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# Fokker–Planck Equation Approach to Fluctuations about Nonequilibrium Steady States

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We examine the properties of steady states in systems which interact at the boundary with a nonequilibrium environment. The examination is based on a nonlinear Fokker–Planck equation, the structure of which is determined by the fact that it also governs the time evolution of the equilibrium fluctuations of the system. The nonlinearities in the Fokker–Planck equation may have two origins: thermodynamic nonlinearities which arise if the thermodynamic potential is not a bilinear function of the state variables, and nonlinear mode coupling which arises if the transport coefficients depend on the state. While these nonlinearities have only a small effect on the equilibrium fluctuations of a system away from critical points, they are shown to be important for the determination of fluctuations about nonequilibrium steady states. In particular the state dependence of the transport coefficients may lead to deviations from local equilibrium and to a breakdown of detail balance. An explicit formula for the time correlations of fluctuations about the nonequilibrium steady state is obtained. The formula leads to long-range correlations in fluids in the presence of a temperature gradient. The result is compared with earlier approaches to the same problem. Finally, we study the linear response to external forces and obtain a generalization of the fluctuation-dissipation formula relating the response functions with the nonequilibrium correlation functions.

**KEY WORDS:** Nonequilibrium steady states; Fokker–Planck equation; correlation functions; response theory; fluctuation-dissipation theorem; fluctuations in fluids; light scattering from nonequilibrium fluids.

## 1. INTRODUCTION

To study the properties of nonequilibrium systems there are two possible approaches: a microscopic approach by statistical mechanical methods and a macroscopic approach using the theory of stochastic processes.

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The macroscopic approach is not necessarily less ambitious. Often the process of the macroscopic variables are approximately Markovian. For Markovian processes, the connection between the macroscopic process and the underlying statistical mechanics is well understood. The molecular nature of the system leads to a particular form of the macroscopic equations of motion in terms of transport coefficients and a thermodynamic potential,(1,2) and those quantities are given by certain molecular averages.(1,3) If this particular form of the equations of motion is correctly incorporated into the macroscopic approach there is generally no need for more detailed microscopic calculations, at least if one does not intend to go beyond the Markovian limit.

In this paper we base our considerations upon a nonlinear Fokker–Planck equation which is of the form derived from statistical mechanics.(1) The nonlinearities in the Fokker–Planck equation may have two origins: thermodynamic nonlinearities which arise if the thermodynamic potential is not a bilinear function of the macroscopic variables, and nonlinear mode coupling which arises if the transport coefficients are not constant but rather depend on the state. The nonlinear Fokker–Planck equation or the equivalent nonlinear Langevin equation are generally used as the basic starting point in the study of critical dynamics(4) where the nonlinearities play a crucial role. Away from critical points the nonlinear mode coupling has only a small effect on the equilibrium fluctuations in three-dimensional systems.(5) In this region Van Kampen's arguments(6) can be used to show that the fluctuations are approximately Gaussian and obey a linear equation of motion.

The Fokker–Planck equations used in the study of fluctuations about equilibrium generally make reference to a particular equilibrium state. This is due to the fact that the thermodynamic potential and the transport coefficients are usually expanded in terms of variables which describe deviations from a particular equilibrium state. However, the basic Fokker–Planck equation(1) makes no reference to a particular equilibrium state. This is why the study of nonequilibrium systems by Fokker–Planck methods is rather straightforward. The thermodynamic functions appearing in the Fokker–Planck equation are now expanded about a reference state which is itself a nonequilibrium state. This reference state is properly chosen as the nonequilibrium solution of the deterministic laws associated with the Fokker–Planck equation.(2)

In this paper we restrict ourselves to nonequilibrium steady states which are not near critical points. This case is particularly simple since the fluctuations about the nonequilibrium steady state are small and they behave in a quasilinear manner. However, the nonlinearities show in the large and must be taken into account to determine the correct steady state.

A corresponding quasilinearization of the Fokker–Planck equation is shown to emerge naturally to first order of an expansion where the Boltzmann constant furnishes a formal expansion parameter.

Recently, a statistical mechanical approach to nonequilibrium steady states has been developed by Oppenheim and his collaborators(7) with interesting results. It has been shown that the nonequilibrium state may not be a local equilibrium state and that the breakdown of time reversal symmetry leads to long-range correlations in hydrodynamic systems. We shall see that these problems can easily be investigated within the Fokker–Planck equation approach.

The outline of the paper is the following: In Section 2 we consider nonequilibrium steady states from a macroscopic deterministic point of view. In particular, we investigate the linear relaxation to time-independent, stable nonequilibrium steady states which lie on the thermodynamic branch of the system.(8,9) In Section 3 we study the fluctuations about the steady state and show that they cannot be described by a local equilibrium distribution if the transport coefficients are functions of the state. Section 4 investigates the time correlation functions of the fluctuations and gives conditions which must be satisfied for processes with detailed balance. Further, we determine the linear response to external forces and obtain a generalization of the fluctuation-dissipation theorem of the first kind. In Section 5 we present our conclusions and discuss the relation to other work. The Appendix illustrates the theory by outlining its application to fluids.

## 2. MACROSCOPIC DETERMINISTIC DESCRIPTION OF STEADY STATES

### 2.1. Deterministic Equations of Motion

We consider a system described by a set $a = (a^1, \ldots, a^i, \ldots)$ of macroscopic variables. The index $i$ may be continuous. In a continuum description the variables $a$ are quantities like energy density, magnetization density, concentrations of chemical constituents. In a lattice or cell description the variables $a$ are quantities like the number of particles in a cell or the energy content of a cell. On a kinetic model the $a$'s are sums of molecular variables.

In a deterministic description the fluctuations of the macroscopic variables are neglected and irreversible processes in the system are described by a set of deterministic equations of motion (transport equations) which we write in Onsager's form

$$\dot{a}^i = L^{i\underline{j}} \chi_{\underline{j}} \equiv f^i \tag{1}$$

Here and in the sequel we understand that a summation or integration is to be carried out for the underlined indices. The $L^{ij}$ are the transport coefficients which may be functions of the state $a$, and the $\chi_i$ are the thermodynamic forces

$$\chi_i = \frac{\partial S}{\partial a^i} \tag{2}$$

where $S(a)$ is the entropy, and where $\partial/\partial a^i$ denotes a partial or functional derivative.

The equations (1) make no reference to a particular equilibrium state as long as the state functions $L^{ij}$ and $S$ are not expanded about some equilibrium values. If the variables are densities of conserved quantities the transport coefficients include derivatives with respect to spatial coordinates, and the deterministic equations (1) have the form of partial differential equations. For fluids the explicit form of these equations is given in the Appendix.

In quite a few systems we can replace the entropy by another thermodynamic potential. For instance, we may often treat the system in an isothermal approximation which may be enforced by a heat bath. This naturally means that we restrict ourselves to nonequilibrium states with constant temperature. In such a case the free energy $F(a)$ is the adequate potential, and $S(a)$ has to be replaced by $-(1/T)F(a)$, where $T$ is the temperature. However, changes of (1) and (2) of this kind are purely formal.

The deterministic equations (1) have certain time reversal symmetries. We choose the variables $a^i$ so that they have definite time reversal signature $\epsilon^i$. Then, the time reversal transformation reads

$$\tilde{a}^i = \epsilon^i a^i, \qquad \epsilon^i = \pm 1 \tag{3}$$

The entropy is invariant under time reversal

$$S(\tilde{a}) = S(a) \tag{4}$$

and the transport coefficients obey the reciprocal relations

$$L^{ij}(\tilde{a}) = \epsilon^i \epsilon^j L^{ji}(a) \tag{5}$$

The matrix $L^{ij}$ is not symmetric in general. The symmetric part

$$D^{ij} = \tfrac{1}{2}(L^{ij} + L^{ji}) \tag{6}$$

is connected with the irreversible part of the deterministic flow, while the antisymmetric part

$$A^{ij} = \tfrac{1}{2}(L^{ij} - L^{ji}) \tag{7}$$

is connected with the reversible part of the deterministic flow.

## 2.2. Steady States

We shall assume that the macroscopic variables $a$ describe local properties of the systems or properties of small subsystems (cells) and that the deterministic equations of motion (1) are at least approximately local in space. We now let the system interact with an environment which has the character of a bath. This means that the state of the environment is not much influenced by the system under consideration (no feedback). The effect of the environment on the dynamics of the system may consist of two parts: a long-range interaction which can be described in terms of external forces $h_i$ that couple to the macroscopic variables $a^i$, and a short-range interaction at the boundaries of the system. On the deterministic level of description the latter interaction specifies the boundary conditions which must be added to the equations of motion in order to have a well-posed problem.

For the sake of simplicity we shall assume that no external forces are present. The effect of external forces could be incorporated into the Hamiltonian of the system. Hence, constant external forces alone do not lead to properties of the system qualitatively different from those of closed systems. Some further discussion of this question will be given below. In the absence of external forces the environment does not change the form of the deterministic equations (1) in the interior of the system. All the environment does is to specify the boundary conditions.

These considerations mainly apply to three-dimensional systems whose state is described by a set of variables $a$ large enough to display variations of the local properties in all dimensions. Sometimes one can neglect spatial variations in one direction and regard the system as two dimensional. Often, spatial variations have been completely disregarded, which leads to a zero-dimensional description in terms of global variables. In those lower-dimensional descriptions the effect of a nonequilibrium environment can be more drastic because even the short-range interactions with the environment may change the form of the equations of motion.

Under time-independent boundary conditions the system often settles down to a steady state $\hat{a}$, where

$$\hat{f}^i = \hat{L}^{i\underline{j}}\hat{\chi}_{\underline{j}} = 0 \tag{8}$$

Here and in the following the ^ indicates that a state function is taken at $a = \hat{a}$. The steady state is an equilibrium state if the thermodynamic forces $\hat{\chi}$ vanish. A nonequilibrium steady state $\hat{a}$ can also be characterized by the nonvanishing thermodynamic forces $\hat{\chi}$ maintained by the environment.

We assume that the steady state $\hat{a}$ is stable. Putting

$$a^i = \hat{a}^i + \Delta^i \tag{9}$$

we obtain from (1), (2) and (8) to linear order in $\Delta$

$$\dot{\Delta}^i = \hat{M}^i{}_{\underline{k}}\Delta^{\underline{k}} = l^i(\hat{a}, \Delta) \tag{10}$$

where the evolution matrix $M^i_k$ reads

$$M^i_k = \frac{\partial f^i}{\partial a^k} = L^{i\underline{j}} S_{\underline{j}k} + \frac{\partial L^{i\underline{j}}}{\partial a^k} \chi_{\underline{j}} \tag{11}$$

and where

$$S_{ij} = \frac{\partial^2 S}{\partial a^i \partial a^j} = \frac{\partial \chi_i}{\partial a^j} \tag{12}$$

Equation (10) governs the linear relaxation to the steady state $\hat{a}$. The evolution matrix (11) naturally decomposes into two parts. The first term on the right-hand side of (11) is of the form of the relaxation matrix in equilibrium systems. The second term only arises if the transport coefficients depend on the state and it is proportional to the thermodynamic forces $\hat{\chi}$. We shall see that this term leads to some interesting features of fluctuations about nonequilibrium steady states.

Next we examine the time reversal properties of the linear relaxation law (10). For a system under the influence of an environment the time reversal transformation consists of two parts$^{(9)}$: a transformation of the state variables

$$a^i \to \tilde{a}^i = \epsilon^i a^i \tag{13}$$

and a transformation of the parameters characterizing the influence of the environment. These parameters are the thermodynamic forces $\hat{\chi}$ maintained by the environment, and the second part of the time reversal transformation reads

$$\hat{\chi}_i \to \tilde{\hat{\chi}}_i = \epsilon^i \hat{\chi}_i \tag{14}$$

which implies

$$\hat{a}^i \to \tilde{\hat{a}}^i = \epsilon^i \hat{a}^i \tag{15}$$

We now decompose the drift vector $l^i(a, \Delta)$ into a reversible part

$$r^i(a, \Delta) = \tfrac{1}{2}\left[ l^i(a, \Delta) - \epsilon^i l^i(\tilde{a}, \tilde{\Delta}) \right] \tag{16}$$

and an irreversible part

$$d^i(a, \Delta) = \tfrac{1}{2}\left[ l^i(a, \Delta) + \epsilon^i l^i(\tilde{a}, \tilde{\Delta}) \right] \tag{17}$$

Using (4), (5), (10), and (11) we find

$$r^i(a, \Delta) = \left( A^{i\underline{j}} S_{\underline{j}\underline{k}} + \frac{\partial A^{i\underline{j}}}{\partial a^{\underline{k}}} \chi_{\underline{j}} \right) \Delta^{\underline{k}} \tag{18}$$

and

$$d^i(a,\Delta) = \left( D^{i\underline{j}} S_{\underline{j}\underline{k}} + \frac{\partial D^{i\underline{j}}}{\partial a^{\underline{k}}} \chi_{\underline{j}} \right) \Delta^{\underline{k}} \tag{19}$$

We will make use of this decomposition of $l^i(a,\Delta)$ below.

At the end of this section we briefly discuss the changes that occur in the presence of constant external forces $h_i$. The equations of motion (1) are replaced by[3]

$$\dot{a}^i = L^{i\underline{j}} \left( \chi_{\underline{j}} - \frac{1}{T_{\underline{j}}} h_{\underline{j}} \right) \tag{20}$$

where $T_j$ is the local temperature at the location associated with variable $a^j$. In a steady state $\hat{a}$ we have

$$\hat{L}^{i\underline{j}} \left( \hat{\chi}_{\underline{j}} - \frac{1}{\hat{T}_{\underline{j}}} h_{\underline{j}} \right) = 0 \tag{21}$$

and the evolution matrix governing the linear relaxation to $\hat{a}$ reads

$$\hat{M}^i_k = \hat{L}^{i\underline{j}} \hat{S}_{\underline{j}k} + \frac{\partial \hat{L}^{i\underline{j}}}{\partial a^k} \left( \hat{\chi}_{\underline{j}} - \frac{1}{\hat{T}_{\underline{j}}} h_{\underline{j}} \right) \tag{22}$$

We see that only that part of the thermodynamic forces which is not maintained by external forces but rather is a consequence of the boundary conditions contributes to the second term in (22).

## 3. FLUCTUATIONS ABOUT STEADY STATES

### 3.1. Fokker–Planck Equation

The stochastic theory of irreversible processes includes the effects of fluctuations about the deterministic path. The basic quantity characterizing the stochastic properties of the system is the conditional probability or transition probability $p_t(a' \mid a)da'$ that the system will reach a state $a'$ in $da'$ within time $t$ if it starts out from the state $a$. Under the assumption that the stochastic process of the fluctuations is a continuous Markov process the conditional probability $p_t(a' \mid a)$ is the Green's function of a Fokker–Planck equation.(10) The statistical mechanical theory shows that this Fokker–Planck equation can be reconstructed from the limiting deterministic law

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[3] This form of the equations of motion can be shown to follow from statistical mechanics.

(1) and that it is of the form(2),[4]

$$\frac{\partial}{\partial t} p_t = \frac{\partial}{\partial a^{\underline{i}}} k_B L^{\underline{i}\,\underline{j}} \left( \frac{\partial p_t}{\partial a^{\underline{j}}} - \frac{p_t}{w} \frac{\partial w}{\partial a^{\underline{j}}} \right) \tag{23}$$

where

$$w(a) \propto \exp\left[ (1/k_B) S(a) \right] \tag{24}$$

$k_B$ is the Boltzmann constant. $w(a)$ is proportional to the equilibrium distribution of the system. The proportionality factor is a function of the globally conserved quantities which characterize the particular equilibrium state. One can absorb such a factor into the definition of $w(a)$ since it cancels in Eq. (23). A detailed discussion of this point is given in Ref. 1.[5] It should, however, be noted that the entropy itself does not depend on the particular equilibrium state.

The deterministic equations of motion (1) are obtained from (23) in the deterministic limit(2) $k_B \to 0$.[6] The explicit $k_B$ dependence of the Fokker–Planck equation can be used to set up an approximation scheme, where $k_B$ is used as a formal expansion parameter in order to determine fluctuation corrections to the deterministic theory.(11) The actual dimensionless expansion parameters depend on the kind of nonlinearities in the specific system under consideration but they are typically very small in noncritical systems.[7] Throughout this paper it will be assumed that we are not in the vicinity of a critical point.

### 3.2. Steady State Fluctuations

The probability distribution of equilibrium fluctuations is basically determined by the thermodynamic potential $S(a)$ and does not depend on the transport coefficients. The probability distribution of fluctuations in a

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[4] We understand that the macroscopic variables $a$ are sums of molecular variables on a kinetic model so that they provide a natural representation of the macroscopic state in the sense of Ref. 2.

[5] An occasional reader not familiar with this approach might find it helpful to look at the example in the Appendix.

[6] The limit $k_B \to 0$ has some features in common with the familiar classical limit of a quantum theory where a constant of Nature is formally approaching zero too.

[7] For instance, in an incompressible fluid the actual expansion parameter is $k_B T/\rho\nu^2\Lambda$, where $T$ is the temperature, $\rho$ the mass density, $\nu$ the kinematic viscosity, and $\Lambda$ the cutoff wavelength or the cell diameter. Even for an extremely small cutoff of 10 Å this parameter is only of order $10^{-2}$–$10^{-3}$ for water at room temperature. This parameter must not be confused with the Reynolds number, which indicates the relevance of the nonlinearities in the deterministic equations. The $k_B$ expansion determines corrections to the deterministic behavior which are due to thermal fluctuations.

nonequilibrium steady state will depend on $S(a)$ and on the thermodynamic forces $\hat{\chi}$ maintained by the environment. However, it is natural that some additional dependence on the transport coefficients arises because a nonequilibrium steady state transports quantities like energy or momentum from one boundary to another. We shall see that the state dependence of the transport coefficients leads to such an influence of the transport properties upon the steady state fluctuations.

In Section 2 we have argued that in the absence of external forces an environment does not change the form of the deterministic laws in the interior of the system. By the same token we may argue that the environment will not affect the validity of the Fokker–Planck equation (23) in the interior. This is more restrictive an assumption in a stochastic description because we generally must take into account external noise due to the molecular nature of the environment. We shall assume that the distance between the "interior" and the boundary is large compared to the attenuation length of the macroscopic modes of the system so that we can neglect the effects of fluctuating boundary conditions in the interior.

Using (6) and (24) we may rewrite the Fokker–Planck equation (23) in the form

$$\frac{\partial}{\partial t} p_t = \frac{\partial}{\partial a^{\underline{i}}}\left(-K^{\underline{i}} + k_B \frac{\partial}{\partial a^{\underline{j}}} D^{\underline{i}\underline{j}}\right) p_t \tag{25}$$

where

$$K^i = L^{i\underline{j}} \frac{\partial S}{\partial a^{\underline{j}}} + k_B \frac{\partial L^{i\underline{j}}}{\partial a^{\underline{j}}} = f^i + k_B \frac{\partial L^{i\underline{j}}}{\partial a^{\underline{j}}} \tag{26}$$

is the Fokker–Planck drift.

It follows that

$$\frac{d}{dt}\langle a^i \rangle_t = \langle K^i \rangle_t \tag{27}$$

and

$$\frac{d}{dt}\langle a^i a^j \rangle_t = \langle a^i K^j \rangle_t + \langle K^i a^j \rangle_t + 2k_B \langle D^{ij} \rangle_t \tag{28}$$

where $\langle \cdots \rangle_t$ denotes the average over the single-event probability $p_t(a)$. The equations (27) and (28) are valid for variables $a^i$ and $a^j$ characterizing properties in the interior of the system. In a steady state the stationary averages $\langle \cdots \rangle$ satisfy

$$\langle K^i \rangle = 0 \tag{29}$$

and

$$\langle a^i K^j \rangle + \langle K^i a^j \rangle + 2k_B \langle D^{ij} \rangle = 0 \tag{30}$$

To evaluate these equations we expand the Fokker–Planck drift $K^i(a)$ about the deterministic steady state $\hat{a}$. Using (8) and (9) we have

$$K^i = \hat{M}^i{}_{\underline{j}}\Delta^{\underline{j}} + \frac{1}{2} M^i{}_{\underline{j}\underline{k}}\Delta^{\underline{j}}\Delta^{\underline{k}} + k_B \frac{\partial \hat{L}^{i\underline{j}}}{\partial a^{\underline{j}}} + O(\Delta^3, k_B\Delta) \tag{31}$$

where $M^i_j$ has been defined previously, while

$$M^i_{jk} = \frac{\partial^2 f^i}{\partial a^j \partial a^k} \tag{32}$$

In the deterministic limit $k_B \to 0$ the deviations $\Delta^i$ of the fluctuating state variables $a^i$ from their deterministic values $\hat{a}^i$ vanish. The mean deviations $\langle\Delta^i\rangle$ and the second moments $\langle\Delta^i\Delta^j\rangle$ are of order $k_B$, while higher moments are at least of order $k_B^2$. Using these orders of magnitude(11) we obtain from (29) and (30)

$$\hat{M}^i{}_{\underline{j}}\langle\Delta^{\underline{j}}\rangle + \frac{1}{2}\hat{M}^i{}_{\underline{j}\underline{k}}\langle\delta a^{\underline{j}}\delta a^{\underline{k}}\rangle + k_B \frac{\partial \hat{L}^{i\underline{j}}}{\partial a^{\underline{j}}} = O(k_B^2) \tag{33}$$

and

$$\hat{M}^i{}_{\underline{k}}\langle\delta a^{\underline{k}}\delta a^j\rangle + \langle\delta a^i\delta a^{\underline{k}}\rangle\hat{M}^j{}_{\underline{k}} + 2k_B\hat{D}^{ij} = O(k_B^2) \tag{34}$$

where the $\delta a^i$ are the fluctuations about the mean values

$$\delta a^i = a^i - \langle a^i\rangle \tag{35}$$

The equations (33) and (34) determine the stationary mean values $\langle a^i\rangle = \hat{a}^i + \langle\Delta^i\rangle$ and the equal-time correlations $\langle\delta a^i\delta a^j\rangle$ of fluctuations about the mean values in leading order in $k_B$. These equations are a truncated form of a systematic cumulant expansion where $k_B$ furnishes a formal expansion parameter. The extension to higher orders is straightforward. However, the present approximation is generally sufficient if the steady state is stable and not near critical points.

### 3.3. Corrections to Local Equilibrium

To elucidate the content of the equations (33) and (34) we show that the nonequilibrium steady state is not a local equilibrium state if the Fokker–Planck equation (23) contains nonlinear mode-coupling terms. A local equilibrium distribution is of the form

$$\bar{p}(a) \propto \exp\left\{\frac{1}{k_B}\left[S(a) - \lambda_{\underline{i}}a^{\underline{i}}\right]\right\} \tag{36}$$

The parameters $\lambda$ vanish in equilibrium. In a nonequilibrium state the $\lambda$'s are determined by the requirement that the local equilibrium mean values $\overline{\langle a^i\rangle}$ coincide with the true mean values $\langle a^i\rangle$.

The local equilibrium distribution associated with the steady state under consideration is characterized by parameters $\lambda$ of the form

$$\lambda_i = \hat{\chi}_i + k_B \kappa_i + O\left(k_B^2\right) \tag{37}$$

Using the method of steepest descent we can easily calculate local equilibrium averages $\langle \overline{\cdots} \rangle$ in powers of $k_B$. In particular, we find

$$\langle \overline{a^i} \rangle = \hat{a}^i - k_B \hat{S}^{i\underline{j}} \left( \kappa_{\underline{j}} - \frac{1}{2} \hat{S}^{\underline{k}\,\underline{l}} \frac{\partial^3 \hat{S}}{\partial a^{\underline{j}} \partial a^{\underline{k}} \partial a^{\underline{l}}} \right) + O\left(k_B^2\right) \tag{38}$$

and

$$\langle \overline{\delta a^i \delta a^j} \rangle = -k_B \hat{S}^{ij} + O\left(k_B^2\right) \tag{39}$$

where $\hat{S}^{ij}$ is the inverse of the matrix $\hat{S}_{ij}$ introduced previously:

$$\hat{S}^{i\underline{k}} \hat{S}_{\underline{k}j} = \hat{S}_{j\underline{k}} \hat{S}^{\underline{k}i} = \delta_j^i \tag{40}$$

The inverse exists, because the steady state is stable by assumption.

The $\kappa$'s are determined by equating the right-hand side of (38) with the mean value $\langle a^i \rangle$ which follows from (33) and (34). Then, $\bar{p}(a)$ yields the correct mean values of the macroscopic variables. However, the local equilibrium correlations $\langle \overline{\delta a^i \delta a^j} \rangle$ of the fluctuations about the mean values may not coincide with the true correlations $\langle \delta a^i \delta a^j \rangle$. Putting

$$\langle \delta a^i \delta a^j \rangle = \langle \overline{\delta a^i \delta a^j} \rangle + \Psi^{ij} \tag{41}$$

we obtain from (34) by use of (6), (11), (39), and (40)

$$\hat{M}^i{}_{\underline{k}} \Psi^{\underline{k}j} + \Psi^{i\underline{k}} \hat{M}^j{}_{\underline{k}} = \hat{R}^{ij} \tag{42}$$

where

$$\begin{aligned} \hat{R}^{ij} &= k_B \left( \frac{\partial \hat{L}^{i\underline{l}}}{\partial a^{\underline{k}}} \hat{S}^{\underline{k}j} + \frac{\partial \hat{L}^{j\underline{l}}}{\partial a^{\underline{k}}} \hat{S}^{i\underline{k}} \right) \hat{\chi}_{\underline{l}} + O\left(k_B^2\right) \\ &= k_B \left( \frac{\partial \hat{L}^{i\underline{l}}}{\partial \chi_j} + \frac{\partial \hat{L}^{j\underline{l}}}{\partial \chi_i} \right) \hat{\chi}_{\underline{l}} + O\left(k_B^2\right) \end{aligned} \tag{43}$$

The equations (42) and (43) determine the deviations $\Psi^{ij}$ from the local equilibrium correlations in leading order in $k_B$. Note, that corrections to local equilibrium arise only if the transport coefficients $L^{ij}$ depend on the state. These nonlinearities do not show in the statics of an equilibrium system but they are important for the statics of nonequilibrium states.

At the end of this section we mention some changes that occur in the presence of external forces $h_i$. The evolution matrix $\hat{M}_k^i$ has the form (22), and instead of (43) one obtains

$$\hat{R}^{ij} = k_B\left(\frac{\partial \hat{L}^{i\underline{l}}}{\partial \chi_j} + \frac{\partial \hat{L}^{j\underline{l}}}{\partial \chi_i}\right)\left(\chi_{\underline{l}} - \frac{1}{T_{\underline{l}}} h_{\underline{l}}\right) \tag{44}$$

which shows that there are no deviations from local equilibrium if the nonequilibrium state is entirely maintained by external forces.

## 4. TIME CORRELATION FUNCTIONS AND LINEAR RESPONSE

### 4.1. Time Correlations of Fluctuations

The evolution law of time correlation functions of variables $a^i$ and $a^j$ characterizing properties in the interior of the system follows from (25):

$$\frac{d}{dt}\langle a^i(t)a^j(0)\rangle_0 = \langle K^i(t)a^j(0)\rangle_0, \qquad \text{for } t > 0 \tag{45}$$

The average $\langle \cdots \rangle_0$ is defined by

$$\langle F(t)G(0)\rangle_0 = \int da\, da'\, F(a')G(a)p_t(a' \mid a)p_0(a) \tag{46}$$

where $p_t(a' \mid a)$ is the conditional probability, while $p_0(a)$ is the single-event probability at time $t_0 = 0$.

For the steady state under consideration we obtain from (31) and (45) an evolution law for the stationary correlations

$$C^{ij}(t) = C^{ji}(-t) = \langle \delta a^i(t)\delta a^j(0)\rangle \tag{47}$$

of fluctuations $\delta a^i(t) = a^i(t) - \langle a^i\rangle$ about the mean values of the form

$$\frac{d}{dt}C^{ij}(t) = \hat{M}^i{}_{\underline{k}}C^{\underline{k}j}(t) + O\left(k_B^2\right) \tag{48}$$

for $t > 0$. The formal solution of (48) reads in obvious notation

$$C^{ij}(t) = \begin{cases} \left(e^{\hat{M}t}\right)^i{}_{\underline{k}}C^{\underline{k}j}(0) & \text{for } t > 0 \\ \left(e^{-\hat{M}t}\right)^j{}_{\underline{k}}C^{i\underline{k}}(0) & \text{for } t < 0 \end{cases} \tag{49}$$

where the equal-time correlations $C^{ij}(0) \equiv \langle \delta a^i \delta a^j\rangle$ are determined by (34).

Introducing the Fourier-transformed correlations

$$C^{ij}(\omega) = e^{-i\omega\underline{t}}C^{ij}(\underline{t}) \tag{50}$$

Eqs. (34) and (49) can be combined to yield

$$C^{ij}(\omega) = 2k_B\left(-i\omega\delta^i{}_{\underline{k}} + \hat{M}^i{}_{\underline{k}}\right)^{-1}\hat{D}^{\underline{k}\underline{l}}\left(i\omega\delta^j{}_{\underline{l}} + \hat{M}^j{}_{\underline{l}}\right)^{-1} + O\left(k_B^2\right) \tag{51}$$

Note that these relations have been obtained without making use of an assumption about the stochastic behavior of the fluctuations in the nonequilibrium steady state. Although the fluctuations about the steady state can be treated in a linear approximation their stochastics have to conform to the fluctuation-dissipation theorem associated with the *nonlinear* process of fluctuations about equilibrium, even if those nonlinearities have only a minor effect on the equilibrium fluctuations themselves. This connection between the equilibrium correlations and the nonequilibrium correlations determines the latter in those areas which are not under the direct influence of the environment.

In equilibrium the correlation functions have the symmetries

$$C^{ij}(t) = \epsilon^i \epsilon^j C^{ji}(t) \tag{52}$$

which are a consequence of the detailed balance of the stochastic process. In order that detailed balance hold for the nonequilibrium steady state under consideration the following potential conditions$^{(12)}$ must be satisfied:

$$D^{ij}(\hat{a}) = \epsilon^i \epsilon^j D^{ji}(\tilde{\hat{a}}) \tag{53}$$

and there must be a potential $\psi(a, \Delta)$ with

$$\psi(\tilde{a}, \tilde{\Delta}) = \psi(a, \Delta) \tag{54}$$

so that

$$\frac{\partial}{\partial \Delta^{\underline{i}}} r^{\underline{i}}(\hat{a}, \Delta) + r^{\underline{i}}(\hat{a}, \Delta) \frac{\partial}{\partial \Delta^{\underline{i}}} \psi(\hat{a}, \Delta) = 0 \tag{55}$$

and

$$d^i(\hat{a}, \Delta) = k_B \hat{D}^{i\underline{j}} \frac{\partial}{\partial \Delta^{\underline{j}}} \psi(\hat{a}, \Delta) \tag{56}$$

where the reversible drift $r^i$ and the irreversible drift $d^i$ have been defined previously.

While (53) is a consequence of (5) and (6) the potential $\psi$ does not exist in general. One finds that $\psi$ only exists if

$$\frac{\partial \hat{A}^{\underline{i}\underline{j}}}{\partial a^{\underline{i}}} \hat{\chi}_{\underline{j}} = 0 \tag{57}$$

and if the equal-time correlations $C^{ij}(0) \equiv \langle \delta a^i \delta a^j \rangle$ following from (34) satisfy

$$C^{ij}(0) = \epsilon^i \epsilon^j C^{ji}(0) \tag{58}$$

as well as

$$\left( \hat{D}^{i\underline{l}} \hat{S}_{\underline{l}\underline{k}} + \frac{\partial \hat{D}^{i\underline{l}}}{\partial a_{\underline{k}}} \hat{\chi}_{\underline{l}} \right) C^{\underline{k}j}(0) = k_B \hat{D}^{ij} \tag{59}$$

The latter relation which relates the irreversible part of the evolution matrix $\hat{M}^i_k$ with the correlation matrix $C^{ij}(0)$ and the diffusion matrix $\hat{D}^{ij}$ reduces to the Einstein relation in equilibrium. However, this condition will generally not be satisfied in a nonequilibrium steady state if the transport coefficients are not constant. State-dependent transport coefficients may lead to a breakdown of detailed balance in nonequilibrium steady states.

In the presence of external forces $h_i$ we have to replace $\hat{\chi}_i$ by $\hat{\chi}_i - (1/T_i)h_i$ on the left-hand sides of (57) and (59). If the thermodynamic forces $\hat{\chi}_i$ are entirely balanced by the external forces the steady state is in local equilibrium and the conditions (57)–(59) for detailed balance are satisfied.

### 4.2. Linear Response

The evolution matrix $\hat{M}^i_k$ governs the linear relaxation to the steady nonequilibrium state according to

$$\frac{d}{dt}\delta\langle a^i(t)\rangle = \hat{M}^i{}_{\underline{k}}\delta\langle a^{\underline{k}}(t)\rangle \tag{60}$$

where $\delta\langle a^i(t)\rangle$ is the deviation of the mean value from the stationary nonequilibrium mean value. In the presence of time-dependent external forces $h_i(t)$ Eq. (60) is modified to

$$\frac{d}{dt}\delta\langle a^i(t)\rangle = \hat{M}^i{}_{\underline{k}}\delta\langle a^{\underline{k}}(t)\rangle + \hat{L}^{i\underline{k}}\frac{1}{\hat{T}_{\underline{k}}}h_{\underline{k}}(t) \tag{61}$$

This equation holds up to corrections of order $k_B$.

The solution of (61) with initial condition $\delta\langle a^i(0)\rangle = 0$ reads

$$\delta\langle a^i(t)\rangle = R^{i\underline{j}}(t-\underline{s})h_{\underline{j}}(\underline{s}) \tag{62}$$

where

$$R^{ij}(\tau) = \theta(\tau)(e^{\hat{M}\tau})^i_{\underline{k}}\hat{L}^{\underline{k}j}(1/\hat{T}_j) \tag{63}$$

is the response tensor. Comparing with (49) we see that the response tensor is related to the time-correlation matrix by a "generalized fluctuation-dissipation theorem" of the form

$$R^{ij}(\tau) = C^{i\underline{k}}(\tau)C^{\underline{k}\underline{l}}(0)^{-1}L^{\underline{l}j}(1/\hat{T}_j) \tag{64}$$

for $\tau \geqslant 0$. This theorem provides a physical realization of a nonequilibrium fluctuation-dissipation theorem and belongs basically to class (III) in Hanggi's classification.(13)

By use of (11) we obtain from (49)

$$\frac{d}{d\tau} C^{ij}(\tau) = C^{i\underline{k}}(\tau) C^{\underline{k}\underline{l}}(0)^{-1} \left( \hat{L}^{\underline{l}\underline{m}} \hat{S}_{\underline{m}\underline{n}} + \frac{\partial \hat{L}^{\underline{l}\underline{m}}}{\partial a^{\underline{n}}} \hat{\chi}_{\underline{m}} \right) C^{\underline{n}j}(0) \qquad (65)$$

from which we see that (64) reduces in equilibrium to the familiar form$^{(13)}$

$$R^{ij}(\tau) = -\frac{1}{k_B T} \frac{d}{d\tau} C^{ij}(\tau) \qquad (66)$$

for $\tau \geqslant 0$. In a nonequilibrium state there is generally no simple connection between the response tensor and the time rate of change of the correlation matrix.

## 5. CONCLUSIONS

Starting from the nonlinear Fokker–Planck equation (23) which determines the stochastic process of a closed Markovian system we have investigated the stochastic properties of the system when it is brought into contact with a nonequilibrium environment. We assumed that the system settles down to a time-dependent nonequilibrium state. This is the case if the nonequilibrium parameters are still below a certain threshold where the system may bifurcate to time-dependent states.$^{(8)}$

For this particular nonequilibrium situation we obtained expressions for the time correlations of fluctuations about the steady state and for the linear response to external forces. To derive those expressions we made the following assumptions: the region where those expressions hold is not directly influenced by the boundary of the system and, second, the fluctuations about the nonequilibrium steady state are small and obey a linear law. The second approximation emerged in the first order of an expansion in terms of $k_B$. In particular, no Langevin assumption or an equivalent fluctuation hypothesis was needed. It should however be noted that our expression (51) for the correlation matrix coincides with an expression [Eq. (7) in Ref. 14] obtained by Tremblay *et al.* using a Langevin assumption. Our procedure justifies their assumption to first order in $k_B$ where the Langevin equations for the fluctuations about the steady state are linear.

Higher-order terms in $k_B$ lead to a nonlinear process of the fluctuations about the steady state. These nonlinearities lead to a renormalization of the transport coefficients characterizing the time evolution of the correlation functions. If the frequency dependence$^{(5,11,15)}$ of the renormalized coefficients can be neglected they just replace the bare coefficients in the final formulas. On the other hand, our approach can also be used to determine the frequency dependence of the renormalized transport coefficients by taking into account higher orders in $k_B$.(11) This is particularly important if one wants to extend the results to states near critical points.

Recently, several calculations(7,14,16,17) of fluctuations in nonequilibrium fluids have been put forward. In particular Ronis *et al.*(16) and Tremblay *et al.*(14) determined the structure factor for light scattering from a fluid in the presence of a thermal gradient. A corresponding evaluation of our relations will be outlined in the Appendix which also serves as an illustration of the theory. In a certain approximation we find an expression for the structure factor for light scattering which coincides with the result obtained by Tremblay *et al.*(14) There is a slight difference between this result and the earlier statistical mechanical calculation of Ronis *et al.*,(16) which comes from the fact that the molecular expressions in Ref. 16 have not been evaluated carefully enough. There is no basic difference between the phenomenological and the statistical mechanical approach. The evolution equations obtained in this paper are in complete agreement with the results of an earlier statistical mechanical examination of nonequilibrium systems.(18,19) The equations (34) and (48) are directly obtained from (7.7) and (7.9) in Ref. 19 if the latter are specialized to time-independent mean values.

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## APPENDIX: FLUCTUATIONS IN FLUIDS

### 1. Deterministic Equations

A simple fluid can be described on the macroscopic level by the densities of the conserved quantities mass, momentum, and energy. We denote the mass density by $\rho(x,t)$, the momentum density by $g^\alpha(x,t)$, and the energy density by $e(x,t)$. The index $\alpha$ runs through 1, 2, and 3 labeling the space components. In a shorthand notation we may introduce a five-component field of macroscopic variables

$$a(x,t) = (\rho(x,t),\ g^\alpha(x,t), e(x,t)) \tag{A1}$$

with components $a^i(x,t)$, where $i$ runs through 0, 1, 2, 3, and 4.

The deterministic equations of motion consist of the continuity equation, the Navier–Stokes equations, and the energy balance equation, and they read[(20,21)]

$$\dot{\rho} = -\frac{\partial}{\partial x^{\underline{\alpha}}}\rho v^{\underline{\alpha}} \tag{A2}$$

$$\dot{g}^{\alpha} = -\frac{\partial}{\partial x^{\underline{\beta}}}\rho v^{\alpha} v^{\underline{\beta}} - \frac{\partial}{\partial x^{\alpha}} p + \frac{\partial}{\partial x^{\underline{\beta}}}\sigma'^{\alpha\underline{\beta}} \tag{A3}$$

$$\dot{e} = -\frac{\partial}{\partial x^{\underline{\alpha}}}(e+p)v^{\underline{\alpha}} + \frac{\partial}{\partial x^{\underline{\alpha}}}\sigma'^{\underline{\alpha}\underline{\beta}}v^{\underline{\beta}} + \frac{\partial}{\partial x^{\underline{\alpha}}}\kappa\frac{\partial}{\partial x^{\underline{\alpha}}}T \tag{A4}$$

where we have introduced the velocity $v^{\alpha}$, the pressure $p$, the temperature $T$, the heat conductivity $\kappa$, and the dissipative part of the stress tensor $\sigma'^{\alpha\beta}$ which reads explicitly

$$\sigma'^{\alpha\beta} = \left(\zeta - \frac{2}{3}\eta\right)\frac{\partial v^{\underline{\gamma}}}{\partial x^{\underline{\gamma}}}\delta^{\alpha\beta} + \eta\left(\frac{\partial v^{\alpha}}{\partial x^{\beta}} + \frac{\partial v^{\beta}}{\partial x^{\alpha}}\right) \tag{A5}$$

where $\zeta$ and $\eta$ are the bulk and shear viscosities. We suppress the space and time dependence of quantities if no confusion arises.

The entropy $S$ of the fluid is a space integral over the entropy density $s(x)$:

$$S = s(\underline{x}) \tag{A6}$$

The functional derivatives of $S$ with respect to the macroscopic variables define the thermodynamic forces

$$\chi_0 = \frac{\delta S}{\delta \rho} = -\frac{\mu - (1/2)v^2}{T} \tag{A7}$$

$$\chi_{\alpha} = \frac{\delta S}{\delta g^{\alpha}} = -\frac{v^{\alpha}}{T} \tag{A8}$$

$$\chi_4 = \frac{\delta S}{\delta e} = \frac{1}{T} \tag{A9}$$

where $\mu$ is the chemical potential.

Now, the deterministic equations (A2)–(A4) can be cast into the form (1):

$$\dot{a}^{i}(x) = L^{i\underline{j}}(x, \underline{y})\chi_{\underline{j}}(\underline{y}) \tag{A10}$$

The transport matrix $L^{ij}(x, y)$ consists of two parts: The antisymmetric part

$$A^{ij}(x,y)=\left[\begin{array}{c|c|c} 0 & -\dfrac{\partial}{\partial x^{\beta}}\dfrac{\partial p}{\partial \chi_0} & 0 \\ \hline \dfrac{\partial}{\partial y^{\alpha}}\dfrac{\partial p}{\partial \chi_0} & -\dfrac{\partial}{\partial x^{\beta}}\dfrac{\partial p}{\partial \chi_{\alpha}}+\dfrac{\partial}{\partial y^{\alpha}}\dfrac{\partial p}{\partial \chi_{\beta}} & \dfrac{\partial}{\partial y^{\alpha}}\dfrac{\partial p}{\partial \chi_4} \\ \hline 0 & -\dfrac{\partial}{\partial x^{\beta}}\dfrac{\partial p}{\partial \chi_4} & 0 \end{array}\right]\delta(x-y) \tag{A11}$$

where $i=0,\alpha,4$ and $j=0,\ \beta,4$, gives rise to the reversible motion (Euler equations), while the symmetric part gives rise to the dissipative motion, and it reads

$$D^{ij}(x,y)=-\frac{\partial}{\partial x^{\underline{\nu}}}\Delta^{i\underline{\nu},j\underline{\mu}}(x)\frac{\partial}{\partial x^{\underline{\mu}}}\delta(x-y) \tag{A12}$$

where

$$\Delta^{i\nu,j\mu}=\left[\begin{array}{c|c|c} 0 & 0 & 0 \\ \hline 0 & T\Xi^{\alpha\nu,\beta\mu} & T\Xi^{\alpha\nu,\underline{\gamma}\mu}v^{\underline{\gamma}} \\ \hline 0 & T\Xi^{\underline{\gamma}\nu,\beta\mu}v^{\underline{\gamma}} & T\Xi^{\underline{\gamma}\nu,\underline{\lambda}\mu}v^{\underline{\gamma}}v^{\underline{\lambda}}+T^2\kappa\delta^{\nu\mu} \end{array}\right] \tag{A13}$$

and

$$\Xi^{\alpha\nu,\beta\mu}=\eta(\delta^{\alpha\beta}\delta^{\nu\mu}+\delta^{\alpha\mu}\delta^{\beta\nu})+(\zeta-\tfrac{2}{3}\eta)\delta^{\alpha\nu}\delta^{\beta\mu} \tag{A14}$$

The equivalence of (A10) and (A2)–(A4) follows after some of the familiar thermodynamic manipulations. For more details and a molecular definition of the various quantities introduced the reader is referred to Ref. 21.

## 2. Fokker–Planck Equation

The Fokker–Planck equation (23) associated with the deterministic laws (A10) is of the form

$$\frac{\partial}{\partial t}p_t=\frac{\delta}{\delta a^{\underline{i}}(\underline{x})}k_B L^{\underline{i}\underline{j}}(\underline{x},\underline{y})\left(\frac{\partial p_t}{\delta a^{\underline{j}}(\underline{y})}-\frac{p_t}{w}\frac{\partial w}{\delta a^{\underline{j}}(\underline{y})}\right) \tag{A15}$$

where $w$ is given by (24). The globally conserved quantities of a fluid in a container with ideal walls are the total mass

$$M=\rho(\underline{x}) \tag{A16}$$

and the total energy

$$E=e(\underline{x}) \tag{A17}$$

Any distribution of the form

$$p_{\mathrm{st}} = wF(M, E), \tag{A18}$$

where $F$ is an arbitrary function of the globally conserved quantities, is a stationary solution of (A15). This is a consequence of the particular form of the transport matrix and the fact that

$$\frac{\delta p_{\mathrm{st}}}{\delta a^{j}(y)} - \frac{p_{\mathrm{st}}}{w}\,\frac{\delta w}{\delta a^{j}(y)}$$

is independent of $y$.

A canonical equilibrium state is of the form

$$p_c \propto w \exp\left[-\frac{1}{k_B T_0}(E - \mu_0 M)\right] \tag{A19}$$

where $T_0$ and $\mu_0$ characterize the particular equilibrium state. Using (A6) the distribution (A19) may be written

$$p_c \propto \exp\left\{\frac{1}{k_B}\left[s(\underline{x}) - \frac{1}{T_0}e(\underline{x}) + \frac{\mu_0}{T_0}\rho(\underline{x})\right]\right\} \tag{A20}$$

This exponential can be substituted for $w$ in Eq. (A15) since the terms which depend on $T_0$ and $\mu_0$ cancel.

To study equilibrium fluctuations the exponent in (A20), which is a function of the state variables, is usually expanded about its maximal value. This leads to an expansion for $w$ of the Ginzburg–Landau type. By truncating this expansion the Fokker–Planck equation acquires a reference to a particular equilibrium state and it can only be used to study fluctuations about this equilibrium state. Such an expansion about equilibrium is not advisable if one wants to study nonequilibrium fluctuations; one rather should base the considerations upon the basic form (A15) with $w$ given by (24).

### 3. A Fluid in a Temperature Gradient

We now consider a particular nonequilibrium state: two heat baths at different temperatures maintain a constant temperature gradient in a fluid layer of thickness $L$. This nonequilibrium steady state is a stationary solution of (A2)–(A4) characterized by

$$\begin{aligned} \hat{v}^{\alpha}(x) &= 0 \\ \hat{p}(x) &= p_0 \\ \hat{T}(x) &= T_0 + \lambda_{\underline{\alpha}} x^{\underline{\alpha}} \end{aligned} \tag{A21}$$

where $\lambda_\alpha$ is the temperature gradient. The origin of the coordinate system lies at the center of the fluid system. To keep things as simple as possible we disregard the temperature and pressure dependence of $\kappa$, $\zeta$, and $\eta$.

The evolution matrix (11) governing the linear relaxation to the steady state is obtained by linearizing (A2)–(A4) about the steady state (A21). We find

$$\hat{M}^{ij}(x, y) =$$

$$\left[\begin{array}{c:c:c} 0 & -\frac{\partial}{\partial x^{\beta}} & 0 \\ \hdashline -\frac{\partial}{\partial x^{\alpha}}\left(\frac{\partial \hat{p}}{\partial \rho}\right)_{\epsilon} & \eta\frac{\partial^2}{\partial x^{\underline{\nu}}\partial x^{\underline{\nu}}}\,\frac{1}{\hat{\rho}}\delta^{\alpha\beta} + \left(\zeta + \frac{1}{3}\eta\right)\frac{\partial^2}{\partial x^{\alpha}\partial x^{\beta}}\,\frac{1}{\hat{\rho}} & -\frac{\partial}{\partial x^{\alpha}}\left(\frac{\partial \hat{p}}{\partial \epsilon}\right)_{\rho} \\ \hdashline \kappa\frac{\partial^2}{\partial x^{\underline{\nu}}\partial x^{\underline{\nu}}}\left(\frac{\partial \hat{T}}{\partial \rho}\right)_{\epsilon} & -\frac{\partial}{\partial x^{\beta}}\,\frac{\hat{e}+\hat{p}}{\hat{\rho}} & \kappa\frac{\partial^2}{\partial x^{\underline{\nu}}\partial x^{\underline{\nu}}}\left(\frac{\partial \hat{T}}{\partial \epsilon}\right)_{\rho} \end{array}\right]\delta(x-y) \tag{A22}$$

where we have noted that $p$ and $T$ are only functions of $\rho$ and the intrinsic energy density,

$$\epsilon = e - \tfrac{1}{2}\rho v^2 \tag{A23}$$

Using (A12)–(A14) we obtain an expression for the symmetric part of the transport matrix in the steady state (A21) of the form

$$\hat{D}^{ij}(x, y) =$$

$$\left[\begin{array}{c:c:c} 0 & 0 & 0 \\ \hdashline 0 & -\eta\frac{\partial}{\partial x^{\underline{\nu}}}\,\hat{T}\frac{\partial}{\partial x^{\underline{\nu}}}\delta^{\alpha\beta} - \eta\frac{\partial}{\partial x^{\beta}}\,\hat{T}\frac{\partial}{\partial x^{\alpha}} - \left(\zeta - \frac{2}{3}\eta\right)\frac{\partial}{\partial x^{\alpha}}\,\hat{T}\frac{\partial}{\partial x^{\beta}} & 0 \\ \hdashline 0 & 0 & -\kappa\frac{\partial}{\partial x^{\underline{\nu}}}\,\hat{T}^2\frac{\partial}{\partial x^{\underline{\nu}}} \end{array}\right]\delta(x-y) \tag{A24}$$

We now have all quantities needed to determine the correlations of fluctuations about the steady state by means of Eq. (51). The evaluation of (51) is itself a complicated problem if the temperature gradient is large because the correlation functions are nonlinear functions of the temperature gradient. For the illustrative purposes of this Appendix we may restrict ourselves to a small gradient and make the simplifying assumption that the pressure is only a function of the density, i.e., $(\partial\hat{p}/\partial\epsilon)_{\rho} = 0$, so that the evolution matrix (A22) couples the density and the longitudinal momentum only to themselves. In this approximation the density–density correlation function is readily obtained from (51) if we introduce a Fourier space representation of the fluctuation

$$a^{i}(k) = \frac{1}{V^{1/2}}\, e^{ik\underline{x}}\delta a^{i}(\underline{x}) \tag{A25}$$

where $V$ is the volume. The requirement that the fluctuating variables describe properties in the interior of the system restricts the $k$ vector to values with $|k|L \gg 1$. Using (A21)–(A25) we obtain from (51)

$$\begin{aligned} C_{\rho\rho}(k,k';\omega) &= e^{-i\omega \underline{t}}\langle \rho(k,\underline{t})\rho(k',0)\rangle \\ &= \frac{2k_B\left\{2\eta(k^{\nu}k'^{\nu})^2 + \left[\zeta - (2/3)\eta\right]k^2k'^2\right\}}{\left(\omega^2 - c^2k^2 - iv_{\|}\omega k^2\right)\left(\omega^2 - c^2k'^2 + iv_{\|}\omega k'^2\right)} \\ &\quad \times\left(T_0 - i\lambda_{\underline{\alpha}}\frac{\partial}{\partial k^{\underline{\alpha}}}\right)\delta(k+k') \end{aligned} \tag{A26}$$

where $k^2 = k^{\nu}_{-}k^{\nu}_{-}$, and where

$$c = \left(\frac{\partial \hat{p}}{\partial \rho}\right)^{1/2}_{\epsilon} \tag{A27}$$

is the sound velocity, while

$$v_{\|} = \frac{\zeta + (4/3)\eta}{\hat{\rho}} \tag{A28}$$

is the longitudinal diffusion constant.

The density–density correlation function is related to the structure factor $S(k,\omega)$ for light scattering by

$$S(k,\omega) = (1/B^2)B(k - \underline{k}')B(k + \underline{k}'')C_{\rho\rho}(\underline{k}',\underline{k}'',\omega) \tag{A29}$$

where $B(k) = B(-k)$ is a weighting function which depends on the bandwidth of the light source focused on a spot around $x = 0$, and where $B^2 = B(\underline{k})B(-\underline{k})$. Using (A26) we find after simple transformations

$$S(k,\omega) = \frac{1}{B^2}B(k - \underline{k}')^2 I(\underline{k}',\omega) \tag{A30}$$

where

$$I(k,\omega) = \frac{2k_B\rho v_{\|}k^4}{(\omega^2 - c^2k^2)^2 + v_{\|}^2\omega^2k^4}\left[T_0 - \frac{2v_{\|}\omega^3\lambda_{\underline{\alpha}}k^{\underline{\alpha}}}{(\omega^2 - c^2k^2)^2 + v_{\|}^2\omega^2k^4}\right] \tag{A31}$$

Since the light source should only illuminate a small portion of the fluid in the interior, the bandwidth $\Delta k$ has to be large compared to $1/L$, but it may still be small compared to $|k|$. In this case the average over $B(k - k')^2$ can be neglected in Eq. (A30) and we have

$$S(k,\omega) = I(k,\omega) \tag{A32}$$

This expression for the spectrum has also been obtained by Tremblay *et al.*(14)

As a consequence of the temperature gradient $\lambda_\alpha$ the structure factor (A32) shows an asymmetry in the Brillouin peaks at $\omega^2 = c^2k^2$. The height difference of the peaks has a pronounced $(1/k^2)$ dependence which can be traced back to long-range static correlations between the density and the longitudinal momentum.(7) The static correlations can be obtained directly from Eq. (42). In the steady state (A21) Eq. (43) yields

$$\hat{R}^{ij}(x,y) = \left[\begin{array}{c|c|c} 0 & -\dfrac{\partial \hat{\rho}\hat{T}}{\partial x^\beta} & 0 \\ \hline -\dfrac{\partial \hat{\rho}\hat{T}}{\partial x^\alpha} & \left(\zeta - \dfrac{5}{3}\eta\right)\left(\dfrac{\partial \hat{T}}{\partial x^\beta}\dfrac{\partial}{\partial x^\alpha} - \dfrac{\partial \hat{T}}{\partial x^\alpha}\dfrac{\partial}{\partial x^\beta}\right) & -\dfrac{\partial(\hat{e}+\hat{p})\hat{T}}{\partial x^\alpha} \\ \hline 0 & -\dfrac{\partial(\hat{e}+\hat{p})\hat{T}}{\partial x^\beta} & 0 \end{array}\right] \delta(x-y) \tag{A33}$$

Using (A22) and (A33) we obtain from (42) for the correlation between the density and the longitudinal momentum $g^{\parallel}$

$$\langle \rho(k)\, g^{\parallel}(-k)\rangle = -\frac{\lambda_{\underline{\alpha}} k^{\underline{\alpha}} \hat{\rho}}{2\Gamma_s |k|}\,\frac{1}{k^2} + O(k^0) \tag{A34}$$

where

$$\Gamma_s = \frac{1}{2}\nu_{\parallel} + \frac{\kappa}{2\hat{\rho}C_p}\left(\frac{C_p}{C_V} - 1\right) \tag{A35}$$

is the sound attenuation constant. This result has also been obtained by Ronis *et al.*(16) If we make the simplifying assumption $p = p(\rho)$, which we have used to calculate the structure factor, $2\Gamma_s$ is replaced by $\nu_{\parallel}$.

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