

On Linearized Hydrodynamic Modes in Statistical Physics

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We formulate the linearized generalized Boltzmann equation as an (asymmetric) eigenvalue problem. This problem has five eigenvalues which tend to zero when the uniformity parameter tends to zero: to second order in this parameter, they correspond to damped sound (two modes), diffusing shear flow (two modes), and diffusing entropy flow (one mode). The microscopic expressions deduced from these results for the transport coefficients agree with the correlation-function formulas. Moreover, the corresponding eigenfunctions are explicitly displayed to lowest order in the uniformity parameter: they are microscopic analogs, in terms of *one*-particle distribution functions, of the well-known linearized hydrodynamic modes of macroscopic physics. All results are established to all orders in the interactions.

KEY WORDS: Generalized Boltzmann equation; hydrodynamic modes; transport coefficients; autocorrelation function formulas.

1. INTRODUCTION

Linearized hydrodynamic modes are well known in macroscopic physics. Let us consider the Laplace-Fourier transform of the linearized hydrodynamic equations^(1,2)

$$-i\omega n_q(\omega) + i\mathbf{q}n\mathbf{g}_q(\omega) = n_q(t=0) \quad (\text{continuity equation}) \quad (1)$$

$$\begin{aligned} -i\omega \mathbf{g}_q(\omega) + i\mathbf{q} \frac{1}{n} \left(\frac{\partial p}{\partial n} \right)_T n_q(\omega) + i\mathbf{q} \frac{1}{n} \left(\frac{\partial p}{\partial T} \right)_n T_q(\omega) + \frac{\eta}{n} [\mathbf{q}(\mathbf{q}\mathbf{g}_q(\omega)) + \mathbf{q}^2 \mathbf{g}_q(\omega)] \\ + \frac{(\zeta - \frac{2}{3}\eta)}{n} [\mathbf{q}(\mathbf{q}\mathbf{g}_q(\omega))] = \mathbf{g}_q(t=0) \quad (\text{Navier-Stokes equation}) \quad (2) \end{aligned}$$

$$\begin{aligned} -i\omega T_q(\omega) + i\mathbf{q} \frac{T}{nC_v} \left(\frac{\partial p}{\partial T} \right)_n \mathbf{g}_q(\omega) + \frac{\kappa}{nC_v} q^2 T_q(\omega) = T_q(t=0) \\ (\text{temperature equation}) \quad (3) \end{aligned}$$

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In these equations, n , p , T , and C_v respectively denote the equilibrium density, pressure, temperature, and specific heat at constant volume; η and ζ are the shear and bulk viscosity, and κ is the thermal conductivity. Moreover, $n_q(\omega)$, $\mathbf{g}_q(\omega)$, and $T_q(\omega)$ are the Laplace–Fourier transforms of the local particle density, local momentum (we always take the mass $m = 1$), and local temperature; for instance, one has

$$n_q(\omega) = \int_0^\infty dt e^{i\omega t} \int d^3r (\exp -i\mathbf{q}\mathbf{r}) \delta n(\mathbf{r}, t) \quad (4)$$

where $\delta n(\mathbf{r}, t)$ is the density fluctuation at point r and time t ; similar definitions hold for $\mathbf{g}_q(\omega)$ and $T_q(\omega)$.

Although the concept of hydrodynamic mode can be formulated in various ways, the most direct one is probably to formally consider the five conserved quantities, $n_q(\omega)$, $\mathbf{g}_q(\omega)$, $T_q(\omega)$, as the components of a vector in a five-dimensional space. The solution of Eqs. (1)–(3) is then easily reduced to the calculation of the eigenvalues and eigenvectors of the homogeneous problem associated with these equations. This eigenvalue problem is equivalent to the diagonalization of a (5×5) (non-Hermitian) matrix; this is readily done and one finds, in the small q -limit and assuming for convenience that \mathbf{q} is oriented along the x axis, the following eigenvalues:

$$\lambda_y = -q^2\eta/n \quad (5a)$$

$$\lambda_z = -q^2\eta/n \quad (5b)$$

$$\lambda_\pm = \pm icq - q^2\Gamma \quad (5c)$$

$$\lambda_T = -q^2\kappa/nC_p \quad (5d)$$

where

$$\Gamma = \frac{1}{2} \left[\frac{\frac{4}{3}\eta + \zeta}{n} + \left(\frac{1}{C_v} - \frac{1}{C_p} \right) \frac{\kappa}{n} \right] \quad (6)$$

and c is the sound velocity:

$$c^2 = \frac{C_p}{C_v} \left(\frac{\partial p}{\partial n} \right)_T \quad (7)$$

Clearly, λ_y and λ_z express the viscous damping of the shear-velocity modes, the λ_\pm describe damped sound-wave propagations, and λ_T corresponds to the diffusion of the thermal mode. The right and left eigenfunctions corresponding to these modes are also easily constructed. However, as we shall not need them and as similar modes will be calculated later from a microscopic viewpoint, we shall not display them here.

This concept of macroscopic modes has been used in statistical physics in at least two important respects:

1. It has served in finding a *microscopic* definition of transport coefficients (the so-called autocorrelation function formulas) by identifying the equations of motion for the average value of the microscopic operators describing the five conserved quantities (in a state taken initially to be the local equilibrium) with the macroscopic system (1)–(3). This is, for instance, the point of view adopted by Mori^(3–5) and by Kadanoff and Martin.⁽²⁾

2. It has also been very useful in the analysis of a series of problems involving *long-wavelength divergences*. Leaving aside the case of long-range forces, we can cite:

(i) The nonanalytic density expansion of transport coefficients (Kawasaki and Oppenheim⁽⁶⁾; for a recent review, see Ernst *et al.*⁽⁷⁾); here, we should mention the recent work of Pomeau,⁽⁸⁾ who has shown that, in order to treat properly the divergence problem in a two-dimensional system, one should carefully take into account the long-wavelength propagation of hydrodynamic modes.

(ii) The critical behavior of transport coefficients (see, e.g., Résibois⁽⁹⁾); here again, the long-distance propagation of hydrodynamic modes plays a crucial role in the determination of the singularities in transport coefficients close to the critical point, as appears clearly in the works of Fixman,⁽¹⁰⁾ Kawasaki,⁽¹¹⁾ and Kadanoff and Swift.⁽¹²⁾

(iii) The van Hove time-dependent correlation function.⁽¹³⁾ The long-wavelength, low-frequency behavior of this function, which is of particular importance, has usually been evaluated from the macroscopic equations (1)–(3); this was done by van Hove himself, and later on by Kadanoff and Martin⁽²⁾ and by Mountain.⁽¹⁴⁾

Although these works share the feature of using hydrodynamic concepts in problems of statistical physics, they use this idea in very different ways. For instance, in the work of van Hove⁽¹³⁾ and Mountain,⁽¹⁴⁾ it is assumed, with no more than heuristic justification, that macroscopic laws can be used to describe the time-dependent density-density correlation function; on the other hand, in the work of Mori and of Kadanoff and Swift, *microscopic* hydrodynamic modes are explicitly constructed in terms of the complete equilibrium *N-particle* distribution function; finally, in the work of Pomeau, microscopic hydrodynamic modes are defined in terms of a *one-particle* distribution function, but for a dilute gas only where effects due to the potential energy between the particles can be neglected.

The generalization of this latter work, namely the *definition of statistical hydrodynamic modes in terms of one-particle functions but for a strongly interacting system*, would be a very useful tool in the microscopic analysis of the abovementioned divergence problems. Indeed, it appears clearly that a full understanding of these questions, in particular, the critical behavior of transport coefficients, requires a detailed analysis of the many-body dynamical problem; such an analysis can only be carried through if one can think, and calculate, in terms of one-body quantities.² The aim of the present paper is to offer such a tool.

Before giving an outline of our work, let us still recall that the calculation of transport coefficients is traditionally based on the generalized Boltzmann equation obeyed by the one-particle distribution function $f_1(\mathbf{r}_1, \mathbf{v}_1; t)$ ^(18–19) We formally write this equation as

$$\partial_t f_1(\mathbf{r}_1, \mathbf{v}_1; t) + \mathbf{v}_1 \frac{\partial f_1}{\partial \mathbf{r}_1} = C(f_1) \quad (8)$$

² For instance, the whole diagrammatic analysis of the *N*-body problem rests heavily upon a description in terms of one-body “propagators” (see, e.g., Abrikosov *et al.*⁽¹⁵⁾ vs Prigogine⁽¹⁶⁾ and Résibois⁽¹⁷⁾ for two very different formulations in terms of graphs).

where C denotes the nonlinear collision operator (which may eventually be nonlocal in space and in time). Using a Chapman–Enskog type of procedure, Eq. (8) is solved for a double purpose: the evaluation of the kinetic part of the transport coefficients, and the explicit determination of the two-particle distribution function f_2 , which can be expressed as a functional of f_1 :

$$f_2(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_2, \mathbf{v}_2; t) = f_2(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_2, \mathbf{v}_2 | f_1) \quad (9)$$

From f_2 , the potential part of the transport coefficients is then computed. Examples of such calculations can be found in works by Choh and Uhlenbeck,⁽²⁰⁾ Résibois,⁽²¹⁾ Severne and Nicolis,⁽²²⁾ Ernst *et al.*,⁽²³⁾ Ernst⁽²⁴⁾ and Garcia-Colin *et al.*⁽²⁵⁾ Let us stress also that this method is not without difficulties, related in particular to the problem of the subsidiary conditions and the closely connected question of temperature definition.^(22,26) Moreover, there exists no extension of these works furnishing a microscopic definition of hydrodynamic modes.

Within the framework of a theory linearized around absolute equilibrium, the present work is precisely intended to furnish such an extension. We shall show indeed that the solution of the linearized, generalized Boltzmann equation (9) can be formulated as an eigenvalue problem whose five particular eigenfunctions, depending on the velocity of one single particle, are microscopic expressions for the above-mentioned hydrodynamic modes. Moreover, we show that the five corresponding eigenvalues, which tend to zero for $q \rightarrow 0$, are exactly the five quantities (5), with, however, an explicit microscopic expression for the transport coefficients. We shall thus obtain the complete transport coefficients, *including their potential parts*, in terms of Eq. (8) only, with no explicit appeal to the functional relation (9).

One immediate remark is in order about this last statement. Indeed, the first BBGKY hierarchy equation provides us with an exact relation between f_1 and f_2 ; dropping vector notation, we have

$$\partial_i f_1 + v_1 \frac{\partial f_1}{\partial r_1} = n \int dr_2 dv_2 \frac{\partial V}{\partial r_{12}} \frac{\partial}{\partial v_1} f_2(r_1, v_1; r_2, v_2; t) \quad (10)$$

Thus, once the functional relation (9) is known, one can immediately calculate the collision operator which appears on the r.h.s. of (8). However the opposite is not true: once $C(f_1)$ is given, we only know the particular combination of f_2 which appears on the r.h.s. of (10), but f_2 itself cannot be determined. Our claim is that it is sufficient to have $C(f_1)$ in order to calculate transport coefficients to arbitrary order in the interaction.

At first sight, it might appear surprising that a kinetic equation for f_1 only suffices to calculate full transport coefficients, including their potential parts. Leaving for later a proof of this assertion, let us give here a heuristic hint suggesting the plausibility of this property.³ Consider the van Hove function $G(r; t)$; it is defined by

$$G(r; t) = \frac{1}{n} \sum_{i,j} \int dr^N dv^N \delta(r - r_i) \exp(-iLt) \delta(r_j) \rho_N^{eq}(r^N, v^N) \quad (11)$$

³ It is gratefully acknowledged that the following argument was developed in the course of a discussion with Prof. J. Lebowitz.

where ρ_N^{eq} denotes the canonical equilibrium distribution:

$$\rho_N^{eq} = \exp -\beta H / \left(\int dr^N dv^N \exp -\beta H \right) \quad (12)$$

and L is the Liouville operator.

Macroscopic physics tells us that, for low frequency and long wavelength, the Laplace–Fourier transform of (11) is given by^(2,13)

$$G_q(\omega) = nkT\chi_T \left[\left(1 - \frac{C_v}{C_p} \right) \frac{1}{-i\omega + q^2\kappa/nC_p} + \frac{1}{2} \sum_{\pm} \frac{C_v}{C_p} \frac{1}{-i\omega \pm icq + q^2\Gamma} \right] \quad (13)$$

where χ_T is the isothermal compressibility.

On the other hand, (11) can be written as

$$G(r; t) = \frac{1}{n} \int dv_1 \bar{f}_1(r_1, v_1; t) \quad (14)$$

where the time-dependent one-body distribution function $\bar{f}_1(r_1, v_1; t)$ is defined by

$$\bar{f}_1(r_1, v_1; t) = N \int dr^{N-1} dv^{N-1} \exp(-iLt) \sum_j \delta(r_j) \rho_N^{eq} \quad (15)$$

The natural way to calculate \bar{f}_1 is of course first to derive for it a generalized Boltzmann equation, which has then to be solved.⁴ Thus, if the macroscopic result (13) is correct, the exact transport coefficients appearing in (13) should come out, in a microscopic calculation, from the kinetic equation for \bar{f}_1 alone, solved to second order in the uniformity parameter q .

The remainder of this paper is organized as follows: in Section 2, we illustrate the philosophy of our method by considering the case of the dilute gas. We formulate the transport problem as the eigenvalue problem associated to the linearized Boltzmann equation. We set up a perturbation scheme, to second order in the uniformity parameter q , starting from the basis formed by the eigenfunction of the linearized Boltzmann collision operator. The usual expressions for the transport coefficients come out as the q^2 -coefficients of the eigenvalues which tend to zero for $q \rightarrow 0$. Although there is of course no potential contribution to the transport coefficients, this example is interesting because it indicates many features of the problem without the complications introduced in the general case by many-body effects. In particular, it shows that the requirements imposed by the subsidiary conditions in the Chapman–Enskog method appear here as natural consequences of a correct perturbation calculus. Moreover, this example might also be of some pedagogical interest: indeed, in the present approach, the calculation of transport coefficients is little more than an exercise in perturbation calculus for any student knowing elementary quantum mechanics.

⁴ This has been done explicitly for many models (see Lebowitz *et al.*⁽²⁷⁾ and references quoted there).

In Section 3, we recall briefly the generalized Boltzmann equation in a strongly interacting system, together with a few useful properties of the operators involved in this equation. Whenever an explicit expression is needed, we shall write it in the formulation developed by Prigogine and co-workers^(16,17); however, the reader will realize that very little many-body analysis is required and that most of the results could equally well be deduced by any of the methods available nowadays in non-equilibrium statistical mechanics.

In Section 4, we develop the nondissipative part of the theory, namely we construct hydrodynamic modes whose eigenvalues are either zero (describing nondissipative shear and thermal modes) or the sound velocity (sound modes).

Section 5 is devoted to the dissipative part of the theory, i.e., we deduce an explicit expression for transport coefficients. Although it will be clear that these expressions involve potential contributions, we shall not prove here in detail the identity of these formulas with the corresponding autocorrelation formulas. Indeed, though the principles involved have been explained before,^(21,22) there are some technical details which require a many body-analysis deeper than the one we want to present here. This point is thus deferred to other publications,⁽²⁸⁾ where the interested reader will also find a first application of the present method, namely an explicit *microscopic* proof of the well-known equation (13) for the van Hove function $G(r; t)$; here again, although in principle straightforward, the calculation involves some subtle points which we do not want to discuss here.

Finally, after some discussion in Section 6, mathematical complements will be found in the Appendices.

2. THE DILUTE GAS

In the dilute gas, the kinetic equation (8) reduces to the well-known Boltzmann equation. We linearize it around absolute equilibrium and we take its Fourier transform with respect to r , assuming that q is oriented along the x axis; we get

$$\partial_t f_q(v; t) + iqv_x f_q(v; t) = C^{1B} f_q(v; t) \quad (16)$$

where C^{1B} is the following linearized integral operator:

$$\begin{aligned} C^{1B} f_q(v_1; t) = n \int dv_2 \int d\Omega \sigma(\Omega; v_{12}) |v_{12}| [f_q(v_1; t) \varphi^{eq}(v_2) + \varphi^{eq}(v_1) f_q(v_2; t) \\ - f_q(v_1'; t) \varphi^{eq}(v_2') - \varphi^{eq}(v_1') f_q(v_2'; t)] \end{aligned} \quad (17)$$

In this equation, $\sigma(\Omega; v_{12})$ is the two-body collision cross section.

We then consider the eigenvalue problem associated to Eq. (16), namely

$$(C^{1B} - iqv_x) \Psi_n^{Bq}(v) = \lambda_n^{Bq} \Psi_n^{Bq}(v) \quad (18)$$

Here, λ_n^{Bq} and Ψ_n^{Bq} respectively denote the eigenvalue and eigenfunction characterized by the index n ; moreover, we have put the superscript q to keep in mind the explicit q -dependence of these eigenvalues and eigenfunctions.

Our program is to solve (18) by a perturbation calculus, considering $(-iqv_\alpha)$ as a small perturbation in the long-wavelength limit $q \rightarrow 0$.

We have thus to discuss first the properties of C^{IB} . Denoting provisionally its eigenfunctions by $\Phi_n(v)$, we consider the problem

$$C^I \Phi_n(v) = \lambda_n^0 \Phi_n(v) \quad (19)$$

where, as everywhere in the remainder of this section, we have dropped the superscript B (Boltzmann).

From the symmetry property⁵

$$\int dv (\varphi^{\text{eq}}(v))^{-1} f(v) C^I g(v) = \int dv (\varphi^{\text{eq}}(v))^{-1} g(v) C^I f(v) \quad (20)$$

where $\varphi^{\text{eq}}(v)$ denotes the Maxwellian distribution,

$$\varphi^{\text{eq}}(v) = \frac{1}{(2\pi kT)^{3/2}} \exp - \frac{v^2}{2kT} \quad (21)$$

it is easily verified that the eigenfunctions $\Phi_n(v)$ can be made to obey the orthogonality requirement:

$$\int dv (\varphi^{\text{eq}}(v))^{-1} \Phi_n(v) \Phi_{n'}(v) = \delta_{n,n'}^{\text{KR}} \quad (22)$$

Indeed, this property is automatically fulfilled if $\lambda_n^0 \neq \lambda_{n'}$, and if the eigenvalues are degenerate, we can always apply the Schmidt orthogonalization method.⁽³²⁾ Moreover, we assume that the $\Phi_n(v)$ form a complete set.

In particular, there are five eigenfunctions with zero eigenvalue corresponding to the five conserved quantities $(1, \mathbf{v}, v^2)$. We denote them generically by $\Phi_\alpha(v)$, where the greek index α runs over the integer values 1–5, as will always be the case in the following. Explicitly, we have

$$\Phi_1(v) = \varphi^{\text{eq}}(v) \quad (23a)$$

$$\Phi_i(v) = \frac{v_i}{(kT)^{1/2}} \varphi^{\text{eq}}(v), \quad i = 2, 3, 4 \equiv x, y, z \quad (23b)$$

$$\Phi_5(v) = \left(\frac{2}{3}\right)^{1/2} \left(\frac{v^2}{2kT} - \frac{3}{2}\right) \varphi^{\text{eq}}(v) \quad (23c)$$

We also assume that the eigenvalues λ_n^0 with $n \notin (\alpha)$ (i.e., $n > 5$) have no accumulation point at the origin. Such an assumption is always implicit in any calculation of transport coefficients; physically, it implies a separation of the relaxation time scale, $\alpha(\lambda_{n \notin (\alpha)}^0)^{-1}$, and the hydrodynamic time scale, $\alpha[q(kT)^{1/2}]^{-1}$.⁶

⁵ For a similar property, see, e.g., Chapman and Cowling.⁽²⁹⁾

⁶ The role of this condition clearly appears in the recent work by Sirovich and Thurber⁽³⁰⁾ in the study of sound propagation. The present analysis in the dilute-gas case is of course closely related to this problem. Moreover, in this paragraph as well as in the general case discussed later on, we will be unable to say anything rigorous about the nature of the expansion in the uniformity parameter. Also see Sirovich^(31a) and Uhlenbeck and Ford.^(31b)

Finally, it is convenient to use an abstract linear vector space notation, by considering $\Phi_n(v)$ as the velocity-space representation of the vector $|n\rangle$:

$$\Phi_n(v) = \langle v | n \rangle \quad (24)$$

In this abstract space, the scalar product between two arbitrary functions $|f\rangle$ and $|g\rangle$ is defined according to (22), namely

$$\langle f | g \rangle = \int dv (\varphi^{eq}(v))^{-1} f(v) g(v) \quad (25)$$

If we now notice that the operator $(C^l - iqv_x)$, although not Hermitian, is symmetric,⁷ the eigenvalue problem (18) can be solved by perturbation calculus in the usual fashion.⁽⁸²⁾ In particular, we want to evaluate

$$\lambda_\alpha^q = q\lambda_\alpha^{(1)} + q^2\lambda_\alpha^{(2)} + \dots \quad (26)$$

for the set of states (α) , $\alpha = 1, \dots, 5$, describing the conserved quantities.

A little care is needed, however, because the set (α) is degenerate when $q = 0$ ($\lambda_\alpha^0 = 0$). Thus, we have first to remove this degeneracy by solving *exactly* the eigenvalue problem

$$(C^l - iqv_x) \Psi_\mu(v) = \bar{\lambda}_\mu \Psi_\mu(v) \quad (27)$$

in the *subspace* spanned by the set (α) .⁸ This is done by expanding $|\Psi_\mu\rangle$ according to

$$|\Psi_\mu\rangle = \sum_{\nu \in (\alpha)} C_{\mu\nu} |\nu\rangle \quad (28)$$

and inserting this into (27).

Using the orthogonality relations (22) and the property $C^l |\nu\rangle = 0$, we immediately obtain the following system of linear equations:

$$-iq \sum_{\nu} \epsilon_{\mu'\nu} c_{\mu\nu} = \bar{\lambda}_\mu c_{\mu\mu'}, \quad \mu, \nu, \mu' \in (\alpha) \quad (29)$$

where

$$\epsilon_{\mu\nu} = \langle \mu | v_x | \nu \rangle \quad (30)$$

From (23), it is easy to evaluate the coefficients $\epsilon_{\mu\nu}$; they all vanish except

$$\epsilon_{12} = \epsilon_{21} = (kT)^{1/2}, \quad \epsilon_{25} = \epsilon_{52} = \left(\frac{2}{3}kT\right)^{1/2} \quad (31)$$

We then calculate the zeros of the determinant $|-iq\epsilon_{\mu\nu} - \bar{\lambda}\delta_{\mu,\nu}^{\text{Kr}}|$; from these, the eigenvalues $\bar{\lambda}_\mu$ and eigenfunctions $|\Psi_\mu\rangle$ are readily computed.

⁷ This means [see (20)] $\langle f | (C^l - iqv_x) g \rangle = \langle (C^l - iqv_x) f | g \rangle$.

⁸ This means that we calculate the eigenfunctions and eigenvalues of the projected operator $\sum_{\mu \in (\alpha)} \sum_{\nu \in (\alpha)} |\mu\rangle \langle \mu | (C^l - iqv_x) | \nu \rangle \langle \nu |$.

One finds, after some simple algebra,

$$\begin{aligned}
 \bar{\lambda}_1 &= -ic^{(0)}q, & |\Psi_1\rangle &= (1/\sqrt{2})[\sqrt{\frac{5}{3}}|1\rangle + |2\rangle + \sqrt{\frac{2}{5}}|5\rangle] \\
 \bar{\lambda}_2 &= +ic^{(0)}q, & |\Psi_2\rangle &= (1/\sqrt{2})[\sqrt{\frac{5}{3}}|1\rangle - |2\rangle + \sqrt{\frac{2}{5}}|5\rangle] \\
 \bar{\lambda}_3 &= 0, & |\Psi_3\rangle &= |3\rangle \\
 \bar{\lambda}_4 &= 0, & |\Psi_4\rangle &= |4\rangle \\
 \bar{\lambda}_5 &= 0, & |\Psi_5\rangle &= \sqrt{\frac{2}{5}}[-|1\rangle + \sqrt{\frac{3}{2}}|5\rangle]
 \end{aligned} \tag{32}$$

where $c^{(0)}$ is the sound velocity in the perfect gas:

$$c^{(0)} = (5kT/3)^{1/2} \tag{33}$$

By direct calculation, one can also check that

$$\langle \Psi_\mu | \Psi_\nu \rangle = \delta_{\mu,\nu}^{\text{Kr}}, \quad \mu, \nu \in (\alpha) \tag{34}$$

$$\langle \Psi_\mu | -iqv_x | \Psi_\nu \rangle = \bar{\lambda}_\nu \delta_{\mu,\nu}^{\text{Kr}}, \quad \mu, \nu \in (\alpha) \tag{35}$$

As will be discussed with more detail in the general case (Section 4), $|\Psi_1\rangle$ and $|\Psi_2\rangle$ represent propagating sound waves, $|\Psi_3\rangle$ and $|\Psi_4\rangle$ undamped shear velocity modes, and $|\Psi_5\rangle$ is a thermal mode. Notice that the spectrum (32) remains degenerate; however, from (35), there is no matrix element of the perturbation between these degenerate states. This is all that is needed in order to develop perturbation calculus.⁹

The strategy of the calculation is now clear; in order to avoid degeneracy difficulties, we have to solve Eq. (18), to second order in q , with the following unperturbed basis:

$$\begin{cases} |\Psi_\alpha\rangle & \alpha = 1, 2, \dots, 5 \\ |\Psi_n\rangle = |n\rangle, & n \notin (\alpha) \end{cases} \tag{36}$$

which of course obeys

$$\langle \Psi_n | \Psi_{n'} \rangle = \delta_{n,n'}^{\text{Kr}}, \quad n, n' \in \text{ or } \notin (\alpha) \tag{37}$$

We then use (26) and a similar expansion for $|\Psi_\alpha^q\rangle$:

$$|\Psi_\alpha^q\rangle = |\Psi_\alpha\rangle + q|\Psi_\alpha\rangle^{(1)} + \dots \tag{38}$$

As the calculation proceeds exactly as in elementary quantum perturbation theory, we merely give the result. We find

$$q\lambda_\alpha^{(1)} = \bar{\lambda}_\alpha \tag{39}$$

a fairly obvious result, and, in complete analogy with elementary quantum mechanics,

$$\lambda_\alpha^{(2)} = \sum_{n \notin (\alpha)} \langle \Psi_\alpha | v_x | \Psi_n \rangle \frac{1}{\lambda_n^0} \langle \Psi_n | v_x | \Psi_\alpha \rangle \tag{40}$$

⁹ See, e.g., Bohn⁽³⁸⁾; the only difference with a symmetric operator is that the scalar product $\langle f | g \rangle$ is defined without taking the complex conjugate of $f(v)$; this is indeed what we have done in (25).

Notice the restriction $n \neq (\alpha)$ which appears in the summation over n ; however from (35) and (36), we can get rid of this restriction by subtracting the following quantity from the third factor of (40):

$$\langle \Psi_n | -g_\alpha | \Psi_\alpha \rangle = -g_\alpha \delta_{n,\alpha}^{\mathbf{K}\mathbf{r}} \quad (41)$$

where we have written

$$\bar{\lambda}_\alpha \equiv i q g_\alpha \quad (42)$$

Then, using the formal relation

$$\lim_{\epsilon \rightarrow 0} \sum_{\text{all } n} | \Psi_n \rangle \frac{1}{\lambda_n^0 - \epsilon} \langle \Psi_n | = \frac{1}{C^l - \epsilon} \quad (43)$$

we obtain formally

$$\lambda_\alpha^{(2)} = \lim_{\epsilon \rightarrow 0} \langle \Psi_\alpha | v_x \frac{1}{C^l - \epsilon} (v_x + g_\alpha) | \Psi_\alpha \rangle \quad (44)$$

With the explicit formulas given in (42) for the eigenfunctions $| \Psi_\alpha \rangle$, we can cast Eq. (44) into more familiar expressions. After some simple algebra, involving the rotation invariance of the operator C^l , we get

$$\lambda_1^{(2)} = \lambda_2^{(2)} = -\frac{1}{2} \left[\frac{4\eta^{(0)}}{3n} + \left(\frac{1}{C_v^{(0)}} - \frac{1}{C_p^{(0)}} \right) \frac{\kappa^{(0)}}{n} \right] \quad (45)$$

$$\lambda_3^{(2)} = \lambda_4^{(2)} = \frac{\eta^{(0)}}{n} \quad (46)$$

$$\lambda_5^{(2)} = -\frac{1}{nC_p^{(0)}} \kappa^{(0)} \quad (47)$$

where $C_v^{(0)}$ and $C_p^{(0)}$ denote respectively the perfect-gas specific heats at constant volume and constant pressure

$$C_v^{(0)} = 3k/2, \quad C_p^{(0)} = 5k/2 \quad (48)$$

while the transport coefficients $\eta^{(0)}$ and $\kappa^{(0)}$ are defined by

$$\eta^{(0)} = -\frac{n}{kT} \lim_{\epsilon \rightarrow 0} \int dv v_x v_y \frac{1}{C^l - \epsilon} v_x v_y \varphi^{\text{eq}} \quad (49)$$

$$\kappa^{(0)} = -\frac{n}{kT^2} \lim_{\epsilon \rightarrow 0} \int dv v_x \frac{v^2}{2} \frac{1}{C^l - \epsilon} v_x \left(\frac{v^2}{2} - \frac{5kT}{2} \right) \varphi^{\text{eq}} \quad (50)$$

These two expressions are of course a formal way of writing

$$\begin{aligned} \eta^{(0)} &= -\frac{n}{kT} \int dv v_x v_y \delta \varphi^{xy} \\ \kappa^{(0)} &= -\frac{n}{kT^2} \int dv v_x \frac{v^2}{2} \delta \varphi^x \end{aligned} \quad (51)$$

where $\delta\varphi^{xy}$ and $\delta\varphi^x$ respectively are the solutions of the following integral equations:

$$C^l \delta\varphi^{xy} = v_x v_y \varphi^{eq}(v), \quad C^l \delta\varphi^x = v_x \left(\frac{v^2}{2} - \frac{5kT}{2} \right) \varphi^{eq}(v) \quad (52)$$

In the form (51)–(52), the equivalence of our formulation with the traditional Chapman–Enskog is transparent. In particular, we should point out the factor $-5kT/2$ in Eq. (50), which ensures that the inverse operator $(C^l)^{-1}$ has a meaning. Of course, the bulk viscosity ζ vanishes in both approaches for the dilute gas.

To summarize the results of this section, we have obtained the sound velocity and the transport coefficients of a dilute gas from the eigenvalue problem associated to the inhomogeneous Boltzmann equation. They appear as the eigenvalues, calculated up to order q^2 , of the hydrodynamic modes, whose microscopic expression has also been displayed to lowest order in the uniformity parameter.

3. THE GENERALIZED BOLTZMANN EQUATION

The extension of the above calculation to arbitrary order in the interaction requires knowledge of the collision operator $C(f_1)$ [see (8)] which generalizes the Boltzmann operator in a strongly interacting system.

To discuss this point, it is convenient to start at the level of the non-Markovian kinetic equation which is obeyed by $f_q(v; t)$. Indeed, it has been shown that, within a theory linearized absolute equilibrium, $f_q(v; t)$ satisfies the following equation:

$$\partial_t f_q(v; t) + iqv_x f_q(v; t) = \int_0^t G_q(v; \tau) f_q(v; t - \tau) d\tau + \mathcal{D}_q(v; t) \quad (53)$$

Here, the kernel $G_q(v; \tau)$ is a non-Markovian collision operator and $\mathcal{D}_q(v; t)$ is an inhomogeneous term which describes the effect of the initial correlations on the time evolution of the one-particle distribution function.

Equation (53) is well known and can be derived by a variety of methods, in particular, by the perturbation method of Prigogine and co-workers,^(16,17) the Bogoliubov streaming operator method,⁽¹⁸⁾ and the Zwanzig projection operator method.⁽³⁴⁾ For this reason, we shall not give here its detailed derivation, although, for completeness, a brief sketch of the proof is given in Appendix 1.

Whenever we shall need the explicit form of $G_q(v; \tau)$, we shall use it as it comes out from the theory of Prigogine and co-workers.^(16,17) We have

$$G_q(v; \tau) \Phi(v) = \frac{-1}{2\pi i} \oint_C dz \exp(-iz\tau) \Psi_q(v; z) \Phi(v) \quad (54)$$

where $\Phi(v)$ denotes an arbitrary function of v and the contour C is parallel to the real axis in the upper half-plane S^+ . The integral operator $\Psi_q(v; z)$ is defined by

$$\begin{aligned} \Psi_q(v_1; z) \Phi(v_1) &= \sum_{j=1}^N \int dv^{N-1} (q_1, \{0\}' | -\delta L \sum_{n=0}^{\infty} \left(\frac{1}{L_0 - z} (-\delta L) \right)^n | q_j, \{0\}')_{irr} \\ &\times \Phi(v_j) \prod_{i \neq j} \varphi^{eq}(v_i) \end{aligned} \quad (55)$$

Here, L_0 and δL respectively are the unperturbed Liouville operator,

$$L_0 = -i \sum_{j=1}^N v_j \frac{\partial}{\partial r_j} \quad (56)$$

and the perturbation due to the interactions,

$$\delta L = i \sum_{k < j=1}^N \frac{\partial V}{\partial r_{kj}} \left(\frac{\partial}{\partial v_k} - \frac{\partial}{\partial v_j} \right) \quad (57)$$

Moreover, the following notation has been used for the Fourier transform of any function or operator¹⁰ $A(r^N, v^N)$:

$$\langle \{k\} | A | \{k'\} \rangle = \frac{1}{\Omega^N} \int dr^N \exp \left(-i \sum_j k_j r_j \right) A(r^N, v^N) \exp \left(i \sum_i k'_i r_i \right) \quad (58)$$

(Ω is the volume of the system).

From translation invariance, we have of course $q_1 = q_j \equiv q$. Finally, the subscript “*irr*” indicates that only “irreducible” contributions should be retained in (55), i.e., all intermediate states involved in the perturbation expansion in δL should have at least two nonvanishing wave numbers.

As is indicated, Eq. (55) is only valid when z is in the upper half-plane S^+ ; when $z \in S^-$, one should take the analytical continuation of the expression (55). More details can be found in Appendix 1, as well as elsewhere.^(16,17,19)

As already said above, only a few general properties of $G_q(v; \tau)$ will be needed here; although we shall always establish these properties on the basis of (55). they could easily be derived by any of the above-mentioned methods. Moreover, we shall not need here the explicit form of $\mathcal{D}_q(v; t)$ except for the property

$$\mathcal{D}_q(v; t) \rightarrow 0, \quad t \gg \tau_c \quad (59)$$

(τ_c is the collision time), which has been established before (see, e.g., Prigogine⁽¹⁶⁾ and Résibois⁽¹⁷⁾).

In order to obtain the generalized Boltzmann equation from Eq. (54), we have to investigate the behavior of this latter equation for long times, of the order of $(cq)^{-1}$ or larger, where c is the sound velocity and where $q \rightarrow 0$.

Using the property (59) and expanding $f_q(v; t - \tau)$ in a Taylor series,

$$f_q(v; t - \tau) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \tau^n \partial_t^n f_q(v; t) \quad (60)$$

we obtain

$$\partial_t f_q(v; t) + iq v_x f_q(v; t) = \sum_{n=0}^{\infty} \left[\int_0^t d\tau G_q(v; \tau) \tau^n \frac{(-1)^n}{n!} \right] \partial_t^n f_q(v; t), \quad t \rightarrow \infty \quad (61)$$

¹⁰ We use round bras and kets, $\langle |$ and $| \rangle$, in order to avoid confusion with states in the one-particle velocity space, $\langle |$ and $| \rangle$.

In the right-hand side of (61), we assume that $G_q(v; \tau)$ decays to zero for times much shorter than t ; it is then a matter of some simple algebra to show that $f_q(v; t)$ obeys the following generalized Boltzmann equation⁽¹⁸⁾:

$$\partial_t f_q(v; t) = i\Omega_q \bar{\Psi}_q(v; 0) f_q(v; t) \tag{62}$$

where $\bar{\Psi}_q(v; 0)$ is the following short-hand notation:

$$\bar{\Psi}_q(v; 0) = [-qv_x + \Psi_q(v; 0)] \tag{63}$$

and where Ω_q is defined by the following implicit equation¹¹:

$$\Omega_q = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left[\frac{\partial^n \Psi_q(v; z)}{\partial z^n} \right]_{z=0} [\Omega_q \bar{\Psi}_q(v; 0)]^{n-1} \Omega_q \tag{64}$$

A word of caution is required here: the validity of the asymptotic form (62) rests upon the convergence of the expansion (60), which is not establish in general. For example, we have studied recently an example showing the danger of this procedure.⁽³⁵⁾ However, we are here considering the evolution of the one-particle distribution function in the hydrodynamic stage; we thus expect that

$$\partial_t^n f_q \leq (cq)^n \tag{65}$$

in which case the expansion in the right hand-side of (61) is really an expansion in the uniformity parameter q and should thus be rapidly converging.

In analogy with (18), the eigenvalue problem associated with the generalized Boltzmann equation reads

$$i(\Omega_q \bar{\Psi}_q) \Psi_n^q(v) = \lambda_n^q \Psi_n^q(v) \tag{66}$$

where we have dropped the arguments of $\bar{\Psi}_q(v; 0)$.

Adopting the same strategy as in the dilute gas, we expand $\Omega_q \bar{\Psi}_q$ in powers of the uniformity parameter:

$$\Omega_q = \Omega_0 + q\Omega_0' + \frac{1}{2}q^2\Omega_0'' \tag{67}$$

$$\bar{\Psi}_q = \Psi_0 + q\bar{\Psi}_0' + \frac{1}{2}q^2\bar{\Psi}_0'' \tag{68}$$

here, the prime means a partial derivative with respect to q ; for example,

$$\Omega_0' = \left. \frac{\partial \Omega_q}{\partial q} \right|_{q=0} \tag{69}$$

Up to order q^2 , we thus get from (66)–(68)

$$(C^l + qV^{(1)} + q^2V^{(2)}) \Psi_n^q(v) = \lambda_n^q \Psi_n^q(v) \tag{70}$$

¹¹ For an analysis leading to (64) when $q = 0$, also see George.⁽³⁶⁾

where the following notation has been used:

$$C^l = i\Omega_0\Psi_0 \quad (71)$$

$$V^{(1)} = i[\Omega_0(-v_x + \Psi_0') + \Omega_0'\Psi_0] \quad (72)$$

$$V^{(2)} = i[\frac{1}{2}\Omega_0''\Psi_0 + \Omega_0'(-v_x + \Psi_0') + \frac{1}{2}\Omega_0\Psi_0''] \quad (73)$$

Consider now the unperturbed eigenvalue problem

$$C^l | \Phi_n \rangle = \lambda_n^0 | \Phi_n \rangle \quad (74)$$

We immediately find a difficulty which did not occur in the dilute-gas limit: as was already stressed by Garcia-Collin *et al.* and by Ernst⁽²⁶⁾ the linearized homogeneous collision operator C^l is in general not symmetric. As a matter of fact, though the symmetric character of $i\Psi_0$ is easily established from the definition (55), namely

$$\langle f | i\Psi_0 | g \rangle = \langle g | i\Psi_0 | f \rangle \quad (75)$$

no similar result holds for $i\Omega_0\Psi_0$! In order to circumvent this difficulty, we will be obliged to work with a biorthonormal set of eigenfunctions⁽³⁷⁾; thus, together with (74), we will have to study the adjoint eigenvalue problem¹²

$$\langle \bar{\Phi}_n | C^l = \langle \bar{\Phi}_n | \lambda_n^0 \quad (76)$$

where $\langle \bar{\Phi}_n |$ is in general different from $\langle \Phi_n |$.

Before considering this point in more detail, let us first discuss some properties of the eigenvalue problem associated with the symmetric operator

$$i\Psi_0 | \chi_n \rangle = \mu_n^0 | \chi_n \rangle \quad (77)$$

Here, the analogy with the Boltzmann case treated in Section 2 is complete. In particular, the eigenfunctions $| \chi_n \rangle$ can be made orthonormal:

$$\langle \chi_n | \chi_{n'} \rangle = \int dv [\varphi^{\text{eq}}(v)]^{-1} \chi_n(v) \chi_{n'}(v) = \delta_{n,n'}^{\text{Kr}} \quad (78)$$

We also assume that the set of functions χ_n is complete.

As can be verified from the definition (55) by the method given by Prigogine⁽¹⁶⁾ and Résibois⁽¹⁷⁾ when proving an H -theorem, there are five eigenfunctions with zero eigenvalue:

$$i\Psi_0 | \chi_\alpha \rangle = 0, \quad \alpha = 1, 2, 3, 4, 5 \quad (79)$$

describing the collisional invariants 1, \mathbf{v} , v^2 . The $| \chi_\alpha \rangle$ are identical to the $| \alpha \rangle$ defined in Section 2 [see Eqs. (23) and (24)]:

$$| \chi_\alpha \rangle \equiv | \alpha \rangle, \quad \alpha = 1, 2, 3, 4, 5 \quad (80)$$

¹² We assume that the eigenvalues λ_n^0 are purely real; there is no difficulty in extending to the case where then λ_n^0 are complex.

[see remark before (23)]. Finally, the symmetric character of $i\Psi_0$ also implies that

$$\langle \alpha | i\Psi_0 = 0, \quad \alpha = 1, \dots, 5 \quad (81)$$

With these preliminary results in mind, let us now go back to the eigenvalue problem (74) and (76). The sets $|\Phi_n\rangle$ and $\langle \bar{\Phi}_n|$ can always be made biorthonormal:

$$\langle \bar{\Phi}_n | \Phi_n \rangle = \delta_{n,n'}^{\text{Kr}} \quad (82)$$

and again we assume that these sets are complete.

Although these eigenfunctions $|\Phi_n\rangle$ and $\langle \bar{\Phi}_n|$ are generally unknown, it is easy to construct five right and left eigenfunctions with zero eigenvalue. Indeed, from (79) and (80), we have

$$C^l |\alpha\rangle \equiv i\Omega_0 \Psi_0 |\alpha\rangle = 0 \quad (83)$$

which implies that

$$|\Phi_\alpha\rangle = |\alpha\rangle, \quad \alpha = 1, \dots, 5 \quad (84)$$

Similarly, from (81), we get

$$\langle \alpha | \Omega_0^{-1} C^l = \langle \alpha | \Omega_0^{-1} i(\Omega_0 \Psi_0) = 0 \quad (85)$$

where we assume that the operator Ω_0^{-1} exists (see Appendix 2). Thus,

$$\langle \bar{\Phi}_\nu' | = \langle \nu | \Omega_0^{-1}, \quad \nu \in (\alpha) \quad (86)$$

is a left eigenfunction of the operator C^l . However, because these functions $\langle \bar{\Phi}_\nu' |$ are degenerate (they all correspond to $\lambda_\nu^0 = 0$), there is no reason why they should be biorthonormal to $|\Phi_\nu\rangle$. In order to ensure this property, we have to apply the Schmidt orthogonalization method.

Using the following results, which are demonstrated in Appendix 2,

$$\langle \mu | \Omega_0^{-1} | \beta \rangle = \delta_{\mu,\beta}^{\text{Kr}}, \quad \mu = 1, 2, 3, 4; \quad \beta \in (\alpha) \quad (87a)$$

$$\langle 5 | \Omega_0^{-1} | 1 \rangle = \left(\frac{2}{3}\right)^{1/2} \left[\frac{1}{kT} \left(\frac{\partial e}{\partial n} \right)_T - \frac{3}{2} - \frac{nV_0}{kT} \right] \quad (87b)$$

$$\langle 5 | \Omega_0^{-1} | i \rangle = 0, \quad i = 2, 3, 4 \equiv x, y, z \quad (87c)$$

$$\langle 5 | \Omega_0^{-1} | 5 \rangle = \frac{2C_v}{3k} \quad (87d)$$

it is easy to verify that the left eigenfunctions are

$$\langle \bar{\Phi}_1 | = \langle 1 | \quad (88a)$$

$$\langle \bar{\Phi}_i | = \langle i |, \quad i = 2, 3, 4 \equiv x, y, z \quad (88b)$$

$$\langle \bar{\Phi}_5 | = \frac{3k}{2C_v} \left[\langle 5 | \Omega_0^{-1} - \left(\frac{2}{3}\right)^{1/2} \frac{1}{kT} \left(\left(\frac{\partial e}{\partial n} \right)_T - \frac{3kT}{2} - nV_0 \right) \langle 1 | \right] \quad (88c)$$

In these equations, we have taken into account that

$$\langle 1 | \Omega_0^{-1} = \langle 1 | \quad (89a)$$

$$\langle i | \Omega_0^{-1} = \langle i |, \quad i = 2, 3, 4 \equiv x, y, z \quad (89b)$$

which are simple consequences respectively of particle and momentum conservation. These eigenfunctions satisfy the required biorthonormality conditions:

$$\langle \bar{\Phi}_{\alpha'} | \bar{\Phi}_{\alpha''} \rangle = \delta_{\alpha', \alpha''}^{\mathbf{K}^{\mathbf{r}}}, \quad \alpha', \alpha'' \in (\alpha) \quad (90)$$

Let us point out that in Eq. (88c), we have to subtract $nv_0 = n \int d^3r V(r)$, which only exists for integrable potentials. This difficulty is a consequence of the perturbation nature of the definition (55); however, it is not a serious drawback because, in the final results, all such terms will exactly compensate each other (see Sections 4 and 5).

To close this section, let us comment about the physical significance of the coefficients of expansion of an arbitrary function $|f_q\rangle$ in terms of the two sets of eigenfunctions which we have introduced thus far, namely $|\chi_n\rangle$ (and $\langle\chi_n|$) and $|\bar{\Phi}_n\rangle$ (and $\langle\bar{\Phi}_n|$). We have, indeed, from the assumed completeness of these two sets,

$$|f_q\rangle = \sum_n \langle\chi_n|f_q\rangle |\chi_n\rangle \quad (91a)$$

$$|f_q\rangle = \sum_n \langle\bar{\Phi}_n|f_q\rangle |\bar{\Phi}_n\rangle \quad (91b)$$

Let us limit ourselves to the coefficients $\langle\chi_\alpha|f_q\rangle$ and $\langle\bar{\Phi}_\alpha|f_q\rangle$, where, as always, $\alpha = 1, 2, 3, 4, 5$. From (23), (80), and (88), we have

$$\langle\chi_1|f_q\rangle = \langle\bar{\Phi}_1|f_q\rangle = \int dv f_q(v; t) = n_q(t)/n \quad (92)$$

where n_q clearly represents the density fluctuation. Similarly,

$$\langle\chi_i|f_q\rangle = \langle\bar{\Phi}_i|f_q\rangle = \int dv \frac{v_i}{(kT)^{1/2}} f_q(v; t) = \frac{ng_q(t)}{(kT)^{1/2}} \quad (93)$$

which, up to a trivial normalization constant, describes the velocity fluctuation.

For the coefficient $\langle\chi_5|f_q\rangle$, we find

$$\langle\chi_5|f_q\rangle = \left(\frac{2}{3}\right)^{1/2} \int dv \left(\frac{v^2}{2kT} - \frac{3}{2}\right) f_q = \left(\frac{2}{3}\right)^{1/2} \frac{3}{2} \frac{T_q}{T} \quad (94)$$

which appears as the natural definition for the *kinetic* temperature fluctuation T_q (up to a trivial normalization factor). On the other hand,

$$\langle\bar{\Phi}_5|f_q\rangle = \frac{3k}{2C_v} \left[\langle 5 | \Omega_0^{-1} f_q \rangle - \left(\frac{2}{3}\right)^{1/2} \frac{1}{kT} \left(\left(\frac{\partial e}{\partial n}\right) - \frac{3kT}{2} - nV_0 \right) \langle 1 | f_q \rangle \right] \quad (95)$$

has in general, a more difficult interpretation. If we limit ourselves to a local equilibrium state, denoted by $|f_q^l\rangle$,

$$|f_q^l\rangle = \sum_{\mu \in (\alpha)} |\Phi_\mu\rangle \langle \bar{\Phi}_\mu | f_q^l \rangle \quad (96)$$

we find from (87) that

$$\langle \bar{\Phi}_5 | f_q^l \rangle = \left(\frac{2}{3}\right)^{1/2} \frac{3}{2} \frac{T_q}{T} \quad (97)$$

where the kinetic temperature T_q is defined by (94). However, in the general case (91), where the sum extends over all n , we get

$$\langle \bar{\Phi}_5 | f_q \rangle = \left(\frac{3}{2}\right)^{1/2} \frac{1}{T} [T_q + T_q^{(1)}] \equiv \left(\frac{3}{2}\right)^{1/2} \frac{T_q^{(e)}}{T} \quad (98)$$

with

$$T_q^{(1)} = \sum_{n \notin (\alpha)} \frac{1}{C_v} \int dv \frac{v^2}{2} \Omega_0^{-1} |\Phi_n\rangle \langle \bar{\Phi}_n | f_q \rangle \quad (99)$$

A more detailed analysis would show that (99) describes the temperature fluctuation $T_q^{(1)}$ coming from the *non*-local-equilibrium part of $|f_q\rangle$; the coefficient $T_q^{(e)}$ may then be interpreted as the temperature defined by the total energy density (kinetic + potential) in the nonequilibrium state $|f_q\rangle$.¹³ However, this physical interpretation plays no role whatsoever in the following mathematical developments; as, moreover, a similar question has already been discussed in the literature from a slightly different point of view,^(22,26) we shall not investigate this point further here.

4. REMOVING THE DEGENERACY (NONDISSIPATIVE HYDRODYNAMICS)

In trying to solve the eigenvalue problem (70) for those eigenvalues which tend to zero when $q \rightarrow 0$, we are immediately confronted with a difficulty similar to one we have already encountered in the dilute gas, namely the set of unperturbed states $|\Phi_\alpha\rangle$ (and $\langle \bar{\Phi}_\alpha |$) is degenerate.

We have thus first to remove this degeneracy by treating exactly the eigenvalue problems

$$(C^l + qV^{(1)}) |\Psi_\mu\rangle = \lambda_\mu |\Psi_\mu\rangle, \quad \mu \in (\alpha) \quad (100a)$$

$$\langle \bar{\Psi}_\mu | (C^l + qV^{(1)}) = \lambda_\mu \langle \bar{\Psi}_\mu |. \quad \mu \in (\alpha) \quad (100b)$$

in the subspace spanned by the set (α) . Exactly as in (28), we expand $|\Psi_\mu\rangle$ according to

$$|\Psi_\mu\rangle = \sum_{\nu \in (\alpha)} c_{\mu\nu} |\Phi_\nu\rangle \quad (101)$$

¹³ The connection between the left eigenfunction of the homogeneous collision operator and the energy density was first pointed out in the elegant paper by Garcia-Colin, Green, and Chaos.⁽²⁵⁾

and we get from (100) a system of five linear equations:

$$iq \sum_{\nu} \epsilon_{\mu'\nu} c_{\mu\nu} = \bar{\lambda}_{\mu} c_{\mu\mu'}, \quad \mu, \nu, \mu' \in (\alpha) \quad (102)$$

where we have set

$$\epsilon_{\mu\nu} = \langle \bar{\Phi}_{\mu} | \Omega_0(-v_x + \Psi_0') | \Phi_{\nu} \rangle \quad (103)$$

As is shown in Appendix 3, the coefficients $\epsilon_{\mu\nu}$ can be evaluated exactly to all orders in the interaction; we find that they all vanish except

$$\epsilon_{12} = -(kT)^{1/2} \quad (103a)$$

$$\epsilon_{21} = -\frac{1}{(kT)^{1/2}} \left(\frac{\partial p}{\partial n} \right)_T \quad (103b)$$

$$\epsilon_{25} = -\left(\frac{2kT}{3} \right)^{1/2} \frac{1}{nk} \left(\frac{\partial p}{\partial T} \right)_n \quad (103c)$$

$$\epsilon_{52} = -\left(\frac{2kT}{3} \right)^{1/2} \frac{1}{nk} \left(\frac{\partial p}{\partial T} \right)_n \frac{3k}{2C_v} \quad (103d)$$

Notice that the asymmetric character of the operators involved in the problem is explicitly displayed in these equations.

From the zeros of the determinant associated with (102), one can easily compute the eigenfunctions $|\Psi_{\mu}\rangle$ and the eigenvalues $\bar{\lambda}_{\mu}$. The result is

$$\bar{\lambda}_1 = -icq, \quad |\Psi_1\rangle = \frac{1}{\sqrt{2}} \left[\frac{(kT)^{1/2}}{c} |1\rangle + |2\rangle + \frac{(3kT/2)^{1/2} (\partial p/\partial T)_n}{ncC_v} |5\rangle \right] \quad (104a)$$

$$\bar{\lambda}_2 = icq, \quad |\Psi_2\rangle = \frac{1}{\sqrt{2}} \left[\frac{(kT)^{1/2}}{c} |1\rangle - |2\rangle + \frac{(3kT/2)^{1/2} (\partial p/\partial T)_n}{ncC_v} |5\rangle \right] \quad (104b)$$

$$\bar{\lambda}_3 = 0, \quad |\Psi_3\rangle = |3\rangle \quad (104c)$$

$$\bar{\lambda}_4 = 0, \quad |\Psi_4\rangle = |4\rangle \quad (104d)$$

$$\bar{\lambda}_5 = 0, \quad |\Psi_5\rangle = \frac{1}{c} \left[-\left(\frac{2}{3} \right)^{1/2} \frac{T}{n} \left(\frac{\partial p}{\partial T} \right)_n |1\rangle + \left(\frac{\partial p}{\partial n} \right)_T |5\rangle \right] \quad (104e)$$

The adjoint problem (100b) is treated similarly, by expanding $\langle \bar{\Psi}_{\mu} |$:

$$\langle \bar{\Psi}_{\mu} | = \sum_{\nu \in (\alpha)} c'_{\mu\nu} \langle \bar{\Phi}_{\nu} | \quad (105)$$

Following the same steps as above, we find

$$\bar{\lambda}_1 = -icq, \quad \langle \bar{\Psi}_1 | = \frac{1}{\sqrt{2}} \left[\frac{1}{c(kT)^{1/2}} \left(\frac{\partial p}{\partial n} \right)_T \langle 1 | + \langle 2 | + \left(\frac{2kT}{3} \right)^{1/2} \frac{1}{ckn} \left(\frac{\partial p}{\partial T} \right)_n \langle \bar{\Phi}_5 | \right] \quad (106a)$$

$$\bar{\lambda}_2 = icq, \quad \langle \bar{\Psi}_2 | = \frac{1}{\sqrt{2}} \left[\frac{1}{c(kT)^{1/2}} \left(\frac{\partial p}{\partial n} \right)_T \langle 1 | - \langle 2 | + \left(\frac{2kT}{3} \right)^{1/2} \frac{1}{ckn} \left(\frac{\partial p}{\partial T} \right)_n \langle \bar{\Phi}_5 | \right] \quad (106b)$$

$$\bar{\lambda}_3 = 0, \quad \langle \bar{\Psi}_3 | = \langle 3 | \quad (106c)$$

$$\bar{\lambda}_4 = 0, \quad \langle \bar{\Psi}_4 | = \langle 4 | \quad (106d)$$

$$\bar{\lambda}_5 = 0, \quad \langle \bar{\Psi}_5 | = \frac{1}{c} \left[-\frac{1}{nC_v} \left(\frac{3}{2} \right)^{1/2} \left(\frac{\partial p}{\partial T} \right)_n \langle 1 | + \langle \bar{\Phi}_5 | \right] \quad (106e)$$

The normalization constants in Eqs. (105) and (106) have been chosen in such a way that

$$\langle \bar{\Psi}_\mu | \Psi_\nu \rangle = \delta_{\mu,\nu}^{Kr}, \quad \mu, \nu \in (\alpha) \quad (107)$$

We also have the important property

$$\langle \bar{\Psi}_\mu | \Omega_0[iq(-v_x + \Psi_0')] | \Psi_\nu \rangle = \bar{\lambda}_\mu \delta_{\mu,\nu}^{Kr} \quad (108)$$

which can be checked by direct calculation from (103), (105), and (106). Notice that, in the noninteracting limit, we recover of course the perfect-gas modes defined in (32).

Before closing this section, let us look at the physical interpretation of the coefficients $\langle \bar{\Psi}_\alpha | f_q \rangle$ in the expansion

$$|f_q\rangle = \sum_{\mu \in (\alpha)} \langle \bar{\Psi}_\mu | f_q \rangle | \Psi_\mu \rangle + \sum_{n \notin (\alpha)} \langle \bar{\Phi}_n | f_q \rangle \langle \Phi_n | \quad (109)$$

In particular, let us study $\langle \bar{\Psi}_5 | f_q \rangle$; from (106c), (92), and (98), we have

$$\langle \bar{\Psi}_5 | f_q \rangle = \frac{1}{c} \left[-\frac{1}{nC_v} \left(\frac{3}{2} \right)^{1/2} \left(\frac{\partial p}{\partial T} \right)_n \frac{n_q}{n} + \left(\frac{3}{2} \right)^{1/2} \frac{T_q^{(e)}}{T} \right] \quad (110)$$

We then use the thermodynamic expression for the entropy density fluctuation,

$$S_q = \frac{e_q}{T} - \frac{p + e}{nT} n_q \quad (111)$$

and the well-known identities

$$e_q = nC_v T_q^{(e)} + \left(\frac{\partial e}{\partial n} \right)_T n_q \quad (112)$$

$$p + e = T \left(\frac{\partial p}{\partial T} \right)_n + n \left(\frac{\partial e}{\partial n} \right)_T \quad (113)$$

These formulas allows us to cast $\langle \bar{\Psi}_5 | \bar{f}_q \rangle$ in the following form:

$$\langle \bar{\Psi}_5 | f_q \rangle = \left(\frac{3}{2} \right)^{1/2} \frac{1}{nC_v} S_q \quad (114)$$

Up to a trivial normalization constant, the mode $|\Psi_5\rangle$ (and $\langle\bar{\Psi}_5|$) thus represents an entropy fluctuation which, to first order in q , is time-independent. Similarly, one can show that $|\Psi_1\rangle$ and $|\Psi_2\rangle$ describe propagating sound waves, while $|\Psi_3\rangle$ and $|\Psi_4\rangle$ correspond to shear viscosity modes.

5. TRANSPORT COEFFICIENTS AS EIGENVALUES

In order to avoid degeneracy difficulties, we have seen in the previous section that the eigenvalue problem (70) should be solved with the following unperturbed basis:

$$\begin{cases} |\Psi_\mu\rangle \text{ (and } \langle\bar{\Psi}_\mu|), & \mu \in (\alpha) \\ |\Psi_n\rangle \equiv |\Phi_n\rangle \text{ (and } \langle\bar{\Psi}_n| = \langle\bar{\Phi}_n|), & n \notin (\alpha) \end{cases} \quad (115)$$

This basis is biorthonormal:

$$\langle\bar{\Psi}_n | \Psi_{n'}\rangle = \delta_{n,n'}^{\text{Kr}}, \quad n, n' \in \text{ or } \notin (\alpha) \quad (116)$$

and is assumed to be complete.

The calculation of the eigenvalues λ_α^0 of the problem (70) is then straightforward. We expand λ_α^q and $|\Psi_\alpha^q\rangle$ in the uniformity parameter q :

$$\lambda_\alpha^q = q\lambda_\alpha^{(1)} + q^2\lambda_\alpha^{(2)} + \dots \quad (117)$$

$$|\Psi_\alpha^q\rangle = |\Psi_\alpha\rangle + q|\Psi_\alpha^{(1)}\rangle + \dots \quad (118)$$

and we insert these expansions into (70). Using the biorthonormality relation (116), one obtains immediately, by a slight modification of the usual perturbation calculus (due to the asymmetry of the operators)

$$q\lambda_\alpha^{(1)} = \bar{\lambda}_\alpha \quad (119)$$

where the $\bar{\lambda}_\alpha$ have been defined in (104), and

$$\lambda_\alpha^{(2)} = - \sum_{n \neq (\alpha)} \langle\bar{\Psi}_\alpha | V^{(1)} | \Psi_n\rangle \frac{1}{\lambda_n^0} \langle\bar{\Psi}_n | V^{(1)} | \Psi_\alpha\rangle + \langle\bar{\Psi}_\alpha | V^{(2)} | \Psi_\alpha\rangle \quad (120)$$

A more explicit formula for $\lambda_\alpha^{(2)}$ is obtained by using the definitions (72) and (73) and by taking into account that

$$\Psi_0 | \Psi_\alpha\rangle = 0 \quad (121)$$

We get then

$$\lambda_\alpha^{(2)} = \lambda_\alpha^{(2)'} + \lambda_\alpha^{(2)''} \quad (122)$$

where

$$\lambda_\alpha^{(2)'} = \sum_{n \neq (\alpha)} \langle\bar{\Psi}_\alpha | \Omega_0(-v_x + \Psi_0') | \Psi_n\rangle \frac{1}{\lambda_n^0} \langle\bar{\Psi}_n | \Omega_0(-v_x + \Psi_0') | \Psi_\alpha\rangle \quad (123)$$

and

$$\begin{aligned} \lambda_\alpha^{(2)''} &= \frac{i}{2} \langle \bar{\Psi}_\alpha | \Omega_0 \Psi_0'' | \Psi_\alpha \rangle + i \langle \bar{\Psi}_\alpha | \Omega_0' (-v_x + \Psi_0') | \Psi_\alpha \rangle \\ &\quad + \sum_{n \neq (\alpha)} \langle \bar{\Psi}_\alpha | \Omega_0' \Psi_0 | \Psi_n \rangle \frac{1}{\lambda_n^0} \langle \bar{\Psi}_n | (-v_x + \Psi_0') | \Psi_\alpha \rangle \end{aligned} \quad (124)$$

The reason for this splitting will be justified later on.

Both $\lambda_\alpha^{(2)'}$ and $\lambda_\alpha^{(2)''}$ can be further simplified. For $\lambda_\alpha^{(2)'}$, we first get rid of the restriction in the sum over n precisely as in (40) and we then use the formal relation

$$\lim_{\epsilon \rightarrow 0} \sum_n | \Psi_n \rangle \frac{1}{\lambda_n^0 - \epsilon} \langle \bar{\Psi}_n | = \lim_{\epsilon \rightarrow 0} \frac{1}{C^l - \epsilon} = \lim_{\epsilon \rightarrow 0} \frac{1}{i(\Omega_0 \Psi_0 + i\epsilon)} = \lim_{\epsilon \rightarrow 0} \frac{1}{i(\Psi_0 + i\epsilon)} \frac{1}{\Omega_0} \quad (125)$$

This leads to

$$\lambda_\alpha^{(2)'} = \lim_{\epsilon \rightarrow 0} \langle \bar{\Psi}_\alpha | \Omega_0 (-v_x + \Psi_0') \frac{1}{i(\Psi_0 + i\epsilon)} (-v_x + \Psi_0' - \Omega_0^{-1} g_\alpha) | \Psi_\alpha \rangle \quad (126)$$

where again $\bar{\lambda}_\alpha = i q g_\alpha$.

In order to simplify $\lambda_\alpha^{(2)'}$, we rewrite the second term on the r.h.s. of (129) as

$$\begin{aligned} i \langle \bar{\Psi}_\alpha | \Omega_0' (-v_x + \Psi_0') | \Psi_\alpha \rangle &= i \langle \bar{\Psi}_\alpha | \Omega_0' \Omega_0^{-1} \Omega_0 (-v_x + \Psi_0') | \Psi_\alpha \rangle \\ &= i \sum_n \langle \bar{\Psi}_\alpha | \Omega_0' \Omega_0^{-1} | \Psi_n \rangle \langle \bar{\Psi}_n | \Omega_0 (-v_x + \Psi_0') | \Psi_\alpha \rangle \end{aligned} \quad (127)$$

while the third term in the same expression is transformed in the following way:

$$\begin{aligned} &\sum_{n \neq (\alpha)} \langle \bar{\Psi}_\alpha | \Omega_0' \Psi_0 | \Psi_n \rangle \frac{1}{\lambda_n^0} \langle \bar{\Psi}_n | \Omega_0 (-v_x + \Psi_0') | \Psi_\alpha \rangle \\ &= \sum_{n \neq (\alpha)} \langle \bar{\Psi}_\alpha | \Omega_0' \Omega_0^{-1} \Omega_0 \Psi_0 | \Psi_n \rangle \frac{1}{\lambda_n^0} \langle \bar{\Psi}_n | \Omega_0 (-v_x + \Psi_0') | \Psi_\alpha \rangle \\ &= -i \sum_{n \neq (\alpha)} \langle \bar{\Psi}_\alpha | \Omega_0' \Omega_0^{-1} | \Psi_n \rangle \langle \bar{\Psi}_n | \Omega_0 (-v_x + \Psi_0') | \Psi_\alpha \rangle \end{aligned} \quad (128)$$

where Eqs. (71) and (74) have been used.

Combining (124), (127), (128), (108), and (42), we get finally

$$\lambda_\alpha^{(2)''} = \frac{i}{2} \langle \bar{\Psi}_\alpha | (\Omega_0 \Psi_0'' + 2\Omega_0' g_\alpha) | \Psi_\alpha \rangle \quad (129)$$

We now claim that $\lambda_\alpha^{(2)}$, as defined by (122), (126), and (129), is identical to the q^2 part of the eigenvalues (5), with an explicit microscopic definition of the transport coefficients η , ζ , and κ .

In order to give an insight into this property, let us use the definitions (104) and (106) of the hydrodynamic modes $|\Psi_\alpha\rangle$ and $\langle \bar{\Psi}_\alpha|$. After some simple manipulations

based on well-known thermodynamic identities and elementary rotation-invariance properties, we get

$$\lambda_1^{(2)} = \lambda_2^{(2)} = \frac{-1}{2n} \left[\left(\frac{4}{3} \eta + \zeta \right) + \left(\frac{1}{C_v} - \frac{1}{C_p} \right) \bar{\kappa} \right] \equiv -\Gamma \quad (130a)$$

$$\lambda_3^{(2)} = \lambda_4^{(2)} = -\eta/n \quad (130b)$$

$$\lambda_5^{(2)} = -\kappa/nC_p \quad (130c)$$

where the following symbols have been introduced:

$$\eta = \eta' + \eta'' \quad (131a)$$

$$\left(\frac{4}{3} \eta + \zeta \right) = \left(\frac{4}{3} \eta + \zeta \right)' + \left(\frac{4}{3} \eta + \zeta \right)'' \quad (131b)$$

$$\kappa = \kappa' + \kappa'' \quad (131c)$$

$$\bar{\kappa} = \bar{\kappa}' + \bar{\kappa}'' \quad (131d)$$

with the definitions

$$\eta' = -n \lim_{\epsilon \rightarrow 0} \langle 3 | (-v_x + \Psi_0') \frac{1}{i(\Psi_0' + i\epsilon)} (-v_x + \Psi_0') | 3 \rangle \quad (132a)$$

$$\eta'' = -\frac{i\hbar}{2} \langle 3 | \Psi_0'' | 3 \rangle \quad (132b)$$

$$\begin{aligned} \kappa' = & -\frac{3kn}{2} \lim_{\epsilon \rightarrow 0} \langle 5 | (-v_x + \Psi_0') \frac{1}{i(\Psi_0' + i\epsilon)} (-v_x + \Psi_0') \\ & \times \left[| 5 \rangle - \left(\frac{2}{3} \right)^{1/2} \frac{T}{n} \left(\frac{\partial n}{\partial T} \right)_p | 1 \rangle \right] \end{aligned} \quad (133a)$$

$$\kappa'' = -\frac{3ikn}{4} \langle 5 | \Psi_0'' \left[| 5 \rangle - \left(\frac{2}{3} \right)^{1/2} \frac{T}{n} \left(\frac{\partial n}{\partial T} \right)_p | 1 \rangle \right] \quad (133b)$$

$$\begin{aligned} \left(\frac{4}{3} \eta + \zeta \right)' = & -n \lim_{\epsilon \rightarrow 0} \langle 2 | (-v_x + \Psi_0') \frac{1}{i(\Psi_0' + i\epsilon)} \\ & \times \left\{ (-v_x + \Psi_0') | 2 \rangle + \Omega_0^{-1} \left[(kT)^{1/2} | 1 \rangle + \frac{(3kT/2)^{1/2} (\partial p / \partial T)_n}{nC_v} | 5 \rangle \right] \right\} \end{aligned} \quad (134a)$$

$$\left(\frac{4}{3} \eta + \zeta \right)'' = -i\hbar \left\{ \frac{1}{2} \langle 2 | \Psi_0'' | 2 \rangle - \langle 2 | \Omega_0' \Omega_0^{-1} \left[(kT)^{1/2} | 1 \rangle + \frac{(3kT/2)^{1/2} (\partial p / \partial T)_n}{nC_v} | 5 \rangle \right] \right\} \quad (134b)$$

$$\begin{aligned} \bar{\kappa}' = & -\frac{3kn}{2} \lim_{\epsilon \rightarrow 0} \langle 5 | (-v_x + \Psi_0') \frac{1}{i(\Psi_0' + i\epsilon)} \left\{ (-v_x + \Psi_0') \right. \\ & \times \left. \left[| 5 \rangle + \left(\frac{2}{3} \right)^{1/2} \left(\frac{\partial e}{\partial p} \right)_n | 1 \rangle \right] + \Omega_0^{-1} \left(\frac{2}{3kT} \right)^{1/2} c^2 \left(\frac{\partial e}{\partial p} \right)_n | 2 \rangle \right\} \end{aligned} \quad (135a)$$

$$\begin{aligned} \bar{\kappa}'' = & -\frac{3ikn}{2} \left\{ \frac{1}{2} \langle 5 | \Psi_0'' \left[| 5 \rangle + \left(\frac{2}{3} \right)^{1/2} \left(\frac{\partial e}{\partial p} \right)_n | 1 \rangle \right] \right. \\ & \left. - \langle 5 | \Omega_0^{-1} \Omega_0' \Omega_0^{-1} | 2 \rangle \left(\frac{2}{3kT} \right)^{1/2} c^2 \left(\frac{\partial e}{\partial p} \right)_n \right\} \end{aligned} \quad (135b)$$

The correctness of the thermodynamic factors appearing in (130) [compare with (5)] strongly suggests that η and ζ should be identified with the shear and bulk viscosity, while we should have

$$\kappa \equiv \bar{\kappa} \quad (136)$$

corresponding to the thermal conductivity.

This is exactly what we have been able to show; more precisely, we have proved that η , ζ , and κ , as given by (131)–(136) are identical to the *reduced* expressions obtained by a many-body analysis of the autocorrelation formulas for transport coefficients. For example, we have shown that Eqs. (131a) and (132) are equivalent to

$$\eta = \lim_{T_1 \rightarrow \infty} \lim_{\Omega \rightarrow \infty} \frac{1}{\Omega k T} \int_0^{T_1} dt \int dr^N dp^N J^{xy} \exp[-iLt] J^{xy} \rho_N^{\text{eq}} \quad (137)$$

where

$$J^{xy} = \sum_i v_i^x v_i^y - \frac{1}{2} \sum_{i \neq j} \frac{\partial V}{\partial r_{ij,y}} r_{ij,x} \quad (138)$$

However, we shall not reproduce these proofs in detail here. Indeed, on the one hand, the principle of these calculations is not new: it follows very closely the analysis given previously by the author⁽²¹⁾ and by Nicolis and Severne⁽²²⁾ when showing the equivalence between the autocorrelation function method and the traditional kinetic-theory approach; and on the other hand, mainly for the case of sound absorption (i.e., $\lambda_1^{(2)}$), there are some nontrivial technical difficulties which require a more careful analysis of the many-body aspects of the problem than we intend to do here; this will be discussed in another publication.⁽²⁸⁾

However, in order to suggest how these proofs can be given, we briefly discuss in Appendix 3 the shear viscosity coefficient (131) and its equivalence with (137); it will appear clearly there that the decomposition of η into two parts, η' and η'' , corresponds to an analogous separation which is naturally made when analyzing (137).

6. DISCUSSION

The central result of this paper is that, formulating the linearized, generalized Boltzmann equation as an eigenvalue problem, we have explicitly constructed five (right and left) eigenfunctions which, to *all* orders in the coupling constant, describe hydrodynamic modes in terms of *one*-body distributions. Moreover, the corresponding eigenvalues, when expanded in powers of the uniformity parameter, give microscopic expressions for transport coefficients which agree with the correlation function formulas.

The idea of getting hydrodynamic eigenmodes, and the corresponding transport coefficients, by an expansion of a transport equation in the uniformity parameter is not new. It was used in the study of sound propagation in dilute gases,⁽³²⁾ in the derivation of the correlation function formulas,^(2,4,5) and in the recent mode-mode coupling approach to critical transport phenomena.⁽¹²⁾ However, to the best of our knowledge, no such approach has been developed in terms of *one*-body distributions

in a strongly coupled system. As explained in the introduction, we expect that this latter feature will provide a useful tool in the analysis of a variety of problems involving long-wavelength divergences. A first, simple but not quite trivial application, namely a microscopic derivation of Eq. (13) for the van Hove function, can be found elsewhere.⁽²⁸⁾

Although Eqs. (131)–(135) offer in principle new microscopic expressions for transport coefficients, it is clear that the present method has not been devised for explicit calculation of these coefficients. In particular, a tentative density expansion of these expressions would lead to the same divergence difficulty as the more traditional method.⁽⁷⁾ On the contrary, the usefulness of our method lies in the fact that whenever an expression of the type $(i\Omega_a \bar{\Psi}_a)^{-1}$, involving the inverse linearized, generalized Boltzmann operator, is encountered in a microscopic expression (and this turns out to be the case in many of these diverging problems!), it does not have to be calculated but can be replaced by

$$\lim_{q \rightarrow 0} (i\Omega_a \bar{\Psi}_a)^{-1} = \sum_{\mu \in (\alpha)} |\Psi_\mu\rangle \frac{1}{iqg_\mu + q^2 \lambda_\mu^{(2)}} \langle \bar{\Psi}_\mu | \quad (139)$$

where the transport coefficients appearing in $\lambda_\mu^{(2)}$ are replaced by the approximation adequate to the problem at hand. This point is further discussed elsewhere⁽²⁸⁾ and other examples are presently studied.

APPENDIX 1

Linearized Kinetic Equations for $f_a(\mathbf{v}; \mathbf{t})$

The formal solution of the Liouville equation for the N -particle distribution $\rho_N(r^N, v^N; t)$ can be written as

$$\rho_N(r^N, v^N; t) = \frac{-1}{2\pi i} \oint_C dz \frac{e^{-izt}}{L - z} \rho_N(r^N, v^N; 0) \quad (A1.1)$$

where the contour C is the same as in (54).

Using the Fourier representation (58) and the formal perturbation expansion

$$(L - z)^{-1} = \sum_{n=0}^{\infty} (L_0 - z)^{-1} [-\delta L (L_0 - z)^{-1}]^n \quad (A1.2)$$

we get from (A1.1)

$$\begin{aligned} (q_1 | \rho_N(r^N, v^N; t) | 0) &= \frac{-1}{2\pi i} \oint_C dz e^{-izt} \sum_{\{k\}} \sum_{n=0}^{\infty} (q_1 | \frac{1}{L_0 - z} [-\delta L \frac{1}{L_0 - z}]^n | \{k\}) \\ &\quad \times (\{k\} | \rho_N(r^N, r^N; 0) | 0) \end{aligned} \quad (A1.3)$$

In the expansion involved in (A1.3), we isolate the intermediate states where one single wave number q_j ($q_j \equiv q_1$) is excited; we then differentiate (A1.3) with respect to time.

The result is

$$\begin{aligned}
 & \partial_t(q_1 | \rho_N(r^N, v^N; t) | 0) + iqv_{1a}(q_1 | \rho_N(r^N, v^N; t) | 0) \\
 &= \frac{-1}{2\pi i} \oint_C dz e^{-izt} \sum_{j=1}^N (q_1 | \Psi(z) | q_j)(q_j | \tilde{\rho}_N(r^N, v^N; z) | 0) \\
 & \quad - \frac{i}{2\pi i} \oint_C dz e^{-izt} \sum_{\{k\}} (q_1 | \mathcal{D}(z) | \{k\})(\{k\} | \rho_N(r^N, v^N; 0) | 0) \quad (A1.4)
 \end{aligned}$$

where $\tilde{\rho}_N(r^N, v^N; z)$ denotes the Laplace transform of $\rho_N(r^N, v^N; t)$. The so-called collision operator $(q_1 | \Psi(z) | q_j)$ and destruction operator $(q_1 | \mathcal{D}(z) | \{k\})$ are respectively defined by

$$(q_1 | \Psi(z) | q_j) = \sum_{n=0}^{\infty} (q_1 | -\delta L \left(\frac{1}{L_0 - z} (-\delta L) \right)^n | q_j)_{irr} \quad (A1.5)$$

where the subscript “*irr*” has the same meaning as in the text, and

$$(q_1 | \mathcal{D}(z) | \{k\}) = \sum_{n=1}^{\infty} (q_1 | \left(-\delta L \frac{1}{L_0 - z} \right)^n | \{k\})_{irr} \quad (A1.6)$$

The subscript “*irr*” implies here that not only the intermediate states of (A1.6), but also the final state $\{k\}$, have at least two nonvanishing wave numbers.

Within the frame of a linearized theory, one can assume, at $t = 0$, the factorization property

$$(q_1 | \rho_N(r^N, v^N; 0) | 0) = f_q(v_1; 0) \prod_{i \neq 1}^N \varphi^{eq}(v_i) \frac{1}{N\Omega^N} \quad (A1.7)$$

where $f_q(v_1; 0)$ is the one-particle distribution function of particle 1. In the thermodynamic limit, it can be proved that this property persists for $t > 0$. We then insert this result into (A1.4) and we integrate over $(N - 1)$ velocities; the result is

$$\begin{aligned}
 \partial_t f_q(v_1; t) + iqv_{1a} f_q(v_1; t) &= -\frac{1}{2\pi i} \oint_C dz e^{-izt} \Psi_q(v_1; z) \tilde{f}_q(v_1; z) \\
 & \quad - \frac{1}{2\pi i} \oint_C dz e^{-izt} \mathcal{D}_q(v_1; z) \quad (A1.8)
 \end{aligned}$$

where $\Psi_q(v_1; z)$ is defined by Eq. (56) and where, when z is in the upper half-plane, one has

$$\mathcal{D}_q(v_1; z) = N\Omega^N \int dv^{N-1} \sum_{\{k\}} (q_1 | \mathcal{D}(z) | \{k\})(\{k\} | \rho_N(r^N, v^N; 0) | 0) \quad (A1.9)$$

For $z \in S^-$, $\mathcal{D}_q(v; z)$ is defined by the analytical continuation of (A1.9) for reasons which are discussed in detail elsewhere.⁽¹⁷⁾

By Laplace inversion, Eq. (A1.8) immediately leads to Eq. (53) in the text.

APPENDIX 2

Properties of Ω_0^{-1}

We here establish Eqs. (87).

The starting point is the definition (64), which we consider only at $q = 0$. We multiply this equation on both sides by Ω_0^{-1} , and get

$$\Omega_0^{-1} = 1 + \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_{z=0} - O\Psi_0 \quad (\text{A2.1})$$

where

$$O = \sum_{n=2}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n \Psi_0}{\partial z^n} \Big|_{z=0} (\Omega_0 \Psi_0)^{n-2} \Omega_0 \quad (\text{A2.2})$$

As we only need $\langle \alpha | \Omega_0^{-1} | \beta \rangle$ where $|\alpha\rangle$ and $|\beta\rangle$ are eigenstates of $i\Psi_0$ with zero eigenvalue [see (79) and (80)], we have

$$\langle \alpha | \Omega_0^{-1} | \beta \rangle = \delta_{\alpha, \beta}^{\text{Kr}} + \langle \alpha | \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_{z=0} | \beta \rangle \quad (\text{A2.3})$$

The definition (55) leads immediately to

$$\langle 1 | \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_{z=0} | \beta \rangle = 0 \quad (\text{particle conservation}) \quad (\text{A2.4})$$

$$\langle i | \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_{z=0} | \beta \rangle = 0, \quad i = 2, 3, 4 \quad (\text{momentum conservation}) \quad (\text{A2.5})$$

We are thus left with $\langle 5 | (\partial \Psi_0 / \partial z)_{z=0} | \beta \rangle$; isolating the front factor $-\delta L(L_0 - z)^{-1}$ in (55), we can write

$$\begin{aligned} \langle 5 | \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_{z=0} | \beta \rangle &= \left(\frac{2}{3}\right)^{1/2} \frac{1}{kT} \sum_{\{k\} \neq 0} \int dv^N \frac{v_1^2}{2} \frac{\partial}{\partial z} (0 | -\delta L \frac{1}{L_0 - z} | \{k\}) \\ &\times (\{k\} | R(z) | 0) \sum_j' \langle v_j | \beta \rangle \prod_{i \neq j} \varphi^{\text{eq}}(v_i) \Big|_{z=0} \end{aligned} \quad (\text{A2.6})$$

where $R(z)$ is defined by

$$(\{k\} | R(z) | 0) = \sum_{n=0}^{\infty} (\{k\} | -\delta L \left[\frac{1}{L_0 - z} (-\delta L) \right]^n | 0)_{\text{irr}} \quad (\text{A2.7})$$

and the prime on the sum over j indicates that we should only retain those particles j that appear in the dynamical parts δL and $R(z)$. This is imposed because Ψ_0 is the $q = 0$ limit of the operator Ψ_q , where a similar condition explicitly occurs [see (55)].

We then transform (A2.6) by: (1) taking into account the symmetric role played by all particles; (2) using the explicit representation

$$(0 | -\delta L \frac{1}{L_0 - z} | \{k\}) = \frac{1}{\Omega} \sum_{s>t} -kV_k \left(\frac{\partial}{\partial v_s} - \frac{\partial}{\partial v_t} \right) \frac{1}{k(v_s - v_t) - z} \delta_{k_s, k}^{\text{Kr}} \delta_{k_t, -k}^{\text{Kr}} \delta_{\{k\}, 0}^{\text{Kr}} \quad (\text{A2.8})$$

(3) performing an integration by parts over v_s and v_t ; (4) taking the derivative with respect to z .

These operations are straightforward and lead to:

$$\begin{aligned} \langle 5 | \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_{z=0} | \beta \rangle &= \left(\frac{2}{3}\right)^{1/2} \frac{1}{kT} \frac{1}{2N\Omega} \sum_{s \neq t} \sum_{k \neq 0} \int dv^N V_k(k_s, -k_t | \frac{\partial R(z)}{\partial z} \Big|_{z=0} | 0) \\ &+ \frac{1}{k(v_s - v_t) - i0} (k_s, -k_t | R(0) | 0) \sum_j' \langle v_j | \beta \rangle \prod_{i \neq j} \varphi^{\text{eq}}(v_i) \end{aligned} \quad (\text{A2.9})$$

The first term in (A2.9) vanishes after integration over v^N because $\partial R(z)/\partial z$ starts with δL ; in the second term, we get

$$\frac{1}{k(v_s - v_t) - i0} (k_s, -k_t | R(0) | 0) \equiv (k_s, -k_t | \mathcal{C} | 0) \quad (\text{A2.10})$$

where \mathcal{C} (creation operator) has been shown previously to play an important role in the determination of the equilibrium correlations in a dense system; as is proved elsewhere,⁽¹⁷⁾ one has indeed

$$(k_s, -k_t | \mathcal{C} | 0) \prod_{i=1}^N \varphi^{\text{eq}}(v_i) = \Omega^N (k_s, -k_t | \rho_N^{\text{eq}} | 0) \quad (\text{A2.11})$$

We thus get

$$\begin{aligned} \langle 5 | \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_{z=0} | \beta \rangle &= \left(\frac{2}{3}\right)^{1/2} \frac{1}{kTN\Omega} \sum_{k \neq 0} \sum_{s > t} \int dv^N V_k \\ &\times (k_s, -k_t | \mathcal{C} | 0) \sum_j' \langle v_j | \beta \rangle \prod_{i \neq j} \varphi^{\text{eq}}(v_i) \end{aligned} \quad (\text{A2.12})$$

From this equation, the calculation of $\langle 5 | [\partial \Psi_0(v; z)/\partial z]_{z=0} | \beta \rangle$ is very direct; indeed, with [see (22)–(24)]

$$\langle v_j | 5 \rangle = \left(\frac{2}{3}\right)^{1/2} T \frac{\partial}{\partial T} \varphi^{\text{eq}}(v_j) \quad (\text{A2.13})$$

and

$$\int dv_j \langle v_j | 5 \rangle = 0 \quad (\text{A2.14})$$

we can transform (A2.12) according to

$$\begin{aligned} \langle 5 | \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_0 | 5 \rangle &= \frac{2}{3} \frac{1}{kN\Omega} \frac{\partial}{\partial T} \sum_{k \neq 0} \sum_{s > t} \int dv^N V_k(k_s, -k_t | \mathcal{C} | 0) \prod_{i=1}^N \varphi^{\text{eq}}(v_i) \\ &= \frac{2}{3} \frac{\Omega^{N-1}}{kN} \frac{\partial}{\partial T} \sum_{k \neq 0} \sum_{s > t} \int dv^N V_k(k_s, -k_t | \rho_N^{\text{eq}} | 0) \\ &= \frac{2}{3k} \left(C_v - \frac{3k}{2} \right) \end{aligned} \quad (\text{A2.15})$$

where use has been made of (A2.11).

The calculation of $\langle 5 | [\partial \Psi_0(v; z) / \partial z]_{z=0} | 1 \rangle$ follows similar lines and leads to

$$\langle 5 | \frac{\partial \Psi_0(v; z)}{\partial z} \Big|_{z=0} | 1 \rangle = \left(\frac{2}{3}\right)^{1/2} \left[\frac{1}{kT} \left(\frac{\partial e}{\partial n}\right)_T - \frac{3}{2} - \frac{nV_0}{kT} \right] \quad (\text{A2.16})$$

Equations (A2.3)–(A2.5), (A2.15), and (A2.16) are equivalent to Eqs. (87).

APPENDIX 3

Evaluation of $\langle \alpha | \Psi_0' | \beta \rangle$ and Discussion of the Shear Viscosity Coefficient

From (88), (89), and (31), the only nontrivial problem in the calculation of $\epsilon_{\mu\nu}$ [defined by (103)] is the evaluation of $\langle \alpha | \Psi_0' | \beta \rangle$.

As a matter of fact, particle conservation and rotation invariance readily show that only $\langle 2 | \Psi_0' | 1 \rangle$, $\langle 2 | \Psi_0' | 5 \rangle$, and $\langle 5 | \Psi_0' | 2 \rangle$ do not vanish.

We devise here a method which allows us to compute easily $\langle 2 | \Psi_0' | 1 \rangle$ and $\langle 2 | \Psi_0' | 5 \rangle$ and which, at the same time, provides us with some important hint in the analysis of the shear viscosity alluded to in Section 5. A similar method would permit the calculation of $\langle 5 | \Psi_0' | 2 \rangle$ and the discussion of the thermal conductivity.

Let us consider the matrix element $\langle i | \Psi_0' | \Phi \rangle$, where $i = 2, 3, 4$, while $|\Phi\rangle$ is an arbitrary one-velocity function.

We have from (55)

$$\begin{aligned} \langle i | \Psi_0' | \Phi \rangle &= \frac{1}{(kT)^{1/2}} \frac{\partial}{\partial q} \left[\int dv^N v_{1,i} \sum_{j=1}^N \sum_{t=1}^N \sum_{k \neq 0, -q_1} (q_1 | -\delta L^{ij} | k_1 + q_1, -k_j) \right. \\ &\quad \left. \times (k_1 + q_1, -k_j | \mathcal{C} | q_t) \langle v_t | \Phi \rangle \prod_{s \neq t} \varphi^{\text{eq}}(v_s) \right]_{q=0} \end{aligned} \quad (\text{A3.1})$$

where we have explicitly displayed the first vertex δL in the collision operator $(q_1 | \Psi | q_t)$; we thus have

$$(k_1 + q_1, -k_j | \mathcal{C} | q_t) = \sum_{n=1}^{\infty} (k_1 + q_1, -k_j | \left[\frac{1}{L_0 - i\epsilon} (-\delta L) \right]^n | q_t)_{i\text{rr}} \quad (\text{A3.2})$$

We notice that all particles play the same role in (A3.1); we may thus write successively:

$$\begin{aligned} \langle i | \Psi_0' | \Phi \rangle &= -\frac{1}{(kT)^{1/2}} \frac{\partial}{\partial q} \left[\frac{1}{N} \sum_{t=1}^N \sum_{j=1}^N \sum_{k \neq 0, -q_1} \int dv^N v_{t,i} \frac{kV_k}{\Omega} \frac{\partial}{\partial v_t} \right. \\ &\quad \left. \times \sum_{t=1}^N (k_t + q_t, -k_j | \mathcal{C} | q_t) \langle v_t | \Phi \rangle \prod_{s \neq t} \varphi^{\text{eq}}(v_s) \right]_{q=0} \\ &= \frac{1}{(kT)^{1/2}} \frac{\partial}{\partial q} \left[\frac{1}{N\Omega} \sum_{l>j=1}^N \sum_{k \neq 0, -q_1} \int dv^N k_i V_k \sum_{t=1}^N [(k_t + q_t, -k_j | \mathcal{C} | q_t) \right. \\ &\quad \left. - (k_j + q_j, -k_t | \mathcal{C} | q_t)] \langle v_t | \Phi \rangle \prod_{s \neq t} \varphi^{\text{eq}}(v_s) \right]_{q=0} \end{aligned}$$

$$\begin{aligned}
 &= \frac{1}{(kT)^{1/2}} \frac{\partial}{\partial q} \left[\frac{1}{N\Omega} \sum_{l>j=1}^N \sum_{k \neq 0, -q_l} \int dv^N [k_i V_k - (k+q)_i V_{k+q}] \right. \\
 &\quad \left. \times \sum_{t=1}^N (k_l + q_l, -k_j | \mathcal{E} | q_t) \langle v_t | \Phi \rangle \prod_{s \neq t} \varphi^{eq}(v_s) \right]_{q=0} \quad (\text{A3.3})
 \end{aligned}$$

In order to get this last equation, we have used the dummy character of the summation variable k . We now remark that the bracketed quantity in (A3.3) vanishes if $q = 0$; the derivative with respect to q is thus immediate to take, and we are lead to

$$\langle i | \Psi'_0 | \Phi \rangle = -\frac{1}{(kT)^{1/2}} \frac{1}{N} \sum_{\{k\} \neq 0} \int dv^N (0 | J^{xy,V} | \{k\}) (\{k\} | \mathcal{E} | 0) \sum_t' \langle v_t | \Phi \rangle \prod_{s \neq t} \varphi^{eq}(v_s) \quad (\text{A3.4})$$

where $J^{xy,V}$ is the potential part of the stress tensor (138).

From this formula, the calculation of $\langle 2 | \Psi'_0 | 5 \rangle$ and $\langle 2 | \Psi'_0 | 1 \rangle$ exactly follows the method used to treat (A2.12); one obtains after some simple algebra

$$\langle 2 | \Psi'_0 | 5 \rangle = -\left(\frac{2}{3}\right)^{1/2} \frac{(kT)^{1/2}}{kn} \left[\left(\frac{\partial p}{\partial T} \right)_n - kn \right] \quad (\text{A3.5})$$

and

$$\langle 2 | \Psi'_0 | 1 \rangle = -\frac{1}{(kT)^{1/2}} \left[\left(\frac{\partial p}{\partial n} \right)_T - kT - nV_0 \right] \quad (\text{A3.6})$$

Applying the same treatment to $\langle 5 | \Psi'_0 | 2 \rangle$, one finds

$$\langle 5 | \Psi'_0 | 2 \rangle = -\left(\frac{2}{3}\right)^{1/2} \frac{1}{(kT)^{1/2}} \left[\frac{h}{n} - nV_0 - \frac{5kT}{2} \right] \quad (\text{A3.7})$$

where h is the enthalpy density.

From Eqs. (A3.5)–(A3.7), the value given in the text for the coefficients $\epsilon_{\mu\nu}$ are easily checked.

Moreover, as already mentioned. Eq. (A3.4) can be used in the discussion of the equivalence between the shear viscosity as defined in the text by Eqs. (131a) and (132) and the result deduced from the correlation function formula (137). To simplify, let us limit ourselves to η' ; it is given by

$$\eta' = -n \lim_{\epsilon \rightarrow 0} \langle 3 | (-v_x + \Psi'_0) \frac{1}{i(\Psi'_0 + i\epsilon)} (-v_x + \Psi'_0) | 3 \rangle \quad (\text{A3.8})$$

The quantity $\langle 3 | (-v_x + \Psi'_0)$ can be obtained by adding to (A3.4) (where $|\Phi\rangle$ was left arbitrary) the trivial kinetic part $\langle 3 | (-v_x)$:

$$\begin{aligned}
 \langle 3 | (-v_x + \Psi'_0) \cdots &= \frac{-1}{(kT)^{1/2}} \frac{1}{N} \int dv^N \left[(0 | J^{xy,K} | 0) \right. \\
 &\quad \left. + \sum_{\{k\} \neq 0} (0 | J^{xy,V} | \{k\}) (\{k\} | \mathcal{E} | 0) \right] \cdots \quad (\text{A3.9})
 \end{aligned}$$

where $J^{xy,K}$ is the kinetic part of the stress tensor. On the other hand, the quantity $(-v_x + \Psi'_0) | 3 \rangle$ has been discussed in detail elsewhere by the author⁽²¹⁾; with a slight change in the notation, it was shown that

$$\begin{aligned} (-v_x + \Psi'_0) | 3 \rangle &= \frac{-1}{(kT)^{1/2}} \int dv^{N-1} \Omega^N [(0 | J^{xy} \rho_N^{\text{eq}} | 0) \\ &+ \sum_{\{k\} \neq 0} (0 | \mathcal{D} |\{k\}\rangle \langle \{k\}| J^{xy} \rho_N^{\text{eq}} | 0) \end{aligned} \quad (\text{A3.10})$$

Since the potential part $J^{xy,V}$ has no component $(0 | J^{xy,V} | 0)$, while the kinetic part $J^{xy,K}$ has no component $(0 | J^{xy,K} |\{k\}\rangle)$, we get formally from (A3.9)

$$\begin{aligned} \eta' &= -\frac{1}{\Omega kT} \lim_{\epsilon \rightarrow 0} \int dv^N [(0 | J^{xy} | 0) + \sum_{\{k'\} \neq 0} (0 | J^{xy} |\{k'\}\rangle \langle \{k'\}| \mathcal{E} | 0) \\ &\times \frac{1}{i[(0 | \Psi | 0) + i\epsilon]} [(J^{xy} \rho_N^{\text{eq}})_0 + \sum_{\{k\} \neq 0} (0 | \mathcal{D} |\{k\}\rangle \langle \{k\}| (J^{xy} \rho_N^{\text{eq}})_{\{k\}} \end{aligned} \quad (\text{A3.11})$$

where linearization has *not* been explicitly written, and where

$$(J^{xy} \rho_N^{\text{eq}})_{\{k\}} = \Omega^N (\{k\} | J^{xy} \rho_N^{\text{eq}} | 0) \quad (\text{A3.12})$$

Equation (A3.11) is *identical* to Eq. (3.18) of Ref. 21; there, it was obtained as one of the two contributions coming out of the many-body analysis of the correlation function formula (137); in order to show the complete equivalence, we have established that the second contribution is identical to η'' , as defined by (132b). The calculation proceeds along similar lines but will not be reproduced here.

Similarly, we have given such an equivalence proof for both the thermal conductivity and the sound absorption coefficient Γ . In this latter case, some subtle technical points arise, which are treated in a separate publication.⁽²⁸⁾

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