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The Influence of Temperature Gradients on the Kinetic Boundary Layer Problem for a Condensing Droplet

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We extend an earlier method for solving kinetic boundary layer problems to the case of particles moving in a *spatially inhomogeneous* background. The method is developed for a gas mixture containing a supersaturated vapor and a light carrier gas from which a small droplet condenses. The release of heat of condensation causes a temperature difference between droplet and gas in the quasistationary state; the kinetic equation describing the vapor is the stationary Klein–Kramers equation for Brownian particles diffusing in a temperature gradient. By means of an expansion in Burnett functions, this equation is transformed into a set of coupled algebrodifferential equations. By numerical integration we construct fundamental solutions of this equation that are subsequently combined linearly to fulfill appropriate mesoscopic boundary conditions for particles leaving the droplet surface. In view of the intrinsic numerical instability of the system of equations, a novel procedure is developed to remove the admixture of fast growing solutions to the solutions of interest. The procedure is tested for a few model problems and then applied to a slightly simplified condensation problem with parameters corresponding to the condensation of mercury in a background of neon. The effects of thermal gradients and thermodiffusion on the growth rate of the droplet are small (of the order of 1%), but well outside of the margin of error of the method.

KEY WORDS: Condensation; kinetic boundary layers; Brownian motion; thermodiffusion; numerical integration methods.

1. INTRODUCTION AND SURVEY

To calculate the growth rate of a liquid droplet condensing from a gas mixture containing its saturated vapor$^{(1-3)}$ during the stage in which its radius is comparable to the mean free path in the gas, one must determine

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the structure of the kinetic boundary layer that develops around the droplet. This in turn requires solving the Boltzmann equation for the space surrounding the droplet, which far enough below the critical point can be assumed to be spherical. Since the temperature of the droplet is typically only a few percent higher than that of the gas at infinity,(3) it appears reasonable to base such a treatment on the *linear* Boltzmann equation, in which the collision operator is linearized around the equilibrium state of the gas at infinity. Recently, methods were developed that allow the determination of the growth rate to an accuracy of better than 1% within the context of the linear Boltzmann equation.(3-6) Once such an accuracy has been reached, one should also try to estimate the magnitude of effects not contained in this simplest linear description. The logical next step is to consider a Boltzmann equation linearized around an appropriate *local equilibrium distribution.*

Though the basic strategy used in our earlier papers to solve kinetic boundary layer problems—writing the solution as a linear combination of fundamental solutions, with coefficients chosen to satisfy the boundary conditions at infinity and at the droplet surface—can still be used, the techniques used to obtain the fundamental solutions must be modified. By expanding around a space-dependent local equilibrium solution, one obtains a linear kinetic equation with a space-dependent collision operator. As a consequence, the space dependence of the fundamental solutions can no longer be expressed in terms of known functions (spherical Hankel functions of imaginary argument); hence, a larger part of our program has to be carried out by purely numerical methods. However, we can still exploit the spherical symmetry of our problem to reduce its complexity. As before,(3,4) this is done by means of an expansion in terms of Burnett functions in the velocity variable. This reduces the partial differential equation for the distribution function to a set of coupled ordinary differential equations for the space-dependent expansion coefficients. For this set of equations we introduce a novel general numerical solution procedure. Our method enables one to solve kinetic boundary layer problems for linear kinetic equations obtained by linearization around a rather arbitrary spherically symmetric local equilibrium state. However, in the present paper we shall confine ourselves to the specific application discussed in the preceding paragraph.

Though one may expect the theory developed in this paper to provide a significant improvement even if the local equilibrium reference state is only a rough approximation to the actual state of the gas mixture, we shall introduce our method for a system for which such a picture is also well justified physically. The system considered is a light carrier gas with a small admixture of a vapor consisting of heavy molecules. In such a system, collisions between the vapor molecules are much less important than collisions of vapor molecules with the carrier gas. Hence, the distribution function for the vapor molecules obeys a *linear* kinetic equation that, moreover, can be well approximated by the Klein–Kramers(7,8) equation for noninteracting Brownian particles. However, one must take into account that the temperature of the background medium is inhomogeneous, due to the heat of condensation released at the droplet. On the other hand, the kinetic boundary layer for the gas is thinner than the one for the vapor, due to the difference in mean free paths. Hence, the gas can be considered to be in local equilibrium till very close to the droplet surface; thus the gas is characterized completely by its temperature profile.

The Klein–Kramers equation for Brownian motion in a medium with inhomogeneous temperature was discussed in an earlier paper.(9) In Section 2 we state the results of that paper and show how the phenomenological parameters appearing in that equation, the friction constant and the thermophoretic force, should be chosen to obtain a correct description of diffusion and thermodiffusion in a gas mixture with a given temperature profile. In Section 3 we then formulate the boundary value problem that must be solved to obtain the droplet growth rate. The treatment closely follows an earlier paper treating condensation from a pure vapor.(3) We also propose a simple first approximation for the temperature profile in the gas.

In Section 4 we show how the modified Klein–Kramers equation can be transformed into an infinite set of coupled equations for the Burnett moments of the distribution function. For the case of constant temperature, a presumably complete set of fundamental solutions of truncated versions of this hierarchy could be constructed explicitly by means of a suitable ansatz, and the boundary problem could be solved by constructing a suitable linear combination of these special solutions. In the presence of a temperature gradient, the explicit form of the fundamental solutions is no longer known, so we chose to construct them by integrating the set of moment equations numerically. The system of equations shows a severe numerical instability, however, for reasons inherent in the physics of the problem. A method to deal with this instability is also proposed in Section 4. In Section 5 we test the proposed numerical procedure, and estimate the accuracy that can be reached with it, by applying it to the case of constant temperature, and comparing with the known semianalytic solution of that problem.

In Section 5 we also treat some simple model problems containing temperature gradients, and study various convergence properties of our procedure. In Section 6 the method is used to treat a simplified version of the actual condensation problem, using parameters that correspond to condensation of mercury vapor in a background of neon. This first semirealistic application allows one to obtain estimates for the influence of the various physical effects included in our description. Since the effects turn out to be small, the simple approximation suffices for the case considered; a more consistent treatment is in principle possible with our method, however. In the concluding section we summarize the results and limitations of our treatment and discuss some possible further applications, both to more realistic condensation problems and to other problems involving kinetic boundary layers.

2. BASIC EQUATIONS

The distribution function $P(\mathbf{v}, \mathbf{r}, t)$ for the velocities $\mathbf{v}$ and positions $\mathbf{r}$ of an assembly of noninteracting Brownian particles moving in a background medium with temperature $T=(k\beta)^{-1}$ evolves in time according to the Klein–Kramers equation$^{(7,8)}$

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}}\right) P(\mathbf{v}, \mathbf{r}, t)=\gamma \frac{\partial}{\partial \mathbf{v}}\cdot\left(\mathbf{v}+\frac{1}{m\beta}\frac{\partial}{\partial \mathbf{v}}\right) P(\mathbf{v}, \mathbf{r}, t) \tag{2.1}$$

where m is the mass and γ the friction coefficient of the particles. In an earlier paper$^{(9)}$ we studied the case where β and γ depend upon position. We showed that the diffusion equation derived from (2.1) by the Chapman–Enskog procedure$^{(10)}$ does not describe thermodiffusion. To include this effect, a term

$$\frac{\mathbf{F}(\mathbf{r})}{m}\cdot\frac{\partial}{\partial \mathbf{v}} P \qquad \text{with} \quad \mathbf{F}(\mathbf{r})=a(\mathbf{r})\frac{dT}{d\mathbf{r}} \tag{2.2}$$

must be added on the left-hand side of (2.1).

As we shall apply (2.1) to the motion of heavy vapor molecules in a light background gas, we must choose $\gamma(\mathbf{r})$ and $a(\mathbf{r})$ in such a way that the equation obtained for $n_V(\mathbf{r}, t)=\int d\mathbf{v}\, P(\mathbf{v}, \mathbf{r}, t)$ by applying the Chapman–Enskog procedure to (2.1) supplemented by (2.2) is identical to the one obtained from kinetic theory for a binary gas mixture.$^{(11)}$ The equation of continuity for n_V reads

$$\begin{aligned} \frac{\partial}{\partial t} n_V(\mathbf{r}, t) &= -\frac{\partial}{\partial \mathbf{r}}\cdot\mathbf{j}_V(\mathbf{r}, t) \\ \mathbf{j}_V(\mathbf{r}, t) &= \int d\mathbf{v}\, \mathbf{v} P(\mathbf{v}, \mathbf{r}, t) \equiv \mathbf{c}_V(\mathbf{r}, t)\, n_V(\mathbf{r}, t) \end{aligned} \tag{2.3}$$

The quantity $\mathbf{c}_V$ is the sum of the hydrodynamic velocity of the mixture and the diffusion velocity. As we shall be considering phenomena on a time scale much slower than the one needed for equalization of the total gas pressure and, moreover, shall be considering the limit

$$\rho_V = m_V n_V \ll m_G n_G = \rho_G \tag{2.4}$$

where quantities with index G refer to the background gas, the hydrodynamic velocity will always be vanishingly small [(2.4) ensures that the vapor flow towards a droplet does not translate into a hydrodynamic flow]. The velocity $\mathbf{c}_V$ is then given by(11)

$$\mathbf{c}_V = -D_{12}\left[\frac{n}{n_V}\frac{\partial}{\partial \mathbf{r}}\left(\frac{n_V}{n}\right) + \alpha_T \frac{\partial}{\partial \mathbf{r}} \ln T\right] \tag{2.5}$$

where n denotes the total density, D_{12} the binary diffusion coefficient for the vapor in the background gas, and α_T the thermal diffusion factor.

For spatially homogeneous β and γ, (2.1) leads to(7,8,10)

$$\frac{\partial n_V}{\partial t} = \frac{1}{m\beta\gamma} \nabla^2 n_V \tag{2.6a}$$

whereas (2.3) and (2.5) result in

$$\frac{\partial n_V}{\partial t} = D_{12} \nabla^2 n_V \tag{2.6b}$$

Hence, $\gamma(\mathbf{r})$ should be chosen in accordance with the Einstein relation

$$\gamma(\mathbf{r}) = [m_V \beta(\mathbf{r}) D_{12}(\mathbf{r})]^{-1} \tag{2.7}$$

The lowest-order stationary solution of (2.1) for the one-dimensional version of (2.1) supplemented with (2.2) reads(9)

$$\frac{n_V(x)}{n(x)} = \frac{n_V(x)}{p\beta(x)} = \text{cst} \cdot \exp\left[\int_{x_0}^{x} dx'\, \beta(x')\, a(x')\, \frac{dT(x')}{dx'}\right] \tag{2.8a}$$

which implies

$$\frac{d}{dx}\left(\frac{n_V}{n}\right) = \frac{n_V}{n} \beta(x)\, a(x) \frac{dT}{dx} \tag{2.8b}$$

whereas putting $\mathbf{c}_V$ equal to zero in (2.5) results in

$$\frac{d}{dx}\left(\frac{n_V}{n}\right) = -\frac{n_V}{n} \alpha_T \frac{1}{T}\frac{dT}{dx} \tag{2.8c}$$

Hence, we should take

$$a(\mathbf{r}) = -k\alpha_T(\mathbf{r}) \tag{2.9}$$

in (2.2) to obtain consistency with the hydrodynamics of binary mixtures.

For the quantities D_{12} and α_T one may take experimental values for the limit of low vapor concentration. In our calculations we shall employ the values derived from kinetic theory (in first order) for a mixture of Lennard-Jones molecules. For D_{12} this means [see (7.3-38b) of ref. 11]

$$D_{12} = \frac{3}{8\sqrt{\pi}} \left[\Omega^{(1,1)*}(T^*)\, n\sigma_{12}^2 \left(\frac{2m_{12}}{kT} \right)^{1/2} \right]^{-1} \tag{2.10a}$$

with

$$T^* = \frac{kT}{\varepsilon_{12}}, \qquad \varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2}, \qquad \sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2), \qquad \frac{1}{m_{12}} = \frac{1}{m_1} + \frac{1}{m_2} \tag{2.10b}$$

with m_i, ε_i, and σ_i the mass and the Lennard-Jones parameters of the two constituents, and $\Omega^{(l,r)*}$ the reduced Ω integrals tabulated in Table I-M of ref. 12. Our choice for ε_i and σ_i will be specified later. For the thermal diffusion ratio $k_T = n_V \alpha_T / n$ we use the expressions (8.2-50), (8.2-36), and (8.2-31) of ref. 12; for α_T in (2.9) we use the limiting value for n_V going to zero.

3. THE BOUNDARY VALUE PROBLEM

As argued in earlier papers,(4,3) it suffices for the discussion of condensation at temperatures far below the critical temperature to study *stationary* solutions of (2.1), supplemented with (2.2), for the space outside of a sphere of given radius. We shall further assume that the gas mixture far away from the condensing droplet is at equilibrium with temperature T_∞ and densities n_∞ and $n_{V\infty}$. It is then convenient to measure velocities and lengths in units of the thermal velocity v_{th} and the velocity persistence length l at infinity

$$v_{\text{th}} = (m_V \beta_\infty)^{-1/2}, \qquad l = \gamma_\infty^{-1} v_{\text{th}} \tag{3.1}$$

where γ_∞ is obtained by substituting the values at infinity in (2.7) and (2.10). We further introduce the abbreviations

$$t = T/T_\infty, \qquad G = \gamma/\gamma_\infty \tag{3.2}$$

For the latter quantity we obtain, using the ideal gas equation of state for the mixture,

$$G(r)=\frac{\Omega^{(1,1)*}[t(r)\,T_\infty^*]}{\Omega^{(1,1)*}(T_\infty^*)}\,t(r)^{-1/2} \tag{3.3}$$

where T_∞^* is related to T_∞ by (2.10b).

In view of the symmetry of the problem, the solution of (2.1) depends only on the magnitudes of $\mathbf{v}$ and $\mathbf{r}$ and on $\mu=\hat{\mathbf{v}}\cdot\hat{\mathbf{r}}$, and it obeys the equation$^{(5)}$

$$\begin{aligned} v\mu\frac{\partial}{\partial r}P(v,\mu,r)=\Bigg[&-v\frac{1-\mu^2}{r}\frac{\partial}{\partial\mu}+G\frac{\partial}{\partial\mathbf{v}}\cdot\left(\mathbf{v}+\frac{\partial}{\partial\mathbf{v}}\right)+(t-1)\,G\nabla_{\mathbf{v}}^2\\ &+\alpha_T\frac{dt}{dr}\left(\mu\frac{\partial}{\partial v}+\frac{1-\mu^2}{v}\frac{\partial}{\partial\mu}\right)\Bigg]P(v,\mu,r) \end{aligned} \tag{3.4}$$

The term on the left and the first term on the right correspond to the streaming term $\mathbf{v}\cdot\partial P/\partial\mathbf{r}$ in (2.1). The second and third terms correspond to the collision term in (2.1); as we shall later expand in terms of the eigenfunctions of the second term, the explicit form of these two terms in the variables v and μ will not be needed. The last term in (3.4) corresponds to the thermal diffusion correction (2.2).

We shall be looking for solutions of (3.4) for a given temperature profile, such that the density $n_V(r)$ approaches $n_{V\infty}$ for $r\to\infty$ and such that the distribution of vapor particles injected *into the gas mixture* at the droplet surface $r=R$ has a prescribed form

$$P(v,\mu,R)=g(v,\mu)\qquad\text{for}\quad \mu>0 \tag{3.5}$$

In general, g may be a functional of the velocity distribution of particles impinging on the droplet, but in this paper we shall confine ourselves to the case of a "black" droplet.$^{(3)}$ Such a droplet absorbs all particles impinging upon it and spontaneously emits particles with a Maxwell distribution at the droplet temperature t_D and the corresponding saturated vapor density $n_S(t_D)$:

$$g_B(v,\mu)=n_S(t_D)\,\phi_0(v;t_D) \tag{3.6a}$$

$$\phi_0(v;t_D)=(2\pi t_D)^{-3/2}\exp(-v^2/2t_D) \tag{3.6b}$$

The solution $P_B(v,\mu,r)$ of (3.4) for a black droplet can be written as a linear combination of the solutions of two classical problems of boundary layer theory. The first is (a three-dimensional variant of) the *Milne* solution(13) P_{M}, defined by

$$g_{\mathrm{M}} = 0, \qquad j_{V\mathrm{M}} = -r^{-2} \tag{3.7}$$

It corresponds to a totally absorbing sphere toward which a steady particle current per solid angle of unity flows; the associated density approaches $n_{\mathrm{M}\infty}$ at infinity. The second constituent of P_B is an *albedo* solution(13) P_A, defined by

$$g_A(v, \mu) = \phi_0(v; t_D); \qquad n_{A\infty} = 0 \tag{3.8}$$

which corresponds to a sphere emitting particles with unit density and Maxwellian velocity distribution, and absorbing all particles returning to it. In terms of these two solutions, the solution sought for can be written as

$$P_B(v, \mu, r) = \frac{n_{V\infty}}{n_{\mathrm{M}\infty}} P_{\mathrm{M}} + n_S(t_D)\, P_A \tag{3.9a}$$

The associated current density equals

$$j_B(r) \equiv \int d\mathbf{v}\; v\mu P_B(v, \mu, r) \tag{3.9b}$$

Solutions for "gray" droplets, which do not absorb all vapor molecules reaching them (and have a correspondingly reduced spontaneous emission),(3) could also be obtained by the present formalism; we shall not consider such variations in the present paper.

In principle, the temperature profile $t(r)$ that enters into (3.4), and that in turn determines $G(r)$ and $\alpha_T(r)$ if we assume uniform pressure and an equation of state (in our case the ideal gas expression) for the background gas, should be determined by solving the Navier–Stokes equation for the background gas, using the appropriate boundary condition at the droplet surface and treating the kinetic energy transfer from the vapor to the gas due to collisions, which follows from a knowledge of P_B, as a heat source. However, since the present paper is devoted mainly to a discussion of our solution procedure for (3.4), and since this procedure will be independent of the expression chosen for $t(r)$, we shall instead use an *assumed* temperature profile of the form

$$t(r) = 1 + (\tilde{t}_D - 1) R/r \tag{3.10}$$

where $\tilde{t}_D$ is the scaled droplet temperature t_D decreased by the temperature jump at the droplet surface. The latter will be determined in a way described in more detail in Section 6, using the results obtained by Hubmer and Titulaer.(14) The temperature profile (3.10) causes a heat current density in the gas given by

$$q(r) = \lambda(\tilde{t}_D - 1)R/r^2 \tag{3.11}$$

where q is measured in units of $kT_\infty v_{\text{th}} l^{-3}$ and λ is the heat conductivity of the background gas, measured in units of $kv_{\text{th}} l^{-2}$. For λ we shall use the first-order kinetic expression [see Eq. (8.2-31) of ref. 12]. To obtain an estimate for the droplet temperature t_D during quasistationary condensation we shall require that the heat carried away by the background gas is balanced by the heat of condensation released by the vapor particles upon absorption by the droplet:

$$-q_0 4\pi R^2 j_B(R) = \lambda(\tilde{t}_D - 1) \cdot 4\pi R \tag{3.12}$$

where we take for q_0 the heat of condensation at t_D in units of kT_∞. The quantity j_B has been defined in (3.9b); it depends on t_D via the profile $t(r)$ entering into (3.4) and via the boundary condition (3.6). Of course, the expression on the left in (3.12) is not exact either: we have neglected the fact that the velocity distribution $P_B(v, \mu, R)$ of the incoming particles differs from the Maxwellian at t_D that would hold for equilibrium condensation.(3) However, the profile (3.10) with t_D determined from (3.12) may at least serve to obtain first estimates for the influence of the various effects included in (3.4) on the rate of condensation, which is our aim in the present paper.

4. THE MOMENT EQUATIONS AND THEIR SOLUTIONS

The partial differential equation (3.4), which can be written in shorthand as

$$\frac{\partial}{\partial r} \mathcal{S}_0 P = \left[-\frac{1}{r} \mathcal{S}_1 + G\mathcal{C}_0 + (t-1)\, G\mathcal{C}_1 + \alpha_T \frac{dt}{dr} \mathcal{T} \right] P \tag{4.1}$$

can be transformed into a set of coupled ordinary differential equations by expanding in terms of the Burnett functions, which are the eigenfunctions of $\mathcal{C}_0$. We therefore write(5,15)

$$P(v, \mu, r) = \phi_0(v) \sum_{n,k=0}^{\infty} \tilde{b}_{nk}(r)\, \psi_{nk}(v, \mu) \tag{4.2}$$

where $\phi_0(v)$ is the Maxwell distribution at $t = 1$. The action of the various terms on the Burnett functions is given by

$$\begin{aligned}\mathcal{S}_0\psi_{nk} &\equiv v\mu\psi_{nk}\\ &= (k+1)\left\{\left[\frac{2n+2k+3}{(2k+1)(2k+3)}\right]^{1/2}\psi_{n,k+1}\right.\\ &\qquad \left.-\left[\frac{2n}{(2k+1)(2k+3)}\right]^{1/2}\psi_{n-1,k+1}\right\}\\ &\qquad +k\left\{\left[\frac{2n+2k+1}{(2k-1)(2k+1)}\right]^{1/2}\psi_{n,k-1}\right.\\ &\qquad \left.-\left[\frac{2n+2}{(2k-1)(2k+1)}\right]^{1/2}\psi_{n+1,k-1}\right\}\end{aligned}\tag{4.3a}$$

$$\begin{aligned}\mathcal{S}_1\psi_{nk} &\equiv v(1-\mu^2)\frac{\partial}{\partial\mu}\psi_{nk}\\ &= k(k+1)\left\{-\left[\frac{2n+2k+3}{(2k+1)(2k+3)}\right]^{1/2}\psi_{n,k+1}\right.\\ &\qquad +\left[\frac{2n}{(2k+1)(2k+3)}\right]^{1/2}\psi_{n-1,k+1}+\left[\frac{2n+2k+1}{(2k-1)(2k+1)}\right]^{1/2}\psi_{n,k-1}\\ &\qquad \left.-\left[\frac{2n+2}{(2k-1)(2k+1)}\right]^{1/2}\psi_{n+1,k-1}\right\}\end{aligned}\tag{4.3b}$$

$$\mathcal{C}_0\phi_0\psi_{nk}\equiv\frac{\partial}{\partial\mathbf{v}}\cdot\left(\mathbf{v}+\frac{\partial}{\partial\mathbf{v}}\right)\phi_0\psi_{nk}=-(2n+k)\,\phi_0\psi_{nk}\tag{4.3c}$$

$$\mathcal{C}_1\phi_0\psi_{nk}\equiv\nabla_{\mathbf{v}}^2\phi_0\psi_{nk}=-[(2n+2)(2n+2k+3)]^{1/2}\,\phi_0\psi_{n+1,k}\tag{4.3d}$$

$$\begin{aligned}\mathcal{T}\phi_0\psi_{nk} &\equiv\left(\mu\frac{\partial}{\partial v}+\frac{1-\mu^2}{v}\frac{\partial}{\partial\mu}\right)\phi_0\psi_{nk}\\ &= -(k+1)\left[\frac{2n+2k+3}{(2k+1)(2k+3)}\right]^{1/2}\phi_0\psi_{n,k+1}\\ &\qquad +k\left[\frac{2n+2}{(2k-1)(2k+1)}\right]^{1/2}\phi_0\psi_{n+1,k-1}\end{aligned}\tag{4.3e}$$

In (4.3a) and (4.3b) we omitted the factor ϕ_0, since $\mathcal{S}_0$ and $\mathcal{S}_1$ commute with it.

Substitution of (4.2) and (4.3) into (4.1) leads to an infinite set of differential equations for the $\tilde{b}_{nk}(r)$, which can be written in the form

$$\frac{d}{dr}\mathbb{S}_0\cdot\tilde{\mathbf{b}}=\left[-\frac{1}{r}\mathbb{S}_1+G\mathbb{C}_0+(t-1)\,G\mathbb{C}_1+\alpha_T\frac{dt}{dr}\mathbb{T}\right]\cdot\tilde{\mathbf{b}}\tag{4.4}$$

where $\tilde{\mathbf{b}}$ is the vector with components $\tilde{b}_{nk}$. For actual calculations this set must be truncated; as in earlier work,$^{(5)}$ we use the truncation prescriptions

$$D_N\colon \quad \tilde{b}_{nk} = 0 \qquad \text{for} \quad n + k > N \tag{4.5}$$

which lead to $(N+1)(N+2)/2$ coupled equations. This prescription was found$^{(4,6)}$ to lead to very good convergence with increasing N for $R > 1.5$, and to reasonable convergence for lower R. We shall use the notations in (4.4) for the truncated version as well.

The truncated matrix $\mathbb{S}_0$ is symmetrical and can therefore be diagonalized. From (4.3a) one sees that it is odd in k. Since, moreover, the prescription (4.5) leaves more even than odd moments, its rank, and therefore its number of nonzero eigenvalues is at most equal to twice the number of odd moments; this maximal rank equals the rank found in practice:

$$\mathscr{r} = \tfrac{1}{2}(N+1)(N+2) - [N/2] - 1 \tag{4.6}$$

with $[n]$ denoting the integer part of n. We shall denote the diagonal form of $\mathbb{S}_0$ by $\mathbb{D}$ and the matrix effecting the diagonalization by $\mathbb{U}$: $\mathbb{S}_0 = \mathbb{U}\mathbb{D}\mathbb{U}'$. If we denote the matrix in square brackets in (4.4) by $\tilde{\mathbb{V}}$, we obtain from (4.4)

$$\frac{d}{dr}\mathbb{D}\cdot\mathbf{b} \equiv \frac{d}{dr}\mathbb{D}\cdot\mathbb{U}'\cdot\tilde{\mathbf{b}} = \mathbb{U}'\cdot\tilde{\mathbb{V}}\cdot\mathbb{U}\cdot\mathbb{U}'\cdot\tilde{\mathbf{b}} \equiv \mathbb{V}\cdot\mathbf{b} \tag{4.7}$$

or, more explicitly, if we assign the last components in $\mathbf{b}$ to the eigenvectors of $\mathbb{D}$ with eigenvalue zero:

$$\frac{d}{dr}\begin{pmatrix} \mathbb{D}_{11} & \mathbb{O} \\ \mathbb{O} & \mathbb{O} \end{pmatrix}\begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \end{pmatrix} = \begin{pmatrix} \mathbb{V}_{11} & \mathbb{V}_{12} \\ \mathbb{V}_{21} & \mathbb{V}_{22} \end{pmatrix}\begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \end{pmatrix} \tag{4.8}$$

The part $\mathbf{b}_2$ can be eliminated, and one arrives at the set of coupled differential equations

$$\frac{d}{dr}\mathbf{b}_1 = \mathbb{D}_{11}^{-1}\cdot[\mathbb{V}_{11} - \mathbb{V}_{12}\cdot\mathbb{V}_{22}^{-1}\cdot\mathbb{V}_{21}]\cdot\mathbf{b}_1 \tag{4.9}$$

For the case of constant $t(r)$, the set of equations (4.4) can be further reduced by postulating$^{(15)}$ for $\tilde{b}_{nk}(r)$ the space dependence $\tilde{b}_{nk}^{(\lambda)}(r) = a_{nk}^{(\lambda)}K_{k+1/2}(q_\lambda r)$ with $K_m(y)$ the Hankel function of imaginary argument. This reduces (4.4) to an algebraic generalized eigenvalue equation for the q_λ which is then solved numerically. One finds a solution with $q = 0$ and a Jordan associated solution; these are the Chapman–Enskog solutions, namely the equilibrium solution and a solution carrying a particle current density proportional to r^{-2}. In addition there are $(\imath/2)-1$ pairs of finite semisimple real eigenvalues q_λ of opposite sign. These values approach square roots of integers for $N \to \infty$; hence the corresponding solutions of (4.8) grow exponentially on the scale of a mean free path in the negative or positive r direction. They are boundary layer solutions of the Boltzmann equation for interior (small-r) and exterior (large-r) spherical boundaries, respectively. The solutions of the Milne and albedo problems are obtained by postulating for the solution a linear combination of the two Chapman–Enskog solutions and the boundary layer solutions for interior boundaries. (Exterior boundary layer solutions would come into play for systems enclosed within a spherical container, a situation not considered in the present paper.) The condition at infinity fixes the coefficient of one of the Chapman–Enskog solutions; the condition (3.5) at $r = R$ is replaced by the Marshak$^{(16)}$ equivalent

$$\int_{\mu > 0} v^2\,dv\,d\mu\,P(v, \mu, R)\,\psi_{n,2k+1}(v, \mu)$$
$$= \int_{\mu > 0} v^2\,dv\,d\mu\,g(v, \mu)\,\psi_{n,2k+1}(v, \mu) \qquad \text{for} \quad n + 2k + 1 \leqslant N \tag{4.10}$$

These are precisely $\imath/2$ conditions; hence, they suffice to determine the solution in D_N approximation uniquely. For slowly varying $t(r)$ it appears reasonable to assume that the *structure* of the space of *local* solutions (two slowly varying solutions and two spaces of dimension $\imath/2 - 1$ of exponentially rapidly decreasing and increasing solutions) remains the same, so the ansatz for solving the boundary value problem may stay the same as well. However, the method used for obtaining the explicit form of the solutions no longer works.

Already the Chapman–Enskog solutions can no longer be written in closed form; for higher D_N approximations one needs Burnett corrections$^{(11)}$ of increasing order, which involve a prohibitive amount of analytical work. Also, efforts to treat the space dependence of t as a perturbation did not lead to a well-convergent scheme. This is not too surprising since $t(r)$ and dt/dr give rise to terms with additional factors of r^{-1} and r^{-2}, respectively, and some other terms in the perturbation involve additional derivatives. However, the possibility that a useful asymptotic perturbation theory would have resulted could not have been excluded *a priori.* We therefore decided to integrate Eqs. (4.9) numerically inward, starting from large r, where the influence of the spatial variation of t can be assumed to be small. For this purpose we first replace $t(r)$ by the modified profile

$$\begin{gathered} \tilde{t}(r) \equiv 1 + [t(r) - 1]\,s(r) \\ s(r) = 0 \quad \text{for } r \geqslant R_+; \qquad s(r) \to 1 \quad \text{for } r \to R \end{gathered} \tag{4.11}$$

The Chapman–Enskog and interior boundary layer solutions for $r \geqslant R_+$ are then known, and the numerical integration may start at R_+. Subsequently, the behavior for increasing cutoff parameter R_+ is considered.

A straightforward numerical integration does not give useful results, however. Since (4.4) [or (4.9)] has solutions that grow exponentially fast with decreasing r, such solutions will build up from roundoff errors, and soon overwhelm the Chapman–Enskog and more slowly increasing boundary layer solutions. However, all that is needed for solving our boundary layer problems is *a complete set of solutions* in the space in which the solution should lie. To obtain such a set we first integrate the solutions at $r = R_+$, obtained by the procedure of ref. 5, inward over an interval Δr. The solutions so obtained from the Chapman–Enskog and interior boundary layer solutions are denoted by $\mathbf{b}_i^0(r)$ $(i = 1, 2)$ and $\mathbf{b}_j^-(r)$ $(j = 1, \ldots, \mathscr{r}/2 - 1)$, respectively. Due to amplified roundoff errors, they all tend to converge to the fastest growing boundary layer solution, i.e., to the one that *decreases* fastest as one moves *away from* the sphere. To remove these unwanted admixtures, we introduce linear combinations of the type

$$\begin{aligned}
&\tilde{\mathbf{b}}_i^0(r') = \mathbf{b}_i^0(r') + \sum_j \alpha_{ij} \mathbf{b}_j^-(r') \qquad [r' = R_+ - \Delta r] \\
&\tilde{\mathbf{b}}_j^-(r') = \tilde{\tilde{\mathbf{b}}}_j^-(r') / \|\tilde{\tilde{\mathbf{b}}}_j^-(r')\| \\
&\tilde{\tilde{\mathbf{b}}}_j^-(r') = \mathbf{b}_j^-(r') + \sum_{k \neq j} \beta_{jk} \mathbf{b}_k^-(r')
\end{aligned} \tag{4.12}$$

with the α_{ij} and β_{jk} chosen such that they minimize the norms $\|\tilde{\mathbf{b}}_i^0\|$ and $\|\tilde{\tilde{\mathbf{b}}}_j^-\|$. In terms of the matrices

$$\mathbb{M}_{jk} \equiv \mathbf{b}_j^- \cdot \boldsymbol{b}_k^-; \qquad \mathbb{N}_{ij} \equiv \mathbf{b}_i^0 \cdot \mathbf{b}_j^- \tag{4.13}$$

these coefficients are

$$\alpha_{ij} = -\sum_k \mathbb{N}_{ik} \cdot \mathbb{M}_{kj}^{-1}; \qquad \beta_{jk} = \mathbb{M}_{jk}^{-1} / \mathbb{M}_{jj}^{-1} \tag{4.14}$$

We now replace the $\mathbf{b}_i^0(r')$ and $\mathbf{b}_j^-(r')$ by $\tilde{\mathbf{b}}_i^0(r')$ and $\tilde{\mathbf{b}}_j^-(r')$, respectively, and repeat the procedure until we have reached $r = R$.

At $r = R$ we so obtain a complete set of solutions with which we may fulfill the boundary condition (3.5) in the approximation (4.10); for this purpose the components $\mathbf{b}_2$, eliminated in (4.9), have to be reconstructed. For later use we note that the solutions $\tilde{\mathbf{b}}_i^0$ contain the "actual" Chapman–Enskog solutions with coefficient unity, since the Chapman–Enskog solutions vary slowly, and hence do not build up from numerical noise to any appreciable extent. In the following sections the numerical procedure just outlined will first be tested for the case of constant $t(r)$, where the "actual" results are known, and then be applied to cases with space-dependent $t(r)$.

5. NUMERICAL TESTS AND CONVERGENCE PROPERTIES

As a first test of our numerical procedure we apply it to the Milne problem with constant temperature [i.e., we put $t(r)=1$, $G(r)=1$ in (4.4)], and compare with the results obtained using the method of ref. 5, which are essentially exact within the respective D_N approximations, defined in (4.5). In Table I we list the relative deviations in the quantity $n_{M\infty}$ defined after (3.7) in D_2 approximation for $R=5$ and for various values of the starting point R_+ of the numerical integration, the step size Δs, and the interval Δr after which the updating procedure (4.12) is carried through. We see that $\Delta s=0.1$, $\Delta r=1$ yields data of sufficient accuracy.

Similar data for $R=5$ in the D_4, D_6, and D_8 approximations are given in Table II. We see that the accuracy obtainable depends only slightly on the order of the approximation. However, for D_6 and D_8 one must use the updating procedure (4.12) after each integration step; this appears reasonable, since with increasing N, boundary layer solutions with ever higher growth rates are introduced.

Table I. Relative Discrepancy Between the Numerical Result for $n_{M\infty}$ and the Value Found by the Semianalytical Treatment of ref. 5 in D_2 Approximation, for $R=5$ and various values of R_+, as a Function of the Step Size Δs of the Numerical Integration and the Interval Δr After Which the Updating (4.12) Is Carried Out

		Discrepancy				
R_+	Δs	$\Delta r=10$	$\Delta r=1$	$\Delta r=10^{-1}$	$\Delta r=10^{-2}$	$\Delta r=10^{-3}$
10^2	1	2×10^{-3}	2×10^{-3}			
	10^{-1}	8×10^{-7}	4×10^{-7}	4×10^{-7}		
	10^{-2}	1×10^{-5}	8×10^{-11}	2×10^{-11}	2×10^{-11}	
	10^{-3}	1×10^{-4}	7×10^{-10}	1×10^{-10}	2×10^{-10}	6×10^{-10}
10^3	1	1×10^{-3}	2×10^{-3}			
	10^{-1}	2×10^{-3}	3×10^{-7}	3×10^{-7}		
	10^{-2}	1×10^{-2}	1×10^{-7}	7×10^{-8}	2×10^{-8}	
10^4	1	—[a]	2×10^{-3}			
	10^{-1}	—[a]	8×10^{-5}	8×10^{-5}		

[a] Bars characterize impracticable combinations of R_+, Δs, and Δr.

Table II. Similar Data As in Table I, for D_4, D_6, and D_8 Approximations

			Discrepancy	
D_N	R_+	Δs	$\Delta r = 1$	$\Delta r = 10^{-1}$
D_4	10^2	10^{-1}	8×10^{-7}	8×10^{-7}
		10^{-2}	1×10^{-10}	1×10^{-10}
	10^3	10^{-1}	8×10^{-7}	8×10^{-7}
		10^{-2}	9×10^{-8}	9×10^{-8}
	10^4	10^{-1}	1×10^{-5}	6×10^{-5}
D_6	10^2	10^{-1}	—	2×10^{-6}
		10^{-2}	—	4×10^{-10}
	10^3	10^{-1}	—	2×10^{-6}
D_8	10^2	10^{-1}	—	4×10^{-6}
	10^3	10^{-1}	—	4×10^{-6}

For a first test of the performance of our procedure in the presence of temperature gradients we considered (4.4) with the temperature profile (3.10), but with $\alpha_T = 0$ and the simplified expression $G(r) = t(r)^{-1/2}$ instead of the full expression (3.3). For $s(r)$ in (4.11) we chose

$$s(r) = \frac{R_+ - r}{R_+ - R} \qquad \text{for} \quad R \leqslant r \leqslant R_+ \tag{5.1}$$

The Milne solution should have $j(r) = r^{-2}$, irrespective of $t(r)$, as a consequence of mass conservation. The same r dependence should appear in $\tilde{b}_{01}$ in (4.7). This behavior was indeed found. In fact, the additional deviations from an r^{-2} dependence introduced by a change from $\tilde{t}_D = 1$ to $\tilde{t}_D = 1.1$ in (3.10) were many orders of magnitude smaller than those already present due to the finiteness of Δr and Δs.

To estimate the influence of the cutoff radius R_+ in (5.1), we solved the simplified Milne problem for $R = 5$ and $\tilde{t}_D = 1.1$ for several values of R_+. The results are given in Table III, together with the extrapolations $n_{M\infty}$ obtained from two successive values using the formula

$$n_{M\infty}(R_+) = n_{M\infty} + cR_+^{-1} \tag{5.2}$$

We see that knowledge of $n_{M\infty}(100)$ and $n_{M\infty}(200)$ suffices to determine $n_{M\infty}$ to a relative accuracy of 10^{-5}; the use of higher R_+, and hence of longer integration intervals, brings no significant improvement. The same result was found in D_6 and D_8 approximations.

The dependence of the results on the order of approximation N is very

Table III. The Dependence of $n_{M\infty}$ on the Cutoff Radius R_+ Introduced in (4.11), for $R=5$ and $\tilde{t}_D=1.1$, Together with the Values $n_{M\infty}$ Obtained by the Fit (5.2)

	D_2		D_4	
R_+	$n_{M\infty}(R_+)$	$n_{M\infty}$	$n_{M\infty}(R_+)$	$n_{M\infty}$
100	0.261219		0.263735	
200	0.261122	0.261024	0.263635	0.263535
300	0.261089	0.261023	0.263601	0.263534
400	0.261072	0.261023	0.263584	0.263534
...	...	...	...	...
1000	0.261043	0.261023	0.263554	0.263534

similar for $\tilde{t}_D=1$ and $\tilde{t}_D=1.1$. By extrapolating the N dependence using the procedure described in ref. 5 we find for the same parameters and simplifications as before

$$n_{M\infty}(\tilde{t}_D=1)=0.2667\pm 0.0002 \tag{5.3a}$$

$$n_{M\infty}(\tilde{t}_D=1.1)=0.2652\pm 0.0002 \tag{5.3b}$$

Thus, the effects of a temperature gradient in our example are about eight times larger than the numerical uncertainty. In the interval $1<\tilde{t}_D<1.1$, $n_{M\infty}(\tilde{t}_D)$ behaves nearly linearly, with deviations of the order of the numerical error given above.

In the case of the albedo problem similar tests were carried out. As a first test we calculated the current density j_{VA} for $t_D=1$ and $\tilde{t}_D=1$. The relation

$$j_{VA}(t_D=\tilde{t}_D=1)=r^{-2}/n_{M\infty}(\tilde{t}_D=1) \tag{5.4}$$

is satisfied within the calculational accuracy in each D_N approximation. For $t_D=1.1$, with $G(r)$ and the other parameters chosen as before, we obtain

$$j_{VA}(t_D=1.1,\ \tilde{t}_D=1.0)=r^{-2}\cdot[4.020\pm 0.005] \tag{5.5a}$$

$$j_{VA}(t_D=1.1,\ \tilde{t}_D=1.1)=r^{-2}\cdot[4.137\pm 0.005] \tag{5.5b}$$

Thus, in this case the effects arising from a temperature gradient are about 25 times larger than the numerical error. In the interval $1<\tilde{t}_D<1.1$ the calculated quantity, $j_{VA}\cdot r^2$, again depends linearly on temperature.

6. FIRST NUMERICAL RESULTS FOR THE CONDENSATION PROBLEM

In this section we apply the method developed in Section 4 to the condensation problem described in Section 3, using the approximate temperature profile (3.10). Vapor and carrier gas consist of Lennard-Jones molecules with parameters corresponding to mercury and neon, respectively. This choice was made to avoid complications arising from internal degrees of freedom; on the other hand, choosing a mixture of noble gases would lead to high densities due to the high saturation pressures, and thus make the use of the Boltzmann equation problematical. The parameters for mercury were determined by first calculating the second virial coefficient $B(T)$ from the critical quantities T_C and p_C using Eq. (4.2-4) of ref. 12 and then using the procedure given in §3.6b of ref. 12. The resulting values are $\sigma_1 = 3.10$ Å and $\varepsilon_1/k = 975$ K.

For neon we used the values $\sigma_2 = 2.78$ Å and $\varepsilon_2/k = 34.9$ K, taken from Table 3.6-1 of ref. 12. Further we chose the temperature T_∞ of the gas mixture far from the droplet equal to 483 K and the total gas density n_∞ far from the droplet equal to $100n_S(T_\infty)$. With these choices, we find the velocity persistence length l of the vapor molecules and the mean free path l_G of the gas, defined by (3.1) together with (2.7), and by Eq. (2.4b) of ref. 4, respectively, as

$$l = 1.18 \times 10^{-5}\ \text{cm} \tag{6.1a}$$

$$l_G = 0.583 \times 10^{-5}\ \text{cm} \tag{6.1b}$$

These values are large compared to the atomic diameters σ_1 and σ_2, justifying the use of the Boltzmann equation; moreover, l is about twice as large as l_G.

To determine the effective droplet temperature $\tilde{t}_D$ entering (3.12), we use the approximate expression

$$\frac{t_D - \tilde{t}_D}{t_D - t(\infty)} = 1 - \frac{1}{1 + x_T R^{-1} + x'_T R^{-2}} \tag{6.2}$$

proposed in ref. 14, with the values $x_T = 2.77$, $x'_T = 4.97$, calculated there for Maxwell molecules (as was noted in ref. 14, at least x_T appears to be rather insensitive to the specific form of the intermolecular interaction). Equation (6.2) is valid only for the case of complete energy accommodation of the gas molecules reflected from the droplet surface; expressions for incomplete energy accommodation are discussed in ref. 14. For the heat conductivity λ, the heat of condensation q_0, and the thermal diffusion ratio α_T we neglect the temperature dependence and use the values for $T_\infty = 483$ K, which in our units are

$$\lambda = 471{,}500 k v_{\text{th}} l^{-2} \tag{6.3a}$$

$$q_0 = 14.8 k T_\infty; \qquad \alpha_T = 0.429 \tag{6.3b}$$

The values for q_0 and the saturation density $n_S(T)$ were taken from ref. 17.

Using these parameters, and the procedures outlined in Section 3, we performed calculations for droplet radii of $2l$, $5l$, and $10l$ and vapor densities $n_{V\infty}$ of $2n_S(T_\infty)$ and $3n_S(T_\infty)$. To obtain a first estimate for the droplet temperature T_D we first carried out the full program described in Section 3 in the D_2 approximation, defined in (4.5); this gives the estimate $t_D^{(2)}$. Next we solved the Milne and albedo problems for two temperatures $t_D^{(-)}$ and $t_D^{(+)}$ with $t_D^{(-)} < t_D^{(2)} < t_D^{(+)}$, using the procedure described in Section 4, in the D_2, D_4, D_6, and D_8 approximations. For the simplified problem obtained by omitting the last two terms on the right in (4.4) and putting $G = 1$ in the second term, we also calculated D_N up to $N = 16$, using the method of ref. 5. The values obtained for $n_{\text{M}\infty}$ and j_{VA} in the latter problem depend very regularly on the order of approximation N and allow one to estimate the exact values by extrapolation.$^{(5)}$ Since the dependence on N is very similar in the simplified and the full problem, this allowed us to estimate the error made by truncation at $N = 8$ in the full problem as well. In view of the linearity of $n_{\text{M}\infty}$ and j_{VA} as functions of t_D, discussed in Section 5, the quantities $n_{\text{M}\infty}(t_D)$ and $j_{VA}(t_D)$ in the interval $t_D^{(-)} < t_D < t_D^{(+)}$ were determined from the values so calculated at $t_D^{(-)}$ and $t_D^{(+)}$ by linear interpolation. These functions were then used to determine the droplet temperature t_D from (3.12), using (3.9) and (6.2). From the current density j_B at that temperature, defined in (3.9), we finally obtain the growth rate $\dot{R}$ of the droplet using

$$\dot{R} = -j_B(t_D)/n_l \tag{6.4}$$

where n_l is the density of liquid mercury for the given temperature and pressure.

Our results for $\dot{R}$, in units of $10^{-5} v_{\text{th}}$, are given in Table IV. In addition to the results obtained from the full equation (last line of the table), we also give the results obtained from the simplified equation, neglecting all effects of temperture gradients (first line). To estimate the influence of the separate terms, we also give results obtained by including only the first three terms on the right in (4.4), omitting thermal diffusion (second line), as well as by including the fourth term, but omitting the third term and putting $G = 1$ in the second (third line).

Table IV. Several Results for the Droplet Growth Rate $\dot{R}$ in Units of $10^{-5}v_{\mathrm{th}}$, for $R=2l$, $5l$, and $10l$ and $n_{V\infty}=2n_S(T_\infty)$ and $3n_S(T_\infty)$[a]

R/l	5	2	5	10
$n_{V\infty}/n_S$	2	3	3	3
$\dot{R}/10^{-5}v_{\mathrm{th}}$	0.1320	0.4460	0.2619	0.15074
	±0.0004	±0.0008	±0.0006	±0.00010
	0.1316	0.4443	0.2613	0.15077
	0.1307	0.4415	0.2584	0.14847
	0.1304	0.4399	0.2578	0.14851

[a] The error bounds (upper bounds on the numerical error) do not change within each row. The last line contains our final results; the significance of the other entries is described in the last two paragraphs of Section 6. The parameters used correspond to mercury condensing in neon.

We see that, except for small R, the effect of thermodiffusion is by far the largest one. Since thermodiffusion impedes the flow of vapor molecules toward the warmer droplet, it must reduce the growth rate. Since, as we saw in the preceding section, the remaining gradient effects act in opposite ways on the Milne and albedo parts of the solution P_B defined in (3.9a), the sign of the net effect cannot be predicted *a priori*, and it appears to change as R increases. The overall effect is small (of the order of 1%), but, in all cases considered, larger than the upper bound for the numerical error, also given in Table IV. Finally, we note that the growth rate $\dot{R}$ is always very small compared with the thermal velocity v_{th}, which justifies our use of the *stationary* Klein–Kramers equation.

7. DISCUSSION AND CONCLUDING REMARKS

The main result of this paper is the development of a reliable method for solving boundary layer problems for linear kinetic equations that involve space-dependent collision operators. Since the method introduced in Section 4 for eliminating the effects of the intrinsic numerical instabilities relies on the preservation of the basic structure of the solution space (Chapman–Enskog, inner and outer boundary layer solutions), it can only be expected to work in cases in which the space-dependent terms vary smoothly on the scale of a mean free path. This condition was clearly fulfilled in the applications treated in this paper. In fact, our basic method should remain applicable when much larger temperature differences between the droplet and the gas mixture at infinity exist. This can be the case when droplets evaporate under the influence of externally supplied heat, or when strongly exothermic chemical reactions occur at the surface of the droplet. In such cases, the simple method we used to determine the droplet temperature would need to be improved, however: in principle, the kinetic equation for the Brownian particles and the hydrodynamic (heat conduction) equation for the background gas should be solved together in a self-consistent manner, in such a way that the sources for the heat conduction equation are deduced from the solution of the kinetic equation for the Brownian particles, as sketched in Section 3.

Clearly, our method is not restricted to spherical geometries; the main requirement is that the space dependence of the distribution is governed by a single generalized coordinate. This is also the case for a half-space, or the space between two parallel plates, as well as for the space outside of a cylinder or between two coaxial cylinders. In cases involving two boundary layers, however, the two should be well separated, since one needs a starting point for the integration that lies well outside of the boundary layers.

Our choice of the basic equation (2.1) with the extra term (2.2) was made for two basic reasons: the fundamental equation is linear, and for the case without temperature gradients highly accurate solutions are available for comparison. However, the method could also be applied to the general Boltzmann equation in cases where a linearization around a local equilibrium distribution is appropriate. In such an application a self-consistent solution of the linearized Boltzmann equation and the Navier–Stokes equations, which determine the local equilibrium solution, would be required. The procedure would be comparable to the usual treatment of the nonlinear BGK equation.(18) The use of the linearized Boltzmann equation in the boundary layer is not without problems: deviations from local equilibrium are known to be far from negligible there. However, since the Boltzmann collision operator involves an integral over the distribution function of the collision partners, their effect on the collision term may not be too severe.

Some of the objections alluded to in the preceding paragraph could also be raised against our application of our formalism to the case of the condensation of mercury in neon. The mass ratio between the components of the mixture as well as the ratio between the characteristic lengths given in (6.1) are small, but not completely negligible. However, in view of the smallness of the effects found, it appears reasonable not to worry too much about effects of higher order in these ratios. On the other hand, the effects calculated, though small, may be of practical importance if one attempts to analyze experiments on droplet growth, especially for not too small droplets, with the purpose of extracting information about absorption and accommodation coefficients at the surface, as discussed in ref. 3. However, since effects of partial absorption and accommodation were not considered in this paper, we shall not pursue this subject here any further.

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