

Theory of evaporation and condensation

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The theory of evaporation and condensation is considered from a kinetic theory approach with a particular interest in the continuum limit. The moment method of Lees is used to solve the problem of the steady flow of vapor between a hot liquid surface and a cold liquid surface. By incorporating the singular nature of the problem, the forms of the continuum flow profiles found by Plesset are recovered. The expression for mass flux has the form of the Hertz–Knudsen formula but is larger by a factor of 1.665. A result of the theory is that the temperature profile in the vapor for the continuum problem is inverted from what would seem physically reasonable. This paradox is significant in that it casts a shadow of doubt on the fundamental theory.

I. INTRODUCTION

The theory of evaporation and condensation has its foundations in the kinetic theory of gases as developed in the latter half of the nineteenth century. Until recently the theory has been little investigated with the notable exception of the work of Schrage.¹ The widely used formulas for net mass flux at an interface, referred to as the Hertz–Knudsen and Schrage formulas, are based on simple analyses which use Maxwellian forms and neglect effects due to collisions of the molecules near the interface. These effects may be significant, and refinements in the theory through approximate solution of the Maxwell–Boltzmann transport equation have appeared in recent years. Underlying all of the treatments of the theory of evaporation and condensation is the assumed boundary condition for emission of molecules from the liquid surface. It is pertinent to review the basis for this boundary condition as well as the development of the Hertz–Knudsen and Schrage formulas.

The most comprehensive accounts of the foundations of the assumed boundary condition at an interface are given by Schrage¹ and by Knacke and Stranski.² Briefly, the argument is as follows. Consider first the equilibrium situation for which the distribution function in the vapor far from the interface is Maxwellian. The interface is a sharp demarcation, and if we assume that the interface itself is not a disturbing influence on the distribution function, then the Maxwellian exists right up to the interface. Because of the net balance of mass, momentum, and energy at equilibrium, we deduce that the molecules are emitted from the liquid according to a Maxwellian with the temperature of the liquid and density equal to the equilibrium vapor density. Now consider a small departure from equilibrium. We imagine that the mechanism of molecules leaving the surface depends only on the state of the liquid and is not affected either by the state of the vapor or by the net transfer of mass, momentum, and energy. Hence, we obtain the usual boundary conditions assumed at a liquid–vapor interface under nonequilibrium conditions: Molecules are emitted with a Maxwell distribution function with the temperature of the liquid T_L and the

density equal to the equilibrium vapor density of the liquid $\rho^e(T_L)$.

Given this boundary condition, we can calculate the mass flux leaving an interface by integrating the mass flux moment over velocity half-space to yield

$$W = \rho^e(T_L)(RT_L/2\pi)^{1/2}.$$

If this result is applied to a free molecular flow between two interfaces, the net mass flux is given by the Hertz–Knudsen formula

$$W = \rho_1^e(RT_1/2\pi)^{1/2} - \rho_2^e(RT_2/2\pi)^{1/2}.$$

Apparently the Hertz–Knudsen formula has been casually extended to continuum flow over the years although little justification for such extension can be found in the literature. Evidently, just outside the interface, the vapor with density ρ_2 and temperature T_2 is represented by a Maxwellian and the effect of collisions is neglected to yield the continuum form

$$W = \rho_1^e(RT_1/2\pi)^{1/2} - \rho_2(RT_2/2\pi)^{1/2}.$$

Furthermore, the temperature of vapor and the temperature of liquid at the interface are often assumed to be approximately the same yielding the continuum form of the Hertz–Knudsen formula

$$W = (\rho_1^e - \rho_2)(RT_1/2\pi)^{1/2}.$$

Schrage¹ proposed a simple correction to this continuum form. He argued that because of the net mass flow the Maxwellian in the vapor must be shifted by the mean velocity. For low flow Mach number with the assumption of equal temperature of liquid and vapor at the interface, Schrage's expression becomes

$$W \cong 2(\rho_1^e - \rho_2)(RT_1/2\pi)^{1/2}.$$

These expressions differ by a factor of 2 and have been the subject of controversy. While recent calculations indicate that a factor of 1.67 is correct, other features of these refined solutions are troublesome. Hence, the current study was undertaken in order to assess the theory.

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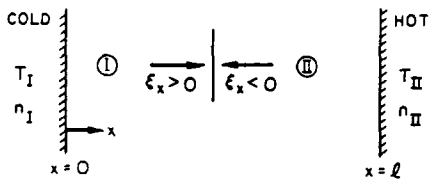


FIG. 1. Geometry for the steady plane two-interface problem.

II. THE STEADY PLANE TWO-INTERFACE PROBLEM

Plesset³ solved the problem of the flow of vapor between liquid surfaces using the continuum equations as an outer solution and the Hertz-Knudsen formula as in an inner solution. Surfaces I and II are kept at constant temperatures T_I and T_{II} with $T_I < T_{II}$ and a steady flow of pure vapor is maintained from II to I (see Fig. 1). We assume for simplicity that liquid is replenished or taken away at each surface so that the surfaces remain a fixed distance l apart. We further assume that the surfaces are infinite so that a one-dimensional problem can be considered. We note that this problem is a particularly good test of the theory because the vapor flow field should be determined from the assumed known boundary conditions at the liquid surfaces.

Plesset's solution provides good insight into the features of the continuum problem. For steady flow, the mass flux ρu is constant, and for low flow Mach number, the momentum equation indicates that the pressure is constant to second order in Mach number. With negligible dissipation the energy equation becomes

$$\frac{dT}{dx} = \frac{k}{\rho u c_p} \frac{d^2T}{dx^2} = -\delta \frac{d^2T}{dx^2},$$

where the length scale δ is a constant since ρu is constant. Hence, the temperature profile has the form

$$T = C_1 \exp(-x/\delta) + C_2.$$

The kinetic theory solutions must recover these features in the continuum limit. Plesset assumed continuity of temperature at the interfaces, and in this case the temperature is constant over most of the field at the temperature of the evaporating surface except for a thin exponential layer with thickness of order δ where the transition to the temperature at the condensing surface occurs.

We have chosen to use the Maxwell moment method as developed by Lees^{4,5} to solve the steady plane two-interface problem. Maxwell converted the Maxwell-Boltzmann transport equation into integral equations of transfer for any quantity Q that is a function of the particle velocity alone. In Cartesian form with no external forces these can be written

$$\frac{\partial}{\partial t} \int Q(\xi) f d\xi + \frac{\partial}{\partial x_i} \int f \xi_i Q d\xi = \Delta Q,$$

where ξ is the vector in velocity space, $f(\mathbf{r}, \xi, t)$ is the velocity distribution function, and ΔQ represents the collision integral. The gas dynamic conservation equations are obtained when Q is set equal to the collisional invariants ($\Delta Q = 0$) of mass, momentum, and energy. Other moments may be used to generate additional equations. As suggested by Maxwell, the collision integral is evaluated using a binary collision

model for molecules which obey an inverse fifth power law of repulsion and satisfy the perfect gas law. Lees notes that this model contains the important physical features of the particle interaction and preserves the nonlinear character of the collision integral.

The approach of Lees is to use the Maxwell moment equations in an approximate integral technique in the spirit of the von Karman-Pohlhausen treatment of boundary layer flow. The basic idea is that integration is a smoothing operation so that mean features are accurately recovered from an approximate distribution function. An approximate form of the distribution function is chosen with N parametric weighting functions to be determined. Then N moment equations are chosen which usually include the conservation equations and other lower moments. With these N equations and N unknowns, a sufficient number of boundary conditions must be specified to close the problem. The success of an approximate integral technique relies to some extent on a discriminating choice of the form of the approximate distribution function. Lees was interested in developing a method which could accurately describe the transition from free molecular flow to continuum flow. Hence, Lees chose a two-stream distribution function which has the two-sided nature of rarified flows but can become almost Maxwellian in the continuum regime. For a six moment method this approximate distribution function takes the form

$$f = \begin{cases} \frac{n_1}{(2\pi RT_1)^{3/2}} \exp\left(-\frac{(\xi_x - u_1)^2 + \xi_y^2 + \xi_z^2}{2RT_1}\right) & \text{for } \xi_x > 0, \\ \frac{n_2}{(2\pi RT_2)^{3/2}} \exp\left(-\frac{(\xi_x - u_2)^2 + \xi_y^2 + \xi_z^2}{2RT_2}\right) & \text{for } \xi_x < 0, \end{cases}$$

where $n_1, n_2, T_1, T_2, u_1, u_2$ are the six parametric weighting functions to be determined. We note that the weighting functions cannot be interpreted directly as physical quantities; the physical quantities must be computed from the total distribution function. An additional motivation for the above form is that the boundary conditions can be satisfied in an elegant way since the liquid is assumed to emit a known Maxwellian distribution over a half-space.

For the steady plane two-interface problem, a six moment method appears most appropriate. Lees' two-sided distribution function is substituted into the moment equations and the integrations are performed. This reduction of the moment equations to differential equations for the weighting functions is documented elsewhere.⁴⁻⁷ For the steady plane one-dimensional case, Sloat⁷ gives the moment equations in full nonlinear form and these are also documented by Koffman.⁸ These equations include the conservation equations of mass ($Q = m$), momentum ($Q = m\xi_x$), and energy ($Q = \frac{1}{2}m\xi^2$). The other three moments are taken to be $\frac{1}{2}m\xi_x \xi_x^2$, $m\xi_x^2$, and $m\xi_x^3$.

We first consider a linearized solution for small Mach number. Sloat⁷ and Labunsov⁹ have presented solutions to the linearized problem. However, they both obtain a linear temperature profile in the continuum limit which is in disagreement with Plesset's continuum solution. We have seen

that the continuum equations are naturally scaled by the length δ whereas the moment equations are naturally scaled by the mean free path λ . If the continuum energy equation is scaled by λ and then linearized, the resulting temperature profile is linear. Hence the problem is a singular perturbation problem. Shankar⁶ realized the singular nature of the plane problem in his treatment of a single interface and he gives the linearized moment equations for the inner Knudsen layer region and for the outer continuum region. We shall use Shankar's form of the linearized equations to solve the steady plane two-interface problem. The parametric weighting functions are taken to be

$$\begin{aligned} n_i &= n_0(1 + \epsilon N_i + \dots), \\ T_i &= T_0(1 + \epsilon t_i + \dots), \quad (i = 1, 2), \\ u_i &= (2\pi RT_0)^{1/2}(\epsilon v_i + \dots), \end{aligned}$$

where n_0 and T_0 are reference values and $\epsilon \ll 1$. It is convenient to define $N_{\pm} = N_1 \pm N_2$, $t_{\pm} = t_1 \pm t_2$, and $v_{\pm} = v_1 \pm v_2$. The linearized inner equations are obtained using the scaling $\bar{x} = (2/\pi)(x/\lambda)$ and retaining $O(\epsilon)$ terms. The resulting linear first-order ordinary differential equations can be integrated to give

$$\begin{aligned} t_- &= \frac{1}{5} C_3 + C_4 \exp\left[-\frac{\pi}{4} \left(\frac{5\pi}{2}\right)^{1/2} \bar{x}\right] \\ &+ C_5 \exp\left[\frac{\pi}{4} \left(\frac{5\pi}{2}\right)^{1/2} \bar{x}\right], \end{aligned} \quad (1a)$$

$$\begin{aligned} v_- &= \frac{3}{2\pi} \left(\frac{5\pi}{2}\right)^{1/2} \left\{ -C_4 \exp\left[-\frac{\pi}{4} \left(\frac{5\pi}{2}\right)^{1/2} \bar{x}\right] \right. \\ &\left. + C_5 \exp\left[\frac{\pi}{4} \left(\frac{5\pi}{2}\right)^{1/2} \bar{x}\right] \right\}, \end{aligned} \quad (1b)$$

$$N_- = \frac{7}{2} t_- - C_3, \quad (1c)$$

$$t_+ = -C_2 + \frac{1}{3} \left[-(\pi/3)C_3\bar{x} + C_6 \right] - \frac{4}{3} v_-, \quad (1d)$$

$$N_+ = C_2 - t_+ - 4v_-, \quad (1e)$$

$$v_+ = (1/2\pi)[C_1 - t_- - 2N_-], \quad (1f)$$

where the C_i are undetermined constants.

Similarly, the linearized outer equations are obtained using the scaling $\eta \equiv \epsilon \bar{x}$ from the cold wall and the resulting equations are

$$2N_-(\eta) + t_-(\eta) + 2\pi v_+(\eta) = A_1, \quad (2a)$$

$$N_+(\eta) + t_+(\eta) + 4v_-(\eta) = A_2, \quad (2b)$$

$$7t_-(\eta) - 2N_-(\eta) = 2A_3, \quad (2c)$$

$$v_-(\eta) = 0, \quad (2d)$$

$$t_+(\eta) = A_5 + A_4 \exp[(\pi^2/3)u_c \eta], \quad (2e)$$

$$2N_-(\eta) - t_-(\eta) = 0, \quad (2f)$$

where u_c is the first-order velocity and is negative for the given geometry. Shankar also gives the physical variables in linearized form. For example,

$$\begin{aligned} \rho u &= \rho_0(RT_0/2\pi)^{1/2} [\epsilon(N_- + \frac{1}{2}t_- + \pi v_+) + \dots], \\ T &= T_0 [1 + \epsilon(\frac{1}{2}t_+ + \frac{1}{3}v_-) + \dots]. \end{aligned}$$

We take an inner solution near each interface and the outer solution in between and try to match. For the inner solution at the cold wall ($x = 0$) we use Eqs. (1) with the constants C_i .

For the inner solution at the hot wall ($x = l$) we use Eqs. (1) with the constants D_i and with x replaced by $(x - l)$. For the outer solution we use Eqs. (2) with the constants A_i . The matching principle is taken to be

$$\lim_{\bar{x} \rightarrow \infty} (\text{inner}) = \lim_{\eta \rightarrow 0} (\text{outer}) \quad \text{at } x = 0,$$

and similarly at $x = l$. Requiring finite values, we obtain the matching conditions

$$A_1 = C_1 = D_1 \quad (\text{mass flux constant}), \quad (3a)$$

$$A_2 = C_2 = D_2 \quad (\text{momentum flux constant}), \quad (3b)$$

$$A_3 = C_3 = D_3 = 0 \quad (\text{heat flux zero for finite inner value in } \lim_{x \rightarrow \infty}; \text{ energy flux constant}), \quad (3c)$$

$$C_5 = D_4 = 0 \quad (\text{for finite inner values in } \lim_{x \rightarrow \infty}), \quad (3d)$$

$$-C_2 + \frac{1}{3} C_6 = A_5 + A_4 \quad (\text{match temperature at } x = 0), \quad (3e)$$

$$-D_2 + \frac{1}{3} D_6 = A_5 \quad (\text{match temperature at } x = l). \quad (3f)$$

The character of the outer continuum solution is established by combining Eqs. (2) and (3) to obtain $v_- = t_- = N_- = 0$ and $v_1 = v_2 = A_1/4\pi$. Hence, the outer solution to first order is a Maxwellian translating with the mean velocity. Note that the temperature and density can change on the continuum scale due to second-order deviations from a Maxwellian. To complete the solution, the boundary conditions must be applied. If the hot surface is taken as the reference so $n_0 = n_{II}^e$ and $T_0 = T_{II}$, then the boundary conditions for the linearized problem become at $x = 0$:

$$N_1 = \frac{n_1^e - n_{II}^e}{\epsilon n_{II}^e} \equiv \Delta v, \quad t_1 = \frac{T_1 - T_{II}}{\epsilon T_{II}} \equiv \Delta \theta, \quad v_1 = 0,$$

and at $x = l$:

$$N_2 = 0, \quad t_2 = 0, \quad v_2 = 0.$$

When these boundary conditions are applied using Eqs. (1), the resulting algebraic equations relate the constants C_i and D_i with Δv and $\Delta \theta$. Then the constants are found by applying the matching conditions in Eqs. (3). The resulting expressions for mass flux and temperature are

$$\begin{aligned} \frac{\rho u}{\rho_{II}^e (RT_{II}/2\pi)^{1/2}} &= \epsilon \frac{C_1}{2} = \frac{1.665}{2} \epsilon (\Delta v + \Delta \theta), \quad (4) \\ T/T_{II} &= 1 + \epsilon \frac{1}{2} \{ 0.21015(\Delta v + \Delta \theta) \\ &+ (1.5797 \Delta \theta - 0.4203 \Delta v) \exp[(\pi^2/3)u_c \eta] \}, \quad (5) \end{aligned}$$

where $u_c = C_1/4\pi < 0$. It is interesting that the mass flux and end values of temperature are the same as in Sloat's solution in which matching is not done. Apparently, matching of the conserved constants of mass, momentum and energy determines the end values. It is significant, however, that our solution correctly recovers the form of the continuum profiles found by Plesset.

A comparison of the mass flux with Plesset's solution is interesting. If Plesset's result for mass flux is linearized, the

TABLE I. Physical values of the latent heat parameter β .

Substance	$T(^{\circ}\text{K})$	$L(\text{m}^2/\text{sec}^2) \times 10^{-6}$	$\beta + 1 \approx L/RT$
Water	273	2.50	19.8
	300	2.44	17.6
	367	2.27	13.4
	373	2.26	13.1
Ethanol	273	0.92	18.7
	351	0.86	13.5
Oxygen	56	0.25	17.0
	100	0.20	7.8
Sodium	1000	4.02	11.1
Argon	87	0.35	19.3
CCl_4	350	0.19	5.3

result is

$$\frac{\rho u}{\rho_{II}^e (RT_{II}/2\pi)^{1/2}} = \frac{1}{2} \epsilon (\Delta v + \Delta \theta).$$

Both expressions are proportional to the vapor pressure difference ($\Delta v + \Delta \theta$) but differ by a factor of 1.665. Recall that Plesset used the Hertz–Knudsen formula. Had he used Schrage’s correction his result would be larger by a factor of 2. Hence, the result (4) agrees qualitatively with Schrage’s correction but alters the correction factor from 2 to 1.665.

Although the more refined solution seems to settle the controversy concerning mass flux, the resulting temperature profile raises serious questions regarding the physics. From Eq. (5) we see that the temperature of the vapor outside the hot surface can be below that outside the cold surface if $\Delta v > 3.76 \Delta \theta$. If we let $\beta = \Delta v/\Delta \theta$ and use the Clausius–Clapeyron equation, then we obtain the approximate relation

$$\beta + 1 = \frac{\Delta p^e/p^e}{\Delta T/T} \approx \frac{L}{RT},$$

where L is the latent heat of vaporization. For most liquids we find that the condition $\beta > 3.76$ is satisfied (see Table I) so that the solution indicates that the temperature profile is inverted. Furthermore, if $\beta > 8.52$ then the temperature jump at each interface is greater than the driving temperature difference. An example is illustrative. Consider water at the boiling point (373 °K) at the hot surface and the cold surface lower by 1 °K. Then from Eq. (5), the temperature of the vapor at the cold surface is 0.38 °K above 373 °K and the temperature of the vapor at the hot surface is 1.38 °K below 373 °K. This clearly does not make sense. We believe that the inverted temperature profiles cast a shadow of doubt on the theory.

Another difficulty with the linearized theory arises when the free molecular and continuum mass fluxes are compared. In linearized form the free molecular mass flux becomes

$$\frac{(\rho u)_{fm}}{\rho_{II}^e (RT_{II}/2\pi)^{1/2}} = \epsilon \left(\Delta v + \frac{1}{2} \Delta \theta \right). \quad (6)$$

Comparing Eqs. (4) and (6) we see that the continuum mass flux may exceed the free molecular mass flux if $\beta < 1.98$. It

would seem that the effect of collisions would be to reduce the net mass flux regardless of the value of β .

Because of our objections to the results of the linearized theory we questioned whether there may be some difficulty with the linearization. Hence, a numerical solution of the full nonlinear equations was attempted. The one-dimensional steady plane two-interface problem is a two-point boundary value problem consisting of six coupled nonlinear first-order ordinary differential equations with three boundary conditions specified at each end. An initial value problem shooting technique was used with an iteration scheme on the initial guess to satisfy the two-point boundary conditions. Since difficulty was experienced in approaching the continuum limit, we just present some results here; Koffman⁸ gives details of the numerical calculation. The calculations proceed by treating the Knudsen number as a parameter. For $\text{Kn} = O(1)$ the numerical results agree with the linearized results of Sloat. We were not able to decrease Knudsen number below a value of 1/6 because of stability problems. However, for $\text{Kn} = 1/6$ the trend of the numerical calculation seems to be in agreement with the linearized theory. There was no evidence that the inverted temperature profiles are a result of linearization.

III. DISCUSSION

The problem of the steady continuum flow of vapor between two liquid surfaces of different temperature has been considered from a kinetic theory approach using the moment method of Lees. This problem is a particularly good test of the theory because the vapor flow field should be determined from the assumed known boundary conditions at the liquid surfaces. Furthermore, for comparison, features of the flow field are available from Plesset’s solution of the continuum conservation equations. Previous kinetic theory solutions reported a linear temperature profile in the continuum limit which is in disagreement with Plesset’s solution. We have resolved this discrepancy by incorporating the singular nature of the plane problem through matching the inner Knudsen layer with the outer continuum region. However, our result for mass flux remained the same as in previous solutions, being a factor of 1.665 greater than the Hertz–Knudsen formula. This result is in qualitative agreement with the mean flow correction of Schrage.

A troublesome result of our solution is that the calculated temperature profile is inverted from what would seem physically reasonable. Other investigators^{7,9–13} have obtained similar solutions. However, these profiles have been regarded as a surprising result or as a new physical effect. It is generally believed that the distribution function at a vapor–liquid interface may deviate considerably from a Maxwellian and that a transition to continuum flow occurs in a layer a few mean free paths in thickness (Knudsen layer). In this case the temperature at the edge of the Knudsen layer may not be the same as the temperature of the liquid so that on the continuum scale there appears to be a temperature jump. We do not object here to the concept of a continuum temperature jump, but we do question the possible magnitude of such a jump. We cannot understand how the tem-

perature jump at the interface can be larger than the temperature difference between the two interfaces, nor can we accept the inverted temperature profiles. We feel that this paradox is significant because it casts a shadow of doubt on the fundamental theory.

We have not been able to pinpoint the difficulty underlying the paradox. However, the difficulty appears to be in the fundamental theory and not in the method of solution. It may be that temperature variation across the Knudsen layer cannot be described in a meaningful way. Another possibility is that the usual boundary conditions assumed at the liquid surface are incorrect for the continuum problem. Fiszdon¹⁴ has also questioned the usual boundary conditions and has suggested an alternative formulation. It seems plausible that the mean continuum flow may affect the emission of molecules from the liquid. In any case, we are not aware of any strong support for these boundary conditions under continuum conditions.

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