

FLUCTUATIONS ABOUT HYDRODYNAMIC NONEQUILIBRIUM STEADY STATES [☆]

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Received 19 December 1979

Using an extension of the Langevin method, we calculate the fluctuations of a fluid about a stationary state held away from global thermal equilibrium by a temperature gradient or shear flow. In the former case, the Brillouin peaks in the light scattering spectrum acquire an asymmetry that is qualitatively similar to earlier results but different in detail.

Fluctuations about nonequilibrium stationary states are not as well understood as fluctuations about thermal equilibrium states where the fluctuation–dissipation theorem and linear response theory can be used effectively. Perhaps the best known nonequilibrium fluctuations are those which lead to $1/f$ noise [1] (flicker noise). In this problem, one must treat both the effect of the applied constant voltage to quadratic order as well as the temperature gradient caused by the Joule heating [2]. A seemingly simpler system is a fluid subjected to a small uniform temperature gradient or shear flow. Here, there are grounds for believing that the local values of hydrodynamic variables will characterize these systems completely.

Recent calculations [3–5] have predicted some small but qualitatively unexpected effects in statically stressed fluids that should be measurable by light scattering. We will show that these can all be simply obtained by a plausible extension of the Langevin method that we have checked by actual microscopic calculations on a model system. Our Langevin calculation has the additional virtue of demonstrating which of the usual equilibrium results [6] (Onsager regression hypothesis, Einstein relation, fluctuation–dissipation theorem) persist in this particular non-equilibrium situation.

On comparison of our predictions for the light scattering spectrum with Ronis et al. [4] we obtain to first order in the external gradient a shift in the height of the Brillouin peaks that is twice as large and a modification to the line shape that falls off as ω^{-5} rather than ω^{-3} . These discrepancies cancel out when static correlation functions are computed. In particular, certain of these functions that would vanish by time reversal symmetry in equilibrium here have a finite value and depend on the momentum transfer as $1/k^2$.

We will derive our results in the context of a general set of hydrodynamic equations for modes A_α , linearized about the nonequilibrium stationary state in question and acted upon by Langevin forces. We will then specialize to the example of a fluid in a uniform temperature gradient or shear flow. Let

$$\frac{\partial A_\alpha(\mathbf{k}, t)}{\partial t} + \int \frac{d^3 k'}{(2\pi)^3} M_{\alpha\beta}(\mathbf{k}, -\mathbf{k}') A_\beta(\mathbf{k}') = \mathcal{F}_\alpha(\mathbf{k}, t). \quad (1)$$

The Langevin force, $\mathcal{F}_\alpha(\mathbf{k}, t)$, should 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 rea-

[☆] This work was supported by the National Science Foundation under Grant #DMR-77-18329 and through the Cornell Materials Science Center, NSF Grant #DMR-76-81083. MSC Report #4189.

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sonable to expect that it will remain uncorrelated at unequal times or points in the nonequilibrium states we are considering. We will further assume that the magnitude of its correlation function has the same form as in equilibrium [7] with local values of the temperature and transport coefficients [8].

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. We have found, however, by explicit calculation in one limit of physical importance that the direct modification of $M_{\alpha\beta}$ by the temperature gradient cancels from the final answer. Hence we will assume $M_{\alpha\beta}$ diagonal in k although the formulae below can be generalized.

Using eq. (1) and the above assumptions about the Langevin forces we find, (in matrix notation)

$$\langle \mathbf{A}(k, t) \mathbf{A}^*(k', 0) \rangle = \theta(t) \exp[-\mathbf{M}(k)t] \langle \mathbf{A}(k, 0) \mathbf{A}^*(k', 0) \rangle + \theta(-t) \langle \mathbf{A}(k, 0) \mathbf{A}^*(k', 0) \rangle \exp[\mathbf{M}^+(k')t], \quad (2)$$

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

$$\langle \mathbf{A}(k, 0) \mathbf{A}^*(k', 0) \rangle \equiv \int_{-\infty}^0 dt \exp[\mathbf{M}(k)t] \mathbf{D}(k, k') \exp[\mathbf{M}^+(k')t], \quad (3)$$

$$\langle \mathcal{F}_\alpha(k, t) \mathcal{F}_\beta^*(k', t) \rangle \equiv D_{\alpha\beta}(k, k') \delta(t - t'). \quad (4)$$

Eq. (4) can be evaluated from our assumptions concerning the Langevin forces. The equal time correlation functions may be obtained from eq. (3) or equivalently from

$$\mathbf{D}(k, k') = [\mathbf{M}(k) \langle \mathbf{A}(k, 0) \mathbf{A}^*(k', 0) \rangle + \langle \mathbf{A}(k, 0) \mathbf{A}^*(k', 0) \rangle \mathbf{M}^+(k')]^{-1}. \quad (5)$$

Note that in general these equations are not diagonal in momentum space, even when \mathbf{M} is. The ensemble implicit in the Langevin equation is stationary but in general not time reversal invariant. Eq. (2) is the generalization of the Onsager regression hypothesis [6] and eq. (5) the generalization of Einstein's relation [6]. Note that these relations follow from the Langevin formalism and our assumptions above without further approximations. Let

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

then, using eq. (2) we find,

$$\boldsymbol{\chi}^\omega(k, k') = (-i\omega \mathbf{1} + \mathbf{M}(k))^{-1} \boldsymbol{\chi}(k, k') + \boldsymbol{\chi}(k, k') (i\omega \mathbf{1} + \mathbf{M}^+(k'))^{-1}, \quad (6)$$

where $\mathbf{1}$ is the identity matrix. Eqs. (5) and (6) also give,

$$\boldsymbol{\chi}^\omega(k, k') = (-i\omega \mathbf{1} + \mathbf{M}(k))^{-1} \mathbf{D}(k, k') (i\omega \mathbf{1} + \mathbf{M}^+(k'))^{-1}. \quad (7)$$

This result may also be obtained directly from eqs. (1) and (4). In equilibrium, eq. (6) reduces to a version of the fluctuation-dissipation theorem which expresses the fluctuations as the imaginary part of a response function.

We now specialize to a fluid in a uniform temperature gradient. In order to display the modifications to the Brillouin spectrum as simply as possible, we will retain in the hydrodynamic description only the density and the longitudinal velocity. This is correct to leading order in the temperature gradient when $(\partial V / \partial T)_p = 0$. Writing the mass density ρ , in terms of the pressure p , the linearized hydrodynamic equations (1) become [7],

$$\partial p / \partial t = -i\rho c^2 \mathbf{k} \cdot \mathbf{v}, \quad \partial \mathbf{k} \cdot \mathbf{v} / \partial t = -i(k^2 / \rho) p - [(\zeta + 4\eta/3) / \rho] k^2 (\mathbf{k} \cdot \mathbf{v}) + (i/\rho) \mathbf{k} \cdot \mathbf{S} \cdot \mathbf{k}, \quad (8)$$

where c is the sound velocity, ζ the bulk and η the shear viscosities. There is no Langevin force associated with the pressure equation while \mathbf{S} in the velocity equation is the fluctuating stress tensor. From ref. [7] and our assumptions we have,

$$\langle S_{ij}(r_1, t_1) S_{lm}(r_2, t_2) \rangle = 2T(r_1) [\eta(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl}) + (\xi - 2\eta/3)\delta_{ij}\delta_{lm}] \delta^3(r_1 - r_2) \delta(t_1 - t_2), \quad (9)$$

with Boltzmann's constant $k_B = 1$.

It is convenient to assume,

$$T(r) = T_0 + \delta T \sin(q \cdot r), \quad (10)$$

which reduces to a linear temperature gradient if the scattering volume is restricted to $|r| \ll q^{-1}$. Using eqs. (7)–(9) we can compute the correlation function,

$$\chi_{pp}^\omega(k', k'') = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle p(k', t) p^*(k'', 0) \rangle = \frac{c^4 2T(k' - k'') [2\eta(k' \cdot k'')^2 + (\xi - 2\eta/3)k'^2 k''^2]}{(\omega^2 - c^2 k'^2 + i\omega D_l k'^2)(\omega^2 - c^2 k''^2 - i\omega D_l k''^2)}, \quad (11)$$

where $D_l \equiv (\xi + 4\eta/3)/\rho$. The light scattering from a volume δk^{-3} of fluid at a frequency in the neighborhood of the Brillouin peaks is proportional to an average of eq. (11) over k' and k'' with a weight function of bandwidth δk centered around k' and k'' equal k . Since the laser must be focused on a spot small compared to the external gradient, $\delta k^{-1} < q^{-1}$. When $T(k' - k'')$ is computed from eq. (10), the average weights equally $k' = k \pm q/2$ and $k'' = k \mp q/2$. If $(\delta k/k) \ll 1$, the remaining average over the bandwidth δk may be neglected. The measured spectrum is then determined from eq. (11) by adding together the three terms obtained with $k' = k \pm q/2$, $k'' = k \mp q/2$ and $k' = k'' = k$. If furthermore $cq/D_l k^2 \ll 1$, we can expand to first order in q . The measured spectrum is thus,

$$\chi_{pp}^\omega = (c^2 \rho T) c^2 k^2 2D_l k^2 / [(\omega^2 - c^2 k^2)^2 + (\omega D_l k^2)^2] + \delta \chi_{pp}^\omega, \quad (12)$$

$$\delta \chi_{pp}^\omega = -(c^2 \rho T) c^2 k^2 \{4\omega^2 (\omega D_l k^2) / [(\omega^2 - c^2 k^2)^2 + (\omega D_l k^2)^2]^2\} (D_l k \cdot (\nabla \ln T)_{r=0}) \quad (13)$$

$$\approx \chi_{vp} c \rho \left\{ \frac{\frac{1}{2} D_l k^2}{(\omega - ck)^2 + (\frac{1}{2} D_l k^2)^2} - \frac{\frac{1}{2} D_l k^2}{(\omega + ck)^2 + (\frac{1}{2} D_l k^2)^2} \right\} \left[\frac{2(\omega D_l k^2)^2}{(\omega^2 - c^2 k^2)^2 + (\omega D_l k^2)^2} \right], \quad (14)$$

where,

$$\chi_{vp} = \chi_{pv} \equiv -(c^2/D_l k^2) [k \cdot \nabla T_{(r=0)}/k], \quad (15)$$

is the static pressure, longitudinal velocity correlation function. It may be obtained from eq. (5) or by using the equation of continuity and performing a frequency integral over eqs. (12), (13).

Comparing eqs. (12)–(14) with the results of Ronis et al. we find the asymmetric shift in the Brillouin peaks at $|\omega| = ck$ to be twice as large as theirs. Its dependence on k^{-2} is the same, however, as is the static correlation function (15)^{†1}. Thus, our line shapes must also disagree since the same integral over χ_{pp}^ω can be done to extract χ_{vp} . Ronis et al. find a $\delta \chi_{pp}^\omega$ similar to eq. (14) but with the term in the second bracket replaced by unity and D_l replaced by $2\Gamma_s$, the sound attenuation constant when the energy mode is coupled to the modes in eq. (8).

The condition $(\partial V/\partial T)_p = 0$ is satisfied by water near 4°C, where however, $(\partial \ln c^2/\partial \ln T) = 1.8$ and $(\partial \ln D_l/\partial \ln T) = -8.7$. We have shown explicitly that the modifications introduced in $M_{\alpha\beta}$ by the dependence of c^2 and D_l on temperature do not influence $\delta \chi_{pp}^\omega$ to first order in the temperature gradient. Since the result of Kirkpatrick et al. [5] for a fluid in a temperature gradient does involve the parameter $\partial \ln D_l/\partial \ln T$, it should be easy to experimentally check which theory is correct.

We believe that the remaining disagreement between our results and those of Ronis et al. can be traced to the latter's treatment of "non-locality" corrections. If eq. (5) is solved for the static correlation functions and the result used in eq. (6) to compute the frequency dependent functions, we see that contributions of order ∇T come not only from the static correlations, χ_{vp} , (as in ref. [4]) but also from the q dependence of the matrices $M_{\alpha\beta}(k \pm q/2)$ and $M_{\alpha\beta}^+(k \mp q/2)$.

^{†1} Note that the sign of that correlation function in ref. [3] differs from our result and that of refs. [4] and [5].

We have also studied the problem of a fluid in a shear [10]. In this case, the matrix \mathbf{D} is diagonal in Fourier space but the matrix \mathbf{M} differs from the equilibrium one. To linear order in the shear, the latter matrix can be taken as diagonal in k . Again, we find the same static correlation functions as those of Machta et al. [9] but our spectrum has a different frequency dependence and the amplitudes at $\omega = \pm |ck|$ again differ by a factor of 2.

It may be asked whether our application of Langevin equations to nonequilibrium stationary states is in fact equivalent to postulating a modified matrix and if so can our results be confirmed by a microscopic calculation. To address these questions simply, we have returned to a system of electrons scattering off impurities studied earlier by one of the authors [2]. The local density, n , satisfies a linear diffusion equation that can easily be studied in a temperature gradient through the Langevin formalism.

Microscopically, we postulated the weight function,

$$\mathcal{P} = \Xi (\text{Tr } \Xi)^{-1}, \quad (16)$$

$$\Xi = \exp \left[-\beta H - \int dr \delta\beta(r) \mathcal{C}(r) \right], \quad (17)$$

where $\mathcal{C}(r)$ is the local energy density, $\beta = 1/T$ and H is the hamiltonian of the system (including the chemical potential). Using the techniques of ref. [2] we calculated,

$$\langle n(k, 0)n(k', t) \rangle = \theta(t) \lim_{\epsilon \rightarrow 0^+} \text{Tr}[\mathcal{P}n(k, \epsilon)n(k', t + \epsilon)] + \theta(-t) \lim_{\epsilon \rightarrow 0^+} \text{Tr}[\mathcal{P}n(k, -t + \epsilon)n(k', \epsilon)], \quad (18)$$

where the trace is over a complete set and where ϵ should be much larger than a microscopic collision time (to establish the dissipative flows) but much smaller than the energy diffusion time [to maintain the local temperature constraint]. Note that the origin of time in eq. (18) is arbitrary. It can also be shown that to first order in $\delta\beta$ and for one-time observables, eq. (18) reduces to the linear response formulae of Kadanoff and Martin [10]. Eq. (18) also reduces to formulae very similar to those of Ronis et al. [4] in the general case.

Both the microscopic and phenomenological calculations yield, (following the approximations that lead to eq. (12)),

$$\chi_{nn}^{\omega} = \chi 2Dk^2 / [\omega^2 + (Dk^2)^2] - \chi \{4\omega Dk^2 / [\omega^2 + (Dk^2)^2]^2\} Dk \cdot (\nabla \ln T)_{r=0}, \quad (19)$$

where χ is a constant and D a diffusion constant. Note the similarity to eqs. (12), (13). This correction is also non-lorentzian, lending some support to our prediction for the fluid. In the above model, the diffusion constant is temperature independent.

Note added in proof. After submitting this paper, we received a preprint from Dr. J.R. Dorfman, where Kirkpatrick, Cohen and him derived independently from us a new prediction for the light scattering spectrum which agrees with our results.

We should like to thank Drs. I. Oppenheim, D. Ronis and I. Procaccia for discussions and correspondence at the early stages of this work and also for sending us preprints of their papers. We should like to thank Andrei Ruckenstein for valuable discussions. M.R. Arai would like to acknowledge the support of an NSF predoctoral scholarship.

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