquad+(\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta}+\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta<\zeta_b(\varepsilon)})[-\partial_\zeta\theta(s,\zeta;\varepsilon)]\mu(s,\varepsilon),
\end{aligned}\tag{58}$$

and

$$\begin{aligned}
&\mu(\zeta,\varepsilon)K_-(\zeta,s,\varepsilon)\\
&\quad=(\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<s}+\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<s<\zeta_b(\varepsilon)})\,\partial_\zeta\theta(\zeta,s;\varepsilon)\mu(s,\varepsilon)\\
&\qquad+\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<\zeta<\zeta_b(\varepsilon)}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}\,\partial_\zeta\theta(\zeta,\zeta_b(\varepsilon);\varepsilon)\\
&\qquad\qquad\times\tfrac{[\theta(s,\zeta_a(\varepsilon);\varepsilon)+\theta(\zeta_a(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}.
\end{aligned}\tag{59}$$

Observe that we have used (40) to transform the terms

$$\tfrac{\partial_s\theta(s,\zeta_b(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_b(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}\quad\text{and}\quad\tfrac{\partial_s\theta(s,\zeta_a(\varepsilon);\varepsilon)-\partial_s\theta(\zeta_a(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}$$

into

$$\tfrac{[\theta(s,\zeta_b(\varepsilon);\varepsilon)+\theta(\zeta_b(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}\quad\text{and}\quad\tfrac{[\theta(s,\zeta_a(\varepsilon);\varepsilon)+\theta(\zeta_a(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)},$$

respectively, and the terms

$$\mu(\zeta,\varepsilon)\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\quad\text{and}\quad\mu(\zeta;\varepsilon)\theta(\zeta,\zeta_b(\varepsilon);\varepsilon)$$

into

$$-\partial_\zeta\theta(\zeta_a(\varepsilon),\zeta;\varepsilon)\quad\text{and}\quad\partial_\zeta\theta(\zeta,\zeta_b(\varepsilon);\varepsilon),$$

respectively.

Then, for $\varepsilon>0$, one has

$$\begin{aligned}
&\int_{\zeta_a(\varepsilon)}^{\infty}K_+(\zeta,s,\varepsilon)\mu(\zeta,\varepsilon)\mathrm{d}\zeta\\
&\qquad=\mathbf{1}_{\varepsilon>0}\mathbf{1}_{s>\zeta_a(\varepsilon)}[1-\theta(\zeta_a(\varepsilon),\infty;\varepsilon)]\theta(\zeta_a(\varepsilon),s;\varepsilon)\mu(s,\varepsilon)\\
&\qquad\quad+\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta_a(\varepsilon)<s}[1-\theta(s,\infty;\varepsilon)]\mu(s,\varepsilon),
\end{aligned}\tag{60a}$$

$$\int_{\zeta_a(\varepsilon)}^{\infty}K_-(\zeta,s,\varepsilon)\mu(\zeta,\varepsilon)\mathrm{d}\zeta=\mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta_a(\varepsilon)<s}[1-\theta(\zeta_a(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon),\tag{60b}$$

while, for $W_{\min}<\varepsilon<0$,

$$
\begin{aligned}
&\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} K_+(\zeta,s,\varepsilon)\mu(\zeta,\varepsilon)\mathrm{d}\zeta \\
&\quad = \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}[1-\theta(s,\zeta_b(\varepsilon);\varepsilon)]\mu(s,\varepsilon) \\
&\qquad + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}[1-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)] \\
&\qquad\qquad \times \tfrac{[\theta(s,\zeta_b(\varepsilon);\varepsilon)+\theta(\zeta_b(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}, \qquad (61a)\\
&\int_{\zeta_a(\varepsilon)}^{\zeta_b(\varepsilon)} K_-(\zeta,s,\varepsilon)\mu(\zeta,\varepsilon)\mathrm{d}\zeta \\
&\quad = \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}[1-\theta(\zeta_a(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon) \\
&\qquad + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}[1-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)] \\
&\qquad\qquad \times \tfrac{[\theta(s,\zeta_a(\varepsilon);\varepsilon)+\theta(\zeta_a(\varepsilon),s;\varepsilon]\mu(s,\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}. \qquad (61b)
\end{aligned}
$$

We here note that the integral in ζ over $(\zeta_a(\varepsilon),\infty)$ and that over $(\zeta_a(\varepsilon),\zeta_b(\varepsilon))$ in (57) are expressed in the unified form

$$
\int_0^\infty [K_+(\zeta,s,\varepsilon)+K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathrm{d}\zeta, \qquad (62)
$$

because of the expressions (58) and (59). Using (60) and (61), this integral is expressed as

$$
\begin{aligned}
&\int_0^\infty [K_+(\zeta,s,\varepsilon)+K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathrm{d}\zeta \\
&\quad = \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta_a(\varepsilon)<s}[1-\theta(\zeta_a(\varepsilon),\infty;\varepsilon)\theta(\zeta_a(\varepsilon),s;\varepsilon)+1-\theta(s,\infty;\varepsilon)]\mu(s,\varepsilon) \\
&\qquad + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}[1-\theta(s,\zeta_b(\varepsilon);\varepsilon)+1-\theta(\zeta_a(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon) \\
&\qquad + \mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}[1-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)] \\
&\qquad\qquad \times \tfrac{[\theta(s,\zeta_b(\varepsilon);\varepsilon)+\theta(s,\zeta_a(\varepsilon);\varepsilon)+\theta(\zeta_b(\varepsilon),s;\varepsilon)+\theta(\zeta_a(\varepsilon),s;\varepsilon)]\mu(s,\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)}. \qquad (63)
\end{aligned}
$$

We shall simplify the last two lines significantly: set

$$
X := \theta(s,\zeta_a(\varepsilon);\varepsilon) > 1 \quad \text{and} \quad \Lambda := \theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon) > 1
$$

for $\zeta_a(\varepsilon) < s < \zeta_b(\varepsilon)$, so that

$$
\theta(\zeta_a(\varepsilon),s;\varepsilon) = 1/X, \quad \theta(\zeta_b(\varepsilon),s;\varepsilon) = \Lambda/X, \quad \theta(s,\zeta_b(\varepsilon);\varepsilon) = X/\Lambda.
$$

Then, one has

$$
\begin{aligned}
&[1-\theta(s,\zeta_b(\varepsilon);\varepsilon)+1-\theta(\zeta_a(\varepsilon),s;\varepsilon)] \\
&+ [1-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)]\tfrac{\theta(s,\zeta_b(\varepsilon);\varepsilon)+\theta(s,\zeta_a(\varepsilon);\varepsilon)+\theta(\zeta_b(\varepsilon),s;\varepsilon)+\theta(\zeta_a(\varepsilon),s;\varepsilon)}{\theta(\zeta_b(\varepsilon),\zeta_a(\varepsilon);\varepsilon)-\theta(\zeta_a(\varepsilon),\zeta_b(\varepsilon);\varepsilon)} \\
&\quad = (2-\tfrac{X}{\Lambda}-\tfrac{1}{X})+(1-\tfrac{1}{\Lambda})\frac{\frac{X}{\Lambda}+X+\frac{\Lambda}{X}+\frac{1}{X}}{\Lambda-\frac{1}{\Lambda}} \\
&\quad = (2-\tfrac{X}{\Lambda}-\tfrac{1}{X})+(1-\tfrac{1}{\Lambda})\frac{(\frac{X}{\Lambda}+\frac{1}{X})(1+\Lambda)}{\frac{(\Lambda+1)(\Lambda-1)}{\Lambda}} \\
&\quad = (2-\tfrac{X}{\Lambda}-\tfrac{1}{X})+(1-\tfrac{1}{\Lambda})\frac{\frac{X}{\Lambda}+\frac{1}{X}}{\frac{\Lambda-1}{\Lambda}} \\
&\quad = 2.
\end{aligned}
$$

Therefore,

$$\begin{aligned}
&\int_0^\infty [K_+(\zeta,s,\varepsilon)+K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathrm{d}\zeta \\
&\quad = \mathbf{1}_{\varepsilon>0}\mathbf{1}_{\zeta_a(\varepsilon)<s}[2-\theta(\zeta_a(\varepsilon),\infty,\varepsilon)\theta(\zeta_a(\varepsilon),s;\varepsilon)-\theta(s,\infty;\varepsilon)]\mu(s,\varepsilon) \\
&\qquad + 2\mathbf{1}_{W_{\min}<\varepsilon<0}\mathbf{1}_{\zeta_a(\varepsilon)<s<\zeta_b(\varepsilon)}\mu(s,\varepsilon). \qquad (64)
\end{aligned}$$

On the other hand, setting

$$L := \theta(\zeta_a(\varepsilon),\infty;\varepsilon) \quad \text{and} \quad Z := \theta(s,\infty;\varepsilon),$$

one has

$$\theta(\zeta_a(\varepsilon),s;\varepsilon) = L/Z\,, \quad L<Z<1.$$

Thus,

$$\theta(\zeta_a(\varepsilon),\infty,\varepsilon)\theta(\zeta_a(\varepsilon),s;\varepsilon)+\theta(s,\infty;\varepsilon) = \tfrac{L^2}{Z}+Z \geq 2L,$$

since

$$\zeta_a(\varepsilon)<s \implies 0<\theta(\zeta_a(\varepsilon),s;\varepsilon)=L/Z<1$$

and $Z \mapsto \frac{L^2}{Z}+Z$ is increasing on $[L,1]$. Thus, it follows that

$$2-\theta(\zeta_a(\varepsilon),\infty;\varepsilon)\theta(\zeta_a(\varepsilon),s;\varepsilon)-\theta(s,\infty;\varepsilon) \leq 2[1-\theta(\zeta_a(\varepsilon),\infty,\varepsilon)].$$

Summarizing, we have proved the following inequality:

$$\begin{aligned}
&\int_0^\infty [K_+(\zeta,s,\varepsilon)+K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathrm{d}\zeta \\
&\qquad \leq 2\mu(s,\varepsilon)\mathbf{1}_{W(s)<\varepsilon}[1-\theta(\zeta_a(\varepsilon),\infty,\varepsilon)\mathbf{1}_{\varepsilon>0}]. \qquad (65)
\end{aligned}$$

3.4.2 Bounding (57)

As noted in the process of deriving (63), the integrals with respect to ζ in (57) are unified in the form (62), so that (57) is recast as

$$\begin{aligned}
&\int_0^\infty \mathcal{K}(\zeta,s)\frac{\mathrm{d}\zeta}{\tau(\zeta)} \\
&\quad = \int_{W_{\min}}^\infty \mathcal{M}(s,\varepsilon)\left(\int_0^\infty [K_+(\zeta,s,\varepsilon)+K_-(\zeta,s,\varepsilon)]\mu(\zeta,\varepsilon)\mathrm{d}\zeta\right)\mathrm{d}\varepsilon. \qquad (66)
\end{aligned}$$

Next, integrating (65) multiplied by $\mathcal{M}(s,\varepsilon)$ in ε from $W_{\min}$ to ∞ and using the resulting inequality in (66), we arrive at the following inequality:

$$\begin{aligned}
&\int_0^\infty \mathcal{K}(\zeta,s)\frac{\tau(s)}{\tau(\zeta)}\mathrm{d}\zeta \\
&\quad \leq 2\int_{W(s)}^\infty \mathcal{M}(s,\varepsilon)\tau(s)\mu(s,\varepsilon)\mathrm{d}\varepsilon \\
&\qquad - 2\int_0^\infty \theta(\zeta_a(\varepsilon),\infty;\varepsilon)\mathcal{M}(s,\varepsilon)\tau(s)\mu(s,\varepsilon)\mathbf{1}_{\zeta_a(\varepsilon)<s}\mathrm{d}\varepsilon \\
&\quad = 1-2\int_0^\infty \theta(\zeta_a(\varepsilon),\infty;\varepsilon)\mathcal{M}(s,\varepsilon)\tau(s)\mu(s,\varepsilon)\mathbf{1}_{\zeta_a(\varepsilon)<s}\mathrm{d}\varepsilon \\
&\quad =: \Upsilon(s). \qquad (67)
\end{aligned}$$

Indeed,

$$\int_{W(s)}^{\infty} \mathcal{M}(s,\varepsilon)\tau(s)\mu(s,\varepsilon)\mathrm{d}\varepsilon = \frac{1}{\sqrt{2\pi}} \int_{W(s)}^{\infty} \frac{e^{W(s)-\varepsilon}\mathrm{d}\varepsilon}{\sqrt{2[\varepsilon - W(s)]}}$$
$$= \frac{1}{\sqrt{2\pi}} \int_0^{\infty} \frac{e^{-u}\mathrm{d}u}{\sqrt{2u}} = \frac{1}{2\sqrt{\pi}}\Gamma(\tfrac{1}{2}) = \frac{1}{2}.$$

Our aim is to find an upper bound for $\Upsilon(s)$, which amounts to finding a lower bound for the integral in the fourth line of (67), i.e.,

$$\int_0^{\infty} \theta(\zeta_a(\varepsilon),\infty;\varepsilon)\mathcal{M}(s,\varepsilon)\tau(s)\mu(s,\varepsilon)\mathbf{1}_{\zeta_a(\varepsilon)<s}\mathrm{d}\varepsilon.$$

In order to do so, we first seek a lower bound for

$$\theta(\zeta_a(\varepsilon),\infty,\varepsilon) = \exp\left(-\int_{\zeta_a(\varepsilon)}^{\infty} \frac{\mathrm{d}t}{\tau(t)\sqrt{2[\varepsilon - W(t)]}}\right),$$

or, equivalently, an upper bound for the integral in the exponential.

This step will use some of the specifics of the potential, summarized in (2) and items (i)–(iv) in Sec. 2.1. Note that the statements in Sec. 2.1 are for the dimensional potential, whereas the potential W considered here is dimensionless [cf. (9) and (25)]. Therefore, we rephrase the specific properties of W that will be used in the following:

- W is decreasing and convex downward on $(0,\zeta_{\min})$, and tends to $+\infty$ at 0^+;
- W is continuous and increasing on $(\zeta_{\min},+\infty)$, and tends to 0^- at $+\infty$.

Thus, for each $\varepsilon > 0$, the point $\zeta_a(\varepsilon)$ is uniquely defined by

$$W(\zeta_a(\varepsilon)) = \varepsilon\,, \quad 0 < \zeta_a(\varepsilon) < \zeta_a(0) < \zeta_{\min};$$

besides

$$W_{\min} = W(\zeta_{\min}) = \min_{\zeta>0} W(\zeta) < 0.$$

On the other hand, we recall, from the properties of the dimensional relaxation time $\tau_{\mathrm{ph,s}}(\zeta)$ in (7) and below in Sec. 2.1, that

$$\tau(\zeta) \geq \tau(0) > 0\,, \quad \text{and} \quad \ell := \int_0^{\infty} \frac{\mathrm{d}s}{\tau(s)} < +\infty,$$

for its dimensionless counterpart $\tau(\zeta)$ considered here.

We first decompose the integral contained in the function $\theta(\zeta_a(\varepsilon),\infty;\varepsilon)$ as

$$\int_{\zeta_a(\varepsilon)}^{\infty} \frac{\mathrm{d}t}{\tau(t)\sqrt{2[\varepsilon - W(t)]}}$$
$$= \int_{\zeta_a(\varepsilon)}^{\zeta_{\min}} \frac{\mathrm{d}t}{\tau(t)\sqrt{2[\varepsilon - W(t)]}} + \int_{\zeta_{\min}}^{\infty} \frac{\mathrm{d}t}{\tau(t)\sqrt{2[\varepsilon - W(t)]}}$$
$$= I + J,$$

and estimate I and J separately.

The easiest term to bound is J: indeed, for $\varepsilon > 0$, one has

$$W|_{(\zeta_{\min},+\infty)} \leq 0 \implies J \leq \int_{\zeta_{\min}}^{\infty} \frac{\mathrm{d}t}{\tau(t)\sqrt{2\varepsilon}} \leq \frac{\ell}{\sqrt{2\varepsilon}}.$$

Bounding the term I is slightly more involved. We first use the convexity of W on the interval $(0, \zeta_{\min})$, which implies that

$$\begin{aligned} W(t) &= W\left(\tfrac{\zeta_{\min}-t}{\zeta_{\min}-\zeta_a(\varepsilon)}\zeta_a(\varepsilon) + \tfrac{t-\zeta_a(\varepsilon)}{\zeta_{\min}-\zeta_a(\varepsilon)}\zeta_{\min}\right) \\ &\leq \tfrac{\zeta_{\min}-t}{\zeta_{\min}-\zeta_a(\varepsilon)}W(\zeta_a(\varepsilon)) + \tfrac{t-\zeta_a(\varepsilon)}{\zeta_{\min}-\zeta_a(\varepsilon)}W(\zeta_{\min}), \end{aligned}$$

or, equivalently,

$$\begin{aligned} W(t) &\leq W(\zeta_a(\varepsilon)) - \tfrac{W(\zeta_a(\varepsilon))-W(\zeta_{\min})}{\zeta_{\min}-\zeta_a(\varepsilon)}[t-\zeta_a(\varepsilon)] \\ &= \varepsilon - \tfrac{\varepsilon-W_{\min}}{\zeta_{\min}-\zeta_a(\varepsilon)}[t-\zeta_a(\varepsilon)]. \end{aligned}$$

The geometric interpretation of this inequality is as follows: it means that the graph of W is below the chord joining the point of coordinates $(\zeta_a(\varepsilon), \varepsilon)$ to the point of coordinates $(\zeta_{\min}, W_{\min})$. This is indeed an obvious consequence of the convexity of W on the interval $(0, \zeta_{\min})$.

Thus

$$t \in (\zeta_a(\varepsilon), \zeta_{\min}) \implies \varepsilon - W(t) \geq \tfrac{\varepsilon-W_{\min}}{\zeta_{\min}-\zeta_a(\varepsilon)}[t-\zeta_a(\varepsilon)],$$

and hence

$$I \leq \tfrac{1}{\tau(0)}\sqrt{\tfrac{\zeta_{\min}-\zeta_a(\varepsilon)}{2(\varepsilon-W_{\min})}}\int_{\zeta_a(\varepsilon)}^{\zeta_{\min}} \tfrac{\mathrm{d}t}{\sqrt{t-\zeta_a(\varepsilon)}} = \tfrac{2}{\tau(0)}\tfrac{\zeta_{\min}-\zeta_a(\varepsilon)}{\sqrt{2(\varepsilon-W_{\min})}} \leq \tfrac{2\zeta_{\min}}{\tau(0)\sqrt{2\varepsilon}}\,.$$

Therefore

$$\int_{\zeta_a(\varepsilon)}^{\infty} \frac{\mathrm{d}t}{\tau(t)\sqrt{2[\varepsilon - W(t)]}} \leq \left(\frac{2\zeta_{\min}}{\tau(0)} + \ell\right)\frac{1}{\sqrt{2\varepsilon}},$$

so that

$$\theta(\zeta_a(\varepsilon), \infty; \varepsilon) \geq e^{-K/\sqrt{\varepsilon}}, \quad \text{with } K := \frac{\sqrt{2}\zeta_{\min}}{\tau(0)} + \frac{\ell}{\sqrt{2}}. \tag{68}$$

Now, we insert the lower bound (68) in the definition of $\Upsilon(s)$ included in (67), that is,

$$\begin{aligned} \frac{1-\Upsilon(s)}{2} &= \int_0^{\infty} \theta(\zeta_a(\varepsilon), \infty; \varepsilon)\mathcal{M}(s,\varepsilon)\tau(s)\mu(s,\varepsilon)\mathbf{1}_{\zeta_a(\varepsilon)<s}\mathrm{d}\varepsilon \\ &\geq \int_0^{\infty} e^{-K/\sqrt{\varepsilon}}\mathcal{M}(s,\varepsilon)\tau(s)\mu(s,\varepsilon)\mathbf{1}_{\zeta_a(\varepsilon)<s}\mathrm{d}\varepsilon \\ &= \frac{1}{\sqrt{2\pi}}\int_0^{\infty} \frac{e^{-K/\sqrt{\varepsilon}}e^{W(s)-\varepsilon}\mathbf{1}_{\zeta_a(\varepsilon)<s}}{\sqrt{2[\varepsilon-W(s)]}}\mathrm{d}\varepsilon \\ &= \frac{1}{\sqrt{2\pi}}\int_{W(s)^+}^{\infty} \frac{e^{-K/\sqrt{\varepsilon}}e^{W(s)-\varepsilon}}{\sqrt{2[\varepsilon-W(s)]}}\mathrm{d}\varepsilon, \end{aligned}$$

with the notation $X^+ = \max(X, 0)$ and $X^- = \max(-X, 0)$. Change variables in the last integral, setting $u = \varepsilon - W(s)$. Since

$$W(s) = W(s)^+ - W(s)^-,$$

one has

$$\frac{1-\Upsilon(s)}{2} \geq \frac{1}{\sqrt{2\pi}} \int_{W(s)^-}^{\infty} \frac{e^{-K/\sqrt{u+W(s)}} e^{-u}}{\sqrt{2u}} \mathrm{d}u$$
$$\geq \frac{1}{\sqrt{2\pi}} \int_{|W_{\min}|+1}^{\infty} \frac{e^{-K/\sqrt{u+W(s)}} e^{-u}}{\sqrt{2u}} \mathrm{d}u$$

since $W(s)^- \leq |W_{\min}| \leq |W_{\min}| + 1$.

Next, observe that the function $v \mapsto e^{-K/\sqrt{v}}$ is increasing on $(0, +\infty)$, so that

$$u \geq |W_{\min}| + 1 \implies e^{-K/\sqrt{u+W(s)}} \geq e^{-K/\sqrt{1+|W_{\min}|+W(s)}} \geq e^{-K}.$$

Therefore

$$\frac{1-\Upsilon(s)}{2} = \int_0^{\infty} \theta(\zeta_a(\varepsilon), \infty; \varepsilon) \mathcal{M}(s, \varepsilon) \tau(s) \mu(s, \varepsilon) \mathbf{1}_{\zeta_a(\varepsilon) < s} \mathrm{d}\varepsilon$$
$$\geq \frac{1}{\sqrt{2\pi}} \int_{|W_{\min}|+1}^{\infty} \frac{e^{-K} e^{-u}}{\sqrt{2u}} \mathrm{d}u > 0.$$

Summarizing, we have proved the following inequality

$$0 \leq \int_0^{\infty} \mathcal{K}(\zeta, s) \frac{\tau(s)}{\tau(\zeta)} \mathrm{d}\zeta$$
$$\leq 1 - 2 \int_0^{\infty} \theta(\zeta_a(\varepsilon), \infty, \varepsilon) \mathcal{M}(s, \varepsilon) \tau(s) \mu(s, \varepsilon) \mathbf{1}_{\zeta_a(\varepsilon) < s} \mathrm{d}\varepsilon$$
$$= \Upsilon(s) \leq \mathcal{L},$$

where

$$\mathcal{L} = 1 - \frac{e^{-K}}{\sqrt{\pi}} \int_{|W_{\min}|+1}^{\infty} \frac{e^{-u}}{\sqrt{u}} \mathrm{d}u < 1.$$

3.4.3 Exponential convergence of n^k and of $F_{\pm}^k$

Now we recall (56) and pass to the limit as $k \to \infty$ in both sides of this equality. Since $n^k \to n$ a.e. on $(0, +\infty)$ by monotone convergence (cf. Lemma 2), one has

$$\int_0^{\infty} n(\zeta) \frac{\mathrm{d}\zeta}{\tau(\zeta)} = \int_0^{\infty} \left(\int_0^{\infty} \mathcal{K}(\zeta, s) \frac{\tau(s)}{\tau(\zeta)} \mathrm{d}\zeta \right) n(s) \frac{\mathrm{d}s}{\tau(s)} + \int_0^{\infty} N(\zeta) \frac{\mathrm{d}\zeta}{\tau(\zeta)},$$

so that

$$0 \leq \int_0^{\infty} [n(\zeta) - n^k(\zeta)] \frac{\mathrm{d}\zeta}{\tau(\zeta)}$$
$$= \int_0^{\infty} \left(\int_0^{\infty} \mathcal{K}(\zeta, s) \frac{\tau(s)}{\tau(\zeta)} \mathrm{d}\zeta \right) [n(s) - n^{k-1}(s)] \frac{\mathrm{d}s}{\tau(s)}$$
$$\leq \mathcal{L} \int_0^{\infty} [n(s) - n^{k-1}(s)] \frac{\mathrm{d}s}{\tau(s)} \leq \mathcal{L}^k \int_0^{\infty} [n(s) - n^0(s)] \frac{\mathrm{d}s}{\tau(s)}$$
$$= \mathcal{L}^k \int_0^{\infty} n(s) \frac{\mathrm{d}s}{\tau(s)} \leq A \mathcal{L}^k \int_0^{\infty} e^{-W(s)} \frac{\mathrm{d}s}{\tau(s)} \leq A \ell e^{|W_{\min}|} \mathcal{L}^k.$$

This proves the first half of Theorem 2.

This result is easily transformed into an exponential convergence statement on $F_\pm^k$. Indeed, by Lemma 2, we know that $F_\pm^k$ is nondecreasing in k and converges pointwise to $F_\pm$, so that

$$\begin{aligned}
&\int_0^\infty\int_{-\infty}^\infty \left[|F_+(\zeta,\varepsilon)-F_+^k(\zeta,\varepsilon)|+|F_-(\zeta,\varepsilon)-F_-^k(\zeta,\varepsilon)|\right]\frac{\mathbf{1}_{\varepsilon>W(\zeta)}\mathrm{d}\varepsilon\mathrm{d}\zeta}{\tau(\zeta)\sqrt{2[\varepsilon-W(\zeta)]}}\\
&\quad=\int_0^\infty\int_{W(\zeta)}^\infty \left[F_+(\zeta,\varepsilon)-F_+^k(\zeta,\varepsilon)+F_-(\zeta,\varepsilon)-F_-^k(\zeta,\varepsilon)\right]\frac{\mathrm{d}\varepsilon\mathrm{d}\zeta}{\tau(\zeta)\sqrt{2[\varepsilon-W(\zeta)]}}\\
&\quad=\int_0^\infty [n(\zeta)-n^k(\zeta)]\frac{\mathrm{d}\zeta}{\tau(\zeta)}\le A\ell e^{|W_{\min}|}\mathcal{L}^k.
\end{aligned}$$

This completes the proof of Theorem 2.

4 Numerical results

In our previous paper [6], the problem (26) was solved approximately to construct models of the boundary condition (24) and also numerically to assess the constructed models. The actual numerical analysis was basically carried out for (32) using a finite-difference method, the details of which are found in Appendix C in [6].

In [6], the presented results were mostly regarding the output distribution function $\hat{f}(\zeta\to\infty,\hat{c}_z>0)$ in response to the input $\hat{f}(\zeta\to\infty,\hat{c}_z<0)$ in (23), since the attention was focused on the boundary condition (24) for the Boltzmann equation. In this section, using the same numerical scheme as in [6], we give some numerical results that visualize the mathematical properties given in Sec. 3 as well as that demonstrate the behavior of the gas in the physisorbate layer.

4.1 Preliminaries

In order to carry out actual numerical computations for the problem (32), one has to specify the interaction potential $W(\zeta)$ and the relaxation time $\tau(\zeta)$ explicitly. Following [6], we adopt the Lennard-Jones (LJ) $(12,6)$ and $(9,3)$ potentials:

$$W(\zeta)=4\kappa\left(\frac{1}{\zeta^{12}}-\frac{1}{\zeta^6}\right), \tag{69a}$$

$$W(\zeta)=\frac{3\sqrt{3}}{2}\kappa\left(\frac{1}{\zeta^9}-\frac{1}{\zeta^3}\right), \tag{69b}$$

and the relaxation times of algebraic and exponential type:

$$\tau(\zeta)=\kappa_\tau\left(1+\frac{\sigma}{\nu}\zeta\right)^\nu, \tag{70a}$$

$$\tau(\zeta)=\kappa_\tau\exp(\sigma\zeta), \tag{70b}$$

where κ, κ_τ, ν, and σ are parameters. Note that (69a), (69b), (70a), and (70b) are in dimensionless form and correspond to (85), (88), (91), and (96) in [6]. The reader is referred to [6] for the related quantities; for instance, $\zeta_a(\varepsilon)$ and $\zeta_b(\varepsilon)$ for (69a) are given by (86) in [6] and those for (69b) are given by (89) there. It is noted that the LJ$(9,3)$ potential (69b) is more realistic as a potential of interactions between a gas molecule and a crystal surface [27, 10, 24]. In fact, it results from a continuous model of the crystal after volume integration.

In addition, the input velocity distribution $F_\infty(c_z)$ in (28d) should be specified. Here, we assume the following shifted Maxwellian:

$$F_\infty(c_z) = \frac{1}{\sqrt{2\pi T_\infty}} \exp\left(-\frac{(c_z - v_{z\infty})^2}{2T_\infty}\right), \tag{71}$$

where $v_{z\infty}$ and T_∞ are the parameters to be specified.

In this Sec. 4, the parameters κ in (69) and κ_τ and σ in (70) are set to be

$$(\kappa, \kappa_\tau, \sigma) = (1, 1, 1) \tag{72}$$

as in [6].

4.2 Monotonicity and exponential convergence with respect to k

The numerical method used in [6] is based on an iteration scheme essentially the same as (34) except that the superscript k on the right-hand side of (34e) is replaced by $k-1$. We also check that the numerical solution enjoys the mathematical properties established in Sec. 3.

In the numerical computation in [6], initial values different from (35) were used for the iteration. In order to mimic the mathematical proofs in Sec. 3, we redo the computation using the scheme in [6] but starting from the initial values (35), i.e., $F_\pm^0 = n^0 = 0$.

The computation is performed in the cases summarized in Table 1. To be more specific, "LJ(12, 6)" indicates (69a), and "LJ(9, 3)" (69b); "algebraic" indicates (70a) (with $\nu = 4$ and 7), and "exponential" (70b); and the parameters T_∞ and $v_{z\infty}$ are chosen as shown in the table. The case (viii) corresponds to the equilibrium solution. Recall that the parameters κ, κ_τ, and σ are set as (72).

Table 1: Computational cases and values of a and b.

		$(T_\infty,\, v_{z\infty})$	a	b
(i)	LJ(12,6), algebraic ($\nu = 7$)	(1, −0.5)	0.06556	−1.127
(ii)	LJ(12,6), exponential	(1, −0.5)	0.06226	−1.221
(iii)	LJ(9,3), algebraic ($\nu = 4$)	(1, −0.5)	0.08827	−0.7568
(iv)	LJ(9,3), exponential	(1, −0.5)	0.08193	−0.9159
(v)	LJ(9,3), algebraic ($\nu = 4$)	(1, 0.5)	0.08827	−1.932
(vi)	LJ(9,3), algebraic ($\nu = 4$)	(0.6, 0)	0.08827	−1.466
(vii)	LJ(9,3), algebraic ($\nu = 4$)	(0.6, −0.5)	0.08827	−0.8125
(viii)	LJ(9,3), algebraic ($\nu = 4$)	(1, 0)	0.08827	−1.266

Figures 3 and 4 show the difference $n^k(\zeta) - n^{k-1}(\zeta)$ versus k at four different positions ζ in the semi-logarithmic scale. Figure 3 contains the cases (i)–(iv) in Table 1, whereas Fig. 4 the cases (v)–(viii) there. The green, red, blue, and orange solid lines indicate the results at $\zeta = 1.371$, $1.122\,(= \zeta_{\min})$, 1, and 0.934, respectively, in panels (a) and (b) in Fig. 3 and indicate the results at $\zeta = 2.293$, $1.201\,(= \zeta_{\min})$, 1, and 0.901, respectively, in panels (c) and (d) in Fig. 3 as well as in all panels in Fig. 4. In Fig. 3, the pair of panels (a) and (b) and that of panels (c) and (d) show the effect of different relaxation times $\tau(\zeta)$, whereas the pair of panels (a) and (c) and that of panels (b) and (d) show the effect of different potentials $W(\zeta)$. Figure 4 shows the effect of the difference in the parameters $(T_\infty, v_{z\infty})$ in the input velocity distribution (71).

In each panel in Figs. 3 and 4, the four solid lines corresponding to the four different positions seem to be straight and parallel for large k. Therefore, it is likely that $n^k(\zeta) - n^{k-1}(\zeta)$ for large k is expressed in the following form:

$$n^k(\zeta) - n^{k-1}(\zeta) = e^{-ak+b}, \qquad \text{(for large } k\text{)},$$

where a and b depend on the parameters, but a is independent of ζ. The values of a and b determined by the least square fitting using the numerical data at $\zeta = \zeta_{\min}$ for $k \geq 50$ are shown in Table 1 for each case, and the line Ce^{-ak} with a in Table 1 and an appropriate constant C is shown by the black dashed line in each panel.

It is seen from Figs. 3 and 4 that $n^k(\zeta) - n^{k-1}(\zeta)$ is always positive. In addition, it is likely from these figures and the above discussion that $n^k(\zeta) - n^{k-1}(\zeta)$ decreases exponentially in k with the convergence rate independent of ζ. This also indicates that $n^k(\zeta)$ is likely to converge to $n(\zeta)$ exponentially fast in k with the same uniform convergence rate, i.e,

$$n(\zeta) - n^k(\zeta) \simeq N(\zeta)e^{-ak},$$

for large k, where $N(\zeta)$ is an appropriate positive function of ζ. These observations numerically confirm a part of the statements in Lemma 2 and Theorem 2, i.e., the fact that the sequence $\{n^k(\zeta)\}$ increases monotonically in k and converges exponentially fast in k. Table 1 shows that the convergence rate is relatively small and is less than 0.1. Although Theorem 2 shows the exponential convergence of n^k in a L^1 norm, the numerical result suggests a pointwise convergence in k with a convergence rate uniform in ζ.

4.3 Behavior in the physisorbate layer

In this section, we give some numerical results for the behavior of the gas and physisorbed molecules inside the physisorbate layer.

4.3.1 Profiles of macroscopic quantities

We recall that $n(\zeta)$ indicates the dimensionless number density of the gas molecules at the zeroth order in ϵ because of the notation agreement in Secs. 2.3 and 2.4 (that is, the superscript $\langle 0 \rangle$ as well as the hat has been omitted) and is expressed as (28b) in terms of the reduced velocity distribution function $F(\zeta, c_z)$.

Figure 5 shows $n(\zeta)$ versus ζ in the cases (i)–(viii) in Table 1; panel (a) contains the cases (i)–(iv), and panel (b) the cases (v)–(viii). The number density naturally increases in the physisorbate layer and exhibits the maximum concentration around $\zeta = \zeta_{\min}$. The result for the case (viii) recovers the equilibrium solution $n(\zeta) = e^{-W(\zeta)}$. In this way, the profiles of $n(\zeta)$ visualizes the physisorbate layer.

Let us denote by $c^\star \hat{\boldsymbol{v}}$ and $T_{\mathrm{w}}\hat{T}$ the (dimensional) flow (or macroscopic) velocity and the (dimensional) temperature, respectively. We follow the notation agreement in Secs. 2.3 and 2.4 and regard $\boldsymbol{v}$ and T as the dimensionless flow velocity and temperature at the zeroth order in ϵ. Then, they are expressed as

$$\boldsymbol{v} = \frac{1}{n}\int_{\mathbf{R}^3} \boldsymbol{c} f \mathrm{d}\boldsymbol{c}, \qquad T = \frac{1}{3n}\int_{\mathbf{R}^3} |\boldsymbol{c} - \boldsymbol{v}|^2 f \mathrm{d}\boldsymbol{c}. \tag{73}$$

It follows from the particle conservation (20) that

$$v_z = \frac{1}{n}\int_{\mathbf{R}^3} c_z f \mathrm{d}\boldsymbol{c} = \frac{1}{n}\int_{-\infty}^{\infty} c_z F(\zeta, c_z) \mathrm{d}c_z = 0,$$

at any ζ, that is, there is no macroscopic motion of the gas molecules in the normal direction in the physisorbate layer. Then, T is expressed as

$$T = \frac{1}{3n}\int_{\mathbf{R}^3}[c_z^2 + (c_x - v_x)^2 + (c_y - v_y)^2]f\mathrm{d}\boldsymbol{c}.$$

This indicates that the temperature T is obtained not by the reduced distribution function $F(\zeta, c_z)$ but by the full distribution $f(\zeta, \boldsymbol{c}_\parallel, c_z)$. However, once $F(\zeta, c_z)$ is obtained, f can be reconstructed as described in the last paragraph in Sec. 2.4. Here, in order to simplify the presentation, we consider, instead of the full temperature T, the *normal* temperature $T_\perp$ defined by

$$T_\perp(\zeta) = \frac{1}{n}\int_{\mathbf{R}^3} c_z^2 f(\zeta, \boldsymbol{c}_\parallel, c_z)\mathrm{d}\boldsymbol{c} = \frac{1}{n}\int_{-\infty}^{\infty} c_z^2 F(\zeta, c_z)\mathrm{d}c_z.$$

The profile of $T_\perp(\zeta)$ is shown in Fig. 6, where panel (a) contains the cases (i)–(iv) in Table 1 and panel (b) the cases (v)–(viii) there. Since $F(\zeta, c_z) \to 0$ as $\zeta \to 0$, the normal temperature $T_\perp$ becomes $0/0$ as $\zeta \to 0$ and does not make sense in the numerical point of view. Therefore, $T_\perp$ is shown only for $\zeta \geq 1$ in Fig. 6. The result for the case (viii) recovers the equilibrium solution $T_\perp = 1$. The profile for each of the cases (i)–(iv) exhibits a sharp downward peak close to $\zeta = 1$, whereas that for each of the cases (v)–(vii) exhibits a sharp upward peak there.

4.3.2 Behavior of velocity distribution function

Next, we consider the reduced velocity distribution function $F(\zeta, c_z)$. In Figs. 7–10, $F(\zeta, c_z)$ versus c_z is plotted at various values of ζ for the cases (iii) and (v)–(vii) in Table 1, respectively. In each figure, panel (a) shows the profiles for $2.239 \leq \zeta \leq \infty$, (b) for $1.201 \leq \zeta \leq 2.293$, (c) for $1 \leq \zeta \leq 1.201$, and (d) for $0.901 \leq \zeta \leq 1$. The vertical dotted line indicates the discontinuities in $F(\zeta, c_z)$.

The profiles of $F(\zeta, c_z)$ in Figs. 7–10 exhibit discontinuities at $\varepsilon = c_z^2/2 + W(\zeta) = 0$, namely, at $c_z = \pm\sqrt{-2W(\zeta)}$ (for $\zeta \geq 1$). The mechanism of generation and propagation of the discontinuity is explained in detail, for the case (iv) in Table 1, in Sec. VII of [6]. Here, we repeat a brief explanation.

Let us consider the characteristic line $c_z^2/2 + W(\zeta) = \varepsilon = 0$ of (28a) for $c_z < 0$. The cases $\varepsilon = 0^+$ and 0^- correspond, respectively, to $F_-(\zeta, 0^+)$ and $F_-(\zeta, 0^-)$ in the (ζ, ε) representation. As $\zeta \to \infty$, $F_-(\zeta, 0^+)$ approaches $F_\infty(0^-)$ because of (32d), whereas $F_-(\zeta, 0^-)$ approaches $F_+(\zeta_b(0^-), 0^-)$ because of (33b). Since $F_\infty(0^-)$ and $F_+(\zeta_b(0^-), 0^-)$ are generally different, $F_-(\zeta, \varepsilon)$ is discontinuous at $\zeta = \infty$ and $\varepsilon = 0$, or equivalently, $F(\zeta, c_z)$ is discontinuous at $\zeta = \infty$ and $c_z = 0$. This discontinuity propagates along the characteristic line $c_z^2/2 + W(\zeta) = 0$ for $c_z \leq 0$, decaying slowly because of the interaction of gas molecules with phonons, toward the solid surface and reaches the *turning* point $(\zeta, c_z) = (\zeta_a(0), 0) = (1, 0)$. Then, it propagates back along the characteristic line $c_z^2/2 + W(\zeta) = 0$ for $c_z > 0$, continuing to decay slowly, toward infinity and finally reaches infinity. The discontinuity does not enter the range $\zeta < \zeta_a(0) = 1$ because the characteristic line $c_z^2/2 + W(\zeta) = 0$ does not enter there. This behavior is well represented by the profiles in Figs. 7–10. The short vertical dotted-line segment at $c_z = 0$ and $\zeta = 1$ in panels (c) and (d) in each of Figs. 7–10, which is upward in Figs. 7 and 10 and downward in Figs. 8 and 9, indicates the height of the discontinuity in $F(\zeta, c_z)$ at $\zeta = 1$.

4.4 Boundary condition for the Boltzmann equation

In this paper, special attention has been focused on the half-space problem (28) for the reduced distribution function $F(\zeta, c_z)$ for the physisorbate layer. The main purpose was to establish some rigorous mathematical results summarized in Theorems 1 and 2 for the problem (28). In addition, some numerical results visualizing rigorous mathematical properties as well as showing the behavior of the gas inside the physisorbate layer were presented. Here, recalling that the original aim of considering the half-space problem (28) or (26) was to establish the boundary condition for the Boltzmann equation, we touch on this aspect of the problem.

In [6], analytical models of the boundary conditions for the Boltzmann equation were proposed. The models were constructed as the first and second approximations for the iteration scheme for (26). The scheme is essentially the same as the scheme (36) for (32) [see (51) in [6]], so that it is omitted here. The point is that the iteration starts not from zero [cf. (35)] but from the equilibrium solution

$$f^0 = \beta \frac{1}{(2\pi)^{3/2}} \exp\left(-\frac{|\boldsymbol{c}|^2}{2} - W(\zeta)\right),$$

where f^0 indicates the zeroth guess for the approximating sequence $\{f^k\}$ $(k = 1, 2, \dots)$ obtained by the iteration scheme mentioned above, and β is a constant to be determined in such a way that the particle conservation (20) is satisfied in each f^k.

The model of the boundary condition (24), based on the first iteration, is obtained in the following form [6]:

$$f_{\rm g}(z, c_z) = [1 - \alpha(c_z^2)] f_{\rm g}(z, -c_z) + \alpha(c_z^2)\beta\,(2\pi)^{-3/2} \exp\left(-|\boldsymbol{c}|^2/2\right), \quad \text{for } c_z > 0, \text{ at } z = 0, \tag{74}$$

where

$$\alpha(c_z^2) = 1 - \left[\theta\left(\zeta_a(c_z^2/2), \infty; c_z^2/2\right)\right]^2 = 1 - \exp\left(-\sqrt{2}\int_{\zeta_a(c_z^2/2)}^{\infty} \frac{{\rm d}\xi}{\tau(\xi)\sqrt{c_z^2/2 - W(\xi)}}\right), \tag{75}$$

$$\beta = -\sqrt{2\pi}\left[\int_0^{\infty} c_z \alpha(c_z^2) \exp\left(-c_z^2/2\right) {\rm d}c_z\right]^{-1} \int_{c_z<0} c_z \alpha(c_z^2) f_{\rm g}(0,\, c_z) {\rm d}\boldsymbol{c}. \tag{76}$$

Here, $\zeta_a(c_z^2/2)$ is the solution of $W(\zeta) = c_z^2/2$, and note that $0 < \alpha(c_z^2) < 1$ holds. In addition, it should be recalled that (74)–(76) are dimensionless and that the arguments t, $\boldsymbol{x}_\parallel$, and $\boldsymbol{c}_\parallel$ are omitted in $f_{\rm g}$ in (74) and (76). The correspondence of the notation here and in [6] is as follows:

$$\begin{aligned}&\left(f_{\rm g},\, \alpha,\, \beta,\, \boldsymbol{x} = (x, y, z),\, \boldsymbol{c} = (c_x, c_y, c_z),\, \tau,\, W\right) \ \text{(here)} \\ &\qquad \Longleftrightarrow \left(\hat{f}_{\rm g},\, \hat{\alpha},\, \hat{\beta},\, \hat{\boldsymbol{x}} = (\hat{x}, \hat{y}, \hat{z}),\, \hat{\boldsymbol{c}} = (\hat{c}_x, \hat{c}_y, \hat{c}_z),\, \hat{\tau}_{\rm ph},\, \hat{\rm W}\right) \ \text{(in [6])}.\end{aligned}$$

The reader is referred to [6] for the dimensional form of (74)–(76) as well as for the generalization, such as the cases of varying wall temperature and curved boundary. The model based on the second iteration, which is also obtained in [6] and detailed in [22], is less explicit, so that it is omitted here.

As one can see from (74), the dependence on c_x and c_y of the reflected distribution $f_{\rm g}(0, c_z)$ $(c_z > 0)$ is determined partially by that of the incident distribution $f_{\rm g}(0, c_z)$

($c_z < 0$) and partially by the thermalizing term $\exp(-|\boldsymbol{c}|^2/2)$. This tendency is more or less the same for the original half-space problem (26). In other words, the problem (26) determines the c_z-dependence of the reflected molecules crucially but not the c_x- and c_y-dependence.

For this reason and in consistency with the main discussions in this paper, we consider the models of the boundary condition only for the reduced distribution function $F(\zeta, c_z)$. Denoting

$$F_{\rm g}(z, c_z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_{\rm g}(z, \boldsymbol{c}_{\parallel}, c_z){\rm d}c_x{\rm d}c_y, \tag{77}$$

and integrating (74) with respect to c_x and c_y each from $-\infty$ to ∞, one obtains

$$F_{\rm g}(z, c_z) = [1-\alpha(c_z^2)]F_{\rm g}(z, -c_z) + \alpha(c_z^2)\beta\,(2\pi)^{-1/2}\exp\left(-c_z^2/2\right), \quad \text{for } \ c_z > 0, \ \text{ at } \ z = 0, \tag{78}$$

where $\alpha(c_z^2)$ is given by (75), and β is recast as

$$\beta = -\sqrt{2\pi}\left[\int_0^{\infty} c_z\alpha(c_z^2)\exp\left(-c_z^2/2\right){\rm d}c_z\right]^{-1}\int_{-\infty}^{0} c_z\alpha(c_z^2)F_{\rm g}(0,\, c_z){\rm d}c_z. \tag{79}$$

Figure 11 shows the reduced velocity distribution for the reflected molecules $F_{\rm g}(0, c_z)$ ($c_z > 0$) in response to that for the incident molecules $F_{\rm g}(0, c_z)$ ($c_z < 0$) when the latter is given by (71), i.e.,

$$F_{\rm g}(0, c_z) = \frac{1}{\sqrt{2\pi T_{\infty}}}\exp\left(-\frac{(c_z - v_{z\infty})^2}{2T_{\infty}}\right), \quad \text{for } \ c_z < 0, \tag{80}$$

for the cases (iii) and (v)–(vii) in Table 1; panels (a), (b), (c), and (d) correspond to the cases (iii), (v), (vi), and (vii), respectively. In the figure, the thin line indicates the result based on the first iteration model, i.e., (78) with (75) and (79), the thick line for $c_z > 0$ that based on the second iteration model (see [6, 22] for its form), and the small circles that based on the numerical solution taken from Figs. 7–10, i.e., $F(\zeta, c_z)$ for $\zeta = \infty$ for $c_z > 0$. The thick line for $c_z < 0$ indicates the incident distribution (80). At least in the cases (iii) and (v)–(vii) in Table 1, the model based on the second iteration shows very good agreement with the numerical solution.

5 Concluding remarks

The present study concerns a kinetic model of gas-surface interactions and resulting boundary conditions for the Boltzmann equation on a solid surface [6]. In the process of the construction of the boundary conditions, a half-space problem of a kinetic equation describing the behavior of the gas molecules in a thin layer on the solid surface (physisorbate layer), in which the molecules are subject to an attractive-repulsive potential and interacting with phonons, plays a crucial role. To be more specific, the solution of this half-space problem establishes the relation between the velocity distribution for the incident molecules and that for the outgoing molecules at infinity, and this relation is nothing but the boundary condition for the Boltzmann equation that is valid outside the physisorbate layer. In [6], this fact was clarified by a formal asymptotic analysis of the kinetic model for gas-surface interactions, and the half-space problem was solved

approximately and numerically to establish the boundary condition for the Boltzmann equation.

In the present paper, we have deepened the analysis and established rigorously the essential mathematical properties of the physisorbate-layer problem. The results are summarized in Theorems 1 and 2 in Sec. 3.1. To be more specific, the existence and uniqueness of the solution have been established. The existence was proved by using an approximating sequence, which turned out to be non-decreasing and to have an upper bound. Furthermore, the approximating sequence was proved to converge to the solution exponentially fast with an explicit estimate of the convergence rate.

In addition to the rigorous mathematical discussions in Sec. 3, we have also carried out some numerical computations, using the method introduced in [6], for some specific potentials and gas-phonon relaxation times, to visualize a part of the mathematical properties shown in Theorems 1 and 2 as well as to demonstrate the behavior of the velocity distribution function and the macroscopic quantities inside the physisorbate layer (Sec. 4). In this connection, the analytical models of the boundary condition for the Boltzmann equation, established in [6] on the basis of first and second approximations for the half-space problem for the physisorbate layer, were also mentioned (Sec. 4.4).

The kinetic approach in [6], which is based on the kinetic scaling in contrast to the fluid scaling considered in [5, 2, 3, 4], can be generalized in various directions. For instance, it would be more practical to consider a confinement potential with a periodic modulation along the solid surface. It would also be important to include chemisorption in addition to physisorption and to consider situations where the phonons are not in equilibrium. Each direction should pose new mathematical problems for relevant kinetic equations, and the mathematical analysis performed in this paper would provide good and useful guidelines for them.

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Data Availability Statement: The data that support Figs. 1–11 are available from the corresponding author, K.A., upon reasonable request. All other data are provided in the paper.

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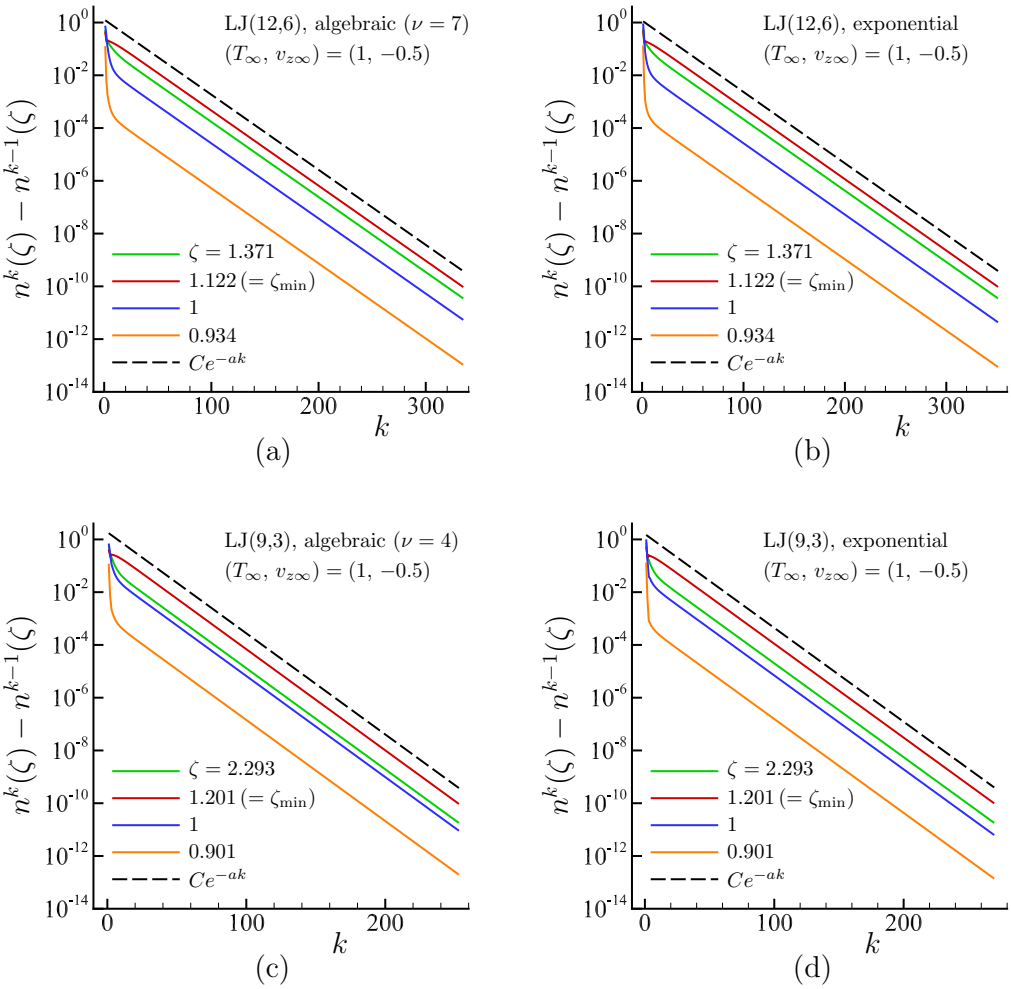

Figure 3: The difference $n^k(\zeta) - n^{k-1}(\zeta)$ versus k at four different positions. Panels (a)–(d) correspond to the cases (i)–(iv) in Table 1. The green, red, blue, and orange solid lines indicate the results at $\zeta = 1.371$, $1.122\,(= \zeta_{\min})$, 1, and 0.934, respectively, in panels (a) and (b) and indicate the results at $\zeta = 2.293$, $1.201\,(= \zeta_{\min})$, 1, and 0.901, respectively, in panels (c) and (d). The function Ce^{-ak} with a in Table 1 and an appropriate constant C is shown by the black dashed line.

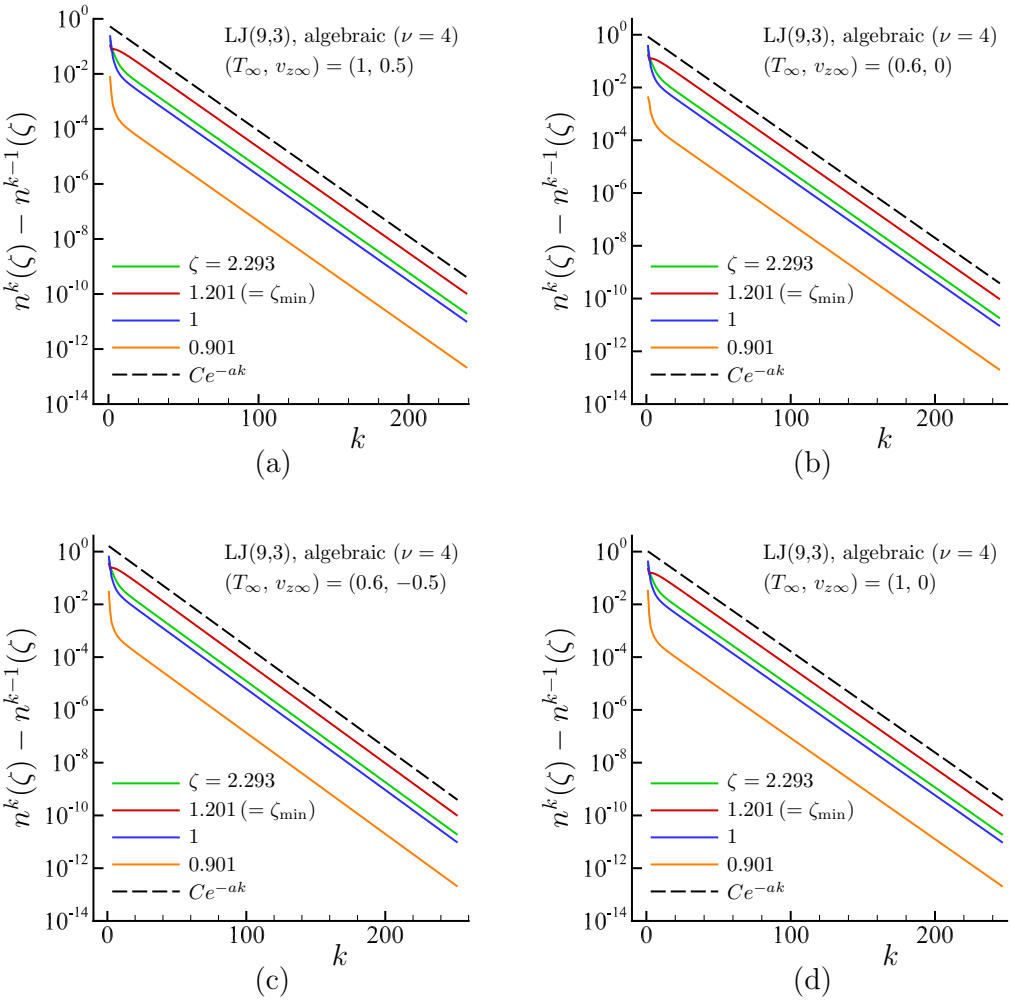

Figure 4: The difference $n^k(\zeta) - n^{k-1}(\zeta)$ versus k at four different positions. Panels (a)–(d) correspond to the cases (v)–(viii) in Table 1. The green, red, blue, and orange solid lines indicate the results at $\zeta = 2.293$, $1.201\,(= \zeta_{\min})$, 1, and 0.901, respectively. The function Ce^{-ak} with a in Table 1 and an appropriate constant C is shown by the black dashed line.

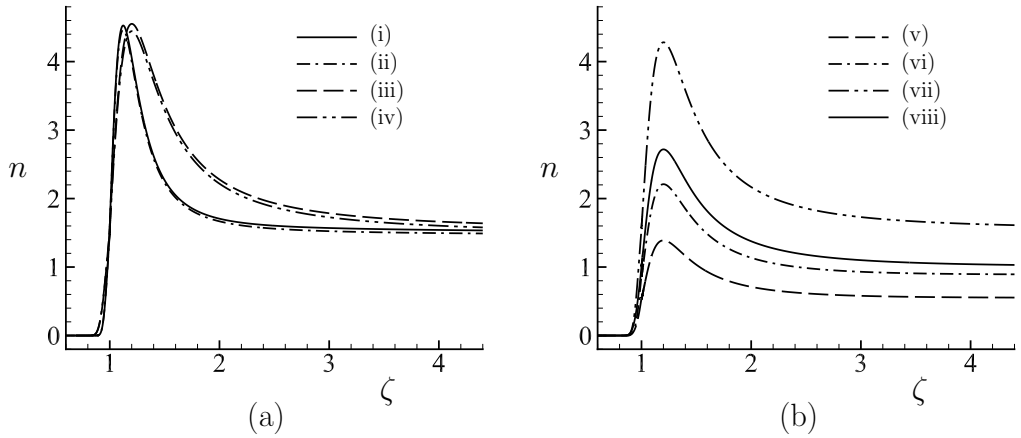

Figure 5: The number density n versus ζ. (a) cases (i)–(iv) in Table 1, (b) cases (v)–(viii) there.

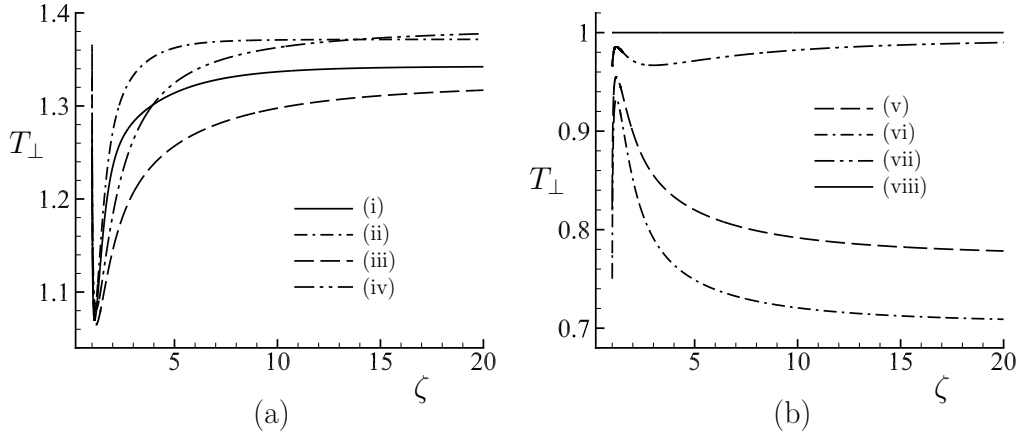

Figure 6: The normal temperature $T_\perp$ versus ζ for $\zeta \geq 1$. (a) cases (i)–(iv) in Table 1, (b) cases (v)–(viii) there.

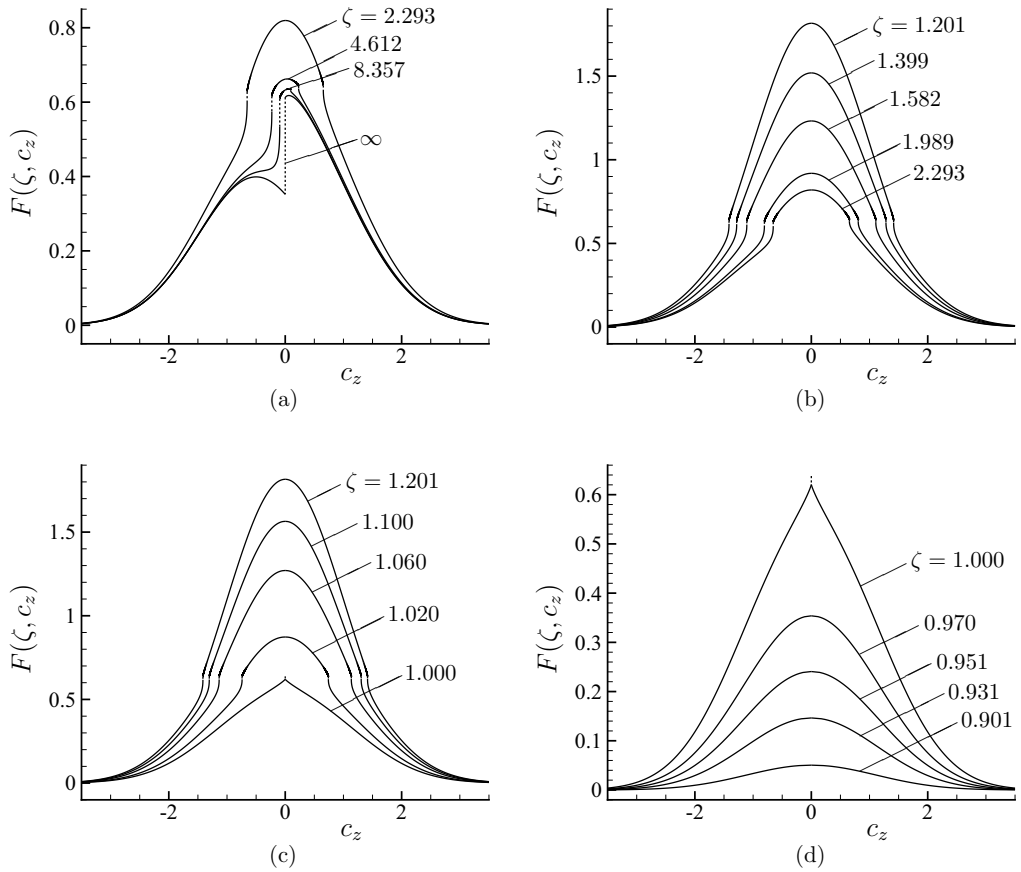

Figure 7: The reduced velocity distribution $F(\zeta, c_z)$ versus c_z in the case (iii) in Table 1. (a) $2.239 \leq \zeta \leq \infty$, (b) $1.201 \leq \zeta \leq 2.293$, (c) $1 \leq \zeta \leq 1.201$, and (d) $0.901 \leq \zeta \leq 1$.

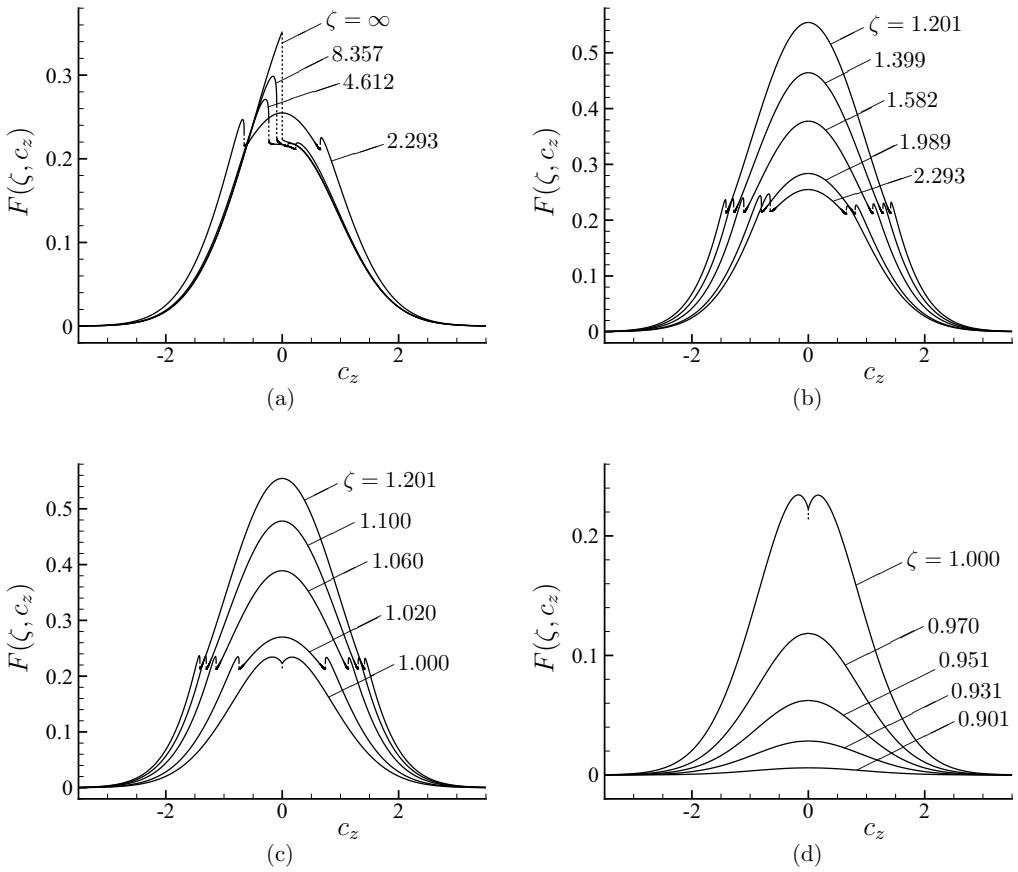

Figure 8: The reduced velocity distribution $F(\zeta, c_z)$ versus c_z in the case (v) in Table 1. (a) $2.239 \leq \zeta \leq \infty$, (b) $1.201 \leq \zeta \leq 2.293$, (c) $1 \leq \zeta \leq 1.201$, and (d) $0.901 \leq \zeta \leq 1$.

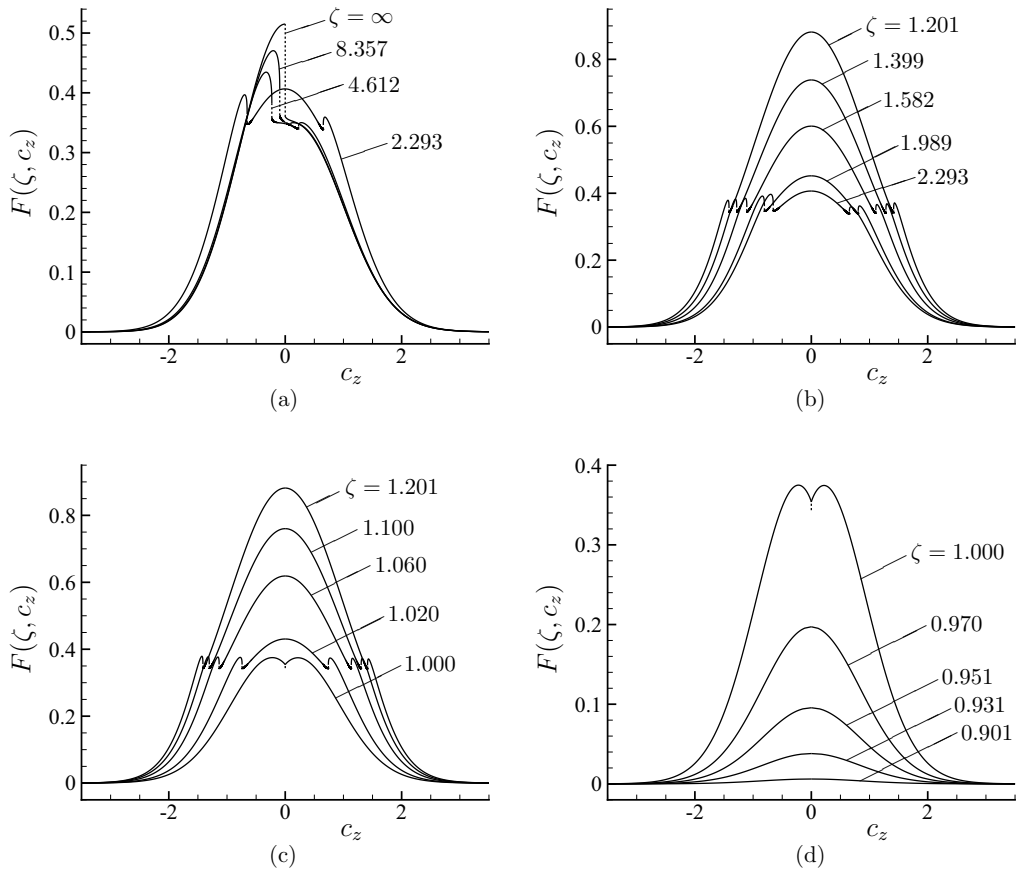

Figure 9: The reduced velocity distribution $F(\zeta, c_z)$ versus c_z in the case (vi) in Table 1. (a) $2.239 \leq \zeta \leq \infty$, (b) $1.201 \leq \zeta \leq 2.293$, (c) $1 \leq \zeta \leq 1.201$, and (d) $0.901 \leq \zeta \leq 1$.

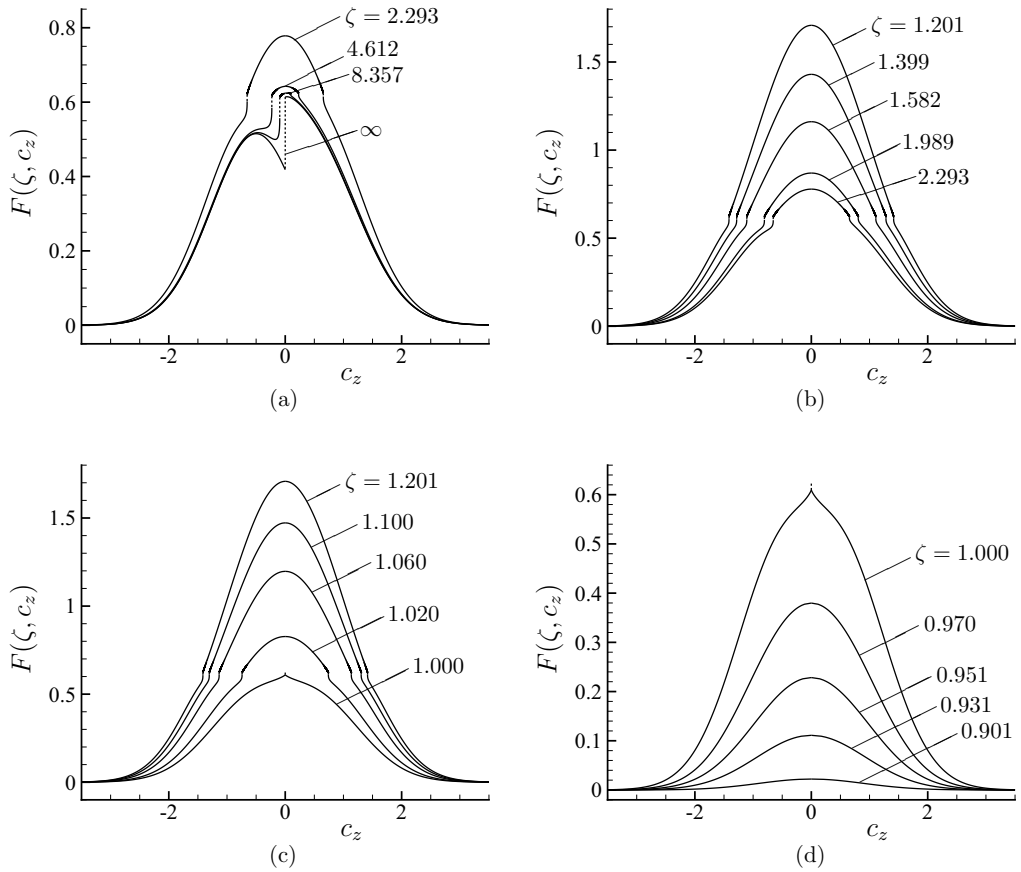

Figure 10: The reduced velocity distribution $F(\zeta, c_z)$ versus c_z in the case (vii) in Table 1. (a) $2.239 \leq \zeta \leq \infty$, (b) $1.201 \leq \zeta \leq 2.293$, (c) $1 \leq \zeta \leq 1.201$, and (d) $0.901 \leq \zeta \leq 1$.

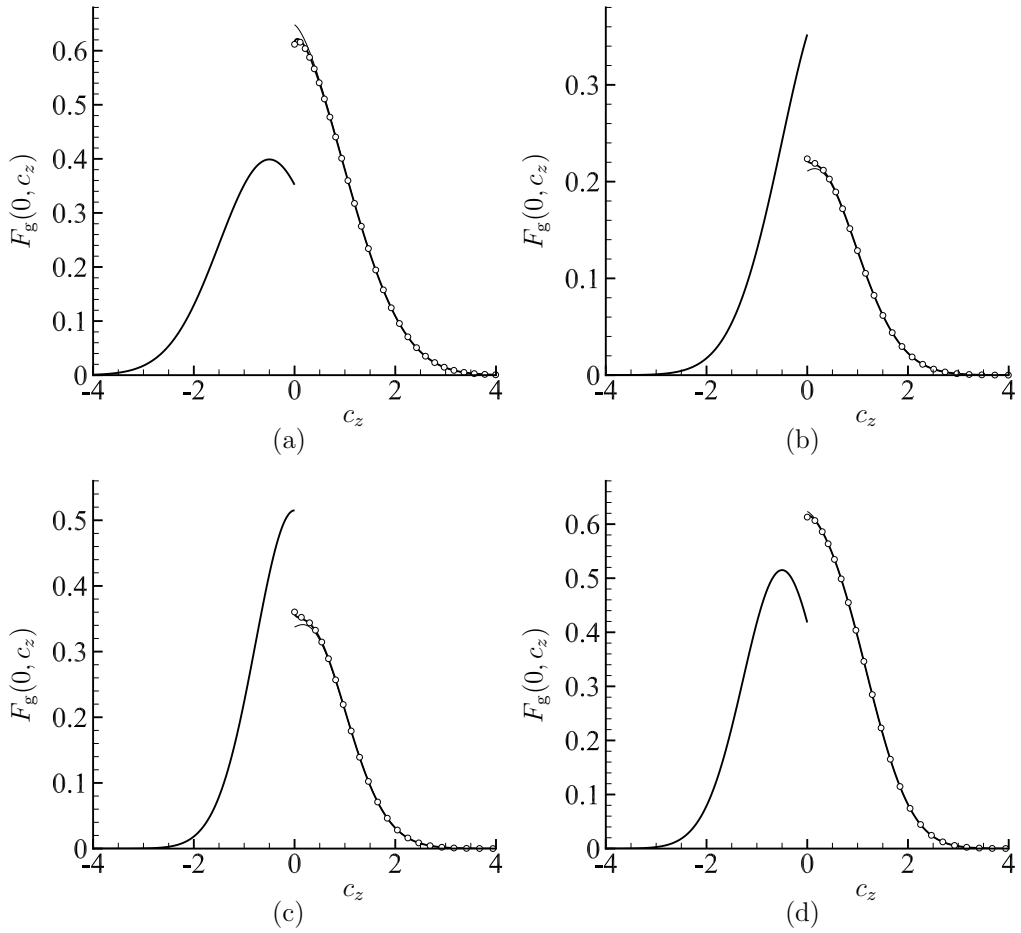

Figure 11: $F_{\rm g}(0, c_z)$ versus c_z. Panels (a), (b), (c), and (d) correspond to the cases (iii), (v), (vi), and (vii) in Table 1, respectively. The thin line indicates the result based on the first iteration model, i.e., (78) with (75) and (79), the thick line for $c_z > 0$ that based on the second iteration model (see [6, 22] for its form), and the circles that based on the numerical solution. The thick line for $c_z < 0$ indicates the incident distribution (80).