

Fluctuations about simple nonequilibrium steady states

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The Langevin formalism that describes fluctuations about thermodynamic equilibrium is extended to study hydrodynamic nonequilibrium steady states. The limitations of our generalization are discussed as well as the connection between experimental and theoretical quantities which is more subtle than in equilibrium. The spectrum for Brillouin scattering from a fluid in a shear flow or temperature gradient is simply obtained by Langevin methods. The latter problem exhibits an asymmetry in the height of the peaks inversely proportional to the square of the scattering wave vector. We also construct a microscopic ensemble that is applicable to a variety of hydrodynamic nonequilibrium steady states, and then verify for a particular model that our extension of the Langevin method agrees with a fully microscopic calculation.

I. INTRODUCTION

Statistical mechanics provides a way to understand the properties of matter on a macroscopic scale from a knowledge of the microscopics. One forgoes a detailed description that is not experimentally accessible in favor of certain conserved quantities (energy, density, etc.), their conjugate forces, and other derived thermodynamic potentials. This coarsened description is accomplished by the assumption that all microstates with prescribed values of energy, number of particles, etc., are *a priori* equally probable. The entropy measures the number of such states subject to the given constraints.

By examining a macroscopic but fractionally small subvolume of the original system one can develop from the microcanonical ensemble other ensembles that are appropriate for various physical situations. From these ensembles, the probability of thermodynamic fluctuations can be calculated and their measurement then provides a nontrivial test of the ensemble and the assumption of equal *a priori* probabilities. The power of statistical mechanics derives in part from the separation of statics and dynamics. The "statics" (time-independent properties) can all be determined from the ensemble.

Thermodynamic fluctuation theory has been generalized in the direction of time-dependent correlation functions and linear response. There we consider infinitesimal perturbations about a state in thermodynamic equilibrium. The fluctuations occur spontaneously with a magnitude set by $k_B T$. The fluctuation-dissipation theorem provides a connection between the spectrum of spontaneous fluctuations in thermal equilibrium and the response to an infinitesimal perturbation. The canonical ensemble is essential to understanding this equivalence. If we restrict ourselves to small frequencies and wave numbers we can equivalently

use the Langevin formalism which realizes the microscopic fluctuations as a fluctuating force coupled to the macroscopic variables.

Even though the above methods allow us to compute certain average quantities such as fluxes (hence transport coefficients) in nonequilibrium situations, they do not tell us the ensemble (and hence the fluctuations) in nonequilibrium states (even if they are steady states). The problem is that in a general nonequilibrium situation one can imagine external forces that keep the system in a state that would be very improbable in equilibrium. The postulate of equal *a priori* probabilities is violated. The notion of an ensemble is also much more tenuous since in general one cannot divorce statics and dynamics. There is in general no analog of the entropy which is independent of the dynamics and gives the probability of equal-time fluctuations.

In a large category of nonequilibrium problems, the external forces are applied only over a large scale. Here hydrodynamics or Ginzburg-Landau theory can frequently be used effectively. Hydrodynamics is restricted to small frequencies and wave numbers but is fully nonlinear. Considerable simplifications are realized because only the dynamics of a few macroscopic fields enter the problem rather than the complete microscopic equations.

In this paper we will consider several systems held away from equilibrium by a static macroscopic "force" such as an external temperature gradient or shear. The stationary profiles of the macroscopic variables are found from hydrodynamics. The nontrivial problem we will address is the calculation of the spectrum of spontaneous fluctuations about these nonequilibrium steady states. We do not know from general arguments the ensemble appropriate to such a stationary state and even equal-time fluctuations require the solution of a time-dependent problem. (As a

consequence, we should not be surprised if transport coefficients appear in the final answer.)

Our approach is to generalize in a physically plausible way the Langevin formalism (usually called the Landau-Lifshitz method in the context of fluids). We assume that the microscopic variables remain uncorrelated over macroscopic lengths and times and that their statistics are completely determined by the local values of the hydrodynamic variables. We have checked for a simple model problem that our generalized Langevin method agrees with a plausible ensemble. This ensemble and the correlation functions we calculate depend greatly on the experiments we intend to describe.

In Sec. II we use a simple example to recall the equilibrium Langevin formalism and indicate how it can be generalized to treat the case of a simple nonequilibrium steady state. This system is treated microscopically in Appendices B and C to lend further support to our formalism. Section III summarizes in a more general and formal way the results of Sec. II. In particular, we establish formal connections to the conventional equilibrium expressions: Einstein relation, Onsager regression hypothesis, and fluctuation-dissipation theorem.

Our work was stimulated partly by a series of papers from M.I.T.^{1,2} and by a Rockefeller-Maryland³ collaboration. They predicted that the Brillouin peaks of a fluid in a temperature gradient would show an asymmetry inversely proportional to the square of the scattering wave vector. They also made the tantalizing suggestion that this asymmetry was intimately related to the breaking of time-reversal symmetry in the nonequilibrium steady state: In classical systems an asymmetry ($\omega \leftrightarrow -\omega$) in the density-density correlation function implies that the equal-time momentum-density correlation function is nonvanishing, in contradiction with time-reversal symmetry.

Consequently, Secs. IV and V are devoted to problems first considered by the M.I.T. group. We study Brillouin scattering off a fluid in a shear flow in Sec. IV and in a temperature gradient in Sec. V. The problems are arranged in order of increasing technical difficulties. Appendices B and C also make a connection with the work of the M.I.T. group at the level of the choice of ensemble. We emphasize in the text and in Appendix A that the choice of correlation function we calculate depends on the experiment performed. A short version of our results appeared in Ref. 4.

In conclusion, we reiterate the physical interpretation of the formalism, and since the problems of Secs. IV and V have been the subject of considerable interest lately, we try to summarize

the results of other workers in the field and mention the points where there is agreement or disagreement. Since there is also a history of generalizations of the Langevin formalism to nonequilibrium situations, we try to mention a few of the papers devoted to that subject.

II. LANGEVIN FORMALISM AND ITS EXTENSION TO SIMPLE NONEQUILIBRIUM PROBLEMS: THE CHOICE OF ENSEMBLE

In this section we use the example of a system with one diffusive mode to recall the Langevin⁵ formalism in equilibrium and to introduce its generalization to a simple nonequilibrium steady state. The calculation we have in mind is that of the density-density correlation function for an uncharged electron-gas scattering off impurities in the presence of a temperature gradient. A "microscopic" calculation for that problem is also presented in Appendices B and C. The ensemble used in these appendices is closely connected to that used by other groups¹⁻³ but the actual calculation is quite different. The fact that our Langevin and microscopic calculations agree for this simple case gives us confidence that our physically motivated hypothesis about the Langevin formalism remains justified for more complicated situations, although by all means *not all* nonequilibrium situations. A counter example is given in the conclusion.

In the calculation we will present in this section, many of the possible complications (due to temperature-dependent transport coefficients, for example) will not be treated explicitly although this could be done. These complications will be introduced in the following sections.

A. Fluctuations about equilibrium

We are interested in long-wavelength density fluctuations about equilibrium. Since the number of particles is conserved, we may write the continuity equation

$$\frac{\partial n}{\partial t} + \vec{\nabla} \cdot \vec{j}_n = 0, \quad (2.1)$$

where n is the number density and $\vec{j}_n$ is the number current. In the long-wavelength limit the average particle current is caused by gradients in the chemical potential μ , i.e.,

$$\vec{j}_n = -\lambda \vec{\nabla} \mu, \quad (2.2)$$

where λ is a transport coefficient.⁶

To close the set of Eqs. (2.1) and (2.2) we need to make the additional hypothesis

$$\delta \mu = \left(\frac{\partial \mu}{\partial n} \right)_T \delta n \equiv \frac{1}{\chi_n} \delta n. \quad (2.3)$$

Relations of this form follow from the assumption of local thermodynamic equilibrium, i.e., that a specification of a complete set of hydrodynamic or thermodynamic variables will fix locally the values of all others.

Equations (2.1)–(2.3) describe the average macroscopic behavior of a perturbation in the density. If we are interested in instantaneous values of the fluctuating quantities in equilibrium, we must replace Eqs. (2.2) and (2.3) by

$$\dot{\mathbf{j}}_n = -\lambda \nabla (\chi_n^{-1} n) + \tilde{\mathbf{f}}. \quad (2.4)$$

Equation (2.1) remains valid if (2.4) is defined as the exact instantaneous current; $\tilde{\mathbf{f}}$ is called a "Langevin force." It is a random-driving term which accounts for the deviations of the instantaneous current $\dot{\mathbf{j}}_n(t)$ from the average macroscopic behavior predicted by hydrodynamics.

Physically, the Langevin force represents the effect of the random-thermal motion of the fast variables on the hydrodynamic variables (here the density n). Accordingly, it is assumed that

$$\langle f^i(\tilde{\mathbf{r}}, t) f^j(\tilde{\mathbf{r}}', t') \rangle = \mathcal{D} \delta_{ij} \delta^3(\tilde{\mathbf{r}} - \tilde{\mathbf{r}}') \delta(t - t'), \quad (2.5)$$

where $\mathcal{D}$ is a constant to be determined from the requirement that the result for the equal-time density-density correlation function coincide with the thermodynamic formula

$$\langle (n - \langle n \rangle)^2 \rangle = \frac{1}{V\beta} \frac{\partial}{\partial \mu} \langle n \rangle = (V\beta)^{-1} \chi_n, \quad (2.6)$$

where $\beta = 1/k_B T$ and V is the volume of the system; from Eqs. (2.1)–(2.6) we can compute $\langle \delta n(\tilde{\mathbf{r}}, t) \delta n(\tilde{\mathbf{r}}', t') \rangle$. Clearly Eqs. (2.5) and (2.6) are related to the choice of the second moment of the ensemble. In equilibrium, Eq. (2.6) is the standard way of finding that second moment, but as we will see, out of equilibrium, Eq. (2.5) is more useful.

To compute the density fluctuations in equilibrium, we substitute Eq. (2.4) in (2.1) and Fourier transform to obtain

$$(-i\omega + Dk^2) n_{k\omega} = -i\tilde{\mathbf{k}} \cdot \tilde{\mathbf{f}}_{k\omega}, \quad (2.7)$$

where $D \equiv \chi_n^{-1} \lambda$. Using Eq. (2.5) we finally obtain

$$\begin{aligned} \int d^3\mathbf{r} dt d^3\mathbf{r}' dt' e^{-i\tilde{\mathbf{k}} \cdot \tilde{\mathbf{r}} + i\omega t} e^{-i\tilde{\mathbf{k}}' \cdot \tilde{\mathbf{r}}' + i\omega' t'} \langle \delta n(\tilde{\mathbf{r}} t) \delta n(\tilde{\mathbf{r}}' t') \rangle &= \langle n_{\tilde{\mathbf{k}}\omega} n_{\tilde{\mathbf{k}}'\omega'} \rangle \\ &= (2\pi)^4 \delta^3(\tilde{\mathbf{k}} + \tilde{\mathbf{k}}') \delta(\omega + \omega') \frac{\mathcal{D} k^2}{\omega^2 + (Dk^2)^2}. \end{aligned} \quad (2.8)$$

The equal-time density-density correlation function (2.6) may be determined from Eq. (2.8) by integrating over ω and then taking the $k \rightarrow 0$ limit. This immediately leads to the identification

$$\mathcal{D} = 2k_B T D \chi_n. \quad (2.9)$$

Equations (2.5) and (2.9) together are often called the second fluctuation-dissipation theorem. Note that for a system of uncharged electrons scattering-off impurities there is another hydrodynamic mode associated with energy conservation. This mode is decoupled from the density here but it will become important in Sec. IIB.

B. Fluctuations about a nonequilibrium steady state

In this section, we set forth the hypotheses which allow us to compute the density fluctuations in a system like the previous one, but in which there is also a temperature gradient. The reader should keep in mind that in all the nonequilibrium problems we shall consider, there are two new lengths which are introduced. First, the length defined by the external perturbation [here $(\nabla \ln T)^{-1}$] and second, the size of the system. Even though the latter length is also present in equilibrium, its importance is much more pronounced in nonequilibrium problems. For example, in the case of a system across which a voltage is applied, the

size of the system will in part determine how fast the Joule heat can be dissipated and hence the steady-state temperature profile.

We divide the problem of calculating fluctuations of slow variables about nonequilibrium steady states in two parts, dynamical and statistical. The dynamics of the slow variables can be computed from the deterministic hydrodynamic equations. First one has to solve for the stationary profiles of density, temperature, etc., using the full (i.e., nonlinear) hydrodynamic equations with appropriate boundary conditions (representing external constraints and forces). Second, one has to linearize about the stationary profiles to compute the behavior of small fluctuations. Note that even with small gradients, the deviations from global equilibrium can be large. Hence the coefficients in the linearized equations (thermodynamic derivatives, transport coefficients, etc.) are determined from the assumption of local thermodynamic equilibrium and may vary in space.

For our example, the boundary conditions and the requirement that the system be in a steady state impose

$$\dot{\mathbf{j}}_n(x=0) = \dot{\mathbf{j}}_n(x=L) = 0, \quad (2.10a)$$

$$T(x=-L/2) = T_0 - \Delta T/2, \quad T(x=L/2) = T_0 + \Delta T/2, \quad (2.10b)$$

$$\frac{\partial T}{\partial t} = 0. \quad (2.10c)$$

To find the temperature profile we have to solve

$$C_v \frac{\partial T}{\partial t} = \vec{\nabla} \cdot (\kappa \vec{\nabla} T) = 0. \quad (2.11)$$

A constant heat flux implies a linear temperature profile provided κ is constant. The temperature dependence of κ can be neglected provided $\Delta T/T \ll 1$. Therefore, from Eqs. (2.10b), (2.10c), and (2.11), we find

$$\vec{\nabla} T = \frac{\Delta T}{L}. \quad (2.12)$$

The chemical potential must be constant in the absence of mass flow [see Eqs. (2.10a) and (2.2)], and if we assume χ_n is temperature independent then the density is constant. Hence the linearized equations of motion for fluctuations of n about the nonequilibrium steady state are

$$\frac{\partial n}{\partial t} = D \nabla^2 n + \vec{\nabla} \cdot \vec{f}. \quad (2.13)$$

To complete the calculation of the density fluctuations from (2.13) we now address the statistical part of the problem, which involves the determination of the Langevin forces away from equilibrium. Our assumption is that the fast degrees of freedom behave as if they were in local equilibrium at the value of the thermodynamic parameters determined from the solution to the steady-state problem. That is, we will continue to use (2.5) and (2.9) but with local values of the parameters T , D , χ_n , etc.

Our ansatz would be compelling in a problem where there was a clear separation of time scales between "fast" and "slow" modes. Consider, for instance, a set of macroscopic masses connected by springs and immersed in a heat bath with a temperature gradient. It is then clear that the correlation function of the oscillator positions can be computed from the usual equations of motions driven by Langevin forces derived from the local temperature. In other words, in a problem where the Langevin forces correspond to degrees of freedom which are correlated only over very short times and distances compared with the correlations of the slow modes, it is perfectly reasonable to assume that the Langevin force correlation is entirely determined by the local value of the thermodynamic variables.

Real problems often do not have an explicit separation of time scales. Thus we will not attempt here to treat the fluctuation-induced enhancement of thermodynamic quantities, such as occurs near a critical point, or the phenomena of long-

time tails.

We believe that the equilibrium value for the correlation function of *slow* variables does not hold for general nonequilibrium situations, even when local values of the thermodynamic parameters are used, simply because slow variables are correlated over large distances (at finite frequencies), hence they can easily probe regions with different temperatures.

A final physical remark on our assumption about Langevin forces: We mentioned earlier that the difficulty with the postulate of equal *a priori* probabilities is that, in nonequilibrium situations, nothing forbids special forces to be devised to favor states which are highly improbable in equilibrium. We believe that solving the correct dynamical problem to find the steady state takes into account the external forces as best as possible. In equilibrium we know that Langevin forces are consistent with the postulate of equal *a priori* probabilities. By analogy, here the Langevin forces allow us to explore phase space around the nonequilibrium steady state with a sort of "equal *a priori* probability consistent with externally imposed stresses."

Returning to the example of this section, we find for the density correlation function from (2.13):

$$\langle n_{\vec{k}\omega} n_{\vec{k}'\omega'} \rangle = \frac{-i\vec{k} \cdot \langle \vec{f}_{\vec{k}\omega} \vec{f}_{\vec{k}'\omega'} \rangle \cdot \vec{k}' i(-)}{(-i\omega + Dk^2)(-i\omega' + Dk'^2)}. \quad (2.14)$$

Since D and χ_n are assumed independent of temperature, we have from (2.5) and (2.9):

$$\langle n_{\vec{k}\omega} n_{\vec{k}'\omega'} \rangle = k_B T_{\vec{k}+\vec{k}'} \chi_n \frac{2D(-)\vec{k} \cdot \vec{k}' 2\pi \delta(\omega + \omega')}{(-i\omega + Dk^2)(-i\omega' + Dk'^2)}, \quad (2.15)$$

where $T_{\vec{k}+\vec{k}'}$ is the Fourier transform of the local temperature. We can choose for our temperature profile and its corresponding Fourier transform:

$$T(\vec{r}) = T_0 + \vec{r} \cdot \vec{\nabla} T, \quad (2.16a)$$

$$T_{\vec{p}} = T_0 (2\pi)^3 \delta^3(\vec{p}) + i \frac{d}{d\vec{p}} [(2\pi)^3 \delta^3(\vec{p})] \cdot \vec{\nabla} T, \quad (2.16b)$$

or

$$T(\vec{r}) = T_0 + \delta \vec{T} \sin \vec{q} \cdot \vec{r}, \quad (2.17a)$$

$$T_{\vec{p}} = T_0 (2\pi)^3 \delta^3(\vec{p}) + \frac{\delta \vec{T}}{2i} [\delta^3(\vec{p} - \vec{q}) - \delta^3(\vec{p} + \vec{q})] (2\pi)^3, \quad (2.17b)$$

$$\vec{\nabla} T \equiv \vec{\nabla} T(\vec{r}=0) = \vec{q} \delta \vec{T}. \quad (2.17c)$$

To first order in q , (2.17) reduces to (2.16). As for many problems in quantum perturbation theory, it is convenient to use (2.17) instead of (2.16).⁷

We digress to discuss the limits of validity of

our calculation which are related to the two macroscopic lengths $L_\nabla = (\nabla \ln T)^{-1}$, and L , the size of the system. First, we must assume that $L_\nabla \gg L$ to keep $T(\vec{r})$ positive in Eq. (2.16) when $|\vec{r}| \leq L$. Note that the assumption $\Delta T/T \ll 1$ made earlier is equivalent to $L_\nabla \gg L$. Second, in addition to the trivial restriction to wavelengths less than L , we must assume that the mean free path of the hydrodynamic modes at the wavelength in question is also much less than L . Otherwise, we could not assume that the periodic continuation in Eq. (2.17) is valid, and most importantly we could not neglect the boundary conditions in the linearized equations for the fluctuations.⁸ This problem is only acute for propagating modes (we will return to it in Sec. IV) but it will significantly circumscribe the domain of validity of our calculated correlation function since the interesting nonequilibrium effects are most pronounced at long wavelengths when fluctuations sample regions of very different temperature.

Note that Eqs. (2.16) and (2.17) are both an approximation when they are used in the calculation of correlation functions in Fourier space [as in Eq. (2.15)] because then $-\infty \leq \vec{r} \leq \infty$ while Eqs. (2.16) and (2.17) clearly apply only when $|\vec{r}| \leq L$. This is no problem, however, if the mean free path of collective modes is shorter than the size of the system and if correlation functions in Fourier space [such as Eq. (2.15)] are used to compute only $\langle n(\vec{r}, t) n(\vec{r}', t') \rangle$ for $|\vec{r}|, |\vec{r}'| \leq L$. In fact, it is quite important to consider carefully which correlation function is really measured in any given experiment. This question is addressed in Appendix A in the case of light scattering. In the past, some authors have been misled to claim that certain imaginary correlation functions could be observed experimentally.² One must thus study the question "what is observed" very carefully.

Returning to our calculation, we substitute (2.17b) in (2.15) and expand to first order in q to obtain⁹

$$[\langle n_{\vec{k}\omega} n_{-\vec{k}-\omega} \rangle + \langle n_{\vec{k}+\vec{q}/2, \omega} n_{-\vec{k}+\vec{q}/2, -\omega} \rangle + \langle n_{\vec{k}-\vec{q}/2, \omega} n_{-\vec{k}-\vec{q}/2, -\omega} \rangle] = (2\pi)^4 \delta^4(0) k_B T_0 \chi_n \left(\frac{2Dk^2}{\omega^2 + (Dk^2)^2} - \frac{4\omega Dk^2}{[\omega^2 + (Dk^2)^2]^2} D\vec{k} \cdot \vec{\nabla} \ln T \right). \quad (2.18)$$

In Appendix A we demonstrate that the left-hand side of (2.18) is the correlation function of interest in a light scattering experiment. We can summarize the results of this appendix as follows. A light scattering experiment measures a quantity proportional to

$$I = \int \frac{d^3 p d^3 p'}{(2\pi)^3 (2\pi)^3} \Delta(\vec{p} - \vec{k}) \Delta(\vec{p}' + \vec{k}) \langle n_{\vec{p}\omega} n_{\vec{p}'-\omega} \rangle, \quad (2.19)$$

where $\Delta(\vec{l})$ is a function which is peaked around $\vec{l} = 0$ with a width δk inversely proportional to the size of the scattering volume and reduces to a Dirac delta function in the infinite volume limit. Using Eqs. (2.15) and (2.17), it is possible to do the integral over $\vec{p}'$ trivially. Since $\delta k > q$ (i.e., $L < L_\nabla$) it is possible to choose the remaining dummy integration variable such that (2.19) looks like an integral over $\vec{p}$ with a weight function peaked at $\vec{p} \sim \vec{k}$, multiplying a sum of three correlation functions. If the width of the weight function is small enough, then the left-hand side of Eq. (2.18) becomes a good approximation to the integral.

Note that the last term of Eq. (2.18) is odd in frequency. This means that the equal-time current-density correlation function, which vanishes in equilibrium by time-reversal symmetry, is nonzero in this nonequilibrium situation. [This can be seen by using the continuity equation (2.1) to compute the frequency-dependent current-density correlation function. The corresponding

equal-time correlation function is obtained by an integration over frequency.] Note also, that the frequency integral of (2.18) shows that the equilibrium result (2.6) holds even in the presence of a temperature gradient. This is consistent with the fact that by construction the density response function χ_n is independent of $\vec{\nabla} T$. The next section gives a more detailed account of the relation between response and fluctuations. One compelling reason to suppose that χ_n is independent of $\vec{\nabla} T$ is that it follows from the full nonlinear hydrodynamic equations which are valid even in the presence of temperature gradients.

In contrast to Eq. (2.18) there is a modification to the Brillouin scattering spectrum of Sec. V which can be interpreted in physical terms because the interesting effects appear not only in the line shape, as here, but also in gross features such as the overall integrated intensity of the line. Modifications to details of the frequency dependence of the spectrum, such as Eq. (2.18), are quite hard to interpret physically.

III. SUMMARY AND FORMAL CONNECTION WITH EQUILIBRIUM RESULTS

In this section, we present the formalism without examples and with a minimum of physical discussion. This will allow us to make a straightforward connection with results familiar from the theory of fluctuations about equilibrium. The dy-

namical part of the problem consists of two steps. We must first solve the full nonlinear hydrodynamic equations with appropriate boundary conditions to find the steady-state value of the thermodynamic parameters. Then we must find the equations of motion for the fluctuations by linearizing the full nonlinear hydrodynamic equations about the steady state. We are left with a set of linear hydrodynamic equations for modes A_α :

$$\frac{\partial A_\alpha(\vec{k}, t)}{\partial t} + \int \frac{d^3 k'}{(2\pi)^3} M_{\alpha\beta}(\vec{k}, -\vec{k}') A_\beta(\vec{k}', t) = f_\alpha(\vec{k}, t). \quad (3.1)$$

The statistical part of the problem has been introduced through a Langevin force $f_\alpha(\vec{k}, t)$, that is to be written as the gradient of a second function where necessary to preserve the conservation laws. The Langevin force is conventionally interpreted as a model of molecular chaos so it is reasonable to expect that it will remain uncorrelated at unequal space-time points in the non-equilibrium states we are considering. As argued in the preceding section, we will further assume that the magnitude of its correlation function has the same form as in equilibrium with local values of the temperature and transport coefficients.

Note that in a temperature gradient, $M_{\alpha\beta}$ becomes off diagonal in k because transport coefficients and thermodynamic derivatives acquire a spatial dependence. The relative importance of such terms is potentially of the order of their logarithmic temperature derivative which in real materials can be large. In the following formal manipulations, a repeated momentum index will imply that there is an integration over that index. In practice, the equations will be solved perturbatively when $M_{\alpha\beta}(\vec{k}, \vec{k}')$ is not diagonal in $\vec{k}$. As we will see, in the cases we have considered, the direct modification of $M_{\alpha\beta}$ by the temperature gradient cancels from the final answer.

Using Eq. (3.1) and the above assumptions about the Langevin forces we find (in matrix notation)

$$\begin{aligned} \langle \underline{A}(\vec{k}, t) \underline{A}^*(\vec{k}', 0) \rangle \\ = \Theta(t) \exp[-\underline{M}(\vec{k}, \vec{p})t] \langle \underline{A}(\vec{p}, 0) \underline{A}^*(\vec{k}', 0) \rangle \\ + \Theta(-t) \langle \underline{A}(\vec{k}, 0) \underline{A}^*(\vec{p}, 0) \rangle \exp[\underline{M}^\dagger(\vec{p}, \vec{k}')t], \end{aligned} \quad (3.2)$$

where $\Theta(t)$ equals one for $t > 0$ and zero for $t < 0$ and

$$\begin{aligned} \langle \underline{A}(\vec{k}, 0) \underline{A}^*(\vec{k}', 0) \rangle &\equiv \int_{-\infty}^0 dt \exp[\underline{M}(\vec{k}, \vec{p})t] \underline{D}(\vec{p}, \vec{p}') \\ &\times \exp[\underline{M}^\dagger(\vec{p}', \vec{k}')t], \end{aligned} \quad (3.3)$$

$$\langle f_\alpha(\vec{k}, t) f_\beta^*(\vec{k}', t') \rangle \equiv D_{\alpha\beta}(\vec{k}, \vec{k}') \delta(t - t'). \quad (3.4)$$

Equation (3.4) can be evaluated from our assumptions concerning the Langevin forces. The equal-

time correlation functions may be obtained from Eq. (3.3) or equivalently from

$$\begin{aligned} \underline{D}(\vec{k}, \vec{k}') &= [\underline{M}(\vec{k}, \vec{p}) \langle \underline{A}(\vec{p}, 0) \underline{A}^*(\vec{k}', 0) \rangle \\ &+ \langle \underline{A}(\vec{k}, 0) \underline{A}^*(\vec{p}, 0) \rangle \underline{M}^\dagger(\vec{p}, \vec{k}')]^{-1}. \end{aligned} \quad (3.5)$$

Note that in general these equations are not diagonal in momentum space even when $\underline{M}$ is. The ensemble implicit in the Langevin equation is stationary but, in general, not time-reversal invariant. Equation (3.2) is the generalization of the Onsager regression hypothesis¹⁰ and Eq. (3.5) is the generalization of Einstein's relation.¹⁰ Note that these relations follow from the Langevin formalism and our assumptions above without further approximations.

Let

$$\chi_{\alpha\beta}^\omega(\vec{k}, \vec{k}') \equiv \int_{-\infty}^{\infty} dt e^{i\omega t} \langle A_\alpha(\vec{k}, t) A_\beta^*(\vec{k}', 0) \rangle$$

and

$$\chi_{\alpha\beta}(\vec{k}, \vec{k}') \equiv \langle A_\alpha(\vec{k}, 0) A_\beta^*(\vec{k}', 0) \rangle$$

then, using Eq. (3.2) we find

$$\begin{aligned} \underline{\chi}^\omega(\vec{k}, \vec{k}') &= [-i\omega \underline{I} + \underline{M}(\vec{k}, \vec{p})]^{-1} \underline{\chi}(\vec{p}, \vec{k}') \\ &+ \underline{\chi}(\vec{k}, \vec{p}) [i\omega \underline{I} + \underline{M}^\dagger(\vec{p}, \vec{k}')]^{-1}, \end{aligned} \quad (3.6)$$

where $\underline{I}$ is the identity matrix. Equations (3.5) and (3.6) also give

$$\underline{\chi}^\omega(\vec{k}, \vec{k}') = [-i\omega \underline{I} + \underline{M}(\vec{k}, \vec{p})]^{-1} \underline{D}(\vec{p}, \vec{p}') [i\omega \underline{I} + \underline{M}^\dagger(\vec{p}', \vec{k}')]^{-1}. \quad (3.7)$$

This result may also be obtained directly from (3.1) and (3.4). In equilibrium (3.6) reduces to a version of the fluctuation-dissipation theorem which expresses the fluctuations as the imaginary part of a response function.

IV. DENSITY FLUCTUATIONS OF A FLUID WITH A UNIFORMLY SHEARED VELOCITY PROFILE

This problem will allow us to introduce the difficulties associated with a hydrodynamic matrix which is not diagonal in momentum space while retaining the equilibrium form for the Langevin forces. First, consider the solution of the full nonlinear hydrodynamic equations for the steady-state problem¹¹

$$\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot (\rho \vec{v}) = 0, \quad (4.1)$$

$$\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \vec{\nabla}) \vec{v} = -\frac{1}{\rho} \vec{\nabla} p + \frac{\eta}{\rho} \nabla^2 \vec{v} + \left(\zeta + \frac{\eta}{3} \right) \frac{1}{\rho} \vec{\nabla} (\vec{\nabla} \cdot \vec{v}). \quad (4.2)$$

ρ is the mass density of the fluid, η and ζ the shear and bulk dynamic viscosities, and p is the pressure. We have assumed that η and ζ are position independent, which is true in the context of hydrodynamics if the only externally imposed perturbation is a shear velocity.

Since the temperature is uniform and the viscous heating small, we can work at constant entropy to find the stationary state. We do not have to supplement (4.1) and (4.2) with an equation for the energy density. When we then linearize and look at frequencies of order the sound frequency, the coupling to the energy must be included. It will greatly simplify the calculations to assume $(\partial\rho/\partial T)_p = 0$ so that the energy can be legitimately neglected throughout [see Eqs. (5.6)–(5.8)]. The interesting nonequilibrium aspects of the shear-flow problem are not compromised. We can therefore use

$$\vec{\nabla}p = c^2 \vec{\nabla}\rho, \quad (4.3)$$

$$\frac{\partial \delta \rho}{\partial t} + (\vec{v}_0 \cdot \vec{\nabla}) \delta \rho + \rho_0 \vec{\nabla} \cdot \delta \vec{v} = 0, \quad (4.6)$$

$$\frac{\partial \delta \vec{v}}{\partial t} + (\vec{v}_0 \cdot \vec{\nabla}) \delta \vec{v} + (\delta \vec{v} \cdot \vec{\nabla}) \vec{v}_0 = -\frac{c^2}{\rho_0} \vec{\nabla} \delta \rho + \frac{\eta}{\rho_0} \nabla^2 \delta \vec{v} + \frac{1}{\rho_0} \left(\zeta + \frac{\eta}{3} \right) \vec{\nabla} (\vec{\nabla} \cdot \delta \vec{v}) + \frac{1}{\rho_0} \vec{\nabla} \cdot \vec{S}, \quad (4.7)$$

where $\vec{S}$ is the fluctuating stress tensor whose correlations are given by¹²

$$\langle S_{ij}(\vec{r}_1, t_1) S_{lm}(\vec{r}_2, t_2) \rangle = 2T [\eta (\delta_{il} \delta_{jm} + \delta_{im} \delta_{jl}) + (\zeta - \frac{2}{3}\eta) \delta_{il} \delta_{lm}] \delta^3(\vec{r}_1 - \vec{r}_2) \delta(t_1 - t_2). \quad (4.8)$$

From now on we will set Boltzmann's constant k_B equal to unity. Recall that T , η , and ζ in (4.8) are position independent. This will not be the case in the following section.

By analogy with the procedure described in Eq. (2.17) we will use instead of (4.5),

$$\vec{v}_0 = [\vec{V}_0 + \vec{\tilde{v}}_0 \sin \vec{q} \cdot \vec{r}], \quad (4.9)$$

where $\vec{q} = \hat{e}_y/L$ and both $\vec{V}_0$ and $\vec{\tilde{v}}_0$ are in the x direction. Using (4.9) and Fourier transforming (4.6) and (4.7) we obtain, in matrix notation,

$$\begin{pmatrix} -i\omega + i\vec{k} \cdot \vec{V}_0 & i\rho_0 \\ \frac{ik^2 c^2}{\rho_0} & (-i\omega + i\vec{k} \cdot \vec{V}_0) + D_I k^2 + \frac{\vec{k} \cdot \vec{\tilde{v}}_0 \vec{q} \cdot \vec{k}}{k^2} \end{pmatrix} \begin{pmatrix} \delta \rho_{\vec{k}} \\ \vec{k} \cdot \delta \vec{v}_{\vec{k}} \end{pmatrix} = \begin{pmatrix} 0 \\ -\frac{i}{\rho_0} \vec{k} \cdot \vec{S}_{\vec{k}} \cdot \vec{k} \end{pmatrix} - \frac{\vec{\tilde{v}}_0}{2i} \cdot \left[i(\vec{k} - \vec{q}) \delta \rho_{\vec{k}-\vec{q}} - i(\vec{k} + \vec{q}) \delta \rho_{\vec{k}+\vec{q}} \right. \\ \left. - \frac{\vec{\tilde{v}}_0}{2i} \cdot \left[i(\vec{k} - \vec{q}) [(\vec{k} - \vec{q}) \cdot \delta \vec{v}_{\vec{k}-\vec{q}}] - i(\vec{k} + \vec{q}) [(\vec{k} + \vec{q}) \cdot \delta \vec{v}_{\vec{k}+\vec{q}}] \right] \right. \\ \left. - \frac{\vec{\tilde{v}}_0}{2i} \cdot \left[i(\vec{k} - \vec{q}) [\vec{q} \cdot \delta \vec{v}_{\vec{k}-\vec{q}}] + i(\vec{k} + \vec{q}) [\vec{q} \cdot \delta \vec{v}_{\vec{k}+\vec{q}}] - 2i\vec{k}\vec{q} \cdot [\hat{k} \times (\hat{k} \times \delta \vec{v}_{\vec{k}})] \right] \right]. \quad (4.10)$$

We have omitted the subscript ω since all Fourier components are at the same frequency. We have also rearranged a term $\vec{q} \cdot \delta \vec{v}_{\vec{k}}$ using the decomposition of $\delta \vec{v}_{\vec{k}}$ into longitudinal and transverse parts

$$\delta \vec{v}_{\vec{k}} = \frac{\vec{k}(\vec{k} \cdot \delta \vec{v}_{\vec{k}}) - \vec{k} \times (\vec{k} \times \delta \vec{v}_{\vec{k}})}{k^2} \quad (4.11)$$

and we defined

$$D_I = (\zeta + \frac{4}{3}\eta) \frac{1}{\rho_0}, \quad (4.12)$$

where $c^2 = (\partial p / \partial \rho)_s$. To solve Eqs. (4.1) and (4.2) for the steady state, we can set $\partial \rho / \partial t = 0$, $\partial \vec{v} / \partial t = 0$, and take as our boundary conditions

$$v_x(x, y = \pm L/2, z) = v_0 \pm \tilde{v}_0/2, \quad (4.4)$$

with all other components of the velocity equal to zero. Then (4.1), (4.2), and (4.3) have as their solution,

$$\rho = \rho_0 = \text{const}, \quad \vec{v}_0(x, y, z) = [v_0 + \tilde{v}_0(y/L)] \hat{e}_x. \quad (4.5)$$

We thus have a fluid moving in the x direction with a velocity increasing linearly from $y = -L/2$ to $y = L/2$ but independent of z . We will take the system as infinite in the x and z directions.

Now let $\vec{v} = \vec{v}_0 + \delta \vec{v}$ and $\rho = \rho_0 + \delta \rho$ in Eqs. (4.1), (4.2), and (4.3). We obtain for the linearized equations for the fluctuations $\delta \rho$ and $\delta \vec{v}$:

$$\hat{k} = \vec{k}/|\vec{k}|. \quad (4.13)$$

Neglecting momentarily the terms proportional to $\vec{v}_0$ on the right-hand side of Eq. (4.10) it is easy to obtain

$$\begin{pmatrix} \delta\rho_{k\omega} \\ \vec{k} \cdot \delta\vec{v}_{k\omega} \end{pmatrix} = \frac{1}{(-\tilde{\omega}^2 - i\tilde{\omega}(\vec{k} \cdot \vec{\nabla}\vec{v}_0 \cdot \vec{k} + D_1 k^2) + c^2 k^2)} \begin{pmatrix} -i\tilde{\omega} + \hat{k} \cdot \vec{\nabla}\vec{v}_0 \cdot \hat{k} + D_1 k^2 & -i\rho_0 \\ \frac{-ic^2 k^2}{\rho_0} & -i\tilde{\omega} \end{pmatrix} \begin{pmatrix} 0 \\ \frac{i}{\rho_0} \vec{k} \cdot \vec{S}_k \cdot \vec{k} \end{pmatrix}. \quad (4.14)$$

In this formula, we have anticipated

$$\hat{k} \cdot \vec{\nabla}\vec{v}_0(\vec{r}=0) \cdot \hat{k} = \hat{k} \cdot \vec{q} \cdot \vec{\nabla}\vec{v}_0 \cdot \hat{k} \quad (4.15)$$

and we defined

$$\tilde{\omega} \equiv \omega - \vec{k} \cdot \vec{v}_0. \quad (4.16)$$

$\tilde{\omega}$ instead of ω enters (4.14) because of the usual Doppler shift. Using (4.8) [see also (3.7)] we can now compute¹³

$$\langle \delta n_{k\omega} \delta n_{-k, -\omega} \rangle = \left(\frac{Tn}{mc^2} \right) \frac{c^2 k^2 (2D_1 k^2)}{[(\tilde{\omega}^2 - c^2 k^2)^2 + [\tilde{\omega}(\hat{k} \cdot \vec{\nabla}\vec{v}_0 \cdot \hat{k} + D_1 k^2)]^2]}, \quad (4.17)$$

where $mn = \rho_0$. We now proceed to show that if we keep only the first order in $\vec{q} \cdot \vec{\nabla}\vec{v}_0$ in (4.17), then we may indeed neglect the terms proportional to $\vec{v}_0$ on the right-hand side of (4.10) to compute $\langle \delta n_{k\omega} \times \delta n_{-k, -\omega} \rangle$. Since these terms are already proportional to $\vec{v}_0$, we can substitute for $(\vec{k} \pm \vec{q}) \cdot \delta\vec{v}_{k\pm q}$ and $\delta\rho_{k\pm q}$ the zeroth-order solution (with k replaced by the appropriate momentum index). Solving iteratively in this manner for $\delta\rho_{k\omega}$, squaring and averaging, the $\mathcal{O}(\vec{v}_0)$ terms in question vanish because

$$\langle \vec{S}_k \cdot \vec{S}_{-k\pm q} \rangle = 0. \quad (4.18)$$

There is also on the right-hand side of (4.10) a term proportional to $\hat{k} \times (\hat{k} \times \delta\vec{v}_k)$. We can substitute for that term the zeroth-order solution for the transverse part of Eq. (4.2). Since from Eq. (4.8),

$$\langle \vec{k} \cdot \vec{S}_k \cdot \vec{k} \vec{k} \times \vec{S}_{-k} \cdot \vec{k} \rangle = 0, \quad (4.19)$$

that term also drops out from the density-density correlation function to first order in $\vec{v}_0$. This conclusion is also even more valid for the terms proportional to $(\vec{k} \pm \vec{q}) \times [(\vec{k} \pm \vec{q}) \times \delta\vec{v}_{k\pm q}]$ which come

from decomposing $\delta\vec{v}_{k\pm q}$ in the last column of Eq. (4.10) into longitudinal and transverse parts. Our final answer is thus (4.17) to first order in $\hat{k} \cdot \vec{\nabla}\vec{v}_0 \cdot \hat{k}$:

$$\langle \delta n_{k\omega} \delta n_{-k, -\omega} \rangle = \left(\frac{Tn}{mc^2} \right) \frac{c^2 k^2 (2D_1 k^2)}{(\tilde{\omega}^2 - c^2 k^2)^2 + (\tilde{\omega} D_1 k^2)^2} \times \left(1 - \frac{2D_1 k^2 \tilde{\omega} \hat{k} \cdot \vec{\nabla}\vec{v}_0 \cdot \hat{k}}{(\tilde{\omega}^2 - c^2 k^2)^2 + (\tilde{\omega} D_1 k^2)^2} \right). \quad (4.20)$$

We also need to calculate the correlation functions $\langle \delta n_{k+q/2, \omega} \delta n_{-k+q/2, -\omega} \rangle$ and $\langle \delta n_{k-q/2, \omega} \delta n_{-k-q/2, -\omega} \rangle$ (or equivalently $\langle \delta n_{k+q/2, \omega} \delta n_{-k-q/2, \omega}^* \rangle$ and $\langle \delta n_{k-q/2, \omega} \times \delta n_{k+q/2, \omega}^* \rangle$), because the hydrodynamic matrix in Eq. (4.10) couples modes whose wave vectors differ by $\pm\vec{q}$. It turns out in the end that these correlation functions vanish but this must be seen by an explicit calculation. We can substitute for $\delta\rho_{k\pm q}$ and $\delta\vec{v}_{k\pm q}$ in Eq. (4.10) the zeroth-order solution because these terms are already multiplied by $\vec{v}_0$. Using (4.18) and (4.19) we also see that to linear order in $\vec{v}_0$ only the longitudinal component of the velocity is important. Hence, approximations such as

$$\vec{k} \cdot \delta\vec{v}_{k-q} \sim \left(1 + \frac{\vec{k} \cdot \vec{q}}{k^2} \right) (\vec{k} - \vec{q}) \cdot \delta\vec{v}_{k-q} \sim \left(1 + \frac{\vec{k} \cdot \vec{q}}{k^2} \right) \left(\frac{\tilde{\omega}}{\rho_0} \right) \frac{(\vec{k} - \vec{q}) \cdot \vec{S}_{k-q} \cdot (\vec{k} - \vec{q})}{[-\tilde{\omega}^2 + c^2 (\vec{k} - \vec{q})^2 - i\tilde{\omega} D_1 (\vec{k} - \vec{q})^2]}$$

can be used in the terms multiplying $\vec{v}_0$ in Eq. (4.10). With all these simplifications we find

$$\delta\rho_{k+} = \frac{\vec{k}_+ \cdot \vec{S}_{k+} \cdot \vec{k}_+}{D_+} - \frac{1}{D_+ D_-} \frac{\tilde{v}_0}{2i} i\vec{k}_- \left[-i\tilde{\omega} \left(2 + \frac{\vec{k} \cdot \vec{q}}{k^2} \right) + D_1 k^2 \right] \vec{k}_- \cdot \vec{S}_{k-} \cdot \vec{k}_-$$

and

$$\delta\rho_{k-}^* = \frac{\vec{k}_- \cdot \vec{S}_{k-}^* \cdot \vec{k}_-}{D_-^*} + \frac{1}{D_+^* D_-^*} \frac{\tilde{v}_0}{2i} i\vec{k}_+ \left[i\tilde{\omega} \left(2 - \frac{\vec{k} \cdot \vec{q}}{k^2} \right) + D_1 k^2 \right] \vec{k}_+ \cdot \vec{S}_{k+}^* \cdot \vec{k}_+,$$

where

$$\vec{k}_\pm \equiv \vec{k} \pm \vec{q}/2$$

and

$$D \equiv -\tilde{\omega}^2 + c^2 k^2 - i\tilde{\omega} D_1 k^2,$$

$$D_\pm \equiv -\tilde{\omega}^2 + c^2 k_\pm^2 - i\tilde{\omega} D_1 k_\pm^2.$$

In $\delta\rho_{\vec{k}_+}$ we dropped the contribution from $\tilde{S}_{\vec{k}+\vec{q}/2}$ because it does not couple to $\delta\rho_{\vec{k}_+}^*$ to linear order in $\tilde{v}_0$. In $\delta\rho_{\vec{k}_+}^*$ we did not include the contribution from $\tilde{S}_{\vec{k}-\vec{q}/2}$ for an analogous reason. With the help of Eq. (4.8) we find

$$\begin{aligned} \langle \delta\rho_{\vec{k}_+, \omega} \delta\rho_{\vec{k}_-, \omega}^* \rangle &= \frac{2T\rho_0 D_1}{D_+ D_-^*} \frac{\tilde{v}_0}{k_+^2 2i} \cdot \frac{i\vec{k}_+}{D_+^* D_-} \left[i\tilde{\omega} \left(2 - \frac{\vec{k} \cdot \vec{q}}{k^2} \right) + D_1 k^2 \right] D_- \\ &\quad - (q \leftrightarrow -q)^*. \end{aligned}$$

Using the expansion

$$\frac{1}{D_- D_+^*} \approx \frac{1}{DD^*} + \frac{2i\omega^3 D_1 \vec{k} \cdot \vec{q}}{(DD^*)^2},$$

we find to linear order in $\tilde{v}_0$ and q ,

$$\langle \delta n_{\vec{k}+\vec{q}/2, \omega} \delta n_{\vec{k}-\vec{q}/2, \omega}^* \rangle + \langle \delta n_{\vec{k}-\vec{q}/2, \omega} \delta n_{\vec{k}+\vec{q}/2, -\omega}^* \rangle = 0.$$

Note that the latter correlation function can be found from the first one rather easily by letting $\vec{q} \rightarrow -\vec{q}$ and remembering that $\tilde{v}_0(\vec{q}) = \tilde{v}_0/2i$ and $\tilde{v}_0(-\vec{q}) = -\tilde{v}_0/2i$. These last equalities mean that only terms linear in q could have possibly contributed to the two correlation functions, but it turns out that even these drop out (we neglect higher-order odd terms).

Let us now discuss the conditions under which our final result (4.20) is valid. In order to proceed from (4.17) to (4.20) and, in fact, for both the damping in (4.17) and the density-density function to be positive, it is certainly necessary to assume

$$\frac{\hat{k} \cdot \tilde{\nabla} \tilde{v}_0 \cdot \hat{k}}{D_1 k^2} < 1. \quad (4.21)$$

This criterion is most stringent for the smallest allowed wave numbers, i.e., $\mathcal{O}(L^{-1})$ where it simply reduces to the condition that the conventionally defined Reynold's number is small. (Of course we have linearized in $\tilde{\nabla} \tilde{v}_0$ and ignored transverse modes and the correct boundary conditions for the fluctuations so our analysis cannot be expected to reproduce the correct critical Reynold's number.) We will always be interested in $k \gg 1/L$. Even if (4.21) is satisfied for such wave numbers, one must always keep in mind that large scale $\mathcal{O}(L)$ hydrodynamic instabilities will be the most stringent limitation on the maximum allowable $\tilde{\nabla} \tilde{v}_0$.

As we discussed in Sec. II, our treatment of the

thermal fluctuations also requires the mean free path for the sound waves to be less than the sample size, i.e.,

$$l = \frac{c}{D_1 k^2} \ll L. \quad (4.22)$$

The modes which we detect by scattering should not propagate ballistically from one side of the container to the other. Equation (4.22) is more stringent than (4.21) since, in general, $c \gg \hat{k} \cdot \tilde{\nabla} \tilde{v}_0 \cdot \hat{k} L$ (or $L < L_\nabla \equiv c / \hat{k} \cdot \tilde{\nabla} \tilde{v}_0 \cdot \hat{k}$). This inequality says that the velocities at the top and bottom of the container differ by an amount less than the speed of sound, which in a macroscopic container is always satisfied if the Reynold's number is kept low enough to avoid hydrodynamic instabilities.¹⁴

There is a physically interesting way of interpreting Eq. (4.20). Since $D_1 k^2 \ll ck$ there are two sharp peaks in the density-density correlation function at $\tilde{\omega} = \pm ck$. For simplicity we may assume $\tilde{v}_0 = 0$. Since the density-density correlation function is proportional to the inelastic cross section for scattering of light from wave vector $\vec{k}_i$ and frequency ω_i into wave vector $\vec{k}_f$ and frequency ω_f , we interpret, for fixed $\vec{k} = \vec{k}_i - \vec{k}_f$, the peak at $\omega = \omega_i - \omega_f = +ck$ as due to the emission of sound waves of wave vector $\vec{k}$ and the peak at $\omega = -ck$ as due to absorption of sound waves of wave vector $-\vec{k}$. (Figure 1 illustrates this point.) It is natural to take as a measure of the number of sound waves traveling in the $+\vec{k}$ direction ($-\vec{k}$) the integral of Eq. (4.20) over positive (negative) frequencies. Performing these integrals [it is easier to integrate Eq. (4.17) using the evenness of the integrand and then to expand], we find that the difference between the number of sound waves predicted by Eq. (4.20) and that for equilibrium ($\tilde{\nabla} \tilde{v}_0 = 0$) normalized by the equilibrium result is

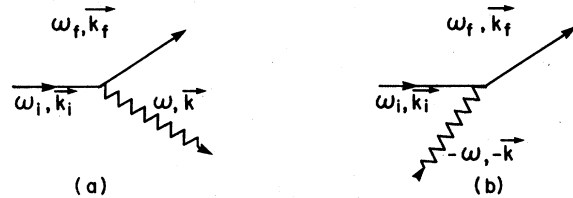


FIG. 1. Scattering processes corresponding to the two peaks in the scattering cross section as a function of frequency $\omega = \omega_i - \omega_f$ for fixed scattering wave vector $\vec{k} = \vec{k}_i - \vec{k}_f$. ω_i and $\vec{k}_i$ (ω_f and $\vec{k}_f$) are the frequency and wave vector of the incident (final) radiation. (a) The peak at $\omega = ck$ corresponds to emission of a sound wave of frequency ω and wave vector $\vec{k}$. (b) The peak at $\omega = -ck$ corresponds to absorption of a sound wave of frequency $-\omega$ and wave vector $-\vec{k}$.

$$\frac{\Delta N}{N} = -\frac{\hat{k} \cdot \vec{\nabla} \vec{v}_0 \cdot \hat{k}}{D_1 k^2}. \quad (4.23)$$

The physical argument for this result is as follows: Referring to Fig. 2, one sees that if there is scattering from a point at which $\vec{v}_0 = 0$, then in a shear there are less sound waves of wave vectors $\vec{k}$ and $-\vec{k}$ coming to that point when $\hat{k} \cdot \vec{\nabla} \vec{v}_0 \times \hat{k} > 0$, than when $\vec{\nabla} \vec{v}_0 = 0$, because the sound waves coming from one mean free path $l = (c/D_1 k^2)$ away have had on the average a smaller sound velocity, $c - l\hat{k} \cdot \vec{\nabla} \vec{v}_0 \cdot \hat{k}$, than if the system had been in equilibrium.¹⁵ Since the temperature is uniform, the absorption and emission rates are uniform and the sound wave flux is proportional to the sound velocity. Hence we find Eq. (4.23).

These physical arguments do not tell us anything about the detailed line shape in Eq. (4.20). If we think of sound waves as elementary excitations (phonons) we would expect a Lorentzian line shape. This was the result obtained by Machta *et al.*¹⁶ who first investigated this problem. The line shape (4.20) predicts that the change in the height of the peaks at the maximum due to the shear is twice that predicted by a Lorentzian having the same integrated intensity. In (4.20) also the correction to the equilibrium result falls off faster at large ω than a Lorentzian. Unfortunately, it is very difficult to resolve experimentally the line shape. We postpone further consideration of this problem to the essentially equivalent discussion at the end of the following section.

V. DENSITY FLUCTUATIONS OF A FLUID IN A UNIFORM TEMPERATURE GRADIENT

A. Steady-state problem

Following our usual procedure, we first solve the full nonlinear hydrodynamic equations for the steady-state problem with appropriate boundary conditions. These equations are¹⁷

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0, \quad (5.1)$$

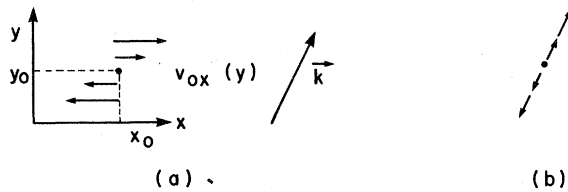


FIG. 2. (a) Velocity field around a point (x_0, y_0) where $\vec{v}_0 = 0$. The (arbitrarily chosen) direction of the scattering wave vector $\vec{k}$ is also shown. (b) Projection $\vec{v}_0 \cdot \hat{k}$ of the velocity field along the direction of $\vec{k}$. Clearly, $\hat{k} \cdot \vec{\nabla} \vec{v} \cdot \hat{k} > 0$ for this case.

$$\frac{\partial v_i}{\partial t} + v_j \nabla_j v_i = -\frac{1}{\rho} \nabla_i p + \frac{1}{\rho} \nabla_j [\eta (\nabla_i v_j + \nabla_j v_i - \frac{2}{3} \nabla_i v_l \delta_{lj}) + \zeta \nabla_i v_l \delta_{lj}], \quad (5.2)$$

$$\rho T \left(\frac{\partial s}{\partial t} + (\vec{v} \cdot \vec{\nabla}) s \right) = \vec{\nabla} \cdot (\kappa \vec{\nabla} T) + \frac{\eta}{2} (\nabla_i v_j + \nabla_j v_i - \frac{2}{3} \nabla_i v_l \delta_{lj})^2 + \zeta (\vec{\nabla} \cdot \vec{v})^2, \quad (5.3)$$

where s is the entropy per unit mass and κ the thermal conductivity. The boundary conditions are

$$T(y = \pm L/2) = T_0 \pm \Delta T/2$$

and zero velocity on the sides of the container. As before, we will think of the system as infinite in the x and z directions. A time-independent solution to Eqs. (5.1) to (5.3) satisfies the relations

$$\vec{v} = 0, \quad p = \text{const}, \quad \vec{\nabla} \cdot (\kappa \vec{\nabla} T) = 0. \quad (5.4)$$

Provided $(\partial \ln \kappa / \partial \ln T) \Delta T / T \ll 1$, we can neglect the temperature dependence of the thermal conductivity to solve the last equation and find

$$T = T_0 + \frac{\Delta T}{L} y. \quad (5.5)$$

Note that the condition $\Delta T / T \ll 1$ is equivalent to $L / L_\nabla \ll 1$ where $L_\nabla = (\nabla \ln T)^{-1}$.

B. Linearized equations for the fluctuations and density-density correlation functions

To simplify the analysis, we will again assume that the thermal expansion coefficient vanishes, i.e., $V^{-1}(\partial V / \partial T)_p = 0$. Water near 4°C, for example, satisfies that condition. This assumption will allow us to neglect the coupling of the sound wave to the energy diffusion mode. This is easiest to see in equilibrium. Then all the terms proportional to velocity drop out from the linearized form of (5.3) so that (5.1) and (5.2) are coupled to (5.3) only because

$$\delta p = \left(\frac{\partial p}{\partial \rho} \right)_s \delta \rho + \left(\frac{\partial p}{\partial s} \right)_\rho \delta s, \quad (5.6a)$$

$$\delta T = \left(\frac{\partial T}{\partial \rho} \right)_s \delta \rho + \left(\frac{\partial T}{\partial s} \right)_\rho \delta s. \quad (5.6b)$$

Hence (5.3) decouples from the other equations when $(\partial p / \partial s)_\rho = 0$ and $(\partial T / \partial \rho)_s = 0$. This is realized when $(\partial V / \partial T)_p = 0$ as can be seen from the thermodynamic identities

$$\left(\frac{\partial p}{\partial s} \right)_\rho = - \left(\frac{\partial p}{\partial \rho} \right)_s \left(\frac{\partial \rho}{\partial s} \right)_p = - \left(\frac{\partial p}{\partial V} \right)_s \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial T}{\partial s} \right)_\rho \quad (5.7)$$

and Maxwell's relation

$$\frac{1}{\rho^2} \left(\frac{\partial p}{\partial s} \right)_\rho = \left(\frac{\partial T}{\partial \rho} \right)_s, \quad (5.8)$$

In a temperature gradient $(\partial V/\partial T)_p = 0$ only on one layer $y = y_0$ of the system. Hence, to linear order in δT the modes become coupled. We will demonstrate that the effect of these couplings shows up only to quadratic order in δT in the density-density correlation function. The assumption $(\partial V/\partial T)_p = 0$ will thus allow us to completely neglect the coupling of the sound waves to the energy mode. Since we are only interested in the Brillouin peaks we do not believe that any essential physics is lost by looking at this mathematically much simpler problem. The effect of a temperature gradient on a diffusive mode, which we have studied in Sec. II, is much less pronounced than the $1/k^2$ effects we will find for the sound waves.

There could be some important physics lost, however, if we assumed that the sound velocity and viscosities were independent of temperature. The effect of their temperature dependence is potentially of the order of their logarithmic temperature derivative which in real fluids can be quite large compared with unity. In water near 4°C, for example, $(\partial \ln c^2/\partial \ln T) = 1.8$ and $(\partial \ln D_1/\partial \ln T) = -8.7$. When we consider these derivatives, there is no effect to first order in the gradients but this cannot be guessed *a priori*. A plausibility argument, however, will be given in Sec. VC. The difficulties will be analyzed in turn in the following subsections.

1. *Fluctuations when $\langle (\partial V/\partial T)_p \rangle_{av} = 0$, $(\partial c^2/\partial T)_p = 0$, and $(\partial D_1/\partial T)_p = 0$.* In the case when the average of $(\partial V/\partial T)_p$ over the system is zero the coupling of the energy mode to the other modes is proportional to δT , i.e., the linearized equations for the velocity and density will contain

terms proportional to δT times the entropy and the linearized equation for the entropy will contain terms proportional to δT times the density and velocity. Adding to Eqs. (5.2) and (5.3) the appropriate fluctuating heat flux and stress tensor¹⁸ we can solve for the density by substituting in the term proportional to δT times the entropy, the zeroth-order solution for the fluctuating hydrodynamic equations. Then it is not hard to see that the term proportional to δT times the entropy is now proportional to δT times the fluctuating Langevin heat flux since to zeroth order the entropy equation is independent of the others. It follows immediately that this term does not contribute to the density-density correlation function to first order in δT because the cross correlation between the fluctuating heat flux and fluctuating stress tensor (to which the density is proportional) vanishes to zeroth order in δT .¹⁸

We are left with the following equations for the Fourier transforms of the fluctuating mass density and velocity:

$$\begin{pmatrix} -i\omega & i\rho_0 \\ \frac{ic^2k^2}{\rho_0} & -i\omega + D_1k^2 \end{pmatrix} \begin{pmatrix} \delta\rho_k \\ \vec{k} \cdot \delta\vec{v}_k \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{i}{\rho_0} \vec{k} \cdot \vec{S}_k \cdot \vec{k} \end{pmatrix} \quad (5.9)$$

We have assumed that the average mass density ρ_0 is a constant to first order in δT . This follows from the fact that the average pressure is constant in Eq. (5.4) and from our assumption $(d\rho/dT)_p = 0$. From Eq. (5.9) we immediately obtain the density-density correlation function:

$$\langle \delta n_{k\omega} \delta n_{k'\omega'}^* \rangle = \frac{1}{m^2} \frac{\langle \vec{k} \cdot \vec{S}_k \cdot \vec{k} \vec{k}' \cdot \vec{S}_{k'}^* \cdot \vec{k}' \rangle}{(-\omega^2 + c^2k^2 - i\omega D_1k^2)(-\omega'^2 + c^2k'^2 + i\omega' D_1k'^2)}. \quad (5.10)$$

The correlation function of the fluctuating stress tensor follows from Eq. (4.8) with a parameter T which depends on position as in Eq. (2.17):

$$\begin{aligned} \langle \vec{k} \cdot \vec{S}_k \cdot \vec{k} \vec{k}' \cdot \vec{S}_{k'}^* \cdot \vec{k}' \rangle &= 2\pi\delta(\omega - \omega')(2\pi)^3 \left[2T_0\delta^3(\vec{k} - \vec{k}') + \frac{2\delta T}{2i} \left(\delta^3(\vec{k} - \vec{k}' - \vec{q}) - \delta^3(\vec{k} - \vec{k}' + \vec{q}) \right) \right] \\ &\times [2\eta(\vec{k} \cdot \vec{k}')^2 + (\zeta - \frac{2}{3}\eta)k'^2k^2]. \end{aligned} \quad (5.11)$$

Equations (5.10) and (5.11) are practically our final result. The reader may immediately skip to Sec. VC for their interpretation.

2. *Fluctuations when $\langle (\partial V/\partial T)_p \rangle_{av} = 0$, $(\partial c^2/\partial T)_p = 0$, and $(\partial D_1/\partial T)_p \neq 0$.* The continuity equation is unchanged but the equation for the velocity becomes

$$\begin{aligned} -i\omega\rho_0\vec{k} \cdot \delta\vec{v}_k &= -ic^2k^2\delta\rho_k - (\frac{4}{3}\eta + \zeta)k^2\vec{k} \cdot \delta\vec{v}_k \\ &- \frac{\delta T}{2i} \left(\frac{\partial\eta}{\partial T} [2\vec{k} \cdot (\vec{k} - \vec{q})(\vec{k} \cdot \delta\vec{v}_{k-q}) - \frac{2}{3}k^2(\vec{k} - \vec{q}) \cdot \delta\vec{v}_{k-q}] + \frac{\partial\zeta}{\partial T} k^2(\vec{k} - \vec{q}) \cdot \delta\vec{v}_{k-q} - (q \cdot -q) \right). \end{aligned} \quad (5.12)$$

The first term multiplying δT may be rewritten $(\partial\eta/\partial T)\{2\vec{k} \cdot (\vec{k} - \vec{q})[(\vec{k} - \vec{q}) \cdot \delta\vec{v}_{k-q} + \vec{q} \cdot \delta\vec{v}_{k-q}]\}$.

The transverse part of the last term, $\vec{q} \cdot \delta \vec{v}_{k-q}$, contributes only to order $\delta \bar{T}^2$. Hence we are left with

$(\partial \eta / \partial T) \{ 2 \vec{k} \cdot (\vec{k} - \vec{q}) [1 + \vec{q} \cdot (\vec{k} - \vec{q}) / |k - q|^2] (\vec{k} - \vec{q}) \cdot \delta \vec{v}_{k-q} \}$ which to linear order in q reduces to

$(\partial \eta / \partial T) [2k^2 (\vec{k} - \vec{q}) \cdot \delta \vec{v}_{k-q}]$. The equations we must solve are thus,

$$\begin{pmatrix} -i\omega & i\rho_0 \\ \frac{ic^2k^2}{\rho_0} & -i\omega + D_l k^2 \end{pmatrix} \begin{pmatrix} \delta \rho_k \\ \vec{k} \cdot \delta \vec{v}_k \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{i}{\rho_0} \vec{k} \cdot \vec{S}_k \cdot \vec{k} \end{pmatrix} - \frac{\partial D_l}{\partial T} \frac{k^2 \delta \bar{T}}{2i} \begin{pmatrix} 0 \\ (\vec{k} - \vec{q}) \cdot \delta \vec{v}_{k-q} - (\vec{k} + \vec{q}) \cdot \delta \vec{v}_{k+q} \end{pmatrix}. \quad (5.13)$$

If we define

$$\vec{k}_\pm = \vec{k} \pm \vec{q} \quad (5.14)$$

we can write the perturbative solution of Eq. (5.13) as follows:

$$\delta \rho_k = \frac{-i}{-\omega^2 + c^2 k^2 - i\omega D_l k^2} \left[i \vec{k} \cdot \vec{S}_k \cdot \vec{k} - \frac{\omega \partial D_l}{\partial T} k^2 \frac{\delta \bar{T}}{2i} \left(\frac{\vec{k}_- \cdot \vec{S}_{k_-} \cdot \vec{k}_-}{-\omega^2 + c^2 k_-^2 - i\omega D_l k_-^2} - \frac{\vec{k}_+ \cdot \vec{S}_{k_+} \cdot \vec{k}_+}{-\omega^2 + c^2 k_+^2 - i\omega D_l k_+^2} \right) \right]. \quad (5.15)$$

The correlation of the Langevin force can be found from Equation (4.8), recalling that the local temperature and viscosities must be used:

$$\begin{aligned} \langle \vec{k} \cdot \vec{S}_k \cdot \vec{k} \vec{k}' \cdot \vec{S}_{k'} \cdot \vec{k}' \rangle &= 2T_0 (\zeta + \frac{4}{3}\eta) k^4 2\pi \delta(\omega - \omega') (2\pi)^3 \delta^3(\vec{k} - \vec{k}') \\ &+ 2 \frac{\delta \bar{T}}{2i} \left[\left(1 + \frac{\partial \ln \eta}{\partial \ln T} \right) 2\eta (\vec{k} \cdot \vec{k}')^2 + \left(1 + \frac{\partial \ln(\zeta - \frac{2}{3}\eta)}{\partial \ln T} \right) (\zeta - \frac{2}{3}\eta) k^2 k'^2 \right] (2\pi) \delta(\omega - \omega') (2\pi)^3 \\ &\times [\delta^3(\vec{k} - \vec{k}' - \vec{q}) - \delta^3(\vec{k} - \vec{k}' + \vec{q})]. \end{aligned} \quad (5.16)$$

Note that for certain symmetrical choices of the variables k and k' , such as those we will be interested in, Eq. (5.16) simplifies considerably if we neglect terms of order q^2 as we will have to do eventually. For example,

$$\begin{aligned} \langle (\vec{k} + \vec{q}/2) \cdot \vec{S}_{k+q/2} \cdot (\vec{k} + \vec{q}/2) (\vec{k} - \vec{q}/2) \cdot \vec{S}_{k-q/2} \cdot (\vec{k} - \vec{q}/2) \rangle &\cong 2 \frac{\delta \bar{T}}{2i} \left(1 + \frac{\partial \ln(\zeta + \frac{4}{3}\eta)}{\partial \ln T} \right) \\ &\times (\zeta + \frac{4}{3}\eta) k^4 (2\pi) \delta(\omega - \omega') (2\pi)^3 \delta^3(0). \end{aligned} \quad (5.17)$$

To be able to write our results in a simpler form, we define

$$\begin{aligned} \vec{k}_\pm &= \vec{k} \pm \vec{q}/2, \\ D &= (-\omega^2 + c^2 k^2 - i\omega D_l k^2), \\ D_\pm &= (-\omega^2 + c^2 k_\pm^2 - i\omega D_l k_\pm^2). \end{aligned} \quad (5.18)$$

Then, from Eqs. (5.15) to (5.18) we find¹³

$$\begin{aligned} \langle \delta \rho_{k\omega} \delta \rho_{k\omega}^* \rangle &+ \langle \delta \rho_{k+q/2, \omega} \delta \rho_{k-q/2, \omega}^* \rangle + \langle \delta \rho_{k-q/2, \omega} \delta \rho_{k+q/2, \omega}^* \rangle \\ &= \frac{2T_0 (\zeta + \frac{4}{3}\eta) k^4}{DD^*} + \left\{ \frac{1}{D_+ D_-^*} 2(\zeta + \frac{4}{3}\eta) \frac{\delta \bar{T}}{2i} k^4 \left[1 - \frac{\partial \ln D_l}{\partial \ln T} \left(\frac{-i\omega D_l k_-^2}{D_-} + \frac{i\omega D_l k_+^2}{D_+^*} \right) + \frac{\partial \ln D_l}{\partial \ln T} \right] - (q + -q) \right\}. \end{aligned} \quad (5.19)$$

Using

$$\frac{1}{D_+ D_-^*} \cong \frac{1}{DD^*} + \frac{2i\omega^3 D_l \vec{k} \cdot \vec{q}}{(DD^*)^2}, \quad (5.20)$$

a few lines of algebra reveal that to linear order in $q\delta \bar{T}$ the terms proportional to $(\partial \ln D_l / \partial \ln T)$ drop out from Eq. (5.19) as we wanted to prove. Note that it was essential to include the temperature dependence of the viscosities in both the Langevin force correlation and the equations of motion.

3. *Fluctuations when* $\langle (\partial V/\partial T)_p \rangle_{av} = 0$, $(\partial c^2/\partial T)_p \neq 0$, and $(\partial D_1/\partial T)_p = 0$. Since we are working to linear order in $\delta\tilde{T}$, the effects of $(\partial c^2/\partial T)_p \neq 0$ and $(\partial D_1/\partial T)_p \neq 0$ on both the linearized hydrodynamic equations and the correlation functions are additive. In this section we consider the implications of $(\partial c^2/\partial T)_p \neq 0$. The linearized equations for the fluctuating quantities are given by (5.13) with the last term replaced by

$$\frac{-ik^2}{\rho_0} \frac{\partial c^2}{\partial T} \frac{\delta\tilde{T}}{2i} \begin{bmatrix} 0 \\ \delta\rho_{k-q} - \delta\rho_{k+q} \end{bmatrix}. \quad (5.21)$$

It is important to notice that the correct way of handling the gradient of the fluctuating pressure is to use Eq. (5.6a) to obtain

$$\vec{\nabla}\delta p = \vec{\nabla} \left[\left(\frac{\partial p}{\partial \rho} \right)_s \delta\rho \right] + \vec{\nabla} \left[\left(\frac{\partial p}{\partial s} \right)_\rho \delta s \right]. \quad (5.22)$$

This quantity is different from

$$\vec{\nabla}\delta p = \left(\frac{\partial p}{\partial \rho} \right)_s \vec{\nabla}\delta\rho + \left(\frac{\partial p}{\partial s} \right)_\rho \vec{\nabla}\delta s \quad (5.23)$$

when the thermodynamic derivatives are functions of position. Equation (5.23) is incorrect. One must apply thermodynamics locally to find the pressure fluctuations caused by mass density or entropy fluctuations *before* taking the gradient, or momentum conservation would be violated. Following the arguments presented in Sec. VB1 above, we have neglected the last term of Eq. (5.22) to obtain Eq. (5.21).

Following Sec. VB2, we finally obtain the analog of Eq. (5.19), which reads

$$\begin{aligned} & \langle \delta\rho_{k\omega} \delta\rho_{k\omega}^* \rangle + \langle \delta\rho_{k+q/2, \omega} \delta\rho_{k-q/2, \omega}^* \rangle + \langle \delta\rho_{k-q/2, \omega} \delta\rho_{k+q/2, \omega}^* \rangle \\ &= \frac{2T_0(\zeta + \frac{4}{3}\eta)k^4}{DD^*} + \left\{ \frac{1}{D_+D_-} \frac{2\delta\tilde{T}}{2i} (\zeta + \frac{4}{3}\eta)k^4 \left[1 - \left(\frac{\partial \ln c^2}{\partial \ln T} \right)_p \left(\frac{c^2 k_-^2}{D_-} + \frac{c^2 k_+^2}{D_+} \right) \right] - (q + -q) \right\}. \end{aligned} \quad (5.24)$$

By the argument given at the beginning of this subsection, to obtain Equation (5.24) we have used Equation (5.16) for the Langevin force correlation with $\partial \ln \eta / \partial \ln T = \partial \ln \zeta / \partial \ln T = 0$ (i.e., Equation (5.11)). In contrast with Sec. VB2, the temperature dependence of the sound velocity influences only the linearized hydrodynamic equations, not the Langevin force correlation. Using Equation (5.20) again, some algebra finally reveals that, to linear order in $q\delta\tilde{T}$, the term proportional to $(\partial \ln c^2 / \partial \ln T)_p$ drops out from Equation (5.24).

It is interesting to remark that to linear order in $\delta\tilde{T}$ again we have the following identity

$$\begin{aligned} & \langle \delta\rho_{k\omega} \delta\rho_{k\omega}^* \rangle + \langle \delta\rho_{k+q/2, \omega} \delta\rho_{k-q/2, \omega}^* \rangle + \langle \delta\rho_{k-q/2, \omega} \delta\rho_{k+q/2, \omega}^* \rangle \\ &= \frac{1}{c^4} [\langle \delta p_{k\omega} \delta p_{k\omega}^* \rangle + \langle \delta p_{k+q/2, \omega} \delta p_{k-q/2, \omega}^* \rangle + \langle \delta p_{k-q/2, \omega} \delta p_{k+q/2, \omega}^* \rangle], \end{aligned} \quad (5.25)$$

i.e., no terms proportional to $\partial c^2/\partial T$ appear even though the sound velocity depends on temperature (and hence on position). The analogous identity for fluctuations of the dielectric constant and density is essential to establish the relation between the scattering cross section and the density-density correlation function. Hence, Eq. (5.25) is essential to prove the experimental relevance of the calculations of this paper. This point is discussed further in Appendix A. The proof of Eq. (5.25) proceeds as follows. Using

$$\delta\rho(\vec{r}) = \frac{1}{c^2(\vec{r})} \delta p(\vec{r}) \quad (5.26)$$

and

$$\frac{1}{c^2(\vec{r})} = \frac{1}{c^2} + \frac{\partial(1/c^2)}{\partial T} [T(\vec{r}) - T_0] \quad (5.27)$$

and Eq. (2.17a) we obtain

$$\langle \delta\rho_k \delta\rho_k^* \rangle = \frac{1}{c^4} \langle \delta p_k \delta p_k^* \rangle + \frac{1}{c^2} \frac{\partial(1/c^2)}{\partial T} \frac{\delta\tilde{T}}{2i} (\langle \delta p_{k-q} \delta p_k^* \rangle - \langle \delta p_{k+q} \delta p_k^* \rangle + \langle \delta p_k \delta p_{k+q}^* \rangle - \langle \delta p_k \delta p_{k-q}^* \rangle). \quad (5.28)$$

Using this result, Eq. (5.25) follows to linear order in $\delta\tilde{T}$ if we also recall that $\langle p_{k+q} p_k^* \rangle$, for example, is of order $\delta\tilde{T}$.

C. Expansion parameters and interpretation of the results and conditions for observability

Our final result can now be obtained from either Eqs. (5.10) and (5.11) or (5.19) or (5.24). To first order in $q\delta\tilde{T}$,

$$\langle \delta n_{k\omega} \delta n_{k\omega}^* \rangle + \langle \delta n_{k+q/2, \omega} \delta n_{k-q/2, \omega}^* \rangle + \langle \delta n_{k-q/2, \omega} \delta n_{k+q/2, \omega}^* \rangle$$

$$= \left(\frac{Tn}{mc^2} \right) c^2 k^2 \left(\frac{2D_1 k^2}{(\omega^2 - c^2 k^2)^2 + (\omega D_1 k^2)^2} - \frac{4\omega^2 (\omega D_1 k^2) D_1 \vec{k} \cdot (\vec{\nabla} \ln T)_{y=0}}{[(\omega^2 - c^2 k^2)^2 + (\omega D_1 k^2)^2]^2} \right) \quad (5.29)$$

$$\cong \left(\frac{Tn}{mc^2} \right) \left(\frac{D_1 k^2 / 2 [1 - \epsilon(\vec{k}, \omega)]}{(\omega - ck)^2 + (\frac{1}{2} D_1 k^2)^2} + \frac{D_1 k^2 / 2 [1 + \epsilon(\vec{k}, \omega)]}{(\omega + ck)^2 + (\frac{1}{2} D_1 k^2)^2} \right), \quad (5.30)$$

where

$$\epsilon(\vec{k}, \omega) = \frac{c}{D_1 k^2} \hat{k} \cdot \vec{\nabla} \ln T \left(\frac{2(\omega D_1 k^2)^2}{(\omega^2 - c^2 k^2)^2 + (\omega D_1 k^2)^2} \right). \quad (5.31)$$

To be able to expand $(D_+ D_-)^{-1}$ we had to assume that (see also Sec. II)

$$\left| \frac{c \hat{k} \cdot \vec{q}}{D_1 k^2} \right| \ll 1. \quad (5.32)$$

Note that $\vec{q} = \vec{\nabla} \ln T$.⁷ Equation (5.32) is implied by the more stringent condition that the phonon mean free path l at the $\vec{k}$ in question satisfy $l \ll L$ while $L \ll L_V$. These restrictions were discussed in Sec. II. Hence, generalizing the theory to the regime $|c \hat{k} \cdot \vec{q} / D_1 k^2| > 1$ does not only involve keeping higher-order terms in $q \delta T$. It also involves at least taking boundary conditions into account in the linearized equations for the fluctuations.¹⁹

If one includes the spatial variation of the sound velocity it might be argued that one of our expansion parameters is

$$\left| \frac{\vec{\nabla} c |Lk|}{D_1 k^2} = \frac{\partial \ln c}{\partial \ln T} (kL) \left(\frac{c |\vec{\nabla} \ln T|}{D_1 k^2} \right) \right| \ll 1. \quad (5.33)$$

This expansion parameter has been proposed by Kirkpatrick *et al.*²⁰ and it represents "the ratio of the magnitude of the broadening of the Brillouin line due to the gradient in the scattering volume $L |\vec{\nabla} c| k$ to the width of the Brillouin lines $D_1 k^2$."²⁰ Kirkpatrick *et al.* agree that the effect of $\vec{\nabla} c$ does not influence the result to linear order but their point is that the expansion parameter is as given above and it must be small for the perturbation series to make sense. In our case, if the terms proportional to $(\partial \ln c / \partial \ln T)$ had not dropped out from Eq. (5.24) then we would have found corrections of order

$$\frac{\partial \ln c^2}{\partial \ln T} \frac{c \hat{k} \cdot \vec{\nabla} \ln T}{D_1 k^2}. \quad (5.34)$$

Hence, we are inclined to think that (5.34) is the expansion parameter involved when taking the position dependence of the sound velocity into account. But we cannot rule out (5.33).

As in Sec. IV [see the discussion accompanying Eq. (4.23)], a physical interpretation to Eq. (5.30) can be found. This equation says that for $\vec{k}$ along $\vec{\nabla} T$ there are more sound waves with wave vector $-\vec{k}$ absorbed ($\omega = -ck$) than sound waves with wave vector $+\vec{k}$ emitted ($\omega = ck$). If we recall that there is a heat flux in the direction $-\vec{\nabla} T$ the effect becomes clear. We can even estimate the magnitude of the effect by a kinetic-theorylike argument (see Fig. 3). The number of sound waves absorbed or emitted is proportional to the temperature. Consequently, there is an excess of sound waves coming from one mean free path l away if they come from a warmer region. We can estimate this excess as $\delta T / T = (\nabla T l) / T = |\hat{k} \cdot \vec{\nabla} \ln T c / D_1 k^2|$. The sign of the effect follows from the previous arguments.

This last result is consistent with Eqs. (5.29)–(5.31). The correction to the equilibrium result is odd in frequency, hence, to estimate the difference in intensity of the peaks, we proceed as follows: Define I_V to be the integral of Eqs. (5.29) or (5.30) multiplied by ω / ck and I , the integral over frequency of the equilibrium line shape. Then we find

$$\frac{\Delta N}{N} = \frac{I_V}{I} = - \frac{c \hat{k} \cdot \vec{\nabla} \ln T}{D_1 k^2}. \quad (5.35)$$

The minus sign comes from the fact that when $\vec{k}$ is along $\vec{\nabla} T$ it is the absorption peak ($\omega = -ck$) which is enhanced compared with the emission peak.

Note that I_V is related to an equal-time longitudinal momentum density correlation function. Indeed, using the linearized continuity Eq. (5.1) we have, to first order in q ,

$$\frac{\omega}{k} \langle \langle n_{k\omega} n_{k\omega}^* \rangle + \langle n_{k+q/2, \omega} n_{k-q/2, \omega}^* \rangle + \langle n_{k-q/2, \omega} n_{k+q/2, \omega}^* \rangle \rangle$$

$$= \frac{n_0}{m} \langle \langle m v_{k\omega} n_{k\omega}^* \rangle + \langle m v_{k+q/2, \omega} n_{k-q/2, \omega}^* \rangle + \langle m v_{k-q/2, \omega} n_{k+q/2, \omega}^* \rangle \rangle. \quad (5.36)$$

Using Eqs. (5.36) and (5.29) and integrating over frequency we find

$$\langle m v_k(t) n_k^*(t) \rangle + \langle m v_{k+q/2}(t) n_{k-q/2}^*(t) \rangle + \langle m v_{k-q/2}(t) n_{k+q/2}^*(t) \rangle = - \frac{T}{D_1 k^2} \hat{k} \cdot \vec{\nabla} \ln T \equiv \chi_{mv, n}. \quad (5.37)$$

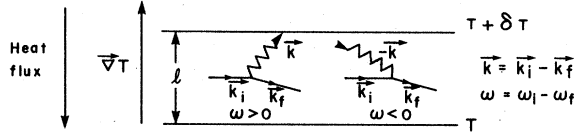


FIG. 3. Scattering processes in a slab of fluid of size l equal to the mean free path ($c/D_1 k^2$) (see also Fig. 1). For $\vec{\nabla}T$ in the upward direction, there are more processes with $\omega < 0$ than processes with $\omega > 0$ because the heat flux is directed downward, i.e., has a positive component along the direction $-\vec{k}$.

Note that this static correlation function can also be computed directly from Eq. (3.5). In equilibrium, the momentum-density correlation function vanishes by time-reversal symmetry. Here, this symmetry is broken by the presence of the fixed external perturbation. Note that in the case of the shear flow, time-reversal symmetry is also broken but the equal-time momentum-density correlation function nonetheless vanishes. It would not be correct either to conclude that an asymmetric density-density correlation function immediately implies that time-reversal symmetry is broken: This is not true in quantum mechanics and it can be false as well in classical systems which are not translationally invariant and where we cannot simply use $\vec{k}$ to replace the divergence operator. What is true is only that $\langle mv(\vec{r}, t) n(\vec{r}', t) \rangle \neq 0$ in classical systems implies that the time-reversal symmetry is broken.

It is interesting to note that the relation of the asymmetric term in (5.30) to the equal-time momentum-density correlation function $\chi_{mv, n}$ allows us to give a plausibility argument as to why the asymmetry is independent of $\partial \ln D_1 / \partial \ln T$ and $\partial \ln c^2 / \partial \ln T$. As can be seen from Eqs. (5.19) and (5.24), if these terms had remained in (5.30), they would have led to an additional contribution to the equal-time momentum-density correlation function proportional to

$$-\frac{T}{D_1 k^2} \hat{k} \cdot \vec{\nabla} \ln T \frac{\partial \ln D_1}{\partial \ln T} = -\frac{T}{D_1 k^2} \hat{k} \cdot \vec{\nabla} \ln D_1$$

or

$$-\frac{T}{D_1 k^2} \hat{k} \cdot \vec{\nabla} \ln T \frac{\partial \ln c^2}{\partial \ln T} = -\frac{T}{D_1 k^2} \hat{k} \cdot \vec{\nabla} \ln c^2.$$

Imagine now an equilibrium fluid, in perhaps an external potential, for which D_1 and c^2 vary in space. The calculations of Secs. VB2 and VB3 could be repeated (with uniform temperature) and must yield $\chi_{mv, n} = 0$ by time-reversal symmetry. The same cancellations between gradients of D_1 and c^2 in the hydrodynamic equations and Lange-

vin forces should continue to hold out of equilibrium when $\nabla \ln D_1$ and $\nabla \ln c^2$ are due to $\nabla \ln T$ instead of to an external field. What cannot be guessed from this argument is whether $\nabla \ln c^2$ and $\nabla \ln D_1$ lead to asymmetries in the detailed line shape which integrate out to zero in $\chi_{mv, n}$.

As in Sec. IV, the physical arguments used in this section "explain" the result but they do not demonstrate why we did not obtain a Lorentzian line shape as we would naively expect from the simple picture of sound waves as elementary excitations. It would thus be extremely interesting to resolve experimentally the line shape predicted by Eq. (5.29). However, as discussed in Appendix A and in (2.19), the experimental result is really an integral of Eq. (5.29) over a bandwidth δk proportional to the inverse of the scattering volume (which cannot be larger than the system size). The main effect of this integral is to add up line shapes of the form (5.29) whose maxima fall within a frequency interval $c \delta k$. If that interval is larger than the intrinsic linewidth $D_1 k^2$, then the line shape (5.29) cannot be resolved experimentally. The condition for observability is thus,

$$\frac{c \delta k}{D_1 k^2} < 1. \quad (5.38)$$

Note that this condition is also required for the resolution of Brillouin peaks at equilibrium.

Since $1/L_\nabla < 1/L$ and $1/L \lesssim \delta k$, we have

$$\left| \frac{c \nabla \ln T}{D_1 k^2} \right| < \frac{c \delta k}{D_1 k^2} < 1. \quad (5.39)$$

At a given scattering angle, to have the largest possible magnitude of the asymmetry consistent with the above string of inequalities, one would try to use a fluid which exists at low temperature where L can be made as close as possible to L_∇ ($\nabla \ln T \sim \Delta T / TL$) consistent with $L < L_\nabla$. One would also try to make δk as close as possible to $1/L$ while remaining one mean free path from the boundaries. We expect that it will be hard to see detailed line shapes and sizable asymmetries at the same time. Nevertheless, the integrated value of the symmetry itself [Eq. (5.35)] may be observed even if $c \delta k / D_1 k^2 \gg 1$ (as long as the other restrictions $l/L \ll 1$, $L \ll L_\nabla$, are satisfied). In that case, Eq. (5.29) is effectively a sum of two delta functions, when looked at on the scale on which the weighting functions in Eqs. (2.19) or (A14) vary. Hence the line shapes are entirely determined by geometrical effects but their intensities are proportional to those of Eq. (5.29). Figure 4 illustrates the above remarks with "realistic" parameters for a light scattering experiment.

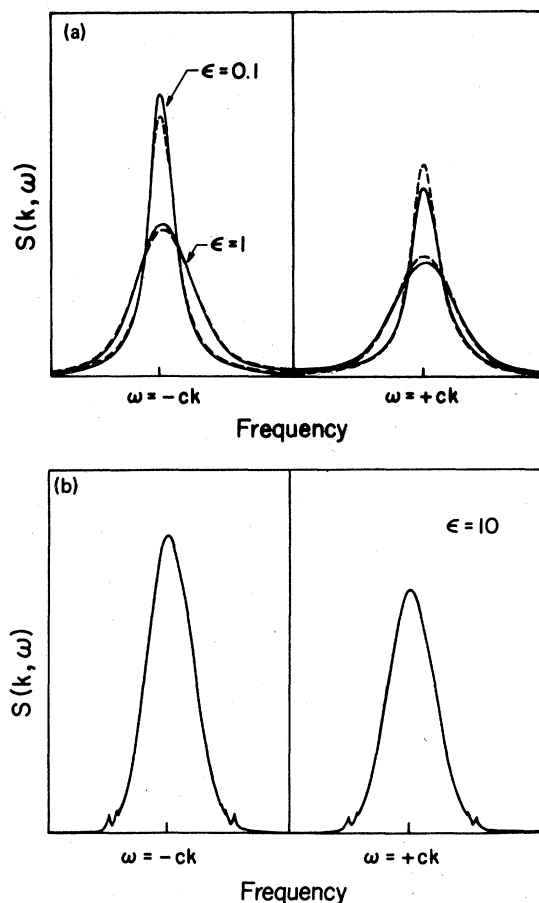


FIG. 4. The observed spectrum for a purely Lorentzian Brillouin peak (dashed) and our line shape (solid) was calculated for three values of $\epsilon = c\delta k/D_1 k^2$ by superimposing many lines with Gaussian-distributed peak centers (width of Gaussian is width of laser line). Owing to sharpness of peaks, only a narrow frequency box about $\omega = \pm ck$ is plotted. For $\epsilon = 0.1, 1$, the width of the box is $10^{-3}ck$; for $\epsilon = 10$, it is $10^{-2}ck$. The vertical scale for $\epsilon = 10$ is also $\frac{1}{20}$ that for $\epsilon = 0.1, 1$. Values for transport coefficients are roughly those for water near 4°C : $c = 1.42 \times 10^5$ cm/sec, $D_1 = 2.09 \times 10^{-2}$ cm²/sec. k was chosen as 852 cm⁻¹ which is the value obtained for a scattering angle of 10 mrad and $\lambda = 4880$ Å.

VI. CONCLUSION

A. Summary

Hydrodynamic nonequilibrium steady states can be characterized as states where the effect of the external perturbation can be taken into account through its modification of the local thermodynamic equilibrium parameters. The first step of the problem is dynamical: It consists of (a) solving the full nonlinear hydrodynamic equations subject

to the externally imposed stresses and boundary conditions to find the steady-state values of the thermodynamic parameters and (b) linearizing the equations of motion for the fluctuations about the steady state.

The second step of the problem is statistical. One assumes that the linearized equations of motion are driven by a stochastic Langevin force whose correlations are delta functions in space and time as in equilibrium with proportionality constants determined by the local values of the thermodynamic parameters. By analogy with the equilibrium result, one can think that the stochastic force explores phase space around the steady state with a sort of equal *a priori* probability consistent with the externally imposed constraints.

The above method has been physically justified in Sec. II. Appendices B and C also presented a microscopic calculation for a simple model which agrees with the Langevin method and thus provides additional support for the theory. We cannot over-emphasize that our Langevin method is probably restricted to states for which the local values of the thermodynamic quantities and transport coefficients provide a complete description. This restriction can perhaps be best understood by giving a counter example. Consider again a system of electrons scattering off impurities to which a potential difference is applied. In the steady state, a temperature gradient is set up which carries away the Joule heat. The current fluctuations to second order in the applied voltage should reflect the existence of both the applied voltage and the temperature gradient.²¹ A naive application of the Langevin formalism would lead to a qualitatively correct answer but would be off by a factor of $\pi^2/9$. One could think that, in general, the Langevin method will always be qualitatively correct but there is no way that we can know in advance and one should be cautious not to apply blindly the results of the present paper to arbitrary nonequilibrium problems.

B. Comparison with the work of others

Our theory depends upon the assumption that the Landau-Lifshitz theory of hydrodynamic fluctuations is valid not only in the linear regime for fluctuations about global equilibrium but also for linear fluctuations about *local* equilibrium (hence in a sense in the nonlinear regime). The work of Keizer²² supports this assumption. Hinton²³ has tried to justify Langevin theory near local equilibrium using a kinetic approach. Interestingly enough, he has concluded that the momentum-density correlation function would vanish in general contradicting our results.²⁴ More recently, Onuki²⁵

has examined fluctuations in inhomogeneous nonequilibrium systems and arrived from microscopic considerations at equal-time correlation functions which are long ranged in space [$1/k^2$ dependence in Fourier space; see his Eqs. (108) and (109)]. He mentioned that the same result could be found from nonlinear fluctuating hydrodynamics. Onuki made no mention of experimental consequences of his theory. Even more recently, Ueyama²⁶ has presented a derivation of nonlinear fluctuating hydrodynamics from a master equation. The reader is also referred to this paper for some references to earlier work on Boltzmann-Langevin equations and the derivation of fluctuating hydrodynamics in the linear and nonlinear regimes. Reference 27 contains some references to the Russian literature. Our point of view is that the assumptions made at the kinetic stage are essentially equivalent to those made at the hydrodynamic level and they are not always more physically justified. Sometimes, however, a kinetic derivation is indeed satisfying and necessary.

We already mentioned that our interest in the problems of Secs. IV and V was stimulated by the work of the M.I.T. group. Their first published results on the problem of Sec. V were essentially identical to Eqs. (5.29)–(5.31), except that the quantity in large parentheses in Eq. (5.31) was replaced by unity. Hence, their line shapes were Lorentzian and they differed by a factor of two with the predictions of Eqs. (5.29)–(5.31) for the maximum height difference of the peaks. Their nonequilibrium effects vanished like ω^{-3} at high frequencies while ours behave like ω^{-5} . On the other hand, the intensity of the lines, which can be estimated from Eq. (5.37), was identical to ours.²⁸ Working independently, the Rockefeller-Maryland collaboration³ published shortly thereafter a rather different result with a non-Lorentzian line shape and an asymmetry depending on $\partial \ln D_i / \partial \ln T$ and other similar parameters. Stimulated by these papers, we performed calculations which gave results⁴ identical to those obtained simultaneously²⁰ by the Rockefeller-Maryland group. New calculations of Ronis (and Puterman)²⁹ and Oppenheim³⁰ of the M.I.T. group also agree with Rockefeller-Maryland and us. Some simultaneous work by van der Zwan and Mazur³¹ destroys, however, the unanimity. As the present paper was being typed we learned of calculations by Grabert³² and Dufty³³ which basically confirm Eqs. (5.29)–(5.31). Finally, a paper by Kirkpatrick and Cohen³⁴ just came out. They claim to have extended the theory beyond its present range of validity.

The recent activity in this area has considerable history. According to the review in the book

of Fabelinskii,³⁵ Mandel'shtam³⁶ first proposed to look at the sound wave spectrum in a temperature gradient as early as 1934. Theoretical calculations were performed by Leontovich in 1939.³⁷ It was suggested that one could measure the sound damping constant by measuring how much the spectrum in a temperature gradient changed as a function of the distance of the scattering volume from the boundary. Experiments on quartz were carried out by Landsberg and Shubin.³⁸ They saw no effect attributable to the temperature gradient. This allowed them to set a lower bound on the value of the sound damping constant. Vladimirsii³⁹ in 1940 even proposed that the asymmetry in the Brillouin doublet [which he correctly found to be given by Eq. (5.35)] be used to measure the sound damping constant which was still the quantity of interest at the time (detailed line shapes could not be resolved). We do not know if the experiment was ever attempted.

Later, Griffin⁴⁰ (1968) considered this problem more microscopically using the Boltzmann equation in a solid with the purpose of devising a method to obtain experimentally the phonon lifetime for momentum nonconserving processes directly. (The usual linewidths are given by a combination of momentum conserving and nonconserving processes.) All of the theories from 1934 until now seem to be based on the assumption that the phonons carry the energy flux caused by the temperature gradient. This is true for phonons in the kinetic (high-frequency) regime but, in the linear approximation, not for hydrodynamic sound waves. (Note that in the quadratic approximation, sound waves do carry energy.⁴¹) Hence, Griffin concluded⁴⁰ that the asymmetry in the Brillouin peaks would not show up in the hydrodynamic regime. We disagree with his conclusion. Even if the slightly loose physical analogies of Secs. IV and V may have led the reader to believe that it is essential that the thermal sound waves carry energy for our results to apply, we believe instead that the essential ingredient for our theory is that the generation rate of thermal sound waves be proportional to the local temperature. Then at a given point, there will be more sound waves coming from one direction than the other because these sound waves can propagate for one mean free path. It is interesting to note that in the kinetic regime, the formula for the asymmetry is identical to that of the hydrodynamic regime as long as the correspondence between mean free paths is made.

The problem of Brillouin scattering in a shear flow, on the other hand, has been investigated first apparently by Machta *et al.*¹⁶ Their results were qualitatively the same as ours but the quanti-

ty in large parentheses in Eq. (4.20) was replaced by $1 - \hat{k} \cdot \vec{\nabla} \hat{v}_0 \cdot \hat{k} / D_1 k^2$. Again, this implies they had a Lorentzian line shape which differs by a factor of two at $\omega = \pm ck$ but leads to the same integrated intensity as (4.20). The results of Kirkpatrick *et al.*²⁰ on this problem are identical to ours.

We should now discuss the different calculational techniques used by the various groups. The M.I.T. group proposed an ensemble which we discuss in Appendix B. In the relevant limit, the ensemble we use in Appendix C to perform a microscopic calculation reduces to that of the M.I.T. group. In their formalism, the nonequilibrium correlation functions are expressed in terms of higher-order equilibrium correlation functions. Contrary to what we do in Appendix C, the equilibrium correlation functions are not evaluated microscopically but instead some sort of Onsager regression hypothesis ("justified" by projection operator methods) is used. In our view, this formalism obscures certain aspects of the phenomena. For example, it is not clear how the temperature dependence of the transport coefficients is taken into account (although it probably is). The physical hypotheses which have to be made are simply hidden in assumptions about the projection operators and about the slow or fast decay of correlation functions. The reason for the discrepancy between the original M.I.T. calculation and the currently accepted result is, according to Oppenheim³⁰ and Ronis,²⁹ that some of the correlation functions which were assumed first to decay fast, in fact, decay slowly due to mode-coupling terms.

Independent of the method of calculation, we believe that the connection between an experimental measurement and a correlation function must be carefully established. For example, in Ref. 2 it was assumed that the measured density-density correlation function could be found from Fourier transforming $\langle n(\vec{r}, \omega) n(\vec{r}', -\omega) \rangle$ with respect to $(\vec{r}' - \vec{r})$ keeping $\vec{r}$ fixed. This leads to the conclusion, for example, that one could measure an imaginary correlation function (corresponding to an imaginary cross section⁴²). The later work of Ronis and Putterman,²⁹ which like ours is based on fluctuating hydrodynamics, avoids the imaginary contributions by keeping $(\vec{r} + \vec{r}')/2$ fixed instead of $\vec{r}$. We believe the correct procedure is that of Appendix A.

We note parenthetically that in the M.I.T. formalism it is apparently clear that the origin of the long-range spatial correlation in the equal-time correlation function is the same as that of the long-time tails⁴³ in equilibrium. In fluctuating hydrodynamics, it is easy to see that the term which leads to the effect of Sec. IV is $\vec{v} \cdot \vec{\nabla} \vec{v}$ which is indeed the same term as that which leads to

long-time tails in equilibrium. For the problem of Sec. V, however, it is not clear whether there is a direct relation to long-time tails although the temperature gradient does couple a density mode of wave vector $\vec{k} + \vec{q}/2$ to one with wave vector $-\vec{k} + \vec{q}/2$.

The work of Kirkpatrick *et al.*^{3,20} is based at least partly on kinetic theory. In their second paper, they took into account the relation between correlation functions and measured quantities. With kinetic theory, one could in principle go continuously from the considerations of Griffin⁴⁰ concerning phonons in solids to the results for sound waves in the hydrodynamic regime. In practice, however, we suspect that the calculation in the intermediate regime would be prohibitively difficult. In the hydrodynamic regime, the kinetic-theory approach is not very convenient and, in fact, in the second paper of Kirkpatrick *et al.*²⁰ it seems that other methods (Kadanoff-Swift mode-coupling theory) have been used for at least part of the calculations. The calculation of Dufty,³³ on the other hand, has been done completely in the kinetic-theory framework. Grabert³² used Fokker-Planck methods which are equivalent to the Langevin method when the random force is assumed to be Gaussian. He also obtained interesting new formal results. Finally, van der Zwan and Mazur³¹ used fluctuating hydrodynamics like us but they arrived to different conclusions. Their results contain, for example, terms proportional to $\partial \ln c^2 / \partial \ln T$.

C. Open problems

As the present paper was being completed, the results of an experiment by Beysens *et al.*⁴⁴ came out. They report an asymmetry in the Brillouin spectrum of a fluid in a temperature gradient. The magnitude of the effect is in agreement with the functional form (5.35) except for an overall numerical factor of about one-third. It would be easier to compare experiment with theory if the sound wave mean free path at the measured scattering angle was much smaller than the system size as all theories have assumed. Hence, it would be valuable to repeat the experiment in more "ideal" conditions even though the fact that the observed effect is somewhat smaller than the predicted one is consistent with a wall effect. Another very important but perhaps even more difficult experiment would measure the detailed line shape in either a temperature gradient or shear flow to confirm both the exact magnitude of the effect and the factor of two difference at the extrema between the "true" result and the Lorentzian prediction. Section VC discussed in

detail the conditions for observability.

The non-Lorentzian line shape of the spectrum is somewhat surprising when one thinks of sound waves as elementary excitations. But sound waves are *not* elementary excitations of the system. For phonons in the kinetic regime, however, it would be quite natural to expect a Lorentzian. Griffin⁴⁰ in his 1968 work did not answer that question and left open the possibility that even for elementary excitations the line shape would be non-Lorentzian.

The above question is related to that of the existence of transportlike equations for sound waves. Since in the usual transport equations one integrates out one of the energy variables (ω or $p^2/2m$) such equations do not give the details of the line shape. Hence they would be appropriate to calculate the magnitude of the line intensity [e.g., Eqs. (4.23) or (5.35)]. Such equations can be written phenomenologically and may lead to results similar to ours.^{45, 46} Appendix 2 of a paper by Andreev and Meierovich⁴⁷ shows how one of the transport equations was derived.

Finally, what about the full probability distribution for fluctuations. We have computed only correlation functions. In equilibrium one usually assumes that the Langevin forces obey Gaussian statistics. Then automatically the distribution function for the fluctuating mass, momentum or energy densities also obey Gaussian statistics since the equations relating these quantities to the Langevin forces are linear. The same statements apply to the nonequilibrium situations we have looked at.⁴⁸ In equilibrium, however, the form of the Gaussian distribution for the equal-time correlation function can be derived from thermodynamic⁴⁹ considerations following well-known arguments of Einstein.¹⁰ Out of equilibrium this cannot apparently be done in general since, for example, in the shear-flow case, the equal-time density-density correlation function contains a term $-\hat{k} \cdot \nabla \hat{v}_0 \cdot \hat{k}/D_1 k^2$ which involves a dissipative quantity D_1 and hence contains information about the dynamics of the system which cannot be inferred from thermodynamics. We know of no general principle which would allow us to guess equal-time correlation functions out of equilibrium.

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APPENDIX A: CORRELATION FUNCTION MEASURED IN A LIGHT SCATTERING EXPERIMENT ON A NONEQUILIBRIUM STEADY STATE

The reader is referred to the text surrounding Eq. (2.19) for a qualitative summary of the results to be derived in this appendix. We follow closely the conventional derivation for light scattering from fluctuations in an equilibrium fluid.⁵⁰ From Maxwell's equation, one finds the field $\vec{E}_s(\vec{R}, t)$ scattered from a fluctuation $\delta\vec{\epsilon}(\vec{r}, t')$ of the dielectric tensor of the medium (c.g.s. units):

$$\vec{E}_s(\vec{R}, t) = \nabla \times \nabla \times \left(\frac{1}{4\pi\epsilon_0} \int_V d^3r \frac{1}{|\vec{R} - \vec{r}|} [\delta\vec{\epsilon}(\vec{r}, t') \cdot \vec{E}_i(\vec{r}, t')] \right). \quad (A1)$$

$\vec{E}_i$ is the incident electric field and the detector is assumed to be immersed in a medium of dielectric constant ϵ_0 . Note that $t' \equiv t - |\vec{R} - \vec{r}| \sqrt{\epsilon_0}/c$ is the retarded time and that the integral is restricted to V the volume of the scattering medium.

We assume that the incident electric field can be written as follows⁵¹:

$$\vec{E}_i(\vec{r}, t) \equiv \vec{n}_i E_0(\vec{r}) e^{i(\vec{k}_i \cdot \vec{r} - \omega_i t)}, \quad (A2)$$

where $\vec{n}_i$ is a polarization vector and $E_0(\vec{r})$ a slowly varying function of position which determines the shape of the incident beam. We neglect the spread in frequency of the incident beam. As usual, it must be much smaller than the frequency shifts we intend to measure. Evaluating Eq. (A1) for large R and assuming, as in equilibrium, that the change in magnitude of the wave vector $\vec{k}_i$ due to scattering is negligible, we obtain

$$\vec{E}_s(\vec{R}, \omega_f) = -\vec{k}_f \times \vec{k}_i \times \left(\frac{e^{i\vec{k}_f \cdot \vec{R}}}{4\pi\epsilon_0 R} \int dt e^{i(\omega_f - \omega_i)t} \int_V d^3r \delta\vec{\epsilon}(\vec{r}, t) \cdot \vec{n}_i E_0(\vec{r}) e^{-i(\vec{k}_f - \vec{k}_i) \cdot \vec{r}} \right). \quad (A3)$$

In this equation $\vec{k}_f = |\vec{k}_i| \vec{R} / |\vec{R}|$. Note also that we have computed the Fourier component ω_f of (A1) because the signal measured using filtering techniques in a light scattering experiment is proportional to $|\vec{E}_s(\vec{R}, \omega_f)|^2$.⁵²

In general, the detector will not see a single Fourier component $\vec{k}_f$ because of the collection optics. This can be accounted for by multiplying $E_0(\vec{r})$ in the integrand of Eq. (A3) by another function of $\vec{r}$, say $E_1(\vec{r})$, which is determined by a classical diffraction problem.⁵¹ We define $E_2(\vec{r}) \equiv E_0(\vec{r})E_1(\vec{r})$.

Computing $|\vec{E}_s(\vec{R}, \omega_f)|^2$, we find that the quantity of interest is proportional to

$$I = \int dt \int dt' \int_V d^3\vec{r} \int_V d^3\vec{r}' e^{-i\vec{k} \cdot (\vec{r}-\vec{r}') + i\omega(t-t')} E_2(\vec{r}) E_2(\vec{r}') \langle \delta n(\vec{r}, t) \delta n(\vec{r}', t') \rangle \quad (A4)$$

where $\vec{k} \equiv \vec{k}_i - \vec{k}_f$ and $\omega \equiv \omega_i - \omega_f$. Note that we made the usual assumption that the fluctuations in dielectric constant are mainly due to density fluctuations. To second order in the external temperature gradient, the thermodynamic derivative $(\partial \epsilon / \partial n)_T$ and all other proportionality constants can be evaluated at the average temperature, density, etc. The proof of this statement is analogous to that of Eq. (5.25). It is given in Eqs. (5.26)–(5.28) and will not be repeated here.

Using the expression for the Fourier transform of the correlation function appearing in Eq. (A4), we obtain

$$I = \int_V d^3\vec{r} \int_V d^3\vec{r}' \int \frac{d^3\vec{p}}{(2\pi)^3} \int \frac{d^3\vec{p}'}{(2\pi)^3} \int dt dt' \int \frac{d\nu}{2\pi} \int \frac{d\nu'}{2\pi} E_2(\vec{r}) E_2(\vec{r}') e^{-i(\vec{k}-\vec{p}) \cdot \vec{r} + i(\vec{k}+\vec{p}') \cdot \vec{r}' + i(\omega-\nu)t - i(\omega+\nu')t'} \langle n_{p\omega} n_{p'\omega'} \rangle. \quad (A5)$$

For simplicity, we will assume that the functions $E_2(\vec{r})$, $E_2(\vec{r}')$, and the restriction to the integration volume lead to integrals over a rectangular region of size $2L_1$, $2L_2$, $2L_3$. This assumption is made for simplicity. It is not much harder to handle analytically a Gaussian form for E_2 such as was used in the calculations that led to Fig. 4.

With the assumption of a rectangular integration region, Eq. (A5) becomes

$$I = 64 \int \frac{d^3\vec{p}}{(2\pi)^3} \int \frac{d^3\vec{p}'}{(2\pi)^3} \prod_{i=1}^3 \left(\frac{\sin(p-k)_i L_i}{(p-k)_i} \right) \prod_{j=1}^3 \left(\frac{\sin(p'+k)_j L_j}{(p'+k)_j} \right) \langle n_{p\omega} n_{p'\omega'} \rangle. \quad (A6)$$

The quantities in large parentheses are proportional to delta functions in the limit $L_i \rightarrow \infty$. Equation (A6) [see also (2.19)] has a simple physical interpretation: It represents the fact that due to the finite size of the system and the laser beam, the measured quantity is an average of correlation functions $\langle \delta n(\vec{p}) \delta n(\vec{p}') \rangle$ over a finite bandwidth $\delta p = \delta p'$ centered around $\vec{p}$ and $\vec{p}'$ equal $\vec{k}$. This effect is present in equilibrium as well.

The choice of the ensemble to evaluate the correlation function in Eq. (A6) has been discussed in Sec.

II. Following Eq. (2.17) we assume that

$$T(\vec{r}) = T_0 + \delta \tilde{T} \sin(\vec{q} \cdot \vec{r}). \quad (A7)$$

Equation (A4) makes more explicit the fact that we always need $r_i \leq L_i$ and hence that if $q_i^{-1} \gg L_i$ then the linear approximation to Eq. (A7) is valid. Consequently, we keep Eq. (A7) in the explicit calculations but at the end we retain only the term linear in q . Appendices B and C clarify the analogy between this procedure and that which is often used to do quantum-mechanical perturbation theory on bulk systems: For example, a constant electric field $\vec{E}$ applied to a system can be represented by a scalar potential having a Fourier component $\tilde{\phi} e^{i\vec{q} \cdot \vec{r} - i\nu t}$ where the limits $\nu \rightarrow 0$ and $\vec{q} \rightarrow 0$ are taken only at the end of the calculation. Only the combination $i\vec{q} \cdot \vec{r} = \vec{E}$ should appear in the final answer. Here, since $r \ll q^{-1}$ only the combination $\vec{q} \cdot \vec{r}$ [standing for $\vec{\nabla} T(\vec{r}=0)$] will appear in the final answer.

Using Eq. (A7) and the properties that it implies for the ensemble [see Eqs. (2.15) and (2.17), for example] we may write, to linear order in the inhomogeneity (no higher harmonics of q appear),

$$\langle n_{p\omega} n_{p'\omega'} \rangle = (2\pi)^4 \delta(\omega + \omega') [\delta^3(\vec{p} + \vec{p}') + \delta^3(\vec{p} + \vec{p}' - \vec{q}) + \delta^3(\vec{p} + \vec{p}' + \vec{q})] \langle n_{p\omega} n_{p'\omega'} \rangle. \quad (A8)$$

This equation is a symbolic way of expressing that Eq. (A7) and the Langevin formalism will lead to three nonvanishing correlation functions corresponding to the three nonvanishing Fourier components of Eq. (A7): $T(\vec{q}=0) = T_0$, $T(\vec{q}) = \delta \tilde{T} / 2i$, and $T(-\vec{q}) = -T(\vec{q}) = -\delta \tilde{T} / 2i = T^*(\vec{q})$. We have neglected the usual overall factors of volume and time necessary to make Eq. (A8) dimensionally correct. The analogous manipulations for the shear flow will be obvious from what will be said for the temperature gradient. Using Eq. (A8) in (A6) we obtain

$$I = I_0 + I_q + I_{-q}, \quad (\text{A9})$$

where

$$I_q = 64 \int \frac{d^3 p}{(2\pi)^3} \prod_{i=1}^3 \left(\frac{\sin(p+q/2-k)_i L_i}{(p+q/2-k)_i} \right) \prod_{j=1}^3 \left(\frac{\sin(-p+q/2+k)_j L_j}{(-p+q/2-k)_j} \right) \langle n_{p+q/2, \omega} n_{-p+q/2, -\omega} \rangle. \quad (\text{A10})$$

The definitions of I_0 and I_{-q} follow from that of I_q by letting $\vec{q} = 0$ or $\vec{q} \rightarrow -\vec{q}$ in the latter.

Basically the result of a light scattering experiment can be found from Eq. (A9). It is helpful, however, to rearrange the terms in such a way that we can factor out the weight functions. This allows certain approximations to be made. If we let $\vec{p} - \vec{k} = \vec{q}'$ in Eq. (A10) then

$$I_q = 64 \int \frac{d^3 q'}{(2\pi)^3} \prod_{i=1}^3 \left(\frac{\sin(q'+q/2)_i L_i}{(q'+q/2)_i} \right) \prod_{j=1}^3 \left(\frac{\sin(q/2-q')_j L_j}{(q/2-q')_j} \right) \langle n_{k+q'+q/2, \omega} n_{-k-q'+q/2, -\omega} \rangle. \quad (\text{A11})$$

Note that the factor multiplying the correlation function is invariant under the change of variable $\vec{q}' \rightarrow -\vec{q}'$ and/or $\vec{q} \rightarrow -\vec{q}$. Using this fact we may write

$$I_q + I_{-q} = 32 \int \frac{d^3 q'}{(2\pi)^3} \prod_{i=1}^3 \left(\frac{\sin(q'+q/2)_i L_i}{(q'+q/2)_i} \right) \prod_{j=1}^3 \left(\frac{\sin(q/2-q')_j L_j}{(q/2-q')_j} \right) \times \langle n_{k+q'+q/2, \omega} n_{-k-q'+q/2, -\omega} \rangle + \langle n_{k-q'+q/2, \omega} n_{-k+q'+q/2, -\omega} \rangle + (q \rightarrow -q). \quad (\text{A12})$$

Clearly we also have

$$I_0 = 32 \int \frac{d^3 q'}{(2\pi)^3} \prod_{i=1}^3 \left(\frac{\sin q'_i L_i}{q'_i} \right) \prod_{j=1}^3 \left(\frac{\sin q'_j L_j}{q'_j} \right) \langle n_{k+q', \omega} n_{-k-q', -\omega} \rangle + \langle n_{k-q', \omega} n_{-k+q', -\omega} \rangle. \quad (\text{A13})$$

In Eq. (A12), correlation functions of the form $\langle n_{p+q/2, \omega} n_{-p+q/2, -\omega} \rangle$ and $\langle n_{p-q/2, \omega} n_{-p-q/2, -\omega} \rangle$ are weighted equally. As is done in the text, we expand the correlation functions in Eq. (A12) in powers of q . Notice that since $\delta T(\vec{q}) = -\delta T(-\vec{q})$, only the odd powers of q survive. Then, to first order in q , we can use in Eq. (A12) the same weight function as in Eq. (A13).⁵³ This proves that if the dependence in q' of the correlation functions over the range of the weight function is negligible, then the quantity we are interested in is indeed proportional to the left-hand side of Eq. (2.18). In a more general case, to linear order in q , we need to evaluate

$$I = 64 \int \frac{d^3 q'}{(2\pi)^3} \prod_{i=1}^3 \left(\frac{\sin q'_i L_i}{q'_i} \right) \prod_{j=1}^3 \left(\frac{\sin q'_j L_j}{q'_j} \right) \langle n_{k+q', \omega} n_{-k-q', -\omega} \rangle + \langle n_{k+q'+q/2, \omega} n_{-k-q'+q/2, -\omega} \rangle + \langle n_{k-q'+q/2, \omega} n_{-k-q'+q/2, -\omega} \rangle. \quad (\text{A14})$$

The equivalent of this integral with a Gaussian weight has been evaluated in Fig. 4.

If we expand the correlation functions of Eqs. (A12) and (A13) in powers of q' , we find that only even powers of q' survive. In general one cannot neglect the terms of order q'^2 compared to those of order q because $q' \sim 1/L_i \gg q$. The conditions for which terms of order q'^2 are negligible are discussed at the end of Sec. V. Their inclusion leads to corrections of order $(cL^{-1}/D_i k^2)^2$. Note that even if the terms of order q'^2 are larger than those of order q , this does not necessarily mean that all manifestations of the external velocity or thermal gradient become unobservable. Indeed, for a fluid in a temperature gradient, the terms of order q lead to effects which are odd in frequency while the terms of order q'^2 are even in frequency. To decide whether the line shape is rendered unobservable by terms of order q'^2 , it suffices to consider the equilibrium case where the effect is present as well. (See also Sec. V and Fig. 4.)

APPENDIX B: EXPLICIT CONSTRUCTION OF A STATIONARY ENSEMBLE IN A TEMPERATURE GRADIENT

Kadanoff and Martin⁵⁴ have shown how to construct an ensemble which describes how a system with nonuniform values of the thermodynamic para-

eters relaxes towards equilibrium. We show how a simple modification of this method can allow us to build a *stationary ensemble* to describe a system in a static temperature gradient. In essence, our ensemble is constructed from a density matrix initially described by a local temperature which then evolves with the exact equations of mo-

tion for a time long enough that the dissipative fluxes are established, but short enough that global equilibrium is not established. We will use this idea first in the context of a one-body observable to show how our formulas reduce to the linear response relations of Kadanoff and Martin.⁵⁴ Then we will show how to modify the formulas to compute correlation functions and discuss what additional hypotheses are involved in using the resulting equations. The ensemble we propose here, which was also used earlier by one of us,⁵⁵ is essentially equivalent to that used by the M.I.T. group, and by Kirkpatrick *et al.* We will present an explicit proof only of the equivalence to the M.I.T. ensemble. As will be seen from the proof of equivalence, there are slightly less assumptions involved in deriving our ensemble although to make practical calculations one has to make the simplification proposed by the M.I.T. group *unless* the calculation is done entirely microscopically as in Appendix C of this paper.

1. One-body observables

Define the density matrix

$$\rho = \Xi(\text{Tr} \Xi)^{-1}, \quad (\text{B1a})$$

$$\Xi = \exp\left(-\beta H + \beta \sum_j \int d^3\vec{r}' A_j(\vec{r}') a_j(\vec{r}')\right) \\ \equiv \exp[-\beta(H + H_{\text{ext}})], \quad (\text{B1b})$$

where $\beta = 1/T$, A_j are conserved one-particle observables such as number, energy, or momentum and a_j their corresponding conjugate thermodynamic variables. For definiteness, think of the case where a_j is nonzero only for the temperature variable and $T(\vec{r}) = \delta T(q) e^{i\vec{q} \cdot \vec{r}}$. We claim that

$$\langle B_i(\vec{r}) \rangle_{ss} = \lim_{\tau \rightarrow \text{plateau}} \text{Tr}[\rho B_i(\vec{r}, t = \tau)], \quad (\text{B2})$$

where (in units $\hbar = 1$)

$$B_i(\vec{r}, t) = e^{iHt} B_i(\vec{r}, 0) e^{-iHt}, \quad (\text{B3})$$

represents the expectation value of the variable B_i in a steady temperature gradient if τ is in the

$$\delta \langle B_i(\vec{r}) \rangle \equiv \langle B_i(\vec{r}) \rangle_{ss} - \langle B_i(\vec{r}) \rangle_e \\ = \sum_j \int d^3\vec{r}' \int_0^\beta d\beta' \langle A_j(\vec{r}', -i\beta') B_i(\vec{r}, \tau) \rangle_e - \langle A_j(\vec{r}', -i\beta') \rangle_e \langle B_i(\vec{r}, \tau) \rangle_e a_j(\vec{r}'). \quad (\text{B6})$$

We momentarily omit the limit in Eq. (B2). The subscript e refers to equilibrium average. It is helpful to define

$$S_{ji}(\vec{r}', \vec{r}; \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} S_{ji}(\vec{r}', t; \vec{r}, 0), \quad (\text{B7a})$$

plateau region defined by

$$\tau_M \ll \tau \ll (D_T q^2)^{-1}, \quad (\text{B4})$$

where τ_M is a microscopic collision time or at worst the equilibration time of the collective modes of the system of size $L \ll q^{-1}$ and $(D_T q^2)^{-1}$ is the relaxation time of the external temperature perturbation. The variable B_i in Eqs. (B2) and (B3) stands for any (not necessarily conserved) one-body observable. The subscript ss to the bracket in Eq. (B2) stands for steady state.

Since we know that the system will eventually relax towards equilibrium, it is certain that Eq. (B2) represents a system with a heat flux. In the regime of times described by Eq. (B4), the system is in a plateau regime where heat fluxes have been established but the system is still far from its final equilibrium state.

We can also understand Eq. (B2) as follows: The density matrix Eq. (B1) is a sort of initial condition which forces the local energy density to have the local equilibrium value consistent with the externally imposed temperature constraint. This cannot correspond, however, to the true ensemble since a purely local equilibrium density matrix cannot account for dissipative fluxes. To find a better approximation to the true density matrix, we let it evolve for an interval of time described by Eq. (B4). [The time evolution operator in Eq. (B3) can be transferred to the density matrix by using the cyclic property of the trace.] The above procedure is similar to methods used in the maximum entropy formalism.⁵⁶

To be able to do a calculation with Eq. (B2), we need to use a perturbation scheme. (The following calculations are not essential to understand the first part of Sec. 2 of this Appendix). Following Kadanoff and Martin again,⁵⁴ we use

$$\exp[-\beta(H + H_{\text{ext}})] = \exp(-\beta H) \exp\left(-\int_0^\beta d\beta' H_{\text{ext}}^I(-i\beta')\right), \quad (\text{B5})$$

$$H_{\text{ext}}^I(-i\beta') = e^{\beta' H} H_{\text{ext}} e^{-\beta' H},$$

where $+$ means time-ordered product. The first-order expansion of Eq. (B5) substituted in Eq. (B2) yields

where

$$S_{ji}(\vec{r}', t; \vec{r}, 0) = \langle \hat{A}_j(\vec{r}', t) \hat{B}_i(\vec{r}, 0) \rangle_e, \quad (\text{B7b})$$

$$\hat{A}_j(\vec{r}', t) \equiv A_j(\vec{r}', t) - \langle A_j(\vec{r}', t) \rangle_e. \quad (\text{B7c})$$

Using (B7) in (B6) we can do the β' integral

$$\begin{aligned} \delta\langle B_i(\vec{r}) \rangle &= \sum_j \int d^3r' \int \frac{d\omega}{2\pi} \left(\frac{1 - e^{-\beta\omega}}{\omega} \right) e^{i\omega\tau} S_{ji}(\vec{r}', \vec{r}; \omega) a_j(\vec{r}') . \end{aligned} \quad (\text{B8})$$

In the classical limit ($\beta\omega \ll 1$) and when there is a single external force $a_j(\vec{r}) = \delta T(q) e^{i\vec{q}\cdot\vec{r}}/T$, Eq. (B8) reduces to

$$\delta\langle B_i(\vec{q}) \rangle = \lim_{\tau \rightarrow \text{plateau}} \int \frac{d\omega}{2\pi} e^{-i\omega\tau} S_{B_i Q}(\vec{q}, \omega) \frac{\delta T(q)}{T^2} , \quad (\text{B9})$$

where Q is the operator which couples to the temperature. It represents a density of heat energy (or T times an entropy density):

$$Q(\vec{r}, t) = \mathcal{E}(\vec{r}, t) - \frac{\langle \mathcal{E} \rangle + p}{n} n(\vec{r}, t) , \quad (\text{B10})$$

where $\mathcal{E}$ is the energy density, n the number density, and p the pressure. Equation (B9) can be used directly to do a microscopic calculation with no additional assumptions. In the rest of this section we will make further assumptions to recover the usual result of linear response theory of Kadanoff and Martin.

Equation (B9) may be rewritten

$$\delta\langle B_i(\vec{q}) \rangle = \lim_{\tau \rightarrow \text{plateau}} S_{B_i Q}(\vec{q}, \tau) \frac{\delta T(q)}{T^2} \quad (\text{B11a})$$

$$= \{ S_{B_i Q}(\vec{q}, \tau) + \lim_{\tau \rightarrow \text{plateau}} [S_{B_i Q}(\vec{q}, 0)] \} \frac{\delta T(q)}{T^2} . \quad (\text{B11b})$$

The first term of this bracket is an equal-time correlation function. It alone will correctly represent what happens if B_i is a conserved variable since in the limit (B4) the conserved variable does not have time to decay and the second term of Eq. (B11b) vanishes. On the other hand, when B_i is a dissipative flux, then $S_{B_i Q}(\vec{q}, t)$ is odd and the first term of Equation (B11b) vanishes. In that case we rewrite the last term of Eq. (B11b) as

$$\begin{aligned} &\lim_{\tau \rightarrow \text{plateau}} [S_{B_i Q}(\vec{q}, \tau) - S_{B_i Q}(\vec{q}, 0)] \\ &= \lim_{\tau \rightarrow \text{plateau}} \int_0^\tau d\bar{t} \frac{\partial}{\partial \bar{t}} \int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{-i\omega\bar{t}} S_{B_i Q}(\vec{q}, \omega) \\ &= \lim_{\tau \rightarrow \text{plateau}} -i \int_0^\tau d\bar{t} \int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{-i\omega\bar{t}} \omega S_{B_i Q}(\vec{q}, \omega) . \end{aligned} \quad (\text{B12})$$

Since $S_{B_i Q}(\vec{q}, t)$ is odd by assumption, $\omega S_{B_i Q}(\vec{q}, \omega)$ is even. If we take the $\vec{q} \rightarrow 0$ limit first (as is always done to find transport coefficients), we

can let $\tau \rightarrow \infty$ in Eq. (B12) [and still have $\tau \ll (Dq^2)^{-1}$]. With these assumptions, the right-hand side of Eq. (B12) reduces to

$$-\frac{i}{2} \int_{-\infty}^\infty d\bar{t} \int_{-\infty}^\infty e^{-i\omega\bar{t}} \omega S_{B_i Q}(\vec{q}, \omega) . \quad (\text{B13})$$

Hence we find a formula which is valid for the two cases discussed above,

$$\begin{aligned} \delta\langle B_i(q) \rangle &= \int \frac{d\omega}{2\pi} S_{B_i Q}(\vec{q}, \omega) \frac{\delta T(q)}{T^2} \\ &= -\frac{i}{2} \lim_{\omega \rightarrow 0} \left(\lim_{\vec{q} \rightarrow 0} \frac{\omega}{q} S_{B_i Q}(\vec{q}, \omega) \right) q \frac{\delta T(q)}{T^2} . \end{aligned} \quad (\text{B14})$$

The hypotheses we made are equivalent to those used in projection operator methods and for the same reason they can be justified only *a posteriori* by using, for example, the hydrodynamic equations⁵⁴ to find the analytic properties of χ'' , a quantity related to S . As for projection operator methods, our hypotheses can sometimes fail.⁵⁷

It is easy to relate Eq. (B14) to the linear response result

$$\begin{aligned} \delta\langle B_i(\vec{q}, \nu) \rangle &= \chi_{ij}(\vec{q}, \nu) \delta a_j(\vec{q}, \nu) \\ &= P \int \frac{d\omega'}{\pi} \frac{\chi_{ij}''(\vec{q}, \omega')}{\omega' - \nu} + i\chi_{ij}'(\vec{q}, \nu) . \end{aligned} \quad (\text{B15})$$

Taking the $\nu \rightarrow 0$ limit of this equation and using the fluctuation-dissipation theorem in the classical limit

$$S(\vec{q}, \omega) = 2T\chi''(\vec{q}, \omega)/\omega \quad (\text{B16})$$

we recover Eq. (B14) except for a change of sign in front of the last term. This sign difference can be understood by noting that the last term represents dissipative effects. For example, consider the case where B_i is the heat current. This current is towards the regions which are to become warm as the temperature perturbation is adiabatically switched on. When the density matrix Eq. (B1) is used, on the other hand, the heat current is toward cold regions because the system is relaxing toward equilibrium.

It is interesting to note that the adiabatic switching-on parameter which leads to the imaginary part in Eq. (B15) is related to τ^{-1} in Eq. (B4). Since $D_T q^2 \ll \tau^{-1} \ll \tau_M^{-1}$, we want to switch on the system at a frequency smaller than microscopic collision frequencies but faster than the system takes to relax back to global thermal equilibrium.

From Eq. (B14), we can "derive", for example, the formula for the specific heat in terms of an equal-time correlation function or, using conservation laws, one can find the Kubo formula for

the thermal conductivity in terms of a current-current correlation function.

2. Two-body observables (correlation functions)

For $t > 0$, by analogy with Eq. (B2) we will assume that⁵⁸

$$\langle A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle = \lim_{\tau \rightarrow \text{plateau}} \text{Tr}[\rho A_i(\vec{r}', \tau) A_j(\vec{r}, t + \tau)] \quad (\text{B17})$$

and use the same ensemble as in part 1. Note that as before, the time evolution over the period τ can all be transferred to the density matrix. For (B17) to be useful, we must also assume that the correlations between A_i and A_j decay in a time τ_c faster than $(D_T q^2)^{-1}$ so that we are always in the plateau region where a dissipative heat flux

exists. This hypothesis will not be valid for an arbitrary pair of quantities A_i, A_j . However, if we look, for example, at the density-density correlation function in a fluid at wave vector k , then we expect that if $(\Gamma k^2)^{-1} \ll (D_T q^2)^{-1}$ where $(\Gamma k^2)^{-1}$ is the damping time of the sound excitations, then Eq. (B17) will be valid.

Note that between time $\tau + 0$ and time $\tau + t$, the system evolves with its own microscopic equations of motion. This is analogous to the Langevin method where a calculation of the same correlation function reveals that between time 0 and time t , the system evolves with its own deterministic equations of motion. [See Eqs. (3.2) and (3.3).]

We have said that Eq. (B17) applies only for $t > 0$. For the case $t < 0$ we can use the stationarity of the ensemble to derive the following formula:

$$\langle A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle = \lim_{\tau \rightarrow \text{plateau}} \{ \Theta(t) \text{Tr}[\rho A_i(\vec{r}', \tau) A_j(\vec{r}, t + \tau)] + \Theta(-t) \text{Tr}[\rho A_i(\vec{r}', \tau - t) A_j(\vec{r}, \tau)] \}. \quad (\text{B18})$$

However, since Eq. (B17) applies only when the correlation time τ_c is less than $(D_T q^2)^{-1}$ one could as well use this equation in the case $t < 0$ by simply choosing τ so that

$$\tau_c \ll \tau \ll (D_T q^2)^{-1}. \quad (\text{B19})$$

τ_M and τ_c can have any value relative to one another. We will check in the explicit example to be worked out in Appendix C that both formulas (B17) and (B18) for the ensemble can be used. Equation (B17), however, is closer to the formulas used by the M.I.T. group. Equation (B18), on the other hand, reminds one of the Onsager regression hypothesis (3.2).

To make a calculation to linear order in δT , we proceed as for Eqs. (B5)–(B9) to obtain for Eq. (B17)

$$\delta \langle A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle = \lim_{\tau \rightarrow \text{plateau}} \int \frac{d\omega}{2\pi} e^{-i\omega(\tau - t)} \int d\vec{r} \int d^3\vec{r}' e^{i\omega\vec{r}} \{ \langle \hat{Q}(\vec{r}, \tau) [A_i(\vec{r}', 0) A_j(\vec{r}, t)] \rangle_e \} \frac{\delta T(\vec{r})}{T^2}. \quad (\text{B20})$$

This equation, or the equivalent one which can be derived for Eq. (B18), is all we need to perform the explicit calculation of Appendix C.⁵⁹ However, to establish a connection with the results of the M.I.T. group, we now proceed to make certain approximations analogous to those used to establish the connection with linear response theory in the previous section of the Appendix.

Using the analogs of Eqs. (B11) and (B12), we find the following exact rearrangement of Eq. (B20):

$$\begin{aligned} \delta \langle A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle &= \int d^3\vec{r} \langle \hat{Q}(\vec{r}, 0) A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle_e \frac{\delta T(\vec{r})}{T^2} \\ &+ \lim_{\tau \rightarrow \text{plateau}} \int_0^{-\tau} d\bar{t} \int d^3\vec{r} \frac{\partial}{\partial \bar{t}} \langle \hat{Q}(\vec{r}, \bar{t}) A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle_e \frac{\delta T(\vec{r})}{T^2}. \end{aligned} \quad (\text{B21})$$

Using the conservation law

$$\frac{\partial \hat{Q}}{\partial t}(\vec{r}, t) = -\vec{\nabla}_r \cdot \vec{J}_Q(\vec{r}, t), \quad (\text{B22})$$

and integrating the last term of Eq. (B21) by parts, (assuming that the correlation function decays fast enough in space that boundary terms can be neglected) we obtain for the last term in Eq. (B21),

$$\lim_{T \rightarrow \text{plateau}} \int_0^{-T} dt \int d^3\vec{r} \langle \bar{j}(\vec{r}, \bar{t}) A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle_e \cdot \vec{\nabla}_{\vec{r}} \frac{\delta T(\vec{r})}{T^2}. \quad (\text{B23})$$

We do not make any assumption about the time-reversal properties of the integrand in Eq. (B23) as we did to derive the linear response formula. However, we do assume that the correlation function decays fast on a time scale $(D_T q^2)^{-1}$. Then, with $\vec{\nabla}_{\vec{r}} \delta T(\vec{r})$ a constant, we take the $q \rightarrow 0$ limit of Eq. (B23) and set $T = \infty$. Combining Eqs. (B21) and (B23) a simple change of variables leads us to the final formula

$$\begin{aligned} \delta \langle A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle &= \int d^3\vec{r} \langle \hat{Q}(\vec{r}, 0) A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle_e \frac{\delta T(\vec{r})}{T^2} \\ &- \int_0^\infty d^3\vec{r} \int d\vec{r}' \langle \vec{j}_Q(\vec{r}, -\bar{t}) A_i(\vec{r}', 0) A_j(\vec{r}, t) \rangle_e \cdot \vec{\nabla}_{\vec{r}} \frac{\delta T(\vec{r})}{T^2}. \end{aligned} \quad (\text{B24})$$

This result is identical to Eq. (3.10) of Ref. 60 and all subsequent work of the M.I.T. group is based on it. The first term is the "local equilibrium" term and the second is the "coupling to dissipative fluxes."

Finally, notice that $\vec{j}_Q$ in Eq. (B24) is a dissipative current simply because it is related to the entropy, and not the energy. Alternatively, the absence of projection operators in Eq. (B24) can probably be understood in a manner analogous to that given in Forster,⁵⁷ p. 119. When the $q \rightarrow 0$ limit is taken first, then the current becomes the dissipative current.

APPENDIX C: MICROSCOPIC CALCULATION OF THE DENSITY-DENSITY CORRELATION FUNCTION IN A TEMPERATURE GRADIENT: IMPURITY SCATTERING MODEL

The ensemble we use is that of Eqs. (B17) or (B18). To compute to first order in the external perturbation, we need the correlation function of Eq. (B20). We do not need to make the approximations which led to Eq. (B24) although the inequality (B4) will often be used to simplify the calculation.

The model is that of a degenerate uncharged electron gas scattering isotropically from impurities. This is a reasonable model for metals in the "residual resistivity" regime (low temperature). Phenomenologically, the density fluctuations are described by the equations of Sec. II.

To solve this model microscopically (i.e., evaluate the correlation functions of Appendix B from first principles) we use methods of quantum-field theory (Green's functions). The diagram technique we use here has been described in detail in Refs. 55 and 21. The technique is due to Kadanoff and Baym. Analytically continued propagators are used instead of the more usual imaginary time-ordered propagators. A particularly lucid description of the method has been given by Langreth.⁶¹ In the present appendix, we will emphasize only the techniques which have not been described in any of the above references. Equations (C11) and (C12), in particular, simplify considerably some of the calculations.

From Eq. (B20), when $\delta T(\vec{r}) = \delta T(q) e^{i\vec{q} \cdot \vec{r}}$, we have

$$\begin{aligned} \delta \langle \hat{n}(-k+q/2, t) \hat{n}(k+q/2, t') \rangle \\ = \frac{\delta T(q)}{T^2} \int \frac{d\omega_0}{2\pi} \frac{d\nu}{2\pi} e^{-i\omega_0(t'-t) - i\nu(t+t'+2T)/2} \langle \hat{Q}(-\vec{q}, -\nu) \hat{n}(-k+q/2, -\omega_0+\nu/2) \hat{n}(k+q/2, \omega_0+\nu/2) \rangle_e, \end{aligned} \quad (\text{C1})$$

where we used the time and space translation invariance of the equilibrium ensemble (angular brackets). The subscript to the angular bracket means that we keep only connected diagrams. The operator Q is defined by Equation (B.10) where the energy density is

$$\mathcal{E}(x) = \sum_s \left[\left(\frac{-\vec{\nabla}}{i} \psi_s^*(x) \right) \frac{1}{2m} \left(\frac{\vec{\nabla}}{i} \psi_s(x) \right) - \left(\mu - \sum_\alpha u(\vec{x} - \vec{R}_\alpha) \right) \psi_s^*(x) \psi_s(x) \right]. \quad (\text{C2})$$

$\psi_s^*(x)$ is the creation operator for an electron of spin s at space-time point $x = (\vec{x}, t)$, μ is the chemical potential, and u the potential of interaction with the impurity at point $\vec{R}_\alpha$. As we will see later, this potential energy term as well as the term proportional to density in Eq. (B10) do not contribute. We omit them immediately and come back to the justification later.

Consider the correlation function

$$\langle \hat{\mathcal{E}}(-\vec{q}, -\nu) \hat{n}(-k+q/2, -\omega_0+\nu/2) \hat{n}(k+q/2, \omega_0+\nu/2) \rangle_e \quad (\text{C3})$$

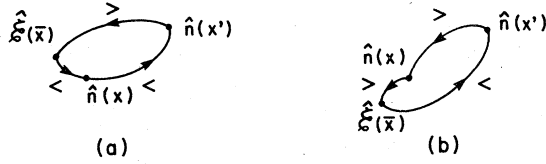


FIG. 5. Lowest-order diagrams for the correlation function of Eqs. (C3) and (C4). The solid lines stand for Green's functions G . The arrow goes from ψ^+ to ψ . The symbols $>$ or $<$ above the line indicate whether the propagator is $G^>$ or $G^<$.

The lowest-order diagrams for that correlation function (in coordinate space) are given in Fig. 5. For Fig. 5(a) one finds the expression

$$\frac{1}{2m} \left(-2i^3 \frac{\nabla_{\bar{x}}}{i} G^>(\bar{x}, x') \frac{\nabla_{\bar{x}}}{-i} G^<(x, \bar{x}) G^<(x', x) \right). \quad (C4)$$

In this equation there is a factor of 2 associated with the spin sum, a minus sign with the closed loop and i^3 because there are three contractions. As usual

$$G^>(x, x') = -i \langle \psi(x) \psi^+(x') \rangle, \quad (C5a)$$

$$G^<(x, x') = i \langle \psi^+(x') \psi(x) \rangle. \quad (C5b)$$

The following quantities will be helpful later:

$$G^R(x, x') = [G^>(x, x') - G^<(x, x')] \Theta(t - t'), \quad (C5c)$$

$$G^A(x, x') = [G^<(x, x') - G^>(x, x')] \Theta(t' - t). \quad (C5d)$$

Equilibrium propagators obey the relations

$$G^<(\vec{p}, \omega) = i f(\omega) i [G^R(\vec{p}, \omega) - G^A(\vec{p}, \omega)], \quad (C6a)$$

$$G^>(\vec{p}, \omega) = -i [1 - f(\omega)] i [G^R(\vec{p}, \omega) - G^A(\vec{p}, \omega)], \quad (C6b)$$

where $f(\omega)$ is a Fermi function and for our model

$$G^R(\vec{p}, \omega) = \frac{1}{\omega - \epsilon + i/2\tau} = [G^A(\vec{p}, \omega)]^*, \quad (C7)$$

where

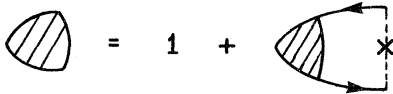


FIG. 6. Diagrammatic definition of the dressed vertex correction (shaded area). The dotted line with a cross represents interaction with impurities. Note that the integral over momentum in a closed loop such as the one in this figure can, in general, be done without problems. All such momentum integrals must be done before the frequency integral can be performed.

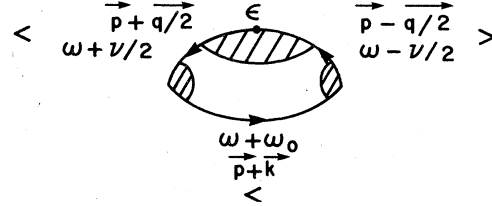


FIG. 7. Dressed version of the diagram of Fig. 5(a). The solid lines now stand for fully dressed propagators. We dropped the symbol n for the density vertices but indicated the energy vertex by an ϵ as a reminder that $\epsilon = p^2/2m - \mu$ multiplies the propagators at this vertex. The momentum and frequency labels of the propagators of the internal loop have been indicated: $\vec{p}$ and ω are to be integrated over. One must use the multiplication rule of Eq. (C10) to find the significance of $G^>$ or $G^<$.

$$\epsilon = p^2/2m - \mu \quad (C8)$$

and

$$1/\tau = 2\pi n_c |u|^2 N(0) \quad (C9)$$

with n_c the impurity concentration, $|u|^2$ the square of the Fourier transform of the impurity potential (a constant in our approximation) and $N(0)$ the single spin density of states at the Fermi surface.

The diagrams of Figs. 5(a) and 5(b) are equal. This can be seen as in Refs. 21 and 55 by using particle-hole symmetry. That symmetry also implies that if we had included the last term of Eq. (B10) in the definition of $\hat{Q}$ it would have given contributions to Figs. 5(a) and 5(b) which would have cancelled each other.⁶²

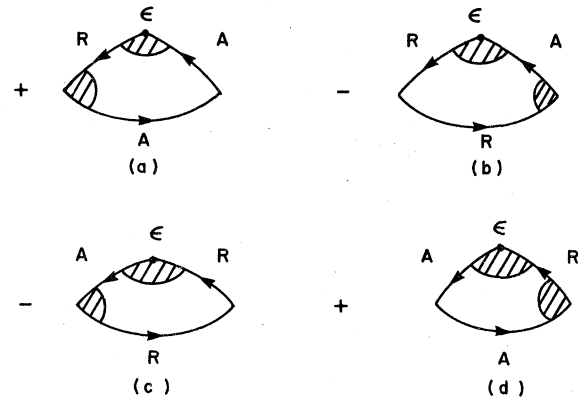


FIG. 8. Diagrams left from Fig. 7 after the identities (C11) and (C12) have been used. R and A indicate whether the Green's functions to be used are G^R or G^A . The momentum and frequency labels in this figure are the same as those of Fig. 7. Note that some of the dressed vertices are not indicated because they vanish (see text).



FIG. 9. Parts of diagrams which vanish upon integration over ϵ . The open circle stands for a density vertex or another impurity interaction.

The conclusions of the preceeding paragraph also hold true for the "dressed" versions of Fig. 5. To dress the diagrams of Fig. 5 we have to insert effective impurity interactions (dotted lines with crosses) and associate with each of these interactions two Green's functions (but no extra factor of i ; they cancel). Diagrams which do not contain the full vertex correction of Fig. 6 decay in a time short compared with hydrodynamic times and thus can be neglected. The dressed analog of Fig. 5(a) which we must compute is given in Fig. 7 with the appropriate momentum labels. By the above arguments, we need not consider further the dressed analog of Fig. 5(b). To evaluate Fig. 7, the following simplification can be made.

Suppose we have three Green's functions multiplied in series. Then the rules of analytic continuation tell us that⁶¹

$$[G_3]^< = G^< G^A G^A + G^R G^< G^A + G^R G^R G^<. \quad (C10)$$

If the frequency labels are the same on each Green's function (as is the case if they are joined by static impurity vertices) then using Eq. (C6a) we find

$$\begin{aligned} [G_3]^< &= if(\omega) \{ (G^R - G^A) G^A G^A \\ &\quad + G^R (G^R - G^A) G^A + G^R G^R (G^R - G^A) \} \\ &= f(\omega) [G^A G^A G^A - G^R G^R G^R]. \end{aligned} \quad (C11)$$

Similarly,

$$[G_3]^> = [1 - f(\omega)] [G^R G^R G^R - G^A G^A G^A]. \quad (C12)$$

The generalization of (C11) and (C12) to N Green's functions is clear. These simple identities would

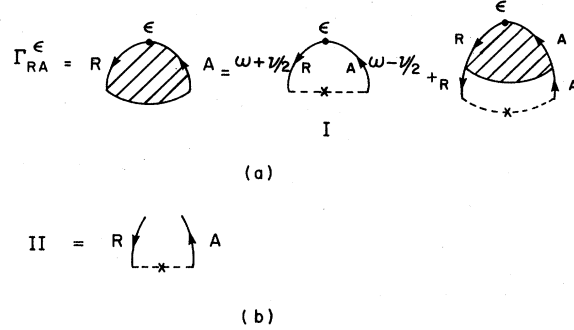


FIG. 10. (a) Equation for the dressed energy vertex. (b) Part of the diagram of (a) which must be iterated.

allow a considerable simplification of the calculations of Refs. 21 and 55.

Using Eqs. (C11) and (C12) in the diagram of Fig. 7 we are left with the diagrams of Fig. 8 to evaluate. Each of the many Green's functions on a line above which there is an $R(A)$ are retarded (advanced). We recall that the analytic continuation rule for retarded (or advanced) Green's functions is quite simple. For example,

$$\begin{aligned} [G_3]^R &= G^R G^R G^R, \\ [G_3]^A &= G^A G^A G^A. \end{aligned} \quad (C13)$$

Equation (C13) should be contrasted with Eq. (C10). To arrive at Fig. 8, we used the fact that a diagram which contains one or more of the loops illustrated in Fig. 9 vanishes because when we do the integral over ϵ [Eq. (C8)] both Green's functions have their poles in the same half-plane. Each diagram of Fig. 8 has a factor $f(\omega + \frac{1}{2}\nu) \times [1 - f(\omega - \frac{1}{2}\nu)] f(\omega + \omega_0)$ in front of the frequency integral which we have not explicitly written.

A further simplification arises when we realize that the only overall factors of i are those appearing in Eq. (C4). Then, using Eq. (C7) we see that Figs. 8(a)–8(c) and 8(b)–8(d) are complex conjugate pairs.

To give an example of how the calculation proceeds, we compute the energy vertex of Fig. 10. The first term (I) on the right-hand side of the Fig. 10(a) gives to zeroth order in q :

$$I = N(0) n_c |u|^2 \int d\epsilon \left(\frac{\epsilon}{\omega + \nu/2 - \epsilon + i/2\tau} \right) \left(\frac{1}{\omega - \nu/2 - \epsilon - i/2\tau} \right). \quad (C14)$$

Terms of order q vanish upon angular integration and we neglected contributions of order q^2 because they do not enter the determination of the frequency (ω_0 and ν) poles.⁶³ Hence they can lead only to corrections of order $q^2 \delta T$ which we do not want to consider. Taking into account the convergence properties of the integral in (C14) we find

$$I = \frac{i/\tau}{\nu + i/\tau} \omega. \quad (C15)$$

The part of Fig. 10(a) which must be iterated is illustrated in Fig. 10(b). This time, the terms of order q^2 must be taken into account since they will eventually determine the position of the pole of ν . We assume $\nu\tau \ll 1$ and $v_F\tau q \ll 1$. Then,

$$\begin{aligned} \Pi &= N(0)n_c|u|^2 2\pi \int \frac{d\epsilon}{2\pi} \int \frac{d\hat{p}}{4\pi} \left(\frac{1}{\omega + \nu/2 - \epsilon - \vec{v}_F \cdot \vec{q}/2 + i/2\tau} \right) \left(\frac{1}{\omega - \nu/2 - \epsilon + \vec{v}_F \cdot \vec{q}/2 - i/2\tau} \right) \\ &\sim \frac{i}{\tau} \frac{1}{\nu + i/\tau} [1 - Dq^2\tau], \quad (D \equiv \frac{1}{3} v_F^2 \tau). \end{aligned} \quad (C16)$$

Using Eqs. (C16) and (C15) we finally find

$$\Gamma_{RA}^{\epsilon} = \frac{\omega i/\tau}{\nu + iDq^2}. \quad (C17)$$

We can now justify why we neglected the potential energy contribution to the energy vertex. Equation (C17) multiplies the contributions coming from the other parts of the diagrams but none of these will depend on ω once the ϵ integrals are done. Hence at the end we have to do the frequency integral

$$J(\eta) \equiv \int d\omega \omega^n f(\omega + \omega_0) [1 - f(\omega - \nu/2)] f(\omega + \nu/2). \quad (C18)$$

We obtain,⁶⁴ to leading order in $\beta\nu \ll 1$ and $\beta\omega_0 \ll 1$:

$$J(1) \sim \frac{-1}{2\beta^2} + \Theta(\beta\nu \text{ and } \beta\omega_0). \quad (C19)$$

For the potential energy contribution, the integral which comes in is

$$J(0) \sim 0 + \Theta(\beta\nu \text{ and } \beta\omega_0). \quad (C20)$$

The results of the calculations for the diagrams give us the correlation function in (C3) which can then be used in Eq. (C1). Doing the integral over ω_0 and then over ν we obtain

$$\begin{aligned} \delta \langle \hat{n}(-k + q/2, t) \hat{n}(k + q/2, t') \rangle \\ = 2N(0)\delta T(q) [\Theta(t' - t)\Theta(t + \tau) e^{-Dq^2(t+\tau) - D(k+q/2)^2(t'-t)} + \Theta(t - t')\Theta(t' + \tau) e^{-Dq^2(t'+\tau) + D(k-q/2)^2(t'-t)} \\ + \Theta(t' - t)\Theta(-t' - \tau) e^{Dq^2(t'+\tau) - D(k-q/2)^2(t'-t)} + \Theta(t - t')\Theta(-t - \tau) e^{Dq^2(t+\tau) + D(k+q/2)^2(t'-t)}], \end{aligned} \quad (C21)$$

Equation (C21) illustrates the abstract discussions of Appendix B on the construction of a stationary ensemble. To construct an ensemble as in Eqs. (B17) and (B20) from Eq. (C21), we set $t=0$ in the latter and assume that

$$\tau \ll T \ll (Dq^2)^{-1}. \quad (C22)$$

The first of these inequalities has already been used in the form $\nu\tau \ll 1$ [see Eq. (C16)]. We also make the assumption equivalent to Eq. (B.19):

$$(Dk^2)^{-1} \ll \tau \ll (Dq^2)^{-1}. \quad (C23)$$

Then when $t=0$, the exponentials in (C21) do not allow $|t'| > \tau$ and we obtain

$$\delta \langle \hat{n}(-k + q/2, 0) \hat{n}(k + q/2, t') \rangle = 2N(0)\delta T(q) [\Theta(t') e^{-D(k+q/2)^2 t'} + \Theta(-t') e^{+D(k-q/2)^2 t'}]. \quad (C24)$$

The correlation function is stationary. Fourier transforming in time and expanding to first order in q we obtain for the corresponding sum of correlation functions the same result as in Eq. (2.18) with $\chi_n = 2N(0)$.

Using Eq. (C21) we can build as well the ensemble corresponding to Eq. (B18). With Eq. (C22) satisfied, the first term of Eq. (B18) can be obtained from Eq. (C21), with $t=0$, $t' \rightarrow t$, in the form

$$2N(0)\delta T(q)\Theta(t)e^{-Dq^2T-D(k+q/2)^2t}\sim 2N(0)\delta T(q)\Theta(t)e^{-D(k+q/2)^2t} \quad (C25)$$

and the second term of (B18) in the form

$$2N(0)\delta T(q)\Theta(-t)\Theta(t+\tau)e^{-Dq^2(t+\tau)+D(k-q/2)^2t}. \quad (C26)$$

If we assume (C23) then (C26) reduces to

$$2N(0)\delta T(q)\Theta(-t)e^{D(k-q/2)^2t} \quad (C27)$$

because then t can never become negative enough for $\Theta(t+\tau)$ to be different from unity.

Comparing Eqs. (C25) plus (C27) to Eq. (C24) we see that the ensembles (B17) and (B18) are really the same, and that both restrictions (C22) and (C23) are needed to obtain sensible results. The most important conclusion of this appendix, however, is that the results of the microscopic calculation agree with the phenomenological results of Sec. II.

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⁷Note that in Eq. (2.17), $\delta \tilde{T} \leq T_0$ if $T(\tilde{r})$ is to remain positive for $-\infty \leq r \leq \infty$. Hence, if $\tilde{q}\delta \tilde{T} = \nabla T$, then the smallest possible value of $\tilde{q}$ is $\tilde{q} = (\nabla \ln T)$.

⁸This last remark applies to fluctuations about equilibrium as well.

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