

Burnett Coefficients and Correlation Functions

J. A. McLennan

Lawrence Livermore Laboratory*, Livermore, California 94550

Lehigh University, Bethlehem, Pennsylvania 18015

(Received 27 December 1972; revised manuscript received 27 March 1973)

Correlation-function expressions are derived for the linearized Burnett and super-Burnett-coefficients for a fluid. The results involve higher spatial moments of correlation functions such as occur in the Green-Kubo theory for the Navier-Stokes transport coefficients. The investigation is stimulated primarily by indications that the Burnett coefficients might actually be infinite, but this problem is not discussed here.

I. INTRODUCTION

The hydrodynamic equations for a gas can be derived from the Boltzmann equation by the Chapman-Enskog¹ approximation method, which in the first approximation gives the Euler equations for an ideal fluid, and in the second approximation the Navier-Stokes equations. The third approximation has been worked out by Burnett.²

To describe Burnett's equations, we write the equation of continuity, energy equation, and equation of motion as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \vec{u} = 0,$$

$$\frac{\partial \epsilon}{\partial t} + \vec{u} \cdot \nabla \epsilon = -h \nabla \cdot \vec{u} - \nabla \cdot \vec{s}^* - t_{ij}^* \partial u_i / \partial x_j, \quad (1)$$

$$\rho \left[\frac{\partial u_i}{\partial t} + \vec{u} \cdot \nabla u_i \right] = - \frac{\partial P}{\partial x_i} - \frac{\partial t_{ij}^*}{\partial x_j}.$$

Here ρ is the mass density, \vec{u} the fluid velocity, ϵ the thermodynamic energy density, h the density of enthalpy, and P the pressure. In addition, \vec{s}^* is the heat flux, and t_{ij}^* the viscous part of the pressure tensor.

In the first approximation, $\vec{s}^* = 0$, $t_{ij}^* = 0$, resulting in Euler's equations. In the next, or Navier-Stokes, approximation,

$$\vec{s}^* = -\lambda \nabla T, \quad (2)$$

$$t_{ij}^* = -\eta \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \nabla \cdot \vec{u} \right) - \kappa \delta_{ij} \nabla \cdot \vec{u},$$

where λ is the thermal conductivity, η the shear viscosity, and κ the bulk viscosity. (Actually for a low-density monatomic gas, $\kappa = 0$.) In Burnett's approximation, there are additional contributions, $\Delta \vec{s}^*$ and Δt_{ij}^* , to be added to the above which are given by^{1,2}

$$\begin{aligned} \Delta s_i^* &= K_1 \nabla^2 u_i + K_2 \frac{\partial D}{\partial x_i} + K_3 D_{ij} \frac{\partial T}{\partial x_j} \\ &+ K_4 A_{ij} \frac{\partial T}{\partial x_j} + K_5 D \frac{\partial T}{\partial x_i} + K_6 D_{ij} \frac{\partial P}{\partial x_j}, \end{aligned}$$

$$\begin{aligned} \Delta t_{ij}^* &= K_7 \left[\frac{\partial^2 T}{\partial x_i \partial x_j} - \frac{1}{3} \delta_{ij} \nabla^2 T \right] + K_8 \left[\frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_j} - \frac{1}{3} \delta_{ij} (\nabla T)^2 \right] \\ &+ K_9 \left\{ \frac{\partial^2 P}{\partial x_i \partial x_j} - \frac{1}{3} \delta_{ij} \nabla^2 P - \frac{1}{P} \left[\frac{\partial P}{\partial x_i} \frac{\partial P}{\partial x_j} - \frac{1}{3} \delta_{ij} (\nabla P)^2 \right] \right\} \\ &+ K_{10} \left\{ \frac{\partial T}{\partial x_i} \frac{\partial P}{\partial x_j} + \frac{\partial T}{\partial x_j} \frac{\partial P}{\partial x_i} - \frac{2}{3} \delta_{ij} \nabla T \nabla P \right\} \\ &+ K_{11} D \bar{D}_{ij} + K_{12} [\bar{D}_{iK} \bar{D}_{jK} - \frac{1}{3} \delta_{ij} \bar{D}_{Kl} \bar{D}_{Kl}] \\ &+ K_{13} [D_{iK} A_{jK} + D_{jK} A_{iK} + A_{iK} A_{jK} - \frac{1}{3} \delta_{ij} A_{Kl} A_{Kl}]. \quad (3) \end{aligned}$$

Here we have introduced the abbreviations

$$D_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right),$$

$$D = D_{ii} = \nabla \cdot \vec{u},$$

$$\bar{D}_{ij} = D_{ij} - \frac{1}{3} \delta_{ij} D,$$

$$A_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i} \right).$$

The K 's are higher-order transport coefficients which can be evaluated, for a given interatomic force law, in much the same way as λ and η .

There are two kinds of terms in Δs_i^* and Δt_{ij}^* , those which are quadratic in first derivatives, and those which are linear in second derivatives. The linear terms are important for small-amplitude, but rapidly varying, processes, such as high-frequency sound. These terms, as well as linear terms occurring in still higher orders (super-Burnett), have been extensively analyzed and compared with the data on sound propagation by Uhlenbeck and Foch.³ Their theory is in excellent agreement with experiment, and is clearly superior to the Navier-Stokes approximation.

The nonlinear terms have apparently not been observed directly in experiments on gases, but

similar terms describe effects which are observed in more complex systems. As an example, consider a shear flow with velocity in the x direction, varying in the y direction. One finds contributions to the pressure tensor as follows:

$$\Delta t_{xx}^* = \left(\frac{1}{12}K_{12} + \frac{7}{12}K_{13}\right) \left(\frac{\partial u_x}{\partial y}\right)^2,$$

$$\Delta t_{yy}^* = \left(\frac{1}{12}K_{12} - \frac{5}{12}K_{13}\right) \left(\frac{\partial u_x}{\partial y}\right)^2,$$

$$\Delta t_{zz}^* = -\frac{1}{6}(K_{12} + K_{13}) \left(\frac{\partial u_x}{\partial y}\right)^2.$$

Thus a shear flow sets up normal stresses. Such normal stresses are responsible for, for example, the Weissenberg effect: If a rod standing in a container of liquid is set into rotation, the resulting shear flow can push the liquid up the rod.⁴

Here the method of correlation functions will be applied to the linearized Burnett coefficients, to obtain formulas analogous to the Green-Kubo expressions for the Navier-Stokes transport coefficients. The motivation for this study stems primarily from the slow decay of a time-dependent correlation function, first observed in self-diffusion by Alder and Wainwright.^{5,6} This slow decay (which is not included in the Boltzmann equation) contradicts the usual assumption of widely separated time scales for hydrodynamics and microscopic relaxation, and so raises a question as to the proper description of hydrodynamics. In particular, the Navier-Stokes coefficients for two-dimensional systems have been shown to be infinite.⁸ In three dimensions Ernst and Dorfman⁷ have obtained a nonanalytic dependence of the hydrodynamic frequencies on the wave number, which is such as to imply that the Burnett coefficients are infinite. This of course also implies that the Chapman-Enskog expansion, used below, is invalid, but the resulting correlation functions might still be interesting objects of study.

II. SELF-DIFFUSION

Consider first the case of self-diffusion (or Brownian motion).⁸ The hydrodynamic equation is the diffusion equation, augmented by Burnett-type terms:

$$\frac{\partial n}{\partial t} = D_1 \nabla^2 n + D_2 \nabla^2 \nabla^2 n + \dots \quad (4)$$

The diffusion process can be described by the correlation function

$$G(\vec{x}, t) = \langle \delta(\vec{q}) \delta(\vec{q}_t - x) \rangle, \quad (5)$$

where \vec{q} denotes the initial position of the particle, \vec{q}_t is its position at time t , and the brackets denote an average over an equilibrium ensemble. It is convenient to make a Fourier transform,

$$\bar{G}(\vec{k}, t) = \int d^3x e^{i\vec{k} \cdot \vec{x}} G(\vec{x}, t) = \langle e^{i\vec{k} \cdot \Delta \vec{q}} \rangle. \quad (6)$$

Here $\Delta \vec{q}$ denotes the displacement of the particle in time t , and we have assumed the particle to occupy unit volume. According to Onsager's assumption on the regression of fluctuations, $G(\vec{x}, t)$ satisfies the diffusion equation for long times, that is,

$$\bar{G}(\vec{k}, t) \underset{t \rightarrow \infty}{\sim} e^{-\rho(\vec{k})t},$$

where $\rho(\vec{k})$ is obtained by Fourier transformation of the diffusion equation,

$$\begin{aligned} p(\vec{k}) &= D_1 k^2 - D_2 k^4 + \dots \\ &= -\sum_{n=1}^{\infty} D_n (-k^2)^n. \end{aligned} \quad (7)$$

We can obtain $p(\vec{k})$ from $\bar{G}(\vec{k}, t)$ by

$$p(\vec{k}) = -\lim_{t \rightarrow \infty} \frac{1}{t} \ln \bar{G}(\vec{k}, t). \quad (8)$$

On the other hand, $\bar{G}(\vec{k}, t)$ is the generating function for the random variable $\Delta \vec{q}$, and its cumulant expansion is

$$\ln \bar{G}(\vec{k}, t) = \sum_{n=1}^{\infty} \frac{(ik)^n}{n!} C_n(\Delta q),$$

where $C_n(\Delta q)$ is the n th-order cumulant, and Δq now denotes the component of the displacement along \vec{k} . The odd-order cumulants vanish because of spherical symmetry, while

$$\begin{aligned} C_2 &= \langle (\Delta q)^2 \rangle, \\ C_4 &= \langle (\Delta q)^4 \rangle - 3[\langle (\Delta q)^2 \rangle]^2, \text{ etc.} \end{aligned}$$

Thus, we can express the diffusion constants D_n in terms of the cumulants:

$$D_n = \frac{1}{(2n)!} \lim_{t \rightarrow \infty} \frac{1}{t} C_n(\Delta q).$$

For D_1 the above formula is just the Einstein expression

$$D_1 = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle (\Delta q)^2 \rangle.$$

An equivalent formula is

$$D_1 = \int_0^{\infty} dt \chi_2(t),$$

where $\chi_2(t)$ is the second-order velocity autocorrelation

$$\chi_2(t) = \langle v(0)v(t) \rangle.$$

Here $v(t)$ is the velocity of the particle at time t , or rather its component along \vec{k} .

For D_2 , we find

$$D_2 = \frac{1}{4!} \lim_{t \rightarrow \infty} \frac{1}{t} \{ \langle (\Delta Q)^4 \rangle - 3[\langle (\Delta Q)^2 \rangle]^2 \}. \quad (9)$$

This can be expressed in terms of the fourth-order velocity autocorrelation $\chi_4(t_1, t_2, t_3)$, defined by

$$\begin{aligned} \chi_4(t_1, t_2, t_3) &= \langle v(0)v(t_1)v(t_2)v(t_3) \rangle \\ &\quad - \langle v(0)v(t_1) \rangle \langle v(t_2)v(t_3) \rangle \\ &\quad - \langle v(0)v(t_2) \rangle \langle v(t_1)v(t_3) \rangle \\ &\quad - \langle v(0)v(t_3) \rangle \langle v(t_1)v(t_2) \rangle. \end{aligned}$$

We obtain immediately

$$\begin{aligned} D_2 &= \frac{1}{4!} \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 \\ &\quad \times \int_0^t dt_4 \chi_4(t_1 - t_4, t_2 - t_4, t_3 - t_4), \end{aligned}$$

which can be manipulated into

$$D_2 = \int_0^\infty dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \chi_4(t_1, t_2, t_3). \quad (10)$$

III. SIMPLE FLUID

In this section, correlation-function expressions for other higher-order transport coefficients will be derived. In the general case, the correlation functions which occur cannot be expressed in the simple form (6) of a generating function, and so the method to be used differs from that of Sec. II. However, it can be verified that both methods yield the same result for the case of self-diffusion.

To identify the coefficients under discussion, we rewrite the earlier equations for ΔS_i^* , Δt_{ij}^* , including only linear terms (and with a slight change in notation):

$$\begin{aligned} \Delta S_i^* &= \alpha \nabla^2 u_i + \beta \nabla^2 \frac{\partial P}{\partial x_i} + \lambda_1 \nabla^2 \frac{\partial T}{\partial x_i}, \\ \Delta t_{ij}^* &= \xi \frac{\partial^2 T}{\partial x_i \partial x_j} + \zeta \frac{\partial^2 P}{\partial x_i \partial x_j} + 2\eta_1 \nabla^2 D_{ij} + \kappa_1 \delta_{ij} \nabla^2 D. \end{aligned} \quad (11)$$

Actually the terms with coefficients β , λ_1 , η_1 , κ_1 (as well as the higher-order diffusion constants of Sec. II) correspond to a super-Burnett approximation. Regarding the terms containing second derivatives, we could have included additional terms by writing, for example,

$$\alpha_1 \nabla^2 u_i + \alpha_2 \frac{\partial}{\partial x_i} \nabla \cdot \vec{u}$$

in place of the first term of ΔS_i^* . However, it is only the divergence of ΔS_i^* which occurs in the hydrodynamic equations, and so only the sum $\alpha = \alpha_1 + \alpha_2$ has significance.

There are five conserved quantities, corresponding to conservation of mass, energy, and momentum. Let ψ_α , $\alpha = 1, \dots, 5$, denote densities of the conserved quantities and φ_α^i their fluxes; the conservation laws are

$$\frac{\partial \psi_\alpha}{\partial t} + \frac{\partial \varphi_\alpha^i}{\partial x_i} = 0.$$

In place of the correlation function $G(\vec{x}, t)$ of Sec. II, we must now consider the matrix $G(\vec{x}, t)$ with elements

$$G_{\alpha\beta}(\vec{x}, t) = \langle \psi_\alpha(\vec{x}, t) \psi_\beta(0) \rangle - \langle \psi_\alpha \rangle \langle \psi_\beta \rangle.$$

In addition, introduce the matrices G^i and G^{ij} with elements

$$\begin{aligned} G^i_{\alpha\beta}(\vec{x}, t) &= \langle \varphi_\alpha^i(\vec{x}, t) \psi_\beta(0) \rangle - \langle \varphi_\alpha^i \rangle \langle \psi_\beta \rangle, \\ G^{ij}_{\alpha\beta}(\vec{x}, t) &= \langle \varphi_\alpha^i(\vec{x}, t) \varphi_\beta^j(0) \rangle - \langle \varphi_\alpha^i \rangle \langle \varphi_\beta^j \rangle. \end{aligned}$$

Their Fourier transforms will be denoted by \bar{G} , \bar{G}^i , \bar{G}^{ij} ; for example,

$$\bar{G}(\vec{k}, t) = \int d^3x e^{i\vec{k} \cdot \vec{x}} G(\vec{x}, t).$$

The conservation laws imply the relations

$$\begin{aligned} \frac{\partial \bar{G}}{\partial t} - ik_i \bar{G}^i &= 0, \\ \frac{\partial \bar{G}^i}{\partial t} - ik_j \bar{G}^{ij} &= 0. \end{aligned} \quad (12)$$

In addition, introduce

$$\begin{aligned} g_{\alpha\beta}(\vec{k}) &= \bar{G}_{\alpha\beta}(\vec{k}, 0), \\ h_{\alpha\beta}^i(\vec{k}) &= \bar{G}_{\alpha\beta}^i(\vec{k}, 0). \end{aligned}$$

The k dependence of g and h^i will be neglected, as it is due only to the short-range equilibrium fluctuations. For $k=0$, g and h^i can be expressed in terms of standard thermodynamic functions. We will find it convenient to choose a representation for the ψ_α such that $g_{\alpha\beta} = \delta_{\alpha\beta}$.

Let $\bar{\psi}_\alpha$ denote the average of the ψ_α . The linearized hydrodynamic equations, written in terms of $\bar{\psi}_\alpha$, will take the form

$$\frac{\partial \bar{\psi}_\alpha}{\partial t} = -p_{\alpha\beta} \bar{\psi}_\beta, \quad (13)$$

where the $p_{\alpha\beta}$ are differential operators, or after Fourier transforming, functions of k . Through fourth order in k , the $p_{\alpha\beta}$ can be determined from the constitutive equations (11).

If an initial distribution of local equilibrium is assumed, the $\psi_\alpha(\vec{k}, t)$ can be related to their

initial values by⁹

$$\bar{\psi}(\vec{k}, t) = G(\vec{k}, t)g^{-1}\bar{\psi}(\vec{k}, 0).$$

Hence,

$$\frac{\partial \bar{\psi}(\vec{k}, t)}{\partial t} = \frac{\partial G(\vec{k}, t)}{\partial t} g^{-1} G^{-1}(\vec{k}, t) g \bar{\psi}(\vec{k}, t).$$

Again, following Onsager, we assume that for large times the above correlation-function equation becomes identical to the hydrodynamic equation (13); hence,

$$\dot{p} = -\lim_{t \rightarrow \infty} \frac{\partial G}{\partial t} g^{-1} G^{-1} g. \tag{14}$$

This equation is analogous to Eq. (8), except that p and G are now matrices.

To make the k expansion, it is convenient to utilize Eqs. (12) to write

$$p = -\lim_{t \rightarrow \infty} ik_j [h^j + ik_m \int_0^t dt_1 \bar{G}^{jm}(\vec{k}, t_1)] \times [1 + ik_i \int_0^t dt_2 \bar{G}^i(\vec{k}, t_2)]^{-1}, \tag{15}$$

where we have assumed the representation $g = 1$. It is next necessary to expand \bar{G}^{jm} and \bar{G}^i in powers of k .

Before proceeding with the general case, it is instructive to first consider the simple situation which occurs if a single hydrodynamic mode can be decoupled and treated independently of the others. As a specific example, consider thermal conduction in a material with negligible coefficient of thermal expansion. (The self-diffusion of Sec. II provides another example.) Let ϵ denote the energy density and s_i its flux, and put

$$\psi = \epsilon/T\sqrt{C}, \quad \varphi^i = s_i/T\sqrt{C},$$

where C is the specific heat and T the Kelvin temperature (in units such that Boltzmann's constant is equal to 1). For the case under consideration, spherical symmetry implies that h^i vanishes, \bar{G}^i is odd in \vec{k} , and \bar{G}^{ij} is even in \vec{k} . One then finds, with the notation of Eq. (7), and again with \vec{k} in the x direction,

$$D_1 = \int_0^\infty dt \bar{G}^{xx}(0, t),$$

$$D_2 = \lim_{t \rightarrow \infty} \int_0^t dt_1 \left[-\frac{1}{2} \frac{\partial^2 \bar{G}^{xx}(\vec{k}, t_1)}{\partial k^2} \right]_{k=0} + i \bar{G}^{xx}(0, t_1) \int_0^t dt_2 \frac{\partial \bar{G}^{xx}(\vec{k}, t_2)}{\partial k} \Big|_{k=0} \Big]. \tag{16}$$

The first of these is essentially the Green-Kubo

formula for the thermal conductivity. The second can be written

$$D_2 = (1/CT^2) \lim_{t \rightarrow \infty} \int_0^t dt_1 \int d^3x \left[\frac{1}{2} x^2 \langle s_x(\vec{x}, t) s_x(0) \rangle - D_1(t) x \langle s_x(\vec{x}, t) \epsilon(0) \rangle \right],$$

where

$$D_1(t) = \int_0^t dt_1 \bar{G}^{xx}(0, t_1) = (1/CT^2) \int_0^t dt_1 \int d^3x \langle s_x(\vec{x}, t_1) s_x(0) \rangle.$$

The results of Sec. II can be recovered by making the substitutions $\epsilon = \delta(\vec{x} - \vec{q})$, $s_i = v_i \delta(\vec{x} - \vec{q})$, $CT^2 = 1$. Then one finds

$$D_2 = \lim_{t \rightarrow \infty} \int_0^t dt_1 \left\{ \frac{1}{2} \langle v(0) v(t_1) [\Delta q(t_1)]^2 \rangle - D_1(t) \langle v(0) \Delta q(t_1) \rangle \right\},$$

$$D_1(t) = \int_0^t dt_1 \chi_2(t_1).$$

This expression can then be reduced to the previous formula (9) for D_2 .

We now return to the problem with five hydrodynamic modes: A convenient choice for the ψ_α is¹⁰

$$\psi_1 = \rho/\bar{\rho} (TK_T)^{1/2},$$

$$\psi_2 = \left[\epsilon - \left(\frac{\partial \epsilon}{\partial \rho} \right)_T \rho \right] / T(\bar{\rho} C_v)^{1/2},$$

$$\psi_3 = g_x/(\bar{\rho} T)^{1/2}, \quad \psi_4 = g_y/(\bar{\rho} T)^{1/2}, \quad \psi_5 = g_z/(\bar{\rho} T)^{1/2}.$$

Here K_T is the isothermal compressibility, C_v the specific heat (per unit mass) at constant volume, ρ the mass density, ϵ the energy density, and \vec{g} the momentum density. With this choice, the matrix $g_{\alpha\beta}$ reduces to the unit matrix,

$$g_{\alpha\beta} = \delta_{\alpha\beta}.$$

The fluxes φ_α^i are

$$\varphi_1^i = g_i/(\bar{\rho} (TK_T)^{1/2}),$$

$$\varphi_2^i = \left[s_i - \left(\frac{\partial \epsilon}{\partial \rho} \right)_T g_i \right] / T(\bar{\rho} C_v)^{1/2},$$

$$\varphi_3^i = t_{xi}/(\bar{\rho} T)^{1/2}, \quad \varphi_4^i = t_{yi}/(\bar{\rho} T)^{1/2}, \quad \varphi_5^i = t_{zi}/(\bar{\rho} T)^{1/2},$$

where t_{ij} is the momentum flux and s_i the energy flux.

With \vec{k} in the x direction, the transverse modes g_y and g_z decouple and can be treated separately. The hydrodynamic equations, with the expressions (11) for Δs_i^* , Δt_{ij}^* included, reduce to

$$\frac{\partial \bar{g}_y}{\partial t} = -[\nu k^2 + \nu_1 k^4] \bar{g}_y,$$

where $\nu = \eta/\bar{\rho}$ is the kinematic viscosity, and

$$\nu_1 = \eta_1/\bar{\rho}.$$

The correlation-function expressions for η , η_1 can be obtained in the same way as Eq. (16); the results are

$$\eta = \frac{1}{T} \int_0^\infty dt \int d^3x \langle t_{xy}(0) t_{xy}(\vec{x}, t) \rangle,$$

$$\eta_1 = \lim_{t \rightarrow \infty} \frac{1}{T} \int_0^t ds \int d^3x \left\{ -\frac{1}{2} x^2 \langle t_{xy}(\vec{x}, s) t_{xy}(0) \rangle + \nu(t) x \langle t_{xy}(\vec{x}, s) g_x(0) \rangle \right\},$$

where

$$\nu(t) = (1/\bar{\rho}T) \int_0^t ds \int d^3x \langle t_{xy}(\vec{x}, s) t_{xy}(0) \rangle.$$

The first of these is the Green-Kubo formula for the shear viscosity.

For the remaining longitudinal modes, it is straightforward to obtain the matrix p of Eq. (13). The result can be expressed as an expansion in powers of k as

$$p = ikA_1 + k^2A_2 + ik^3A_3 + k^4A_4,$$

$$A_1 = -\frac{1}{(\bar{\rho}K_T)^{1/2}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & (\gamma-1)^{1/2} \\ 1 & (\gamma-1)^{1/2} & 0 \end{pmatrix},$$

$$A_2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \lambda/\bar{\rho}C_v & 0 \\ 0 & 0 & \eta'/\bar{\rho} \end{pmatrix},$$

$$A_3 = \frac{1}{(\bar{\rho}K_T)^{1/2}} \times \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha(K_T/T\bar{\rho}C_v)^{1/2} \\ \xi(\gamma-1)^{1/2} & [\xi + \xi(\bar{\rho}C_v/TK_T)^{1/2}] & 0 \end{pmatrix},$$

$$A_4 = \frac{1}{(T\bar{\rho}C_vK_T)^{1/2}} \begin{pmatrix} 0 & 0 & 0 \\ \beta & (\gamma-1)^{1/2}\beta & 0 \\ 0 & 0 & \eta'_1(TC_vK_T/\bar{\rho})^{1/2} \end{pmatrix}.$$

Here $\gamma = C_p/C_v$, $\eta' = \frac{4}{3}\eta + \kappa$, and $\eta'_1 = \frac{4}{3}\eta_1 + \kappa_1$.

It is now necessary to expand the right-hand side of Eq. (15) in powers of k . The transport coefficients are then determined by comparing the coefficients of this expansion with those in the expansion for p . The calculations are straightforward but tedious, and we simply list the results:

$$\alpha = (1/T) \int_0^\infty dt \int d^3x x \langle t_{xx}(\vec{x}, t) s'_x(0) \rangle,$$

$$\beta = \lim_{t \rightarrow \infty} (1/\bar{\rho}T) \int_0^t dt_1 \int d^3x \left\{ D_T(t) x \langle \epsilon'(\vec{x}, t_1) g_x(0) \rangle - \frac{1}{2} x^2 \langle s'_x(\vec{x}, t_1) g_x(0) \rangle \right\},$$

$$\xi = (1/T^2) \int_0^\infty dt \int d^3x x \langle t'_{xx}(\vec{x}, t) s_x(0) \rangle,$$

$$\zeta = (1/\bar{\rho}T) \int_0^\infty dt \int d^3x x \langle t'_{xx}(\vec{x}, t) g_x(0) \rangle,$$

$$\eta_1 = \lim_{t \rightarrow \infty} (1/T) \int_0^t dt_1 \int d^3x \left\{ \nu(t) x \langle t_{xx}(\vec{x}, t_1) g_x(0) \rangle - \frac{1}{2} x^2 \langle t_{xx}(\vec{x}, t_1) t'_{xx}(0) \rangle \right\},$$

$$\lambda_1 = \lim_{t \rightarrow \infty} (1/T^2) \int_0^t dt_1 \int d^3x \left\{ D_T(t) x \langle s'_x(\vec{x}, t_1) \epsilon'(0) \rangle - \frac{1}{2} x^2 \langle s_x(\vec{x}, t_1) s'_x(0) \rangle \right\}.$$

Here

$$\epsilon' = \epsilon - \left(\frac{\partial \epsilon}{\partial \rho} \right)_T \rho,$$

$$\vec{s}' = \vec{s} - (h/\bar{\rho}) \vec{g},$$

$$t'_{ij} = t_{ij} - \delta_{ij} \left[\left(\frac{\partial P}{\partial \epsilon} \right)_\rho \epsilon + \left(\frac{\partial P}{\partial \rho} \right)_\epsilon \rho \right],$$

$$D_T(t) = (1/\bar{\rho}C_vT^2) \int_0^t dt_1 \int d^3x \langle s'_x(\vec{x}, t_1) s'_x(0) \rangle,$$

$$\nu(t) = (1/\bar{\rho}T) \int_0^t dt_1 \int d^3x \langle t_{xy}(\vec{x}, t_1) t_{xy}(0) \rangle.$$

Expressions having a resemblance to the above have been obtained previously¹¹ by a method which allowed for dependence on frequency and wave number separately. The resemblance is, however, only superficial, since the Burnett coefficients as obtained above are defined by an expansion (the Chapman-Enskog expansion) which in effect requires a specific relation between frequency and wave number.

ACKNOWLEDGMENTS

It is a pleasure to thank T. E. Wainwright for discussions which stimulated the investigation. I am also indebted to J. R. Dorfman for uncovering an error in an early draft of the manuscript.

APPENDIX

The general expressions from which Burnett's coefficients for a low-density gas can be determined are not given by Burnett or Chapman and Cowling, and so will be listed for reference.

Let I denote the linearized collision operator, defined by

$$I\psi = \int d^3v_1 f_0(v_1) g d\sigma [\psi + \psi_1 - \psi' - \psi'_1],$$

where f_0 is the Maxwellian

$$f_0 = (m/2\pi T)^{3/2} e^{-mv^2/2T},$$

$d\sigma$ is the differential cross section, and the notation otherwise follows that of Chapman and Cowling. In addition, define the bilinear functional $J(\psi, \varphi)$,

$$J(\psi, \varphi) = \frac{1}{2} \int d^3v_1 f_0(v_1) g d\sigma [\psi\varphi_1 + \psi_1\varphi - \psi'\varphi'_1 - \psi'_1\varphi].$$

The average over a Maxwellian will be denoted by angular brackets,

$$\langle \psi \rangle = \int d^3v f_0 \psi.$$

Introduce the abbreviations

$$t_{ij} = m(v_i v_j - \frac{1}{3} \delta_{ij} v^2),$$

$$s_i = (\frac{1}{2} m v^2 - \frac{5}{2} T) v_i.$$

Let T_{ij} denote that solution to the integral equation

$$IT_{ij} = t_{ij}$$

which satisfies the conditions

$$\langle T_{ij} \psi_\alpha \rangle = 0, \quad \psi_\alpha = \{1, v_i, v^2\}.$$

Similarly, let S_i denote that solution to

$$IS_i = s_i$$

which satisfies

$$\langle S_i \psi_\alpha \rangle = 0.$$

Then the thermal conductivity and viscosity are given by

$$\lambda = \frac{1}{T^2} \langle s_x S_x \rangle, \quad \eta = \frac{1}{T} \langle t_{xy} T_{xy} \rangle.$$

The Burnett coefficients are given by

$$K_1 = \langle S_x v_y T_{xy} \rangle / P,$$

$$K_2 = \langle S_x [v_y T_{xy} - 2S_x] \rangle / 3P,$$

$$K_3 = (2/PT^2) \langle S_x [-TS_x + s_y T_{xy} + T v_x \partial S_x / \partial v_x + T^2 v_x \partial T_{xx} / \partial T - 2J(S_x, T_{xx})] \rangle,$$

$$K_4 = (K_1 - 3K_2) / T,$$

$$K_5 = (1/3PT) \langle S_x [8S_x - 2T \partial S_x / \partial T - 5v_x \partial S_x / \partial v_x] \rangle,$$

$$K_6 = -(2/\rho P) \langle T_{xx} \partial S_x / \partial v_x \rangle,$$

$$K_7 = 2K_1 / T,$$

$$K_8 = (2/PT^3) \langle T_{xx} [s_x S_x - T v_x S_x + T^2 v_x \partial S_x / \partial T - J(S_x, S_x)] \rangle,$$

$$K_9 = -(2/\rho P) \langle T_{xx} T_{xx} \rangle,$$

$$K_{10} = -(1/PT) [K_1 - \frac{1}{2} P (K_9 - K_6)],$$

$$K_{11} = (2/3P) \langle T_{xx} [T_{xx} - 2T \partial T_{xx} / \partial T] \rangle,$$

$$K_{12} = (3/\rho T) \langle T_{xx} [\frac{1}{2} T T_{xx} + t_{xx} T_{xx} - \frac{3}{2} T v_x \partial T_{xx} / \partial v_x - J(T_{xx}, T_{xx})] \rangle,$$

$$K_{13} = -\rho K_9.$$

The dimensionless parameters $\theta_1, \dots, \theta_5$ and $\omega_1, \dots, \omega_6$ defined in Chapman and Cowling are given in terms of the K 's by

$$\theta_1 = (\rho T / \eta^2) (K_5 + \frac{2}{3} K_4),$$

$$\theta_2 = (\rho T / 2\eta^2) K_4,$$

$$\theta_3 = (\rho P / \eta^2) K_6,$$

$$\theta_4 = (2\rho / \eta^2) K_1$$

$$\theta_5 = (\rho T / \eta^2) (K_3 + K_4),$$

$$\omega_1 = (P / \eta^2) (K_{11} - \frac{4}{3} \rho K_9),$$

$$\omega_2 = -(\rho P / \eta^2) K_9,$$

$$\omega_3 = \theta_4,$$

$$\omega_4 = -(\theta_3 + \theta_4),$$

$$\omega_5 = (\rho T^2 / \eta^2) K_8,$$

$$\omega_6 = (P / \eta^2) (K_{12} - 3\rho K_9).$$

Numerical values for the θ 's and ω 's have been worked out for Maxwellian molecules and for hard spheres, and are given in Chapman and Cowling, and in Wang Chang and Uhlenbeck.¹²

Expressions similar to those above have been given by Ernst,¹³ for the linearized Burnett coefficients. We note the following relations with the coefficients χ , γ , and ξ of Ernst:

$$K_1 = \chi/2, \quad K_4 = 2\gamma, \quad K_9 = -\xi/\rho.$$

*Work was performed under the auspices of the U. S. Atomic Energy Commission.

[†]Research supported by National Science Foundation.

¹S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge U. P., Cambridge, England, 1953).

²D. Burnett, Proc. London Math. Soc. **40**, 382 (1935).

³G. E. Uhlenbeck and J. D. Foch, Phys. Rev. Letters **19**, 1025 (1967); also J. D. Foch and G. W. Ford, *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck; (North-Holland, Amsterdam, 1970), Vol. V, and other references cited therein.

⁴Cf. M. Reiner, *Deformation and Flow* (H. K. Lewis, London, 1949).

⁵B. J. Alder and T. E. Wainwright, Phys. Rev. Letters **18**, 988 (1969).

⁶B. J. Alder and T. E. Wainwright, Phys. Rev. A **1**, 18 (1970); M. H. Ernst, J. H. Hauge, and J. M. J. Van Leeuwen, Phys. Rev. Letters **25**, 1254, (1970); J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Letters **25**, 1257 (1970); M. Bixon and R. Zwanzig, Phys. Rev. A **2**, 2005 (1970); B. J. Alder, T. E. Wainwright, and D. M. Gass, Phys. Rev. A **4**, 233 (1971); K. Kawasaki, Phys. Rev. Letters **34A**, 12 (1971); J. W. Dufty, Phys. Rev. A **5**, 2247 (1972); Y. Pomeau, Phys. Rev. A **5**, 2569 (1972).

⁷M. H. Ernst and J. R. Dorfman, Physica **61**, 157 (1972).

⁸Higher-order effects in self-diffusion, with particular

- reference to computer experiments, have been considered by W. W. Wood, in *The Boltzmann Equation—Theory and Applications*, edited by E. G. D. Cohen and W. Thirring (Springer-Verlag, Vienna, 1973).
- ⁹J. W. Dufty, *Phys. Rev.* **176**, 398 (1968).
- ¹⁰J. A. McLennan, *Helv. Phys. Acta* **40**, 645 (1967).
- ¹¹J. A. McLennan, *Phys. Fluids* **3**, 493 (1960).
- ¹²C. S. Wang Chang and G. E. Uhlenbeck, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck, (North-Holland, Amsterdam, 1970), Vol. V.
- ¹³M. H. Ernst, *Am. J. Phys.* **38**, 908 (1970).