Equilibrium Fluctuations in Fluid Layers: Effects of Transport Across Fluid-Solid Interfaces

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The effects of momentum and energy transport across the fluid-solid interfaces on the dynamic structure factor of a fluid layer have been studied. New spectral features have been found; their positions and line shapes are sensitive to the boundary conditions. This theory suggests that experiments that probe the dynamic structure factor (such as light scattering) may be important for studying the nature of interfacial transport.

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The transport of momentum and energy across fluid-solid interfaces may significantly affect the dynamic properties of fluids, which are typically confined by solid walls. Traditionally, in the hydrodynamic theory of fluids,[1,2] the interfaces are modeled by empirical boundary conditions on the hydrodynamic variables, without a detailed understanding of the complicated nature of the dynamics of the interfacial transport. In addition to the theoretical difficulties,[3-5] to date there has been no sensitive experimental probe of interfacial transport over a wide range of frequencies.

In this Letter, we report theoretical analysis of the equilibrium dynamic structure factor of a fluid layer confined by two parallel solid walls. We show that the dynamic structure factor is affected by the energy and momentum transport across the interfaces. It exhibits novel peaks whose positions and line shapes depend sensitively on the boundary conditions, and may prove to be a useful probe of the transport porperties of interfaces, over a wide frequency range.

Consider an equilibrium fluid layer of infinite extent in the xy plane, bounded by solid walls at $z = \pm L/2$. The fluctuations $\delta\rho$ (mass density), δT (temperature), and $\vec{u}$ (velocity) are given by the solutions of the linearized hydrodynamic equations

$$\partial \delta\rho/\partial t + \rho_0(\nabla\cdot\vec{u}) = 0, \tag{1}$$

$$\partial\vec{u}/\partial t + c^2(\nabla\delta\rho + \alpha\rho_0\nabla\delta T)/\rho_0\gamma - \nu\nabla^2\vec{u} - (\zeta + \nu/3)\nabla(\nabla\cdot\vec{u}) = 0, \tag{2}$$

$$\partial\delta T/\partial t + (\gamma - 1)(\nabla\cdot\vec{u})/\alpha - \gamma\kappa\nabla^2\delta T = 0, \tag{3}$$

where ρ_0 is the mean density, c is the adiabatic speed of sound, α is the thermal expansion coefficient, ν and ζ are shear and bulk kinematic viscosities, $\gamma \equiv C_p/C_v$, and κ is the thermal diffusivity. The quantity of experimental interest is the dynamic structure factor,[6] which is the Fourier transform of the time-dependent density autocorrelation function

$$S(\vec{r},\vec{r}\,';t) \equiv \langle \delta\rho(\vec{r},t)\delta\rho(\vec{r}\,',0)\rangle. \tag{4}$$

Equations (1)–(3) are solved most easily by first Fourier transforming in the xy plane and Laplace transforming in time so that a hydrodynamic variable δA assumes the form

$$\delta A(k_{\parallel},z;s) = (2\pi)^{-2}\int_0^\infty dt \int_{-\infty}^{\infty} dx\,dy\, \exp[-st - i(k_x x + k_y y)]\delta A(\vec{r},t), \tag{5}$$

where $k_{\parallel}{}^2 = k_x{}^2 + k_y{}^2$. The set of Eqs. (1)–(3) then poses a boundary-value problem in z, in terms of the initial values of the variables $\delta A(k_{\parallel},z;0)$.

The empirical boundary condition on the velocity normal to the surface, u_z, is $u_z = 0$, corresponding to no mass transport. The parallel velocity components (u_x or u_y) are customarily believed[2] to vanish at a solid wall ("stick" boundary conditions). This corresponds to a very efficient transfer of tangential momentum across the interface. In many applications, a "slip" condition has been employed for mathematical simplicity. In this case $\partial u_x/\partial z = \partial u_y/\partial z = 0$, corresponding to no tangential momentum transport. While well established at low frequencies, the validity of the "stick" boundary condition at high frequencies is untested. The interfacial energy transport is assumed to be given by the heat flux, leading to boundary conditions on temperature. A common form is

$$\delta T = \delta T_s; \quad \rho_0 C_p \kappa(\partial \delta T/\partial z) = \rho_s C_p{}^s \kappa_s(\partial \delta T_s/\partial z),$$

where subscript s refers to the solid. For the simple case in which T_s obeys the heat equation ($\partial \delta T_s/\partial t = \kappa_s \nabla^2 \delta T_s$) the boundary condition on $\delta T(k_\parallel, z; s)$ of the fluid becomes

$$\partial \delta T/\partial z \pm \epsilon_T(k_\parallel, s)\delta T = 0; \quad z = \pm \tfrac{1}{2}L, \tag{6}$$

where

$$\epsilon_T(k_\parallel, s) \equiv (\rho_s C_p{}^s/\rho_0 C_p)(\kappa_s/\kappa)(\kappa_\parallel{}^2 + s/\kappa_s)^{1/2}. \tag{7}$$

Notice that in the limit $\kappa_s/\kappa \to \infty$ Eq. (6) reduces to $\delta T = 0$ (perfectly conducting wall). For $\kappa_s/\kappa \to 0$ we see that $\partial \delta T/\partial z \to 0$, which is the perfect insulator limit.

We have found the exact solutions of Eqs. (1)–(3) for arbitrary values of ϵ_T and for both "stick" and "slip" conditions. With the solution for $\delta\rho(\vec{k}_\parallel, z; s)$ at hand, one can find the dynamic correlation function $\langle \delta\rho(k_\parallel, z; s)\delta\rho(k_\parallel, z'; t=0)\rangle$ in terms of the static correlation function $\langle \delta\rho(k_\parallel, z; t=0)\delta\rho(k_\parallel, z'; t=0)\rangle$. This is a quantity of great interest since it is observable in a variety of experimental techniques, particularly light scattering. In the present case, it is quite involved algebraically and it is convenient to present the nature of our findings by considering its projection on the Fourier modes defined by

$$S(k_\parallel, k_z, k_{z'}; \omega) \equiv \pi^{-1}\,\mathrm{Re}\iint_{-L/2}^{L/2} dz\,dz'\,\exp(-i2n\pi z/L + i2n'\pi z'/L)\langle \delta\rho(k_\parallel, z; s = i\omega)\delta\rho(k_\parallel, z'; t=0)\rangle, \tag{8}$$

where $k_z \equiv 2n\pi/L$. As a result of lack of translational invariance in z, there are off-diagonal elements in the dynamic structure factor. Here we discuss only the diagonal elements, denoted by $S(k, k_2; \omega)$, since they are more readily probed experimentally, e.g., by light scattering. We assume that the off-diagonal elements in the static structure factor are negligible.

In the case of "stick" boundary conditions, there are two new peaks in the dynamic structure factor, for which, if the layer thickness is such that $\exp[k_\parallel L(\Gamma' k_\parallel/c)^{1/2}] \gg 1$, the dispersion relation depends only on $k_\parallel$ and is

$$\omega = \pm k_\parallel c + i[\Gamma + \Lambda(k_\parallel)]k_\parallel{}^2, \tag{9}$$

where $\Gamma = \frac{1}{2}[(\zeta + \frac{4}{3}\nu) + (\gamma - 1)\kappa]$ is the usual sound attenuation coefficient,

$$[2\Lambda(k_\parallel)]^{1/2} \equiv (2\Gamma')^{1/2} - (\gamma - 1)\kappa^{1/2}\{(\rho_s C_p{}^s/\rho_0 C_p)[(\kappa_s/\kappa)(1 \pm ik_\parallel \kappa_s/c)]^{1/2} + 1\}^{-1}, \tag{10}$$

and $\Gamma' \equiv \frac{1}{2}[\nu^{1/2} + (\gamma - 1)\kappa^{1/2}]^2$. Since $\Lambda(k_\parallel)$ is explicitly complex, the positions of these new peaks can be shifted from $\pm k_\parallel c$ depending on the ratio of κ_s/κ. Thus, for $\kappa_s k_\parallel/c \gg 1$ the dispersion relation becomes

$$\omega \cong \pm k_\parallel c\left[1 + (\gamma - 1)\left(\frac{\Gamma' k_\parallel}{c}\right)^{1/2} \frac{\rho_0 C_p}{\rho_s C_p{}^s}\frac{\kappa}{\kappa_s}\right] + i\left[\Gamma + \Gamma' - (\gamma - 1)\left(\frac{\Gamma' c}{k_\parallel}\right)^{1/2}\left(\frac{\rho_0 C_p}{\rho_s C_p{}^s}\right)\frac{\kappa}{\kappa_s}\right]k_\parallel{}^2, \tag{11a}$$

whereas for $\kappa_s/\kappa \ll 1$, we have

$$\omega \cong \pm k_\parallel c + i[\Gamma + \tfrac{1}{2}\nu + (\gamma - 1)(\nu\kappa_s)^{1/2}(\rho_s C_p{}^s/\rho_0 C_p)]k_\parallel{}^2. \tag{11b}$$

Therefore, for $\kappa_s k_\parallel/c \gg 1$, the effective speed of sound depends on $k_\parallel{}^{1/2}$.

The physical origin of these new peaks is clear. The component of the sound wave which propagates parallel to the "sticky" boundaries experiences additional dissipation due to the shear created by the wall (reflected by the appearance of ν in Λ). For $\kappa_s > 0$, the walls can also act as a heat sink. Since the sound is not isothermal, there is also extra dissipation due to heat conduction between fluid and solid walls (reflected by the appearance of κ and κ_s in Λ). With this picture, one would expect that in the limit of "slip," at thermally insulating boundaries there should be no extra dissipation and, consequently, no new peaks in the dynamic structure factor; direct calculation confirms this.[7]

The contribution of these peaks to the dynamic structure factor is, in general, very complicated and will not be given here. However, in the limit of perfectly conducting solid walls ($\kappa_s/\kappa \to \infty$) and for $k_z{}^2$

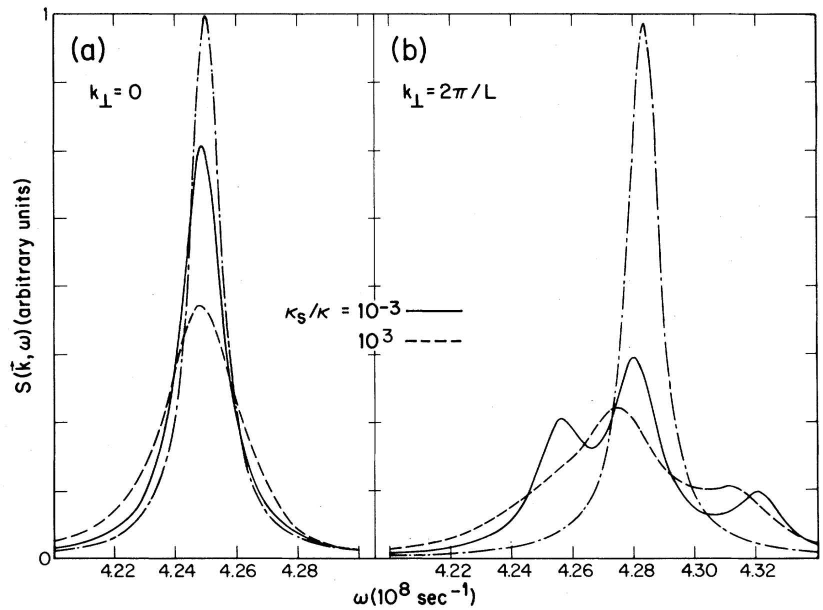

FIG. 1. The dynamic structure factor $S(k_{\parallel}, k_z; \omega)$ for ω in the vicinity of $\omega = kc$, at two values of k_z. The fluid parameters are of argon at 85 K: $\kappa = 2.3\times10^{-2}$ cm^2/sec, $\nu = \zeta = 9\times10^{-3}$ cm^2/sec, $c = 8.5\times10^4$ cm/sec, $\gamma = 2.2$. Also $\rho_0 C_p = \rho_s C_p^s$ is assumed. In all cases $k_{\parallel} = 5\times10^3$ cm^{-1} and the velocity field is assumed to vanish at the boundaries ("stick" boundary conditions). The Brillouin line (dot-dashed curve) of the infinite system is shown for comparison. The solid curve pertains to poor thermal diffusivity of the solid ($\kappa_s/\kappa = 10^{-3}$), while the dashed curve to high thermal diffusivity ($\kappa_s/\kappa = 10^3$).

$\gg 2\Gamma' k_{\parallel}^3/c$ this contribution is simply

$$\frac{\Delta S(k_{\parallel}, k_z; \omega)}{S(k_{\parallel}, k_z; t=0)} = \frac{2}{\pi\gamma(k_{\parallel}L)}\left(\frac{k_{\parallel}\Gamma'}{c}\right)^{1/2}\left(\frac{k_{\parallel}}{k_z}\right)^2\left[\frac{\delta + k_{\parallel}c - \omega}{\delta^2 + (\omega - k_{\parallel}c)^2} + \frac{\delta + k_{\parallel}c + \omega}{\delta^2 + (\omega + k_{\parallel}c)^2}\right], \tag{12}$$

where $\delta \equiv (\Gamma + \Gamma')k_{\parallel}^2$. Hence, this contribution to $S(k_{\parallel}, k_z; \omega)$ becomes significant only for sufficiently small values of L such that $k_{\parallel}L \sim (\Gamma' k_{\parallel}/c)^{1/2}$; i.e., for parameters typical for fluids and $k_{\parallel}$ typical for light scattering experiments, the new peaks should be observable for $L \sim 100$ μm, in which case there will be L-dependent corrections to the dispersion given in Eq. (10). Even more important is the fact that for such small values of L the fluid layer acts as a waveguide. Neglecting dissipation for a moment, we can use the theory of ideal waveguides[8] to realize that there exist a series of standing waves in the z directions which are the *natural* modes (rather than those calculated by the Fourier transform), which are supported by the waveguide whenever the dispersion relation

$$k_{\parallel}^2 = (\omega/c)^2 - (k_z^s)^2 \tag{13}$$

is satisfied. For rigid boundaries we have $k_z^s = m\pi/L$, $m = 0, 1, 2, 3 \ldots$. In our analysis, we have fixed $k_{\parallel}$ and looked at the projection of $S(k_{\parallel}, z, z'; \omega)$ on the Fourier mode $\exp(i2n\pi z/L)$ as a function of ω. Whenever $[(\omega/c)^2 - k_{\parallel}^2]^{1/2}$ hits a value of $k_z^s = m\pi/L$, we should see resonance. However, the Fourier projection used eliminated the standing waves which are orthogonal to it (i.e., $2m\pi/L = k_z^s, m \neq n$) and leaves those that are not [i.e., $(2m+1)\pi/L$, and $2n\pi/L$ itself]. The amplitudes of these peaks depend on their proximity to the Brillouin peak of the infinite system. Therefore, particularly revealing is the dynamic structure factor in the neighborhood of frequencies that characterize the Brillouin peak.[6] In Fig. 1, we present a typical plot of $S(k_{\parallel}, k_z; \omega)$ [evaluated from the exact solutions to Eqs. (1)–(3)] for a simple fluid (argon at 85 K) for the two first values of k_z (0, $2\pi/L$), superimposed on the Brillouin line of the infinite system. Shown are the results for a fluid layer which is 100 μm thick with "stick" boundary conditions on the velocity field, and two different thermal diffusivities of the solid walls. The infinite system lines

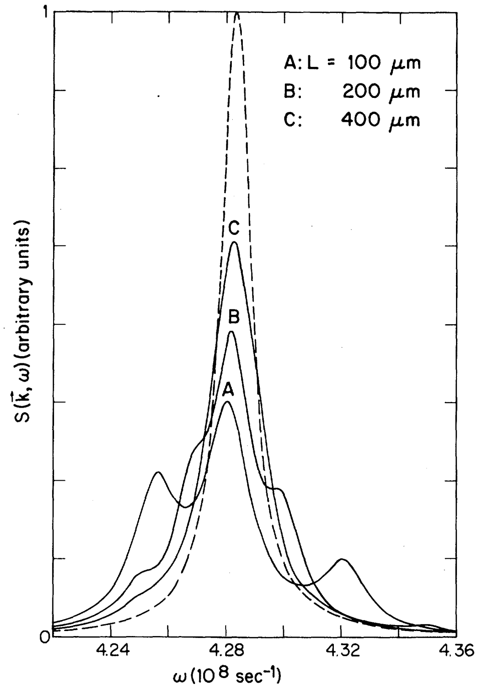

FIG. 2. The dynamic structure factor $S(k_{\|}, k_z; \omega)$ near the Brillouin frequency for three values of the layer thickness. The dashed curve is the infinite-system Brillouin line. The parameters are as in Fig. 1, with $k_z = 2\pi/L$.

correspond to $k = (k^2 + k_z^{\,2})^{1/2}$. In the layer the spectrum consists of more lines, quite distinct in the case of poor heat conductivity but somewhat smeared out in the case of high heat conductivity. Notice the high sensitivity to boundary conditions. In Fig. 2, we show the thickness dependence of the fine structure. Evidently, we are discussing thin-layer effects, although the thickness is orders of magnitude larger than that involved in light scattering from thin films[9] (i.e., order of nanometers).

It is seen in Fig. 1 that the new "dissipative" peaks and the peaks due to standing waves are not resolved since fluid parameters were chosen to demonstrate the effect on the dynamic structure factor of the coupling of the temperature fluctuations in the fluid to the solid walls. The detailed line shapes are determined, of course, by the overall dissipation. However, one expects that an efficient heat-conducting solid would cause broader spectral features due to increased dissipation through heat conduction to the walls. Indeed this effect is seen very clearly in Fig. 1.

All the effects discussed here occur when the dynamics of the solid consists only of heat diffusion. The influence of the propagating modes in the solid on the dynamic structure factor in the fluid will be considered elsewhere.[7]

The above theory suggests that experiments that probe the dynamics of the structure factor (light and neutron scattering, sound attenuation and dispersion) may prove to be a useful probe of interfacial transport.

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