PHYSICAL REVIEW A VOLUME 8, NUMBER 4 OCTOBER 1973

Frequency-Dependence Correction to the Order-Parameter Decay Rates near the Critical Point of Fluids*

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(Received 31 January 1973)

The correction to the order-parameter decay rates near the critical point of fluids arising from the frequency dependence of shear viscosity was calculated, and was found to be generally small ranging from 0.6% at $q\xi = 0.1$ to 6% at $q\xi = 30$, where q and ξ are the wave number and the range of correlations of order-parameter fluctuations, respectively.

In a recent paper[1] (hereafter referred to as I) we obtained the formula for the order-parameter decay rate Γ_{qs} (I7), near the critical point of fluids where the new linewidth function $K(x)$ was determined by solving the simultaneous integral equation involving the nonlocal shear viscosity (I6) and (I9). However, we disregarded all the memory effects (or, equivalently, frequency dependence) associated with the shear viscosity and the order parameter decay rate. On the other hand, Perl and Ferrell[2] considered the memory effects (called the retardation effects by them) associated with the shear viscosity and showed that the memory effects virtually cancel the nonlocal effects for $q\xi=\infty$. Thus we undertook to investigate the importance of the memory effects in the context of our theory.

We now introduce the wave-number- and frequency-dependent decay rate $\Gamma_{qs}(\omega)$ and $\eta(\xi, q, \omega)$ by one-sided Fourier transforms as in Ref. 3 and define the frequency-dependent linewidth function $K(\xi, q, \omega)$ by

$$\Gamma_{qs}(\omega)=\frac{k_B T}{6\pi\eta(T)\xi^3}K(\xi, q, \omega). \tag{1}$$

The self-consistent equation for determining η and K then takes the form

$$K(\xi, q, \omega)=\frac{3}{(2\pi)^3}\frac{\eta(T)\xi^3}{\rho}q^2\int d\vec{k}\frac{\chi_{\vec{q}-\vec{k}}}{\chi_{\vec{q}}}\sin^2\theta\int_{-\infty}^{\infty}d\omega'\frac{1}{i(\omega-\omega')+(k^2/\rho)\eta(\xi,\vec{k},\omega-\omega')}\,\frac{1}{i\omega'+(k_BT/6\pi\eta\xi^3)K(\xi,\vec{q}-\vec{k},\omega')}, \tag{2}$$

$$\eta(\xi, q, \omega)=\eta^0+\frac{k_BT}{2(2\pi)^4q^2}\int d\vec{k}\,k^2\sin^2\theta\,\chi_{\vec{k}}\chi_{\vec{q}-\vec{k}}\left(\frac{1}{\chi_{\vec{k}}}-\frac{1}{\chi_{\vec{q}-\vec{k}}}\right)$$
$$\times\int_{-\infty}^{\infty}d\omega'\frac{1}{i(\omega-\omega')+(k_BT/6\pi\eta\xi^3)K(\xi,\vec{q}-\vec{k},\omega-\omega')}\,\frac{1}{i\omega'+(k_BT/6\pi\eta\xi^3)K(\xi,\vec{k},\omega')}. \tag{3}$$

For small wave numbers and frequencies involved the integrand of (2) as a function of complex ω' has one pole in the upper half plane and another in the lower half plane. Thus, converting the path of integration over ω' into the semicircle enclosing the upper half plane, (2) becomes

$$K(\xi, q, \omega)=\frac{3}{(2\pi)^2}\frac{\eta(T)\xi^3}{\rho}q^2\int d\vec{k}\frac{\chi_{\vec{q}-\vec{k}}}{\chi_q}\sin^2\theta\left(i\omega+\frac{k^2}{\rho}\eta(\xi,k,\omega-\Omega(\vec{q}-\vec{k}))+\frac{k_BT}{6\pi\eta(T)\xi^3}K(\xi,\vec{q}-\vec{k},\Omega(\vec{q}-\vec{k}))\right)^{-1}$$
$$\times\left[1-\frac{ik_BT}{6\pi\eta(T)\xi^3}\left(\frac{\partial}{\partial\omega'}K(\xi,\vec{q}-\vec{k},\omega')\right)_{\omega'=\Omega(\vec{q}-\vec{k})}\right]^{-1}, \tag{4}$$

where $\Omega(\vec{q}-\vec{k})$ is the pole in the upper half plane determined by

$$\Omega(\vec{k})=\frac{ik_BT}{6\pi\eta(T)\xi^3}K(\xi,k,\Omega(\vec{k})). \tag{5}$$

Since the viscous relaxation rate $\xi^{-2}\eta/\rho$ is much greater than $\Gamma_{\vec{k}s}\sim\Omega(\vec{k})$ and we are interested in ω much smaller than the viscous relaxation rate, we have

$$\frac{k_BT}{6\pi\eta(T)\xi^3}\left(\frac{\partial K(\xi,\vec{q}-\vec{k},\omega')}{\partial\omega'}\right)_{\omega'=\Omega(\vec{q}-\vec{k})}\sim\frac{\Gamma_{\vec{k}s}}{\eta/\rho\xi^2}\ll 1, \tag{6}$$

and (4) simplifies to

$$K(\xi, q, \omega)=\frac{3}{(2\pi)^2}\eta(T)\xi^3\times\int d\vec{k}\frac{\chi_{\vec{q}-\vec{k}}}{\chi_{\vec{q}}}\frac{q^2}{k^2\eta(\xi,k,\omega-\Omega(\vec{q}-\vec{k}))}. \tag{7}$$

TABLE I. Linewidth function $K(x)$ and the frequency-dependence correction $\Delta K(x, 0)$. The numbers in the third column are subjected to the error of 0.02.

x	$K(x)/x^3$	$\Delta K(x,0)/x^3$	$\Delta K(x,0)/K(x)$ (%)
0.1	10.6	0.09	0.8
0.3	3.73	0.03	1
1	1.61	0.02	1
3	1.35	0.04	3
7	1.41	0.05	4
10	1.44	0.06	4
20	1.53	0.08	5
30	1.59	0.09	6
200	2	0.3	15

One can also simplify (3) in a similar fashion although we shall not write down the results explicitly at this stage.

We now introduce the corrections to K and η arising from the frequency dependence as

$$K(\xi, q, \omega) = K(q\xi) + \Delta K(\xi, q, \omega), \tag{8}$$

$$\eta(\xi, q, \omega) = \eta(T)[1 - F(q\xi) - \Delta F(q, \xi, \omega)], \tag{9}$$

where $K(q\xi)$ and $F(q\xi)$ were obtained previously[1] and include the corrections due to the nonlocal shear viscosity. The resulting equations for ΔK and ΔF can be expressed in terms of the dimensionless variables defined by

$$\vec{q} = \vec{x}/\xi, \quad \vec{k} = \vec{y}/\xi, \quad \omega = \frac{k_B T}{6\pi\eta\xi^3} z, \quad iK(\xi, k, \Omega(\vec{k})) = Z(\vec{k}\xi), \tag{10}$$

and we finally obtain using the Ornstein-Zernike form for $\chi_{\vec{k}}$,

$$\Delta K(x,z) = \frac{3}{4\pi^2} x^2(1+x^2) \int d\vec{y} \frac{\sin^2\theta}{y^2(1+|\vec{x}-\vec{y}|^2)} \left(\frac{1}{1-F(y)-\Delta F(y, z-Z(|\vec{x}-\vec{y}|))} - \frac{1}{1-F(y)} \right), \tag{11}$$

$$\Delta F(x,z) = -\frac{3}{8\pi^2 x^2} \int d\vec{y}\, y^2 \sin^2\theta \frac{(2\vec{x}\cdot\vec{y}-x^2)^2}{(1+y^2)(1+|\vec{x}-\vec{y}|^2)} \times \left(\frac{1}{iZ + K(y) + K(|\vec{x}-\vec{y}|) + \Delta K(y, z - Z(|\vec{x}-\vec{y}|)) + \Delta K(|\vec{x}-\vec{y}|, Z(|\vec{x}-\vec{y}|))} - \frac{1}{K(y)+K(|\vec{x}-\vec{y}|)} \right), \tag{12}$$

where, of course, Z is still an unknown function related to K through the last equation of (10).

Since (11) and (12) are an enormously complicated set of equations, we have estimated the importance of the correction ΔK by substituting (12) without ΔK terms into (11) with $z=0$ where we only need $\Delta F(x, -iK(|\vec{x}-\vec{y}|))$. The results of this first iterative solution of (11) and (12) for $\Delta K(x, 0)$ are presented in Table I for representative values of x. Thus the frequency dependence of shear viscosity results in a further increase in the relaxation rate but its magnitude is insignificant in the hydrodynamic regime and amounts to only several percent even in the critical regime. (Here we have excluded the result for $x=200$ which will be subject to larger errors.) Because of the smallness of the correction we have not attempted further iterations of (11) and (12).

In contrast to the expectation of Ref. 1, ΔK is positive, which is natural since the frequency dependent shear viscosity is expected to be smaller than its zero frequency value. In this connection we draw attention to the fact that the nonlocal correction to the shear viscosity in Ref. 2 was in fact meant to be $\eta(\infty, q, 0) - \eta(q^{-1}, 0, 0)$ in our notation, which is positive and is independent of temperature, whereas in our case it is $\eta(\xi, q, 0) - \eta(\xi, 0, 0)$ which is negative. The retardation correction to the order-parameter decay rate for $q\xi \to \infty$ in the work of Perl and Ferrell[2] is given roughly by

$$\left(\frac{\Delta\eta}{\eta}\right)_{\text{ret}} = \frac{8}{15\pi^2}\sigma_{\text{AVE}}$$

in their notation. This amounts to about 3%, which is smaller than the values obtained here for large x. We have not yet understood the cause for this discrepancy although for small values of x we seem to be in agreement.[4]

The authors are indebted to Professor R. A. Ferrell for the very informative conversations.

*Work supported by the National Science Foundation.

[1]K. Kawasaki and S.-M. Lo, Phys. Rev. Lett. 29, 48 (1972). Equations (1) and (2) in the paper are referred to as (I1), (I2), etc. We generally follow the notation of this reference.

[2]R. Perl and R. A. Ferrell, Phys. Rev. Lett. 29, 51 (1972); Phys. Rev. A 6, 2358 (1972).

[3]K. Kawasaki, Ann. Phys. (N.Y.) 61, 1 (1970). Note we here changed the sign of ω.

[4]R. A. Ferrell (private communications).