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Space and Time Dependent Fluctuations in a Continuous Medium

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Abstract. Space and time dependent correlation functions for a continuous medium are discussed, on the basis of Onsager's assumption on the regression of fluctuations. The correlation functions are separated into two parts corresponding to slow hydrodynamic behavior, plus rapid microscopic relaxation. The hydrodynamic parts are then obtained, as functions of the thermodynamic variables and transport coefficients. In contrast to previous treatments based on a suggestion of Landau and Placzek, the method can be readily extended to arbitrary order in the wave number, and in addition provides an alternative derivation of the correlation-function formulas for transport coefficients. The effect of long-range critical point fluctuations on the hydrodynamic behavior, and on the correlation functions, is also treated.

I. Introduction

Space and time dependent correlation functions are of interest both because of their connection with the scattering properties of a continuous medium [1], and because of their basic role in the theory of irreversible processes [2]. The correlation functions (or rather their "hydrodynamic parts") have been determined [3] by a method suggested by LANDAU and PLACZEK [4]: They are assumed to satisfy the hydrodynamic equations, and these equations are then solved subject to initial conditions which are provided by the initial values of the correlation functions; the latter are known from equilibrium statistical mechanics.

The basis for this procedure is Onsager's assumption on the regression of fluctuations [5]. However an additional assumption is involved: As was pointed out by Onsager, the hydrodynamic equations can be satisfied only after an ageing period of the order of the microscopic relaxation times. This ageing period is neglected in the Landau-Placzek procedure. One can argue that the error involved is small, since the hydrodynamic variables do not change by large amounts over such short intervals. Nevertheless it is clearly desirable to avoid the extra assumption, and indeed a closer analysis reveals that it limits the calculation to lowest order in the wavenumber. The difficulty is more acute when the relation between transport coefficients and the correlation functions is at hand, since it is just the microscopic relaxation

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which is responsible for such irreversible processes as thermal conduction and viscosity.

Here we will discuss the correlation functions with an approach which is based on Onsager's assumption, but which explicitly takes into account the ageing period. The method enables one to see clearly how the two phenomena, hydrodynamics and microscopic relaxation, are reflected in the correlation functions. The calculations will be carried through in detail far enough to obtain the Landau-Placzek contribution, but the extension to higher order in wave number is straightforward. In addition, the method provides an alternative derivation of the correlation-function formulas for the transport coefficients [2].

The method is such that the effect of long-range equilibrium (*i.e.*, time-independent) correlations is easily included. Such correlations occur near a critical point, or in a system with Coulomb interactions. The effect of critical point fluctuations on the hydrodynamic behavior, and on the time-dependent fluctuations, is discussed in detail. As will be seen, this effect can be described by wave-number dependent (*i.e.*, non-local) heat capacities and sound speed [6]. (We consider only a one-component fluid, but the extension to critical mixtures is straightforward.)

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II. Single Hydrodynamic Mode

To illustrate the basic points while avoiding algebraic complications, we first consider a system with only a single hydrodynamic mode. Examples are provided by Brownian motion, selfdiffusion in a gas, and thermal conduction in a solid which is sufficiently rigid that sound propagation can be neglected. Considering the latter, let $\varepsilon(\boldsymbol{x})$ denote the energy density, or rather the deviation of the energy density from its equilibrium average value and let $\boldsymbol{s}(\boldsymbol{x})$ denote the energy flux. Consider the correlation functions

$$\begin{aligned} G(\boldsymbol{x}, t) &= \langle \varepsilon(0)\, \varepsilon(\boldsymbol{x}, t) \rangle\,, \\ G_i(\boldsymbol{x}, t) &= \langle \varepsilon(0)\, s_i(\boldsymbol{x}, t) \rangle\,, \\ G_{ij}(\boldsymbol{x}, t) &= \langle s_i(0)\, s_j(\boldsymbol{x}, t) \rangle\,, \end{aligned} \tag{1}$$

where the brackets denote an equilibrium average, and the time dependence is determined by the microscopic equations of motion. We consider an isolated system which is homogeneous and isotropic, so that the correlation functions are invariant to space and time translations and time-reversal, and transform under spatial rotations and reflections of $\boldsymbol{x}$ as a scalar, vector, and second-rank tensor respectively. Conservation of energy leads to the relations

$$\frac{\partial G}{\partial t} + \frac{\partial G_i}{\partial x_i} = 0\,, \qquad \frac{\partial G_i}{\partial t} + \frac{\partial G_{ij}}{dx_j} = 0\,. \tag{2}$$

We will work with transformed correlation functions, defined by

$$\overline{G}(\boldsymbol{k}, z) = \int_0^\infty e^{zt}\, dt \int dv\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\, G(\boldsymbol{x}, t)\,, \tag{3}$$

with similar definitions for $\overline{G}_i(\boldsymbol{k}, z)$ and $\overline{G}_{ij}(\boldsymbol{k}, z)$. The integral (3) can be shown to converge (for real $\boldsymbol{k}$) in the half-plane Re $z < 0$, and there defines an analytic function of z. In the right-half plane, $\overline{G}$, $\overline{G}_i$, and $\overline{G}_{ij}$ are to be obtained by analytic continuation.

The "conservation laws" (2) lead to

$$z\,\overline{G}(\boldsymbol{k}, z) + ik_i\,\overline{G}_i(\boldsymbol{k}, z) = -\,g(\boldsymbol{k})\,,$$
$$z\,\overline{G}_i(\boldsymbol{k}, z) + ik_j\,\overline{G}_{ji}(\boldsymbol{k}, z) = 0\,, \tag{4}$$

where

$$g(\boldsymbol{k}) = \int dv\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\,\langle\varepsilon(0)\,\varepsilon(\boldsymbol{x})\rangle\,. \tag{5}$$

From Eqs. (4) it follows that singularities in $\overline{G}(\boldsymbol{k}, z)$ must also occur in $\overline{G}_i(\boldsymbol{k}, z)$ and $\overline{G}_{ji}(\boldsymbol{k}, z)$. The nature of these singularities has been determined for a monatomic gas described by the Boltzmann equation [7]. For $|\,k\,| \leqslant k_0$, where $1/k_0$ is of the order of the mean-free-path, there is a hydrodynamic pole, whose location we denote by $p(\boldsymbol{k})$. In addition there are singularities corresponding to microscopic relaxation. Accordingly, we write

$$\overline{G}(\boldsymbol{k}, z) = \overline{G}^h(\boldsymbol{k}, z) + \overline{G}^m(\boldsymbol{k}, z) \tag{6}$$

where

$$\overline{G}^h(\boldsymbol{k}, z) = \frac{A(\boldsymbol{k})}{p(\boldsymbol{k}) - z}\,. \tag{7}$$

The functions $A(\boldsymbol{k})$ and $p(\boldsymbol{k})$ are analytic for $|\,k\,| \leqslant k_0$, while $\overline{G}^m(\boldsymbol{k}, z)$ is, depending on the value of z, analytic in k up to values of the order of k_0. For larger values of k, it is unlikely that the separation into hydrodynamic and microscopic singularities can be maintained.

For small values of k, the hydrodynamic pole lies close to the origin. In contrast, the microscopic relaxation is very rapid, and the singularities in $\overline{G}^m(\boldsymbol{k}, z)$ lie well to the right of the imaginary axis. For $t = 0$ both $G^h(\boldsymbol{x}, t)$ and $G^m(\boldsymbol{x}, t)$ contribute to $G(\boldsymbol{x}, t)$, but after an ageing period of the order of the (largest) microscopic relaxation time, only $G^h(\boldsymbol{x}, t)$ is important.

The analytic behavior as described above has been demonstrated for gases [7], but is a reasonable expectation for more general systems. Indeed the occurence of a hydrodynamic pole near the origin, with the remaining singularities lying far to the right, is essentially Onsager's assumption. We will henceforth accept Onsager's assumption, in the form of Eqs. (6) and (7), while recognizing that its proof for general normal systems presents a fundamental problem [8].

As follows from Eqs. (4), $\overline{G}_i(\boldsymbol{k}, z)$ and $\overline{G}_{ji}(\boldsymbol{k}, z)$ can also be separated into hydrodynamic and microscopic parts:

$$\overline{G}_i = \overline{G}_i^h + \overline{G}_i^m\,, \qquad \overline{G}_{ji} = \overline{G}_{ji}^h + \overline{G}_{ji}^m\,. \tag{8}$$

Assuming spherical symmetry, we write

$$\overline{G}_i^h = ik_i\,\frac{B(\boldsymbol{k})}{p(\boldsymbol{k}) - z}\,, \qquad \overline{G}_{ji}^h = k_i k_j\,\frac{C(\boldsymbol{k})}{p(\boldsymbol{k}) - z}\,. \tag{9}$$

We have supposed $\overline{G}^h_{ji}$ to be entirely longitudinal. The presence of a transverse part, proportional to $k_i k_j - \delta_{ij} k^2$, is excluded by the condition imposed earlier that there be only a single hydrodynamic mode; a transverse part would be completely decoupled from the energy fluctuations, and would correspond to a different, independent, mode.

As a consequence of Eqs. (4), the combinations

$$z\,\overline{G}^h + ik_i\,\overline{G}^h_i\,, \quad z\,\overline{G}^h_i + ik_j\,\overline{G}^h_{ji}\,, \tag{10}$$

must be analytic in z, that is, the hydrodynamic pole must drop out. The coefficients $B(\boldsymbol{k})$ and $C(\boldsymbol{k})$ can then be determined in terms of $A(\boldsymbol{k})$, with the result

$$\begin{aligned} \overline{G}^h_i(\boldsymbol{k}, z) &= ik_i\,[p(\boldsymbol{k})/k^2]\,\overline{G}^h(\boldsymbol{k}, z) \\ \overline{G}^h_{ji}(\boldsymbol{k}, z) &= -k_i k_j\,[p(\boldsymbol{k})/k^2]^2\,\overline{G}^h(\boldsymbol{k}, z)\,. \end{aligned} \tag{11}$$

We now determine $p(\boldsymbol{k})$ and $A(\boldsymbol{k})$ by contour integration. Let C denote a contour around the origin, enclosing the pole at $z = p(\boldsymbol{k})$ but none of the microscopic singularities. Then

$$\begin{aligned} -A(\boldsymbol{k}) &= \frac{1}{2\pi i}\int_C dz\,\overline{G}(\boldsymbol{k}, z) \\ &= \frac{1}{2\pi i}\int_C dz\,\frac{1}{z}\,[-g(\boldsymbol{k}) - ik_i\,\overline{G}_i(\boldsymbol{k}, z)] \\ &= -g(\boldsymbol{k}) - ik_i\,\frac{1}{2\pi i}\int_C dz\,\frac{1}{z}\,\overline{G}_i(\boldsymbol{k}, z)\,. \end{aligned} \tag{12}$$

Now

$$\frac{1}{2\pi i}\int_C dz\,\frac{1}{z}\,\frac{1}{p(\boldsymbol{k}) - z} = 0\,, \tag{13}$$

so only the part $\overline{G}^m_i(\boldsymbol{k}, z)$ gives a contribution to the last integral in (12). Since this part is analytic within the contour, the integral is readily evaluated, with the result

$$A(\boldsymbol{k}) = g(\boldsymbol{k}) + ik_i\,\overline{G}^m_i(\boldsymbol{k}, 0)\,. \tag{14}$$

Similarly, we have

$$\begin{aligned} -A(\boldsymbol{k})\,p(\boldsymbol{k}) &= \frac{1}{2\pi i}\int_C dz\,z\,\overline{G}(\boldsymbol{k}, z) \\ &= \frac{1}{2\pi i}\int_C dz\,[-g(\boldsymbol{k}) - ik_i\,\overline{G}_i(\boldsymbol{k}, z)]\,. \end{aligned} \tag{15}$$

The first term gives no contribution, and continuing we obtain

$$A(\boldsymbol{k})\,p(\boldsymbol{k}) = ik_i\,\frac{1}{2\pi i}\int_C dz\,\frac{1}{z}\,[-ik_j\,\overline{G}_{ji}(\boldsymbol{k}, z)] = k_i k_j\,\overline{G}^m_{ji}(\boldsymbol{k}, 0)\,. \tag{16}$$

Combining (14) and (16), we find the general dispersion relation for $p(\boldsymbol{k})$,

$$p(\boldsymbol{k}) = \frac{k_i k_j\,\overline{G}^m_{ij}(\boldsymbol{k}, 0)}{g(\boldsymbol{k}) + ik_i\,\overline{G}^m_i(\boldsymbol{k}, 0)}\,. \tag{17}$$

To lowest order in k,

$$A(\boldsymbol{k}) = g(0) \,. \tag{18}$$

This is the mean-square fluctuation in energy, or

$$g(0) = T^2 C \tag{19}$$

where C is the specific heat per unit volume, and T the Kelvin temperature. (We use units for temperature such that Boltzmann's constant is equal to 1.) The lowest order approximation for $p(\boldsymbol{k})$ is

$$p(\boldsymbol{k}) = \frac{1}{3} k^2 \frac{\overline{G}^m_{ii}(0,0)}{g(0)} \tag{20}$$

The coefficient of k^2 is the thermal diffusivity

$$D = \lambda / C \,, \tag{21}$$

which identifies the thermal conductivity λ as

$$\lambda = \frac{1}{3T^2} \overline{G}^m_{ii}(0, 0) \,. \tag{22}$$

The correlation function $G(\boldsymbol{k}, z)$ in this approximation is

$$\overline{G}(\boldsymbol{k}, z) = \frac{T^2 C}{Dk^2 - z} + \overline{G}^m(\boldsymbol{k}, z) \,. \tag{23}$$

In scattering experiments with small energy and momentum transfer, the scattering is dominated by the hydrodynamic part. For this part, the result (23) is in agreement with that obtained from the Landau-Placzek procedure. (Actually it is the fluctuations in density, rather than energy, which are important for scattering.)

To show that the result (22) agrees with the usual correlation-function expression for the thermal conductivity [2], note that from Eq. (11)

$$\lim_{\boldsymbol{k} \to 0} \overline{G}^h_{ii}(\boldsymbol{k}, z) = 0 \,. \tag{24}$$

Hence we may write in place of (22)

$$\lambda = \frac{1}{3T^2} \lim_{z \to 0} \lim_{\boldsymbol{k} \to 0} \overline{G}_{ii}(\boldsymbol{k}, z) \,, \tag{25}$$

which is the usual formula. The order of the limits is immaterial for $\overline{G}^m_{ii}(\boldsymbol{k}, z)$, which is analytic at $\boldsymbol{k} = 0$, $z = 0$. However the hydrodynamic part has a more complicated limiting behaviour, and it is essential that the limits be taken in the order given in (25).

The above procedure can be readily extended to higher orders in $\boldsymbol{k}$. Except near a critical point, the equilibrium correlations described by $g(\boldsymbol{k})$ extend only over distances of the order of the force range, and $g(\boldsymbol{k})$ can be safely replaced by $g(0)$ up to the highest wavenumbers for which the separation into hydrodynamics and microscopic relaxation occurs. The significant corrections come from expanding $\overline{G}^m_i(\boldsymbol{k}, 0)$ and $\overline{G}^m_{ji}(\boldsymbol{k}, 0)$ in powers of $\boldsymbol{k}$. The validity of the lowest order equation (20) (or, more

generally, of the Navier-Stokes equations) even for quite large wavenumbers shows that $\overline{G}_i^m(\boldsymbol{k}, 0)$ and $\overline{G}_{ji}^m(\boldsymbol{k}, 0)$ are only weakly dependent on $\boldsymbol{k}$.

Near the critical point $g(\boldsymbol{k})$ obtains a strong k-dependence. However there is no reason to expect a similar behavior for $\overline{G}_i^m(\boldsymbol{k}, 0)$ and $\overline{G}_{ji}^m(\boldsymbol{k}, 0)$; to the contrary these are still presumably analytic for those values of $\boldsymbol{k}$ pertinent to hydrodynamics. It is then consistent to replace Eq. (20) by

$$p(\boldsymbol{k}) = \frac{\lambda\, T^2}{g(\boldsymbol{k})}\, k^2 \tag{26}$$

with λ still given by Eq. (22). In the same approximation,

$$\overline{G}(\boldsymbol{k}, z) = \frac{g(\boldsymbol{k})}{p(\boldsymbol{k}) - z}\,. \tag{27}$$

Thus the equilibrium critical-point fluctuations have an effect on the hydrodynamic equation (26), as well as on the dynamic fluctuations (27). This effect can be described by a $\boldsymbol{k}$-dependent (or non-local) specific heat,

$$C(\boldsymbol{k}) = g(\boldsymbol{k})/T^2\,.$$

The effect of critical-point fluctuations will be discussed more fully in Section IV.

III. General One-component Fluid

In this Section we give a treatment which is basically the same as that given above, but which includes the additional hydrodynamic modes corresponding to sound propagation and shear flow. Diffusion in a multi-component fluid will not be considered, but the generalization to this case is straightforward.

For a one-component fluid there are five conserved quantities, the mass density ϱ, energy density ε, and momentum density $\boldsymbol{p}$. (Again, ϱ and ε will actually be used to denote the deviations of the mass and energy densities from their equilibrium values.) The flux of mass is equal to the momentum density, and the flux of momentum is the stress tensor t_{ij}.

It is convenient to introduce certain linear combinations of ϱ, ε, and $\boldsymbol{p}$. Denoting these by ψ_α, $\alpha = 1, \ldots, 5$, we will require that the ψ_α be orthonormal in the sense that

$$\int dv\, \langle \psi_\alpha(0)\, \psi_\beta(x) \rangle = \delta_{\alpha\beta}\,. \tag{28}$$

To construct the ψ_α one needs certain correlations whose values are known from equilibrium statistical mechanics; these are

$$\begin{aligned}
&\int dv\, \langle \varrho(0)\, \varrho(\boldsymbol{x}) \rangle = (\partial\overline{\varrho}/\partial\nu)_\beta \\
&\int dv\, \langle \varrho(0)\, \varepsilon(\boldsymbol{x}) \rangle = (\partial\overline{\varepsilon}/\partial\nu)_\beta = -(\partial\overline{\varrho}/\partial\beta)\nu \\
&\int dv\, \langle \varepsilon(0)\, \varepsilon(\boldsymbol{x}) \rangle = -(\partial\overline{\varepsilon}/\partial\beta)\nu \\
&\int dv\, \langle p_i(0)\, p_j(\boldsymbol{x}) \rangle = \delta_{ij}\, \overline{\varrho}\, T
\end{aligned} \tag{29}$$

Here $\bar{\varrho}$ and $\bar{\varepsilon}$ denote the equilibrium averages of the mass density and energy density, $\beta = 1/T$, and $\nu = \beta\mu$ where μ is the chemical potential per unit mass. It can then be verified, after some manipulation involving thermodynamic identities, that the set

$$\psi_1 = \frac{1}{\sqrt{TK_T}} \frac{\varrho}{\bar{\varrho}} ,$$
$$\psi_2 = \frac{1}{T\sqrt{C_V}} [\varepsilon - (\partial\bar{\varepsilon}/\partial\bar{\varrho})_\beta \varrho]$$
$$\psi_3 = \frac{p_x}{\sqrt{\bar{\varrho}T}} , \quad \psi_4 = \frac{p_y}{\sqrt{\bar{\varrho}T}} , \quad \psi_5 = \frac{p_z}{\sqrt{\bar{\varrho}T}}$$

satisfies Eqs. (28). Here K_T is the isothermal compressibility and C_V the specific heat at constant volume.

Associated with the ψ_α are fluxes φ^i_α, satisfying the conservation laws

$$\frac{\partial\psi_\alpha}{\partial t} + \frac{\partial}{\partial x_i} \varphi^i_\alpha = 0 . \tag{31}$$

They are given by

$$\varphi^i_1 = \frac{1}{\varrho\sqrt{T K_T}} p_i ,$$
$$\varphi^i_2 = \frac{1}{T\sqrt{C_V}} [s_i - (\partial\bar{\varepsilon}/\partial\bar{\varrho})_\beta p_i] ,$$
$$\varphi^i_3 = \frac{1}{\sqrt{\bar{\varrho}T}} t_{xi} , \quad \varphi^i_4 = \frac{1}{\sqrt{\bar{\varrho}T}} t_{yi} , \quad \varphi^i_5 = \frac{1}{\sqrt{\bar{\varrho}T}} t_{zi} . \tag{32}$$

It is convenient to introduce a compact notation for the transformed correlation functions. For any phase functions A, B, define $(A, B; \boldsymbol{k}, z)$ by

$$(A, B; \boldsymbol{k}, z) = \int_0^\infty dt\, e^{zt} \int dv\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \langle A(0)\, B(\boldsymbol{x}, t)\rangle . \tag{33}$$

We will sometimes suppress the dependence on $\boldsymbol{k}$, z and write simply (A, B).

The conservation laws (31) lead to relations similar to (4),

$$z(\psi_\alpha, \psi_\beta) + ik_i(\psi_\alpha, \varphi^i_\beta) = -g_{\alpha\beta}(k) ,$$
$$z(\psi_\alpha, \varphi^j_\beta) + ik_i(\varphi^i_\alpha, \varphi^j_\beta) = -h^j_{\alpha\beta}(k) , \tag{34}$$

where

$$g_{\alpha\beta}(\boldsymbol{k}) = \int dv\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \langle\psi_\alpha(0)\, \psi_\beta(\boldsymbol{x})\rangle ,$$
$$h^j_{\alpha\beta}(\boldsymbol{k}) = \int dv\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \langle\psi_\alpha(0)\, \varphi^j_\beta(\boldsymbol{x})\rangle . \tag{35}$$

It follows from invariance to space and time reflections that $(\psi_\alpha, \psi_\beta)$ is symmetric

$$(\psi_\alpha, \psi_\beta) = (\psi_\beta, \psi_\alpha) \tag{36}$$

and in addition

$$(\varphi^i_\alpha, \varphi^j_\beta) = (\varphi^j_\beta, \varphi^i_\alpha) ,$$
$$k_i(\psi_\alpha, \varphi^i_\beta) = k_i(\psi_\beta, \varphi^i_\alpha) ,$$
$$k_j\, h^j_{\alpha\beta}(\boldsymbol{k}) = k_j\, h^j_{\beta\alpha}(\boldsymbol{k}) . \tag{37}$$

To formulate Onsager's assumption, we introduce hydrodynamic normal modes χ_μ which are certain linear combinations of the ψ_α:

$$\chi_\mu = \sum_\alpha S^{-1}_{\alpha\mu}\, \psi_\alpha \tag{38}$$

The coefficients $S^{-1}_{\alpha\mu}$, and the χ_μ, are $\boldsymbol{k}$-dependent. Corresponding to the five conserved quantities there are five hydrodynamic poles at $p_\mu(\boldsymbol{k})$. (Actually only four are distinct, since the two transverse modes have a degenerate eigenvalue.) The normal modes are defined to have only a single hydrodynamic pole, so that

$$(\chi_\mu, \chi_\nu) = \frac{\delta_{\mu\nu}}{p_\mu - z} + (\chi_\mu, \chi_\nu)^m\,. \tag{39}$$

In terms of the original ψ_α, this is

$$(\psi_\alpha, \psi_\beta) = \sum_\alpha \frac{S_{\mu\alpha}\, S_{\mu\beta}}{p_\mu - z} + (\psi_\alpha, \psi_\beta)^m\,. \tag{40}$$

The singularities of the microscopic parts will again be assumed to lie well to the right of the imaginary axis.

We must now determine the p_μ and the coefficients $S_{\mu\alpha}$. Proceeding as before

$$\begin{aligned} -\sum_\mu S_{\mu\alpha}\, S_{\mu\beta} &= \frac{1}{2\pi i}\int_C dz\, (\psi_\alpha, \psi_\beta) \\ &= \frac{1}{2\pi i}\int_C dz\, \frac{1}{z}\, [-\, g_{\alpha\beta} - ik_i(\psi_\alpha, \varphi^i_\beta) \\ &= -\, g_{\alpha\beta} - ik_i\, (\psi_\alpha, \varphi^i_\beta;\, \boldsymbol{k}, 0)^m\,; \end{aligned} \tag{41}$$

the contour C includes all poles p_μ as well as the origin. Equation (41) is conveniently written in matrix form as

$$S^T\, S = X \tag{42}$$

where S^T is the transpose of S, and X denotes the matrix

$$X_{\alpha\beta}(\boldsymbol{k}) = g_{\alpha\beta}(\boldsymbol{k}) + ik_i\, (\psi_\alpha, \varphi^i_\beta;\, \boldsymbol{k}, 0)^m\,. \tag{43}$$

In addition we find

$$\begin{aligned} -\sum_\mu S_{\mu\alpha}\, p_\mu\, S_{\mu\beta} &= \frac{1}{2\pi i}\int_C dz\, z(\psi_\alpha, \psi_\beta) \\ &= \frac{1}{2\pi i}\int_C dz\, [-\, ik_j\, (\psi_\alpha, \psi^j_\beta)] \\ &= -\, ik_j\, \frac{1}{2\pi i}\int_C dz\, \frac{1}{z}\, [-\, h^j_{\alpha\beta} - ik_i\, (\varphi^i_\alpha, \varphi^j_\beta)] \\ &= ik_j\, h^j_{\alpha\beta} - k_i k_j\, (\varphi^i_\alpha, \varphi^j_\beta;\, \boldsymbol{k}, 0)^m \end{aligned} \tag{44}$$

This can be written

$$S^T\, P\, S = Y \tag{45}$$

where P is a diagonal matrix with elements p_μ, and

$$Y_{\alpha\beta}(\boldsymbol{k}) = -ik_j\, h^j_{\alpha\beta}(\boldsymbol{k}) + k_i k_j\, (\varphi^i_\alpha, \varphi^j_\beta; \boldsymbol{k}, 0)^m \tag{46}$$

Multiplying Eq. (45) by X^{-1} and using Eq. (42), we find

$$X^{-1}Y = S^{-1}\, P\, S \tag{47}$$

or

$$P = S\, X^{-1}\, Y\, S^{-1}\,. \tag{48}$$

This shows that the p_μ are the eigenvalues of the matrix $X^{-1}Y$, and S is a matrix which diagonalizes it. In addition S must satisfy Eq. (42) or (45); that such an S exists is shown in the Appendix.

It is now necessary to evaluate the matrices X and Y. To save labor, we remark that $(\psi_\alpha, \varphi^i_\beta; \boldsymbol{k}, 0)^m$ is at least of order k, and its retention in Eq. (43) would lead to contributions of a higher order than will be considered here. Neglecting it, we have simply

$$X_{\alpha\beta} = g_{\alpha\beta}(\boldsymbol{k})\,. \tag{49}$$

Except near the critical point, the equilibrium correlations described by $g_{\alpha\beta}(\boldsymbol{k})$ extend only over distances of the order of the force range, and $g_{\alpha\beta}(\boldsymbol{k})$ can be replaced by its value for $\boldsymbol{k} = 0$. This, because of the orthonormality (28), is simply $\delta_{\alpha\beta}$, and hence

$$X_{\alpha\beta} = \delta_{\alpha\beta} \tag{50}$$

Consider next the matrix Y. Most of the elements of $h^i_{\alpha\beta}$ vanish from time-reversal invariance or spherical symmetry; in addition one may again put $\boldsymbol{k} = 0$ because of the short-range of the equilibrium fluctuations. For convenience we take $\boldsymbol{k}$ to point in the x-direction; the non-vanishing elements of $h^x_{\alpha\beta}$ are $h^x_{31} = h^x_{13}$ and $h^x_{23} = h^x_{32}$. We have explicitly

$$\begin{aligned} h^x_{13} &= \int dv\, \langle \psi_1(0)\, \varphi^x_3(\boldsymbol{x}) \rangle \\ &= \frac{1}{\bar{\varrho} T \sqrt{\bar{\varrho} K_T}} \int dv\, \langle \varrho(0)\, t_{xx}(\boldsymbol{x}) \rangle \\ &= \frac{1}{\bar{\varrho} T \sqrt{\bar{\varrho} K_T}} \left(\frac{\partial P}{\partial v}\right)_\beta \end{aligned} \tag{51}$$

where P is the equilibrium pressure. A thermodynamic identity enables one to reduce this to

$$h^x_{13} = \frac{1}{\sqrt{\bar{\varrho} K_T}}\,. \tag{52}$$

In addition,

$$\begin{aligned} h^x_{23} &= \int dv\, \langle \psi_2(0)\, \varphi^x_3(\boldsymbol{x}) \rangle \\ &= \frac{1}{T\sqrt{\bar{\varrho}\, TC_V}} \int dv\, \left\langle \left[\varepsilon(0) - \left(\frac{\partial \bar{\varepsilon}}{\partial \bar{\varrho}}\right)_\beta \varrho(0)\right] t_{xx}(\boldsymbol{x}) \right\rangle \\ &= \frac{1}{T\sqrt{\bar{\varrho}\, TC_V}} \left[-\left(\frac{\partial P}{\partial \beta}\right)_v - \left(\frac{\delta \bar{\varepsilon}}{\partial \bar{\varrho}}\right)_\beta \left(\frac{\partial P}{\partial v}\right)_\beta \right] \\ &= -\frac{1}{T\sqrt{\bar{\varrho}\, TC_V}} \left(\frac{\partial P}{\partial \beta}\right)_{\bar{\varrho}}\,. \end{aligned} \tag{53}$$

Use of a standard formula for the difference $C_P - C_V$ of the specific heats at constant pressure and volume yields

$$h^x_{23} = \sqrt{\frac{\gamma - 1}{\bar{\varrho}\, K_T}} \tag{54}$$

where

$$\gamma = C_P / C_V \tag{55}$$

In the remaining contribution to Y we consider only the lowest order, replacing $(\varphi^i_\alpha, \varphi^j_\beta; \boldsymbol{k}, 0)^m$ by $(\varphi^i_\alpha, \varphi^j_\beta; 0, 0)^m$. Many of the latter vanish from spherical symmetry. In addition those for $\alpha = 1$ or $\beta = 1$ vanish since $\boldsymbol{p}$ is a conserved quantity as well as a flux: for $k = 0$ the Fourier transform converts the momentum density to the total momentum which is time-independent, and the correlations contain only the "hydrodynamic pole" at $z = 0$. The only non-vanishing elements are then those with $\alpha = \beta = 2$, $\alpha = \beta = 3$, $\alpha = \beta = 4$, and $\alpha = \beta = 5$. To save writing we anticipate the connection between the correlation functions and the transport coefficients; they are in fact

$$\begin{aligned}
&(s_x, s_x; 0, 0)^m = \lambda\, T^2\,, \\
&(t_{xx}, t_{xx}; 0, 0)^m = \bar{\eta}\, T, \bar{\eta} = \left(\frac{4}{3}\,\eta + \eta'\right), \\
&(t_{yx}, t_{yx}; 0, 0)^m = (t_{zx}, t_{zx}; 0, 0)^m = \eta\, T,
\end{aligned} \tag{56}$$

where η and η' are the shear and bulk viscosities, and λ the thermal conductivity. The non-vanishing elements of $\varphi^x_\alpha, \varphi^x_\beta; 0, 0)^m$ are then

$$\begin{aligned}
&(\varphi^x_2, \varphi^x_2; 0, 0)^m = \lambda / C_V \\
&(\varphi^x_3, \varphi^x_3; 0, 0)^m = \bar{\eta}/\bar{\varrho} \\
&(\varphi^x_4, \varphi^x_4; 0, 0)^m = (\varphi^x_5, \varphi^x_5; 0, 0)^m = \eta/\bar{\varrho}
\end{aligned} \tag{57}$$

To summarize, we display the matrix Y, to the approximation considered,

$$Y = -ik\,\frac{1}{\sqrt{\bar{\varrho}\, K_T}} \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & \sqrt{\gamma-1} & 0 & 0 \\ 1 & \sqrt{\gamma-1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} + k^2 \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & \lambda/C_V & 0 & 0 & 0 \\ 0 & 0 & \bar{\eta}/\bar{\varrho} & 0 & 0 \\ 0 & 0 & 0 & \eta/\bar{\varrho} & 0 \\ 0 & 0 & 0 & 0 & \eta/\varrho \end{pmatrix} \tag{58}$$

It now remains to determine the eigenvalues p_μ, and the matrix S. Since X has been reduced to the unit matrix, the p_μ are the eigenvalues of Y. A straightforward calculation gives, to order k^2,

$$\begin{aligned}
&p_1 = D\, k^2\,, \\
&p_2 = ikc + \Gamma k^2\,, \\
&p_3 = -\,ikc + \Gamma k^2\,, \\
&p_4 = p_5 = \eta\, k^2/\bar{\varrho}
\end{aligned} \tag{59}$$

Here c is the sound speed, D the thermal diffusivity,

$$D = \lambda / C_P \,, \tag{60}$$

and Γ the damping constant

$$\Gamma = \frac{\bar{\eta}}{2\,\bar{\varrho}} + \frac{(\gamma-1)\lambda}{2\,C_P} \,. \tag{61}$$

The results (59) agree with those obtained from the Navier-Stokes equations, justifying the identification (56) of the transport coefficients λ, η, and η'.

The matrix S is to be determined from Eqs. (42) and (48), with $X = 1$. We give the result for S to lowest order; it is obtained as the orthogonal matrix which diagonalizes the leading contribution to Y as given in (58). One finds

$$S = \begin{pmatrix} \sqrt{\frac{\gamma-1}{\gamma}} & -\frac{1}{\sqrt{\gamma}} & 0 & 0 & 0 \\ \frac{1}{\sqrt{2\gamma}} & \sqrt{\frac{\gamma-1}{2\gamma}} & -\frac{1}{\sqrt{2}} & 0 & 0 \\ \frac{1}{\sqrt{2\gamma}} & \sqrt{\frac{\gamma-1}{2\gamma}} & \frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \tag{62}$$

(Actually the diagonalization of Y is not sufficient to determine S uniquely, because of the degeneracy $p_4 = p_5$. However it follows from spherical symmetry that $(\psi_4, \psi_\beta) = 0$, $\beta \neq 4$, and $(\psi_5, \psi_\beta) = 0$, $\beta \neq 5$. As a consequence there are the additional conditions on S that $S_{4\beta} = 0$, $\beta \neq 4$ and $S_{5\beta} = 0$, $\beta \neq 5$.)

Having S, it is now possible to obtain the hydrodynamic parts of the correlation functions. Considering in particular the density-density correlation, we find for its hydrodynamic part

$$(\varrho, \varrho)^h = T\,K_T\,\bar{\varrho}^2\,(\psi_1, \psi_1)^h = T\,K_T\,\bar{\varrho}^2 \sum_{\mu} \frac{S_{\mu 1}\,S_{\mu 1}}{p_\mu - z} \,. \tag{63}$$

Introducing the elements of S, one obtains

$$(\varrho, \varrho)^h = \bar{\varrho}^2 T\,K_T\,\frac{1}{\gamma}\left\{\frac{\gamma-1}{p_1 - z} + \frac{1}{2}\left[\frac{1}{p_2 - z} + \frac{1}{p_3 - z}\right]\right\} . \tag{64}$$

The result (64) is in agreement with that obtained by the method of LANDAU and PLACZEK [3]. Our argument therefore provides a justification of this method, to lowest order in $\boldsymbol{k}$. On the other hand, if it is desired to continue to higher order, it is necessary to follow the procedure given here, since there are then contributions from the microscopic parts which are not obtained of the ageing period is ignored.

We remark, without a detailed demonstration, that the results (56) are equivalent to the usual [2] correlation-function formulas.

IV. Behavior Near a Critical Point

In this Section we will consider how the results of the previous Section must be modified when long-range critical point fluctuations are present. As already mentioned

in Section II, there is presumably no strong effect on the microscopic parts, that is, on the transport coefficients. (This is not to say that the transport coefficients do not change rapidly near the critical point; indeed one expects significant variations near any phase change. The point is that they do not have a strong $\boldsymbol{k}$-dependence.) On the other hand, the $\boldsymbol{k}$-dependence of the equilibrium correlations $g_{\alpha\beta}(\boldsymbol{k})$ cannot be neglected.

The analysis proceeds as far as Eq. (48) unchanged. In addition it is found that $h^j_{\alpha\beta}$ does not have a long-range character; h^x_{31} and h^x_{32} describe correlations with the momentum density and these involve only single-particle correlations, which are short-ranged.

Thus the long-range correlations manifest themselves only in $g_{\alpha\beta}(\boldsymbol{k})$. We again neglect the contribution $(\psi, \varphi^i_\beta; \boldsymbol{k}, 0)^m$ to X, and so have

$$X_{\alpha\beta}(\boldsymbol{k}) = g_{\alpha\beta}(\boldsymbol{k}) \tag{65}$$

in place of Eq. (50). From Eqs. (30) one finds for the $g_{\alpha\beta}(\boldsymbol{k})$,

$$\begin{aligned}
g_{11}(\boldsymbol{k}) &= \frac{1}{T\,K_T\,\bar{\varrho}^2} \int dv\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \langle \varrho(0)\, \varrho(\boldsymbol{x}) \rangle \\
g_{12}(\boldsymbol{k}) &= \frac{1}{T\bar{\varrho}\sqrt{T\,K_T\,C_V}} \int dv\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \langle \varrho(0) \left[\varepsilon(\boldsymbol{x}) - \left(\frac{\partial\bar{\varepsilon}}{\partial\bar{\varrho}}\right)_\beta \varrho(\boldsymbol{x})\right] \rangle \\
g_{22}(\boldsymbol{k}) &= \frac{1}{C_V\,T^2} \int dv\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \langle \left[\varepsilon(0) - \left(\frac{\partial\bar{\varepsilon}}{\partial\bar{\varrho}}\right)_\beta \varrho(0)\right] \left[\varepsilon(\boldsymbol{x}) - \left(\frac{\partial\bar{\varepsilon}}{\partial\bar{\varrho}}\right)_\beta \varrho(\boldsymbol{x})\right] \rangle
\end{aligned} \tag{66}$$

The correlation $g_{11}(\boldsymbol{k})$ can be related to the pair-distribution function, but $g_{12}(\boldsymbol{k})$ and $g_{22}(\boldsymbol{k})$ depend on higher-order distribution functions. One finds that g_{33}, g_{44}, and g_{55} do not contain longrange correlations, for the same reason as applied to $h^j_{\alpha\beta}$. These are therefore again

$$g_{33} = g_{44} = g_{55} = 1\,. \tag{67}$$

It is now a straightforward matter to obtain the eigenvalues of $X^{-1}\,Y$. One finds that

$$p_4 = p_5 = \eta\, k^2/\bar{\varrho} \tag{68}$$

as before. Thus the critical point fluctuations have no effect on the nature of pure shear flow. (However, as already commented, the value of the viscosity may change rapidly near the critical point.) The remaining eigenvalues are determined by a cubic scalar equation. Depending on the values of the parameters, it might be necessary to obtain a numerical solution. More simply, one can expand in powers of $\boldsymbol{k}$, ignoring the $\boldsymbol{k}$-dependence of the $g_{\alpha\beta}(\boldsymbol{k})$. The results then have the form of Eq. (59), but with a $\boldsymbol{k}$-dependent diffusivity, sound speed, and damping constant. It is convenient to express the results in terms of the three functions

$$\begin{aligned}
\Delta(k) &= g_{11}(k)\, g_{22}(k) - [g_{12}(k)]^2\,, \\
\alpha(k) &= \frac{\sqrt{\gamma-1}\, g_{11}(k) - g_{12}(k)}{\sqrt{(\gamma-1)\,\Delta(k)}} \\
\beta(k) &= \frac{g_{22}(k) - \sqrt{\gamma-1}\, g_{12}(k)}{\sqrt{\Delta(k)}}\,.
\end{aligned} \tag{69}$$

We note that α, β, and Δ all approach unity for $k \to 0$. The eigenvalues are found to be

$$\begin{aligned} p_1 &= \lambda k^2/C_P(k) \,, \\ p_2 &= i\, c(k)k + \Gamma(k)k^2 \,, \\ p_3 &= -\, i\, c(k)k + \Gamma(k)k^2 \,, \end{aligned} \tag{70}$$

where the k-dependent specific heat is

$$C_P(k) = C_{P_0} \sqrt{\Delta(k)}\, \frac{1}{\gamma}\, [(\gamma - 1)\, \alpha(k) + \beta(k)] \,, \tag{71}$$

C_{P_0} being its value for $k = 0$. The sound speed $c(k)$ is given by

$$\left[\frac{c(k)}{c_0}\right]^2 = \frac{C_P(k)}{C_{P_0}\, \Delta(k)} \,, \tag{72}$$

with c_0 its value for $k = 0$, and $\Gamma(k)$ is

$$\Gamma(k) = \frac{1}{2}\, \frac{\bar{\eta}}{\bar{\varrho}} + \frac{1}{2}\, \frac{\lambda}{C_{P_0}}\, (\gamma - 1)\, \frac{\gamma\, \alpha^2(k)}{(\gamma - 1)\, \alpha(k) + \beta(k)} \,. \tag{73}$$

Since the transverse modes are completely decoupled, it is only necessary to give the matrix $S_{\mu\alpha}$ for $\mu, \alpha = 1, 2, 3$. The result, which may be verified by explicit calculation to satisfy Eqs. (42) and (45), is

$$S = \frac{c_0}{c(k)} \begin{pmatrix} \sqrt{\dfrac{\gamma-1}{\gamma}}\, \alpha(k) & -\dfrac{1}{\sqrt{\gamma}}\, \beta(k) & 0 \\ \dfrac{1}{\sqrt{2\gamma}} & \sqrt{\dfrac{\gamma-1}{2\gamma}} & -\dfrac{1}{\sqrt{2}}\, \dfrac{c(k)}{c_0} \\ \dfrac{1}{\sqrt{2\gamma}} & \sqrt{\dfrac{\gamma-1}{2\gamma}} & \dfrac{1}{\sqrt{2}}\, \dfrac{c(k)}{c_0} \end{pmatrix} . \tag{74}$$

It is then a straightforward matter to obtain the hydrodynamic contribution to the density-density correlation function. In place of Eq. (64), we now find

$$\begin{aligned} (\varrho, \varrho)^h = \bar{\varrho}^2 T\, K_T \Bigg\{ \left[g_{11}(k) - \frac{C_{P_0}}{C_P(k)}\, \frac{\Delta(k)}{\gamma} \right] \frac{1}{p_1 - z} \\ + \frac{1}{2}\, \frac{C_{P_0}}{C_P(k)}\, \frac{\Delta(k)}{\gamma} \left[\frac{1}{p_2 - z} + \frac{1}{p_3 - z} \right] \Bigg\} \,. \end{aligned} \tag{75}$$

The above results can be simplified if the relative magnitudes of the various parameters are recognized. Since g_{12} vanishes for $k = 0$, it is reasonable to neglect it for small k. In addition, γ becomes large as one approaches the critical point, and only the leading terms in $1/\gamma$ need be retained. These two approximations give, in place of Eqs. (11), (12), (13), and (15),

$$\begin{gathered} C_P(k) = C_{P_0}\, g_{11}(k) \,, \\ \left[\frac{c(k)}{c_0}\right]^2 = \frac{1}{g_{22}(k)} \,, \qquad \Gamma(k) = \frac{1}{2}\, \frac{\bar{\eta}}{\bar{\varrho}} + \frac{1}{2}\, \frac{\lambda}{C_{V_0}} \sqrt{\frac{g_{11}(k)}{g_{22}(k)}} \,, \end{gathered} \tag{76}$$

and, introducing the adiabatic compressibility K_S,

$$(\varrho, \varrho)^h = \bar{\varrho}^2\, T \left\{ K_T\, g_{11}(k)\, \frac{1}{p_1 - z} + K_S\, g_{22}(k)\, \frac{1}{2} \left[\frac{1}{p_2 - z} + \frac{1}{p_3 - z} \right] \right\} . \tag{77}$$

Appendix

It is necessary to show the existence of a matrix satisfying two of the conditions (42), (45), or (48); the third then follows automatically.

First put $\boldsymbol{k}' = i\boldsymbol{k}$ and assume $\boldsymbol{k}'$ to be real; the case of real $\boldsymbol{k}$ can be obtained by analytic continuation. The matrices X and Y are symmetric, and for real $\boldsymbol{k}'$ are also real. In addition, X is non-negative (*i.e.*, its eigenvalues are non-negative) for sufficiently small $\boldsymbol{k}$; this is evident from the fact that the leading term $g_{\alpha\beta}(\boldsymbol{k})$ forms a non-negative matrix. Such a matrix has a unique real, symmetric, non-negative, square root, R:

$$X = R^2, \quad R^T = R\,. \tag{A1}$$

The matrix

$$Y' = R^{-1}\, Y R^{-1} \tag{A2}$$

is real and symmetric, and can therefore be brought into diagonal form by an orthogonal matrix Q:

$$Q\, Y'\, Q^{-1} = \text{diagonal}\,, \tag{A3}$$

$$Q^T = Q^{-1}, \quad Q \text{ real}\,.$$

Furthermore Q is unique except for labeling of rows and columns, and except for the degeneracy associated with the transverse modes. It is readily verified that

$$S = Q\, R \tag{A4}$$

satisfies the necessary conditions.

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