Condensation and Evaporation of a Dilute Vapour on a Spherical Droplet

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The behaviour of a dilute vapour, diffusing in a non-condensable gas, has been investigated. The vapour condenses on, and evaporates from, a spherical droplet, and the appropriate Boltzmann equation has been formulated thus enabling the condensation rate to be calculated in a precise manner. In contrast to previous work on this problem, the saturation temperature of the droplet differs from that of the non-condensable gas and this leads to certain differences and difficulties in the calculations. Despite these difficulties, an approximate method has been developed which uses the integral form of the transport equation to express the condensation rate in a form which includes any type of vapour-gas interaction. This is an advance on previous work which was confined to simple model problems and restricted to isotropic scattering. An expression for the heat flux to the droplet is obtained and a method for calculating the vapour density and temperature is outlined. Finally, we stress the limitations of the method and suggest ways in which these may be overcome.

1. Introduction

The evaporation and condensation of a vapour on a surface is a significant field of research because it has important implications in aerosol growth, in heat transfer calculations and in related areas such as meteorology, astrophysics and environmental pollution. A useful survey and extensive bibliography on the subject has recently been presented by Fuchs and Sutugin [1]. In this survey, the problems of mass, heat and electric charge transfer to droplets are discussed and several simple methods of calculating the rates at which these processes proceed are outlined. Particular attention was payed to the case of mass transfer to a spherical droplet situated in a non-condensable gas. It was assumed that the vapour is at so low a density compared with that of the non-condensable gas that collisions between vapour molecules could be neglected, thus simplifying the problem and obviating the need for linearization. Indeed, an analogy with neutron transport theory exists [2] and results obtained in that field by Sahni [3] were employed directly to calculate the mass transfer to a droplet. This problem was subsequently treated by Loyalka [4] who used a one-term separable kernel (quasi-BGK model) with what amounted to a constant collision frequency. In the parlance of neutron transport theory this is equivalent to instantaneous thermalization on collision of a vapour molecule with a gas molecule together with the assumption of a mean free path proportional to velocity. In all cases considered, the scattering of vapour molecules by gas molecules was assumed to be isotropic in the laboratory system which, in turn, implied that the mass of a vapour molecule, m, was much smaller than the mass of a gas molecule, m_g. Thus the so-called "persistence of velocity" effect was neglected. A further assumption in the works cited above was that of a constant temperature throughout. Thus the temperatures of the vapour, the gas and the evaporated molecules were supposed to be equal.

The purpose of the present paper is to discuss the above phenomenon in greater generality. In particular, we shall formulate equations which allow an arbitrary degree of anisotropic scattering, thereby including persistence of velocity. We shall allow for any type of scattering interaction between vapour and gas molecules and, finally, we shall assume that, whilst the host gas is at a uniform temperature, the evaporated molecules are emitted at the appropriate saturation temperature; which is in general different from that of the gas.

This more general approach will reduce the ease with which the previous authors have calculated the mass transfer rate and other associated parameters, but will have the advantage of highlighting the sensitivity of the results to the physical properties of the gas and the vapour.

We shall apply our equations to condensation on a spherical droplet and develope an approximate expression for the condensation rate. Our results will be compared with those of previous calculations.

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2. The Equation of Transport and the Boundary Conditions

We consider a spherical droplet surrounded by a non-condensable gas and a dilute vapour. The situation is spherically symmetric and the distribution function of the vapour molecules is specified by the function $f(r, v, \mu)$. In this function, r is the radius vector taken from the centre of the droplet, v the speed and μ the cosine of the angle that the direction of the molecule makes with the radius vector. It is assumed that there are no vapour-vapour collisions and we may therefore write the Boltzmann transport equation for the vapour molecules as [5]

$$v\left\{\mu \frac{\partial}{\partial r} + \frac{1-\mu^2}{r} \frac{\partial}{\partial \mu}\right\} f(r, v, \mu) + V(v) f(r, v, \mu) = \int \mathrm{d}\boldsymbol{v}'\, v'\, \Sigma(\boldsymbol{v}' \to \boldsymbol{v})\, f(r, v', \mu') \qquad (1)$$

where $\mathrm{d}\boldsymbol{v}' \equiv 2\pi v'^2\, \mathrm{d}v'\, \mathrm{d}\mu'$.

$\Sigma(\boldsymbol{v}' \to \boldsymbol{v})\,\mathrm{d}\boldsymbol{v}$ is the differential cross section for a vapour molecule of velocity $\boldsymbol{v}'$ to be cast into the velocity range $(\boldsymbol{v}, \boldsymbol{v} + \mathrm{d}\boldsymbol{v})$ after collision with a gas molecule. $\Sigma(\boldsymbol{v}' \to \boldsymbol{v})$ depends linearly upon the density, N_g, and in a more complicated fashion on the temperature, T_g, of the non-condensable gas. Thus if N_g and T_g vary with position then $\Sigma(\boldsymbol{v}' \to \boldsymbol{v})$ will do so also. We shall assume that N_g and T_g are spatially independent, although in the immediate neighbourhood of the droplet this assumption may well be open to question.

The collision frequency $V(v) = v\,\Sigma(v)$ is related to $\Sigma(\boldsymbol{v}' \to \boldsymbol{v})$ in the following manner:

$$\Sigma(v) = \int_0^\infty \mathrm{d}v'\, v'^2\, \Sigma_0(v \to v') \qquad (2)$$

where we have expanded $\Sigma(\boldsymbol{v}' \to \boldsymbol{v})$ in spherical harmonics; viz.

$$\Sigma(\boldsymbol{v}' \to \boldsymbol{v}) = \sum_{l=0}^{\infty} \frac{2l+1}{4\pi} \Sigma_l(v' \to v)\, P_l(\mu_0)\,, \qquad (3)$$

μ_0 being the cosine of the angle between $\boldsymbol{v}$ and $\boldsymbol{v}'$ and $P_l(\mu_0)$ the Legendre polynomials. The boundary condition at $r = a$ may be stated as follows:

$$f(a, v, \mu) = F_s(v)\,; \quad 0 < \mu \leqq 1 \qquad (4)$$

where $F_s(v)$ is the Maxwellian distribution, i. e.

$$F_s(v) = N_s \left(\frac{m}{2\pi k T_s}\right)^{3/2} \exp\left(-\frac{m v^2}{2 k T_s}\right). \qquad (5)$$

In this expression N_s is the saturation density of the vapour and T_s the corresponding saturation temperature. The relation $N_s(T_s)$ is determined from an appropriate equation of state.

The boundary condition at infinity depends upon whether we have a source of vapour at infinity or on whether the vapour is generated only by evaporation from the droplet. The exact nature of the solution can best be described if we seek solutions to Eq. (1) in the following form:

$$f(r, v, \mu) = \sum_{l=0}^{\infty} \frac{2l+1}{4\pi} f_l(r, v)\, P_l(\mu)\,. \qquad (6)$$

Then by a generalization, to include velocity dependence, of some work due to Davison [2], we can note that the f_l assume the form

$$f_l(r, v) = 4\pi F_v(v) \left\{\Delta \delta_{0l} - \frac{l!}{2l+1} \frac{Q_l(r, v)}{r^{l+1}}\right\}. \qquad (7)$$

$F_v(v)$ is the equilibrium Maxwellian at the temperature of the host gas, viz:

$$F_v(v) = N_\infty \left(\frac{m}{2\pi k T_g}\right)^{2/2} \exp\left(-\frac{m v^2}{2 k T_g}\right) \qquad (8)$$

where N_∞ is the density of vapour at large distances from the droplet. Δ is unity when there is a current of particles (to be defined) from infinity, and zero when there is no such current.

The $Q_l(r, v)$ are functions which have the property

$$\lim_{r \to \infty} Q_l(r, v) = U_l(v) \qquad (9)$$

and only depend significantly on position within a mean free path of the droplet surface. A deeper discussion of the significance of the Q_l may be found in Williams [6].

Equations for the $U_l(v)$ may be found by inserting the asymptotic form of (6) into (1) and collecting up coefficients of $P_l(\mu)$. The result is that

$$-U_{l-1}(v) + \Sigma(v)\, U_l(v) = \int_0^\infty \mathrm{d}v'\, v'^2\, \Sigma_l(v \to v')\, U_l(v') \qquad (10)$$

where we have employed the detailed balance condition [7]:

$$v'\, \Sigma_l(v' \to v) F_v(v') = v\, \Sigma_l(v \to v') F_v(v)\,. \qquad (11)$$

In the set of Eqs. (10), $U_{-1} \equiv 0$ and U_0 is equal to a constant which is denoted by A. Thus setting $U_l = A\, \widetilde{U}_l$ we can obtain the $\widetilde{U}_l$ as universal functions of the scattering kernel $\Sigma(\boldsymbol{v}' \to \boldsymbol{v})$. As an example, in the case of isotropic scattering, we have $\Sigma_l(v' \to v) = 0,\ l > 0$ and hence

$$\widetilde{U}_1(v) = 1/\Sigma(v) \tag{12}$$

i. e. $\widetilde{U}_1$ is equal to the mean free path.

3. The Integral Equations

It is convenient for the study of this problem to convert the integro-differential Eq. (1) into a purely integral form. This may be readily, though somewhat laboriously done by using the method of characteristics. The result may be written thus:

$$\begin{aligned} r\,v\,f_l(r,v) = {} & 2\pi\,r\,v\,F_s(v) \int\limits_{(1-a^2/r^2)^{1/2}}^{1} \mathrm{d}\mu\,P_l(\mu)\,\exp\{\Sigma(v)\,[(a^2-r^2+r^2\mu^2)^{1/2} - r\mu]\} \\ & + \sum_{l'=0}^{\infty} \frac{2l'+1}{2} \int\limits_a^\infty \mathrm{d}r'\,r'\,K_{ll'}(r,r';v) \int\limits_0^\infty \mathrm{d}v'\,v'^3\,\Sigma_{l'}(v'\to v)\,f_{l'}(r',v') \end{aligned} \tag{13}$$

where

$$K_{ll'}(r,r';v) = \int\limits_{|r-r'|}^{\sqrt{r^2-a^2}+\sqrt{r'^2-a^2}} \frac{\mathrm{d}t}{t}\,e^{-\Sigma(v)t}\,P_l\left(\frac{r^2-r'^2+t^2}{2rt}\right) P_{l'}\left(\frac{r^2-r'^2-t^2}{2r't}\right). \tag{14}$$

We now insert (7) into (13) and after some reduction obtain

$$\begin{aligned} \frac{l!}{2l+1} F_v(v)\,\frac{Q_l(r,v)}{r^l} = {} & \tfrac{1}{2} F_v(v) \sum_{l'=0}^{\infty} l'! \int\limits_a^\infty \frac{\mathrm{d}r'}{r'^{l'}} K_{ll'}(r,r';v) \int\limits_0^\infty \mathrm{d}v'\,v'^2\,\Sigma_{l'}(v\to v')\,Q_{l'}(r',v') \\ & + F_v(v)\{r\,\delta_{0l} - \tfrac{1}{2}\Sigma(v) \int\limits_0^\infty \mathrm{d}r'\,r'\,K_{l0}(r,r';v)\}\,\Delta \\ & - \tfrac{1}{2} F_s(v)\,r \int\limits_{(1-a^2/r^2)^{1/2}}^{1} \mathrm{d}\mu\,P_l(\mu)\,\exp\{\Sigma(v)\,[(a^2-r^2+r^2\mu^2)^{1/2} - r\mu]\}\,. \end{aligned} \tag{15}$$

However, it may be shown with some effort that

$$\frac{\Sigma}{2} \int\limits_a^\infty \mathrm{d}r'\,r'\,K_{l0}(r,r';v) - r\,\delta_{0l} \equiv -\tfrac{1}{2} r \int\limits_{(1-a^2/r^2)^{1/2}}^{1} \mathrm{d}\mu\,P_l(\mu)\,\exp\{\Sigma(v)\,[(a^2-r^2+r^2\mu^2)^{1/2} - r\mu]\}\,. \tag{16}$$

Let us denote this quantity by $S_l(r,v)$ whence (15) can be written as

$$\begin{aligned} \frac{l!}{2l+1} F_v(v)\,\frac{Q_l(r,v)}{r^l} = {} & \tfrac{1}{2} F_v(v) \sum_{l'=0}^{\infty} l'! \int\limits_a^\infty \frac{\mathrm{d}r'}{r'^{l'}} K_{ll'}(r,r';v)\,, \\ & \cdot \int\limits_0^\infty \mathrm{d}v'\,v'^2\,\Sigma_{l'}(v\to v')\,Q_{l'}(r',v') + [F_s(v) - F_v(v)\Delta]\,S_l(r,v)\,. \end{aligned} \tag{17}$$

Solutions of this coupled set of equations will lead to the quantities of interest.

4. The Condensation Rate

To calculate the amount of vapour condensing on the droplet per unit time, it is necessary to obtain the net current $\mathcal{J}(a)$. This quantity is by definition

$$\mathcal{J}(a) = 2\pi \int\limits_{-1}^{1} \mathrm{d}\mu\,\mu \int\limits_0^\infty \mathrm{d}v\,v^3\,f(a,v,\mu)\,. \tag{18}$$

The net condensation rate Φ is therefore

$$\Phi = 4\pi\,a^2\,m\,\mathcal{J}(a)\,. \tag{19}$$

Now it is readily seen by integrating Eq. (1) over all velocities that $\mathcal{J}(r)$ has the simple behaviour

$$r^2\,\mathcal{J}(r) = \mathrm{const}\,. \tag{20}$$

Thus, using (18), (6) and (7) we find that

$$\Phi = -\frac{4\pi}{3}\,4\pi\,m \int\limits_0^\infty \mathrm{d}v\,v^3\,Q_1(a,v)\,F_v(v) \tag{21}$$

which, since Φ is constant for all values of r, we may also write as

$$\Phi = -\frac{4\pi}{3}\,4\pi m\int_0^\infty \mathrm{d}v\,v^3\,Q_1(\infty,v)\,F_v(v) \quad \text{or} \quad \Phi = -\frac{4\pi}{3}\,4\pi m A\int_0^\infty \mathrm{d}v\,v^3\,\widetilde{U}_1(v)\,F_v(v)\,. \tag{22}$$

A knowledge of A, together with $\widetilde{U}_1$ from Eq. (10), will therefore enable us to compute Φ. Setting $l=1$ in (17) and then $r=a$, we find that the integral in (21) is given as follows:

$$\begin{aligned}\int_0^\infty \mathrm{d}v\,v^3\,Q_1(a,v)\,F_v(v) &= \frac{3\,a^2}{4}\int_0^\infty \mathrm{d}v\,v^3\,[\varDelta F_v(v) - F_s(v)]\\ &\quad + 3\sum_{l=0}^\infty l!\,(-)^l\int_0^\infty \mathrm{d}v\,v^3\,F_v(v)\int_0^\infty \mathrm{d}v'\,v'^2\,\Sigma_l(v\rightarrow v')\int_a^\infty \mathrm{d}r'\,S_l(r',v)\,\frac{Q_{l'}(r',v')}{r'^l}\end{aligned} \tag{23}$$

where we have used the readily, but tediously, proved relation:

$$S_l(r,v) = (-)^l\,\frac{a}{2}\,K_{1l}(a,r;v)\,. \tag{24}$$

Evaluating the integral over F_v and F_s in (23) we find that Φ may be written

$$\Phi = \Phi_f + (4\pi)^2\,m\sum_{l=0}^\infty l!\,(-)^l\int_0^\infty \mathrm{d}v\,v^3\,F_v(v)\int_0^\infty \mathrm{d}v'\,v'^2\,\Sigma_l(v\rightarrow v')\int_a^\infty \mathrm{d}r'\,S_l(r',v)\,\frac{Q_l(r',v')}{r'^l} \tag{25}$$

where

$$\Phi_f = \pi\,a^2\,m\,\{N_\infty\,\tilde{v}_g\,\varDelta - N_s\,\tilde{v}_s\} \tag{26}$$

is the condensation rate for free molecule flow, $\tilde{v}$ being equal to $(8\,k\,T/\pi\,m)^{1/2}$. The remaining term, involving the summation, represents the effect of collisions of the vapour molecules with gas molecules and, as will be seen, tends to reduce the condensation rate.

At this stage no further exact analysis can be carried out and in order to compute Φ it would in general be necessary to specify the scattering kernel and to numerically integrate the equations. It has, however, been customary to seek variational principles for Φ which can lead to a reduction in computational effort with only a small loss of accuracy. This has the advantage that an explicit algebraic form results, from which the importance on Φ of the physical parameters of the system can be deduced.

In the present case, it is possible to construct a variational principle but, unfortunately, unlike the work of previous investigators of this topic, the adjoint function is required. Whilst this does not preclude the use of the variational method it does make it less useful and less accurate. The reason for this additional complication can be traced to our boundary condition, Eq. (4), where the temperature $T_s \neq T_g$. This leads to the source term in (17) containing $F_s(v)$ which prevents detailed balance being used to simplify the equations. In the work of Sahni and of Loyalka it is assumed that $T_s = T_g$ and thus the source term can be written

$$S_l(r,v)\,(N_s - N_\infty\,\varDelta)\left(\frac{m}{2\pi\,k\,T_g}\right)^{3/2}\exp\left(-\frac{m\,v^2}{2\,k\,T_g}\right) \equiv S_l(r,v)\,(N_s - N_\infty\,\varDelta)\,\tilde{F}_v(v) \tag{27}$$

which allows the simplification mentioned, with $(N_s - N_\infty\,\varDelta)$ as the driving term in the equation. It seems clear, however, that this assumption is open to question. In the next section we shall discuss an approximate method of solution which enables an explicit analytical formula to be obtained for Φ thereby avoiding the necessity of a direct numerical treatment and of introducing adjoint functions.

5. Approximate Values for the Condensation Rate

Let us recall that at distances slightly greater than a mean free path from the droplet surface, the values of $Q_l(r,v)$ are virtually constant and equal to $A\,\widetilde{U}_l(v)$. Our approximation, therefore, is that in (25) we replace Q_l by its asymptotic value. This does not cause any significant error.

Let us define the average of a quantity $a(v)$ as follows

$$\langle a \rangle = \int_0^\infty \mathrm{d}v\, v^3 \tilde{F}_v(v)\, a(v) \tag{28}$$

then using (22) we see that the approximation described above leads to the following equation for Φ:

$$\frac{\Phi}{\Phi_\mathrm{f}} = 1 + \frac{3}{\langle U_1 \rangle} \frac{\Phi}{\Phi_\mathrm{f}} \sum_{l=0}^{\infty} l!\,(-)^l \int_0^\infty \mathrm{d}v\, v^3 \tilde{F}_v(v) \cdot \int_0^\infty \mathrm{d}v'\, v^2 \Sigma_l(v \to v')\, \tilde{U}_l(v') \int_a^\infty \mathrm{d}r\, \frac{S_l(r,v)}{r^l}. \tag{29}$$

This can be solved for Φ/Φ_f and leads to

$$\frac{\Phi}{\Phi_\mathrm{f}} \left\{ 1 - \frac{3}{\langle \tilde{U}_1 \rangle} \sum_{l=0}^{\infty} l!\,(-)^l [\langle \Sigma \tilde{U}_l \mathcal{T}_l \rangle - \langle \tilde{U}_{l-1} \mathcal{T}_l \rangle] \right\}^{-1} \tag{30}$$

where

$$\mathcal{T}_l(v) = \int_a^\infty \frac{\mathrm{d}r}{r^l} S_l(r,v) \tag{31}$$

and we have used (10) to eliminate any explicit dependence on $\Sigma_l(v \to v')$.

Consider now the cases examined by Sahni and Loyalka, both of whom assumed isotropic scattering. The general result for this case leads to

$$\Phi/\Phi_\mathrm{f} = \{1 - (3/\langle l \rangle)\, \langle \Sigma\, \mathcal{T}_0 \rangle\}^{-1} \tag{32}$$

with $l = \Sigma^{-1}$ being the mean free path. $\mathcal{T}_0$ can be evaluated analytically and we can write

$$\frac{\Phi_\mathrm{f}}{\Phi} = \frac{1}{2} + \frac{3a}{4} \frac{\langle 1 \rangle}{\langle l \rangle} + \frac{3}{2\langle l \rangle} \left\langle l \int_0^\infty \frac{s E_3(s)\, \mathrm{d}s}{\sqrt{s^2 + a^2 \Sigma^2}} \right\rangle. \tag{33}$$

For $a \to 0$, $\Phi \to \Phi_\mathrm{f}$ as we expect and as indeed is obeyed by the general expression (30). For large values of a we find

$$\Phi \sim \frac{4}{3a} \frac{\langle l \rangle}{\langle 1 \rangle} \Phi_\mathrm{f} \equiv \Phi_\infty = 4\pi a D_0 m N_\infty \left\{ \Delta - \frac{N_\mathrm{s}}{N_\infty} \left(\frac{T_\mathrm{s}}{T_\mathrm{g}} \right)^{3/2} \right\} \tag{34}$$

where D_0, the diffusion coefficient of vapour molecules in the non-condensable gas, is defined as

$$D_0 = \frac{4\pi}{3} \langle \tilde{U}_1 \rangle \cong \frac{4\pi}{3} \langle l \rangle \tag{35}$$

and $\langle 1 \rangle = \tilde{v}_g/4\pi$.

Equation (34) is the correct continuum limit as given by others, except that we have $T_\mathrm{s} \neq T_\mathrm{g}$. If $\Delta = 0$, the rate of loss of mass of the droplet is given.

Φ/Φ_f as described by (33) can be cast into a more convenient form if we write it as

$$\Phi = \Phi_\infty/(1 + \lambda/a) \tag{36}$$

λ being the conventional slip coefficient, or in neutron transport jargon the extrapolation distance. Comparing (36) with (33) we note that

$$\lambda = \frac{2}{3} \frac{\langle l \rangle}{\langle 1 \rangle} \left\{ 1 + \frac{3}{\langle l \rangle} \left\langle l \int_0^\infty \frac{s E_3(s)\, \mathrm{d}s}{\sqrt{s^2 + a^2 \Sigma^2}} \right\rangle \right\}. \tag{37}$$

For $a \to 0$, $\lambda \to 4\langle l \rangle / 3\langle 1 \rangle$, whilst for large a, $\lambda \to 2\langle l \rangle / 3 \langle 1 \rangle$. For the case of a cross section independent of velocity we have $4/3 \geqq \lambda/l \geqq 2/3$ as $0 \leqq a \leqq \infty$ which is to be compared with Sahni's very accurate result $4/3 \geqq \lambda/l \geqq 0.71\ldots$

In the case of a constant collision frequency such that

$$l(v) = \tilde{l}_0 (m/2kT_\mathrm{g})^{1/2}\, v$$

we find that $\langle l \rangle / \langle 1 \rangle = 3\sqrt{\pi}\, \tilde{l}_0/4$, which leads to the limits $\sqrt{\pi} \geqq \lambda/\tilde{l}_0 \geqq \sqrt{\pi}/2$ $(= 0.887)$. Loyalka, using the variational method, obtains $\sqrt{\pi} \geqq \lambda/\tilde{l}_0 \geqq (\sqrt{\pi}/4 + 1/\sqrt{\pi}) = 1.0073$. Thus the large a limits differ by about 12% in this case and in Sahni's case by about 6%. We have not computed any intermediate values but it is clear that our method of approximation is a reasonable one.

For the general case of anisotropic scattering, (30) may be cast into the form of (36) with D_0 defined exactly by (35) and with λ given by

$$\lambda = \frac{16\pi}{3 v_\mathrm{g}} \left\{ \langle \tilde{U}_1 \rangle - \frac{1}{2} \langle l \rangle + \frac{3}{2} \left\langle l \int_0^\infty \frac{\mathrm{d}s\, s E_3(s)}{\sqrt{s^2 + a^2 \Sigma^2}} \right\rangle - 3 \sum_{l=0}^{\infty} l!\,(-)^l [\langle \Sigma \tilde{U}_l \mathcal{T}_l \rangle - \langle \tilde{U}_{l-1} \mathcal{T}_l \rangle] \right\}. \tag{38}$$

Again the limiting cases are of interest. As $a \to 0$ we note that

$$\lambda \to (16\pi/3\tilde{v}_\mathrm{g})\, \langle U_1 \rangle = \tfrac{4}{3}\, (D_0/\tilde{v}_\mathrm{g}). \tag{39}$$

For $a \to \infty$, we use the fact that

$$\mathcal{T}_l \sim -\frac{1}{2\Sigma a^{l-1}} \int_0^1 \mu P_l(\mu)\, \mathrm{d}\mu \tag{40}$$

and hence that

$$\lambda \to \tfrac{2}{3}\, D_0/\tilde{v}_{\mathrm{g}}\,. \tag{41}$$

$D_0/\tilde{v}_{\mathrm{g}}$ is the mean free path corrected for persistence of velocity.

One important point that should be stressed in this analysis is that no specific knowledge of $\Sigma_0(v' \to v)$ is required, only its weighted average $\Sigma(v)$. It is true that the higher components $\Sigma_l(v' \to v)$, $l > 0$, are required but the sensitivity of λ to the *differential* nature of these quantities is of second order. Thus it would be quite sufficient for many purposes to set

$$\Sigma_l(v' \to v) = \Sigma(v)\, b_l(v)\, \delta(v - v')/v^2\,,$$

where $b_1(v)$ for example is the mean cosine of scattering in the laboratory system [7]. Moreover, as we have seen, λ does not depend at all on the $\Sigma_l(v' \to v)$, $l > 1$, for small and large a. The sensitivity to the $\Sigma_l(v' \to v)$ for intermediate values of a remains to be calculated.

6. Approximations for the Density, Temperature and Heat Flux

From the conventional definitions, we find that the vapour density N, temperature T and heat flux Ψ are given by

$$N(r) = \Delta N_\infty - \frac{4\pi}{r} \int_0^\infty \mathrm{d}v\, v^2 F_v(v)\, Q_0(r, v)\,, \tag{42}$$

$$\tfrac{3}{2} k N(r) T(r) = \Delta\, \tfrac{3}{2}\, k N_\infty T_{\mathrm{g}} - \frac{2\pi m}{r} \int_0^\infty \mathrm{d}v\, v^4 F_v(v)\, Q_0(r, v) \tag{43}$$

and

$$\mathcal{J}_{\mathrm{h}}(r) = -\frac{2\pi m}{3 r^2} \int_0^\infty \mathrm{d}v\, v^5 F_v(v)\, Q_1(r, v) \qquad \text{where} \quad \Psi = 4\pi a^2 \mathcal{J}_{\mathrm{h}}(a)\,. \tag{44}$$

Estimates of the integral terms are readily obtained from (17), thus

$$F_v(v) Q_0(r, v) = [F_{\mathrm{s}}(v) - F_v(v)\Delta]\; S_0(r, v) + \tfrac{1}{2} F_v(v) \sum_{l=0}^{\infty} l! \int_0^\infty \frac{\mathrm{d}r'}{r'^l} K_{0l}(r, r'; v) \int_0^\infty \mathrm{d}v'\, v'^2\, \Sigma_l(v \to v')\; Q_l(r', v')\,. \tag{45}$$

We can estimate this term by the process described above in which, on the right hand side, $Q_l(r, v)$ is set equal to its asymptotic value. Since A has already been calculated, an accurate description of the macroscopic parameters $N(r)$ and $T(r)$ can be obtained even up to the droplet surface. Indeed it is the values at the droplet surface that are of most interest since we wish to obtain the jump conditions $N(a) - N_{\mathrm{s}}$ and $T(a) - T_{\mathrm{s}}$. We shall not continue this process any further at this time for N or T, but the value of the heat flux Ψ at the surface will be calculated in more detail. This can be obtained rather easily from (23) with a change in velocity weighting. Thus, with $\Psi = 4\pi a^2 \mathcal{J}_{\mathrm{h}}(a)$,

$$\Psi = -\frac{2\pi m}{3}\, 4\pi \int_0^\infty \mathrm{d}v\, v^5 F_v(v)\, Q_1(a, v) \tag{46}$$

where

$$\int_0^\infty \mathrm{d}v\, v^5 F_v(v) Q_1(a, v) = \frac{3a^2}{4} \int_0^\infty \mathrm{d}v\, v^5 [\Delta F_v(v) - F_s(v)] + 3A \sum_{l=0}^{\infty} l!\,(-)^l \int_0^\infty \mathrm{d}v\, v^5 F_v(v) \int_0^\infty \mathrm{d}v'\, v'^2\, \Sigma_l(v \to v')\, \tilde{U}_l(v')\, \mathcal{J}_l(v)\,. \tag{47}$$

Rearranging, we find

$$\Psi = \Psi_{\mathrm{f}} + 2\pi \frac{\Phi}{D_0} \sum_{l=0}^{\infty} l!\,(-)^l \int_0^{\infty} \mathrm{d}v\, v^5 \tilde{F}_v(v)\, \mathcal{T}_l(v) \quad [\Sigma(v)\tilde{U}_l(v) - \tilde{U}_{l-1}(v)] \tag{48}$$

where

$$\Psi_{\mathrm{f}} = 2\pi a^2 [\Delta N_\infty k T_{\mathrm{g}} \tilde{v}_{\mathrm{g}} - N_{\mathrm{s}} k T_{\mathrm{s}} \tilde{v}_{\mathrm{s}}] \tag{49}$$

is the heat flux for free molecule flow. Thus for $a \to 0$, $\Psi \to \Psi_{\mathrm{f}}$.

For the general case with the $l = 0$ term only, we can write

$$\Psi = 2\pi a^2 k N_{\mathrm{s}} \tilde{v}_{\mathrm{s}} (T_{\mathrm{g}} - T_{\mathrm{s}}) + 2\pi a^2 k T_{\mathrm{g}} [\Delta N_\infty \tilde{v}_{\mathrm{g}} - N_{\mathrm{s}} \tilde{v}_{\mathrm{s}}] \frac{\lambda}{\lambda + a}$$

$$+ \frac{4\pi a^2}{a+\lambda} [\Delta N_\infty \tilde{v}_{\mathrm{g}} - N_{\mathrm{s}} \tilde{v}_{\mathrm{s}}] \frac{\pi m}{\tilde{v}_{\mathrm{g}}} \left[\tfrac{1}{3} \langle l \rangle^* - \left\langle l \int_0^{\infty} \frac{\mathrm{d}s\, s\, E_3(s)}{\sqrt{s^2 + a^2 \Sigma^2}} \right\rangle^* \right] \tag{50}$$

where $\langle \ldots \rangle^*$ is defined as

$$\langle a \rangle^* = \int_0^{\infty} \mathrm{d}v\, v^5 \tilde{F}_v(v)\, a(v)\,.$$

For large values of radius

$$\Psi \sim 2\pi a^2 k N_{\mathrm{s}} \tilde{v}_{\mathrm{s}} (T_{\mathrm{g}} - T_{\mathrm{s}}) + 2\pi a k T_{\mathrm{g}} [\Delta N_\infty \tilde{v}_{\mathrm{g}} - N_{\mathrm{s}} \tilde{v}_{\mathrm{s}}] (\lambda + \lambda^*) \tag{51}$$

where

$$\lambda^* = \frac{\pi m}{\tilde{v}_{\mathrm{g}}} \frac{2}{3} \frac{\langle l \rangle^*}{k T_{\mathrm{g}}} \equiv \frac{2}{3} \int_0^{\infty} \mathrm{d}x\, x^5 e^{-x^2} l(x) \tag{52}$$

and is analogous to the normal slip coefficient λ.

The physical explanation of this is as follows: the first term in (51) is due to the temperature difference between gas and droplet at the surface. The second term, however, is due to diffusion of particles towards the droplet surface thereby either enhancing or decreasing the heat flux according to whether $\Delta N_\infty v_{\mathrm{g}} \gtreqless N_{\mathrm{s}} \tilde{v}_{\mathrm{s}}$.

If we consider the case when $T_{\mathrm{s}} = T_{\mathrm{g}}$, the heat flux is not zero unless $N_\infty = N_{\mathrm{s}}$. Furthermore, in the case of $\Delta = 0$, the droplet will lose heat at the rate

$$\Psi \sim -2\pi a k T_{\mathrm{g}} N_{\mathrm{s}} v_{\mathrm{g}} (\lambda + \lambda^*)\,. \tag{53}$$

7. Discussion and Conclusions

We have discussed in some detail the nature of vapour diffusion through a host gas, including also the influence of boundaries. It has not been necessary to restrict the basic analysis to small perturbations or to a small ratio of m/m_{g}. Indeed, in the situation discussed in this paper none of the usual gas-kinetic assumptions has been made or was even needed. This convenient fact arose simply from the neglection of vapour-vapour molecular collisions, thus converting the problem to one in the related field of neutron thermalization, about which much is known[7]. For the case of a pure vapour the situation would have been very different, for in that case linearization would have been essential and the usual restrictions implied by it would operate. As it is, the problem is very simple and the only type of mechanism causing condensation is that due to diffusion; Stefan flow, which arises from mass motion of the bulk fluid, is absent.

Despite the apparent simplicity of the problem considered here, there is one important restriction which has not been investigated. This concerns the temperature and density distribution of the host gas. Quite clearly, since $T_{\mathrm{s}} \neq T_{\mathrm{g}}$, there will be some effect on the host medium near the droplet surface giving rise, possibly, to temperature and density gradients and thereby making N_{g} and T_{g} functions of position. The only situation in which this would not arise is that of specular scattering of the gas molecules by the droplets: an unlikely situation. In principle, then, the problem should be considered as two separate calculations. In the first, the behaviour of the non-condensable gas is studied, with the vapour ignored but with the correct boundary conditions at the surface of the sphere. Naturally, such a calculation would require the linearization technique. Having obtained $N_g(r)$ and $T_g(r)$ and possibly $U_g(r)$, the bulk flow velocity, these would be inserted into the cross section $\Sigma(\boldsymbol{v}' \rightarrow \boldsymbol{v})$ for the vapour problem and then the calculation for that would be carried out. Whilst no linearization is required, the dependence of the cross section on position would complicate the analysis considerably and make a direct numerical approach the most suitable method [5].

In spite of the objections listed above, we believe that the results obtained in this paper are of value and demonstrate how the previous work, as reported by Fuchs and Sutugin and by Loyalka, can be consistently improved upon.

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