

The Kinetic Boundary Layer for the Linearized Boltzmann Equation around an Absorbing Sphere

G. F. Hubmer¹ and U. M. Titulaer¹

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We construct approximate solutions of the linearized Boltzmann equation for a gas outside of a completely absorbing sphere, a simple model for a liquid droplet growing in a supersaturated vapor. The solutions are linear combinations of two Chapman–Enskog-type solutions, which carry heat and particle currents, and boundary layer eigenfunctions that decay with increasing distance from the sphere on a distance of the order of a mean free path. To construct the boundary layer eigenfunctions and the linear combination that satisfies the boundary condition at the sphere, we expand the solution in Burnett functions and truncate the resulting system of equations for the expansion coefficients. For one particular truncation prescription, which generalizes Grad's 13-moment scheme, good initial convergence with increasing order of truncation is obtained for both moderately small and large radii of the sphere; the results for small radii extrapolate smoothly toward the known limit of zero radius. We present results for the reaction rate (the particle current arriving at the sphere divided by the density at infinity) and for the density and temperature profiles in the boundary layer. The explicit calculations are carried out for Maxwell molecules, but the method appears to be suitable for more general intermolecular potentials.

KEY WORDS: Boltzmann equation; kinetic boundary layer; moment expansions; droplet growth; Maxwell molecules.

1. INTRODUCTION

The system considered in this paper is a not too dense, one-component gas, described by the Boltzmann equation, surrounding an absorbing sphere. The sphere can be thought of as a liquid droplet or crystallite placed in a highly supersaturated vapor, but we shall not attempt to describe complications that occur in this actual physical system, except briefly in the

¹ Institut für Theoretische Physik, Johannes Kepler Universität Linz, A-4040 Linz, Austria.

concluding section. Far away from the sphere, the gas is kept in thermal equilibrium; hence, the flow not too close to the sphere can be described by the Navier–Stokes equations. These can be derived from the Boltzmann equation by means of the Chapman–Enskog procedure.^(1–3) However, this procedure is based on the assumption that the gradients in the hydrodynamic variables are small on the scale of a mean free path, and that the distribution function $f(\mathbf{v}, \mathbf{r}, t)$ for the velocities \mathbf{v} and positions \mathbf{r} of the gas molecules is everywhere close to (local) thermal equilibrium. In particular the latter condition is certainly violated near the surface of the sphere, where there are no particles with outwardly-directed velocities. Thus, in a layer around the sphere, the Chapman–Enskog procedure breaks down, and we have to go back to the Boltzmann equation: there appears a *kinetic boundary layer*.

Kinetic boundary layers occur in various problems in kinetic theory, in particular near walls that have a velocity⁽⁴⁾ or temperature^(5,6) different from the bulk of the gas. They can be studied by moment expansion and by variational methods.^(7,8) Most treatments thus far have been confined to planar or cylindrical geometries,⁽⁹⁾ however. In recent years, a number of papers have appeared^(10–13) on the problem of an absorbing sphere in a gas of Brownian particles moving in a stationary background. We mention in particular a paper by Kumar and Menon⁽¹²⁾ using the moment expansion method, and one by Widder and Titulaer⁽¹³⁾ using a refinement of this method to obtain a systematic expansion in the inverse radius of the sphere.

In the present paper we study the possibility of extending and modifying these treatments to apply them to the Boltzmann case. Since the paper is in part a feasibility study, we confine ourselves to the *linearized* Boltzmann equation. Linearization may appear to be unrealistic for the completely absorbing sphere; it can be justified, however, for the case of a droplet in a moderately supersaturated vapor. As we shall show in Section 5, the solution of the latter case can be obtained very simply from the one for a completely absorbing sphere. As an additional simplification, we shall confine ourselves in the actual calculations to the case of Maxwell molecules. This has the advantage that the eigenfunctions of the Boltzmann collision operator are known explicitly. Compared to the even simpler BGK model, the Maxwell model has the advantage that the Prandtl number has the rather realistic value $2/3$; this is relevant since heat currents will turn out to play an important role in the solution we obtain.

In Section 2 we rewrite the stationary Boltzmann equation in spherical geometry as a set of coupled equations for the expansion coefficients in terms of the Burnett functions.⁽¹⁴⁾ This hierarchy of equations turns out to have boundary layer solutions, which decay with definite decay lengths (of

the order of a mean free path) with increasing distance from the sphere, as well as four constant or slowly decaying solutions, which approach Chapman–Enskog-type solutions far away from the sphere. Some details of the derivation and some theorems about the spectrum of decay lengths are given in an Appendix.

In Section 3 we describe the construction of a linear combination of these fundamental solutions that obeys the boundary conditions at infinity and at the surface of the sphere. To obtain results from the infinite hierarchy of coupled moment equations, the hierarchy must be truncated; two alternative truncation schemes are discussed. In Section 4 we present some explicit results. We see that one of the truncation schemes, similar to the ones customarily used in the literature, yields results that rapidly become useless as the sphere radius R decreases and becomes comparable to the mean free path. The other scheme, designed as a generalization of Grad's 13-moment method,⁽¹⁵⁾ yields results that stay reasonable down to small radii (where they eventually break down for numerical reasons) and connect smoothly to the known limit for $R \downarrow 0$. The physical picture is completely different from the Brownian motion case. In a freely streaming gas the particle transport is convective rather than diffusive. Hence, the total current arriving at the sphere is proportional to R^2 for large spheres, rather than to R as in the Brownian case; the coefficient of R^2 depends sensitively on the structure of the boundary layer, and therefore on details of the intermolecular potential; it cannot be obtained from hydrodynamics. In the concluding section we discuss some limitations of our treatment and some possibilities to extend it to more general, and more realistic, cases.

2. THE FUNDAMENTAL BOUNDARY LAYER SOLUTIONS

In this section we consider special solutions of the linearized Boltzmann equation^(2,16) for a gas of point particles of mass m ,

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \right) \Phi(\mathbf{v}, \mathbf{r}, t) = n_0 \mathcal{R}_0 \Phi(\mathbf{v}, \mathbf{r}, t) \quad (2.1)$$

The function Φ describes the deviation of the one-particle distribution function $f(\mathbf{v}, \mathbf{r}, t)$ from a reference equilibrium state,

$$f(\mathbf{v}, \mathbf{r}, t) = n_0 f_M(v; T_0) [1 + \Phi(\mathbf{v}, \mathbf{r}, t)] \quad (2.2)$$

where $f_M(v; T_0)$ is the Maxwell distribution at the temperature T_0 ; $n_0 \mathcal{R}_0$ is the linearized Boltzmann operator.⁽¹⁶⁾ We are interested in stationary problems with spherical symmetry; hence Φ can be written as

$$\Phi(\mathbf{v}, \mathbf{r}, t) = \Phi(v, \mu, r); \quad \mu = \hat{\mathbf{v}} \cdot \hat{\mathbf{r}} \quad (2.3)$$

Moreover, from now on we shall use dimensionless units, with v measured in units of the thermal velocity

$$v_{\text{th}} = (m\beta)^{-1/2} \equiv (kT_0/m)^{1/2} \quad (2.4a)$$

and r measured in terms of the mean free path l , for which we use the definition

$$l = \eta(m\beta)^{1/2}/mn_0 \quad (2.4b)$$

where η denotes the shear viscosity. The linearized Boltzmann equation then becomes⁽¹¹⁾

$$v \left(\mu \frac{\partial}{\partial r} + \frac{1 - \mu^2}{r} \frac{\partial}{\partial \mu} \right) \Phi(v, \mu, r) = \beta\eta\mathcal{R}_0\Phi \quad (2.5)$$

We now write Φ as a linear combination of the Burnett functions $\psi_{nk}(v, \mu)$ ($n, k = 0, 1, 2, \dots$)

$$\Phi(v, \mu, r) = \sum_{n,k} A_{nk}(r) \psi_{nk}(v, \mu) \quad (2.6)$$

with

$$\psi_{nk}(v, \mu) = N_{nk} v^k S_{k+1/2}^{(n)}(v^2/2) P_k(\mu) \quad (2.7)$$

where $S_{k+1/2}^{(n)}$ and P_k are the Sonine and Legendre polynomials, respectively, and

$$N_{nk} = [2^n n! (2k+1)/(2k+2n+1)!!]^{1/2} \quad (2.8)$$

The Burnett functions are complete and satisfy the orthogonality relations

$$2\pi \int d\mu \int dv v^2 f_M(v) \psi_{nk}(v, \mu) \psi_{n'k'}(v, \mu) = \delta_{nn'} \delta_{kk'} \quad (2.9)$$

The functions ψ_{00} , ψ_{10} , and ψ_{01} are eigenfunctions of \mathcal{R}_0 with eigenvalue zero; they are connected with the excess density, the excess kinetic energy, and the radial component of the mean velocity, respectively. For the special case of *Maxwell molecules*, the other ψ_{nk} are eigenfunctions of \mathcal{R}_0 as well^(17,18):

$$\mathcal{R}_0 \psi_{nk}(v, \mu) = -\omega_{nk} \psi_{nk}(v, \mu) \quad (\text{Maxwell}) \quad (2.10)$$

with $\omega_{02} = (\beta\eta)^{-1}$; all other ω_{nk}/ω_{02} are numbers obtainable by simple quadratures.^(18,19) In the remainder of this paper we confine ourselves to

the case of Maxwell molecules, though all our procedures can be extended to the general case without difficulty.

Substitution of (2.7) and (2.10) into (2.5), and use of the properties of the Burnett functions, leads to a set of coupled equations for the A_{nk} ,^(12,17)

$$\begin{aligned}
 & (k+1) \left(\frac{d}{dr} + \frac{k+2}{r} \right) \left[\left(\frac{2n+2k+3}{(2k+3)(2k+1)} \right)^{1/2} A_{n,k+1} \right. \\
 & \quad \left. - \left(\frac{2n}{(2k+3)(2k+1)} \right)^{1/2} A_{n-1,k+1} \right] \\
 & + k \left(\frac{d}{dr} - \frac{k-1}{r} \right) \left[\left(\frac{2n+2k+1}{(2k+1)(2k-1)} \right)^{1/2} A_{n,k-1} \right. \\
 & \quad \left. - \left(\frac{2(n+1)}{(2k+1)(2k-1)} \right)^{1/2} A_{n+1,k-1} \right] \\
 & = - \frac{\omega_{nk}}{\omega_{02}} A_{nk}
 \end{aligned} \tag{2.11}$$

[Different coefficients, e.g. in ref. 12, are caused by a scaling different from our convention (2.4).] Following Kumar and Menon,⁽¹²⁾ we look for *special solutions* of the form

$$A_{nk}(r) = a_{nk}^{(q)} \left(\frac{2}{\pi qr} \right)^{1/2} K_{k+1/2}(qr) \tag{2.12}$$

where $K_{k+1/2}(qr)$ denotes the modified Bessel function. This ansatz satisfies (2.13), provided q and $a_{nk}^{(q)}$ satisfy the generalized eigenvalue equation

$$\begin{aligned}
 & q \left\{ (k+1) \left[\left(\frac{2n+2k+3}{(2k+3)(2k+1)} \right)^{1/2} a_{n,k+1}^{(q)} \right. \right. \\
 & \quad \left. \left. - \left(\frac{2n}{(2k+3)(2k+1)} \right)^{1/2} a_{n-1,k+1}^{(q)} \right] \right. \\
 & \quad \left. + k \left[\left(\frac{2n+2k+1}{(2k+1)(2k-1)} \right)^{1/2} a_{n,k-1}^{(q)} \right. \right. \\
 & \quad \left. \left. - \left(\frac{2(n+1)}{(2k+1)(2k-1)} \right)^{1/2} a_{n+1,k-1}^{(q)} \right] \right\} \\
 & = - \frac{\omega_{nk}}{\omega_{02}} a_{nk}^{(q)}
 \end{aligned} \tag{2.13}$$

which can be written more compactly as

$$q \mathbf{B} \cdot \mathbf{a}^{(q)} = \mathbf{A} \cdot \mathbf{a}^{(q)} \tag{2.14}$$

where $\mathbf{a}^{(q)}$ is a vector containing the components $a_{nk}^{(q)}$.

The eigenvalue problem (2.14) is discussed more fully in the Appendix. There we find that there is a fourfold degenerate eigenvalue $q=0$, and that all other eigenvalues are real and semisimple. From the invariance of (2.13) under the transformation

$$q \rightarrow -q; \quad a_{nk}^{(q)} \rightarrow (-1)^k a_{nk}^{(q)} \tag{2.15}$$

one sees that they occur in pairs of opposite sign. Two of the eigenvectors belonging to $q=0$ are trivial: they have only a_{00} and a_{10} , respectively, different from zero and correspond to a uniform change in density or temperature. There are two associated vectors that can be obtained by substituting, instead of (2.12),

$$A_{nk}(r) = a_{nk} g_k(r); \quad g_0(r) = \frac{1}{r}; \quad g_k(r) = \frac{(2k-1)!!}{r^{k+1}} \tag{2.16}$$

One finds that the coefficients a_{01} and a_{11} can be chosen freely. The remaining coefficients turn out to be

$$\begin{aligned} a_{00} &= \left(\frac{8}{45}\right)^{1/2} a_{11} \\ a_{0k} &= \frac{\omega_{20}}{\omega_{0k}} \frac{k}{(2k-1)^{1/2}} \left[a_{0,k-1} - \left(\frac{2}{2k+1}\right)^{1/2} a_{1,k-1} \right] \quad (k \geq 2) \\ a_{10} &= \frac{2}{\sqrt{15}} a_{11} \\ a_{1k} &= \frac{\omega_{20}}{\omega_{1k}} k \left[\frac{2k+3}{(2k+1)(2k-1)} \right]^{1/2} a_{1,k-1} \quad (k \geq 2) \\ a_{nk} &= 0 \quad \text{for } n \geq 2 \end{aligned} \tag{2.17}$$

Thus, there are two independent solutions: one, with $a_{01} = 1, a_{11} = 0$, describes a radial particle flow; the other, with $a_{11} = 1, a_{01} = 0$, describes a radial heat flow. Only the latter is associated with modifications of particle density (a_{00}) and kinetic energy density (a_{10}). Note, however, that the a_{01} solution does contain components a_{nk} with $n+k > 1$, which become more prominent for small r ; these are associated with entropy production, as should be expected, since the velocity field is not shear-free.

In conclusion, we have constructed in this section four types of special solutions of the linearized Boltzmann equation:

(a) Solutions for which the $A_{nk}(r)$ in (2.6) are given by (2.12) with $q = q_i > 0$ and q_i and $\mathbf{a}^{(q)}$ obeying (2.13). These solutions, further denoted by $\Phi_i^{(+)}(v, \mu, r)$, decay like $r^{-1}e^{-qir}$ for $r \rightarrow \infty$.

(b) Similar solutions $\Phi_i^{(-)}(v, \mu, r)$ with $q = -q_i$; these solutions increase exponentially for $r \rightarrow \infty$.

(c) The homogeneous solutions $\Phi_d = \psi_{00}$ and $\Phi_k = \psi_{10}$, corresponding to excess density and excess kinetic energy.

(d) The solutions $\Phi_{pc}(v, \mu, r)$ and $\Phi_{hc}(v, \mu, r)$ obtained by putting $a_{01} = 1, a_{11} = 0$ and $a_{11} = 1, a_{01} = 0$, respectively, in (2.17). These solutions decrease like powers of r^{-1} at $r \rightarrow \infty$ and they carry a particle and a heat current, respectively.

3. BOUNDARY PROBLEMS AND TRUNCATION SCHEMES

The aim of the present paper is the construction of a solution of (2.1) that vanishes for $r \rightarrow \infty$, which means that $f(v, \mu, r)$ approaches the reference equilibrium state there, and that obeys a prescribed boundary condition at the surface of a sphere with radius R for particles leaving the sphere. The simplest such boundary condition, which is the only one we shall consider in detail, is the one for a completely absorbing sphere,⁽⁹⁾

$$f_a(v, \mu, R) = n_0 f_M(v) [1 + \Phi_a(v, \mu, R)] = 0 \quad \text{for } \mu > 0 \quad (3.1)$$

In view of the boundary condition at $r \rightarrow \infty$, we look for a solution constructed out of solutions of types (a) and (d) from the list in the last section:

$$\Phi_a(v, \mu, r) = C(R) \Phi_{pc} + D(R) \Phi_{hc} + \sum_i d_i(R) \Phi_i^{(+)} \quad (3.2)$$

As yet there is no proof that a solution of the form (3.2) satisfying the boundary condition (3.1) exists, and that it is unique. We shall, however, assume this is the case. A few remarks on this question will be made in the concluding section.

Moreover, the $\Phi_i^{(+)}$ are not known explicitly. Approximate solutions can be obtained, however, by truncating the infinite set of equations (2.13). The so-called $L_N P_K$ approximations⁽¹⁰⁾ are obtained by putting $a_{nk}^{(q)} = 0$ for $n > N$ or $k > K$. We shall use as one of our truncation schemes

$$Q_N = L_N P_N: \quad a_{nk}^{(q)} = 0 \quad \text{for } n > N \quad \text{or } k > N \quad (3.3)$$

As an alternative, we shall also consider the diagonal truncations

$$D_N: \quad a_{nk}^{(q)} = 0 \quad \text{for } n+k > N; \quad a_{N0}^{(q)} = 0 \quad (3.4)$$

[The last condition is not essential; it has the advantage that Grad's 13-moment approximation is equal to D_2 .] The choice (3.4) offers the advantage that, except for $a_{N-1,1}^{(q)}$, at most one term on the lhs of (2.13) is dropped. For both truncation schemes one obtains a rather regularly spaced spectrum of q values between a lower limit that has reached about 0.23 for Q_{15} or D_{22} , but is still slightly decreasing with N , and an upper limit that still increases without apparent bound for those ranges of N . The spectrum is roughly similar to the one obtained in ref. 5 by a method using separate expansions of $\Phi(v, \mu, r)$ for positive and negative μ . The individual q values do not converge very well with increasing N ; this behavior is similar to the one obtained by a similar scheme⁽²⁰⁾ for the one-dimensional BGK model, where the actual spectrum is known to be continuous. For most N there are one or more eigenvectors with infinite q [i.e., $\mathbf{B} \cdot \mathbf{a}^{(q)} = 0$, $\mathbf{A} \cdot \mathbf{a}^{(q)} \neq 0$ in the truncated version of (2.14)]; the number of positive eigenvalues is always exactly two less than the number of a_{nk} with odd k that are considered in the schemes D_N or Q_N . As we show in the Appendix, this is the highest possible number of positive q for each scheme. This latter feature ensures that the coefficients in (3.2) are determined uniquely when we include all finite q_i obtained in the scheme D_N or Q_N in the sum in (3.2), replace Φ_{pc} and Φ_{hc} by their truncation according to D_N or Q_N , and replace (3.1) by the Marshak-type condition⁽²¹⁾

$$\int_0^1 d\mu \int_0^\infty v^2 dv f(v, \mu, R) \psi_{n,2k+1}(v, \mu) = 0 \quad (3.5a)$$

with

$$n \leq N, \quad 2k+1 \leq N \quad \text{for } Q_N \quad (3.5b)$$

$$n+2k+1 \leq N \quad \text{for } D_N \quad (3.5c)$$

Since the $\psi_{nk}(v, \mu)$ with odd k alone are complete on the half range $0 < \mu < 1$; $0 < v < \infty$, the condition (3.5) becomes equivalent to (3.1) for $N \rightarrow \infty$. Substitution of (3.1) and the truncation of (3.2) into (3.5a) leads to a number of conditions on the elements of the vector $\mathbf{d} \equiv (C, D, d_1, \dots, d_n)$ that can be written in the general form

$$\mathbf{M} \cdot \mathbf{d} + \mathbf{e} = 0 \quad (3.6)$$

where the rows of \mathbf{M} contain the half range moments (3.5a) of the truncated fundamental solutions Φ_{pc} , Φ_{hc} , and $\Phi_i^{(+)}$, and \mathbf{e} contains the corresponding moments of the equilibrium distribution $f_M(v)$. The coefficient vector \mathbf{d} is then obtained from (3.6) by a matrix inversion.

4. RESULTS AND DISCUSSION

The procedure outlined in the preceding section was carried out for several sphere radii R and for several truncation schemes Q_N and D_N . The most important quantity to be derived from those results is the reaction rate coefficient k , i.e., the total number of particles absorbed by the sphere per unit time divided by the density at infinity. From (3.2) and (2.16) one finds

$$k = \frac{4\pi R^2}{n_0(m\beta)^{1/2}} \int d\mathbf{v} (-v\mu) f(v, \mu, R) = \frac{-4\pi}{(m\beta)^{1/2}} C(R) \tag{4.1}$$

where we restored the factor $(m\beta)^{1/2}$ to obtain k in regular units. The limit of k for $R \downarrow 0$ is easily obtained: spheres with radii very small compared to l do not influence the distribution of incoming particles to any appreciable extent, so we may put

$$f(v, \mu, R) \rightarrow n_0 f_M(v) \Theta(-\mu) \quad \text{for } R \downarrow 0 \tag{4.2}$$

and k approaches the kinetic limit

$$k_{\text{kin}} = 4\pi R^2 (2\pi m\beta)^{-1/2} \tag{4.3}$$

In Fig. 1 we present our results for the ratio

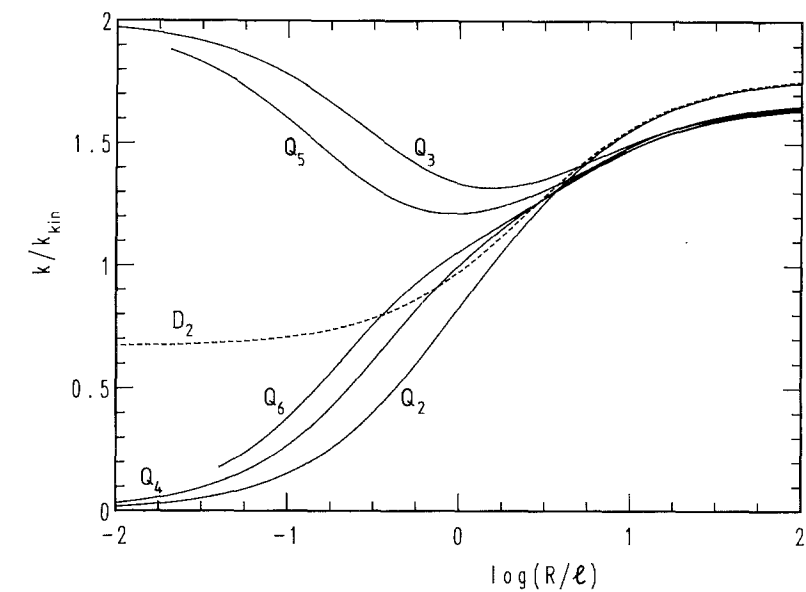
$$k/k_{\text{kin}} = -(2\pi)^{1/2} C(R) \tag{4.4}$$

as a function of $\log(R/l)$ for several D_N and Q_N truncation schemes. For small R and large N the determination of the coefficients in (3.2) becomes unreliable, since the elements of \mathbf{M} in (3.6) contain the Bessel functions $K_{k+1/2}(R)$ and the $g_k(R)$ of (2.16), which for large k and small R become very large. The curves in Fig. 1 are continued toward small R until the ensuing numerical errors no longer allow one to satisfy (3.6) to an accuracy better than 10^{-6} .

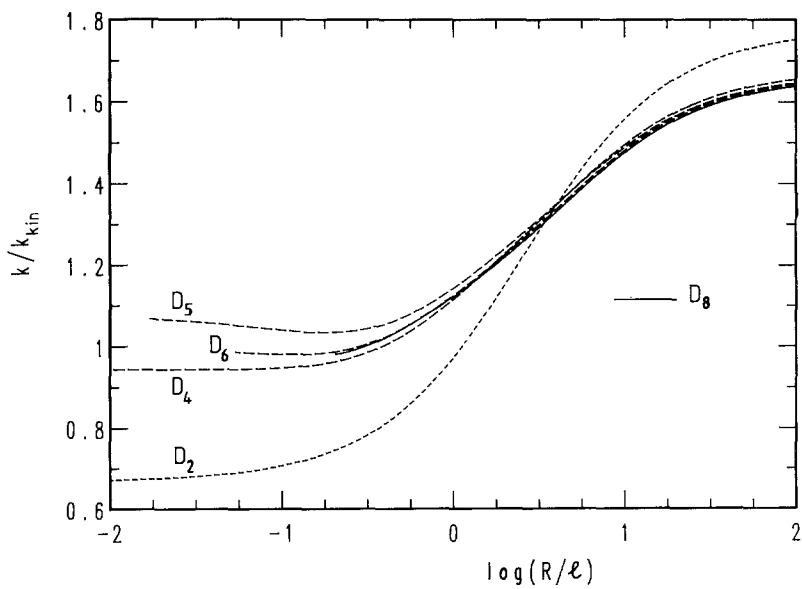
In Fig. 1 there is a clear difference between the D_N and Q_N approximants. The former converge quickly for not too small R , and the values at the point where numerical uncertainties become too large are close to the theoretical limit $k(R) = k_{\text{kin}}(R)$ for not too small N . The Q_N approximants converge much more slowly and they are still far away from the theoretical limit at low R .

For large R the values for k are not too much different in the two schemes; the values $k^N(R)$ in the D_N scheme depend more smoothly on N , and they can be extrapolated empirically according to

$$k^N(R) = k^\infty(R) + \gamma N^{-\delta} \tag{4.5}$$



(a)



(b)

Fig. 1. The ratio of the reaction rate coefficient to the kinetic theory value for (a) quadratic and (b) diagonal approximations. Note the different scales in the ordinate.

The convergence exponent δ varies from $\delta \simeq 1.40$ for $R = 10^6$ to $\delta \simeq 1.30$ for $R = 10$. The dependence of $k^N(R)$ on R for $\log R \geq 0.5$ can be fitted well by an expression of the type

$$R^{-2}k^N(R) = k_0^N + k_1^N R^{-1} + k_2^N R^{-2} + k_3^N R^{-3} + k_4^N R^{-4} \quad (4.6)$$

The extrapolation procedure (4.5) can be used to obtain an estimate for the k_i^∞ ; this leads to our best estimate

$$\frac{k(R)}{k_{\text{kin}}(R)} = 1.652\underline{3} - 2.444\underline{4}R^{-1} + 5.7\underline{7}R^{-2} \quad (R \geq 10l) \quad (4.7)$$

where the estimated error is about 3 units in the underlined decimal.

When we compare the result (4.7) with the analogous result for Brownian particles,⁽¹³⁾ two differences are apparent. First, the reaction rate remains of order R^2 for all R , whereas it becomes of order R for large R in the Brownian case. This decrease in the Brownian case is caused by the friction the Brownian particles experience when moving through the background gas; to maintain a flow, a concentration gradient must be maintained, and the density near the absorbing sphere is of order l/R compared to the one at infinity. A one-component gas can flow without any density gradient, as we saw in discussing (2.17), and resistance to flow occurs mainly in the boundary layer, where ψ_{nk} with $n+k \geq 2$ become important. This is connected with the second main difference: the leading term in (4.7) depends sensitively on the structure of the boundary layer [the D_2 approximation, which contains no $\Phi_i^{(+)}$ in the ansatz (3.2), would yield $k(\infty) = (16/9)k_{\text{kin}}$], but does not contain any transport coefficient, although the precise value of course depends on ratios of the ω_{nk} . In the Brownian case the leading term can be determined from hydrodynamics and is proportional to the diffusion coefficient.

In addition to the results for $k(R)$, our calculations produced results for the distribution function itself. Some of them can be found elsewhere⁽²³⁾; here, we merely present a few illustrative aspects. In Fig. 2 we show the density profile

$$n(r) = \int d\mathbf{v} f(v, \mu, r) \quad (4.8)$$

in the boundary layer for a few D_N and for $R = 10l$. In the higher D_N we find a steep decline of $n(r)$, but the profile is less steep than in the analogous Brownian case. The convergence with increasing N is more rapid well away from the surface, where the exponent in a fit of type (4.5) is 1.3, than immediately at the surface, where the exponent is 0.6. The latter value

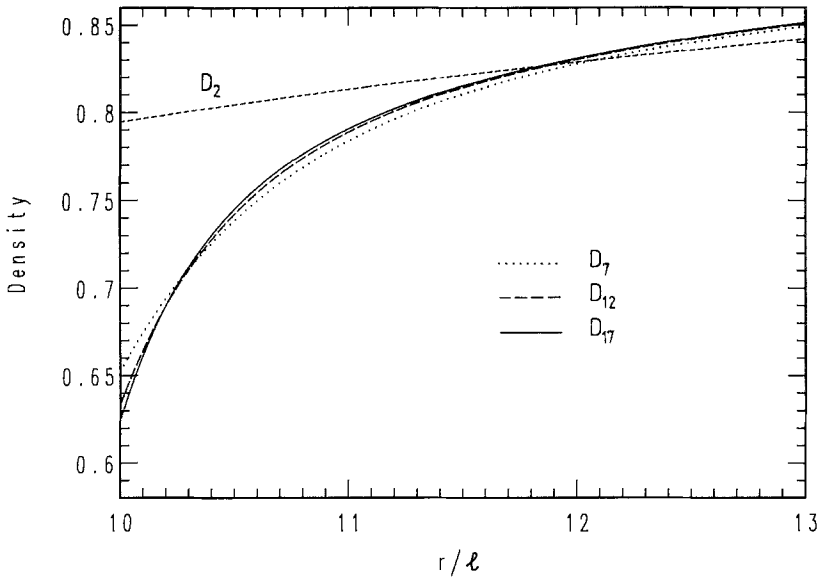


Fig. 2. The particle density $n(r)$ near the surface of a completely absorbing sphere of radius $R = 10l$ in various approximations.

is roughly the same as in the Brownian particle case. Attempts to fit $n(r - R)$ as a function of $(r - R)$ gave no indications for a nonanalytic $(r - R)$ dependence, though our method is not sensitive enough to detect logarithmic singularities.

In Fig. 3 we present the temperature profile in the boundary layer, given by

$$\frac{3}{2} n(r) kT(r) = \frac{1}{2} m \int d\mathbf{v} \mathbf{V}^2 f(v, \mu, r) \tag{4.9a}$$

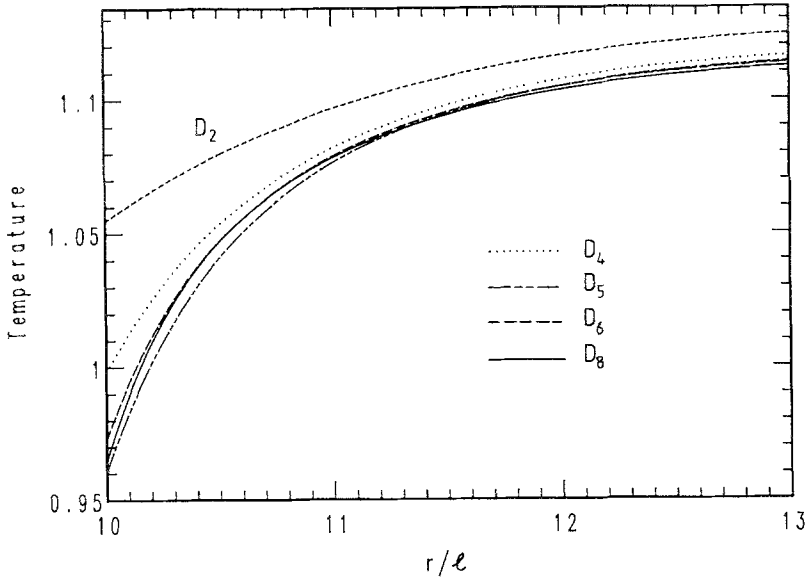
with

$$\mathbf{V} = \mathbf{v} - \mathbf{u}(r); \quad n(r) \mathbf{u}(r) = \int d\mathbf{v} \mathbf{v} f(v, \mu, r) \tag{4.9b}$$

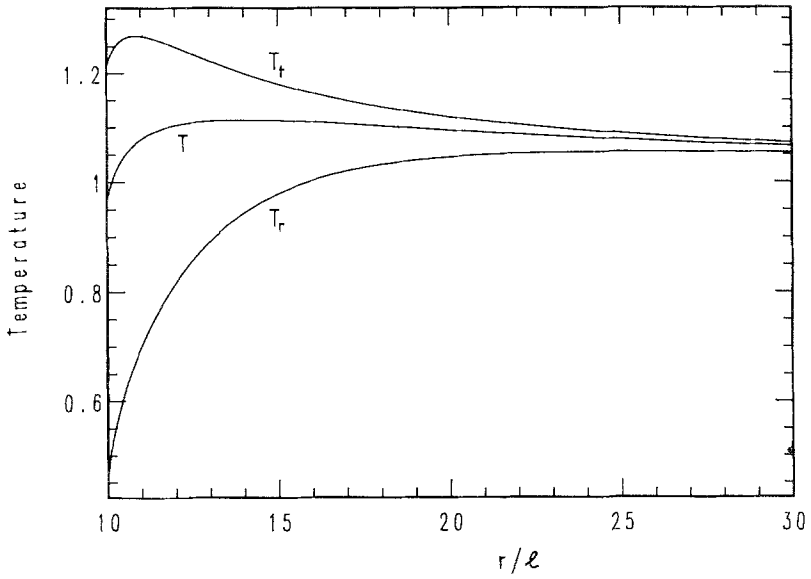
Of course, $\mathbf{u}(r)$ is directed in the negative \mathbf{r} direction. In terms of the $A_{nk}(r)$, $T(r)$ can be written as

$$\frac{T(r)}{T_0} = \frac{1 + A_{00}(r) - (2/3)^{1/2} A_{10}(r)}{1 + A_{00}(r)} - \frac{\frac{1}{3} [A_{01}(r)]^2}{[1 + A_{00}(r)]^2} \tag{4.10}$$

In Fig. 3 we also present the radial and transverse parts $T_r(r)$ and $T_t(r)$ of the temperature, obtained by taking only the radial and transverse com-



(a)



(b)

Fig. 3. (a) The temperature profile near a totally absorbing sphere of radius $R=10l$ in various approximations. (b) The division of temperature into a radial and a transverse part (see text) for the D_8 approximation.

ponents of V^2 in (4.9a), and changing the $3/2$ into $1/2$ and 1 , respectively. One sees that the rather small effect in $T(r)$ is the result of much larger effects, of opposite sign, in $T_r(r)$ and $T_t(r)$. The much higher values for $T_t(r)$ are the effect of collisions that partly transform the directed kinetic energy associated with the systematic velocity $\mathbf{u}(r)$ into undirected kinetic energy in the transverse components of \mathbf{v} . The curves in Fig. 3 also clearly demonstrate that the gas in the boundary layer is far from thermal equilibrium.

Finally, we provide in Table I some numerical values for $k(R)/k_{\text{kin}}(R)$ and for the ratio $D(R)/C(R)$ in (3.2), i.e., for the ratio between heat and particle current. The "need" for an additional heat current is clear from Fig. 3: clearly, the average kinetic energy of an absorbed particle exceeds the thermal value $(3/2)kT_0$, at least when the directed kinetic energy is also taken into account. The exact value for the ratio D/C in the limit of small radii is obtained by considerations analogous to the ones given before (4.2):

$$D(R)/C(R) = 1/\sqrt{10} = 0.316\dots \quad \text{for } R \downarrow 0 \quad (4.11)$$

On the other hand, one expects in the limit of large radii

$$D(R)/C(R) = \text{const}/R \quad \text{for } R \rightarrow \infty \quad (4.12)$$

where the constant in D_2 equals $3(5\pi)^{1/2}/16$ ($=0.743\dots$). Table I shows that for small radii the D_2 approximation becomes completely inadequate, whereas for large radii the correction due to the boundary layer amounts to about 7% for the reaction rate coefficient and to merely 2% for the ratio D/C .

Table I. Values for the Reaction Rate Coefficient k and the Ratio D/C between Heat and Particle Current in Various Approximations for Several Values of the Radius R

$\log(R/l)$	k/k_{kin}			D/C	
	D_2	D_8	Extrapolated ^a	D_2	D_8
-1	0.706	—	—	1.401734	—
0	0.973	1.122	1.117	0.642238	0.287473
1	1.558	1.475	1.461	0.078424	0.075176
2	1.751	1.637	1.628	0.007491	0.007617
3	1.775	1.658	1.650	0.000744	0.000758

^a The extrapolated values are obtained by fits of type (4.5).

5. CONCLUDING REMARKS

A droplet in a supersaturated vapor does not merely absorb particles impinging upon it; it also emits molecules into the gas. Absorption and emission balance when the gas has the saturation density $n_s(R)$, which depends on R due to surface tension effects.⁽²⁴⁾ Hence a more realistic boundary condition instead of (3.1) is

$$f(v, \mu, R) = n_s(R) f_M(v) \quad \text{for } \mu > 0 \quad (5.1)$$

This boundary condition, together with the one at $r \rightarrow \infty$, is clearly satisfied by

$$f(v, \mu, r) = f_M(v) \{ n_s + (n_0 - n_s) [1 + \Phi_a(v, \mu, r)] \} \quad (5.2)$$

with Φ_a the solution discussed in the preceding sections. The solution (5.2) has the additional advantage that, for n_0 not too different from n_s , it does not differ as much from the equilibrium distribution as $f_a(v, \mu, r)$; hence, the use of the *linearized* Boltzmann equation is better justified. We note in passing that (5.2) with $n_s > n_0$ can be used to describe the situation around an evaporating superheated droplet.

Our treatment is also generalizable without much difficulty to more general boundary conditions, in particular to partial absorption and to emission with a distribution corresponding to a temperature different from T_0 . This is of particular importance for the case of growing droplets, where the heat of condensation may cause appreciable temperature differences between the droplet and the surrounding gas. We shall not discuss these more general boundary conditions any further, since they will be subject of a forthcoming paper.⁽²⁵⁾

The restriction to Maxwell molecules was made mainly for calculational convenience. For more general potentials the matrix \mathbf{A} in (2.14) is no longer a diagonal one, but it remains symmetric, and the conclusions in the Appendix still hold. We do not expect qualitative differences in the solution; there is no assurance, however, that the results in the D_N truncation scheme will approach the known limit for small R equally well.

The formal limiting case $R \downarrow 0$ of course does not refer to the very first stages of nucleation of a droplet from the vapor. For droplet radii near the critical value for droplet growth our boundary conditions are much too simple. However, for not too high n_s , there is a range of radii large compared to the critical radius (typically about 10 \AA) and still small compared to the mean free path (typically of the order of 1000 \AA), where the limiting form (4.3) can be expected to hold. The situation may be different for high n_s , and in particular near the critical point, where the densities of vapor

and liquid become comparable. In that region the treatment of the droplet surface as a sharp mathematical surface also becomes problematic. Finally, the use of *stationary* solutions of the Boltzmann equation in our treatment presupposes that the velocity with which the droplet grows is small compared to the thermal velocity in the vapor. Since the gas flow arriving at the surface has a mean velocity comparable to the thermal velocity in our case (where the particle transport is convective), this requires an appreciable difference in density between liquid and vapor.

As we remarked after (3.2), the existence and uniqueness of the solutions constructed in Section 3 have not been proved for our case. Rigorous proofs, based, e.g., on half range completeness theorems, exist for a number of one-dimensional problems: the Klein–Kramers case⁽²⁶⁾ and the one-speed neutron transport equation⁽²⁷⁾; the BGK case is discussed in ref. 9. The success of our approximate procedure, in particular the smooth dependence of type (4.5) of various results on the number of moments, can be considered as evidence in favor of the half-space completeness conjecture for our problem.

The main result of this paper is the demonstration that the Burnett moment expansion with the truncation prescription D_N converges down to quite low values of the droplet radius, and that its results connect smoothly to the known limit of vanishing radius. The specific numerical results are certainly less significant, due to the assumption of Maxwell molecules and to several other simplifications, discussed earlier in this section; some of these simplifications will be removed in subsequent work.⁽²⁵⁾ On the other hand, we expect that our qualitative results on the adequacy of the D_2 (or 13-moment) approximation, and thus on the importance of “genuine” boundary layer effects, will have broader validity.

APPENDIX

In this Appendix we discuss the generalized eigenvalue problem (2.14) by extending the treatment proposed by Kumar and Menon⁽¹²⁾ for the Brownian motion case. We arrange the coefficients in $\mathbf{a}^{(q)}$ according to [we henceforth omit the index (q)]

$$\mathbf{a}^t = (a_{00}, a_{01}, a_{10}, a_{11}; a_{02}, a_{20}, a_{12}, \dots) \quad (\text{A.1})$$

where the arrangement of the further a_{nk} is immaterial for our purposes. If we denote the first four components by \mathbf{a}'_1 and the remainder of the vector by \mathbf{a}'_2 , (2.14) for Maxwell molecules can be decomposed into the pair of equations

$$q(\mathbf{B}_{11} \cdot \mathbf{a}_1 + \mathbf{B}_{12} \cdot \mathbf{a}_2) = \mathbf{A}_{11} \cdot \mathbf{a}_1 \quad (\text{A.2a})$$

$$q(\mathbf{B}'_{12} \cdot \mathbf{a}_1 + \mathbf{B}_{22} \cdot \mathbf{a}_2) = \mathbf{A}_{22} \cdot \mathbf{a}_2 \quad (\text{A.2b})$$

The matrix \mathbf{A}_{11} has the diagonal form

$$\mathbf{A}_{11} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2/3 \end{pmatrix} \tag{A.3}$$

For different potentials the nonzero matrix element may have a different value and there may be \mathbf{A}_{12} matrices that connect a_{11} to higher a_{nk} . In any case, one can conclude from (2.13) that the \mathbf{a}_1 for $q \neq 0$ must have the form

$$\mathbf{a}'_1 = (a_{00}, 0, a_{10}, 0) \tag{A.4}$$

i.e., the vectors $\mathbf{a}^{(q)}$ for $q \neq 0$ carry no heat or particle current. Thus, the right-hand side of (A.2a) vanishes and one obtains for $q \neq 0$

$$\mathbf{a}_1 = -\mathbf{B}_{11}^{-1} \cdot \mathbf{B}_{12} \cdot \mathbf{a}_2 \tag{A.5}$$

{The matrix \mathbf{B}_{11} , given by [see (2.13)]

$$\mathbf{B}_{11} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & -\sqrt{2/3} & 0 \\ 0 & -\sqrt{2/3} & 0 & \sqrt{5/3} \\ 0 & 0 & \sqrt{5/3} & 0 \end{pmatrix} \tag{A.6}$$

turns out to be invertible.} Substitution into (A.2) gives (even for general potentials, since $a_{11} = 0!$)

$$q[\mathbf{B}_{22} - \mathbf{B}'_{12} \cdot \mathbf{B}_{11}^{-1} \cdot \mathbf{B}_{12}] \cdot \mathbf{a}_2 = \mathbf{A}_{22} \cdot \mathbf{a}_2 \tag{A.7}$$

After substitution of the expression for \mathbf{B}_{12} , one sees that the matrix $\mathbf{B}'_{12} \cdot \mathbf{B}_{11}^{-1} \cdot \mathbf{B}_{12}$ vanishes identically. The matrix \mathbf{A}_{22} is diagonal with positive eigenvalues for Maxwell molecules, and symmetric and positive definite for general potentials.⁽¹⁶⁾ Hence $\mathbf{A}_{22}^{1/2}$ exists and is invertible, and (A.7) can be transformed into the regular eigenvalue problem

$$\mathbf{A}_{22}^{-1/2} \cdot \mathbf{B}_{22} \cdot \mathbf{A}_{22}^{-1/2} \cdot [\mathbf{A}_{22}^{1/2} \cdot \mathbf{a}_2] \equiv \tilde{\mathbf{B}}_{22} \cdot [\mathbf{A}_{22}^{1/2} \cdot \mathbf{a}_2] = q^{-1} \mathbf{A}_{22}^{1/2} \cdot \mathbf{a}_2 \tag{A.8}$$

Since $\mathbf{A}_{22}^{-1/2} \cdot \mathbf{B}_{22} \cdot \mathbf{A}_{22}^{-1/2}$ is real and symmetric, the eigenvalues q^{-1} are real and semisimple, and the associated eigenvectors are complete in the \mathbf{a}_2 space. Moreover, none of the q can be zero. The transformation just carried out therefore shows that there are no generalized eigenvectors of (2.14) with $q = 0$ beyond the four already found in Section 2 [strictly speaking, all this follows rigorously only for truncated versions of (2.14); for the infinite system one would have to prove self-adjointness of $\tilde{\mathbf{B}}_{22}$].

It is clear from (2.13) that \mathbf{B}_{22} has matrix elements only between ψ_{nk} and $\psi_{n'k'}$ with k and k' of different parity. On the other hand, for a centrally symmetric potential, \mathbf{A}_{22} connects only ψ_{nk} with equal k parity. Hence \mathbf{B}_{22} also connects ψ_{nk} with different k parity. One now easily shows (e.g., by rearranging the components of \mathbf{a}_2 in such a way that all a_{nk} with odd k precede those with even k) that the rank of $\tilde{\mathbf{B}}_{22}$ is at most twice the number of odd- k or twice the number of even- k moments, whichever is smaller. Since in Q_N or D_N the number of odd- k moments never exceeds the number of even- k ones, the number of nonzero q values is at most twice the number of odd moments in \mathbf{a}_2 ; since the q 's occur in pairs of opposite sign, the number of positive q 's is thus at most equal to the number of odd moments in \mathbf{a}_2 , or two less than the number of odd moments in $\mathbf{a}' = (\mathbf{a}'_1, \mathbf{a}'_2)$ (note that \mathbf{a}_1 contains two odd moments). As we reported in Section 3, this maximal value is found in all of our calculations.

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