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A kinetic theory of steady condensation

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This paper pertains to the steady condensation on to, or evaporation from, a liquid droplet suspended in a mixture of its vapour and an inert gas. The treatment is from a kinetic theory viewpoint. The Maxwell moment method is used with Lees' two stream Maxwellian representations for the distribution functions, to obtain a closed form result valid through the whole range from free molecule to continuum. In the diffusion control limit the formula reduces to approximate results obtained by Maxwell, Fuchs and others. In the limit where no inert gas is present the formula reduces to a result obtained earlier by the author. The formulae presented here for the mass and energy flux can now be used to calculate the growth rate of very small droplets, under a wide range of conditions.

1. Introduction

The growth or dimunition of liquid droplets, by condensation and evaporation respectively, is of great importance in various areas of technology. The performance of supersonic nozzles, the erosion of steam turbine buckets, the efficiency of vapour-droplet separators all depend to various degrees on droplet sizes. The phenomenon is also of importance in droplet combustion, and liquid metal vapour power cycles. In all of these cases knowledge of droplet size and growth rate are of considerable importance.

The phenomenon of condensation droplet growth is a transient one. The moving boundary and the changing droplet temperature pose hard mathematical problems. In order to reduce the difficulty one can attempt to solve the problem by a quasi-steady approach, i.e. solve the problem of steady condensation and then use this solution for the transient problem in a quasi-steady manner. In this paper we consider only steady condensation and evaporation.

Let a droplet of liquid of radius r_0 (figure 1), at a temperature T_L be surrounded by a mixture of its vapour (subscript A) and an inert gas (subscript B). Far from the droplet, let the partial pressures of the vapour and inert gas (called gas from now on) be $p_{A\infty}$ and $p_{B\infty}$ respectively. Let the temperature far away be T_∞. The saturation vapour pressure of the liquid, corresponding to a temperature T_L and radius r_0, is p_L^*. The problem is to calculate the evaporation or condensation rate when the ambient temperature and vapour pressure are not equal to the droplet temperature and the corresponding vapour pressure.

Maxwell (1877) was the first to attempt a solution to this problem. He assumed that diffusion was the controlling mechanism, i.e. the amount of vapour evaporated or condensed depended only on its ability to diffuse outward or inward. Then, if Γ_A is the total mass of vapour crossing the spherical surface of radius r,

$$\Gamma_A = 4\pi r^2 \dot{m}_A = -4\pi r^2 D_{AB}\frac{d\rho_A}{dr}, \tag{1}$$

where D_{AB} is the diffusion coefficient and $\dot{m}_A$ is the mass flux. Maxwell now assumed that ρ_A, the vapour density, took the value ρ_L^*, corresponding to saturation, at the droplet surface. Then

$$\Gamma_A = \Gamma_{A0} = 4\pi r_0 D_{AB}(\rho_L^* - \rho_{A\infty}). \tag{2}$$

Among many things neglected in this analysis was the mean motion of the gas and vapour. If the vapour diffuses in one direction, the gas has to diffuse in the other direction to keep the pressure approximately constant. But, since there can be no net flow of the inert gas, there must be a mean motion to counteract the diffusion. Stefan (1881) took this into account and showed that

$$\Gamma_A \approx 4\pi r_0 D_{AB}(\rho_L^* - \rho_{A\infty})\left[1 + \frac{p_L^* + p_{A\infty}}{2(p_{A\infty} + p_{B\infty})}\right]. \tag{3}$$

The correction term is not significant if the vapour partial pressure is small.

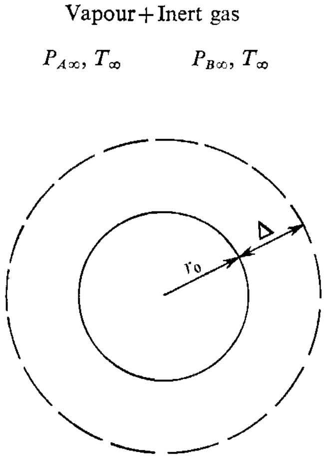

FIGURE 1. The geometry used for the continuum analyses.

The assumption that the vapour pressure at the droplet surface is equal to ρ_L^* is in general a poor one. The non-equilibrium processes occurring close to the surface cause rapid changes to occur in the vapour concentration. This was pointed out first by Langmuir (1915), and Schäfer (1932) and Fuchs (1934) attempted to take this effect into account. They assumed (figure 1) that diffusion was rate controlling up to a distance Δ (of the order of the mean free path) from the surface, but that within this distance the transport was governed by free molecular kinetics. At $r = r_0 + \Delta$ let the vapour concentration be ρ_{A1} which is initially unknown. Then from Fick's law (with $\rho_{A\infty} = 0$)

$$\rho_A = \frac{\Gamma_A}{4\pi r D_{AB}}; \tag{4}$$

and at $r = r_0 + \Delta$

$$\Gamma_A = 4\pi D_{AB}(r_0 + \Delta)\,\rho_{A1}. \tag{5}$$

But from elementary kinetic theory, the mass flux from the droplet is given by $\alpha_m \rho_L^* (R_A T_L)^{\frac{1}{2}}/2\pi$ and the flux to the droplet is given by $\alpha_m \rho_{A1} (R_A T_{A1})^{\frac{1}{2}}/2\pi$, where α_m is the sticking or mass accommodation coefficient. Therefore if $T_{A1} \simeq T_L$, the net rate of vapour mass flow from the droplet is

$$\Gamma_A = 4\pi r_0^2 \alpha_m \frac{(R_A T_L)^{\frac{1}{2}}}{2\pi} (\rho_L^* - \rho_{A1}). \tag{6}$$

Between (5) and (6) the unknown ρ_{A1} can be eliminated to give the evaporation rate

$$\Gamma_A = \frac{\Gamma_{A0}}{\left[1 - \dfrac{\Delta}{r_0 + \Delta} + \dfrac{D_{AB}}{r_0 \alpha_m} \left(\dfrac{2\pi}{R_A T_L}\right)^{\frac{1}{2}}\right]}. \tag{7}$$

Now the distance Δ is normally taken to be some multiple α of the mean free path l at the droplet surface, i.e. $\Delta = \alpha l$.

There are two major unsatisfactory features in the above mentioned analyses. First, they are based on the assumption that diffusion is the rate controlling mechanism. Now, when the density of the inert gas is low, diffusion will give way to kinetic control. Diffusion based continuum theories cannot describe this transition to the limit where no inert gas is present. The second unsatisfactory feature is the *ad hoc* introduction of kinetic effects by a mean free path approach. Not only is the multiple α in the definition of Δ unknown, but the mean free path l at liquid surface is itself not a clearly defined quantity.

The limitations of the continuum analyses originate from one basic fact. The evaporation–condensation problem is not properly posed in a continuum formulation. The boundary conditions at the liquid surface cannot be specified in terms of continuum thermodynamic variables. In fact, the problem is really a two-point boundary-value problem for the molecular velocity distribution functions, where the complete distribution functions are known at infinity and half the distribution functions are known at the liquid surface.

The purpose of the present analysis is to obtain, from a kinetic theory formulation, a solution valid through the range from free molecule to continuum and capable of describing the transition from pure diffusion to pure kinetic control. This will be done by solving the Boltzmann equations approximately for the distribution functions f_ν by the Maxwell moment method, as developed by Lees (1959, 1965). This technique, in spite of its recognized limitations, offers the most tractable approach to a problem of this degree of complexity.

Before passing on to the present formulation, we note that Monchick & Reiss (1954) attempted a kinetic theory treatment of the problem. However, they used the Chapman–Enskog theory which is quite unsuitable for boundary-value problems of this type. Also, the Chapman–Enskog expansion is really in inverse powers of the density. Thus it will always fail to give the free molecule or nearly free molecule solution. The result of Monchick & Reiss suffers from precisely this defect.

2. A kinetic theory formulation

2.1. *The governing equations and boundary conditions*

The knowledge of the molecular velocity distribution function $f_\nu(\mathbf{r}, \boldsymbol{\xi}, t)$ constitutes the most complete knowledge of the state of a gas, above the individual molecular level. If we know the distribution function f_ν, all the macroscopic quantities such as density, velocity, pressure, etc., can be obtained as moments of f_ν:

$$\rho_\nu(\mathbf{r}, t) = \int m_\nu f_\nu \, d\boldsymbol{\xi}_\nu, \tag{8a}$$

$$\mathbf{u}_\nu(\mathbf{r}, t) = \int m_\nu \boldsymbol{\xi}_\nu f_\nu \, d\boldsymbol{\xi}_\nu, \tag{8b}$$

etc. Here $\boldsymbol{\xi}$ is the molecular velocity vector, m is the molecular mass and the subscript ν refers to the particular species (no sum over ν). In this particular case ν takes the values A and B, where A refers to the condensable vapour and B to the inert gas. The problem then is to solve for f_A and f_B which satisfy the Boltzmann equations

$$\boldsymbol{\xi} \cdot \nabla f_\nu = \left(\frac{\partial f_\nu}{\partial t}\right)_{\text{Coll.}}, \quad \nu = A, B. \tag{9}$$

where we have left out the time dependence, since we are considering the steady case. $(\partial f_\nu / \partial t)_{\text{Coll.}}$ are the collision integrals.

We shall consider the boundary conditions in some detail. Far from the droplet the gas and vapour pressures $p_{B\infty}$ and $p_{A\infty}$ are known; also, the temperature T_∞ is the same for both vapour and gas and is known.

From the equation of state the two number densities n_ν are also known. Hence the boundary conditions for $r \to \infty$ may be written

$$\left.\begin{array}{ll} n_A \to n_{A\infty}, & n_B \to n_{B\infty}, \\ T_A \to T_\infty, & T_B \to T_\infty, \end{array}\right\} \tag{10}$$

The situation at the surface of the droplet is somewhat more complicated. One obvious boundary condition is that the net mass flux of inert gas must be zero

$$\dot{m}_B(r = r_0) = \int m_B \xi_r f_B \, d\boldsymbol{\xi}_B = 0. \tag{11}$$

We now assume that the inert gas molecules striking the liquid are absorbed by it, and are then diffusely re-emitted with a Maxwellian distribution corresponding to the temperature T_L of the liquid

$$f_B = \frac{n_{B0}}{[2\pi R_B T_L]^{\frac{3}{2}}} \exp\left\{-\frac{\xi^2}{2R_B T_L}\right\} \quad \text{for} \quad \xi_r > 0. \tag{12}$$

Note that n_{B0} the number density of the re-emitted molecules is not known in advance.

As for the vapour, we now have to introduce the mass accommodation or sticking coefficient α_m and the thermal accommodation coefficient α_T. These coefficients just manifest our uncertainty as to the physics of the actual molecular processes occurring at the surface. They are defined as follows:

$$\alpha_m = \frac{\dot{m}_{Ai} - \dot{m}_{AR}}{\dot{m}_{Ai} - \dot{m}_{AL}}, \tag{13a}$$

$$\alpha_T = \frac{q'_{Ai} - q'_{AR}}{q'_{Ai} - q'_{AL}}, \tag{13b}$$

where i refers to the incident stream, R to the net receding stream and L to the stream of molecules from the liquid. q'_{Aj} are the energy fluxes. Thus, when the receding stream of molecules is composed only of the stream emitted from the liquid and contains no molecules reflected from the incident beam, both α_m and $\alpha_T = 1$, i.e. for diffuse re-emission the accommodation coefficients are unity. Now we shall assume that the liquid emits vapour molecules in a Maxwellian distribution corresponding to the liquid temperature T_L and number density corresponding to the saturation value at T_L and radius r_0, i.e.

$$f_{AL} = \frac{n_L^*}{[2\pi R_A T_L]} \exp\left\{-\frac{\xi_A^2}{2R_A T_L}\right\} \quad \text{for} \quad \xi_{Ar} > 0. \tag{14}$$

Note that this constitutes two boundary conditions, since the number density and temperature are specified. It is true that n_L^* is a function of T_L and the radius r_0 through the saturation vapour pressure–temperature relationship (the Clausius–Clapeyron equation modified by the Kelvin correction). But, as far as the vapour is concerned, the liquid is a black box which specifies two quantities n_L^* and T_L.

In summary, we have four boundary conditions (10) at infinity, two boundary conditions (11) and (12) at $r = r_0$ for the inert gas, and two boundary conditions (14) modified or complicated by (13) for the vapour at $r = r_0$. In the case of diffuse re-emission ($\alpha_T = \alpha_m = 1$) the molecules from the liquid surface are made up entirely of the molecules emitted by it

$$f_A(r = r_0) = f_{AL} \quad \text{for} \quad \xi_{Ar} > 0. \tag{15}$$

2.2. *The Maxwell moment method*

In § 2.1 we noted that a solution to the problem necessitated the solutions of the Boltzmann equations (9) for the distribution functions f_A and f_B. However, we are not particularly interested in distribution functions themselves. The gross macroscopic quantities such as mass flux and heat flux are our main concern. We shall therefore not attempt to solve (9) directly, but we shall solve the transport equation for the lower moments. In so doing we shall be satisfying (9) in some average sense. Multiplying (9) by some function $Q(\xi_{\nu i})$ of the molecular velocity components, and integrating over the velocity space,

$$\int Q(\xi_{\nu i})\, \boldsymbol{\xi}_\nu . \nabla f_\nu \, d\boldsymbol{\xi}_\nu = \int Q(\xi_{\nu i})\, (\partial f_\nu / \partial t)_{\text{Coll.}}\, d\boldsymbol{\xi}_\nu, \tag{16}$$

or

$$\int Q(\xi_{\nu i})\, \boldsymbol{\xi}_\nu . \nabla f_\nu \, d\boldsymbol{\xi}_\nu = \Delta Q, \tag{17}$$

where ΔQ is the change in Q due to collisions. This is the basic transport equation due to Maxwell. For a pure gas, setting $Q = m, m\xi_i$ and $\frac{1}{2}m\xi^2$ leads to the equations of conservation of mass, momentum and energy ($\Delta Q = 0$).

For details of the present method due to Lees (1959, 1965) we refer to the original papers. In brief, the procedure is as follows:

(i) Represent the distribution function f by a number of unknown functions.

(ii) Take as many moments (17) as necessary to determine the unknown functions.

(iii) Satisfy the boundary conditions.

In choosing the form of the distribution function and the arbitrary functions one is guided by the following requirements:

(i) It should have the two-sided character essential to rarified flows.

(ii) Its form must be such that the boundary conditions are easily satisfied.

(iii) It should be capable of providing a smooth transition from rarified flow to the Navier–Stokes limit.

Lees's two-stream Maxwellian is admirably suited for most purposes involving simple geometries.

2.3. *Moment formulation of the droplet problem*

For a spherically symmetric geometry (refer to figure $2a, b$) the transport equation (17) takes the form,

$$\begin{aligned}\frac{1}{r^2}\frac{d}{dr}\int r^2 f_\nu\,\xi_{\nu r}\,Q\,d\boldsymbol{\xi}_\nu+\frac{1}{r}\frac{\cos\theta}{\sin\theta}\int f_\nu\,\xi_{\nu\theta}Q\,d\boldsymbol{\xi}_\nu\\ -\frac{1}{r}\int f_\nu\left[(\xi^2_{\nu\theta}+\xi^2_{\nu\phi})\frac{\partial Q}{\partial\xi_{\nu r}}+\left(\frac{\cos\theta}{\sin\theta}\,\xi^2_{\nu\phi}-\xi_{\nu\theta}\,\xi_{\nu r}\right)\frac{\partial Q}{\partial\xi_{\nu\theta}}\right.\\ \left.+\left(\xi_{\nu\phi}\,\xi_{\nu r}+\frac{\cos\theta}{\sin\theta}\,\xi_{\nu\phi}\,\xi_{\nu\theta}\right)\frac{\partial Q}{\partial\xi_{\nu\phi}}\right]d\boldsymbol{\xi}_\nu=\Delta Q,\ldots\nu=A,B.\end{aligned}\qquad(18)$$

We shall assume both species to be Maxwell molecules, i.e. ones that have an inverse fifth power law of force between the molecules. This permits us to evaluate ΔQ without knowing the form of f. Since we have two species,

$$\left.\begin{aligned}\Delta Q&=(\Delta Q)_{AA}+(\Delta Q)_{AB}\quad\text{for molecules } A,\\ \Delta Q&=(\Delta Q)_{BB}+(\Delta Q)_{AB}\quad\text{for molecules } B.\end{aligned}\right\}\qquad(19)$$

That is, the change in Q is due to collisions with the same species plus that due to collisions with the other. For Maxwell particles it can be shown (Jeans 1954; Lees 1959) that

$$\left.\begin{aligned}(\Delta Q)_{\nu\nu}&=0\quad\text{for}\quad Q=m_\nu,\ m_\nu\,\xi_{\nu i},\ \tfrac{1}{2}m_\nu\,\xi^2_\nu,\\ (\Delta Q)_{\nu\nu}&=(p_\nu/\mu_\nu)\cdot p_{\nu jk}\quad\text{for}\quad Q=m_\nu\,\xi_{\nu j}\,\xi_{\nu k},\\ (\Delta Q)_{\nu\nu}&=(p_\nu/\mu_\nu)\,[-\tfrac{2}{3}q_{\nu j}+\sum_k p_{\nu jk}u_{\nu k}]\quad\text{for}\quad Q=\tfrac{1}{2}m_\nu\,\xi_{\nu j}\,\xi^2_\nu.\end{aligned}\right\}\qquad(20)$$

The collision integrals for the gas mixture yield complicated $(\Delta Q)_{AB}$. They have been derived by Kolodner (1957), Weinstein (1965) and others. The details

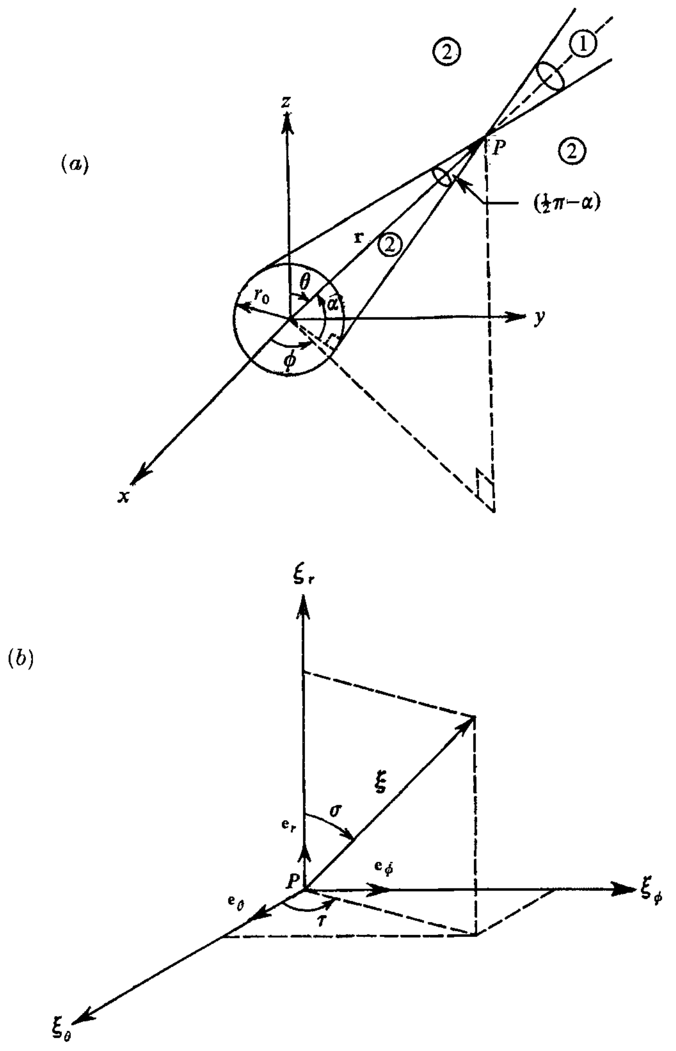

FIGURE 2. (*a*) Geometry for the two stream Maxwellian representation.
(*b*) The velocity space at the point $P(r, \theta, \phi)$.

for the present calculation are given in a report by the author (Shankar 1969); we shall not present them here.

The two distribution functions f_ν will be assumed to be two stream Maxwellians (refer to figures 2*a*, *b*) of the following form:

$$f_\nu(r,\xi) = \left\{ \begin{aligned} & f_{\nu 1} = \frac{n_{\nu 1}(r)}{[2\pi R_\nu T_{\nu 1}(r)]^{\frac{3}{2}}} \exp\left\{ -\frac{\xi_\nu^2}{2R_\nu T_{\nu 1}(r)} \right\} \quad \text{in} \quad (1), \\ & f_{\nu 2} = \frac{n_{\nu 2}(r)}{[2\pi R_\nu T_{\nu 2}(r)]^{\frac{3}{2}}} \exp\left\{ -\frac{\xi_\nu^2}{2R_\nu T_{\nu 2}(r)} \right\} \quad \text{in} \quad (2). \end{aligned} \right\} \tag{21}$$

We therefore have eight unknown functions $n_{\nu 1}$, $n_{\nu 2}$, $T_{\nu 1}$ and $T_{\nu 2}$, all of which are functions of r only. This form permits us to have a cone of influence which is essential for free molecular flow.

With such a choice for $f_\nu(r, \xi)$ it is easy to show that the mass density of ν at r is given by

$$\rho(r) = \int m_\nu f_\nu(r, \xi)\, d\boldsymbol{\xi} = \tfrac{1}{2} m_\nu [n_{\nu 1}(r)\,(1-x) + n_{\nu 2}(r)\,(1+x)], \tag{22}$$

where

$$x = \left(1 - \frac{r_0^2}{r^2}\right)^{\frac{1}{2}}. \tag{23}$$

All other quantities such as radial velocity, heat flux, pressure, etc., can also be evaluated in terms of the unknown functions $n_{\nu 1}$, $n_{\nu 2}$, $T_{\nu 1}$ and $T_{\nu 2}$.

Having defined each distribution function by four unknown functions it is necessary to use four moment equations for each f_ν; the three conservation equations plus one higher moment each. Now the choice of the higher moment is in a sense arbitrary and the solution will, at least numerically, be dependent on the particular choice. Experience with the heat transfer problem (Lees 1965), which bears considerable similarity to the condensation problem, leads us to choose the moment corresponding to radial heat flux. Setting $Q = m_\nu, m_\nu \xi_{\nu r}, m_\nu \frac{1}{2}\xi_\nu^2$ and $m_\nu \xi_{\nu r} \frac{1}{2}\xi_\nu^2$ respectively, (18) yields the following eight moment equations:

$$\frac{d}{dr}(r^2 \rho_\nu v_\nu) = 0, \tag{24a}$$

$$\rho_\nu v_\nu \frac{dv_\nu}{dr} - \frac{d}{dr} P_{\nu rr} - \frac{1}{r}(2P_{\nu rr} - P_{\nu\theta\theta} - P_{\nu\phi\phi}) = (\Delta Q)_{AB}, \tag{24b}$$

$$\frac{d}{dr}[r^2(q_{\nu r} + \tfrac{3}{2} p_\nu v_\nu - v_\nu P_{\nu rr} + \tfrac{1}{2}\rho_\nu v_\nu^3)] = (\Delta Q)_{AB}, \tag{24c}$$

$$\frac{1}{r^2}\frac{d}{dr}\int r^2 f_\nu m_\nu \xi_{\nu r}^2 \tfrac{1}{2}\xi_\nu^2\, d\boldsymbol{\xi}_\nu - \frac{1}{r}\int f_\nu m_\nu \tfrac{1}{2}\xi_\nu^2 (\xi_{\nu\theta}^2 + \xi_{\nu\phi}^2)\, d\boldsymbol{\xi}_\nu = \frac{p_\nu}{\mu_\nu}[-\tfrac{2}{3} q_{\nu r} + v_\nu p_{\nu rr}] + (\Delta Q)_{AB}. \tag{24d}$$

These equations can now be rewritten as equations for the eight unknown functions.

The boundary conditions (10), (11) and (14) can also be quite simply written, as boundary conditions on $T_{\nu 1}$, $T_{\nu 2}$, $n_{\nu 1}$ and $n_{\nu 2}$. Thus we have eight non-linear first-order equations and eight boundary conditions for the unknowns $T_{\nu 1}$, $T_{\nu 2}$, $n_{\nu 1}$ and $n_{\nu 2}$.

3. A perturbation solution

Our main interest here is to calculate the vapourization rate for departures from equilibrium that are not too large. It is then natural to seek a perturbation solution about the equilibrium state. We first write the functions defining $f_\nu(r, \xi)$ in perturbation series of the form,

$$n_{\nu 1}(r) = n_{\nu\infty}[1 + N_{\nu 1}(r) + \ldots], \tag{25a}$$

$$T_{\nu 1}(r) = T_\infty[1 + t_{\nu 1}(r) + \ldots], \tag{25b}$$

$$n_{\nu 2}(r) = n_{\nu\infty}[1 + N_{\nu 2}(r) + \ldots], \tag{25c}$$

$$T_{\nu 2}(r) = T_\infty[1 + t_{\nu 2}(r) + \ldots]. \tag{25d}$$

$N_{\nu 1}$, $t_{\nu 1}$, $N_{\nu 2}$ and $t_{\nu 2}$ are the dimensionless first-order perturbation quantities to be calculated. It is convenient to introduce the following notation:

$$\left.\begin{aligned} N_{\nu +} &= N_{\nu 1}(r)+N_{\nu 2}(r), \quad & N_{\nu -} &= N_{\nu 1}(r)-N_{\nu 2}(r), \\ t_{\nu +} &= t_{\nu 1}(r)+t_{\nu 2}(r), \quad & t_{\nu -} &= t_{\nu 1}(r)-t_{\nu 2}(r). \end{aligned}\right\} \tag{26}$$

In terms of these variables the dynamic and thermodynamic gross quantities are to first order

$$\rho_\nu(r) = \rho_{\nu\infty}[1+\tfrac{1}{2}(N_{\nu +}-\tfrac{1}{2}xN_{\nu -})+\ldots], \tag{27a}$$

$$v_\nu(r) = \frac{\beta_\nu(1-x^2)}{2\pi}[(N_{\nu -}+\tfrac{1}{2}t_{\nu -})+\ldots], \tag{27b}$$

$$T_\nu(r) = T_\infty[1+\tfrac{1}{2}(t_{\nu +}-\tfrac{1}{2}xt_{\nu -})+\ldots], \tag{27c}$$

$$p_\nu(r) = p_{\nu\infty}[1+\tfrac{1}{2}(N_{\nu +}-xN_{\nu -}+t_{\nu +}-xt_{\nu -})+\ldots], \tag{27d}$$

$$q_{\nu r}(r) = \frac{p_{\nu\infty}\beta_\nu(1-x^2)}{2\pi}[(\tfrac{7}{4}t_{\nu -}-\tfrac{1}{2}N_{\nu -})+\ldots], \tag{27e}$$

where $\beta_\nu = (2\pi R_\nu T_\infty)^{\frac{1}{2}}$. We note that the radial velocity $v_{\nu r}$ and the radial heat flux $q_{\nu r}$ have only first-order components, i.e. they vanish at equilibrium, as they should. Substituting the forms (27) into the moment equations (24) we obtain after some simplification the following eight linearized moment equations:

$$N_{A-}+\tfrac{1}{2}t_{A-} = F_1, \tag{28a}$$

$$N_{B-}+\tfrac{1}{2}t_{B-} = G_1 \ (=0), \tag{28b}$$

$$\frac{d}{dr}(N_{A+}+t_{A+})-x^3\frac{d}{dr}(N_{A-}+t_{A-}) = -\left\{\frac{n_{B\infty}}{n_{A\infty}+n_{B\infty}}\frac{r_0\beta_A}{\pi D_{AB}}\right\}\frac{r_0}{r^2}F_1, \tag{29a}$$

$$\frac{d}{dr}\left\{(N_{A+}+t_{A+})+\frac{n_{B\infty}}{n_{A\infty}}(N_{B+}+t_{B+})\right\}-x^3\frac{d}{dr}\left\{(N_{A-}+t_{A-})+\frac{n_{B\infty}}{n_{A\infty}}(N_{B-}+t_{B-})\right\} = 0, \tag{29b}$$

$$\frac{d}{dr}\left\{N_{A-}+\tfrac{3}{2}t_{A-}\right\} = \frac{3\pi}{8}M_A\left\{\frac{n_{B\infty}}{n_{A\infty}+n_{B\infty}}\frac{r_0\beta_A}{\pi D_{AB}}\right\}\frac{r^2}{r_0^3}\left\{(t_{B+}-xt_{B-})-(t_{A+}-xt_{A-})\right\}, \tag{30a}$$

$$(N_{A-}+\tfrac{3}{2}t_{A-})+\frac{n_{B\infty}\beta_B}{n_{A\infty}\beta_A}(N_{B-}+\tfrac{3}{2}t_{B-}) = \text{const.}, \tag{30b}$$

$$\begin{aligned} &\frac{d}{dr}[N_{A+}+2t_{A+}]-x^3\frac{d}{dr}[N_{A-}+2t_{A-}] \\ &\quad = -\frac{2}{15}\left(\frac{p_{A\infty}r_0}{\beta_A\mu_{A\infty}}\right)\frac{r_0}{r}[7t_{A-}-2N_{A-}]+\frac{2}{15}\left\{\frac{n_{B\infty}}{n_{A\infty}+n_{B\infty}}\frac{\beta_A r_0}{\pi D_{AB}}\right\}\frac{r_0}{r^2} \\ &\qquad \times\left[-6F_2+M_B\left(5\frac{m_A}{m_B}F_1+12F_2\right)+M_B^2\left(-10\frac{m_A}{m_B}F_1+8\frac{m_A}{m_B}\frac{\beta_B}{\beta_A}G_2-8F_2\right)\right. \\ &\qquad\qquad \left.+\frac{A_2}{A_1}\left\{-8M_BF_2+M_B^2\left(10\frac{m_A}{m_B}F_1-8\frac{m_A}{m_B}\frac{\beta_B}{\beta_A}G_2+8F_2\right)\right\}\right], \end{aligned} \tag{31a}$$

$$\begin{aligned}\frac{d}{dr}[N_{B+}+2t_{B+}]-x^3\frac{d}{dr}[N_{B-}+2t_{B-}] &= -\frac{2}{15}\left(\frac{p_{B\infty}r_0}{\beta_B\mu_{B\infty}}\right)\frac{r_0}{r^2}[7t_{B-}-2N_{B-}]\\ &+\frac{2}{5}\left\{\frac{n_{A\infty}}{n_{B\infty}+n_{A\infty}}\frac{r_0\beta_A}{\pi D_{AB}}\right\}\frac{r_0}{r^2}\bigg[\frac{5}{2}F_1-6G_2+M_A\left(12\frac{\beta_B}{\beta_A}G_2-10F_1\right)\\ &+M_A^2\left(10F_1+8\frac{m_B}{m_A}F_2-8\frac{\beta_B}{\beta_A}G_2\right)+\frac{A_2}{A_1}\bigg\{M_A\left(-8\frac{\beta_B}{\beta_A}G_2+10F_1\right)\\ &+M_A^2\left(10F_1-8\frac{m_B}{m_A}F_2+8\frac{\beta_B}{\beta_A}G_2\right)\bigg\}\bigg],\end{aligned} \qquad (31b)$$

where F_1, G_1 are constants proportional to the radial velocities and

$$F_2 = N_{A-}+\tfrac{3}{2}t_{A-}, \quad G_2 = N_{B-}+\tfrac{3}{2}t_{B-},$$

$$M_A = \frac{m_A}{m_A+m_B}, \quad M_B = \frac{m_B}{m_A+m_B}.$$

A_1 and A_2 are constants from the collision integral and D_{AB} is the binary diffusion coefficient defined (Jeans 1954) by

$$D_{AB} = \frac{kT_\infty}{m_A m_B A_1}\left(\frac{m_A+m_B}{K_{AB}}\right)^{\frac{1}{2}}\frac{1}{n_{A\infty}+n_{B\infty}}. \qquad (32)$$

Note that $(28a, b)$ state that the mass flux of each species is inversely proportional to the square of the radius. Since the inert gas has no velocity at the surface of the sphere, G_1 must be zero. This fact has been used in simplifying the collision terms. Equations $(29a, b)$ are the mass diffusion equations, $(30a, b)$ the energy conservation equations, and $(31a, b)$ the heat flux moment equations.

The eight equations (28)–(31) can be solved for the eight functions. However, it is possible to make an assumption that leads to great simplification with, probably, little loss in detail. Let us assume that the two species have the same mean temperature at any point, i.e.

$$T_A(r) = T_B(r), \qquad (33a)$$

or

$$(t_{A+}-xt_{A-}) = (t_{B+}-xt_{B-}). \qquad (33b)$$

This is obviously valid in the continuum limit. In the free molecule limit the temperatures are exactly equal when the accommodation coefficients are unity. We therefore expect $(33a)$ to be a good assumption. It is possible now to drop one moment equation, the last one, $(31b)$. In so doing the dependence of the flow quantities on $2p_{B\infty}/\beta_B\mu_{B\infty}$, the mean free path of the inert gas based on its partial density, will be lost. This dependence is however weak in the problem of evaporation and condensation, where diffusion and vapour kinetic control are the dominant factors. In any case, we assume (33) and drop the last moment equation, $(31b)$. Now, F_2 and G_2 are constants and the system of equations is readily integrated to give

$$N_{A-} = \tfrac{3}{2}F_1-\tfrac{1}{2}F_2, \quad t_{A-} = F_2-F_1, \qquad (34a,b)$$

$$N_{B-} = -\tfrac{1}{2}G_2, \quad t_{B-} = G_2, \qquad (34c,d)$$

$$t_{A+} = \frac{r_0}{r}[(I_1 - H_3)F_1 + I_2F_2 + I_3G_2] + (I_0 - H_2), \tag{34e}$$

$$N_{A+} = \frac{r_0}{r}[(2H_3 - I_1)F_1 - I_2F_2 - I_3G_2] + (2H_2 - I_0), \tag{34f}$$

$$t_{B+} = t_{A+} + \left(1 - \frac{r_0^2}{r^2}\right)^{\frac{1}{2}}(t_{B-} - t_{A-}), \tag{34g}$$

$$N_{B+} = H_1 - \frac{n_{A\infty}}{n_{B\infty}}(N_{A+} + t_{A+}) - t_{B+}, \tag{34h}$$

where

$$\frac{2r_0p_{A\infty}}{\beta_A\mu_{A\infty}} = \frac{r_0}{l_{A\infty}}, \quad L_1 = \frac{m_A}{m_B},$$

$$H_3 = \frac{n_{B\infty}}{n_{A\infty} + n_{B\infty}}\frac{r_0\beta_A}{\pi D_{AB}},$$

$$I_1 = -\frac{2}{3}\frac{r_0}{l_{A\infty}} - \frac{2}{5}H_3\left(5M_A - 10L_1M_B^2 + 10\frac{A_2}{A_1}L_1M_B^2\right),$$

$$I_2 = \frac{8}{15}\frac{r_0}{l_{A\infty}} - \frac{2}{5}H_3\left(-6 + 12M_B - 8M_B^2 - 8\frac{A_2}{A_1}M_B + 8\frac{A_2}{A_1}M_B^2\right),$$

$$I_3 = -\tfrac{16}{5}H_3L_1^{\frac{3}{2}}M_B^2\left(1 - \frac{A_2}{A_1}\right),$$

Note that we have six constants of integration, F_1, F_2, G_2, H_1, H_2 and I_0. The constant G_1 was set equal to zero earlier as it is proportional to the gas mass flux. In setting $T_A = T_B$ we lost another constant and also one of the temperature conditions at infinity.

Now the boundary conditions at infinity (10) imply that, for $r \to \infty$;

$$t_{A2} \to 0, \quad N_{A2} \to 0, \quad N_{B2} \to 0. \tag{35a, b, c}$$

The condition (12) on the inert gas implies that

$$t_{B1} = \frac{T_L - T_\infty}{T_\infty} = \frac{\Delta T}{T_\infty} \quad \text{at} \quad r = r_0. \tag{36}$$

The boundary conditions (14) subject to the accommodation coefficient restrictions (13) yield at $r = r_0$

$$N_{A1} + \tfrac{1}{2}t_{A1} = (1 - \alpha_m)(N_{A2} + \tfrac{1}{2}t_{A2}) + \alpha_m(N_L + \tfrac{1}{2}t_L), \tag{37a}$$

$$N_{A1} + \tfrac{3}{2}t_{A1} = (1 - \alpha_T)(N_{A2} + \tfrac{3}{2}t_{A2}) + \alpha_T(N_L + \tfrac{3}{2}t_L). \tag{37b}$$

The six constants can, now, be evaluated from the solutions (34) and the boundary conditions (35), (36) and (37).

Our chief interest is in the vapour mass flux which is given to first order by

$$\dot{m}_A = \rho_Av_A = \rho_{A\infty}\frac{\beta_A}{2\pi}F_1 = \frac{\rho_{A\infty}(2\pi R_AT_\infty)^{\frac{1}{2}}}{2\pi}F_1. \tag{38}$$

Some algebraic manipulations lead to the result,

$$F_1 = \frac{\alpha_m \left[\{1 + \tfrac{1}{2}\alpha_T a_2 R_A + (b_3 - \tfrac{1}{2}\alpha_T b_3 + \tfrac{1}{2}\alpha_T b_2)\, R_{AB}\} \dfrac{\Delta p}{p_{A\infty}} - \dfrac{1}{2}\dfrac{\Delta T}{T_\infty} \right]}{[1 + e_1 R_A + e_2 R_{AB} + e_3 R_A R_{AB} + e_4 R_{AB}^2]}, \tag{39}$$

where

$$\Delta p = p_L^* - p_{A\infty}, \quad \Delta T = T_L - T_\infty,$$

$$R_A = \frac{r_0}{l_{A\infty}}, \quad R_{AB} = \frac{n_{B\infty}}{n_{A\infty} + n_{B\infty}} \frac{r_0 \beta_A}{\pi D_{AB}},$$

$$a_1 = -\tfrac{2}{3}, \quad a_2 = \tfrac{8}{15},$$

$$b_1 = -\frac{2}{5}\left[5 \frac{m_A}{m_A + m_B} - 10 \left(\frac{m_A}{m_B}\right) \frac{m_B^2}{m_A + m_B} + 10 \frac{m_A m_B}{(m_A + m_B)^2}\right],$$

$$b_2 = -\frac{2}{5}\left[-6 + 12 \frac{m_B}{m_A + m_B} - 8 \frac{A_2}{A_1} \frac{m_B}{m_A + m_B} - 8 \frac{m_B^2}{(m_A + m_B)^2} \left(1 - \frac{A_2}{A_1}\right)\right],$$

$$b_3 = -\frac{16}{5} \frac{m_A (m_A m_B)^{\frac{1}{2}}}{(m_A + m_B)^2} \left(1 - \frac{A_2}{A_1}\right),$$

$$e_1 = \tfrac{1}{6}\alpha_m + \tfrac{2}{15}\alpha_T,$$

$$e_2 = -\tfrac{1}{4}\alpha_m b_1 + \tfrac{1}{4}\alpha_T b_2 + \tfrac{3}{4}\alpha_m + (1 - \tfrac{1}{4}\alpha_m - \tfrac{1}{4}\alpha_T)\, b_3,$$

$$e_3 = \tfrac{1}{4}\alpha_m \alpha_T a_2,$$

$$e_4 = \tfrac{1}{4}\alpha_m (2b_3 - \alpha_T b_3 + \alpha_T b_2).$$

4. Discussion

The result (39) gives the dependence of the evaporation rate on the pressure difference $(p_L^* - p_{A\infty})$ and the temperature difference $(T_L - T_\infty)$. Similar expressions exist for the energy fluxes, which are proportional to F_2 and G_2 respectively. We note that two dimensionless inverse Knudsen numbers R_A and R_{AB} enter the result. R_A is the ratio of the droplet radius to the mean free path of the vapour in the absence of the inert gas; R_{AB} is proportional to the ratio of the droplet radius to the diffusion coefficient divided by the sound speed in the vapour alone. From elementary kinetic theory, when the two species are of the same mass and size, the common mean free path l will be proportional to the ratio of the diffusion coefficient divided by the sound speed. In such a case only will R_{AB} be inversely proportional to the mean free path. We shall now consider various limiting cases.

The free molecule limit corresponds to the case where the two Knudsen numbers tend to infinity or $R_A \to 0$, $R_{AB} \to 0$. The formula for the mass flux then reduces to

$$\dot{m}_A = \alpha_m \frac{p_{A\infty}}{(2\pi R_A T_\infty)^{\frac{1}{2}}} \left[\frac{\Delta p}{p_{A\infty}} - \frac{1}{2} \frac{\Delta T}{T_\infty}\right].$$

This is precisely the linearized form of the effusion based Hertz–Knudsen formula. In the free molecule limit the inert gas cannot affect the transport of the vapour. This would be true for 'very small' droplets irrespective of the ambient conditions.

When no inert gas is present, we can set $n_{B\infty} = 0$. Since this implies that $R_{AB} = 0$, the result (39) for F_1 reduces to

$$F_1 = \frac{\alpha_m\left[\left\{1+\frac{4}{15}\alpha_T\frac{r_0}{l_{A\infty}}\right\}\frac{\Delta p}{p_{A\infty}}-\frac{1}{2}\frac{\Delta T}{T}\right]}{\left[1+(\frac{1}{6}\alpha_m+\frac{2}{15}\alpha_T)\frac{r_0}{l_{A\infty}}\right]}.$$

This is the kinetic controlled limit; diffusion is nonexistent and the mass flux depends on the Knudsen number of the vapour alone. This formula agrees with the result obtained earlier by the author (Shankar 1968). In the continuum limit we note that the mass flux depends on the pressure difference alone.

The other limiting case is when diffusion is rate controlling. This corresponds to: $R_{AB} \gg 1$, $R_{AB} \gg R_A$ and the formula for F_1 takes the form,

$$F_1 = \frac{(2/R_{AB})\,(\Delta p/p_{A\infty})}{\left[1+\frac{2}{R_{AB}}\left(\frac{e_2}{e_4}+\frac{e_3}{e_4}R_A\right)\right]}.$$

The net evaporation rate in this limit is given by

$$\Gamma_A = 4\pi r_0^2\rho_{A\infty}\frac{(2\pi R_A T_\infty)^{\frac{1}{2}}}{2\pi}F_1$$

$$= \frac{4\pi r_0\rho_{A\infty}D_{AB}\left(1+\frac{n_{A\infty}}{n_{B\infty}}\right)\left(\frac{p_L^*-p_{A\infty}}{p_{A\infty}}\right)}{\left[1+\frac{\pi D_{AB}}{r_0\beta_A}\left\{\frac{e_2}{e_4}+\frac{e_3}{e_4}\frac{r_0}{l_{A\infty}}\right\}\right]}.$$

In the continuum limit when $D_{AB}/r_0\beta_A \ll 1$ the formula reduces to Maxwell's result modified by the hydrodynamic flow correction $(1+n_{A\infty}/n_{B\infty})$.

Now Fuchs' results (7) applies to the case when $p_{A\infty} = 0$ or $l_{A\infty} = \infty$. This result can be rewritten in the form,

$$F_1\,(\text{Fuchs}) = \frac{1}{\left[1+\frac{2\pi D_{AB}}{r_0\beta_A}-\frac{\alpha l}{r_0+\alpha l}\right]}\,\frac{p_L^*-p_{A\infty}}{p_{A\infty}},$$

where we have set $\Delta = \alpha l$, where l is the mean free path and α is a constant. It is clear that Fuchs' result is of the right form, but, since e_2/e_4 is a complicated function of the mass ratios and the accommodation coefficients, detailed comparison is not possible in general. The numerical calculations presented next show that for the cases considered. Fuchs' result is excellent with α set equal to zero.

The theory developed here is strictly valid only for monatomic Maxwell molecules. However, the calculation should have a wider range of applicability, since (i) the intermolecular potential is of no importance in the free molecule limit, and (ii) in the continuum limit the form of the potential will affect only the gas properties. The restriction to monatomic gases is not a serious one, since vibrational and rotational exchanges will be unimportant at moderate temperatures. Bearing these remarks in mind, we present some calculations made for the practically useful case of water vapour–air mixtures at temperatures of 20 °C and 150 °C. The total pressure was assumed to be atmospheric in each case and the molecular mass ratio was taken to be 18/29 = 0·62. Then writing the vapour mass flux in the form,

$$\dot{m}_A = \frac{p_{A\infty}}{(2\pi R_A T_\infty)^{\frac{1}{2}}}\left[C_1\frac{\Delta p}{p_{A\infty}} - C_2\frac{\Delta T}{T_\infty}\right].$$

Figure 3 shows the variation of the coefficient C_1, of the pressure difference, with the droplet radius for the $T_\infty = 20$ °C case. It is clear that Maxwell's result is valid for droplets greater than $2\,\mu$. Fuchs's formula shows excellent agreement with the present calculation when the unknown factor α is set equal to zero (we have taken the mean free path to be $= 2\pi D_{AB}/\beta_A$). Droplets of radius $2 \times 10^{-3}\,\mu$ are within 1 % of the free molecule limit.

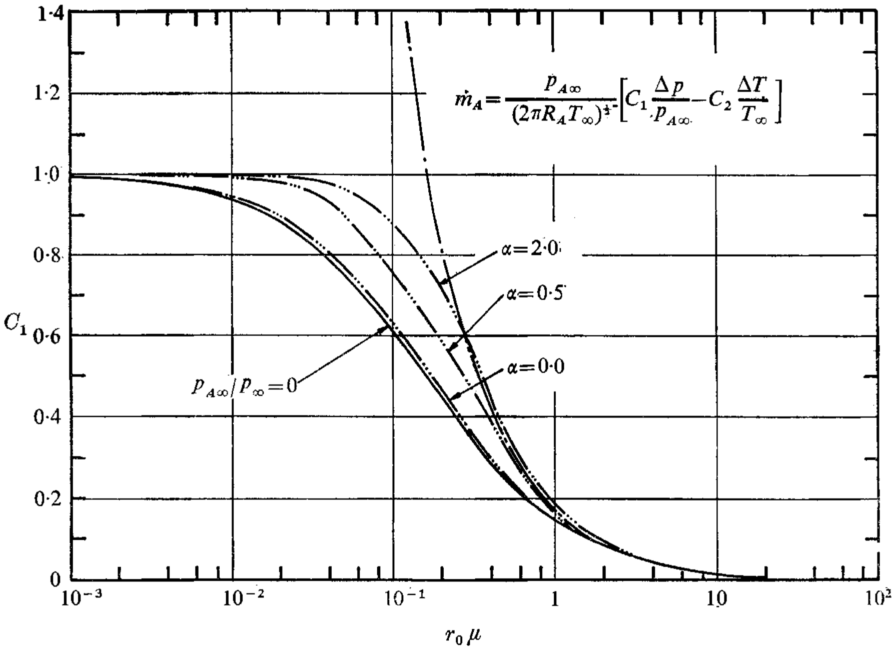

FIGURE 3. The dependence of the coefficient C_1 of the pressure difference on the droplet radius. The calculations are for a water vapour–air mixture, $T_\infty = 20$ °C, $\rho_{A\infty} = 0$, $\alpha_T = \alpha_m = 1$, $D_{AB} = 0{\cdot}25$ cm²/sec, $\mu_{A\infty} = 9{\cdot}7 \times 10^{-5}$ gm/cm sec. —·—, Maxwell; —···—, Fuchs; ——, moment calculation.

Figures 4a, b show the dependence of the coefficients C_1 and C_2 on the droplet radius and on the pressure ratio $p_{A\infty}/p_\infty$. The wide scope of the present calculation is clearly illustrated here: the free molecule limit, the continuum limit, the diffusion control limit and the kinetic control limit are all obtained from one formula. Once again the Maxwell result is valid for $r_0 > 4\mu$, and Fuchs' result is excellent with α set equal to zero. One particularly interesting feature is the

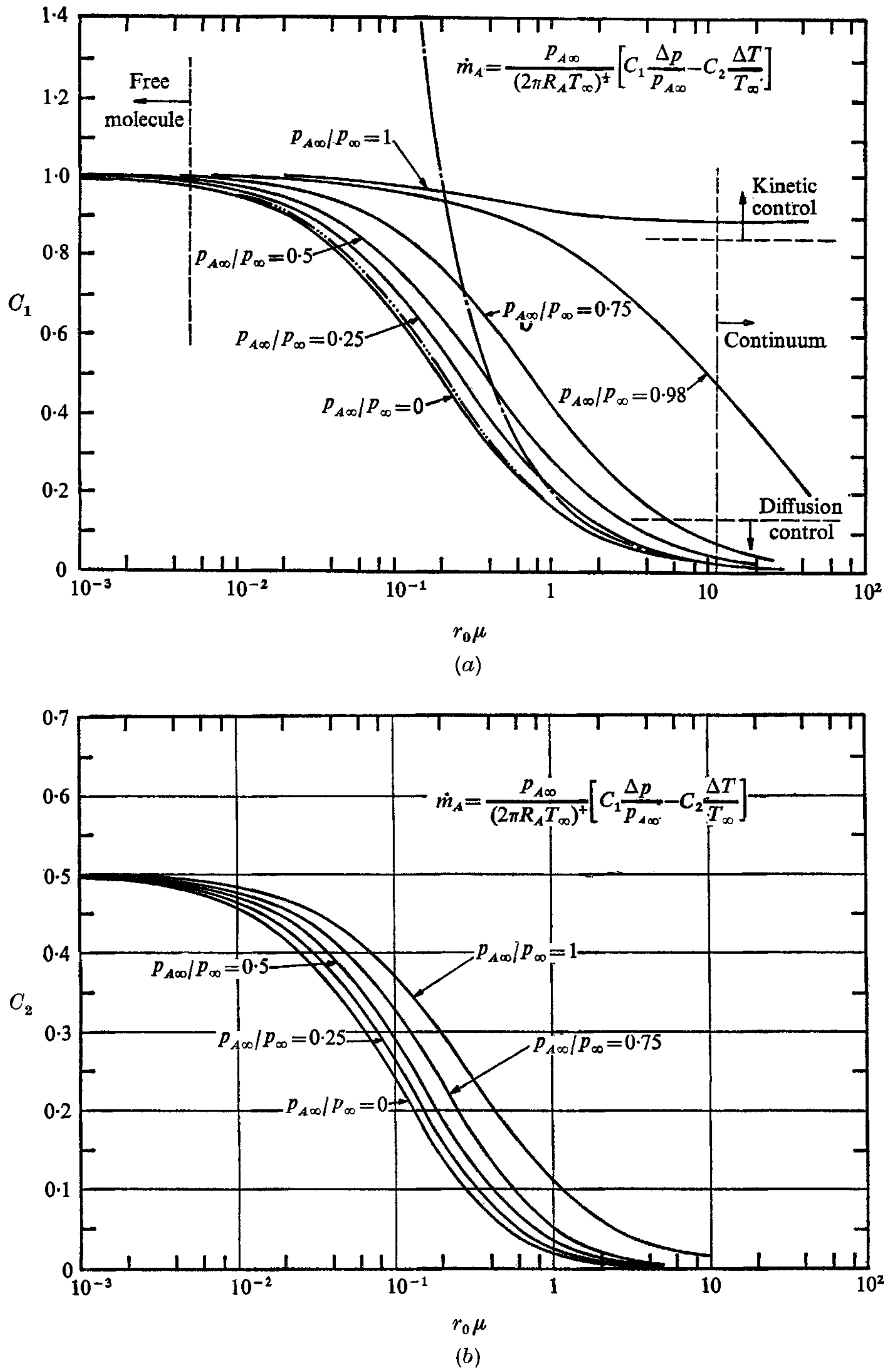

FIGURE 4. (a) The dependence of the coefficient C_1 on the droplet radius and the pressure ratio, $p_{A\infty}/p_\infty$. The calculations are for a steam–air mixture. $T_\infty = 150°$ C, $\alpha_T = \alpha_m = 1$, $D_{AB} = 0{\cdot}361\,\mathrm{cm^2/sec}$, $\mu_{A\infty} = 1{\cdot}54 \times 10^{-4}$ gm/cm sec. —·—, Maxwell; —···—, Fuchs, $\alpha = 0$; ——, moment calculation. (b) The dependence of the coefficient C_2 on the droplet radius and the pressure ratio $p_{A\infty}/p_\infty$. The steam–air conditions are the same as for (a).

considerable effect of a small quantity of inert gas. With just 2 % inert gas, diffusion becomes important for droplets greater than 0·5μ. However, in this case kinetic condensation is of equal importance for droplets of the order of 10–50μ.

The formulae obtained in this paper for the mass and energy fluxes can now be used to calculate the transient growth of small droplets by a quasi-steady analysis under a wide variety of conditions. We caution, however, that in view of all the approximations made in the analysis a quasi-steady calculation may give only a qualitative description of the actual transient problem.

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