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The condensation and evaporation of liquid droplets in a pure vapour at arbitrary Knudsen number

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Abstract—A new set of equations describing the growth and evaporation of small liquid droplets in a pure vapour are presented. The equations, which model both mass and heat transfer between the droplet and the vapour, are in simple closed form solution and are suitable for practical calculations at any Knudsen number. The physical model on which the theory is based is essentially that of Langmuir but some novel features are incorporated. For example, the velocity distribution function for molecules approaching the liquid surface is described by a simplified Grad, thirteen-moment distribution. The results of the analysis are in close agreement with other, more complicated and less general theories to be found in the literature. In particular, the temperature jump across the Knudsen layer in the continuum limit is accurately predicted. It is also shown that Maxwell moment methods based on the Lees, two-stream Maxwellian distribution lead to incorrect results.

INTRODUCTION

THE GROWTH rate of small spherical liquid droplets by condensation from the surrounding vapour has been the subject of much investigation since the pioneering analyses of Hertz [1] and Knudsen [2]. Most work has been concerned with condensation or evaporation in an inert gas environment (particularly for meteorological applications) where the droplet growth rate is controlled by diffusive mass transfer. The simpler problem of heat transfer limited growth in a pure vapour has received less attention and forms the subject of the present article.

In recent years the focus of theoretical work has been to describe the complex molecular interaction processes in the vapour phase close to the liquid surface on which condensation is occurring. Most of this work is highly mathematical and often the underlying physics is obscured by the complexity of the mathematics. Also, many investigators concentrate on just one aspect of the problem (e.g. the continuum limit) with the result that a set of equations for practical calculations valid for all Knudsen numbers is not currently available. The present paper attempts to rectify this omission.

Those acquainted with the literature of condensation will be aware of the confusion which exists in the subject. Referring specifically to droplet growth in a pure vapour, the following points all require clarification:

(1) Droplet growth under continuum conditions. (Theoretical studies of condensation kinetics have postulated the existence of a temperature jump at the liquid–vapour interface but simple models do not predict this effect.)

(2) Droplet growth at slip and transition Knudsen numbers. (Little attempt has been made to assess the accuracy of the various proposed interpolation formulae.)

(3) The role of the Schrage correction [3] in droplet growth theory.

(4) The roles of the condensation and evaporation coefficients and their possible inequality under non-equilibrium conditions.

(5) The complementary roles of the mass and energy transfer equations. (Many investigators choose to ignore one or other of these equations altogether when computing the dynamics of droplet growth or evaporation.)

(6) The definitions and interpretation of the various relaxation times characterizing vapour–droplet flows. (These are frequently defined in physically misleading ways and, in particular, a correct expression for the droplet temperature relaxation time has never appeared in the literature).

Definitive solutions are not yet available for all the above problems but much progress can be obtained by a careful reappraisal and extension of existing ideas. Here, we focus on the equations describing the quasi-steady mass and energy transfer between a single spherical droplet and the surrounding vapour rather than on the overall dynamics of droplet growth itself.

The transport processes in the vapour are first considered from the standpoint of macroscopic irreversible thermodynamics in order to obtain the form of the required equations. The coefficients of these phenomenological equations can only be determined via a molecular kinetic theory and we make use of the well-known Langmuir model whereby the vapour field close to the droplet surface is considered to be a

NOMENCLATURE

A, B, C, D	coefficients defined by equations (40) and (42)
c_p	isobaric specific heat capacity of vapour
$\dot{E}$	total energy flow rate from droplet
f	molecular velocity distribution function
h	specific enthalpy
J_m, J_q	mass and heat fluxes from droplet
Kn	Knudsen number, $\lambda/2r_d$
k	thermal conductivity of vapour
$L_{mm}, L_{mq}, L_{qm}, L_{qq}$	phenomenological coefficients
$\dot{M}$	mass flow rate from droplet
Pr	Prandtl number of vapour, $c_p\eta/k$
p	pressure
Δp	$p_s - p_v$
$\dot{Q}$	heat flow rate from droplet
q_c, q_e	condensation and evaporation coefficients
R	specific gas constant of vapour
r	radius
S	entropy
T	temperature
ΔT	$T_d - T_v$
u	bulk velocity.

Greek symbols

α_p, α_T	coefficients in expansion of q_c/q_e
β	constant to define position of Knudsen/continuum interface
γ	ratio of specific heat capacities
η	dynamic viscosity of vapour
λ	mean free path of vapour molecule
μ	chemical potential per unit mass
$\xi_r, \xi_\theta, \xi_\phi$	molecular velocity components
ρ	density
σ	surface tension of liquid.

Subscripts

d	droplet
i	interface of Knudsen and continuum regions
ne	non-equilibrium region
s	saturated
v	vapour (far from droplet)
+	away from droplet
−	towards droplet.

collision-free zone, while outside this volume continuum behaviour is assumed to operate. Unlike most other treatments, however, we model the molecular velocity distribution by a simplified Grad distribution function and are therefore able to reflect correctly (in the shape of the distribution function) the mass motion (Schrage effect) and heat transfer to or from the droplet. By making suitable approximations, the resulting equations for the mass and heat transfer rates can be expressed in simple algebraic forms which agree quantitatively with numerically accurate, but more complex and less general, solutions of the Boltzmann equation.

We begin with a brief résumé of the thermodynamics and kinetics of vapour–droplet equilibrium.

VAPOUR–DROPLET EQUILIBRIUM

Consider a small spherical liquid droplet of radius r_d at rest and in equilibrium in an infinite expanse of its own pure vapour. The droplet temperature T_d, internal pressure p_{di} and density ρ_d are uniform throughout the droplet and the vapour is assumed to behave as a perfect gas with specific gas constant R. The vapour pressure and temperature are denoted by p_v and T_v. The thermodynamic and mechanical conditions for equilibrium are

$$T_v = T_d$$

$$\mu_v(T_v, p_v) = \mu_d(T_d, p_{di})$$

$$p_{di} = p_v + \frac{2\sigma}{r_d} \tag{1}$$

where μ is the chemical potential per unit mass and σ the liquid surface tension. Note that, for very small droplets such as occur during the early stages of homogeneous nucleation, the internal pressure p_{di} may be very much higher than the vapour pressure p_v due to the large surface curvature. The second of equations (1) can be transformed to the alternative, Kelvin–Helmholtz, form

$$p_v = p_s(T_d, r_d) = p_s(T_d, \infty)\exp\left(\frac{2\sigma}{\rho_d R T_d r_d}\right) \tag{2}$$

where $p_s(T_d, \infty)$ is the saturated vapour pressure at temperature T_d for a flat liquid–vapour interface. (Subsequently, we denote $p_s(T_d, r_d)$ simply by p_s.)

From a molecular-kinetic viewpoint, the condition of equilibrium is a dynamic one where the rate of condensation of molecules arriving from the vapour is exactly balanced by the rate of evaporation of molecules from the droplet surface. The molecular condensation rate $\dot{M}$ is given by^{-}

$$\dot{M} = 4\pi r_d^2 q_c \frac{p_v}{\sqrt{(2\pi R T_v)}} \tag{3}$$

where q_c, the condensation coefficient, represents the fraction of incident molecules which condense (as opposed to being reflected).

At equilibrium $p_v = p_s$, $T_v = T_d$ and equation (3) also represents the mass evaporation rate $\dot{M}_+$. The maximum value of $\dot{M}_+$ occurs when $q_e = 1$ and, in general, $\dot{M}_+$ is defined by

$$\dot{M}_+ = 4\pi r_d^2 q_e \frac{p_s}{\sqrt{(2\pi R T_d)}} \quad (4)$$

where q_e is the evaporation coefficient and is necessarily equal to q_c, *but only under equilibrium conditions.*

All theories of droplet growth now make the experimentally unconfirmed assumption that the evaporation rate is a function only of droplet temperature and radius and hence that $\dot{M}_+$ can be represented by equation (4) *even under non-equilibrium conditions.*

IRREVERSIBLE THERMODYNAMICS OF DROPLET GROWTH

Consider now the non-equilibrium situation characterized by a finite net condensation or evaporation rate. Such conditions are achievable in two independent ways. Starting from the equilibrium state, the vapour temperature can be altered while maintaining the vapour pressure constant at the value p_s. Alternatively, the vapour pressure can be adjusted while maintaining the vapour temperature constant at the value T_d. The condensation or evaporation rate thus depends on the temperature difference $\Delta T = (T_d - T_v)$ and the pressure difference $\Delta p = (p_s - p_v)$. Many treatments of droplet growth incorrectly neglect one or other of these thermodynamic driving forces.

It should be appreciated that Δp does not represent a real vapour–droplet pressure difference. In varying p_v from the equilibrium value p_s, the actual vapour pressure at the droplet surface (and also the internal pressure of the droplet) establishes itself at a level just sufficient to drive the bulk flow of vapour to or from the droplet. The pressure difference associated with this bulk flow is always small and is usually neglected.

To apply the formalism of irreversible thermodynamics, consider the system (closed to the transfer of mass) shown in Fig. 1. Region D is the droplet and includes the surface transition layer. (In keeping with the Gibbs treatment of surface thermodynamics, liquid properties are assumed to be uniform up to the discontinuous liquid–vapour interface, which is positioned to satisfy the condition of zero excess surface mass.) The bulk liquid is assumed to be in a quasi-equilibrium state characterized by the droplet temperature T_d and internal pressure p_{di} and to be in thermodynamic equilibrium with the surface at all times. Region V is a vapour reservoir at uniform constant pressure p_v and temperature T_v. Region NE is a non-equilibrium region.

It is assumed that quasi-steady condensation is occurring and conditions in region NE are time independent. The outer boundary of the system therefore moves radially inward at a steady state. The rate of heat transfer crossing this boundary (in the *outward* direction) is denoted by $\dot{Q}_v$. The mass flow rate from the droplet (also in the *outward* direction) is denoted by $\dot{M}$.

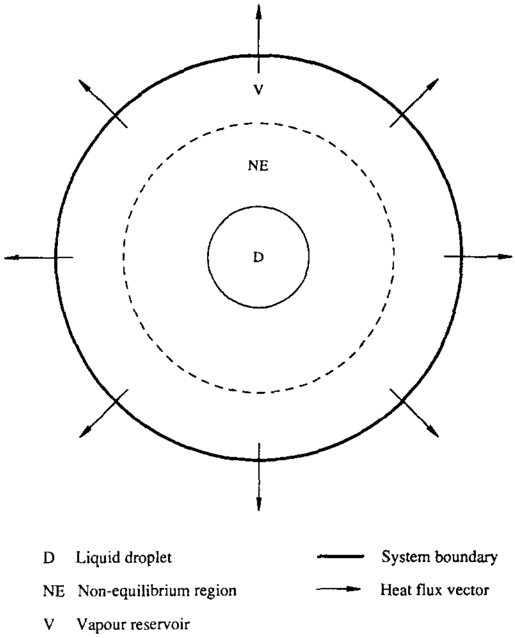


FIG. 1. Closed system for the analysis of irreversible entropy production.

The rate of entropy production due to irreversibilities in region NE has been considered by Lang [4], who did not specifically include the effects of surface energy and entropy. A more formal derivation, including these effects, is presented in Appendix A, where it is shown that the rate of entropy production $\dot{S}$ is given by

$$\frac{\dot{S}}{R} = 4\pi r_d^2 \left\{ J_m \left(\frac{\Delta p}{p_s}\right) + J_q \left(\frac{\Delta T}{T_d}\right) \right\}. \quad (5)$$

The fluxes J_m and J_q are defined by

$$\dot{M} = 4\pi r_d^2 J_m$$

$$\frac{\dot{Q}_v}{R T_v} = 4\pi r_d^2 J_q. \quad (6)$$

Equation (5) defines the conjugate fluxes and thermodynamic forces for the application of Onsager's theory. Assuming linear deviations from equilibrium, we therefore have

$$J_m = \frac{p}{\sqrt{(2\pi R T)}} \left[L_{mm} \left(\frac{\Delta p}{p}\right) + L_{mq} \left(\frac{\Delta T}{T}\right) \right]$$

$$J_q = \frac{p}{\sqrt{(2\pi r T)}} \left[L_{qm} \left(\frac{\Delta p}{p}\right) + L_{qq} \left(\frac{\Delta T}{T}\right) \right] \quad (7)$$

where L_{mm}, L_{mq}, L_{qm} and L_{qq} are dimensionless phenomenological coefficients. (The factor $p/\sqrt{(2\pi R T)}$ has been introduced for convenience and, as equation (7) describes linear departures from equilibrium, p and T can be evaluated at either droplet or vapour conditions.)

The problem, therefore, is to obtain expressions for L_{mm}, L_{mq}, L_{qm} and L_{qq}. These cannot be determined from a thermodynamic analysis and must be derived from a molecular kinetic model. However, Onsager's reciprocal theorem ensures the equality $L_{mq} = L_{qm}$.

KINETIC THEORIES OF CONDENSATION

The essential problem in formulating a kinetic theory of droplet growth is to obtain an expression for the velocity distribution function of those molecules situated in the vapour directly adjacent to the liquid surface which have velocity vectors pointing in the direction of the surface. (The distribution function for molecules leaving the surface is assumed known.) The Knudsen number is here defined by $Kn = \lambda/2r_d$ (as opposed to the more common $Kn = \lambda/r_d$), where λ is the mean free path of a vapour molecule and is given by the kinetic theory expression

$$\lambda = \frac{\eta}{2}\frac{\sqrt{(2\pi RT_v)}}{p_v} \tag{8}$$

η being the dynamic viscosity of the vapour.

The simplest model of heat transfer in arbitrarily rarefied gases can be traced to Langmuir [5]. In the Langmuir model, shown in Fig. 2, the non-equilibrium region is divided into two parts. Far from the droplet the continuum equations of fluid mechanics are assumed to apply, while close to the liquid surface molecular collisions are supposedly unimportant and the exchange processes can be described by the equations of free molecule kinetic theory. The inner region is known as the Knudsen layer and its interface with the continuum region is arbitrarily fixed at a radius $r_i = r_d + \beta\lambda$ where β is an unknown constant of order unity.

The Langmuir model has been used for several studies of condensation on plane [6] and spherical surfaces [7, 8]. Unfortunately, however, it has serious shortcomings. In reality, the transition from the continuum to the kinetic region is gradual rather than instantaneous and the velocity distribution of inwardly moving molecules is modified somewhat by collisions in the Knudsen layer. Nevertheless, as we shall see, the Langmuir model, in a refined form, can yield results which are comparable to those obtained by much more complicated methods.

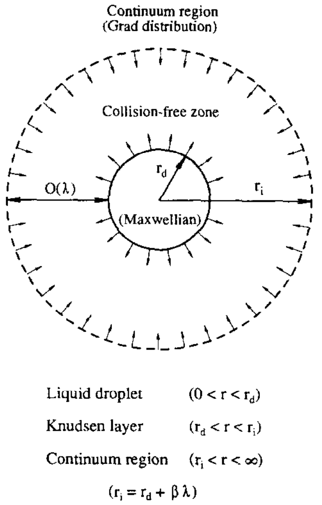


FIG. 2. The Langmuir model.

Ideally, the droplet condensation problem would be solved by integrating the Boltzmann equation across the Knudsen layer subject to suitable boundary conditions. This approach has been adopted for studies of plane evaporation and condensation [9–14] but the analyses are mathematically complicated and major simplifications are required. Recently, however, Chernyak and Margilevskiy [15] have obtained a numerical solution of a model Boltzmann equation in the vicinity of a condensing droplet for a monatomic vapour and their results provide a useful test of accuracy for the theory described below.

Direct solutions of the Boltzmann or BGK-type equations are complete in that they give the spatial variation of the molecular velocity distribution function. An alternative, and simpler, approach is the Maxwell moment method which seeks to satisfy the first few moments of the Boltzmann equation using an assumed test form of the velocity distribution function. (It is worth noting that Langmuir-type methods are fundamentally Maxwell moment methods where the test function only satisfies the moment equations corresponding to mass and energy conservation.)

Maxwell moment methods for droplet growth were pioneered by Sampson and Springer [16] and Shankar [17] using a linearized four-moment method with Lees' two-stream Maxwellian as the test distribution function. Both papers have been very influential and have formed the basis for later developments on the same theme, notably refs. [4, 18, 19]. Unfortunately, however, the four-moment method based on Lees' distribution function gives an equation of mass transfer which is seriously incorrect. Such a conclusion was presented in ref. [15] and is confirmed by the present analysis. The physical reasons for the failure of the two-stream Maxwellian to describe the kinetics of calculation are discussed below and must call into question the validity of this approach for other rarefied gas problems.

We now present a new theory of droplet condensation based on the Langmuir model shown in Fig. 2.

CONTINUUM REGION ANALYSIS

For $r_i < r < \infty$ the conservation equations of continuum fluid mechanics are valid. (Properties at the Knudsen/continuum interface are denoted by subscript i and far from the droplet, where the bulk velocity is zero, by subscript v.) Assuming steady-state condensation and neglecting viscous normal stresses, the conservation equations of mass, momentum and energy can be written as

$$\frac{\mathrm{d}}{\mathrm{d}r}(r^2\rho u) = 0$$

$$r^2\frac{\mathrm{d}p}{\mathrm{d}r} + (r^2\rho u)\frac{\mathrm{d}u}{\mathrm{d}r} = 0$$

$$(r^2\rho u)\frac{\mathrm{d}}{\mathrm{d}r}\left(h + \frac{u^2}{2}\right) - \frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 k\frac{\mathrm{d}T}{\mathrm{d}r}\right) = 0 \qquad (9)$$

where u is the radial (outward) bulk velocity, h the specific enthalpy and k the thermal conductivity (assumed constant).

The mass continuity and energy equations can be integrated directly to give

$$\dot{M} = 4\pi r^2 \rho u \qquad = \text{constant}$$

$$\dot{E} = \dot{M}\left(h + \frac{u^2}{2}\right) - 4\pi r^2 k\frac{\mathrm{d}T}{\mathrm{d}r} = \text{constant} \qquad (10)$$

where $\dot{M}$ and $\dot{E}$ are the mass and total energy flow rates *from* the droplet.

Approximate integration of the momentum equation from the far field to the interface $r = r_i$ and substitution of the perfect gas equation gives

$$\frac{p_v - p_i}{p_v} = \frac{u_i^2}{2RT_{av}} \qquad (11)$$

where T_{av} is a suitably defined average vapour temperature. The analysis is now restricted to slow, subsonic condensation ($|u_i/\sqrt{(2RT_i)}| = O(\varepsilon)$, where $\varepsilon \ll 1$). Neglecting terms of $O(\varepsilon^2)$, then justifies the approximation

$$p_i = p_v \qquad (12)$$

which will subsequently be adopted.

The above approximation also allows the neglect of the kinetic energy term in the energy equation (10) which can then be integrated subject to the boundary conditions $T = T_i$ at $r = r_i$ and $T \to T_v$ as $r \to \infty$. The solution for the temperature distribution is

$$\frac{T - T_v}{T_i - T_v} = \frac{1 - \exp\left(-\dot{M}c_p/4\pi r k\right)}{1 - \exp\left(-\dot{M}c_p/4\pi r_i k\right)} \qquad (13)$$

where c_p is the isobaric specific heat capacity of the vapour. We now make the assumption $|\dot{M}c_p/4\pi r_i k| \ll 1$ (see Appendix B) so that equation (13) reduces to

$$\frac{T - T_v}{T_i - T_v} \simeq \frac{r_i}{r}. \qquad (14)$$

The total energy flow rate is then

$$\dot{E} = \dot{M}h_i + \dot{Q}_i = \dot{M}h_v + \dot{Q}_v \qquad (15)$$

where $\dot{Q}$ is the heat flow rate, at arbitrary radius $r > r_i$, given by

$$\dot{Q} = -4\pi r^2 k\frac{\mathrm{d}T}{\mathrm{d}r} = 4\pi r_i k(T_i - T_v) - \dot{M}c_p(T - T_v). \qquad (16)$$

THE MOLECULAR VELOCITY DISTRIBUTION FUNCTION

For $r > r_i$ the vapour is in a non-equilibrium state and the molecular velocity distribution is not well approximated by a Maxwellian distribution even with a superposed bulk velocity as suggested by Schrage [3]. A much better approximation which is compatible with the Navier–Stokes equations is Grad's thirteen-moment distribution [20]. Neglecting viscous normal stresses and assuming spherical symmetry, the Grad velocity distribution is given by

$$f = \frac{\rho}{(2\pi RT)^{3/2}}\left\{1 - \frac{q(\xi_r - u)}{pRT}\left[1 - \frac{(\xi_r - u)^2 + \xi_\theta^2 + \xi_\phi^2}{5RT}\right]\right\}$$
$$\times \exp\left\{-[(\xi_r - u)^2 + \xi_\theta^2 + \xi_\phi^2]/2RT\right\} \qquad (17)$$

where (ξ_r, ξ_θ, ξ_ϕ) are the molecular velocity components in spherical polar coordinates, ρ is the local density, T the temperature, u the bulk velocity and q the radial heat flux ($\dot{Q}/4\pi r^2$).

The Grad distribution is an approximation for a monatomic gas but it can be applied to polyatomic gases if it is assumed that the rotational and vibrational energy is not correlated with the translational kinetic energy.

Equation (17) should be a good representation of the real molecular velocity distribution in the continuum region and, in particular, we assume it to apply at the interface $r = r_i$. It is further assumed that the distribution function for molecules arriving at the liquid surface ($\xi_r < 0$) is unaltered from that at $r = r_i$. This assumption is crucial and would only be correct if the molecules suffered no collisions whatsoever in travelling from $r = r_i$ to the droplet surface. Unfortunately, this approximation is patently untrue, because molecules evaporating from the droplet surface undergo a transformation from a half-Maxwellian to a half-Grad distribution during their outward passage across the Knudsen layer and this is brought about purely by the effect of molecular collisions. However, in order to introduce more flexibility into the specification of the distribution function at the droplet surface, it is necessary to include equations for the momentum exchange and higher moments of the Boltzmann equation. The analysis in spherical geometry then becomes very awkward if a simple, closed form solution is required.

Despite these difficulties, there is some evidence which suggests that the approximations involved in specifying the molecular velocity distribution as described above are not as serious as they appear at first glance. In ref. [6], Labuntsov and Kryukov used a rather similar Grad moment method to analyse condensation at a plane surface. Their assumed distribution function (at the liquid surface for $\xi_r < 0$) was similar to equation (17) except that it was multiplied by a constant C to allow for variations across the Knudsen layer. The conservation of momentum as well as of mass and energy was applied to fix the value of C, although this required that the equations be solved numerically rather than algebraically. In all examples considered, the calculated value of C was very close to unity and this applied even when the bulk velocity was a significant fraction of the speed of sound.

We therefore assume the velocity distribution in the vapour at the *liquid–vapour interface* to be as follows:

(i) for $(0 < \xi_r < \infty)$

$$f_+ = \frac{\rho_s}{(2\pi RT_d)^{3/2}} \exp\left[-(\xi_r^2+\xi_\theta^2+\xi_\phi^2)/2RT_d\right] \qquad (18)$$

(ii) for $(-\infty < \xi_r < 0)$

$$f_- = \frac{\rho_i}{(2\pi RT_i)^{3/2}}\left\{1-\frac{q_i(\xi_r-u_i)}{p_iRT_i}\right.$$
$$\left.\times\left[1-\frac{(\xi_r-u_i)^2+\xi_\theta^2+\xi_\phi^2}{5RT_i}\right]\right\}$$
$$\times\exp\left\{-[(\xi_r-u_i)^2+\xi_\theta^2+\xi_\phi^2]/2RT_i\right\}. \qquad (19)$$

In equation (18), $\rho_s = p_s/RT_d$.

KNUDSEN LAYER ANALYSIS

The rate of mass transfer from the droplet surface is given by

$$\dot{M} = q_c\dot{M}_+ + (1-q_c)\dot{M}_- - \dot{M}_- = q_c\dot{M}_+ - q_c\dot{M}_- \qquad (20)$$

where

$$\dot{M}_+ = 4\pi r_d^2\int_0^\infty\iint_{-\infty}^{\infty}\xi_r f_+\,\mathrm{d}\xi_r\,\mathrm{d}\xi_\theta\,\mathrm{d}\xi_\phi$$
$$= 4\pi r_d^2\frac{p_s}{\sqrt{(2\pi RT_d)}} \qquad (21)$$

and

$$\dot{M}_- = 4\pi r_d^2\int_0^\infty\iint_{-\infty}^{\infty}\xi_r f_-\,\mathrm{d}\xi_r\,\mathrm{d}\xi_\theta\,\mathrm{d}\xi_\phi$$
$$\simeq 4\pi r_d^2\frac{p_i}{\sqrt{(2\pi RT_i)}}\left[1-\frac{u_i\sqrt{\pi}}{\sqrt{(2RT_i)}}\right]. \qquad (22)$$

The triple integrals of the above and later equations can be performed analytically by substituting equations (18) and (19) and using tables of standard integrals. The procedure is straightforward but algebraically tedious. In deriving equation (22), we have assumed that the dimensionless heat flux $|(q_i/RT_i)\sqrt{(2\pi RT_i)}/p_i| = O(\varepsilon)$, and have neglected terms of $O(\varepsilon^2)$ (see Appendix B).

Substituting equations (21) and (22) into equation (20) gives

$$\dot{M} = 4\pi r_i^2\rho_iu_i = 4\pi r_i^2(2\sqrt{\pi})\frac{p_i}{\sqrt{(2\pi RT_i)}} - \frac{u_i}{\sqrt{(2RT_i)}}$$
$$\left.\times\left[1-\frac{u_i\sqrt{\pi}}{\sqrt{(2RT_i)}}\right]\right\}. \qquad (23)$$

Noting from equations (10) that

$$\dot{M} = 4\pi r_i^2\rho_iu_i = 4\pi r_i^2(2\sqrt{\pi})\frac{p_i}{\sqrt{(2\pi RT_i)}}\frac{u_i}{\sqrt{(2RT_i)}} \qquad (24)$$

results in

$$\dot{M}\left(1-\frac{q_c}{2}\frac{r_d^2}{r_i^2}\right) = 4\pi r_d^2\left[\frac{q_cp_s}{\sqrt{(2\pi RT_d)}}-\frac{q_cp_i}{\sqrt{(2\pi RT_i)}}\right]. \qquad (25)$$

From equation (12), we have $p_i = p_v$. As $Kn \to \infty$, $r_i \to \infty$, $T_i \to T_v$ and we recover the Hertz–Knudsen equation. As $Kn \to 0$, $r_i/r_d \to 1$ and apart from the fact that $T_i \neq T_v$, we have Schrage's result [3] for a plane liquid–vapour interface. Equation (25) thus shows how Schrage's correction enters into droplet growth theory in a logically consistent and physically satisfying manner. Unlike Schrage, however, we shall introduce a correction due to the dependence of T_i on $\dot{M}$ and this will have the effect of making an adjustment to the coefficient in parentheses on the left-hand side of equation (25).

We now derive an expression for the total energy flow rate from the droplet assuming that the rotational and vibrational energies of polyatomic molecules are uncorrelated with their translational kinetic energies. We also assume that molecules reflected from the droplet surface emerge with a half-Maxwellian distribution characterized by the liquid temperature (i.e. complete thermal accommodation). Thus

$$\dot{E} = [q_c\dot{M}_+ + (1-q_c)\dot{M}_-]\left(c_p-\frac{R}{2}\right)T_d$$
$$-\left[\dot{E}_- + \dot{M}_-\left(c_p-\frac{5R}{2}\right)T_i\right] \qquad (26)$$

where $\dot{E}_-$ is the translational kinetic energy flow rate of molecules directed towards the surface. $\dot{E}_-$ is given by

$$\dot{E}_- = 4\pi r_d^2\int_0^\infty\iint_{-\infty}^{\infty}\frac{1}{2}\xi_r(\xi_r^2+\xi_\theta^2+\xi_\phi^2)f_-\,\mathrm{d}\xi_r\,\mathrm{d}\xi_\theta\,\mathrm{d}\xi_\phi$$
$$\simeq 4\pi r_d^2\left\{\frac{p_i(2RT_i)}{\sqrt{(2\pi RT_i)}}\left[1-\frac{5u_i\sqrt{\pi}}{4\sqrt{(2RT_i)}}\right]-\frac{q_i}{2}\right\} \qquad (27)$$

where terms of $O(\varepsilon^2)$ have been neglected. Note that the term in equation (27) involving u_i is equivalent to Schrage's correction applied to the energy rather than the mass transfer process. The term involving q_i is due to the distortion of the distribution function from the equilibrium Maxwellian form at $r = r_\mathrm{i}$ to allow the representation of the heat flux.

Substituting equations (21), (22), (24) and (27) into equation (26) gives

$$\dot{E} = 4\pi r_\mathrm{d}^2 \frac{p_\mathrm{i}}{\sqrt{(2\pi R T_\mathrm{i})}} \left(c_p - \frac{R}{2}\right)(T_\mathrm{d} - T_\mathrm{i}) + \left(\frac{r_\mathrm{d}^2}{2r_\mathrm{i}^2}\right)\dot{Q}_\mathrm{i} + \dot{M} c_p T_\mathrm{i} + \dot{M}\left(1 - \frac{r_\mathrm{d}^2}{2r_\mathrm{i}^2}\right) \times \left[\left(c_p - \frac{R}{2}\right)(T_\mathrm{d} - T_\mathrm{i}) - \frac{RT_\mathrm{i}}{2}\right]. \tag{28}$$

Equations (25) and (28) are expressions for the mass and energy transfer rates in terms of the thermodynamic properties at the droplet surface and the Knudsen–continuum interface.

THE INTERFACE TEMPERATURE T_i AND THE TEMPERATURE JUMP AT THE LIQUID SURFACE

The interface temperature T_i can be obtained by equating the continuum and Knudsen layer expressions for $\dot{E}$. Thus, combining equations (15), (16) and (28) and rearranging, we have

$$4\pi r_\mathrm{i} k (T_\mathrm{i} - T_\mathrm{v})\left(1 - \frac{r_\mathrm{d}^2}{2r_\mathrm{i}^2}\right) = 4\pi r_\mathrm{d}^2 \frac{p_\mathrm{i}}{\sqrt{(2\pi R T_\mathrm{i})}} \times \left(c_p - \frac{R}{2}\right)(T_\mathrm{d} - T_\mathrm{i}) + \dot{M}\left(1 - \frac{r_\mathrm{d}^2}{2r_\mathrm{i}^2}\right) \times \left[\left(c_p - \frac{R}{2}\right)(T_\mathrm{d} - T_\mathrm{v}) - \frac{RT_\mathrm{v}}{2}\right]. \tag{29}$$

We now make the assumption (valid for most practical cases of droplet growth), that the droplet–vapour temperature difference is small compared with the absolute temperature, $|(T_\mathrm{d} - T_\mathrm{v})/T_\mathrm{v}| \ll 1$. The final bracket in equation (29) therefore becomes: $(c_p - R/2)(T_\mathrm{d} - T_\mathrm{v}) - RT_\mathrm{v}/2 \simeq -RT_\mathrm{v}/2$.

Defining the vapour Prandtl number by $Pr = c_p \eta / k$ and using equation (8), we have

$$\frac{p_\mathrm{v}}{\sqrt{(2\pi R T_\mathrm{v})}} \simeq \frac{p_\mathrm{i}}{\sqrt{(2\pi R T_\mathrm{i})}} = \frac{Pr\, k}{2\lambda c_p}. \tag{30}$$

Introducing equation (30) into equation (29) gives

$$\left\{\frac{r_\mathrm{d}/r_\mathrm{i}}{(1 - r_\mathrm{d}^2/2r_\mathrm{i}^2)} + \left(\frac{8\gamma}{\gamma+1}\right)\frac{Kn}{Pr}\right\}\left(\frac{T_\mathrm{d} - T_\mathrm{i}}{T_\mathrm{v}}\right) = \left(\frac{8\gamma}{\gamma+1}\right)\frac{Kn}{Pr}\left(\frac{T_\mathrm{d} - T_\mathrm{v}}{T_\mathrm{v}}\right) + \left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{r_\mathrm{d}}{r_\mathrm{i}}\right)\frac{\sqrt{(2\pi R T_\mathrm{i})}}{p_\mathrm{i}} J_m \tag{31}$$

where J_m is the mass flux defined by equation (6).

Equation (31) is an expression for the temperature difference $(T_\mathrm{d} - T_\mathrm{i})$ between the droplet and the interface at $r = r_\mathrm{i}$ in terms of the overall droplet vapour temperature difference $(T_\mathrm{d} - T_\mathrm{v})$ and the mass flux J_m. It is valid for all values of the Knudsen number and includes the effects of surface curvature for very small droplets. The ratio $r_\mathrm{i}/r_\mathrm{d}$ is a function of the Knudsen number only and is given by

$$\frac{r_\mathrm{i}}{r_\mathrm{d}} = \frac{r_\mathrm{d} + \beta\lambda}{r_\mathrm{d}} = 1 + 2\beta\, Kn \tag{32}$$

where β is an, as yet, unknown constant of order unity. (Subsequently, we show by comparison with a direct numerical solution of the Boltzmann equation that $\beta \approx 0.75$.)

For droplet growth under free molecule conditions, $Kn \to \infty$, $r_\mathrm{d}/r_\mathrm{i} \to 0$ and $T_\mathrm{i} \to T_\mathrm{v}$ as expected. For droplet growth under continuum conditions, $Kn \to 0$, $r_\mathrm{d}/r_\mathrm{i} \to 1$ and

$$\left(\frac{T_\mathrm{d} - T_\mathrm{i}}{T_\mathrm{v}}\right) \to \left(\frac{\gamma-1}{\gamma+1}\right)\frac{\sqrt{(2\pi R T_\mathrm{i})}}{p_\mathrm{i}}\frac{J_m}{2} = \sqrt{\pi}\left(\frac{\gamma-1}{\gamma+1}\right)\frac{u_\mathrm{i}}{\sqrt{(2RT_\mathrm{i})}}. \tag{33}$$

Evidently, in the continuum limit, the model predicts a temperature jump across the Knudsen layer (the thickness of which tends to zero) which is proportional to the mass condensation rate.

Most theories of condensation in the continuum limit assume that the temperature is continuous at the droplet surface ($T_\mathrm{i} \to T_\mathrm{d}$ as $Kn \to 0$). However, it can be seen from equation (33) that this is only true as the condensation rate itself tends to zero. The true boundary condition for applying the continuum equations at a condensing or evaporating droplet surface in the limit $Kn \to 0$ is, $T = T_\mathrm{i} \neq T_\mathrm{d}$ in the vapour at $r = r_\mathrm{d}$.

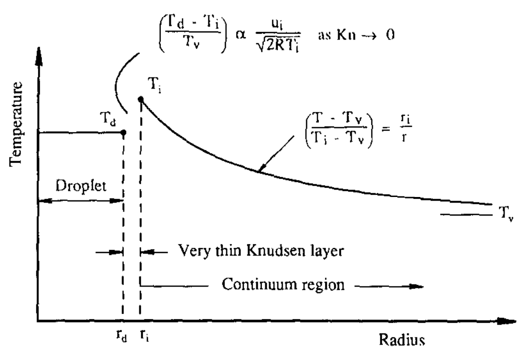
The temperature jump across the Knudsen layer and the effective boundary conditions to be applied to the continuum equations has provoked considerable discussion in the literature in the context of plane condensation. A solution of the linearized BGK equation for this problem has been given by Sone and Onishi [12] for a monatomic gas which can be written as

$$\left(\frac{T_\mathrm{d} - T_\mathrm{i}}{T_\mathrm{v}}\right) \to 0.447\frac{u_\mathrm{i}}{\sqrt{(2RT_\mathrm{i})}} \quad \text{as } Kn \to 0. \tag{34}$$

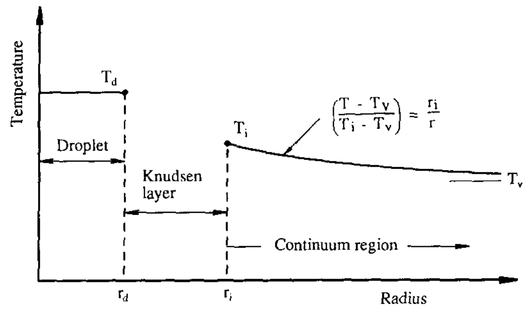
Substituting $\gamma = 5/3$ for a monatomic gas into equation (31) gives

$$\left(\frac{T_\mathrm{d} - T_\mathrm{i}}{T_\mathrm{v}}\right) \to 0.443\frac{u_\mathrm{i}}{\sqrt{(2RT_\mathrm{i})}} \quad \text{as } Kn \to 0 \tag{35}$$

which is, indeed, a remarkable agreement. Unlike the analysis of ref. [12], however, equations (31) and (33) also apply to polyatomic vapours, although, as yet, there are no analytical or numerical solutions of the Boltzmann equation available for assessing the accuracy of the result.



a) Condensing droplet, Kn→0.



b) Condensing droplet, Kn = O(1).

FIG. 3. Schematic diagram of the temperature distribution near a condensing droplet at different Knudsen numbers.

Equation (35) shows that, for droplet condensation under continuum conditions ($u_i < 0$), the temperature T_i is always *higher* than the temperature T_d of the condensing surface. (The opposite effect is found for evaporation ($u_i > 0$).) For steady condensation (when the droplet temperature remains constant with time), the enthalpy of phase change is conducted *away* from the liquid surface and the temperature distribution surrounding the droplet takes the (initially surprising) form shown schematically in Fig. 3(a). At higher Knudsen numbers, the temperature difference $(T_d - T_i)$ must be calculated from equation (31) rather than equation (33) and it is then found that, for $u_i < 0$, the temperature T_i falls below T_d, see Fig. 3(b).

The physical reason for the existence of a temperature jump $(T_d - T_i)$ in the continuum limit has been discussed by Sone and Onishi [12]. Briefly, it is caused by the selective effect of the absorbing liquid surface which removes molecules arriving at the surface (having a velocity distribution characterized by a finite bulk velocity and radial heat flux) and replaces them with an evaporative flux which is precisely half-Maxwellian.

THE CONDENSATION AND EVAPORATION COEFFICIENTS

At thermodynamic equilibrium, the coefficients q_c and q_e are equal, but this is not necessarily so when net condensation or evaporation is occurring. For a linearized analysis, $\Delta p/p \ll 1$, $\Delta T/T \ll 1$ and

$$\frac{q_c}{q_e} \simeq 1+\alpha_p\frac{\Delta p}{p}+\alpha_T\frac{\Delta T}{T} \tag{36}$$

where α_p and α_T are defined by

$$\alpha_p = \left[\frac{\partial(q_c/q_e)}{\partial(\Delta p/p)}\right]_{\Delta p = \Delta T = 0};$$

$$\alpha_T = \left[\frac{\partial(q_c/q_e)}{\partial(\Delta T/T)}\right]_{\Delta p = \Delta T = 0}. \tag{37}$$

As shown below, α_p and α_T are not independent and are constrained by the Onsager reciprocal relation.

Due to lack of experimental evidence to the contrary, it is normal practice to set $\alpha_p = \alpha_T = 0$ for practical calculations. Maximum growth or evaporation rates are then obtained when $q_c = q_e = 1$. Reduced growth rates correspond to $q_c = q_e < 1$ and the specification of $q_c < 1$ is then a useful artifice for matching theory to experiment (see Mozurkewich [21] for a discussion on measurements of the condensation coefficient). However, as noted in ref. [22], some (indirect) experimental evidence exists to suggest that the Hertz–Knudsen theory underpredicts the free molecule growth rate of small water droplets in low pressure, pure steam by a factor of about 2. The only way to reconcile this discrepancy with droplet growth theory appears to involve specifying $q_e = 1$ and $q_c/q_e < 1$ for non-equilibrium condensation.

GENERALIZED EQUATIONS FOR DROPLET CONDENSATION AND EVAPORATION

Assuming $\Delta p/p \ll 1$ and $\Delta T/T \ll 1$, the mass transfer equation (25) can be written as

$$J_m\frac{\sqrt{(2\pi RT_i)}}{p_i}\left(1-\frac{q_c}{2}\frac{r_d^2}{r_i^2}\right) = q_c\left[(1+\alpha_p)\frac{\Delta p}{p}+\alpha_T\frac{\Delta T}{T}-\frac{\Delta T_i}{2T}\right] \tag{38}$$

where $\Delta T_i = T_d - T_i$ and α_p and α_T are defined by equations (36) and (37). Introducing equation (31), we obtain

$$J_m\frac{\sqrt{(2\pi RT_i)}}{p_i}\left\{1-\frac{q_c}{2}\frac{r_d}{r_i}\left[\frac{r_d}{r_i}-\frac{(\gamma-1)/(\gamma+1)}{(A+B)}\right]\right\} = q_c(1+\alpha_p)\frac{\Delta p}{p}-q_c\left(\frac{C}{2}-\alpha_T\right)\frac{\Delta T}{T} \tag{39}$$

where

$$A = \frac{r_d/r_i}{(1-r_d^2/2r_i^2)}$$

$$B = \left(\frac{8\gamma}{\gamma+1}\right)\frac{Kn}{Pr}$$

$$C = \frac{B}{(A+B)}. \tag{40}$$

The coefficients L_{mm} and L_{mq} in the phenomenological mass transfer equation (7) are therefore given by

$$L_{mm} = \left[\frac{q_c(1+\alpha_p)}{D}\right]$$

$$L_{mq} = \left[\frac{-q_c(C/2-\alpha_T)}{D}\right] \tag{41}$$

where

$$D = 1 - \frac{q_c}{2}\frac{r_d}{r_i}\left[\frac{r_d}{r_i} - \frac{(\gamma-1)/(\gamma+1)}{(A+B)}\right] \tag{42}$$

and

$$\frac{r_i}{r_d} = 1 + 2\beta\,Kn \tag{43}$$

β being an (as yet) undetermined constant. Due to the linearized nature of the analysis, the factor $p/\sqrt{(2\pi RT)}$ can be evaluated at the equilibrium vapour pressure and temperature. It should also be noted that A is a function of β and Kn only.

An equation for the heat flux J_q can be derived in a similar way. From equation (16) evaluated at $T = T_v(r \to \infty)$, and definition (6) of J_q

$$J_q = \left(\frac{r_i}{r_d}\right)\left(\frac{k}{r_d}\right)\left[\left(\frac{T_d - T_v}{RT_v}\right) - \left(\frac{T_d - T_i}{RT_v}\right)\right]. \tag{44}$$

In terms of the definitions (40), equation (31) can be written as

$$\left(\frac{T_d - T_i}{T_v}\right) = \left(\frac{B}{A+B}\right)\left(\frac{T_d - T_v}{T_v}\right) + \left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{r_d}{r_i}\right)\frac{\sqrt{(2\pi RT_i)}}{p_i}\frac{J_m}{(A+B)}. \tag{45}$$

Hence

$$J_q = \left(\frac{k}{r_d}\right)\left(\frac{r_i}{r_d}\right)\left(\frac{A}{A+B}\right)\frac{\Delta T}{RT_v} - \left(\frac{B}{A+B}\right)\frac{J_m}{2} \tag{46}$$

where use has been made of relationship (30).

The form of equation (46) stresses the link with the continuum heat transfer coefficient (k/r_d) in the absence of condensation. The factor $(r_i/r_d)(A/(A+B))$ can then be interpreted in the usual way as a correction for rarefied gas effects. The term proportional to J_m is related to the continuum temperature jump at the liquid surface discussed in the previous section and does not appear in simpler theories of droplet growth. Note that, as $r_i \to \infty$ $(Kn \to \infty)$, the Hertz–Knudsen expression for J_q is recovered.

The phenomenological coefficients L_{qm} and L_{qq} are obtained by combining equations (39) and (46)

$$L_{qm} = \left[\frac{-q_c C(1+\alpha_p)}{2D}\right]$$

$$L_{qq} = \left[\left(\frac{\gamma+1}{\gamma-1}\right)\left(\frac{AC}{2}\right)\left(\frac{r_i}{r_d}\right) + \frac{q_c}{2}\frac{C}{D}\left(\frac{C}{2} - \alpha_T\right)\right]. \tag{47}$$

The inclusion of the factor $p/\sqrt{(2\pi RT)}$ in equation (7) suggests that the variation of Kn is with respect to the free molecule limit. The equations can also be written with respect to the continuum limit and this is achieved simply by substituting equation (30).

Comparing equations (41) and (47), Onsager reciprocity requires

$$\alpha_T = -\left(\frac{C}{2}\right)\alpha_p \tag{48}$$

so that, for the limiting cases

$$\alpha_T \to -\left(\frac{2\gamma}{\gamma+1}\right)\left(\frac{Kn}{Pr}\right)\alpha_p \quad (Kn \to 0)$$

$$\alpha_T \to -\frac{\alpha_p}{2} \quad (Kn \to \infty). \tag{49}$$

It must be conceded that, from physical considerations, such behaviour seems unlikely and, despite the experimental evidence cited previously, it is most probable that $\alpha_p = \alpha_T = 0$ and $q_e = q_c$ even under non-equilibrium conditions.

COMPARISON WITH OTHER THEORIES

A numerical solution of a simplified Boltzmann equation for droplet condensation in a pure monatomic gas has been obtained by Chernyak and Margilevskiy [15]. Their results, converted to the present notation, are reproduced in Figs. 4–6. Figure 4 shows L_{mm}, Fig. 5 shows $-L_{mq}$ and Fig. 6 shows L_{qq}. All curves are plotted as functions of Kn for the particular case $q_c = q_e = 1$. Also included are results from the present theory computed from equations (41) and (47) for $\gamma = 5/3$, $Pr = 2/3$ and various values of β (see equation (43)). Best agreement is obtained with $\beta = 0.75$, although the coefficients L_{mq} and L_{qq} are comparatively insensitive to the value chosen.

Taking $\beta = 0.75$, excellent agreement between the present theory and that of ref. [15] is obtained for Knudsen numbers in the continuum and slip regimes. The correct free molecule limit is also recovered for $Kn \to \infty$. The largest discrepancies occur for $Kn = O(1)$, although even here variations in calculated growth rate due to such discrepancies are small. It must also be remembered that the comparison is with a numerical solution of a model Boltzmann equation and not with experimentally measured values. Comparison with the results of ref. [15] for other values of q_c (with $\beta = 0.75$) shows equally impressive agreement.

Figures 4–6 also show curves calculated from the

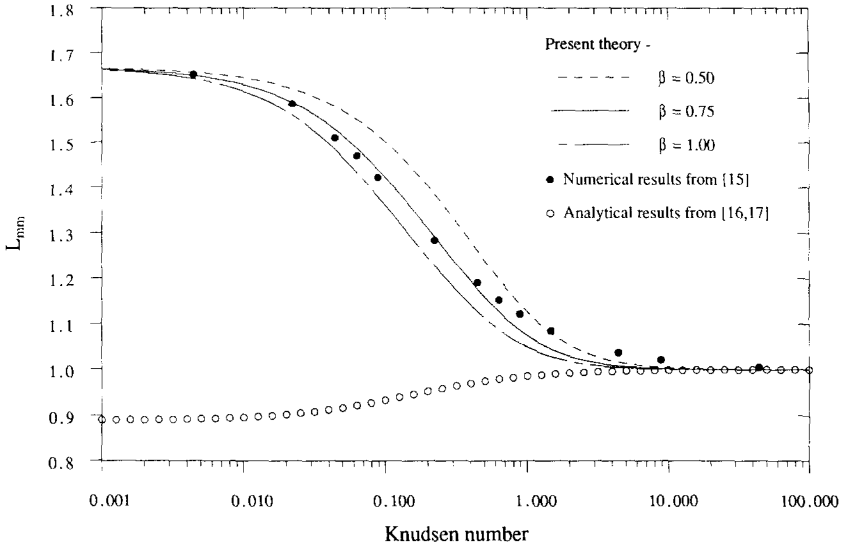


FIG. 4. Variation of L_{mm} with Knudsen number for $q_c = q_e = 1$.

theories of Sampson and Springer [16] and Shankar [17]. It is evident that these theories predict quite a different trend for the coefficient L_{mm}. (The coefficient L_{mq} also displays significant differences.) The discrepancies stem from the representation of the molecular velocity distribution function at the liquid surface. Molecules are assumed to leave the surface with a half-Maxwellian distribution and this is correctly modelled by all theories (f_+ of equation (17) in the present paper). The distribution function of molecules approaching the liquid surface, however, is perturbed from the Maxwellian shape by the net bulk velocity and heat transfer. Both refs. [16, 17] adopt Lees' distribution function which is constrained to represent f_- by a half-Maxwellian and which does not allow sufficient flexibility for modelling the true distribution function which is much closer to the representation f_- of equation (19).

Finally, it should be noted that the analytical results of refs. [16, 17] satisfy the Onsager reciprocal theorem. Evidently, satisfaction of this theorem is no guarantee of the accuracy of the solution.

CONCLUSIONS

A new set of equations describing the condensation and evaporation of small liquid droplets in a pure vapour has been derived. The equations (which are in explicit, algebraic form) specify the heat and mass transfer between the droplet and vapour in terms of

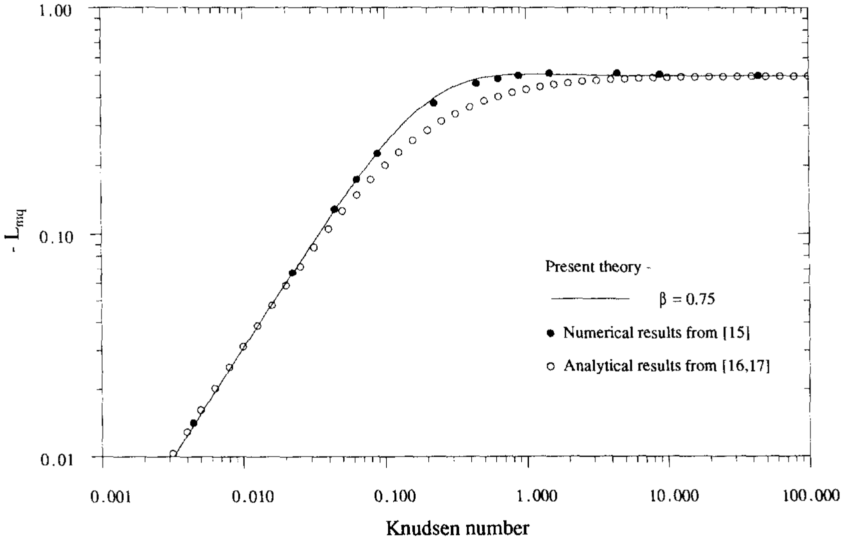


FIG. 5. Variation of $-L_{mq}$ with Knudsen number for $q_c = q_e = 1$.

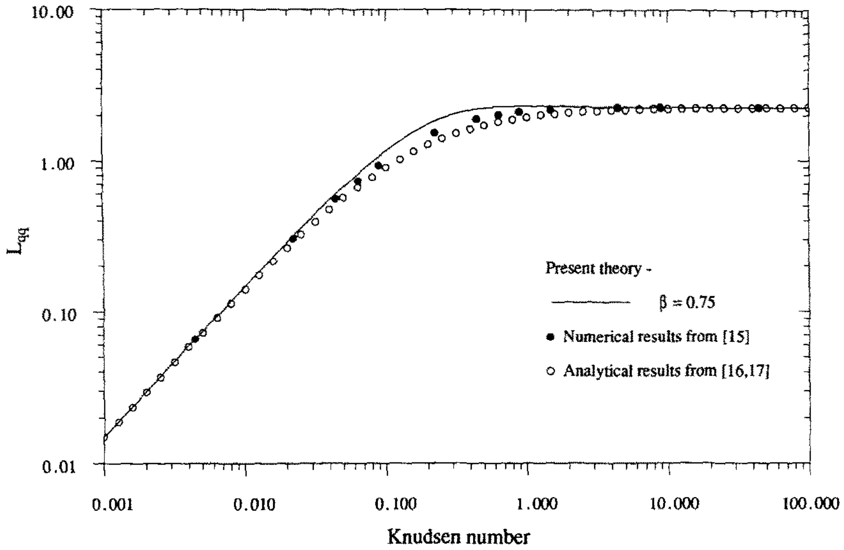


FIG. 6. Variation of L_{qq} with Knudsen number for $q_c = q_e = 1$.

the temperature difference $\Delta T = (T_d - T_v)$ and the pressure difference $\Delta p = (p_s - p_v)$. The relevant expressions are given by equations (7) with the phenomenological coefficients defined by equations (41) and (47). The theory is valid for polyatomic gases at arbitrary Knudsen number and, apart from the condensation and evaporation coefficients, contains no arbitrary constants.

Unlike other simple theories of droplet growth, the present theory successfully models most features of the kinetics of condensation which are usually only revealed by complex analytical and numerical solutions of Boltzmann-type equations. Thus, the temperature jump across the Knudsen layer in the continuum limit agrees closely with the analysis of ref. [12]. The arbitrary constant β which specifies the blending of the Knudsen and continuum regions has been fixed by comparison with a numerical solution of a BGK-type equation for a monatomic gas [15]. Hitherto, the impossibility of specifying this interpolation constant has been a serious weakness of theories which do not utilize the higher moments of the Boltzmann equation invoking the collision integrals. The present theory also illustrates the precise way in which the much discussed Schrage correction [3] is incorporated in droplet growth theory in a physically satisfying way.

Finally, the theory reinforces a conclusion of ref. [15] and demonstrates the inadequacy of Maxwell moment methods using the Lees, two-stream Maxwellian distribution [4, 16–19].

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APPENDIX A. ENTROPY PRODUCTION RATE

The rate of entropy production $\dot{S}$ due to irreversibilities originating in the non-equilibrium region of the system shown in Fig. 1 is given by

$$\dot{S} = \dot{S}_{\mathrm{d}} + \dot{S}_{\mathrm{ne}} + \dot{S}_{\mathrm{v}} + \dot{Q}_{\mathrm{v}}/T_{\mathrm{v}} \tag{A1}$$

where S_{d}, S_{ne} and S_{v} are the entropies of regions D, NE and V, respectively. Invoking the quasi-steady assumption, $\dot{S}_{\mathrm{ne}} = 0$.

S_{d} is composed of contributions from the bulk liquid (S'_{d}) and the droplet surface (S''_{d}). Thus

$$\dot{S}_{\mathrm{d}} = \dot{S}'_{\mathrm{d}} + \dot{S}''_{\mathrm{d}}. \tag{A2}$$

Treating region D as an open system and assuming $S'_{\mathrm{d}} = S'_{\mathrm{d}}(E'_{\mathrm{d}}, V_{\mathrm{d}}, M_{\mathrm{d}})$ where E'_{d} is the contribution to the droplet energy from the bulk liquid, V_{d} the droplet volume and M_{d} its mass, then

$$\dot{S}'_{\mathrm{d}} = \frac{1}{T_{\mathrm{d}}}\dot{E}'_{\mathrm{d}} + \frac{p_{\mathrm{di}}}{T_{\mathrm{d}}}\dot{V}_{\mathrm{d}} - \frac{\mu_{\mathrm{d}}}{T_{\mathrm{d}}}\dot{M}_{\mathrm{d}} \tag{A3}$$

where $\mu_{\mathrm{d}} = \mu_{\mathrm{d}}(T_{\mathrm{d}}, p_{\mathrm{di}})$ is the chemical potential per unit mass of the droplet.

Assuming $S''_{\mathrm{d}} = S''_{\mathrm{d}}(E''_{\mathrm{d}}, A_{\mathrm{d}})$ where E''_{d} is the contribution to the droplet internal energy from the surface and A_{d} the droplet surface area, then

$$\dot{S}''_{\mathrm{d}} = \frac{1}{T_{\mathrm{d}}}\dot{E}''_{\mathrm{d}} - \frac{\sigma}{T_{\mathrm{d}}}\dot{A}_{\mathrm{d}} \tag{A4}$$

where σ is the surface free energy per unit area (surface tension).

Combining equations (A2)–(A4) and noting that $\dot{A}_{\mathrm{d}} = 2\dot{V}_{\mathrm{d}}/r_{\mathrm{d}}$ gives

$$\dot{S}_{\mathrm{d}} = \frac{1}{T_{\mathrm{d}}}\dot{E}_{\mathrm{d}} + \frac{p_{\mathrm{d}}}{T_{\mathrm{d}}}\dot{V}_{\mathrm{d}} - \frac{\mu_{\mathrm{d}}}{T_{\mathrm{d}}}\dot{M}_{\mathrm{d}} \tag{A5}$$

where $E_{\mathrm{d}} = E'_{\mathrm{d}} + E''_{\mathrm{d}}$ and $p_{\mathrm{d}} = p_{\mathrm{di}} - 2\sigma/r_{\mathrm{d}}$ is the pressure in the *vapour* at the droplet surface.

Treating region V as an open system and assuming $S_{\mathrm{v}} = S_{\mathrm{v}}(E_{\mathrm{v}}, V_{\mathrm{v}}, M_{\mathrm{v}})$ where E_{v}, V_{v} and M_{v} represent the internal energy, volume and mass of the region respectively, then

$$\dot{S}_{\mathrm{v}} = \frac{1}{T_{\mathrm{v}}}\dot{E}_{\mathrm{v}} + \frac{p_{\mathrm{v}}}{T_{\mathrm{v}}}\dot{V}_{\mathrm{v}} - \frac{\mu_{\mathrm{v}}}{T_{\mathrm{v}}}\dot{M}_{\mathrm{v}} \tag{A6}$$

where $\mu_{\mathrm{v}} = \mu_{\mathrm{v}}(T_{\mathrm{v}}, p_{\mathrm{v}})$ is the chemical potential per unit mass of the vapour.

Application of the conservation of mass and the first law of thermodynamics to the complete system gives

$$\dot{M}_{\mathrm{v}} + \dot{M}_{\mathrm{d}} = 0 \tag{A7}$$

$$(\dot{E}_{\mathrm{v}} + \dot{E}_{\mathrm{d}}) + p_{\mathrm{v}}(\dot{V}_{\mathrm{v}} + \dot{V}_{\mathrm{d}}) + \dot{Q}_{\mathrm{v}} = 0. \tag{A8}$$

Hence

$$\dot{S} = \left(\frac{1}{T_{\mathrm{d}}} - \frac{1}{T_{\mathrm{v}}}\right)\dot{E}_{\mathrm{d}} + \left(\frac{p_{\mathrm{d}}}{T_{\mathrm{d}}} - \frac{p_{\mathrm{v}}}{T_{\mathrm{v}}}\right)\dot{V}_{\mathrm{d}} - \left(\frac{\mu_{\mathrm{d}}}{T_{\mathrm{d}}} - \frac{\mu_{\mathrm{v}}}{T_{\mathrm{v}}}\right)\dot{M}_{\mathrm{d}}. \tag{A9}$$

Because there is bulk flow in region V, $\dot{E}_{\mathrm{v}} + p_{\mathrm{v}}\dot{V}_{\mathrm{v}} = h_{\mathrm{v}}\dot{M}_{\mathrm{v}}$, where h_{v} is the specific enthalpy of the vapour in region V. Substituting in equation (A8) and combining with equation (A9) gives

$$\dot{S} = \left(\frac{1}{T_{\mathrm{v}}} - \frac{1}{T_{\mathrm{d}}}\right)\dot{Q}_{\mathrm{v}} + \left[h_{\mathrm{v}}\left(\frac{1}{T_{\mathrm{v}}} - \frac{1}{T_{\mathrm{d}}}\right) - \left(\frac{\mu_{\mathrm{v}}}{T_{\mathrm{v}}} - \frac{\mu_{\mathrm{d}}}{T_{\mathrm{d}}}\right)\right]\dot{M} - \frac{(p_{\mathrm{v}} - p_{\mathrm{d}})}{T_{\mathrm{d}}}\dot{V}_{\mathrm{d}} \tag{A10}$$

where use has been made of the equality $\dot{M}_{\mathrm{d}} = -\dot{M}$ (the negative of the mass condensation rate).

A droplet of radius r_{d} and temperature T_{d} would be in equilibrium with vapour at temperature T_{d} and pressure $p_{\mathrm{s}} = p_{\mathrm{s}}(T_{\mathrm{d}}, r_{\mathrm{d}})$. The internal pressure of such a droplet would be $p_{\mathrm{si}} = p_{\mathrm{s}} + 2\sigma/r_{\mathrm{d}}$. Using the thermodynamic relationship for a pure substance, $(\partial\mu/\partial p)_T = 1/\rho$, we can therefore write

$$\mu_{\mathrm{d}}(T_{\mathrm{d}}, p_{\mathrm{di}}) = \mu_{\mathrm{d}}(T_{\mathrm{d}}, p_{\mathrm{si}}) + \frac{(p_{\mathrm{di}} - p_{\mathrm{si}})}{\rho_{\mathrm{d}}}. \tag{A11}$$

From the second of equations (1), $\mu_{\mathrm{d}}(T_{\mathrm{d}}, p_{\mathrm{di}}) = \mu_{\mathrm{v}}(T_{\mathrm{d}}, p_{\mathrm{s}})$. Noting that $(p_{\mathrm{di}} - p_{\mathrm{si}}) = (p_{\mathrm{d}} - p_{\mathrm{s}})$, we have

$$\mu_{\mathrm{d}}(T_{\mathrm{d}}, p_{\mathrm{di}}) = \mu_{\mathrm{v}}(T_{\mathrm{d}}, p_{\mathrm{s}}) + \frac{(p_{\mathrm{d}} - p_{\mathrm{s}})}{\rho_{\mathrm{d}}}. \tag{A12}$$

Making the approximation $\rho_{\mathrm{v}}/\rho_{\mathrm{d}} \ll 1$ (i.e. neglecting the liquid specific volume compared with that of the vapour), the final terms in equations (A10) and (A12) may be discarded. Substituting equation (A12) into equation (A10) then gives

$$\dot{S} = \left(\frac{1}{T_{\mathrm{v}}} - \frac{1}{T_{\mathrm{d}}}\right)\dot{Q}_{\mathrm{v}} + \left[h_{\mathrm{v}}\left(\frac{1}{T_{\mathrm{v}}} - \frac{1}{T_{\mathrm{d}}}\right) - \left(\frac{\mu_{\mathrm{v}}(T_{\mathrm{v}}, p_{\mathrm{v}})}{T_{\mathrm{v}}} - \frac{\mu_{\mathrm{d}}(T_{\mathrm{d}}, p_{\mathrm{s}})}{T_{\mathrm{d}}}\right)\right]\dot{M}. \tag{A13}$$

Assuming the vapour to behave as a perfect gas and using the definitions and approximations $(T_{\mathrm{d}} - T_{\mathrm{v}})/T_{\mathrm{d}} = \Delta T/T_{\mathrm{d}} \ll 1$ and $(p_{\mathrm{s}} - p_{\mathrm{v}})/p_{\mathrm{s}} = \Delta p/p_{\mathrm{s}} \ll 1$, gives

$$\frac{\dot{S}}{R} = \dot{M}\left(\frac{\Delta p}{p_{\mathrm{s}}}\right) + \frac{\dot{Q}_{\mathrm{v}}}{RT_{\mathrm{v}}}\left(\frac{\Delta T}{T_{\mathrm{d}}}\right). \tag{A14}$$

Introducing the definitions of the fluxes J_m and J_q, equations (6), finally result in

$$\frac{\dot{S}}{R} = 4\pi r_{\mathrm{d}}^2\left\{J_m\left(\frac{\Delta p}{p_{\mathrm{s}}}\right) + J_q\left(\frac{\Delta T}{T_{\mathrm{d}}}\right)\right\}. \tag{A15}$$

APPENDIX B. ASSUMPTIONS OF THE THEORY

The physical interpretation of the assumptions introduced into the analysis is not obvious and requires explanation.

Firstly, the analysis is restricted to slow, subsonic condensation or evaporation, $|u_{\mathrm{i}}/\sqrt{(2RT_{\mathrm{i}})}| \ll 1$. A further restriction is also imposed by the condition, $|\dot{M}c_p/4\pi r_{\mathrm{i}}k| \ll 1$. Using the definitions of J_m, Pr and Kn, this can also be written as

$$\left|\frac{J_m\sqrt{(2\pi RT)}}{p}\,\frac{Pr}{4Kn}\,\frac{r_{\mathrm{d}}}{r_{\mathrm{i}}}\right| \ll 1. \tag{B1}$$

Equation (B1) takes its strongest form in the continuum limit, $r_{\mathrm{i}} \to r_{\mathrm{d}}$, where it becomes (using the first of equations (7))

$$\left|\frac{Pr}{4Kn}\left(L_{mm}\frac{\Delta p}{p}+L_{mq}\frac{\Delta T}{T}\right)\right| \ll 1. \tag{B2}$$

The results of the analysis (equations (41)), show that, as $Kn \rightarrow 0$ and assuming $q_c = q_e$, $L_{mm} = O(q_c)$ and $L_{mq} = O(q_c\,Kn)$. The satisfaction of equation (B2) therefore requires

$$\frac{\Delta p}{p} \ll \frac{Kn}{q_c}$$

$$\frac{\Delta T}{T} \ll \frac{1}{q_c}. \tag{B3}$$

The condition on $\Delta p/p$ is therefore more restrictive than that on $\Delta T/T$.

In developing equations for the Knudsen layer, we also introduced the assumption that the dimensionless heat flux $|(q_i/RT_i)\sqrt{(2\pi RT_i)}/p_i| \ll 1$. Noting that $J_q = (q_i/RT_i)$ and introducing the second of equations (7), we therefore require

$$\left(L_{qm}\frac{\Delta p}{p}+L_{qq}\frac{\Delta T}{T}\right) \ll 1. \tag{B4}$$

An examination of equation (47) for L_{qm} and L_{qq} shows that equation (B4) is always satisfied if

$$\frac{\Delta p}{p} \ll \frac{1}{q_c}$$

$$\frac{\Delta T}{T} \ll 1. \tag{B5}$$

In order to relax the constraint on $\Delta p/p$ implied by equation (B3), a non-linear analysis is required. This has been performed (but only for a monatomic gas with $Kn \ll 1$) by Onishi [23] using a theory developed by Onishi and Sone [24] which is based on an approximate analytical solution of the BGK equation. In this connection, it is interesting to note that the requirement, equation (B1), can be expressed in an equivalent form, $|Ma/Kn| \ll 1$, where Ma is the Mach number of the vapour flow. This is exactly the condition necessary for the validity of the earlier linearized analysis of Sone and Onishi [12].

CONDENSATION ET EVAPORATION DE GOUTTELETTES LIQUIDES DANS UNE VAPEUR PURE A UN NOMBRE DE KNUDSEN QUELCONQUE

Résumé—On présente un nouveau système d'équations qui décrit la croissance et l'évaporation de gouttelettes liquides dans une vapeur pure. Les équations qui modélisent le transfert de masse et de chaleur entre la gouttelette et la vapeur conviennent aux calculs pratiques pour un nombre de Knudsen quelconque. Le modèle physique, sur lequel la théorie est basée, est essentiellement celui de Langmuir mais des idées nouvelles y sont introduites. Par exemple, la fonction de distribution des vitesses pour les molécules qui sont proches de la surface du liquide est décrite par une distribution de treizième moment simplifiée de Grad. Les résultats de l'analyse sont en bon accord avec d'autres théories plus compliquées et moins générales que l'on connaît. En particulier le saut de température à travers la couche de Knudsen, à la limite du milieu continu, est correctement prédit. On montre aussi que les méthodes de moment de Maxwell, basées sur la distribution maxwellienne, conduisent à des résultats incorrects.

KONDENSATION UND VERDAMPFUNG VON FLÜSSIGEN TRÖPFCHEN IN REINEM DAMPF BEI BELIEBIGER KNUDSEN-ZAHL

Zusammenfassung—Wachstum und Verdampfung von kleinen Flüssigkeitströpfchen in einem reinen Dampf werden mit Hilfe eines neuen Gleichungssystems beschrieben. Die Gleichungen, mit denen der Stoff- und der Wärmeübergang zwischen Tropfen und Dampf modelliert wird, sind in einfacher geschlossener Form lösbar und für praktische Berechnungen bei beliebiger Knudsen-Zahl zu verwenden. Das zugrundeliegende physikalische Modell entspricht im wesentlichen demjenigen von Langmuir, jedoch werden einige neue Merkmale mit eingegliedert. So wird z. B. der funktionale Zusammenhang für die Geschwindigkeitsverteilung der Moleküle bei Annäherung an die Flüssigkeitsoberfläche mittels einer vereinfachten Verteilung mit 13 Momenten nach Grad beschrieben. Die Ergebnisse der Berechnung stimmen gut mit solchen aus der Literatur überein, die auf komplizierteren und weniger allgemeinen theoretischen Vorstellungen beruhen. Insbesondere wird der Temperatursprung in der Knudsen-Schicht an der Grenze des Kontinuums genau vorhergesagt. Es zeigt sich auch, daß die Impulsverfahren nach Maxwell, die auf der Zweistrom-Maxwell-Verteilung nach Lees beruhen, zu falschen Ergebnissen führen.

КОНДЕНСАЦИЯ И ИСПАРЕНИЕ КАПЕЛЬ ЖИДКОСТИ В ЧИСТОМ ПАРЕ ПРИ ПРОИЗВОЛЬНОМ ЧИСЛЕ КНУДСЕНА

Аннотация—Предложена новая система уравнений, описывающих рост и испарение небольших капель жидкости в чистом паре. Уравнения, моделирующие тепло-и массоперенос между каплей и паром, имеют простую замкнутую форму и пригрдны для практических расчетов при любом значении числа Кнудсена. Физическая модель, на которой основана теория, является, по существу, моделью Ленгмюра, но включает также и некоторые новые характеристики. Например, функция распределения скоростей для молекул, приближающихся к поверхности жидкости, описывается упрощенным тринадцатимоментным распределением Грэда. Результаты анализа хорошо согласуются с другими, более сложными и менее обобщенными теориями, имеющимися в литературе. В частности, точно определен температурный скачок в слое Кнудсена в пределах сплошной среды. Показано также, что применение метода моментов Максвелла на основе приближения Лиса с использованием двухстороннего максвелловского распределения приводит к неверным результатам.