the short-range details of the impurity potential. A more refined theory should contain both a better impurity potential[1] and a better description of the screening. The authors wish to thank Dr. M. Altarelli, Dr. A. Baldereschi, Dr. K. Maschke, and Dr. E. Tosatti for helpful discussions. One of us (A.S.) is partially supported by Landis and Gyr AG, Zug, Switzerland.

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Light Scattering and Pair-Correlation Functions in Fluids with Nonuniform Velocity Fields

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We study fluctuations in a fluid with a stationary, linear shear. We find that the pair-correlation function gains a long-ranged part. The Brillouin components of scattered light are enhanced or reduced compared to equilibrium depending on the scattering angle. The Landau-Placzek ratio no longer holds and the total scattering intensity is k dependent. We suggest a simple light-scattering experiment to test our predictions. The new features are explained by the differential attenuation of sound modes.

Fluctuations in fluids with nonuniform velocity fields are of great current interest, in the context of the hierarchy of hydrodynamic instabilities[1,2] and the transition to turbulence.[3] In this Letter we report some results of a theoretical investigation of hydrodynamic fluctuations in systems with stable nonuniform velocity field, and we argue that the existence of a dissipative momentum flux is accompanied by the appearance of a long-ranged part in the pair-correlation function as well as interesting and measurable new effects in the spectrum of light scattering.

The method of calculating the correlation functions in the presence of a velocity field is based on our statistical-mechanical theory of nonequilibrium stationary states. The theory was presented in great detail in Refs. 4–6 and a shortened version was outlined in a previous Letter.[7] We do not repeat the derivations here, and simply remind the reader that the main result of the formal theory is that when the macroscopic gradients are sufficiently small we have an expression for the nonequilibrium ensemble average of any dynamical variable $B(\vec{r},t)$[4]:

$$\langle B(\vec{r},t)\rangle_{\rm NE} = \langle B(\vec{r})\rangle_{\rm L}{}^{\rm hom} - \int_0^\infty d\tau \langle B(\vec{r},\tau)\underline{I}_T\rangle_{\rm L}{}^{\rm hom} * \nabla[\beta\underline{\Phi}(\vec{r},t)], \tag{1}$$

where the symbol $\langle\ \rangle_{\rm L}{}^{\rm hom}$ denotes an average over a "local equilibrium" distribution function

$$f_{\rm L}(X|\vec{r},t) \equiv \frac{f_{\rm G.C.}(X)\exp[\beta\underline{\Phi}(\vec{r},t)*\int\underline{A}(\vec{r}_1)d^3r_1]}{\sum_N\int dX f_{\rm G.C.}(X)\exp[\beta\underline{\Phi}(\vec{r},t)*\int\underline{A}(\vec{r}_1)d^3r_1]}, \tag{2}$$

where $f_{\rm G.C.}$ is the grand canonical distribution function, X is the phase-space point, and in a simple fluid the set $\underline{A}(\vec{r},t)$ is composed of the densities of number energy and momentum. The set $\beta\underline{\Phi}$ is related to the local chemical potential, temperature, and velocity, respectively. The set $\underline{I}_T$ is composed of the microscopic dissipative fluxes, integrated over the volume: $\underline{I}_T \equiv \int d^3r\underline{I}(\vec{r})$. Here the asterisk denotes an inner product in the space of such sets, but now with the spatial integration explicitly written out (see notation in Ref. 7).

In a simple fluid with a nonuniform velocity field as the only dissipative mechanism (i.e., the system is isothermal) the only contribution to Eq. (1) comes from the dissipative momentum flux $\overleftrightarrow{I}_p$, which is contracted with $\nabla[\beta\vec{v}(\vec{r})]$, where $\vec{v}(\vec{r})$ is the local velocity field and $\beta = 1/k_{\rm B}T_{\rm eq}$. Equation (1) can be used, after simple manipulations, to compute the static correlation functions in k space in a nonequilibrium stationary state (NESS) with velocity gradients:

$$\langle \underline{A}_{\vec{k}}(t)\underline{A}_{-\vec{k}}(t)\rangle_{\rm NE}(\vec{r}) = \langle \underline{A}_{\vec{k}}\underline{A}_{-\vec{k}}\rangle_{\rm L}{}^{\rm hom}(\vec{r}) - \int_0^\infty d\tau\langle \underline{A}_{\vec{k}}(\tau)\underline{A}_{-\vec{k}}(\tau)\overleftrightarrow{I}_{p,\tau}\rangle_{\rm L}{}^{\rm hom}(\vec{r}):\nabla[\beta\vec{v}(\vec{r})]. \tag{3}$$

We have shown[5] that the dominant part of the second term on the right-hand side (RHS) of Eq. (3) can be obtained by writing

$$\underline{A}_{\vec{k}}(t) \simeq \exp(\underline{\underline{M}}_{\vec{k}}t)\underline{A}_{\vec{k}}(0), \tag{4}$$

where $\underline{\underline{M}}_{\vec{k}}$ is the matrix that governs the linearized macroscopic relaxation to the steady state. For NESS that are not too far from equilibrium we can identify $\underline{\underline{M}}_{\vec{k}}$ with the matrix that governs the relaxation to equilibrium.[4] For simplicity, we can compute the quantities appearing in Eq. (3) in the rest frame of a fluid element, and at the end transform to the laboratory frame. Thus, denoting the second term on the RHS of Eq. (3) by $\underline{\underline{W}}^p(\vec{k}|\vec{r})$ we have

$$\underline{\underline{W}}^p(\vec{k}|\vec{r}) \equiv -\int_0^\infty d\tau\,\exp(\underline{\underline{M}}_{\vec{k}}\tau)\langle\underline{A}_{\vec{k}}\underline{A}_{-\vec{k}}\overleftrightarrow{I}_{p,\tau}\rangle(r)\exp(\underline{\underline{M}}_{\vec{k}}{}^{\dagger}\tau):\nabla[\beta\vec{v}(\vec{r})], \tag{5}$$

where now the average is in an equilibrium system with uniform thermodynamic parameters that are the same as the actual ones at the point $\vec{r}$. Since $\overleftrightarrow{I}_p$ is even under time reversal, the only nonvanishing entries of $\underline{\underline{W}}^p(\vec{k}|\vec{r})$ are the NN, EN, NE, EE, and PP ones. Since we are interested here in the modifications of the light-scattering spectrum, we do not evaluate $\langle\vec{P}_{\vec{k}}\vec{P}_{-\vec{k}}\rangle_{\rm NE}$ or $\langle E_{\vec{k}}E_{-\vec{k}}\rangle_{\rm NE}$ which will be given elsewhere.[8] Remembering that the light-scattering spectrum is determined[9] by $\langle N_{\vec{k}}(t)N_{-\vec{k}}\rangle_{\rm NE}$, which is

$$\langle N_{\vec{k}}(t)N_{-\vec{k}}\rangle_{\rm NE} = [\exp(\underline{\underline{M}}_{\vec{k}}t)]_{N\underline{A}}\langle\underline{A}_{\vec{k}}N_{-\vec{k}}\rangle_{\rm NE} \tag{6}$$

we see that we have to compute only the entries NN and EN of $\underline{\underline{W}}^p(\vec{k}|\vec{r})$.

The matrix $\exp(\underline{\underline{M}}_{\vec{k}}t)$ was computed in Ref. 5. With use of symmetry arguments and the fact that $\nabla\cdot\vec{v}(\vec{r})\approx 0$ in the NESS it can be shown that only $\langle P_{\vec{k}}{}^xP_{-\vec{k}}{}^xI_p{}^{xx}\rangle$ contributes appreciably to the matrix multiplication in Eq. (5). Here $P_{\vec{k}}{}^x$ is the longitudinal component of the momentum[10] (i.e., x is chosen to point in the $\vec{k}$ direction). Performing the calculation involved in Eq. (5), which contain only integrals over thermodynamic and hydrodynamic quantities, we find (details are given elsewhere)[8]

$$W_{NN}{}^p(\vec{k}|\vec{r}) = -\frac{1}{2}\frac{k_{\rm B}T}{mc_0{}^2\Gamma_s}\frac{\hat{k}\hat{k}}{k^2}:\nabla[\vec{v}(\vec{r})], \tag{7a}$$

$$W_{EN}{}^p(\vec{k}|\vec{r}) = -\frac{1}{2}\frac{hk_{\rm B}T}{mc_0{}^2\Gamma_s}\frac{\hat{k}\hat{k}}{k^2}:\nabla[\vec{v}(\vec{r})], \tag{7b}$$

where ρ, h, T, m, c_0, and Γ_s are the density, the enthalpy density, the temperature, the molecular mass, the speed of sound, and the attenuation of sound, respectively, all computed at the point $\vec{r}$. $\hat{k}$

is a unit vector in the direction of $\vec{k}$.

The first interesting conclusion is that the static density autocorrelation function gains a long-ranged part. The $1/k^2$ dependence appearing in Eqs. (7) is equivalent to a $1/r$ decay in physical space. Here we caution the reader that the theory is only valid for systems in which the shear remains constant over a length scale several times larger than $c_0/2\Gamma_s k^2$, the characteristic attenuation length of sound with wave vector k. Thus $1/k^2$ is not to be interpreted as a true divergence, since the limit $k \to 0$ is not accessible within the present theory. However, the $1/k^2$ dependence means that for distances that are not too large the pair-correlation function has a part that decays like $1/r$ in space, in contrast to equilibrium systems far from critical points where the pair-correlation function is extremely short ranged. We stress that the present finding is associated with a *stable* NESS and is not related to any instability.

Secondly, we can combine Eqs. (6), (3), and (7) to find the density time autocorrelation function. Performing a Fourier transformation according to

$$S_{\vec{k}\omega}(\vec{r}) \equiv \int_{-\infty}^{\infty} dt \langle N_{\vec{k}}(t) N_{-\vec{k}}\rangle_{\mathrm{NE}}(\vec{r}) e^{-i\omega t}$$

we find the following result for the dynamic structure factor[9,10]:

$$S_{\vec{k}\omega}(\vec{r}) = \left[\frac{2k_B T\rho}{mc_0^2}\left(\frac{C_p}{C_v}-1\right)\frac{\Gamma_T k^2}{\omega^2+(\Gamma_T k^2)^2}\right] + \left\{\frac{2k_B T\rho\Gamma_s k^2}{mc_0^2}\left(\frac{1-\epsilon(\vec{r})}{(\omega-kc_0)^2+(\Gamma_s k^2)^2}+\frac{1-\epsilon(\vec{r})}{(\omega+kc_0)^2+(\Gamma_s k^2)^2}\right)\right\}, \tag{8}$$

where

$$\epsilon(\vec{r}) = \frac{c_0}{2\Gamma_s k^2}\hat{k}\hat{k}:\frac{\nabla[\vec{v}(\vec{r})]}{c_0}. \tag{9}$$

Here C_p, C_v, and Γ_T are the specific heats at constant pressure and volume and the heat attenuation coefficient, respectively. We remind the reader that Eq. (8) is calculated in the rest frame. It can be shown that the transformation to the laboratory frame involves only a Doppler shift [i.e., $\omega \to \omega + \vec{k}\cdot\vec{v}(\vec{r})$ in all the frequencies].

As is well known, the spectrum of scattered light is proportional to $S_{\vec{k}\omega}$. Two facts concerning Eq. (8) are immediately obvious; first, the total scattering intensity has become $\vec{k}$ dependent. Secondly, the central peak is not affected. Thus the Landau-Placzek ratio[9,10] no longer holds. The ratio between the intensities of the Brillouin and Rayleigh components is not purely thermodynamic but is now k dependent.

In Fig. 1 we depict $S_{\vec{k}\omega}$ for a fluid subject to a linear shear with the velocity in the x direction and the gradient of velocity in the y direction. The two panels are associated with two $\vec{k}$ vectors, $\vec{k}^{(1)}$ and $\vec{k}^{(2)}$. The following relations are chosen:

$$|\vec{k}^{(1)}| = |\vec{k}^{(2)}|, \quad k_y^{(1)} = k_y^{(2)}, \quad k_x^{(1)} = -k_x^{(2)}. \tag{10}$$

The fact that the Landau-Placzek ratio does not hold is related to the long-ranged part in the pair-correlation function. In equilibrium, the static correlations of the sound and heat modes, respectively, which determine the intensities of the Brillouin and Rayleigh lines, can be computed (as all other static correlation functions) in the $k \to 0$ limit, which yields a purely thermodynamic result. Once the pair correlation gains a long-ranged part, the computation of the static correlation cannot be done in the $k=0$ limit and the Landau-Placzek ratio should not hold.[11]

A simple light-scattering experiment can be suggested to test our predictions. One can place a fluid within two coaxial cylinders and then rotate the outer one (to avoid instability). In this way an almost linear shear can be produced. Denoting the velocity direction as x and its gradient as y, one can send a laser beam in the z direction. The spectra depicted in Fig. 1 can be obtained by observing two scattered beams that share a small polar angle but differ in their azimuthal angles (in the $\vec{v}$-∇v plane) by 90°. The $\vec{k}$ vectors can be then chosen according to Eq. (10).

The experimental setup must obey several con-

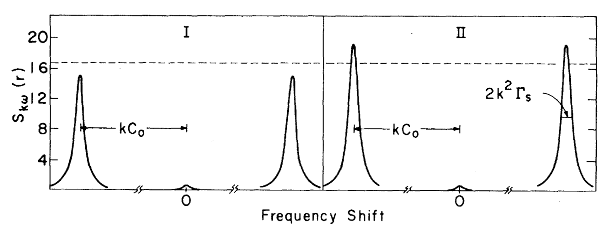

FIG. 1. A schematic spectrum of light scattered from a fluid with a linear shear. In panel I, $\hat{k}\hat{k}:(\nabla\vec{v}/c_0)$ is positive, whereas in panel II it is negative. The dashed line marks the height of the Brillouin components in the same system at equilibrium. Notice that the Landau-Placzek ratio no longer holds.

straints in order to allow a measurable effect [i.e., $\epsilon(\vec{r}) \sim 10^{-1}$]. Firstly, the shear flow must remain laminar. With the suggested geometry, laminar flow can be maintained up to Reynolds numbers of $O(10^3-10^4)$. Secondly, the difference between the inner and outer radii, l, must be several times larger than $c_0/2k^2\Gamma_s$ (see the last paragraph for an intuitive reason for this constraint). Finally, k must be sufficiently small to allow a detectable $\epsilon(\vec{r})$.

Choosing $l \sim 4(C_0/2k^2\Gamma_s)$ we find a relationship between the Reynolds number $R = v_0 l/\nu$ and the scattering vector k,

$$k = [R/4l^2\epsilon(\vec{r})]^{1/2}$$

and the kinematic viscosity,

$$\nu \sim \Gamma_s \sim 8c_0\epsilon(\vec{r})l/R\,.$$

A good compromise between the above-mentioned constraints can be found if the fluid is sufficiently viscous[12] [$\Gamma_s \sim O(1-10\ \mathrm{cm}^2/\mathrm{sec})$ and $k \sim O(500\ \mathrm{cm}^{-1})$]. This means scattering angles $\theta \sim O(0.5°)$ which are accessible with modern light-scattering techniques.

To conclude this Letter we present a nonrigorous, intuitive argument that may help to explain the novel features reported above. The height of the Brillouin components of $S_{\vec{k}\omega}$ can be identified with the intensity of sound waves having wave vector $\vec{k}$. These sound waves propagate over relatively large distances in the fluid. In fact, their characteristic attenuation length is $c_0/2\Gamma_s k^2$, which is precisely the coefficient in $\epsilon(\vec{r})$ [Eq. (9)]. For light-scattering wave vectors this attenuation length is of the order of 1 cm and thus the sound waves contributing to the Brillouin part of the spectrum are able to "see" the macroscopic velocity gradient. Consider now the way in which sound propagation is changed by the presence of a velocity gradient. If we choose $\vec{k}$ to lie on the x axis, then we are interested only in sound propagation along the x axis. Further, if we choose our frame of reference so that the scattering point is at rest, then there are two possible projections of the surrounding velocity field onto the x axis as shown in Figs. 2(a) and 2(b). In Fig. 2(a), $\nabla\vec{v}:\hat{x}\hat{x}$ is positive and fluid moves away from the scattering point along the x axis, whereas in Fig. 2(b), $\nabla\vec{v}:\hat{x}\hat{x}$ is negative and fluid moves toward the scattering point along the x axis. We see that, if $\nabla\vec{v}:\hat{x}\hat{x}$ is positive, the velocity field

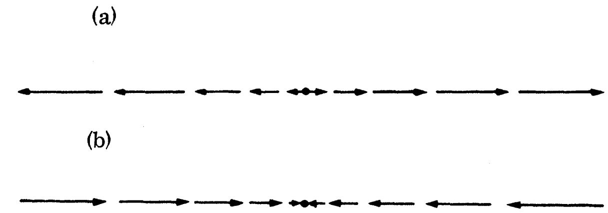

FIG. 2. Two possible projections of the velocity field onto the x axis. (a) $\hat{x}\hat{x}:\nabla\vec{v} > 0$; (b) $\hat{x}\hat{x}:\nabla\vec{v} < 0$.

works against incoming sound waves; the effective distance over which they propagate to reach the scattering point is increased and they arrive more strongly attenuated. Thus both Brillouin peaks are diminished from their equilibrium height. On the other hand, if $\nabla\vec{v}:\hat{x}\hat{x}$ is negative, the reverse holds and the Brillouin peaks are increased.

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