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Surprisingly high probability of evaporation for a molecule passing through the Knudsen layer

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The most important characteristics of the Knudsen layer are the temperature jump ΔT between the liquid and vapor and the probability θ_K that a molecule, emitted by the liquid into the vapor, reaches infinity (as opposed to bouncing back due to collisions). In the present paper, the linearized Bhatnagar-Gross-Krook model is used to calculate ΔT and θ_K and show that, in the absence of macroscopic gradients of temperature and density, $\theta_K \approx 96.3\%$. It is then examined how ΔT and θ_K are affected by a combination of a temperature gradient (heat flux) and the matching density gradient, such that the resulting pressure field is uniform.

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I. INTRODUCTION

When studying evaporation, one can distinguish two transient regions: the liquid-vapor interface where the van der Waals force creates a barrier for molecules escaping from the liquid, and the Knudsen layer where the escaped molecules gradually equilibrate with the rest of the vapor (see Fig. 1). Within the framework of the classical Hertz-Knudsen-Schrage approach [1–3] and its modifications [4,5], the Knudsen layer is characterized by the evaporation probability θ_K (also called the "mass adjustment coefficient") and the liquid-vapor temperature jump ΔT. The interface, in turn, is characterized just by the corresponding probability θ_I, as interfaces are typically too thin to accommodate a significant temperature change. If θ_K, ΔT, and θ_I are known, the Hertz-Knudsen-Schrage theory predicts the evaporation rate, i.e., the mass flux into the macroscopic region.

There can be several approaches to finding θ_K, ΔT, and θ_I. The last of these can be calculated using the Enskog-Vlasov kinetic theory [6] or its moment approximation [7], but this task has not been accomplished yet, probably because of the mathematical difficulties involved. Exploring the Knudsen layer is easier: it is described by the Boltzmann kinetic theory which is much simpler that its Enskog-Vlasov counterpart, and there exist many papers where the Knudsen layer is examined using the Boltzmann equation (e.g., [8,9]) or its moment approximation (e.g., [10–21]), or Bhatnagar-Gross-Krook-style kinetic models (e.g., [22–24]).

Note, however, that the flux exiting the interface provides a boundary condition for the Knudsen layer. Thus, even if one knows everything about the latter, the overall evaporation rate still cannot be calculated without the parameter θ_I of the interface.

This difficulty is best illustrated using the Hertz-Knudsen-Schrage approach. First, it will be applied to the Knudsen layer alone.

Let the distribution f_0 of molecules exiting the interface be Maxwellian and correspond to the temperature T_0 and pressure p_0 (the subscript 0 implies that these parameters are measured at $z = 0$, where z is the vertical coordinate; see Fig. 1). Integrating f_0 over molecules with velocities directed away from the interface, one can calculate the mass flux entering the Knudsen layer from the liquid side,

$$F_{0\to K} = \frac{p_0}{\sqrt{2\pi T_0}}.$$

When the molecules are passing through the Knudsen layer, they generally collide with liquid-bound molecules, and sometimes the former bounce back toward the liquid whereas the latter do *not* bounce back toward infinity. As a result, the flux escaping to infinity is

$$F_{0\to K\to\infty} = \theta_K \frac{p_0}{\sqrt{2\pi T_0}}, \tag{1}$$

where θ_K is the probability that a molecule either passes through the Knudsen layer and evaporates or bounces back into the liquid, but sends a "replacement" to infinity.

To estimate the flux of molecules moving in the opposite direction, observe that, at infinity, the vapor is in equilibrium; hence, its distribution f_∞ is definitely Maxwellian, with a temperature T_∞, pressure p_∞, and the macroscopic velocity equal to E/ρ_∞ (where E is the evaporation rate). Integrating f_∞ over liquid-bound molecules, one obtains

$$F_{\infty\to K} = \frac{\rho_\infty T_\infty}{\sqrt{2\pi T_\infty}} \exp\left(-\frac{E^2}{2\rho_\infty^2 T_\infty}\right) + \frac{E}{2}\,\mathrm{erf}\left(\frac{E}{\rho_\infty\sqrt{2T_\infty}}\right) - \frac{E}{2} \tag{2}$$

(for more details, see a similar calculation in Ref. [25]). The bounce-back probability for liquid-bound molecules is the

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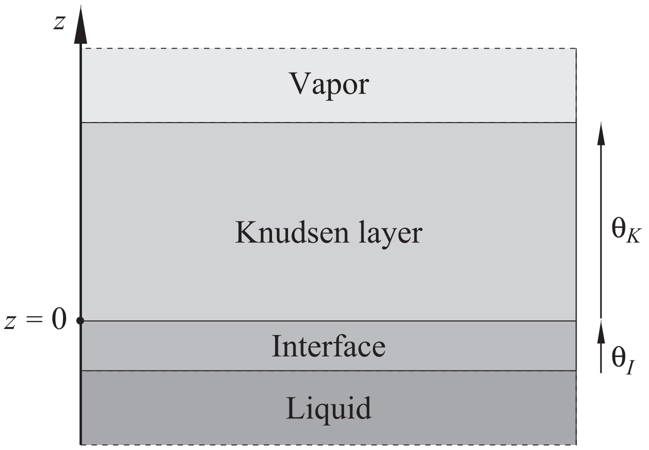

FIG. 1. Steady evaporation (a schematic). It is implied that the liquid is pumped from below with a flux matching the evaporation rate. θ_I and θ_K are the probabilities for a molecule to pass through the interface and Knudsen layer, respectively.

same as that for their infinity-bound counterparts [4]; hence, the flux exiting the Knudsen layer on the liquid side is

$$F_{\infty\to K\to 0} = \theta_K F_{\infty\to K}. \tag{3}$$

Recalling that the evaporation rate is

$$E = F_{0\to K\to\infty} - F_{\infty\to K\to 0},$$

one can reduce Eqs. (1)–(3) to a single equation for E,

$$E = \theta_K \frac{p_0}{\sqrt{2\pi T_0}} - \theta_K \left[\frac{\rho_\infty T_\infty}{\sqrt{2\pi T_\infty}} \exp\left(-\frac{E^2}{2\rho_\infty^2 T_\infty} \right) + \frac{E}{2} \operatorname{erf}\left(\frac{E}{\rho_\infty \sqrt{2T_\infty}} \right) - \frac{E}{2} \right]. \tag{4}$$

In this paper, evaporation is examined under two extra assumptions:

$$T_\infty \approx T_0, \quad p_\infty \approx p_0,$$

in which case Eq. (4) yields to leading order

$$E \approx \frac{2\theta_K}{2-\theta_K} \frac{p_0}{\sqrt{2\pi T_0}} \left(\frac{p_0 - p_\infty}{p_0} + \frac{1}{2} \frac{T_\infty - T_0}{T_0} \right). \tag{5}$$

This expression relates the evaporation rate to the relative humidity (the first term in parentheses) and liquid-vapor temperature jump (the second term). The latter is unknown, and, thus, E can be determined only if formula (5) is complemented with an expression for T_∞.

Note that the above derivation does not rely on the specifics of the Knudsen layer, so (5) can be just as well applied to the interface: one only needs to replace $\theta_K \to \theta_I$. One can even apply (5) to the whole system—the interface plus the Knudsen layer—by replacing θ_K with the overall probability

$$\theta = \frac{\theta_I \theta_K}{\theta_I + \theta_K - \theta_I \theta_K}.$$

Thus, even if one calculates θ_K, one still cannot find θ and eventually E without knowing θ_I.

There is a notable exception to this rule, however: the simulations of Refs. [26,27] suggest that, at low temperatures, the overall probability θ is close to unity–which can occur only if θ_K and θ_I are *both* close to unity. Not only does this result deliver a value for θ_I, but also provides a means to check the value of θ_K when it is found theoretically. Unfortunately, the conclusions of Refs. [26,27] cannot be confirmed via experiments due the discord among those: the values of θ measured by different authors for the same fluid at the same temperature vary between 0.01 and 1 [28,29].

In the present paper, the probability θ_K is calculated, together with the temperature jump $\Delta T = T_\infty - T_0$, using a kinetic model formulated in Sec. II. In Sec. III A, it is shown that, in the absence of macroscopic gradients of temperature and density, $\theta_K \approx 1$. This conclusion holds for all temperatures and, thus, extends the low-temperature result of Refs. [26,27].

The effect of density and temperature gradients is examined in Sec. III B, and estimated for water in Sec. III C. According to the latter, the gradients associated with the vaporization-heat flux is too weak to be important, but a sufficiently strong external gradient can even make undersaturated vapor condense.

II. FORMULATION

A. The Bhatnagar-Gross-Krook model

Consider a liquid and its vapor, occupying the domains $z < 0$ and $z > 0$, respectively, and let the latter be undersaturated, so the former evaporates. If the evaporation is steady in time and homogeneous in the directions perpendicular to the z axis, the distribution function $f(z, v, u)$ of the vapor depends on z, the vertical component v of the molecular velocity, and its horizontal component u.

The mean density ρ, vertical velocity V, and temperature T depend on z and are given by

$$\rho = 2\pi \int_{-\infty}^{\infty} \int_0^{\infty} f\, u \, du \, dv, \tag{6}$$

$$V = \frac{2\pi}{\rho} \int_{-\infty}^{\infty} \int_0^{\infty} v f u \, du \, dv, \tag{7}$$

$$RT = \frac{2\pi}{3\rho} \int_{-\infty}^{\infty} \int_0^{\infty} (v - V)^2 f\, u \, du \, dv, \tag{8}$$

where R is the specific gas constant and the factor of 2π appears because the integration over the polar angle has already been carried out.

According to the steady-state Bhatnagar-Gross-Krook (BGK) model [30], f satisfies the following equation:

$$v \frac{\partial f}{\partial z} = \frac{M - f}{\tau}, \tag{9}$$

where

$$M = \frac{2\pi\rho}{(2\pi RT)^{3/2}} \exp\left[-\frac{u^2 + (v - V)^2}{2RT} \right], \tag{10}$$

is the local Maxwellian distribution, and τ is an empiric parameter representing the characteristic time between two successive collisions experienced by the same molecule. The dependence of τ on the local ρ and T is supposed to be deduced from experimental data, but it will not be discussed here.

To apply Eqs. (6)–(10) to the Knudsen layer, introduce the temperature T_0 of the liquid and the corresponding saturated vapor density ρ_0. Let the vapor passing through the interface due to evaporation have a Maxwellian distribution and be saturated (the latter corresponds to the hypothesis $\theta_I = 1$ assumed by Hertz [1]). Then one obtains the following boundary condition:

$$v > 0 \quad \Rightarrow \quad f = \frac{\rho_0}{(2\pi R T_0)^{3/2}} \exp\left(-\frac{u^2 + v^2}{2RT_0}\right) \qquad \text{at} \quad z = 0. \tag{11}$$

The vapor coming from infinity, in turn, is also Maxwellian, but with different characteristics,

$$v < 0 \quad \Rightarrow \quad f \to \frac{\rho_\infty}{(2\pi R T_\infty)^{3/2}} \exp\left[-\frac{u^2 + (v - V_\infty)^2}{2RT_\infty}\right] \quad \text{as} \quad z \to \infty, \tag{12}$$

where ρ_∞ and T_∞ are related to the relative humidity H at infinity via

$$\frac{\rho_\infty T_\infty}{\rho_0 T_0} = H, \tag{13}$$

i.e., H is determined as the ratio of the vapor pressure to its saturated value.

It is worth noting that condition (11) is a *hypothesis* (as it is not obvious that the vapor emitted by the liquid is necessarily Maxwellian), whereas condition (12) reflects the *fact* that the vapor at infinity is in equilibrium.

B. Nondimensionalization

The following nondimensional variables will be used:

$$z_{nd} = \frac{z}{\lambda_0}, \quad v_{nd} = \frac{v}{(RT_0)^{1/2}},$$

$$\rho_{nd} = \frac{\rho}{\rho_0}, \quad V_{nd} = \frac{V}{(RT_0)^{1/2}}, \quad T_{nd} = \frac{T}{T_0},$$

$$M_{nd} = \frac{(RT_0)^{3/2}}{\rho_0} M, \quad f_{nd} = \frac{(RT_0)^{3/2}}{\rho_0} f, \quad \tau_{nd} = \frac{\tau}{\tau_0},$$

where τ_0 is the BGK collision time corresponding to ρ_0 and T_0, and

$$\lambda_0 = (RT_0)^{1/2}\tau_0 \tag{14}$$

is the mean-free path.

Rewriting boundary-value problem (6)–(13) in terms of the above variables and omitting the subscript $_{nd}$, one can verify that the resulting problem is identical to the original one, but with

$$\rho_0 = 1, \quad T_0 = 1.$$

C. Linearization

To simplify the problem, assume that the vapor is close to saturation, i.e.,

$$H = 1 + \tilde{H},$$

where $|\tilde{H}| \ll 1$. Assume also that

$$\rho = 1 + \tilde{\rho}, \quad V = \tilde{V}, \quad T = 1 + \tilde{T},$$

$$\rho_\infty = 1 + \tilde{\rho}_\infty, \quad V_\infty = \tilde{V}_\infty, \quad T_\infty = 1 + \tilde{T}_\infty,$$

$$f = \frac{1}{(2\pi)^{3/2}} \exp\left(-\frac{u^2 + v^2}{2}\right) + \tilde{f}, \quad \tau = 1 + \tilde{\tau},$$

where the tilded variables are $O(\tilde{H})$, hence, small. Substituting the above expressions into Eqs. (6)–(13), one obtains to leading order

$$\tilde{\rho} = 2\pi \int_{-\infty}^{\infty}\int_0^{\infty} \tilde{f} u \, \mathrm{d}u \, \mathrm{d}v, \quad \tilde{V} = 2\pi \int_{-\infty}^{\infty}\int_0^{\infty} v \tilde{f} u \, \mathrm{d}u \, \mathrm{d}v, \quad \tilde{T} = 2\pi \int_{-\infty}^{\infty}\int_0^{\infty} \frac{u^2 + v^2 - 3}{3} \tilde{f} u \, \mathrm{d}u \, \mathrm{d}v, \tag{15}$$

$$v \frac{\partial \tilde{f}}{\partial z} = \frac{1}{(2\pi)^{3/2}} \left(\tilde{\rho} + \frac{u^2 + v^2 - 3}{2} \tilde{T} + v\tilde{V}\right) \exp\left(-\frac{u^2 + v^2}{2}\right) - \tilde{f}, \tag{16}$$

$$v > 0 \Rightarrow \tilde{f} = 0 \quad \text{at} \quad z = 0, \tag{17}$$

$$v < 0 \Rightarrow \tilde{f} = \frac{1}{(2\pi)^{3/2}} \left(\tilde{\rho}_\infty + \frac{u^2 + v^2 - 3}{2} \tilde{T}_\infty + v\tilde{V}_\infty\right) \exp\left(-\frac{u^2 + v^2}{2}\right) \quad \text{as} \quad z \to \infty, \tag{18}$$

$$\tilde{\rho}_\infty + \tilde{T}_\infty = \tilde{H}. \tag{19}$$

It can be readily deduced from Eqs. (15)–(19) that

$$\frac{\mathrm{d}\tilde{V}}{\mathrm{d}z} = 0,$$

which comes as no surprise as $\tilde{V}$ represents the linear part of the nondimensional mass flux and, hence, must be spatially uniform (because the problem is steady). Thus, in what follows, $\tilde{V}$ will be treated as a constant. The boundary-value problem (15)–(19) involves three independent variables (z, u, v), but it can be reduced (see Appendix A) to a much simpler one-variable problem,

$$\tilde{\rho}(z) + \tilde{V} A_{\rho V}(z) = \int_0^{\infty} [B_{\rho\rho}(z - z')\,\tilde{\rho}(z') + B_{\rho T}(z - z')\,\tilde{T}(z')]\mathrm{d}z', \tag{20}$$

$$\tilde{T}(z)+\tilde{V}A_{TV}(z)=\int_0^{\infty}[B_{T\rho}(z-z')\,\tilde{\rho}(z')+B_{TT}(z-z')\,\tilde{T}(z')]\mathrm{d}z', \tag{21}$$

$$\frac{1}{2}\tilde{V}=-\int_0^{\infty}[B_{V\rho}(z')\,\tilde{\rho}(z')+B_{VT}(z')\,\tilde{T}(z')]\mathrm{d}z', \tag{22}$$

where the coefficients are

$$A_{\rho V}=C_1,\quad A_{TV}=\frac{C_3-C_1}{3}, \tag{23}$$

$$B_{\rho\rho}=C_{-1},\quad B_{\rho T}=\frac{C_1-C_{-1}}{2}, \tag{24}$$

$$B_{T\rho}=\frac{C_1-C_{-1}}{3},\quad B_{TT}=\frac{C_3-2C_1+5C_{-1}}{6}, \tag{25}$$

$$B_{V\rho}=C_0,\quad B_{VT}=\frac{C_2-C_0}{2}, \tag{26}$$

and

$$C_n(z)=\frac{1}{(2\pi)^{1/2}}\int_0^{\infty}v^n\exp\left(-\frac{v^2}{2}-\frac{|z|}{v}\right)\mathrm{d}v. \tag{27}$$

As shown in Appendix B, the function $C_{-1}(z)$ is singular as $z\to 0$ – hence, $B_{\rho\rho}(z)$, $B_{\rho T}(z)$, $B_{T\rho}(z)$, and $B_{TT}(z)$ are singular too. These singularities are integrable, however, so they do not pose a problem for Eqs. (20)–(22) (where $B_{\rho\rho}$, etc. are the kernels). It is also shown in Appendix B that both A and B coefficients decay exponentially as $z\to\infty$.

Next, boundary condition (19) can be rewritten in the form

$$\tilde{\rho}+\tilde{T}\to\tilde{H}\quad\text{as}\quad z\to\infty. \tag{28}$$

It turns out that the solution of Eqs. (20)–(22) subject to condition (28) is not unique. To understand why, note that there must be a solution describing steady transfer of heat from, or to, infinity, i.e., such that

$$\tilde{T}=-\tilde{Q}z+O(1)\quad\text{as}\quad z\to\infty, \tag{29}$$

where $\tilde{Q}$ is the nondimensional heat flux. Given the above asymptotics, boundary condition (28) implies that

$$\tilde{\rho}=\tilde{Q}z+O(1)\quad\text{as}\quad z\to\infty. \tag{30}$$

The fact that asymptotics (29) and (30) are mathematically consistent with Eqs. (20)–(22) is shown in Appendix C.

Thus, a heat flux must be accompanied by a density gradient—which comes as no surprise, as the pressure field must be spatially uniform (otherwise an accelerating flow would arise).

For given $\tilde{H}$ and $\tilde{Q}$, Eqs. (20)–(22) and boundary conditions (28) and (29) fully determine $\tilde{\rho}(z)$, $\tilde{T}(z)$, and $\tilde{V}$.

III. SOLUTIONS DESCRIBING THE KNUDSEN LAYER

This section examines solutions with $\tilde{Q}=0$ and $\tilde{Q}\neq 0$ (Secs. III A and III B, respectively). In both cases, Eqs. (20)–(22) were solved numerically, using the algorithm described in Appendix D.

A. Solutions with zero heat flux, $\tilde{Q}=0$

Due to linearity of Eqs. (20)–(22) and (28)–(30), their solution depends linearly on $\tilde{H}$ (the deviation of the humidity from unity). Thus, it is sufficient to solve the problem for a single value of $\tilde{H}$ – say, $\tilde{H}=-1$ (where the minus makes the vapor at infinity undersaturated). The solution for this case was computed and plotted in Fig. 2, and the corresponding evaporation rate is $\tilde{V}\approx 0.663$. Observe that the global variability of the

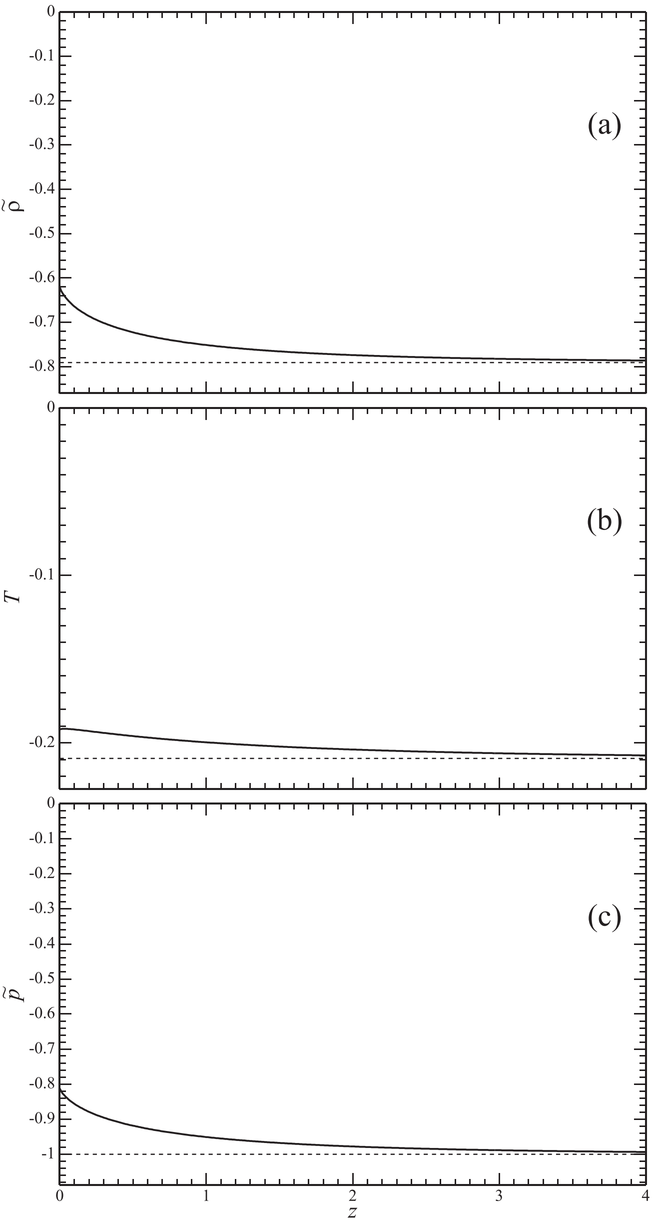

FIG. 2. The solution of boundary-value problem (20)–(22) and (28)–(30) with $\tilde{H}=-1$ and $\tilde{Q}=0$: (a) the density $\tilde{\rho}(z)$, (b) the temperature $\tilde{T}(z)$, (c) the pressure $\tilde{p}(z)=\tilde{\rho}(z)+\tilde{T}(z)$. The horizontal dotted lines show the limiting ($z\to\infty$) values of $\tilde{\rho}$, $\tilde{T}$, and $\tilde{p}$. Note that the global change of $\tilde{\rho}$ is 22% and that of $\tilde{T}$, 8% (in both cases, relative to their respective values at infinity).

vapor characteristics is small, and the large amount of white space in this figure illustrates this smallness.

Figure 2 also shows that, near the interface, the vapor density differs from its saturated value ($\tilde{\rho}(0) \neq 0$), and the vapor temperature differs from the liquid temperature ($\tilde{T}(0) \neq 0$). This observation, however, does not contradict to boundary condition (11), which constrains the distribution of the *incoming* molecules, so that the *full* density ρ and temperature T can differ from ρ_0 and T_0, respectively.

Thus, $\tilde{V}$ is related to $\tilde{H}$ by

$$\tilde{V} \approx -0.6632\,\tilde{H}. \tag{31}$$

Let $\tilde{T}_\infty$ be the value of $\tilde{T}(z)$ as $z \to \infty$. Physically, this quantity is the nondimensional liquid-vapor temperature jump, and computationally, it is related to $\tilde{H}$ by

$$\tilde{T}_\infty \approx 0.2094\,\tilde{H}. \tag{32}$$

The physical meaning of results (31)–(32) becomes clear if they are "redimensionalized," i.e., rewritten in terms of the dimensional evaporation rate $E = \rho_0 (RT_0)^{1/2}\tilde{V}$, the dimensional temperature jump $\Delta T = T_0 \tilde{T}_\infty$, and the full humidity $H = 1 + \tilde{H}$,

$$E \approx 0.6632\,\rho_0 (RT_0)^{1/2}(1 - H), \tag{33}$$

$$\Delta T \approx -0.2094\,T_0(1 - H). \tag{34}$$

Comparing formula (33) to the Hertz-Knudsen-Schrage equation (5), one can deduce that the coefficient θ_K in the latter is

$$\theta_K \approx 0.9629.$$

Thus, the probability for a molecule to bounce back when passing through the Knudsen layer is less than 4%.

The surprisingly low value of the "bounce-back probability" $1 - \theta_K$ is probably connected to the weak variability of the vapor characteristics noted above. Indeed, imagine for the sake of argument that the vapor's density and temperature in the Knudsen layer are fully uniform—in which case the numbers of molecules entering it and leaving it on the other side should be equal—so that θ_K is exactly unity. Then, it is reasonable to conjecture that, if the vapor variability is weak, then $1 - \theta_K$ is small.

It is also interesting to estimate the temperature jump across the Knudsen layer for, say, 90% humidity and a "room temperature" $T_0 = 25\,^\circ\mathrm{C}$, in which case expression (34) yields $\Delta T \approx -8\,^\circ\mathrm{C}$. Such a value is large enough to be important for heat and mass transfer in the outer region (due to the sensitivity of the saturated pressure of water to the temperature; see, for example, Fig. 1 of Ref. [31]).

B. Solutions with nonzero heat flux, $\tilde{Q} \neq 0$

To examine the effect of nonzero $\tilde{Q}$, one can set $\tilde{H} = 0$. This does not cause loss of generality, as the problem's linearity allows one to simply add the contribution of $\tilde{H}$ computed in the previous section. For the same reason, one needs to examine a single value of the heat flux—say, $\tilde{Q} = 1$—and eventually find

$$\tilde{V} \approx -0.5246\,\tilde{Q}, \tag{35}$$

$$T_\infty \approx -1.6743\,\tilde{Q}, \tag{36}$$

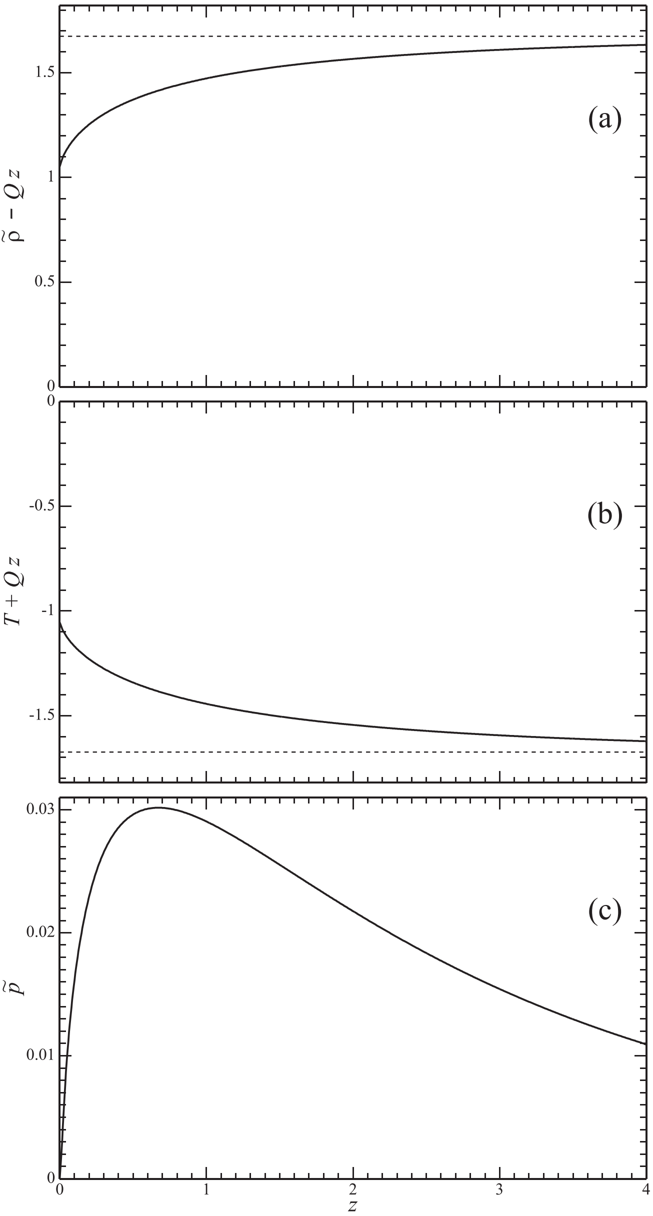

FIG. 3. The solution of boundary-value problem (20)–(22) and (28)–(30) with $\tilde{H} = 0$ and $\tilde{Q} = 1$: (a) the nonlinear part of the density, $\tilde{\rho}(z) - \tilde{Q}z$, (b) the nonlinear part of the temperature, $\tilde{T}(z) + \tilde{Q}z$, (c) the pressure $\tilde{p}(z) = \tilde{\rho}(z) + \tilde{T}(z)$. The horizontal dotted lines in panels (a)–(b) show the limiting ($z \to \infty$) values of the quantities plotted, and in panel (c) the dotted line coincides with the horizontal axis. Note that the quantities plotted in panels (a)–(b) change both by 37% (relative to their values at infinity).

where $\tilde{T}_\infty$ is defined as the limit of $\tilde{T}(z) + \tilde{Q}z$ as $z \to \infty$. The solution computed for this case is illustrated in Fig. 3. Note that, to make comparison between Figs. 2 and 3 meaningful, the latter shows $\tilde{\rho}(z)$ and $\tilde{T}(z)$ with their linear components subtracted. Observe the noticeably stronger variability of the solution in the latter figure (the quantitative characteristics of variability are given in the captions of Figs. 2 and 3).

To "redimensionalize" Eqs. (35) and (36), introduce the dimensional heat flux by

$$Q = \frac{\kappa_0 T_0}{\lambda_0}\tilde{Q},$$

where the mean free path λ_0 is given by (14), and the vapor's thermal conductivity, by

$$\kappa_0 = \frac{5\rho_0 R^2 T_0}{2}\tau.$$

These two formulas were derived similarly to the derivation of Ref. [32] for a similar model.

Thus, the dimensional analogs of (35) and (36) are

$$E \approx -\frac{0.2098\,Q}{RT_0}, \tag{37}$$

$$\Delta T \approx -\frac{0.6697\,T_0 Q}{\rho_0 (RT_0)^{3/2}}. \tag{38}$$

C. Discussion

(1) Combining formulas (33) and (34) ($\tilde{Q} = 0$) and (37) and (38) ($\tilde{H} = 0$), one obtains

$$\frac{E}{\rho_0 (RT_0)^{1/2}} \approx 0.6632(1 - H) - \frac{0.2098\,Q}{\rho_0 (RT_0)^{3/2}}, \tag{39}$$

$$\frac{\Delta T}{T_0} \approx -0.2094(1 - H) - \frac{0.6697\,Q}{\rho_0 (RT_0)^{3/2}}, \tag{40}$$

where E is the dimensional evaporation rate and H, the full humidity.

Equations (39) and (40) are the main result of the present paper. To draw a connection between them and the existing literature, rewrite (39)–(40) in the form

$$\begin{bmatrix} 1 - H \\ \frac{-\Delta T}{T_0} \end{bmatrix} = \mathbf{G} \begin{bmatrix} \frac{E}{\rho_0 (RT_0)^{1/2}} \\ \frac{Q}{\rho_0 (RT_0)^{3/2}} \end{bmatrix},$$

where

$$\mathbf{G} = \begin{bmatrix} 1.5078 & 0.3163 \\ 0.3157 & 0.7359 \end{bmatrix}$$

is sometimes referred to as the "matrix of interfacial coefficients." As shown in Refs. [22,23] for the linearized BGK model, and in Ref. [8] for its Boltzmann-equation equivalent, **G** should be positive-definite and symmetric. The latter property can be used to estimate the numerical accuracy of this paper's results: evidently, the diagonal terms of **G** equal 0.316 ± 0.0003, suggesting that the accuracy is 0.1%. Note also that $\det \mathbf{G} \approx 1.0097$, and it is unclear whether its proximity to unity has a physical meaning (for example, it might somehow be connected to the fact that $\theta_K \approx 1$).

(2) To estimate the importance of nonzero Q, recall that evaporation implies continuous delivery of vaporization heat to the interface. The corresponding heat fluxes come from both sides of the interface: Q is the flux coming from the vapor side, and that coming from the liquid side will be denoted by $Q^{(l)}$. Their sum should amount to the total heat required for evaporation, i.e.,

$$Q^{(l)} - Q = E\Delta, \tag{41}$$

where Δ is the vaporization heat per unit mass.

For a flat interface in an unbounded space, the fluxes satisfy the following proportion (derived in Ref. [33] and, in a simpler way, in Appendix E):

$$\frac{-Q}{Q^{(l)}} = \frac{(\rho_0 c_0 \kappa_0)^{1/2}}{\left(\rho_0^{(l)} c_0^{(l)} \kappa_0^{(l)}\right)^{1/2}}, \tag{42}$$

where ρ_0, c_0, and κ_0 are the vapor's density, specific heat at constant pressure, and thermal conductivity, respectively; and $\rho_0^{(l)}$, $c_0^{(l)}$, and $\kappa_0^{(l)}$ are the corresponding parameters of the liquid.

Expressing Q from Eqs. (41) and (42) and substituting it into (39), one obtains

$$E\left[1 - \frac{(\rho_0 c_0 \kappa_0)^{1/2}}{(\rho_0 c_0 \kappa_0)^{1/2} + \left(\rho_0^{(l)} c_0^{(l)} \kappa_0^{(l)}\right)^{1/2}} \frac{0.2098\,\Delta}{RT_0}\right] \approx 0.6632\,\rho_0 (RT_0)^{1/2}(1 - H). \tag{43}$$

To estimate the importance of the heat flux (the second term in the square brackets), consider water at, say, $T_0 = 25\,^{\circ}\mathrm{C}$. Using Ref. [34] to specify Δ, and Ref. [35] for the other parameters, one obtains

$$\frac{(\rho_0 c_0 \kappa_0)^{1/2}}{(\rho_0 c_0 \kappa_0)^{1/2} + \left(\rho_0^{(l)} c_0^{(l)} \kappa_0^{(l)}\right)^{1/2}} \frac{0.2098\,\Delta}{RT_0} \approx 2.11 \times 10^{-3}.$$

As follows from this estimate and Eq. (43), the heat flux from the vapor side is unimportant in this case. Physically, this occurs because most of the heat is delivered from the liquid side.

Next, consider an *external* heat flux—created, for example, using a flat heating element mounted above the interface (as done in Ref. [36]). To see if such a flux can be important, assume, for the sake of an argument, that it supplies all the vaporization heat needed for evaporation, i.e., $Q = -E\Delta$, in which case Eqs. (39) and (40) yield

$$E\left(1 - \frac{0.2098\,\Delta}{RT_0}\right) \approx 0.6632\,\rho_0 (RT_0)^{1/2}(1 - H). \tag{44}$$

Estimating the Q-related term in this equation for water at $T_0 = 25\,^{\circ}\mathrm{C}$, one can see that the contribution of the heat flux is an order-one effect,

$$\frac{0.2198\,\Delta}{RT_0} \approx 3.726.$$

Furthermore, Eq. (44) shows that the sign of E in this case is opposite to that of $(1 - H)$, i.e., the heat flux makes undersaturated vapor condense!

One should realize, however, that the density gradient is probably just as important in this case as the heat flux. Indeed, boundary condition (30) makes $\tilde{\rho}$ change linearly toward infinity, and this circumstance ought to affect the evaporation rate just as strongly as the linear change of $\tilde{T}$ does.

As much as one might be interested in separating the effects of the heat flux and density gradient, one cannot do so for the case of a pure fluid, where the two are interlinked by boundary conditions (29) and (30). This will have to be done for a mixture.

IV. CONCLUDING REMARKS

The main result of this paper are expressions (39) and (40) for the evaporation rate E and temperature jump ΔT across the Knudsen layer, in terms of the relative humidity H and macroscopic heat flux Q (the latter is also a measure of the density gradient).

It follows from expression (39) that a heat flux and the matching density gradient can strongly affect the Knudsen layer, but it is impossible to clarify which one of the two is more important. They do not arise separately in pure fluids: if it is at rest or moving as a whole, the temperature and density gradients have to add up to a uniform pressure field (pressure inhomogeneities give rise to an accelerating flow, physically irrelevant to evaporation).

This effect of the heat flux alone can only be clarified if one considers evaporation of a liquid into a *mixture*, say, of vapor and air. If the partial density of the vapor is smaller than that of air (which it indeed is in Earth's atmosphere), the pressure field typically equilibrates at the expense of a slight change of the air density, so that the vapor density gradient does not have to be present. One's intuition suggests that, in this case, the heat flux alone would be unable to make undersaturated vapor condense, but it should still be important quantitatively.

Note also that all existing multicomponent BGK models do not satisfy the Onsager reciprocal relations [37]. As a result, they cannot be calibrated, i.e., their parameters cannot be fixed to make the transport properties of the model match the properties of the vapor–air mixture. This means that the problem of evaporation of a liquid into a mixture of vapor and air will have to be examined using the multicomponent Boltzmann equation.

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DATA AVAILABILITY

No data were created or analyzed in this study.

APPENDIX A: DERIVATION OF EQS. (20)–(22)

Eq. (24) can be viewed as an ordinary differential equation (linear, first order) where $\tilde{f}$ is the unknown, z is the independent variable, and the dependence of $\tilde{f}$ on u and v is treated as parametric (this approach was suggested for a similar problem in Ref. [22–24]). Subject to boundary conditions (17) and (18), the solution of Eq. (24) is

$$\tilde{f} = \pm\frac{1}{(2\pi)^{3/2} v}\int_0^z \left[\tilde{\rho}(z') + \frac{u^2+v^2-3}{2}\tilde{T}(z') + v\tilde{V}(z')\right]\exp\left(-\frac{u^2+v^2}{2} - \frac{z-z'}{v}\right)\mathrm{d}z' \quad \text{for} \quad v \gtrless 0.$$

Substituting this expression into Eqs. (15) and changing the order of integration $\mathrm{d}z'\mathrm{d}v \to \mathrm{d}v\,\mathrm{d}z'$, one obtains

$$\tilde{\rho}(z) = \int_0^\infty [B_{\rho\rho}(z-z')\,\tilde{\rho}(z') + B_{\rho T}(z-z')\,\tilde{T}(z') + D_{\rho V}(z-z')\,\tilde{V}(z')]\mathrm{d}z', \tag{A1}$$

$$\tilde{T}(z) = \int_0^\infty [B_{T\rho}(z-z')\,\tilde{\rho}(z') + B_{TT}(z-z')\,\tilde{T}(z') + D_{TV}(z-z')\,\tilde{V}(z')]\mathrm{d}z', \tag{A2}$$

$$\tilde{V}(z) = \int_0^\infty [D_{V\rho}(z-z')\,\tilde{\rho}(z') + D_{VT}(z-z')\,\tilde{T}(z') + D_{VV}(z-z')\,\tilde{V}(z')]\mathrm{d}z', \tag{A3}$$

where

$$D_{\rho V} = C_0 \operatorname{sgn} z, \quad D_{TV} = \frac{C_2 - C_0}{3}\operatorname{sgn} z, \quad D_{V\rho} = C_0 \operatorname{sgn} z, \quad D_{VT} = \frac{C_2 - C_0}{2}\operatorname{sgn} z, \quad D_{VV} = C_1, \tag{A4}$$

and the rest of the coefficients are given by expressions (24)–(26), with C_n given by (27).

One can simplify Eqs. (A1)–(A3) by taking advantage of the fact that $\tilde{V}$ does not dependent on z. Letting $\tilde{V} = \text{const}$ and using expressions (23) and (A4) to show that

$$\int_0^\infty B_{\rho V}(z-z')\,\mathrm{d}z' = -A_{\rho V}(z),$$

$$\int_0^\infty B_{TV}(z-z')\,\mathrm{d}z' = -A_{TV}(z),$$

one can verify that Eqs. (A1) and (A2) reduce to (20) and (21), as required. To reduce Eq. (A3) to (22), one needs to first set $z = 0$ in the former (which is allowable because both sides of (A3) are constants) and then use expressions (A4) to show that

$$D_{V\rho}(-z') = -B_{V\rho}(z'), \quad D_{VT}(-z') = -B_{VT}(z'),$$

$$\int_0^\infty D_{VV}(-z')\,\mathrm{d}z' = \frac{1}{2}.$$

APPENDIX B: PROPERTIES OF THE COEFFICIENTS IN EQS. (20)–(22)

Consider definition (27) of $C_n(z)$, let $z \to \infty$, and use the steepest descent method to show that

$$C_n \sim \frac{|z|^{n/3}}{2\sqrt{3}}\exp\left(-\frac{3|z|^{2/3}}{2}\right) \quad \text{as} \quad z \to \infty.$$

Thus, C_n decay exponentially as $z \to \pm\infty$, and so do the coefficients $A_{\rho V}$, $B_{\rho\rho}$, etc., because they are related to C_n by Eqs. (23)–(26).

Next, observe that the integral in Eq. (27) converges for non-negative n; hence, $C_n(z)$ with $n \geqslant 0$ are finite and continuous at all z. This property and the exponential decay at infinity (proved above) makes them integrable. Thus, to ensure that the coefficients $A_{\rho V}$, $B_{\rho\rho}$, etc., are integrable too, one needs to also prove integrability of C_{-1} [which is the only C_n with a negative n in Eqs. (23)–(26)].

To examine the behavior of C_{-1} as $z \to 0$, consider first C_1 and use definition (27) to show that

$$z\frac{\mathrm{d}^3 C_1}{\mathrm{d}z^3} + C_1 = \frac{1}{(2\pi)^{1/2}}\int_0^\infty \left(v - \frac{|z|}{v^2}\right) \times \exp\left(-\frac{v^2}{2} - \frac{|z|}{v}\right)\mathrm{d}v \quad \text{for} \quad z > 0.$$

The integral on the right-hand side of this equality can readily be evaluated and shown to equal zero, resulting in the following differential equation:

$$z\frac{\mathrm{d}^3 C_1}{\mathrm{d}z^3} + C_1 = 0 \quad \text{for} \quad z > 0. \tag{B1}$$

Definition (27) of C_n implies also that

$$C_1 = \frac{1}{(2\pi)^{1/2}}, \quad \frac{\mathrm{d}C_1}{\mathrm{d}z} = -\frac{1}{2} \quad \text{at} \quad z = 0. \tag{B2}$$

Applying the Frobenius method to Eq. (B1), one can find the expansions of its three linearly independent solutions, and then use (B2) to obtain

$$C_1(z) \sim \frac{1}{(2\pi)^{1/2}}\left[1 - \frac{1}{2}z^2\ln z + O(z^4\ln z)\right] - \frac{1}{2}[z + O(z^3)] + b[z^2 + O(z^4)] \quad \text{as} \quad z \to +0, \tag{B3}$$

where b is an undetermined constant.

Now, one can use (27) to verify that

$$C_{-1} = \frac{\mathrm{d}^2 C_1}{\mathrm{d}z^2} \quad \text{for} \quad z > 0.$$

This equality and asymptotics (B3) show that $C_{-1}(z)$ has an integrable singularity at $z = 0$:

$$C_{-1} \sim -\frac{\ln z}{(2\pi)^{1/2}} \quad \text{as} \quad z \to +0.$$

Thus, all C_n with $n \geqslant -1$ are integrable, and so are all the coefficients of Eqs. (20)–(22) [because the latter are related to the former by Eqs. (23)–(26)].

APPENDIX C: ASYMPTOTICS (29)–(30)

To prove that asymptotics (29) and (30) are consistent with Eqs. (20)–(22), one needs to show that, as $z \to \infty$, the linearly growing terms in the first two of these equations cancel out. Equation (22), in turn, does not involve z, and hence is irrelevant to the limit $z \to \infty$. Note also that the coefficients $A_{\rho V}$ and A_{TV} decay exponentially as $z \to \infty$ and, thus, should be omitted from the limiting form of Eqs. (20) and (21). Note also, the exponential decay of the kernels $B_{\rho\rho}$, $B_{\rho T}$, $B_{T\rho}$, and B_{TT} suggests that the main contribution to the integrals in Eqs. (20) and (21) comes from the region $z' \sim z$. As a result, one can change in the limiting form of Eqs. (20) and (21) the integration intervals from $(0, \infty)$ to $(-\infty, \infty)$.

Letting also $\tilde{\rho}(z) = \tilde{Q}z$ and $\tilde{T}(z) = -\tilde{Q}z$, one can reduce Eqs. (20) and (21) to

$$\tilde{Q}z = \int_{-\infty}^{\infty} [B_{\rho\rho}(z - z') - B_{\rho T}(z - z')]Qz'\mathrm{d}z',$$

$$-\tilde{Q}z = \int_{-\infty}^{\infty} [B_{T\rho}(z - z') + B_{TT}(z - z')]Qz'\mathrm{d}z'.$$

To prove that these equalities are identities, one should substitute into them expressions (24), (25), and (27), and then evaluate the resulting integrals with respect to z' and v (in that order).

APPENDIX D: NUMERICAL ALGORITHM FOR SOLVING EQS. (20)–(22)

When solving numerically Eqs. (20)–(22), the main difficulty stems from the singularity of kernels $B_{\rho\rho}(z - z')$, etc. at $z' = z$. It was handled by replacing $\tilde{\rho}(z')$ and $\tilde{T}(z')$ with

$$[\tilde{\rho}(z') - \tilde{\rho}(z)] + \tilde{\rho}(z) \quad \text{and} \quad [\tilde{T}(z') - \tilde{T}(z)] + \tilde{T}(z),$$

respectively, and evaluating the integrals involving $\tilde{\rho}(z)$ and $\tilde{T}(z)$ in Eqs. (20)–(22) using expressions (23)–(27). Eventually, one obtains

$$\tilde{\rho}(z)A_{\rho\rho}(z) + \tilde{T}(z)A_{\rho T}(z) + \tilde{V}A_{\rho V}(z) = \int_0^\infty \{B_{\rho\rho}(z - z')[\tilde{\rho}(z') - \tilde{\rho}(z)] + B_{\rho T}(z - z')[\tilde{T}(z') - \tilde{T}(z)]\}\mathrm{d}z' + \tilde{Q}D_\rho(z), \tag{D1}$$

$$\tilde{\rho}(z)A_{T\rho}(z) + \tilde{T}(z)A_{TT}(z) + \tilde{V}A_{TV}(z) = \int_0^\infty \{B_{T\rho}(z - z')[\tilde{\rho}(z') - \tilde{\rho}(z)] + B_{TT}(z - z')[\tilde{T}(z') - \tilde{T}(z)]\}\mathrm{d}z' + \tilde{Q}D_T(z), \tag{D2}$$

$$\frac{1}{2}\tilde{V} + \frac{\tilde{\rho}(0) + \frac{1}{2}\tilde{T}(0)}{(2\pi)^{1/2}} = -\int_0^\infty \{B_{V\rho}(z')[\tilde{\rho}(z') - \tilde{\rho}(0)] + B_{VT}(z')[\tilde{T}(z') - \tilde{T}(0)]\}\mathrm{d}z', \tag{D3}$$

where

$$A_{\rho\rho} = C_0, \quad A_{\rho T}(z) = \frac{C_2 - C_0}{2}, \quad A_{T\rho} = \frac{C_2 - C_0}{3}, \quad A_{TT} = \frac{C_4 - 2C_2 + 5C_0}{6},$$

and the rest of the coefficients and the functions C_n are determined by (23)–(27). The singularity of the integrands in Eqs. (D1) and (D2) is $O(|z - z'|\ln|z - z'|)$, which is weaker than the $\ln|z - z'|$ singularity in the original equations (20) and (21), and the singularity in Eq. (D3) is $O(|z - z'|^2\ln|z - z'|)$, which is weaker than the $|z - z'|\ln|z - z'|$ singularity in the original equation (22).

Equations (D1)–(D3) were discretized on a mesh with constant step and solved as a large set of linear algebraic equations. At all interior nodes (with nonzero z), the integrals involved where computed using the trapezoidal rule which has a reduced error near the singularity (because the integrand is locally odd). At $z = 0$, the singularity occurs at the boundary of the integration interval in z', so that the error of the trapezoidal rule is relatively large. In this case, the integral over the first two steps in z' was computed using a formula specifically designed for functions with this kind of singularity, and the trapezoidal rule was used for the rest of the domain.

APPENDIX E: DERIVATION OF EQ. (42)

Even though evaporation is steady, one cannot derive the fluxes delivering vaporization heat to the interface from the *steady* heat-conduction problem (whose solutions include an arbitrary spatially uniform heat flux, and it is unclear which of its values corresponds to the naturally arising pattern). Instead, one should consider the *initial-value* problem and let the evolution choose in which proportion the heat comes to the interface from the liquid and vapor.

Consider the following heat-conduction problem:

$$\rho_0^{(l)} c_0^{(l)} \frac{\partial \tilde{T}}{\partial t} = \kappa_0^{(l)} \frac{\partial^2 \tilde{T}}{\partial z^2} \quad \text{if} \quad z < 0, \tag{E1}$$

$$\rho_0 c_0^{(v)} \frac{\partial \tilde{T}}{\partial t} = \kappa_0^{(v)} \frac{\partial^2 \tilde{T}}{\partial z^2} \quad \text{if} \quad z > 0, \tag{E2}$$

where ρ_0, c_0, and κ_0 are the vapor's density, specific heat at constant pressure, and thermal conductivity, respectively; and $\rho_0^{(l)}$, $c_0^{(l)}$, and $\kappa_0^{(l)}$ are the corresponding parameters of the liquid. Observe that Eqs. (E1) and (E2) do not include the terms describing the temperature advection by the evaporative flow: such terms are quadratic in $\tilde{H}$ (the deviation of the humidity from unity)—hence, they are beyond the linear approximation used in this paper. Note also that Eqs. (E1) and (E2) assume that the interfacial thickness is zero, which is a reasonable assumption in a calculation of *macroscopic* fluxes.

Equations (E1) and (E2) are to be solved with the following matching conditions at the interface:

$$(\tilde{T})_{z\to+0} = (\tilde{T})_{z\to-0}, \tag{E3}$$

$$-\kappa_0 \left(\frac{\partial \tilde{T}}{\partial z}\right)_{z\to+0} + \kappa_0^{(l)} \left(\frac{\partial \tilde{T}}{\partial z}\right)_{z\to-0} = -E\,\Delta, \tag{E4}$$

where the right-hand side of condition of (E4) describes consumption of vaporization heat. Assume also that there are no external heat sources,

$$\frac{\partial \tilde{T}}{\partial z} \to 0 \quad \text{as} \quad z \to \pm\infty, \tag{E5}$$

and that the initial temperature field is uniform,

$$\tilde{T} = 0 \quad \text{at} \quad t = 0. \tag{E6}$$

Equations (E1)–(E6) form an initial-boundary-value problem for $\tilde{T}(z, t)$.

To derive Eq. (42), one does not need the full solution of Eqs. (E1)–(E6), but only the following characteristics:

$$Q^{(l)} = -\kappa_0^{(l)} \left(\frac{\partial \tilde{T}}{\partial z}\right)_{z\to-0}, \tag{E7}$$

$$Q = -\kappa_0 \left(\frac{\partial \tilde{T}}{\partial z}\right)_{z\to+0}. \tag{E8}$$

To calculate them, introduce the Laplace transform of $\bar{T}(z, t)$,

$$\hat{T}(s, t) = \int_0^\infty \tilde{T}(z, t)\, \mathrm{e}^{-st}\, \mathrm{d}t,$$

and apply the Laplace transformation to Eqs. (E1)–(E5). Solving the resulting boundary-value problem for an ODE with piecewise-constant coefficients, one obtains

$$\hat{T}(s, t) = -\frac{E\,\Delta}{(\rho_0 c_0 \kappa_0)^{1/2} + \left(\rho_0^{(l)} c_0^{(l)} \kappa_0^{(l)}\right)^{1/2}} s^{-3/2} \exp\left[\left(\frac{c_l s}{\kappa_l}\right)^{1/2} z\right] \quad \text{if} \quad z < 0, \tag{E9}$$

$$\hat{T}(s, t) = \frac{E\,\hat{\Delta}}{(\rho_0 c_0 \kappa_0)^{1/2} + \left(\rho_0^{(l)} c_0^{(l)} \kappa_0^{(l)}\right)^{1/2}} s^{-3/2} \exp\left[-\left(\frac{c_v s}{\kappa_v}\right)^{1/2} z\right] \quad \text{if} \quad z > 0. \tag{E10}$$

Calculation of the inverse transforms of these expressions is cumbersome, but possible, yet unnecessary. Instead, apply the Laplace transformation to the flux expressions (E7) and (E8) and, taking into account Eqs. (E9) and (E10), obtain

$$\hat{Q}^{(l)}(s) = \frac{\left(\rho_0^{(l)} c_0^{(l)} \kappa_0^{(l)}\right)^{1/2} E\,\Delta}{(\rho_0 c_0 \kappa_0)^{1/2} + \left(\rho_0^{(l)} c_0^{(l)} \kappa_0^{(l)}\right)^{1/2}} s^{-1}, \qquad \hat{Q}(s) = -\frac{(\rho_0 c_0 \kappa_0)^{1/2} E\,\Delta}{(\rho_0 c_0 \kappa_0)^{1/2} + \left(\rho_0^{(l)} c_0^{(l)} \kappa_0^{(l)}\right)^{1/2}} s^{-1}.$$

Since the inverse transform of s^{-1} is 1, the above expressions entail Eq. (42), as required.

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