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The condensation and evaporation of liquid droplets at arbitrary Knudsen number in the presence of an inert gas

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Abstract—A new set of equations describing the growth and evaporation of stationary liquid droplets in a mixture of pure vapour and inert gas is presented. The equations, which model the heat and mass transfer between the droplet and its environment, are presented in a simple algebraic form and are suitable for practical calculations of droplet growth at any Knudsen number and at any concentration of inert gas. In particular, they are not restricted to the so-called *quasi-steady* regime of droplet growth when the droplet surface temperature has relaxed to its steady-state value. The physical model on which the theory is based is essentially that of Langmuir but some novel features are incorporated. Thus, the velocity distribution functions for vapour and inert gas molecules approaching the liquid surface are assumed to correspond to simplified Grad thirteen-moment distributions and this allows correct representation at a molecular level of the heat and mass fluxes at the outer edge of the Knudsen layer. In contrast to most simple models of condensation and evaporation, the theory predicts finite (as opposed to zero) temperature and vapour pressure jumps across the Knudsen layer in the continuum limit and shows that the former is directly proportional to the concentration of vapour present. The analysis also provides a physical interpretation for the origins of the *reversed temperature gradient phenomenon* in the Kundsen layer, an unusual feature predicted by more complex solutions of the Boltzmann equation itself. The transition from diffusion to kinetic control as the pure vapour limit is approached is also modelled by the theory which shows that the range of Knudsen numbers over which this occurs is of the same order as the mole fraction of inert gas present.

INTRODUCTION

PREDICTING the growth and evaporation rates of small, spherical liquid droplets in a mixture of pure vapour and inert gas is a scientific problem of interest in a variety of technological areas including mechanical engineering, chemical engineering and meteorology. In order to calculate the condensation or evaporation rates of such droplets, equations are required describing the mass, momentum and energy transfer between the droplet and its surroundings and the literature addressing these problems at various levels of complexity is now very large. (For recent reviews see Gyarmathy [1] and Mozurkewich [2].) Theoretical analysis is difficult because the equations must represent a continuous transition through all Knudsen numbers from the free molecule to the continuum limit and must be valid for all concentrations of inert gas including the limiting case of pure vapour.

In a previous paper [3], equations describing the quasi-steady mass and energy transfer between a stationary droplet and a pure vapour were presented. Using a simplfied Grad distribution function to represent the molecular velocity distribution in the vapour near the liquid surface, it was possible to model the temperature jump across the Knudsen layer in the continuum limit in close agreement with other more complex analytical solutions of Boltzmann-type equations. (Simple theories predict zero temperature jump in the continuum limit.) The heat and mass transfer rates at intermediate Knudsen numbers were obtained by 'tuning' the equations to match a numerical solution of a model Boltzmann equation for a monatomic gas (although the resulting equations were not themselves subject to the constraint of monatomicity). The condition for Onsager reciprocity was satisfied as required by the theory of linear irreversible thermodynamics but it was noted that such agreement is no guarantee of accuracy. Indeed, some well-known Maxwell moment solutions based on the Lees' two stream Maxwellian distribution function [4, 5] (which also satisfy the Onsager requirement), were shown to give results for the mass transfer equation which are at variance with more direct solutions of the Boltzmann equation.

The analysis of droplet growth in the presence of an inert gas presented below is an extension of the method described in ref. [3]. As in that paper, the focus is on the mass and energy transfer between a single spherical droplet and the surrounding vapour–gas mixture rather than on the overall dynamics of droplet growth itself. Consideration is first given to the thermodynamics and kinetics of vapour–droplet equilibrium. The transport processes are then discussed from the standpoint of the theory of linear irreversible thermodynamics and the general form of the phenomenological equations describing heat and mass transfer is established. The coefficients of these

NOMENCLATURE

c_p	isobaric specific heat capacity
D	diffusion coefficient
$\dot{E}$	energy flow rate from droplet
f	molecular velocity distribution function
h	specific enthalpy
J_m, J_{qc}	mass and conduction heat fluxes from droplet
Kn	Knudsen number, $\lambda/2r_d$
k	thermal conductivity of vapour–gas mixture
$L_{mm}, L_{mq}, L_{qm}, L_{qq}$	phenomenological coefficients
$\dot{M}$	mass flow rate from droplet
Pr	Prandtl number of vapour–gas mixture, $\gamma R\eta/(\gamma-1)k$
p	pressure
p_s	saturation pressure at T_d and r_d
$\dot{Q}_c$	conduction heat flow rate from droplet
q	radial heat flux
q_c, q_e	condensation and evaporation coefficients
R	specific gas constant
r	radius
$\dot{S}$	rate of entropy creation
Sc	Schmidt number, $\eta/\rho D$
T	temperature
u	radial bulk velocity
v	radial diffusive velocity.

Greek symbols

β_m, β_q	constants defining Knudsen continuum interface
γ	ratio of specific heat capacities
Δp_v	$p_s - p_{v,\infty}$
ΔT	$T_d - T_\infty$
η	dynamic viscosity of vapour–gas mixture
λ	mean free path
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
di	internal to the droplet
e	equilibrium region
g	inert gas component
i	Knudsen–continuum interface
ne	non-equilibrium region
s	saturated
v	vapour component
∞	far from droplet
+	away from droplet
−	towards droplet.

No subscript generally refers to the vapour–gas mixture.

equations can only be determined from a molecular-kinetic theory and, as in ref. [3], an extension of the well-known Langmuir model is employed. The molecular velocity distributions for the vapour and inert gas components are assumed to be Grad distribution functions as these provide physically correct representations of the convective and diffusive mass and heat fluxes at the outer edge of the Knudsen layer. With suitable approximations, the resulting equations for the interphase transfer rates can be expressed in simple algebraic forms which are easily programmable for practical calculations of droplet growth and evaporation.

VAPOUR–DROPLET EQUILIBRIUM

Consider a small spherical liquid droplet of radius r_d at rest and at equilibrium in an infinite expanse of a mixture of its own vapour and an inert, non-condensable gas. The droplet temperature T_d, internal pressure p_{di} and density ρ_d are assumed uniform throughout the droplet. The vapour–gas environment is assumed to behave as a mixture of perfect gases, the specific gas constant of the vapour being denoted by R_v and that of the inert gas by R_g. The temperature and total pressure are denoted by p and T, respectively, and the partial pressures of the vapour and gas by p_v and p_g so that $p = p_v + p_g$. The thermodynamic and mechanical conditions for equilibrium are given by

$$\begin{aligned} T &= T_d \\ \mu_v(T, p_v) &= \mu_d(T_d, p_{di}) \\ p_{di} &= p + \frac{2\sigma}{r_d} \end{aligned} \qquad (1)$$

where μ is the chemical potential per unit mass and σ is the liquid surface tension. The internal pressure of the droplet is p_{di} which, for very small droplets, may be very much higher than the external pressure p. If the effect of the partial pressure of the inert gas component on the chemical potential of the liquid is neglected (i.e. if p_{di} in the *second* of equations (1) can be approximated by $p_v + 2\sigma/r_d$), an approximation which is normally acceptable, then the second of equations (1) can be transformed to the alternative, Kelvin–Helmholtz, form

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

where $p_s(T_d, \infty)$ is the saturated vapour pressure at temperature T_d for a flat liquid–vapour interface. Throughout the rest of the paper, $p_s(T_d, r_d)$ is denoted simply by p_s.

From a molecular–kinetic viewpoint, the condition of equilibrium represents a state where the rate of condensation of vapour molecules arriving at the liquid surface is exactly balanced by the rate of evaporation of molecules from the surface. Inert gas molecules also strike the liquid surface, but play no part at equilibrium (apart from the small influence of p_g on μ_d noted above) as the droplet and vapour–gas temperatures are equal. At equilibrium, the velocity distribution of vapour molecules is Maxwellian and hence the mass condensation rate of these molecules $\dot{M}_{v-}$ is given by

$$\dot{M}_{v-} = -4\pi r_d^2 q_c \frac{p_v}{\sqrt{(2\pi R_v T)}} \tag{3}$$

where q_c, the condensation coefficient, is defined as in the case of a pure vapour [3]. (Note that all fluxes are considered positive when they are directed away from the droplet.) The mass evaporation rate of vapour molecules is likewise given by

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

where q_e is the evaporation coefficient and is equal to q_c at equilibrium, but not necessarily otherwise. The theory assumes that $\dot{M}_{v+}$ is a function of droplet temperature and radius only and hence that equation (4) represents $\dot{M}_{v+}$ even under non-equilibrium conditions. The presence of the inert gas is assumed to have no effect in this respect.

IRREVERSIBLE THERMODYNAMICS OF CONDENSATION

Equations (1) show that equilibrium can be disturbed in three ways. Firstly, the vapour temperature can be altered while maintaining the vapour *partial* pressure constant at the equilibrium value p_s. Secondly, the vapour partial pressure can be adjusted while maintaining the vapour–gas temperature constant at the value T_d. Thirdly, a sudden change in the *total* pressure of the vapour–gas mixture can disturb the condition of mechanical equilibrium. The relaxation time associated with this last process is very short, however, and it is assumed that the third of equations (1) is always satisfied.

These considerations imply that the net condensation or evaporation rate depends independently on the temperature difference $\Delta T = (T_d - T_\infty)$ and the *partial* pressure difference $\Delta p_v = (p_s - p_{v\infty})$, the subscript ∞ denoting conditions far from the droplet. (Although departures from equilibrium can be instigated, apparently independently, by variations in either the mixture *total* pressure or the vapour mass fraction, it is the combined effect on the vapour *partial* pressure which is the decisive factor affecting the rate of phase change.) Throughout the analysis, it is assumed that departures from equilibrium as measured by $|\Delta T/T_\infty|$ and $|\Delta p_v/p_{v\infty}|$ are small. The satisfaction of these conditions is discussed in Appendix B of ref. [3].

To apply the formalism of irreversible thermodynamics, an expression for the entropy production rate $\dot{S}$ in the dissipative region surrounding the droplet is required in order to identify the conjugate *fluxes* and thermodynamic *forces* appearing in the *phenomenological equations*. The open thermodynamic system used in deriving an expression for $\dot{S}$ is shown in Fig. 1. Region D is the droplet and includes the surface transition layer. The bulk liquid is assumed to be in a quasi-equilibrium state characterized by a uniform temperature T_d and internal pressure p_{di} and to be in thermodynamic equilibrium with the surface at all times. Region NE is a non-equilibrium vapour–gas region surrounding the droplet. Region E is an infinite vapour–gas reservoir external to the system with uniform constant total pressure p_∞ and temperature T_∞. The vapour partial pressure in region E is $p_{v\infty}$.

It is assumed that quasi-steady condensation or evaporation is occurring and conditions in region NE are time-independent. The rate of heat transfer *due solely to thermal conduction* crossing the system boundary in the radial *outward* direction is denoted by $\dot{Q}_c$. The total mass flow rate of vapour (also crossing the boundary in the *outward* direction) is denoted by $\dot{M}$. As shown in Appendix 1, the rate of entropy creation $\dot{S}$ due to irreversibilities in region NE is,

$$\frac{\dot{S}}{R_v} = 4\pi r_d^2 \left\{ J_m\left(\frac{\Delta p_v}{p_{v\infty}}\right) + J_{qc}\left(\frac{\Delta T}{T_\infty}\right) \right\} \tag{5}$$

where the fluxes J_m and J_{qc} are defined by

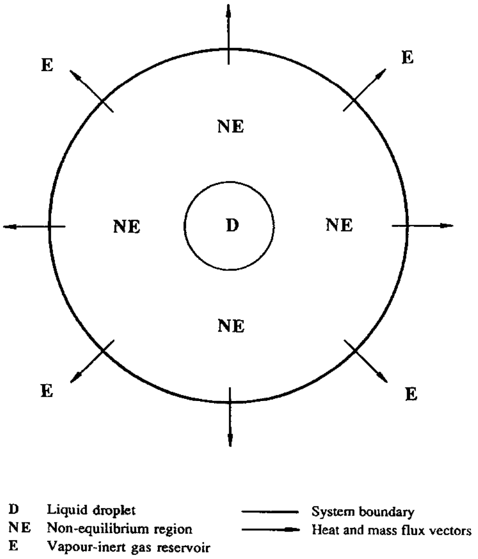

FIG. 1. Open system for the analysis of irreversible entropy production.

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

$$\frac{\dot{Q}_c}{R_v T_\infty} = 4\pi r_d^2 J_{qc}. \tag{6}$$

In equations (5) and (6), it is important to note that it is the heat transfer due to conduction $\dot{Q}_c$ (rather than the total heat transfer as normally defined for a binary mixture) which is associated with the production of entropy.

Equation (5) defines the conjugate fluxes and thermodynamic forces for the application of Onsager's theory. For linear departures from equilibrium, the phenomenological equations therefore take the form

$$J_m = \frac{p}{\sqrt{(2\pi R_v T_\infty)}}\left\{L_{mm}\left(\frac{\Delta p_v}{p_{v\infty}}\right)+L_{mq}\left(\frac{\Delta T}{T_\infty}\right)\right\}$$

$$J_{qc} = \frac{p}{\sqrt{(2\pi R_v T_\infty)}}\left\{L_{qm}\left(\frac{\Delta p_v}{p_{v\infty}}\right)+L_{qq}\left(\frac{\Delta T}{T_\infty}\right)\right\} \tag{7}$$

where L_{mm}, L_{mq}, L_{qm} and L_{qq} are dimensionless phenomenological coefficients. (The factor $p/\sqrt{(2\pi R_v T_\infty)}$ has been introduced for convenience only.)

The problem 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 requires the equality $L_{mq} = L_{qm}$.

THEORIES OF DROPLET GROWTH IN VAPOUR–GAS MIXTURES

In formulating a theory of droplet condensation, expressions are required for the phenomenological coefficients L_{mm}, L_{mq}, L_{qm} and L_{qq} in equations (7) which accurately model the transfer processes at all Knudsen numbers and concentrations of inert gas. (The Knudsen number is defined as $Kn = \lambda/2r_d$, where λ is a mean free path to be specified later.)

The basis of the continuum theory ($Kn \to 0$) was laid by J. C. Maxwell in 1877 when he derived equations for the mass and heat fluxes assuming thermodynamic equilibrium between the liquid surface and the vapour in direct contact with it. This boundary condition is now known to require modification and recent theoretical research on the behaviour of the Boltzmann equation for a pure vapour close to a condensing or evaporating surface has revealed the presence of a temperature jump across the Knudsen layer *even in the continuum limit as the thickness of that layer tends to zero* [6]. Such advances have not yet found their way into most droplet growth theories, with the result that the older theories are inconsistent under certain limiting conditions when compared with the predictions of more recent (but often more restrictive) models. For example, it is not immediately clear how the correction due to Schrage [7], originally derived for the case of plane condensation and much discussed in the literature, should be adapted to the spherical geometry of a growing droplet at arbitrary Knudsen number in the presence of a carrier gas.

Rarefied gas effects were first introduced into the theory by Langmuir and many later developments have utilized his approach. The Langmuir model, shown in Fig. 2, divides the flowfield into an outer region where the equations of continuum fluid mechanics apply and an inner Knudsen layer where transfer processes are kinetically controlled to the extent that intermolecular collisions are deemed unimportant. The matching process is assumed to take place, rather arbitrarily, on a sphere of radius $r_d+\beta\lambda$, where β is an unknown constant of order unity and may take different values for the mass and energy transfer processes. The equation in most common use obtained by this technique is that of Fuchs and Sutugin [8] which compares favourably with the excellent measurements of Davis *et al.* [9, 10]. These authors concentrate on the mass transfer equation in the near isothermal situation of very low vapour concentration, but a similar approach in a more general context and including energy transfer has been presented by Gyarmathy [1].

Other approaches to the problem include the Maxwell moment methods using the Lees' two-stream Maxwellian velocity distribution function pioneered by Sampson and Springer [4] and Shankar [5]. Unfortunately, despite the elegance and apparent universality of the method, it now appears that the results are at variance with more direct solutions of the Boltzmann equation [3, 11]. A similar type of analysis was performed by Sitarski and Nowakowski [12] using the Grad moment method but, for reasons which are not clear, they obtained incorrect behaviour in the free molecule limit.

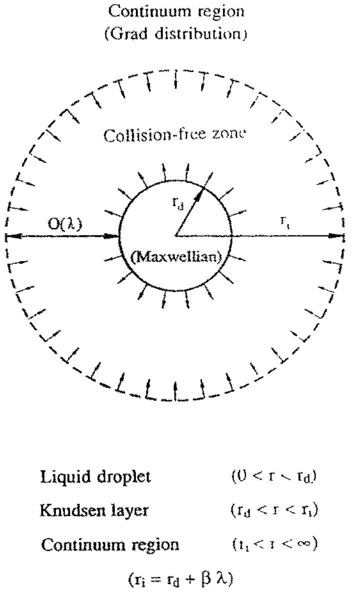

FIG. 2. The Langmuir model.

Direct analytical or numerical solutions of the Boltzmann equation itself (or model versions such as the BGK equation), although sometimes restricted to a narrow class of problem, are extremely useful for calibrating the arbitrary constants which appear in the simpler theories. In this connection, the papers of Loyalka [13, 14], Onishi and Dohara [15] and Onishi [16] are cited.

Familiarity with the literature shows that most research has concentrated on droplet growth or evaporation at the diffusion-controlled continuum or near-continuum limit when the vapour mass fraction is very low. This problem corresponds to the case of well-established water droplets growing or evaporating in air and has obvious applications in meteorology and cloud physics. The equations derived, for example, by Fuchs and Sutugin [8] with minor amendments by Davis *et al.* [10], are very accurate in this regime. Difficulties arise, however, both in the free molecule limit with large inert gas concentrations and in the pure vapour limit as the inert gas concentration tends to zero. Both these cases are of technological importance: the former during the early stages of many homogeneous nucleation processes and the latter when condensation of almost pure vapour occurs in the undesirable presence of small quantities of non-condensable in-leakage. Under these circumstances, transfer processes across the Knudsen layer may dominate and it is important to model as accurately as possible the velocity distribution functions of vapour and gas molecules incident on the droplet surface.

The analysis presented below is an extension of that described in ref. [3] and is based on the Langmuir model of Fig. 2. Whereas previous theories of this type have assumed that the velocity distribution of molecules approaching the surface is half-Maxwellian, the present analysis adopts a more realistic half-Grad distribution function which is fully compatible with the macroscopic processes of diffusion and heat conduction occurring in the continuum region near the Knudsen–continuum interface. For the plane condensation problem, a similar technique was employed by Pong and Moses [17], following the work of Labuntsov and Kryukov [18] for a pure vapour. The equations derived in ref. [17], however, are algebraically complex and are inconvenient for practical computation. In contrast, the equations derived below introduce a few minor simplifications which allow the results to be presented in an algebraically much simpler closed form. The analysis is, however, only valid for small departures from equilibrium.

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 ∞.) Assuming steady-state condensation and neglecting viscous normal stresses, the conservation equations of mass (vapour plus gas and vapour alone), momentum and energy can be written

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

$$\frac{\mathrm{d}}{\mathrm{d}r}[r^2\rho_v(u+v_v)] = 0$$

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

$$\frac{\mathrm{d}}{\mathrm{d}r}\left[r^2\rho u\left(h+\frac{u^2}{2}\right)+r^2 q\right] = 0 \tag{8}$$

where u is the outward radial bulk velocity of the mixture, ρ the mixture density, ρ_v the vapour density, h the mixture specific enthalpy, v_v the outward radial diffusive velocity of the vapour and q is the outward radial heat flux. Neglecting thermal and pressure diffusion

$$\rho_v v_v = -\rho D\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho_v}{\rho}\right) \tag{9}$$

where D is the binary diffusion coefficient. The sum of the diffusive fluxes is zero, $\rho_v v_v + \rho_g v_g = 0$.

The first two of equations (8) can be integrated immediately to give

$$\dot{M} = 4\pi r^2\rho u = 4\pi r^2\rho_v(u+v_v) = \text{constant} \tag{10}$$

where $\dot{M}$ is the total mass flow rate of vapour from the droplet. (The subscript v is disposable because the inert gas remains stationary.) Introducing pressures in favour of densities via the perfect gas equation, gives (without any approximation, see Appendix 2)

$$\dot{M}\left(1-\frac{p_v}{p}\right) = -4\pi r^2\left(\frac{pD}{R_v T}\right)\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{p_v}{p}\right). \tag{11}$$

(Despite the analysis of Wagner [19], it is easier to work in terms of partial pressures rather than densities as this avoids the introduction of a term proportional to the temperature gradient.)

Adopting an average total pressure and temperature and neglecting the variation of D with temperature, equation (11) may be integrated subject to the boundary conditions $p_v = p_{vi}$ at $r = r_i$ and $p_v \to p_{v\infty}$ as $r \to \infty$. The resulting vapour partial pressure distribution is

$$\frac{p_v - p_{v\infty}}{p_{vi} - p_{v\infty}} = \frac{1-\exp(-\dot{M}R_v T/4\pi r p D)}{1-\exp(-\dot{M}R_v T/4\pi r_i p D)} \tag{12}$$

and the total vapour mass flow rate is

$$\dot{M} = 4\pi r_i\left(\frac{pD}{R_v T}\right)\ln\left(\frac{1-p_{v\infty}/p}{1-p_{vi}/p}\right). \tag{13}$$

For small departures from equilibrium, equation (12) reduces to

$$\frac{p_v - p_{v\infty}}{p_{vi} - p_{v\infty}} \approx \frac{r_i}{r} \tag{14}$$

and equation (13) to

$$\begin{aligned}\dot{M} &\approx \frac{4\pi r_i D}{R_v T(1 - p_{v\infty}/p)}(p_{vi} - p_{v\infty}) \\ &= \frac{4\pi r_i D}{R_v T(p_{g\infty}/p)}(p_{vi} - p_{v\infty}).\end{aligned} \tag{15}$$

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

$$\frac{p_\infty - p_i}{p_\infty} = \frac{u_i^2}{2RT_{av}} \tag{16}$$

where R is the specific gas constant for the mixture and T_{av} is a suitably defined average temperature. Restricting the analysis to condensation or evaporation at low Mach numbers ($u_i/\sqrt{(2RT_i)} \ll 1$) justifies the assumption of constant total pressure everywhere.

The conservation of energy can also be integrated immediately to give,

$$\dot{E} = \dot{M}\left(h + \frac{u^2}{2}\right) + 4\pi r^2 q = \text{constant} \tag{17}$$

where $\dot{E}$ is the total energy flow rate from the droplet. Neglecting diffusion thermal, the heat flux q is given by

$$q = -k\frac{dT}{dr} + (h_v - h_g)\rho_v v_v \tag{18}$$

where k is the thermal conductivity of the vapour–gas mixture (assumed constant) and h_v and h_g are the partial specific enthalpies of the vapour and inert gas, respectively. The mixture specific enthalpy is given by

$$h = \left(\frac{\rho_v}{\rho}\right)h_v + \left(1 - \frac{\rho_v}{\rho}\right)h_g. \tag{19}$$

Noting that $4\pi r^2 \rho_v v_v = (1 - \rho_v/\rho)\dot{M}$ and substituting (18) and (19) into (17) gives

$$\dot{E} = \dot{M}\left(h_v + \frac{u^2}{2}\right) - 4\pi r^2 k\frac{dT}{dr} = \text{constant} \tag{20}$$

which expresses the fact that the inert gas is stationary and the enthalpy flux is carried by the vapour alone. Neglecting the bulk kinetic energy flux

$$\dot{E} = \dot{M}c_{pv}T - 4\pi r^2 k\frac{dT}{dr} = \text{constant} \tag{21}$$

where c_{pv} is the isobaric specific heat capacity of the vapour.

Equation (21) can be integrated subject to the boundary conditions $T = T_i$ at $r = r_i$ and $T \rightarrow T_\infty$ as $r \rightarrow \infty$. The solution for the temperature distribution is

$$\frac{T - T_\infty}{T_i - T_\infty} = \frac{1 - \exp(-\dot{M}c_{pv}/4\pi rk)}{1 - \exp(-\dot{M}c_{pv}/4\pi r_i k)}. \tag{22}$$

For small departures from equilibrium, equation (22) reduces to

$$\frac{T - T_\infty}{T_i - T_\infty} \approx \frac{r_i}{r}. \tag{23}$$

The total energy flow rate is then

$$\dot{E} = \dot{M}c_{pv}T_i + \dot{Q}_{ci} = \dot{M}c_{pv}T_\infty + \dot{Q}_{c\infty} \tag{24}$$

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

$$\begin{aligned}\dot{Q}_c &= -4\pi r^2 k\frac{dT}{dr} \\ &= 4\pi r_i k(T_i - T_\infty) - \dot{M}c_{pv}(T - T_\infty).\end{aligned} \tag{25}$$

In summary, the mass flow rate of vapour from the droplet is given by equation (15) and the total energy flow rate by equation (24) with $\dot{Q}_c$ defined by equation (25).

THE MOLECULAR VELOCITY DISTRIBUTION FUNCTION

In the region of continuum flow the vapour is in a non-equilibrium state and the molecular velocity distribution is not well approximated by a Maxwellian distribution function. As discussed in ref. [3], a much better approximation (and one that is compatible with the Navier–Stokes equations) is the Grad distribution function [20].

The basic Grad distribution for a single-component gas can be extended to represent a binary mixture of inter-diffusing perfect gases, see for example ref. [17]. Neglecting viscous normal stresses and assuming spherical symmetry, the velocity distribution function for *vapour* molecules in the continuum region $r > r_i$ is postulated to be

$$\begin{aligned}f_v = \frac{\rho_v}{(2\pi R_v T)^{3/2}}&\left\{1 - \frac{q_v(\xi_{vr} - u)}{p_v R_v T}\right. \\ &\times\left[1 - \frac{(\xi_{vr} - u)^2 + \xi_{v\theta}^2 + \xi_{v\phi}^2}{5R_v T}\right] \\ &\left. + \frac{v_v(\xi_{vr} - u)}{R_v T}\left[\frac{7}{2} - \frac{(\xi_{vr} - u)^2 + \xi_{v\theta}^2 + \xi_{v\phi}^2}{2R_v T}\right]\right\} \\ &\times\exp\left\{-\left[\frac{(\xi_{vr} - u)^2 + \xi_{v\theta}^2 + \xi_{v\phi}^2}{2R_v T}\right]\right\}\end{aligned} \tag{26}$$

where $(\xi_{vr}, \xi_{v\theta}, \xi_{v\phi})$ are the molecular velocity components in spherical polar coordinates, ρ_v is the local vapour density, T is the temperature, q_v is the contribution to the radial heat flux carried by the vapour molecules, v_v is the diffusive velocity of the vapour and u is the bulk velocity of the mixture. The corresponding velocity distribution function for the inert gas molecules is identical to equation (26) with subscript v replaced by subscript g.

Equation (26) should be a good representation of the real molecular velocity distribution in the continuum region and, in particular, it is assumed to apply at $r = r_i$. It is further assumed that the distribution function for molecules arriving at the liquid surface ($\xi_{vr} < 0$, $\xi_{gr} < 0$) is unaltered from that at $r = r_i$. The justification for this assumption in the case of a pure vapour is discussed in ref. [3] and the considerations when an inert gas is present are similar.

The velocity distribution of vapour molecules emitted from the liquid surface by pure evaporation is assumed to be a half-Maxwellian characterized by the droplet temperature T_d. Vapour and inert gas molecules which reflect from the surface are also assumed to emerge with a similar velocity distribution. In other words, diffuse reflection with perfect thermal accommodation for both species is assumed. (The analysis can, of course, be performed with thermal accommodation coefficients other than unity but this introduces the added complication of extra unknown parameters for which no experimental data exist. The *mass* accommodation (or condensation) coefficient for the vapour is retained, however, in order to provide a certain degree of flexibility in the final equations.) The velocity distributions of vapour and inert gas molecules *at the liquid–vapour interface* are thus specified as follows:

(i) For the vapour for ($0 < \xi_{vr} < \infty$)

$$f_{v+} = \frac{\rho_s}{(2\pi R_v T_d)^{3/2}} \exp\left\{-\left[\frac{\xi_{vr}^2+\xi_{v\theta}^2+\xi_{v\phi}^2}{2R_v T_d}\right]\right\}. \tag{27}$$

(ii) For the vapour for ($-\infty < \xi_{vr} < 0$)

$$\begin{aligned} f_{v-} = \frac{\rho_{vi}}{(2\pi R_v T_i)^{3/2}} & \left\{1 - \frac{q_{vi}(\xi_{vr}-u_i)}{p_{vi} R_v T_i}\right. \\ & \times \left[1 - \frac{(\xi_{vr}-u_i)^2+\xi_{v\theta}^2+\xi_{v\phi}^2}{5R_v T_i}\right] \\ & \left. + \frac{v_{vi}(\xi_{vr}-u_i)}{R_v T_i}\left[\frac{7}{2} - \frac{(\xi_{vr}-u_i)^2+\xi_{v\theta}^2+\xi_{v\phi}^2}{2R_v T_i}\right]\right\} \\ & \times \exp\left\{-\left[\frac{(\xi_{vr}-u_i)^2+\xi_{v\theta}^2+\xi_{v\phi}^2}{2R_v T_i}\right]\right\} \end{aligned} \tag{28}$$

where $\rho_{vi} = p_s/R_v T_d$ and subscript i refers to properties at the *Knudsen–continuum interface*.

(iii) For the inert gas for ($0 < \xi_{gr} < \infty$)

$$f_{g+} = \frac{\rho_{gs}}{(2\pi R_g T_d)^{3/2}} \exp\left\{-\left[\frac{\xi_{gr}^2+\xi_{g\theta}^2+\xi_{g\phi}^2}{2R_g T_d}\right]\right\}. \tag{29}$$

(iv) For the inert gas for ($-\infty < \xi_{gr} < 0$)

$$\begin{aligned} f_{g-} = \frac{\rho_{gi}}{(2\pi R_g T_i)^{3/2}} & \left\{1 - \frac{q_{gi}(\xi_{gr}-u_i)}{p_{gi} R_g T_i}\right. \\ & \times \left[1 - \frac{(\xi_{gr}-u_i)^2+\xi_{g\theta}^2+\xi_{g\phi}^2}{5R_g T_i}\right] \\ & \left. + \frac{v_{gi}(\xi_{gr}-u_i)}{R_v T_i}\left[\frac{7}{2} - \frac{(\xi_{gr}-u_i)^2+\xi_{g\theta}^2+\xi_{g\phi}^2}{2R_g T_i}\right]\right\} \\ & \times \exp\left\{-\left[\frac{(\xi_{gr}-u_i)^2+\xi_{g\theta}^2+\xi_{g\phi}^2}{2R_g T_i}\right]\right\}. \end{aligned} \tag{30}$$

In equation (29), ρ_{gs} is a density compatible with the boundary condition that the reflected mass flux of inert gas must equal the incident mass flux calculated from equation (30).

KNUDSEN LAYER ANALYSIS

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

$$\dot{M} = q_e \dot{M}_{v+} - (1-q_c)\dot{M}_{v-} + \dot{M}_{v-} = q_e \dot{M}_{v+} + q_c \dot{M}_{v-} \tag{31}$$

where

$$\begin{aligned} \dot{M}_{v+} &= 4\pi r_d^2 \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \xi_{vr} f_{v+} \, d\xi_{vr} \, d\xi_{v\theta} \, d\xi_{v\phi} \\ &= 4\pi r_d^2 \frac{p_s}{\sqrt{(2\pi R_v T_d)}} \end{aligned} \tag{32}$$

and

$$\begin{aligned} \dot{M}_{v-} &= 4\pi r_d^2 \int_{-\infty}^0 \int_{-\infty}^\infty \int_{-\infty}^\infty \xi_{vr} f_{v-} \, d\xi_{vr} \, d\xi_{v\theta} \, d\xi_{v\phi} \\ &\approx -4\pi r_d^2 \frac{p_{vi}}{\sqrt{(2\pi R_v T_i)}}\left[1 - \frac{(u_i+v_{vi})\sqrt{\pi}}{\sqrt{(2R_v T_i)}}\right] \\ &\approx -4\pi r_d^2 \frac{p_{vi}}{\sqrt{(2\pi R_v T_i)}} + \left(\frac{r_d^2}{2r_i^2}\right)\dot{M} \end{aligned} \tag{33}$$

where the final form has been obtained with the help of equation (10) for $\dot{M}$. The triple integrals can be evaluated by substituting the relevant expression for the velocity distribution (equations (27)–(30)) and using tables of standard integrals. It should be noted that $\dot{M}_{v+}$, $\dot{M}_{v-}$ and all similarly subscripted variables are considered positive when the flux is directed away from the droplet.

For future reference, an expression is also derived for $\dot{M}_{g-}$, the mass flux of inert gas molecules incident on the droplet. This is identical to equation (33) with subscript v replaced by subscript g. The inert gas is stationary, however, the inward convective velocity just balancing the outward diffusive velocity, and hence $u_i + v_{gi} = 0$. Thus

$$\dot{M}_{g-} = -4\pi r_d^2 \frac{p_{gi}}{\sqrt{(2\pi R_g T_i)}}. \tag{34}$$

Substituting equations (32) and (33) into equation (31) gives the required equation for $\dot{M}$

$$\dot{M}\left(1-\frac{q_c r_d^2}{2r_i^2}\right) = 4\pi r_d^2\left[\frac{q_e p_s}{\sqrt{(2\pi R_v T_d)}} - \frac{q_c p_{vi}}{\sqrt{(2\pi R_v T_i)}}\right]. \tag{35}$$

Linearizing the right hand side of the equation

$$\dot{M}\left(1-\frac{q_c r_d^2}{2r_i^2}\right) = 4\pi r_d^2 \frac{p_{v\infty}}{\sqrt{(2\pi R_v T_\infty)}} \times \left\{q_e\left[1+\frac{p_s-p_{v\infty}}{p_{v\infty}}-\frac{T_d-T_\infty}{2T_\infty}\right] - q_c\left[1+\frac{p_{vi}-p_{v\infty}}{p_{v\infty}}-\frac{T_i-T_\infty}{2T_\infty}\right]\right\}. \tag{36}$$

Equation (35) is almost identical to equation (25) in ref. [3] (derived for the case of a pure vapour), the only difference being the replacement of the total pressure p_i by the partial pressure p_{vi} in the final term on the right-hand side. When the inert gas concentration is very low, $p_{vi} \approx p_i$ and the Knudsen layer provides the resistance to mass transfer. As the concentration of inert gas is increased, p_{vi} falls below p_i due to the increased resistance due to diffusion in the continuum region.

The comments in ref. [3] following equation (25) of that paper concerning the relationship of the theory for a pure vapour with Schrage's analysis [7] are equally applicable here. In the isothermal continuum limit ($r_i \to r_d$), Schrage's correction appears unmodified as the bracketed term on the left-hand side of equation (35). In the free molecule limit ($r_i \to \infty$), the original Hertz–Knudsen equation is recovered. The Schrage effect therefore decreases in importance with increasing Knudsen number, a conclusion which agrees with qualitative physical intuition.

An expression is now derived 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. It is also assumed that molecules reflected from the droplet surface emerge with a half-Maxwellian distribution characterized by the liquid surface temperature (i.e. complete thermal accommodation). There are contributions to the energy flow rate from both the vapour and the inert gas and hence

$$\begin{aligned}\dot{E} = {} & \{[q_e\dot{M}_{v+}-(1-q_e)\dot{M}_{v-}](c_{pv}-R_v/2)T_d\} \\ & +\{\dot{E}_{v-}+\dot{M}_{v-}(c_{pv}-5R_v/2)T_i\} \\ & -\{\dot{M}_{g-}(c_{pg}-R_g/2)T_d\} \\ & +\{\dot{E}_{g-}+\dot{M}_{g-}(c_{pg}-5R_g/2)T_i\}.\end{aligned} \tag{37}$$

The first and second terms in braces represent the energy flow rates carried by the vapour molecules. The third and fourth terms represent the energy flow rates for the inert gas molecules. $\dot{E}_{v-}$ and $\dot{E}_{g-}$ are the *translational* kinetic energy flow rates of vapour and inert gas molecules incident on the droplet. $\dot{E}_{v-}$ is given by

$$\begin{aligned}\dot{E}_{v-} & = 4\pi r_d^2 \int_{-\infty}^{0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \tfrac{1}{2}\xi_{vr}(\xi_{vr}^2+\xi_{v\theta}^2+\xi_{v\phi}^2) \\ & \quad \times f_{v-}\,\mathrm{d}\xi_{vr}\,\mathrm{d}\xi_{v\theta}\,\mathrm{d}\xi_{v\phi} \\ & \approx -4\pi r_d^2\left[\frac{p_{vi}(2R_v T_i)}{\sqrt{(2\pi R_v T_i)}} - \frac{\rho_{vi}u_i}{2}\left(\frac{5R_v T_i}{2}\right) - \frac{q_{vi}}{2}\right].\end{aligned} \tag{38}$$

q_{vi} is the heat flux carried by the vapour molecules and can be written

$$q_{vi} = q_{cvi} + \rho_{vi}v_{vi}\left(\frac{5R_v T_i}{2}\right) \tag{39}$$

where q_{cvi} is the contribution by the vapour molecules to the conduction heat flux at $r = r_i$. Substituting equation (39) into (38) defining $\dot{Q}_{cvi} = 4\pi r_i^2 q_{cvi}$

$$\dot{E}_v = -4\pi r_d^2 \frac{p_{vi}(2R_v T_i)}{\sqrt{(2\pi R_v T_i)}} + \frac{r_d^2}{2r_i^2}\left[\left(\frac{5R_v T_i}{2}\right)\dot{M} + \dot{Q}_{cvi}\right]. \tag{40}$$

$\dot{E}_{g-}$ can be evaluated in a similar fashion. Noting again that $u_i + v_{gi} = 0$, results in

$$\dot{E}_{g-} = -4\pi r_d^2 \frac{p_{gi}(2R_g T_i)}{\sqrt{(2\pi R_g T_i)}} + \frac{r_d^2}{2r_i^2}\dot{Q}_{cgi} \tag{41}$$

where $\dot{Q}_{cgi}$ is the contribution from the inert gas to the conduction heat transfer rate.

Substituting equations (32)–(34), (40) and (41) into equation (37) and rearranging it gives

$$\dot{E} = 4\pi r_d^2\left\{\frac{p_{vi}(c_{pv}-R_v/2)}{\sqrt{(2\pi R_v T_i)}} + \frac{p_{gi}(c_{pg}-R_g/2)}{\sqrt{(2\pi R_g T_i)}}\right\}(T_d-T_i) + \frac{r_d^2}{2r_i^2}\dot{Q}_{ci} + \dot{M}c_{pv}T_i - \frac{\dot{M}R_v T_d}{2}\left[1-\frac{r_d^2}{2r_i^2}\right] \tag{42}$$

where $\dot{Q}_{ci} = \dot{Q}_{cvi} + \dot{Q}_{cgi}$ is the total conduction heat transfer rate at $r = r_i$. (The final term of equation (42) has been simplified by the assumption, $c_{pv}(T_d-T_i)-R_v T_d/2 \approx -R_v T_d/2$ corresponding to $|(T_d-T_\infty)/T_\infty| \ll 1$.)

In summary, the mass flow rate of vapour from the droplet is given by equation (36) and the total energy flow rate by equation (42). An equation for momentum conservation is not required because of the assumption (introduced in the previous section) that the distribution function for molecules incident on the liquid surface is unaltered from that at $r = r_i$. (Intuitively, it would seem that the full set of conservation equations should result in a more accurate solution but in practice the resulting equations are far too cumbersome for analytical development.)

THE KNUDSEN LAYER TEMPERATURE JUMP

The interface temperature T_i can be obtained by equating the continuum and Knudsen layer expressions for $\dot{E}$. Combining equations (24), (25) and (42) with equation (6) gives

$$\left[1-\frac{r_d^2}{2r_i^2}\right]J_{qc} = \left[1-\frac{r_d^2}{2r_i^2}\right]\frac{k}{r_d}\frac{r_i}{r_d}\frac{(T_i-T_\infty)}{R_vT_\infty}$$

$$= \left\{\left(\frac{\gamma_v+1}{2\gamma_v}\right)\frac{p_{vi}c_{pv}}{\sqrt{(2\pi R_vT_i)}} + \left(\frac{\gamma_g+1}{2\gamma_g}\right)\frac{p_{gi}c_{pg}}{\sqrt{(2\pi R_gT_i)}}\right\}\frac{(T_d-T_i)}{R_vT_\infty}$$

$$-\left[1-\frac{r_d^2}{2r_i^2}\right]\frac{J_m}{2} \qquad (43)$$

where γ_v and γ_g are the ratios of the specific heat capacities for the vapour and inert gas. Equation (43) can be simplified by *defining* a quantity γ by the identity

$$\left(\frac{\gamma+1}{\gamma-1}\right)\frac{pR}{\sqrt{(2\pi RT_i)}} = \left\{\left(\frac{\gamma_v+1}{\gamma_v-1}\right)\frac{p_{vi}R_v}{\sqrt{(2\pi R_vT_i)}} + \left(\frac{\gamma_g+1}{\gamma_g-1}\right)\frac{p_{gi}R_g}{\sqrt{(2\pi R_gT_i)}}\right\} \qquad (44)$$

where R is the specific gas constant of the mixture and $p = p_i = p_{vi}+p_{gi} = p_{v\infty}+p_{g\infty}$ is the mixture total pressure. γ is a 'mass flux' weighted average of γ_v and γ_g and is not the same as the ratio of specific heat capacities for the mixture. When calculating γ it is normally acceptable to replace p_{vi} and p_{gi} in equation (44) by $p_{v\infty}$ and $p_{g\infty}$, both these quantities being known at the outset. A mean free path λ is also *defined* by the kinetic theory formula

$$\lambda = \frac{\eta}{2}\frac{\sqrt{(2\pi RT)}}{p} \qquad (45)$$

where η is the viscosity of the *vapour–gas mixture.* Finally, a Prandtl number is *defined* by

$$Pr = \frac{\gamma R\eta}{(\gamma-1)k}. \qquad (46)$$

Substituting equations (44)–(46) into equation (43) and rearranging, results in an expression for the temperature difference across the Knudsen layer (T_d-T_i)

$$\left\{\frac{r_d/r_i}{(1-r_d^2/2r_i^2)}+\left(\frac{8\gamma}{\gamma+1}\right)\frac{Kn}{Pr}\right\}\left(\frac{T_d-T_i}{T_\infty}\right)$$

$$= \left(\frac{8\gamma}{\gamma+1}\right)\left(\frac{Kn}{Pr}\right)\left(\frac{T_d-T_\infty}{T_\infty}\right)$$

$$+\left(\frac{r_d}{r_i}\right)\left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{R_v}{R}\right)\frac{\sqrt{(2\pi RT_i)}}{p}J_m \qquad (47)$$

where Kn is a Knudsen number *defined* by

$$Kn = \frac{\lambda}{2r_d}. \qquad (48)$$

No new physical principles have been introduced by rewriting equation (43) as equation (47). (In particular, the exact location of the Knudsen–continuum interface at $r = r_i$ has not yet been specified.) When calculating the value of Pr by equation (46), the viscosity and thermal conductivity of the mixture can be obtained by any suitable procedure for computing the transport properties of perfect gas mixtures. (Note that, in the limiting cases of pure vapour and pure inert gas, the values of R, γ, Pr and λ all become equal to the conventional, single component, property values.)

Equation (47) expresses the temperature difference across the Knudsen layer (T_d-T_i) in terms of the overall temperature difference (T_d-T_∞) and the mass evaporation flux J_m. In particular, it is evident that, in the continuum limit ($Kn \to 0$, $r_i \to r_d$) as the thickness of the Knudsen layer tends to zero, *there remains a temperature jump across the layer which is proportional to the mass flux.* The magnitude of the temperature jump in the limit $Kn \to 0$ is

$$\frac{T_d-T_i}{T_\infty} \to \left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{R_v}{R}\right)\frac{\sqrt{(2\pi RT_i)}}{2p}J_m$$

$$\approx \sqrt{\pi}\left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{p_{v\infty}}{p}\right)\left(\frac{R_v}{R}\right)^{1/2}\frac{(u+v_v)_i}{\sqrt{(2R_vT_\infty)}} \qquad (49)$$

where the second form is obtained by substituting equations (6) and (10).

Most simple theories of droplet growth under continuum conditions start from the premise $T_d = T_i$ and hence cannot predict the Knudsen layer temperature jump. Its existence has been established, however, by direct solution of Boltzmann-like equations, although currently such solutions are restricted to monatomic vapours in near-continuum regimes. A solution of the BGK equation for a mixture of a condensing vapour and an inert gas in the vicinity of a liquid droplet is given by Onishi [16]. For monatomic mixtures, his expression for the Knudsen layer temperature jump in the continuum limit (equation (4.24) of ref. [16]) is

$$\frac{T_d-T_i}{T_\infty} = -d_4^M\frac{(u+v_v)_i}{\sqrt{(2R_vT_\infty)}} \qquad (50)$$

where d_4^M is the *temperature jump coefficient* and depends on the molar masses (m_v and m_g) and relative concentration of the vapour and inert gas components. Some typical values were calculated by Onishi and are reproduced in Table 1. The present analysis gives a simple expression for d_4^M which is valid also for polyatomic vapours and inert gases. From equations (49) and (50)

$$d_4^M = -\sqrt{\pi}\left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{p_{v\infty}}{p}\right)\left(\frac{R_v}{R}\right)^{1/2}. \qquad (51)$$

Values of d_4^M computed from equation (51) with

Table 1. Predictions of the Knudsen layer temperature and vapour pressure jump coefficients in the continuum limit

$\frac{m_g}{m_v}$	$\frac{p_{g\infty}}{p_{v\infty}}$	$-d_4^M$ (Onishi)	$-d_4^M$ equation (51)	$-C_4^A$ (Onishi)	$-C_4^A$ equation (56)
	0.1	0.380	0.388	2.121	1.967
0.5	1.0	0.162	0.183	2.082	1.864
	10.0	0.024	0.029	2.053	1.787
	0.1	0.406	0.403	2.124	1.974
1.0	1.0	0.223	0.221	2.089	1.883
	10.0	0.041	0.040	2.053	1.793
	0.1	0.422	0.414	2.126	1.979
2.0	1.0	0.284	0.260	2.097	1.902
	10.0	0.067	0.055	2.058	1.800
Pure vapour		0.447	0.443	2.132	1.994

$\gamma_v = \gamma_g = 5/3$ are compared with those of Onishi in Table 1. The agreement is excellent and gives great confidence that the fundamental physical processes of condensation and evaporation are accurately modelled by the present theoretical treatment.

In the absence of the inert gas component, equations (47) and (49) become identical to equations (31) and (33) derived in ref. [3] for the case of a pure vapour. In this situation, $p_{vi} = p$ and the Knudsen layer temperature jump takes its maximum value for a given condensation or evaporation rate. An increase in concentration of inert gas corresponds to $p_{vi} < p$ and, according to equation (49), the temperature jump decreases.

Equation (49) shows that the Knudsen layer temperature jump in the continuum limit is directly proportional to the dimensionless vapour velocity at the liquid surface and also to the mole fraction of vapour in the mixture $(p_{v\infty}/p)$. The latter conclusion is not obvious from the much more complex analysis of Onishi [16]. The sign of the temperature jump has been discussed in ref. [3] and similar conclusions apply when an inert gas is present. In particular, the *reversed temperature gradient phenomenon* can manifest itself within the Knudsen layer. Thus, in quasi-steady droplet *condensation* when heat is being transferred *away* from the droplet, the temperature may *increase* through the Knudsen layer before *decreasing* (in accordance with Fourier's law) in the outer continuum region. This behaviour is shown qualitatively in Fig. 3 and graphically illustrates how strongly non-equilibrium is the molecular velocity distribution function in the Knudsen layer.

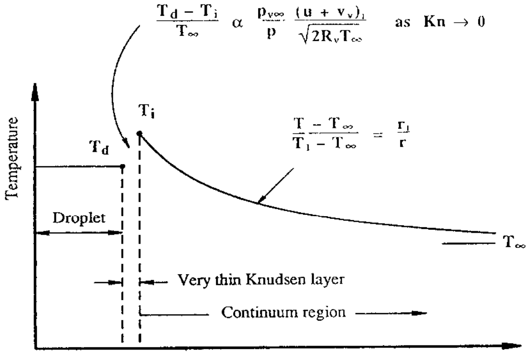

FIG. 3. Schematic diagram of the temperature distribution near a condensing droplet in the continuum limit.

THE KNUDSEN LAYER VAPOUR PRESSURE JUMP

When net phase change is occurring, the vapour partial pressure at the Knudsen–continuum interface p_{vi} differs from the (curvature corrected) droplet saturation pressure p_s. Although this is not surprising for the case of pure vapour (momentum considerations requiring $p_{vi} = p_{v\infty} \neq p_s$), most simple theories of droplet growth under continuum conditions in the presence of an inert gas *assume* the boundary condition at the droplet surface to be $p_{vi} = p_s$. The difference $(p_s - p_{vi})$ has been referred to as the *pressure jump across the Knudsen layer* but the terminology is misleading as a real pressure imbalance would violate the conservation of momentum.

An expression for p_{vi} can be obtained by equating the continuum and Knudsen layer expressions for $\dot{M}$, equations (15) and (36). Equation (15) is manipulated to a more convenient form by introducing a Schmidt number *defined* by

$$Sc = \frac{\eta}{\rho D} \tag{52}$$

where η and ρ are the dynamic viscosity and density of the *vapour–gas mixture*. Introducing the definitions of the mean free path and Knudsen numbers from equations (45) and (48), together with the definition of the mass flux J_m from equation (6)

$$\begin{aligned} &\left(1 - \frac{q_c r_d^2}{2r_i^2}\right) \frac{\sqrt{(2\pi R_v T_\infty)}}{p_{v\infty}} J_m \\ &\quad = \left(1 - \frac{q_c r_d^2}{2r_i^2}\right) \frac{r_i}{r_d} \frac{4Kn}{Sc} \left(\frac{R}{R_v}\right)^{1/2} \frac{p}{p_{g\infty}} \frac{(p_{vi} - p_{v\infty})}{p_{v\infty}} \\ &\quad = q_e \left[1 + \frac{p_s - p_{v\infty}}{p_{v\infty}} - \frac{T_d - T_\infty}{2T_\infty}\right] \\ &\qquad - q_c \left[1 + \frac{p_{vi} - p_{v\infty}}{p_{v\infty}} - \frac{T_i - T_\infty}{2T_\infty}\right]. \end{aligned} \tag{53}$$

(p_{vi} (unlike T_i) depends on the condensation and evaporation coefficients q_c and q_e.)

Investigation of the Knudsen layer vapour pressure jump as the layer shrinks to zero thickness requires care in proceeding to the limit. An expression for $(p_s - p_{vi})$ in terms of the mass flux J_m can be obtained from the second of equations (53). For the purposes of illustration it is assumed that $q_c = q_e = q$. Setting $r_i = r_d$ and introducing equation (49) for $(T_d - T_i)$ gives

$$\frac{p_s - p_{vi}}{p_{v\infty}} \to \left\{\frac{2-q}{2q} + \frac{p_{v\infty}}{4p}\left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{R_v}{R}\right)^{1/2}\right\}\frac{\sqrt{(2\pi R_v T_\infty)}}{p_{v\infty}} J_m$$

$$= 2\sqrt{\pi}\left\{\frac{2-q}{2q} + \frac{p_{v\infty}}{4p}\left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{R_v}{R}\right)^{1/2}\right\}\frac{(u+v_v)_i}{\sqrt{(2R_v T_\infty)}}. \tag{54}$$

An expression for the vapour pressure jump based on an analytical solution of the BGK equation for a monatomic vapour and $q = 1$ is given by Onishi [16] in the form

$$\frac{p_s - p_{vi}}{p_{v\infty}} = -C_4^A \frac{(u+v_v)_i}{\sqrt{(2R_v T_\infty)}} \tag{55}$$

where C_4^A is the *vapour pressure jump coefficient* and depends on the molar masses and relative concentration of the vapour and inert gas components. From equations (54) and (55), the present analysis gives,

$$C_4^A = -2\sqrt{\pi}\left\{\frac{2-q}{2q} + \frac{p_{v\infty}}{4p}\left(\frac{\gamma-1}{\gamma+1}\right)\left(\frac{R_v}{R}\right)^{1/2}\right\}. \tag{56}$$

Values computed by Onishi [16] are compared with the predictions of equation (56) for $\gamma_v = \gamma_g = 5/3$ and $q = 1$ in Table 1. Agreement is within about 10% and it is evident that, with increase in inert gas concentration, similar trends are predicted by both analyses.

The behaviour of the Knudsen layer vapour pressure jump $(p_s - p_{vi})$ compared with the overall pressure difference $(p_s - p_{v\infty})$ in the continuum limit can be found by combining equations (53) with (49). Assuming $q_c = q_e = q$ and setting $r_i = r_d$ gives, after some manipulation

$$\frac{p_s - p_{vi}}{p_s - p_{v\infty}} = \frac{\chi}{1+\chi} \tag{57}$$

where

$$\chi = \frac{Kn}{Sc}\frac{p_{v\infty}}{p_{g\infty}}\left[\frac{\gamma-1}{\gamma+1} + \frac{2-q}{q}\frac{2p}{p_{v\infty}}\left(\frac{R}{R_v}\right)^{1/2}\right]. \tag{58}$$

In the limiting case of pure vapour, $p_{g\infty} = 0$, $\chi \to \infty$, and $p_{vi} = p_{v\infty}$ for any Knudsen number, however small. This is the kinetically controlled limit with zero diffusive resistance in the outer continuum layer. However, if the concentration of inert gas is non-zero ($p_{g\infty}/p \neq 0$), then $\chi \to 0$ as $Kn \to 0$ and hence $p_{vi} \to p_s$ as $Kn \to 0$. This represents the diffusion controlled limit with negligible kinetic resistance across the Knudsen layer. Evidently, for any finite concentration of inert gas, the equilibrium boundary condition $p_{vi} = p_s$ is justifiable *providing the Knudsen number is sufficiently small.* (Note that this conclusion is not in conflict with equation (54) if $J_m = O(Kn)$.) The transition from the kinetic to the diffusion controlled limit occurs in the range $\chi = O(1)$ which, according to equation (58), corresponds to $p_{g\infty}/p_{v\infty} = O(Kn)$.

Figure 4 shows the variation of $(p_s - p_{vi})/(p_s - p_{v\infty})$ with $p_{g\infty}/p_{v\infty}$ computed from equation (58) for Knudsen numbers of 0.1, 0.01 and 0.001 (representing the approach to the continuum limit). The calculations were performed with the parameter values $Sc = 1$, $q = 1$, $\gamma = 5/3$ and $R = R_v$. Evidently, for small Knudsen numbers, only a very low concentration of inert gas is required to effect the transition from kinetic to diffusion control.

GENERALIZED EQUATIONS FOR THE HEAT AND MASS FLUXES

Equations (43) and (53) describe the heat and mass fluxes J_{qc} and J_m in terms of the temperature differences $(T_d - T_i)$ and $(T_i - T_\infty)$ and the vapour pressure

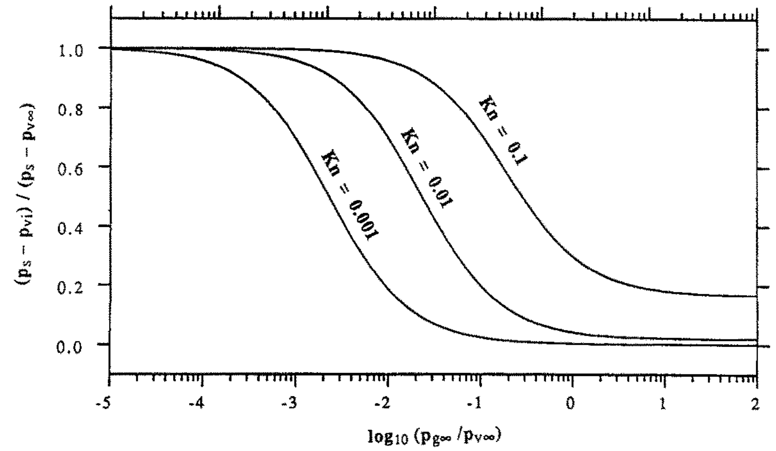

FIG. 4. The Knudsen layer pressure jump computed from equation (57).

differences $(p_{\mathrm{s}}-p_{\mathrm{vi}})$ and $(p_{\mathrm{vi}}-p_{\mathrm{v}\infty})$. The equations are reproduced here in slightly modified forms to highlight their similarities. (In particular, equation (43) is combined with equations (44)–(46) and in equation (53) it is assumed that $q_{\mathrm{e}} = q_{\mathrm{c}} = q$.) Thus

$$\left[\frac{1}{q}-\frac{r_{\mathrm{d}}^2}{2r_{\mathrm{im}}^2}\right]\frac{\sqrt{(2\pi R_{\mathrm{v}}T_\infty)}}{p_{\mathrm{v}\infty}}J_{\mathrm{m}}$$

$$=\left[\frac{1}{q}-\frac{r_{\mathrm{d}}^2}{2r_{\mathrm{im}}^2}\right]\frac{r_{\mathrm{im}}}{r_{\mathrm{d}}}\left(\frac{R}{R_{\mathrm{v}}}\right)^{1/2}\frac{4Kn}{Sc}\frac{p}{p_{\mathrm{g}\infty}}\frac{(p_{\mathrm{vi}}-p_{\mathrm{v}\infty})}{p_{\mathrm{v}\infty}}$$

$$=-\frac{(T_{\mathrm{d}}-T_{\mathrm{i}})}{2T_\infty}+\frac{(p_{\mathrm{s}}-p_{\mathrm{vi}})}{p_{\mathrm{v}\infty}}$$

$$\left[1-\frac{r_{\mathrm{d}}^2}{2r_{\mathrm{iq}}^2}\right]\frac{\sqrt{(2\pi RT_\infty)}}{p}J_{\mathrm{qc}}$$

$$=\left[1-\frac{r_{\mathrm{d}}^2}{2r_{\mathrm{iq}}^2}\right]\frac{r_{\mathrm{iq}}}{r_{\mathrm{d}}}\frac{\gamma}{\gamma-1}\frac{R}{R_{\mathrm{v}}}\frac{4Kn}{Pr}\frac{(T_{\mathrm{i}}-T_\infty)}{T_\infty}$$

$$=\frac{\gamma+1}{\gamma-1}\frac{R}{R_{\mathrm{v}}}\frac{(T_{\mathrm{d}}-T_{\mathrm{i}})}{2T_\infty}-\left[1-\frac{r_{\mathrm{d}}^2}{2r_{\mathrm{iq}}^2}\right]\frac{\sqrt{(2\pi RT_\infty)}}{p}\frac{J_{\mathrm{m}}}{2}. \tag{59}$$

As yet, the positions of the Knudsen–continuum interfaces have not been specified. The subscripts m and q have therefore been added to r_{i} in order to stress the fact that the ratios $r_{\mathrm{i}}/r_{\mathrm{d}}$ in the heat and mass transfer equations may not be identical. In physical terms, this is an acknowledgement that the mean free paths for heat and mass transfer are likely to differ. The interface radii r_{im} and r_{iq} are given in terms of the two constants β_{m} and β_{q} *defined* by

$$\frac{r_{\mathrm{im}}}{r_{\mathrm{d}}} = 1+2\beta_{\mathrm{m}}Kn, \quad \frac{r_{\mathrm{iq}}}{r_{\mathrm{d}}} = 1+2\beta_{\mathrm{q}}Kn. \tag{60}$$

Simplification of equations (59) is facilitated by defining the following parameters:

$$A_1 = \frac{4}{Sc}\left(\frac{R}{R_{\mathrm{v}}}\right)^{1/2}, \quad A_2 = \frac{p_{\mathrm{v}\infty}}{p},$$

$$B_1 = \frac{8}{Pr}\frac{\gamma}{\gamma+1}, \quad B_2 = \frac{\gamma+1}{2(\gamma-1)}\left(\frac{R}{R_{\mathrm{v}}}\right)^{1/2},$$

$$F_1 = \left[\frac{1}{q}-\frac{r_{\mathrm{d}}^2}{2r_{\mathrm{im}}^2}\right], \quad F_2 = \frac{r_{\mathrm{d}}}{r_{\mathrm{im}}},$$

$$G_1 = \left[1-\frac{r_{\mathrm{d}}^2}{2r_{\mathrm{iq}}^2}\right], \quad G_2 = \frac{r_{\mathrm{d}}}{r_{\mathrm{iq}}}. \tag{61}$$

A_1, A_2, B_1 and B_2 are thermodynamic properties of the mixture (with γ, Pr and Sc defined by equations (44), (46) and (52), respectively). F_1, F_2, G_1 and G_2 are functions of β_{m}, β_{q} and Kn only and take the following limiting values:

$$Kn \to 0: \quad F_1 \,\&\, G_1 \to 0.5 \quad F_2 \,\&\, G_2 \to 1$$

$$Kn \to \infty: \quad F_1 \,\&\, G_1 \to 1 \quad F_2 \,\&\, G_2 \to 0.$$

Introducing the definitions (61), equations (59) take the form

$$A_{\mathrm{mm}}J_{\mathrm{m}}+A_{\mathrm{mq}}J_{\mathrm{qc}} = B_{\mathrm{m}}\frac{p}{\sqrt{(2\pi R_{\mathrm{v}}T_\infty)}}\frac{(p_{\mathrm{s}}-p_{\mathrm{v}\infty})}{p_{\mathrm{v}\infty}} \tag{62}$$

$$A_{\mathrm{qm}}J_{\mathrm{m}}+A_{\mathrm{qq}}J_{\mathrm{qc}} = B_{\mathrm{q}}\frac{p}{\sqrt{(2\pi R_{\mathrm{v}}T_\infty)}}\frac{(T_{\mathrm{d}}-T_\infty)}{T_\infty} \tag{63}$$

where

$$A_{\mathrm{mm}} = \left[F_2\frac{p_{\mathrm{g}\infty}}{p}+F_1A_1Kn+\frac{A_1A_2G_1Kn}{4B_2}\right]$$

$$A_{\mathrm{mq}} = \left[\frac{A_1A_2G_1Kn}{2B_2}\right]$$

$$A_{\mathrm{qm}} = \left[\frac{G_1B_1Kn}{2}\right]$$

$$A_{\mathrm{qq}} = G_2+G_1B_1Kn$$

$$B_{\mathrm{m}} = A_1A_2Kn$$

$$B_{\mathrm{q}} = B_1B_2Kn. \tag{64}$$

Equations (62) and (63) are multi-range equations for the mass and heat fluxes in terms of $(p_{\mathrm{s}}-p_{\mathrm{v}\infty})$ and $(T_{\mathrm{d}}-T_\infty)$. They are valid for all Knudsen numbers and all concentrations of inert gas including the pure vapour limit. (Indeed, setting $p_{\mathrm{g}\infty} = 0$, $R = R_{\mathrm{v}}$, $\gamma = \gamma_{\mathrm{v}}$ and $Pr = Pr_{\mathrm{v}}$ generates equations (39) and (46) of ref. [3], derived for the case of a pure vapour.)

Expressions for the phenomenological coefficients of equations (6) are easily obtained by simultaneous solution of equations (62) and (63). Thus

$$L_{\mathrm{mm}} = \frac{A_{\mathrm{qq}}B_{\mathrm{m}}}{\Delta}, \quad L_{\mathrm{mq}} = -\frac{A_{\mathrm{mq}}B_{\mathrm{q}}}{\Delta},$$

$$L_{\mathrm{qm}} = -\frac{A_{\mathrm{qm}}B_{\mathrm{m}}}{\Delta}, \quad L_{\mathrm{qq}} = \frac{A_{\mathrm{mm}}B_{\mathrm{q}}}{\Delta} \tag{65}$$

where $\Delta = (A_{\mathrm{mm}}A_{\mathrm{qq}}-A_{\mathrm{mq}}A_{\mathrm{qm}})$. Substitution of the relevant expressions from equation (64) confirms that the Onsager reciprocal requirement $(L_{\mathrm{mq}} = L_{\mathrm{qm}})$ is satisfied.

The parameters β_{m} and β_{q} can only be established by comparison with experimental measurements of droplet growth rates or by comparison with solutions of the Boltzmann equation which include a model for molecular collisions. However, numerical calculations of the phenomenological coefficients from equations (65) for a wide variety of mixture conditions show a negligible dependence of the coefficients on β_{q} within the range $0.5 < \beta_{\mathrm{q}} < 1.5$. The effect of β_{m} on L_{qq} and $L_{\mathrm{mq}} = L_{\mathrm{qm}}$ is likewise negligible. It is only in the effect on L_{mm} near the pure vapour limit for Knudsen numbers in the range $0.1 < Kn < 1.0$, where the choice of β_{m} is at all important. As shown in ref. [3], a value giving good agreement with the numerical calculations of Chernyak and Margilevskiy [11] for pure monatomic vapours in this region is $\beta_{\mathrm{m}} = 0.75$. It is therefore suggested that the parameter values

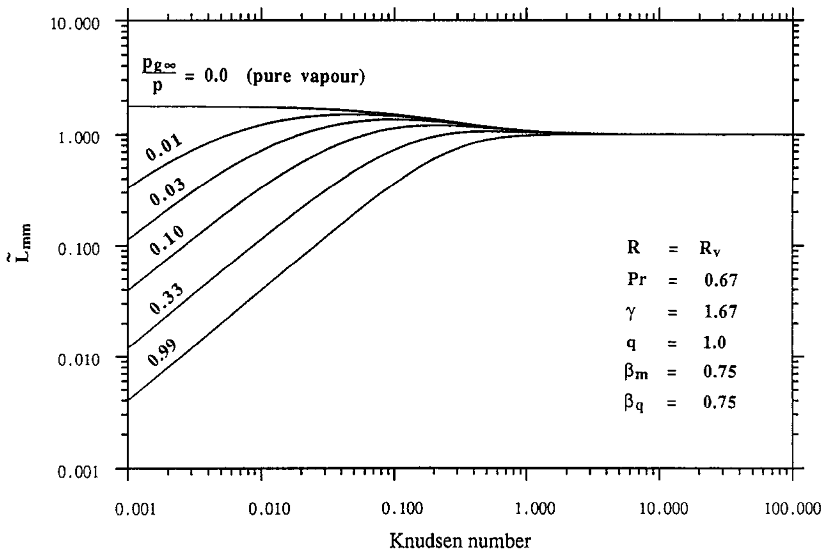

FIG. 5. Variation of $\tilde{L}_{mm}$ with Knudsen number and inert gas concentration.

$\beta_m = \beta_q = 0.75$ be adopted for practical calculations until further experimental or computational evidence is forthcoming.

Figures 5–7 are graphs of the phenomenological coefficients plotted as functions of the Knudsen number for a condensation coefficient of unity. Each coefficient is normalised with respect to its free molecule limiting value at very large Knudsen number. Thus

$$\tilde{L}_{mm} = \frac{L_{mm}}{L_{mm\infty}}, \quad \tilde{L}_{mq} = \tilde{L}_{qm} = \frac{L_{mq}}{L_{mq\infty}}, \quad \tilde{L}_{qq} = \frac{L_{qq}}{L_{qq\infty}} \tag{66}$$

where $L_{mm\infty}$, $L_{mq\infty}$ and $L_{qq\infty}$ are obtained from equation (65) as

$$L_{mm\infty} = A_2, \quad L_{mq\infty} = L_{qm\infty} = -\frac{A_2}{2},$$

$$L_{qq\infty} = B_2 + \frac{A_2}{4}. \tag{67}$$

When normalised in this way, the coefficients $\tilde{L}_{mq}$ and $\tilde{L}_{qq}$ are remarkably insensitive to variations in the inert gas concentration and the ratio of the molar masses of the diffusing species. Figures 6 and 7 are plotted for the parameter values notated in the diagrams but alternative values have little effect on the curves. In the free molecule limit $\tilde{L}_{mq}$ and $\tilde{L}_{qq}$ both tend to constant values and in the approach to the continuum limit both become directly proportional to the Knudsen number. The normalised coefficient $\tilde{L}_{mm}$

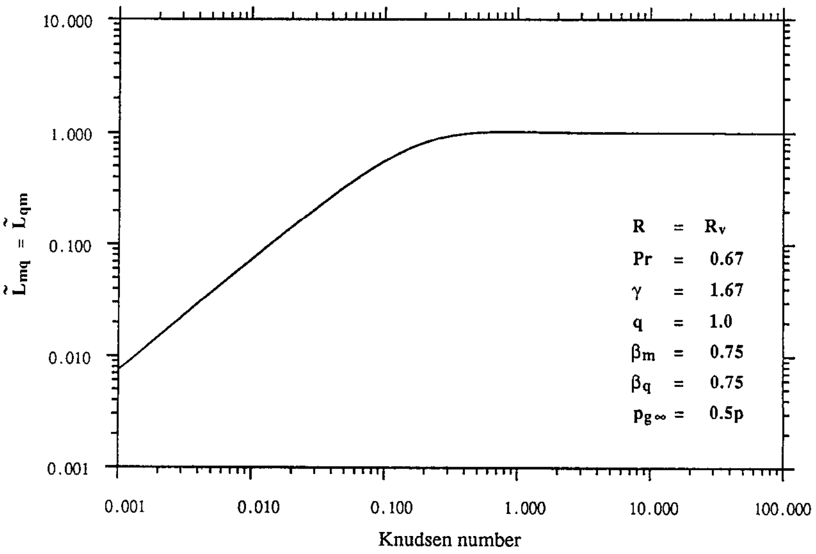

FIG. 6. Variation of $\tilde{L}_{mq} = \tilde{L}_{qm}$ with Knudsen number.

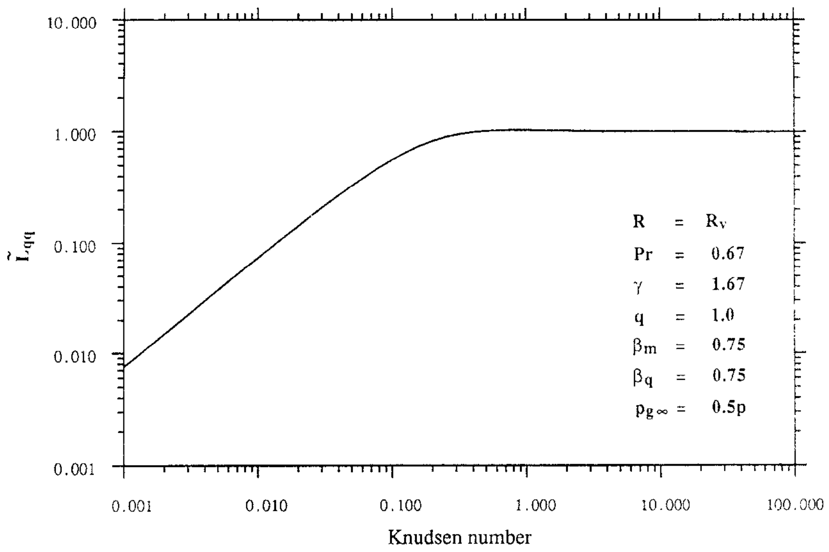

FIG. 7. Variation of $\tilde{L}_{qq}$ with Knudsen number.

displays more interesting behaviour as can be seen in Fig. 5. For a pure vapour, it remains of order unity over the whole range of Knudsen numbers. However, for very high concentrations of inert gas, mass transfer is governed by diffusion and $\tilde{L}_{mm}$ varies directly with the Knudsen number in the continuum regime. The transition from kinetic to diffusion control with increase of inert gas concentration can be clearly seen. For a given inert gas concentration, transition occurs over a range of Knudsen numbers of the same order of magnitude as $p_{g\infty}/p$. This is in agreement with the analysis leading to equation (57) and Fig. 4.

CONCLUSIONS

A new set of equations describing the growth and evaporation of stationary liquid droplets in a mixture of pure vapour and inert gas has been derived. The equations (which are in explicit, algebraic form) specify the heat and mass transfer between the droplet and the vapour–gas mixture in terms of the temperature difference $\Delta T = T_d - T_\infty$ and the vapour pressure difference $\Delta p_v = p_s - p_{v\infty}$. Expressions for the mass flux J_m and the conductive heat flux J_{qc} are given by equations (7) with the phenomenological coefficients defined by equations (65). The equations are not restricted to the so-called *quasi-steady* regime of droplet growth when the droplet surface temperature has relaxed to its steady-state value but can also be used to model transient situations. The theory is valid for polyatomic vapours and gases at arbitrary Knudsen number and for any concentration of inert gas. The transition from diffusion to kinetic control with decrease in inert gas concentration at low Knudsen numbers is successfully described by the theory which predicts the transition to occur over a range of Knudsen numbers of the same order of magnitude as the mole fraction of inert gas, $p_{g\infty}/p$. The case of a pure vapour (zero inert gas concentration) is obtained as a limiting case in exact ageement with an earlier analysis described in ref. [3].

Unlike most simple theories of droplet growth, the analysis can be used to predict many features of the kinetics of condensation which are usually only revealed by more complex solutions of the Boltzmann equation itself. Thus, simple and illuminating expressions for the Knudsen layer temperature and vapour pressure jump coefficients in the continuum limit are obtained (equations (51) and (56)) which are in good agreement with analytical solutions of the BGK equation presented in ref. [16]. An interesting deduction from equation (51) is that the Knudsen layer temperature jump in the continuum limit is directly proportional to the mole fraction of vapour in the mixture and therefore tends to zero at high concentrations of inert gas. It has also been shown that the Knudsen layer vapour pressure jump tends to zero providing at least some inert gas is present and that the Knudsen number is sufficiently small to ensure that diffusion rather than kinetic control predominates.

An important conclusion from the analysis is that, when computing droplet growth under continuum conditions, it is incorrect to apply the Navier–Stokes equations over the whole region from the far-field to the droplet surface with the surface boundary conditions prescribed by $T_i = T_d$ and $p_{vi} = p_s$. Account should be taken of the Knudsen layer temperature and vapour pressure jumps given by equations (49) and (54), respectively. At high condensation or evaporation rates the correction to the boundary conditions may be quite significant.

The analysis also provides a physical interpretation for the origins of the so-called *reversed temperature* *gradient phenomenon* within the Knudsen layer, an effect predicted by solutions of the BGK and other Boltzmann-like equations. The phenomenon is associated with condensation or evaporation under continuum conditions when the mass and heat fluxes are in opposite directions (i.e. the normal situation for quasi-steady condensation or evaporation) and is an indication of the highly non-equilibrium nature of the distribution of molecular velocities close to the liquid surface.

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APPENDIX 1. ENTROPY PRODUCTION RATE

With reference to the system of Fig. 1, open to the transfer of mass, condensation or evaporation is assumed to be occurring under quasi-steady conditions. The small change in volume of the droplet is accommodated by allowing the system boundary to expand or contract at such a rate that the volume, mass and thermodynamic properties of the non-equilibrium transition region remain constant.

The rate of entropy production $\dot{S}$ due to irreversibilities originating in region NE is therefore given by

$$\dot{S} = \dot{S}_d + \dot{S}_e \tag{A1.1}$$

where $\dot{S}_d$ is the rate of increase of the entropy of region D and $\dot{S}_e$ the rate of increase of entropy of fluid external to the system. $\dot{S}_d$ is composed of contributions from the bulk liquid and the droplet surface. In the appendix of ref. [3], it is shown that

$$\dot{S}_d = \frac{1}{T_d}\dot{E}_d + \frac{p_d}{T_d}\dot{V}_d - \frac{\mu_{di}}{T_d}\dot{M}_d. \tag{A1.2}$$

E_d, V_d and M_d are the total (bulk liquid plus surface) energy, volume and mass, respectively, of the droplet. $\mu_{di} = \mu_d(T_d, p_{di})$ is the chemical potential per unit mass of the droplet evaluated at its temperature T_d and (possibly high) internal pressure p_{di}. $p_d = p_{di} - 2\sigma/r_d$ is the pressure in the vapour–gas mixture at the droplet surface. The rate of increase of entropy of the fluid external to the system is given by

$$\dot{S}_e = \frac{1}{T_\infty}\dot{E}_e + \frac{p_\infty}{T_\infty}\dot{V}_e - \frac{\mu_{v\infty}}{T_\infty}\dot{M}_{ve} \tag{A1.3}$$

where $\dot{E}_e$, $\dot{V}_e$ and $\dot{M}_{ve}$ are the rates of increase of energy, volume and mass of vapour in that region. The temperature and total pressure are T_∞ and p_∞, and $\mu_{v\infty} = \mu_v(T_\infty, p_{v\infty})$ is the chemical potential per unit mass of the vapour with partial pressure $p_{v\infty}$. Note that (apart from the effect of the change in volume of the droplet), the inert gas does not move and hence there is no transfer of this component across the system boundary.

By the conservation of mass, energy and volume

$$\dot{M}_d + \dot{M}_{ve} = 0, \tag{A1.4}$$

$$\dot{E}_d + \dot{E}_e = 0 \tag{A1.5}$$

$$\dot{V}_d + \dot{V}_e = 0. \tag{A1.6}$$

Hence

$$\dot{S} = \left(\frac{1}{T_d} - \frac{1}{T_\infty}\right)\dot{E}_d + \left(\frac{p_d}{T_d} - \frac{p_\infty}{T_\infty}\right)\dot{V}_d - \left(\frac{\mu_{di}}{T_d} - \frac{\mu_{v\infty}}{T_\infty}\right)\dot{M}_d. \tag{A1.7}$$

Equation (A1.7) can be rewritten in terms of the rate of heat transfer crossing the system boundary by introducing the first law of thermodynamics. Applying this principle to the system of Fig. 1 (neglecting the bulk kinetic energy of the fluid crossing the boundary)

$$\dot{E}_d + p_\infty \dot{V}_d + h_\infty \dot{M} + \dot{Q} = 0 \tag{A1.8}$$

where ($\dot{M} = -\dot{M}_d$) and $\dot{Q}$ are the rates at which mass and heat are transferred across the system boundary and h_∞ is the specific enthalpy of the vapour–gas mixture far from the droplet. The heat transfer rate $\dot{Q}$ embodies contributions from pure thermal conduction and also diffusion. Noting that the diffusive mass transfer rate is $\dot{M}(1 - \rho_{v\infty}/\rho_\infty)$, we have

$$\dot{Q} = \dot{Q}_{\mathrm{c}} + (h_{\mathrm{v}\infty} - h_{\mathrm{g}\infty})(1 - \rho_{\mathrm{v}\infty}/\rho_{\infty})\dot{M} \qquad \text{(A1.9)}$$

where $\dot{Q}_{\mathrm{c}}$ is the heat transfer rate due solely to thermal conduction and $h_{\mathrm{v}\infty}$ and $h_{\mathrm{g}\infty}$ are the partial enthalpies of the vapour and inert gas, respectively. The mixture specific enthalpy is

$$h_{\infty} = \left(\frac{\rho_{\mathrm{v}\infty}}{\rho_{\infty}}\right)h_{\mathrm{v}\infty} + \left(1 - \frac{\rho_{\mathrm{v}\infty}}{\rho_{\infty}}\right)h_{\mathrm{g}\infty} \qquad \text{(A1.10)}$$

from which it follows that

$$\dot{Q} + h_{\infty}\dot{M} = \dot{Q}_{\mathrm{c}} + h_{\mathrm{v}\infty}\dot{M}. \qquad \text{(A1.11)}$$

Substituting equations (A1.8) and (A1.11) in (A1.7) gives

$$\dot{S} = \left(\frac{1}{T_{\infty}} - \frac{1}{T_{\mathrm{d}}}\right)\dot{Q}_{\mathrm{c}} + \left[h_{\mathrm{v}\infty}\left(\frac{1}{T_{\infty}} - \frac{1}{T_{\mathrm{d}}}\right) - \left(\frac{\mu_{\mathrm{v}\infty}}{T_{\infty}} - \frac{\mu_{\mathrm{dl}}}{T_{\mathrm{d}}}\right)\right]\dot{M} + \left(\frac{p_{\infty} - p_{\mathrm{d}}}{T_{\mathrm{d}}}\right)\dot{V}_{\mathrm{d}}. \qquad \text{(A1.12)}$$

Simplification of equation (A1.12) is exactly as described in ref. [3] subject to the approximations, $|(T_{\mathrm{d}} - T_{\infty})/T_{\infty}| = |\Delta T/T_{\infty}| \ll 1$, $|(p_{\mathrm{s}} - p_{\mathrm{v}\infty})/p_{\mathrm{v}\infty}| = |\Delta p_{\mathrm{v}}/p_{\mathrm{v}\infty}| \ll 1$ and $(\rho_{\mathrm{v}}/\rho_{\mathrm{d}}) \ll 1$. In terms of the fluxes J_{m} and J_{qc} defined by equations (6), the result is

$$\frac{\dot{S}}{R_{\mathrm{v}}} = 4\pi r_{\mathrm{d}}^{2}\left\{J_{\mathrm{m}}\left(\frac{\Delta p_{\mathrm{v}}}{p_{\mathrm{v}\infty}}\right) + J_{\mathrm{qc}}\left(\frac{\Delta T}{T_{\infty}}\right)\right\}. \qquad \text{(A1.13)}$$

APPENDIX 2. DERIVATION OF EQUATION (11)

Equation (11) is so frequently quoted incorrectly in the literature that it is worthwhile outlining its derivation.

Combining equations (9) and (10) gives

$$\dot{M}\left(1 - \frac{\rho_{\mathrm{v}}}{\rho}\right) = -4\pi r^{2}\rho D\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho_{\mathrm{v}}}{\rho}\right). \qquad \text{(A2.1)}$$

From the perfect gas equations for the vapour and inert gas components

$$\frac{\rho_{\mathrm{v}}}{\rho} = \frac{(R_{\mathrm{g}}/R_{\mathrm{v}})(p_{\mathrm{v}}/p)}{1 + (p_{\mathrm{v}}/p)(R_{\mathrm{g}}/R_{\mathrm{v}} - 1)}. \qquad \text{(A2.2)}$$

Hence

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho_{\mathrm{v}}}{\rho}\right) = \frac{(R_{\mathrm{g}}/R_{\mathrm{v}})}{[1 + (p_{\mathrm{v}}/p)(R_{\mathrm{g}}/R_{\mathrm{v}} - 1)]^{2}}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{p_{\mathrm{v}}}{p}\right). \qquad \text{(A2.3)}$$

Introducing equation (A2.2) gives

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho_{\mathrm{v}}}{\rho}\right) = \frac{(1 - \rho_{\mathrm{v}}/\rho)}{(1 - p_{\mathrm{v}}/p)}\left(\frac{\rho_{\mathrm{v}}}{\rho}\right)\left(\frac{p}{p_{\mathrm{v}}}\right)\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{p_{\mathrm{v}}}{p}\right). \qquad \text{(A2.4)}$$

Substitution in equation (A2.1) then gives equation (11).