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Reverse Temperature Gradient in the Kinetic Theory of Evaporation

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The singular-eigenfunction-expansion method for solving the transport equation is applied to a modeled kinetic-theory Boltzmann equation to solve the problem of evaporation and condensation between parallel surfaces. A remarkable result is obtained for the temperature profile which seems to confirm previous predictions made on the basis of asymptotic approximations.

In a recent paper, Pao¹ suggested that the slope of the temperature profile of a saturated vapor between two parallel surfaces at different temperatures could be in opposition to the imposed gradient for certain values of β , where $\Delta N = \beta \Delta T$ in a saturated liquid-vapor system. Here N represents the molecular density and T the temperature. Pao's prediction was based on an asymptotic analysis for large gap width, and used results obtained for the half-space problem² by applying the Wiener-Hopf technique to a modeled Boltzmann equation.

We have approached the same problem through the singular-eigenfunction analysis of Kriese, Chang, and Siewert,³ also used by Thomas and co-workers,⁴⁻⁶ and have avoided any asymptotic approximations. Thus for the first time, inverted temperature profiles and critical values of β are calculated explicitly. The surprising result is that our analysis seems to confirm Pao's novel prediction.

We consider the problem of a vapor between two interphase (vapor-liquid or vapor-solid) surfaces maintained at $x = \pm d/2$; we assume that the condensed phase in $x < -d/2$ is kept at temperature $T_0 - \frac{1}{2}\Delta T$ and that the condensed phase in $x > d/2$ is kept at temperature $T_0 + \frac{1}{2}\Delta T$. As a result of evaporation and condensation there is a flow of mass and energy from $x = +d/2$ to $x = -d/2$. Within the vapor, we assume the state of the fluid to be described by the linearized single-relaxation model of the Boltzmann equation⁷:

$$c_x \partial f(x, \vec{c}) / \partial x + f(x, \vec{c}) = \pi^{-3/2} [N(x) + (c^2 - \frac{3}{2})T(x) + 2c_x U(x)]. \quad (1)$$

Here $f(x, \vec{c})$ is the perturbation of the particle-distribution function, x is the spatial variable, \vec{c} is the molecular velocity, and c_x is the x component of the velocity, all in dimensionless units. In addition, $N(x)$, $T(x)$, and $U(x)$ represent perturbations of the number density, the temperature, and the x com-

ponent of mass flow:

$$N(x) = \int f(x, \vec{c}) \exp(-c^2) d^3c, \quad (2a)$$

$$T(x) = \frac{2}{3} \int f(x, \vec{c}) (c^2 - \frac{3}{2}) \exp(-c^2) d^3c, \quad (2b)$$

and

$$U(x) = \int f(x, \vec{c}) c_x \exp(-c^2) d^3c. \quad (2c)$$

Since it follows from Eqs. (1) and (2c) that $U(x)$ is a constant, we find it convenient to introduce

$$h(x, \vec{c}) = f(x, \vec{c}) - (2/\pi^{3/2}) c_x U, \quad (3)$$

and subsequently consider the equation

$$c_x \partial h(x, \vec{c}) / \partial x + h(x, \vec{c}) = \pi^{-3/2} [N(x) + (c^2 - \frac{3}{2}) T(x)]. \quad (4)$$

We are interested here only in density and temperature effects, so we may decompose the equation in the manner discussed by Cercignani⁸ to obtain

$$\mu \partial \bar{\Psi}(x, \mu) / \partial x + \bar{\Psi}(x, \mu) = \pi^{-1/2} \underline{Q}(\mu) \int_{-\infty}^{\infty} \underline{Q}^T(\mu') \bar{\Psi}(x, \mu') \exp(-\mu'^2) d\mu', \quad (5)$$

where $\underline{Q}(\mu)$ is a matrix of polynomials.³ The variable μ now represents the x component of the velocity, and $\bar{\Psi}(x, \mu)$ is a two-vector simply related to the density and temperature of the gas:

$$N(x) = \pi^{1/2} \begin{pmatrix} 1 \\ 0 \end{pmatrix}^T \int_{-\infty}^{\infty} \bar{\Psi}(x, \mu) \exp(-\mu^2) d\mu, \quad (6)$$

and

$$T(x) = \frac{2}{3} \pi^{1/2} \int_{-\infty}^{\infty} \begin{pmatrix} \mu^2 - \frac{1}{2} \\ 1 \end{pmatrix}^T \bar{\Psi}(x, \mu) \exp(-\mu^2) d\mu. \quad (7)$$

We use the superscript T to denote the transpose operation.

At the two interphase surfaces, we assume that the vapor molecules striking the surface are absorbed and re-emitted with a Maxwellian distribution of velocities characterized by the temperature at the respective surface. Hence the linearized boundary conditions are

$$f(\mp \frac{1}{2} \delta, \vec{c}) = \mp \frac{1}{2} [\Delta N + (c^2 - \frac{3}{2}) \Delta T], \quad c_x > 0, \quad (8)$$

where δ is a nondimensional distance and $\Delta N = \beta \Delta T$, with β the slope of the saturated-vapor-density-temperature curve. Couched in terms of the vector $\bar{\Psi}(x, \mu)$, we find this boundary condition to be

$$\bar{\Psi}(\mp \frac{1}{2} \delta, \pm \mu) = \mp \sqrt{\pi} \begin{pmatrix} \mu^2 - \frac{1}{2} + \beta + 2\pi^{-3/2} U \mu \\ 1 \end{pmatrix}, \quad \mu > 0. \quad (9)$$

In Eq. (9), for notational convenience we have absorbed into U and $\bar{\Psi}$ a factor $(\Delta T)^{-1}$.

From an asymptotic solution for large δ , Pao¹ has predicted that for certain values of β the slope of the temperature profile in the main body of the vapor will be in opposition to the imposed temperature gradient. It is our purpose here to investigate this prediction by solving for the temperature profile with the use of the singular-eigenfunction-expansion technique, developed for Eq. (5) by Kriese, Chang, and Siewert.³

Kriese, Chang, and Siewert³ have expressed a general solution of Eq. (5) as

$$\bar{\Psi}(x, \mu) = \sum_{\alpha=1}^2 A_{\alpha} \bar{\Phi}_{\alpha}(\mu) + \sum_{\alpha=3}^4 A_{\alpha} \bar{\Psi}_{\alpha}(x, \mu) + \sum_{\alpha=1}^2 \int_{-\infty}^{\infty} A_{\alpha}(\eta) \bar{\Phi}_{\alpha}(\eta, \mu) e^{-x/\eta} d\eta, \quad (10)$$

where the $\bar{\Phi}_{\alpha}(\mu)$, $\bar{\Psi}_{\alpha}(x, \mu)$, and $\bar{\Phi}_{\alpha}(\eta, \mu)$ are the normal modes given explicitly in Ref. 3, and the A_{α} , $\alpha = 1, \dots, 4$, and $A_{\alpha}(\eta)$, $\alpha = 1$ and 2, are expansion coefficients. Substituting this general solution into Eq. (7) for the temperature perturbation, we find

$$T(x) = -(2/3\pi)^{1/2} A_3 x - (2/\pi) \int_0^{\infty} A_1(\eta) \sinh(x/\eta) \exp(-\eta^2) d\eta, \quad (11)$$

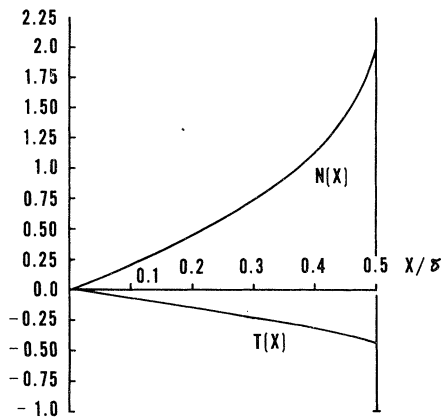


FIG. 1. Temperature and density profiles for $\beta = 8$ and $\delta = 2$.

so that it is clear that we must determine the expansion coefficients A_3 and $A_1(\eta)$ in order to establish the temperature profile. Using the solution (10) in the boundary conditions given by Eq. (9), we find a coupled pair of singular integral equations for the expansion coefficients. We then may apply the half-range ($\mu > 0$) orthogonality theorem of Kriese, Chang, and Siewert³ to convert these singular integral equations into a coupled pair of Fredholm integral equations. We have found that iterative solutions of these Fredholm equations converge very rapidly, so that solutions for the expansion coefficients may be straightforwardly obtained, with great precision.

In Fig. 1, we give a plot of a typical temperature profile obtained from our calculations. It is clear that in the center of the gap, the slope of the profile is in opposition to the imposed gradient and thus very large temperature slips occur at the boundaries. The accompanying density profile is consistent with this temperature profile. We found that for all values of β greater than a "critical" value, $\beta_c(\delta)$, the computed temperature profile was in opposition to the imposed gradient. We define $\beta_c(\delta)$ as that β for which

$$dT(x)/dx|_{x=0} = 0. \quad (12)$$

By solving the coupled Fredholm equations mentioned above in conjunction with the constraint of Eq. (12), we were able to compute $\beta_c(\delta)$. In Fig. 2 we plot $\beta_c(\delta)$ versus δ for $0 < \delta < \infty$. It will be noted that as δ increases, $\beta_c(\delta)$ approaches an asymptotic value of 3.7723... , whereas Pao's approximate value is 3.5. For δ approaching zero, it appears that $\beta_c(\delta)$ also approaches zero; however, we were unable to confirm this since we did not obtain converged solutions to the Fred-

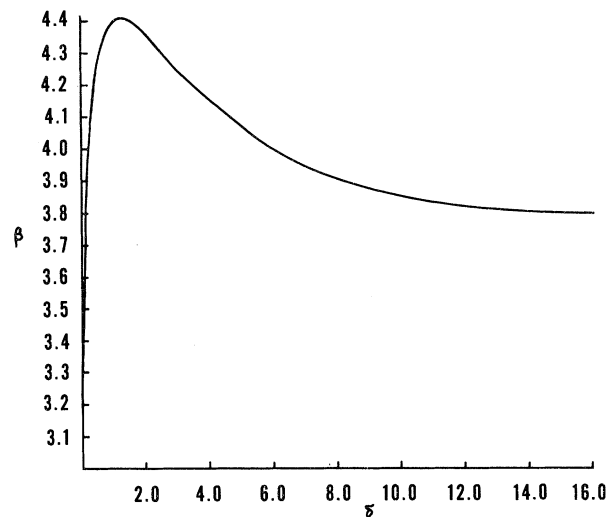


FIG. 2. Critical $\beta_c(\delta)$.

holm equations for $\delta < 0.01$.

An apparent explanation for the unexpected temperature behavior is that for large β evaporation is so rapid that energy transfer by mass flow must be counterbalanced by heat conduction in the opposite direction. We hope that our results will invite attempts to study this phenomenon experimentally. The superheating and supercooling effects of the vapor phase adjacent to the condensate should be readily observable.

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