particle ($R = 1500$ Å) case. We would emphasize, however, that we were never able to prepare large-particle colloids that were stable enough to avoid particle settling and possible ambiguities in interpretation for these cases. Bonchev *et al.*[4] apparently encountered similar difficulties.

In conclusion we find that, for the highly stable sol of cobaltous hydroxy stannate in glycerol, glycerol-ethanol, and glycerol-water, the Singwi-Sjölander theory gives a very satisfactory description of the diffusive broadening of the Mössbauer line. Rapid falloff in the recoil-free fraction in the temperature interval where diffusive effects are observed has not been satisfactorily explained, and more theoretical investigation of this point seems necessary.

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Decoupled-Mode Theory of Critical Viscosity and Diffusion in the Binary-Liquid Phase Transition*

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The fluctuation-dissipation formula for the viscosity in terms of the stress-tensor fluctuations reproduces the experimental logarithmic temperature dependence of the hydrodynamic viscosity. Using the theoretical wave-number- and frequency-dependent viscosity in the problem of critical diffusion, we find that the effects of nonlocality and retardation practically cancel, resulting in satisfactory agreement with a recent light scattering determination of the effective viscosity.

I. INTRODUCTION

It is well known that the binary liquid exhibits interesting critical behavior as the critical point is approached, just before it begins to separate into two distinct liquid phases. The most striking example is the critical opalescence or the scattering of light by the concentration fluctuations. A less-evident critical phenomenon which has been recently firmly established experimentally is the diverging behavior of the viscosity as the critical point is approached. It is customary[1] to separate the viscosity into a so-called "ideal" background component $\eta_{\rm id}$ and a critical component $\Delta\eta$. The fraction by which the critical component accounts for the total viscosity is established experimentally[2,3] to follow the temperature dependence as the temperature T approaches T_c,

$$\Delta\eta/\eta = A_{\rm EXPT} \ln q_D \xi \ , \qquad (1.1)$$

where the correlation length is $\xi = 2.56$ Å $(T/T_c - 1)^{0.616}$, q_D is a Debye cutoff, and $A_{\rm EXPT} = 0.051$. This relationship which gives a good fit to the experimental data is shown in Fig. 1 by the line labeled "HYD." (In this case the abscissa represents the inverse correlation length.) The purpose of the present paper is to give a theory of the viscosity not only in a hydrodynamic context, but also in its

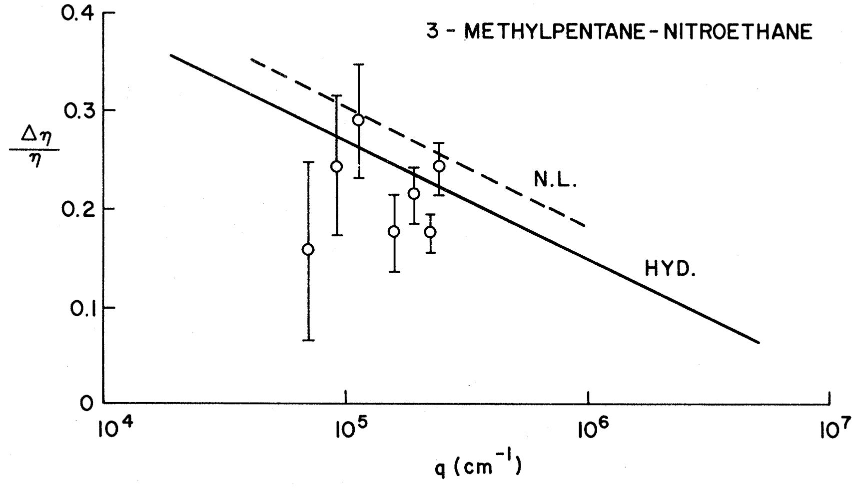

FIG. 1. Fractional critical viscosity vs wave number. The solid line labeled "HYD" represents the experimental logarithmic dependence of the hydrodynamic viscosity upon the inverse correlation length (Refs. 2 and 3). The dashed line labeled "N.L." shows the static nonlocal correction for the theoretically computed value of $a_{\mathrm{N.L.}} = 0.496$. This would be the result for a crude theory which did not include retardation. In the complete theory the correction for redardation cancels the effect of static nonlocality and brings the theory back down to the solid line. Thus the solid line represents both the hydrodynamic viscosity and the theoretically expected effective viscosity. This line is in satisfactory agreement with the circles, which show the light scattering linewidths measured by Chang, Keyes, Sengers, and Alley (Ref. 4).

more indirect form in which it determines the relaxation of concentration fluctuations. This "effective" viscosity has been measured recently[4] and is shown by the circles and error bars in Fig. 1. A theory of the critical viscosity has been presented by Kawasaki[5] and by Deutch and Zwanzig.[6] Following the latter approach, which is based on the fluctuation-dissipation theorem,[7,8] we have to integrate over the correlation function of the off-diagonal component of the stress tensor T_{xy}, where x and y are Cartesian coordinates and angular brackets indicate the thermal average:

$$\eta = (1/2T) \int d^4 21 \langle T_{xy}(2) T_{xy}(1) \rangle \ . \tag{1.2}$$

The integration is over the entire range of the relative space-time coordinate $(\vec{x}_{21}, t_{21})$. The temperature T is measured in natural units so that Boltzmann's constant is unity. Computation carried out using Eq. (1.2) will be presented in the subsequent sections. For the moment we want to describe the connection between the viscosity and the linewidth measurements. The measured linewidth in a light scattering experiment is given by

$$\Gamma_q = D(q) q^2 \ , \tag{1.3}$$

where $D(q)$ is in general a nonlocal diffusion coefficient depending on the wave number q of the concentration fluctuation. It is given by the ratio of $\lambda(q)$, the conductivity (for material to flow in response to a gradient in a chemical potential), to the generalized susceptibility $\chi(q)$:

$$D(q) = \lambda(q)/\chi(q) \ . \tag{1.4}$$

The conductivity is also expressed as an integral over the correlation function of the fluctuations in current $\vec{J}$. The wave-number-dependent generalization of the relevant fluctuation-dissipation theorem is

$$\lambda(q) = (1/2T) \int d^4 21 \langle J_{\hat{q}}(2) J_{\hat{q}}(1) \rangle e^{-i\vec{q}\cdot\vec{x}_{21}}. \tag{1.5}$$

The subscript indicates the component of J in the direction of the unit vector $\hat{q} = \vec{q}/q$.

The current density which appears in the integrand in Eq. (1.5) is the product

$$\vec{J} = s\vec{v} \ , \tag{1.6}$$

where s is the concentration fluctuation and v is the velocity fluctuation. It is not necessary to repeat here the derivation[9,10] of the critical variation in the diffusion coefficient which leads to

$$D(0) = T\mu_\xi \ , \tag{1.7}$$

where

$$\mu_\xi = 1/6\pi\eta\xi \tag{1.8}$$

is Stokes's formula for the mobility of a sphere of radius ξ moving through a medium of viscosity η. Substitution of Eqs. (1.8), (1.7), and (1.4) into Eq. (1.3) yields

$$\Gamma_q = (Tq^2/6\pi\eta\xi^2)\kappa^{-1} \ , \tag{1.9}$$

provided that $\kappa = \xi^{-1} \gg q$. But as the critical point is approached, $T \to T_c$, $\xi \to \infty$, and this condition is violated. It is then necessary according to dynamical-scaling theory[11,12] to replace all factors of κ by q, according to

$$\kappa_{\text{eff}} = a_{\text{eff}} q \ . \tag{1.10}$$

The qualitative theory of dynamical scaling does not attempt to calculate the numerical value of a_{eff} and consequently yields only proportionalities. The decoupled-mode dynamical scaling theory[10] or theories[9] equivalent to it attempt to calculate this numerical factor and therefore constitute a more complete theory of dynamical critical behavior. In Eq. (1.9) we have made a distinction between the appearances of the correlation length in the denominator and in the numerator. In the denominator, according to static scaling, ξ^{-1} simply becomes replaced by q, with no further numerical factor required. The numerator, on the other hand, involves the dynamics and we have to use Eq. (1.10). Explicit calculation[9,10] of the numerical factor yields

$$a_{\text{eff}} = 8/3\pi \tag{1.11}$$

which then substituted into Eq. (1.9) gives for the linewidth at the critical point

$$\Gamma_q^c = Tq^3/16\eta_{\text{eff}}(q) \ . \tag{1.12}$$

Here we have explicitly taken cognizance of the fact that the viscosity which appears in the denominator of Eq. (1.9) has critical variation and consequently has to be regarded as a function of κ. Thus according to Eq. (1.10) we must introduce an effective-wave-number dependence and have therefore labeled the viscosity which appears in Eq. (12) as an "effective" viscosity function. It is the task of the rest of this paper to calculate the theoretically expected effective viscosity and to compare it with the data[4] shown as the circles and error bars in Fig. 1.

II. CRITICAL VISCOSITY

As explained above, the calculation of the critical viscosity depends upon studying the fluctuations in the off-diagonal components of the stress tensor:

$$T_{xy} = s_x \frac{\partial F}{\partial s_y} = Z^{-1} s_x s_y \ . \tag{2.1}$$

This canonical expression for the stress tensor in terms of the Landau–Ginzburg expression for the free-energy density F is derived in Appendix A. It depends only opon the partial derivatives of the concentration $s_{x,y}$ through the gradient term $(\nabla s)^2/2Z$. Equation (2.1) shows that for studying the fluctuations in the stress tensor we will need the time-dependent correlation function for the concentration fluctuations themselves,

$$G(21) = \langle s(2)s(1)\rangle = (2\pi)^{-3}\int d^3q \, e^{i\vec{q}\cdot\vec{x}_{21} - \Gamma_q|t_{21}|} g(q) \ . \tag{2.2}$$

The Fourier transform of the equal-time correlation function is assumed to have the usual Ornstein-Zernike form for arbitrary values of wave number q and inverse correlation length κ,

$$g(q) = ZT/(q^2+\kappa^2) \ . \tag{2.3}$$

The time-dependent correlation function of the stress tensor can be expressed in terms of G by the decoupling, or factoring approximation,

$$\begin{aligned}\langle T_{xy}(2)T_{xy}(1)\rangle &\cong Z^{-2}\langle s_x(2)s_x(1)\rangle\langle s_y(2)s_y(1)\rangle \\ &\quad + Z^{-2}\langle s_x(2)s_y(1)\rangle\langle s_y(2)s_x(1)\rangle \\ &= Z^{-2}\left[\frac{\partial^2 G(21)}{\partial x_{21}^2}\,\frac{\partial^2 G(21)}{\partial y_{21}^2} + \left(\frac{\partial^2 G(21)}{\partial x_{21}\,\partial y_{21}}\right)^2\right] .\end{aligned} \tag{2.4}$$

The validity of this approximation is discussed below in Sec. VI. Substituting this factored form into Eq. (1.2) and carrying out the time integration, we obtain the critical hydrodynamic viscosity in the form of an integral over wave number,

$$\Delta\eta = \frac{T^{-1}Z^{-2}}{(2\pi)^3}\int d^3q \frac{g(q)^2}{\Gamma_q}\, q_x^2\, q_y^2 \ . \tag{2.5}$$

In order to proceed further we require an expression for Γ_q. In principle, Γ_q could be determined entirely theoretically from a self-consistent treatment of both the viscosity and the linewidth. As we have already mentioned above, and will see in more detail below, the linewidth is given by an integral over the wave-number- and frequency-dependent viscosity. Rather than attack this set of coupled integral equations for η and Γ_q in a purely abstract theoretical fashion, abstaining from the use of any empirical information, we have found it more convenient to use the experimental data as an "ansatz" for Γ_q. The self-consistency condition will then be shown in Sec. V to be satisfied. The Γ_q which we obtain there agrees with the input ansatz, so that further iteration is unnecessary.

As an ansatz for Γ_q we choose the following expression, which gives a good fit to the experimental data:

$$\Gamma_q = \frac{Tq^2(q^2+\kappa^2)^{1/2}}{16\eta((q^2+\kappa^2)^{1/2})} \ . \tag{2.6}$$

Here η is the empirical hydrodynamical viscosity of Eq. (1.1) with the argument $\xi^{-1}=\kappa$ replaced by $(q^2+\kappa^2)^{1/2}$. This fit[13] is illustrated in Fig. 2, which shows the experimental linewidth values divided by the wave-number-dependent factors of the numerator of Eq. (2.7). The data exhibited in this way have a flat behavior, as is seen by the location of the points in Fig. 2. This is compatible with the slow logarithmic variation of the denominator of Eq. (2.6). The normalization is effected

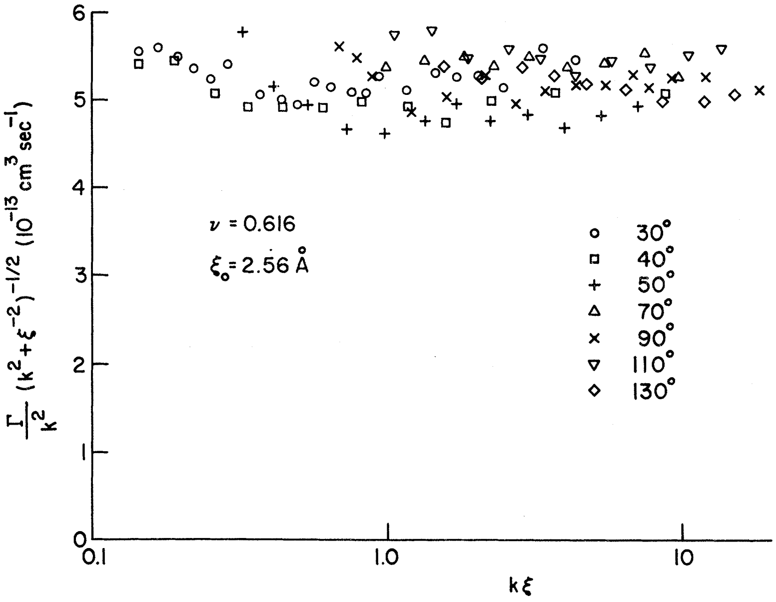

FIG. 2. Rate Γ_k for relaxation of a concentration fluctuation of wave number k vs $k\xi$. ξ is the correlation length. Dividing by the factor $k^2\ (k^2+\xi^{-2})^{1/2}$ has removed the main wave number and temperature dependence. The remaining dependence, shown by the data points of Chang *et al.* (Ref. 4), is consistent with the weakly varying viscosity factor in Eq. (2.6). Equation (2.6) thus can be regarded as a good empirical fit to the data, and serves as a starting point for the theory of critical viscosity.

in the $q/\kappa \gg 1$ limit and corresponds to representing the circles in Fig. 1 by the solid line. Because of the slow variation of η, when Eq. (2.6) is substituted into Eq. (2.5), η can be taken outside the integral and approximated by setting the argument equal to κ. Dividing by η, we obtain the fractional critical viscosity,

$$\frac{\Delta\eta(\kappa)}{\eta(\kappa)}=\frac{8}{\pi^2}\int_0^{q_c} dq\frac{q^4}{(q^2+\kappa^2)^{5/2}}\left\langle\frac{q_x^2 q_y^2}{q^4}\right\rangle_{\mathrm{ANG}}$$
$$=\frac{8}{\pi^2}\left\langle\frac{q_x^2 q_y^2}{q^4}\right\rangle_{\mathrm{ANG}}\int_0^{q_c/\kappa}\frac{v^4\,dv}{(1+v^2)^{5/2}}\ , \qquad (2.7)$$

where the angular average appearing in the integrand is

$$\langle q_x^2 q_y^2/q^4\rangle_{\mathrm{ANG}}=\tfrac{1}{15}\ . \qquad (2.8)$$

The radial integration is cut off at q_c, a free parameter in the theory, and yields

$$\int_0^{q_c/\kappa}\frac{v^4\,dv}{(1+v^2)^{5/2}}=\ln\frac{2q_c}{\kappa}-\frac{4}{3}\ . \qquad (2.9)$$

Substituting Eqs. (2.8) and (2.9) into Eq. (2.7) gives[14]

$$\frac{\Delta\eta(\kappa)}{\eta(\kappa)}=A\left(\ln\frac{2q_c}{\kappa}-\frac{4}{3}\right). \qquad (2.10)$$

This is of the form of Eq. (1.1), which fits the experimental data. The theoretical value for the coefficient[15] is

$$A=8/15\pi^2=0.054\ , \qquad (2.11)$$

and is in good agreement with the experimental value $A_{\mathrm{EXPT}}=0.051$. This confirms the validity of the decoupled-mode approximation as applied to the critical viscosity and encourages us to proceed to employ it below in its more complicated wave-number- and frequency-dependent form. We note finally that we can fix q_c by matching the logarithms of Eqs. (2.10) and (1.1):

$$\ln q_c=\ln q_D+\tfrac{4}{3}-\ln 2. \qquad (2.12)$$

III. NONLOCAL VISCOSITY

The critical viscosity found in Eq. (2.10) is a function of only one variable, the reciprocal correlation length κ, and is applicable only in the hydrodynamic limit. This viscosity cannot be used for studying the relaxation of concentration fluctuations in a fluid because these take place at finite frequency. It is therefore necessary to calculate a generalized viscosity by introducing two more variables into the viscosity function. The straightforward generalization of Eq. (1.1) involves taking the Fourier transform of the correlation function for the stress-tensor fluctuations in both space and time. It will be more convenient for our purposes, however, to treat the time dependence by the Laplace transform, in which we write the "frequency" as the relaxation rate Γ_q times the dimensionless variable γ^3. In this notation the hydrodynamic viscosity is the limiting case $\eta(\kappa)=\eta(\kappa,\ q,\ \gamma)_{q=\gamma=0}=\eta(\kappa,0,0)$. The general case is given by the generalized fluctuation-dissipation theorem,

$$\eta(\kappa,q,\gamma)=(1/2T)\int d^4 21\, e^{i\vec{q}\cdot\vec{x}_{21}-\Gamma_q\gamma 3|t_{21}|}$$
$$\times\langle T_{xy}(2)T_{xy}(1)\rangle\ . \qquad (3.1)$$

The wave number $\vec{q}$ is taken in the direction of the

y Cartesian axis. We use the same factorization as in Eq. (2.4) and in converting the integration in Eq. (3.1) to wave-number space we denote the Fourier components of the two different factors by $\vec{k}$ and $\vec{k}'$, respectively. Because these two vectors must add up to the given wave number $\vec{q}$, and because $\vec{q}$ is entirely in the y direction, we have the following equations:

$$k_x + k_x' = 0 \ , \tag{3.2}$$

$$k_y + k_y' = q \ . \tag{3.3}$$

From Eq. (3.2) it follows that we can eliminate one of the x components and obtain for the angle-dependent factor in the integrand the expression

$$\begin{aligned} k_x{}^2 k_y{}'^2 + k_x k_y k_x{}' k_y{}' &= k_x{}^2 k_y{}'(k_y{}' - k_y) \\ &= \tfrac{1}{2} k_x{}^2 (k_y{}' - k_y)^2 + \tfrac{1}{2} k_x{}^2 (k_y{}'^2 - k_y{}^2) \ . \end{aligned} \tag{3.4}$$

In the final line we have substituted for $k_y{}'$ in terms of the sum and difference of the y wave-number components. This introduces in the last term of Eq. (3.4) a factor which is odd under interchange between $\vec{k}$ and $\vec{k}'$. As the remaining factors in the integrand are even under this interchange, the resulting contribution to the integrand vanishes. Therefore only the first term in the last line of Eq. (3.4) need be retained. This gives us the critical wave-number- and frequency-dependent viscosity as the integral

$$\Delta\eta(\kappa, q, \gamma) = \frac{T^{-1}Z^{-2}}{2(2\pi)^3} \int d^3k \frac{g(k) g(k') k_x{}^2 (k_y{}' - k_y)^2}{\Gamma_k + \Gamma_{k'} + \Gamma_q \gamma^3} \ . \tag{3.5}$$

We now proceed with the task of evaluating this integral. Because of the symmetry about the y axis we obtain a factor of 2π in rotating about this axis. The remaining integration can in principle be carried out by using polar coordinates consisting of the magnitude of k and the angle describing its direction relative to $\vec{q}$. But it is more convenient to eliminate the angle variable in terms of the magnitude of the other vector $\vec{k}'$. The resulting bipolar coordinate system converts the element of volume into the symmetrical form

$$d^3k = 2\pi q^{-1} k k' \, dk \, dk' \ . \tag{3.6}$$

In terms of these bipolar coordinates the remaining angle-dependent factors assume the form

$$k_y{}' - k_y = q^{-1}(k'^2 - k^2) \tag{3.7}$$

and

$$k_x{}^2 = (4q^2)^{-1} [2(k^2 + k'^2) q^2 - q^4 - (k^2 - k'^2)^2] \ . \tag{3.8}$$

In the rest of this paper we will concentrate on the nonlocal limit $\kappa \to 0$, where $\eta((q^2 + \kappa^2)^{1/2}) \to \eta(q) = \eta(q, 0, 0)$. Equation (2.6) then assumes the simpler critical relaxation form

$$\Gamma_q^c = T q^3 / 16 \eta(q) \ . \tag{3.9}$$

Factoring out the critical relaxation rate for the wave number q from the denominator of the integrand of Eq. (3.5) leaves the ratio

$$\frac{\Gamma_k^c}{\Gamma_q^c} = \frac{k^3}{q^3} \frac{\eta(q)}{\eta(k)} \simeq \left(\frac{k}{q}\right)^3 = u^3 \ , \tag{3.10}$$

and similarly $u'^3 = (k'/q)^3$ for the ratio $\Gamma_{k'}^c / \Gamma_q^c$. Here we have neglected the slow logarithmic variation in the ratio of the hydrodynamic viscosity at two different values of its argument and we have introduced the dimensionless variables u and u' to denote k and k' measured in units of q. Dividing now by the hydrodynamic viscosity function we obtain the fractional critical nonlocal viscosity,

$$\frac{\Delta\eta(0, q, \gamma)}{\eta(q)} = \frac{1}{4\pi^2} \iint_{\substack{u+u' \geq 1 \\ |u-u'| \leq 1 \\ u, u' \leq q_c/q}} \frac{du \, du'}{u u'} \frac{(u^2 - u'^2)^2}{u^3 + u'^3 + \gamma^3} \times [2(u^2 + u'^2) - 1 - (u^2 - u'^2)^2] \ . \tag{3.11}$$

The restrictions on the integration variables are illustrated in Fig. 4. The condition $|u - u'| \leq 1$ limits the integration for large values of u and u' to the narrow strip running along the line $u' = u$. The dashed lines in Fig. 4 represent a change from u, u' to new Cartesian variables x, x', with the new variable

$$x = u' + u \tag{3.12a}$$

running in the direction of the strip and having the range $1 \leq x < \infty$. The other coordinate

$$x' = u' - u \tag{3.12b}$$

measures the distance across the strip and has the range $-1 \leq x' \leq +1$. This change of coordinates puts the quantity appearing in square brackets in Eq. (3.11) into the simple factored form

$$2(u^2 + u'^2) - 1 - (u^2 - u'^2)^2 = (1 - x'^2)(x^2 - 1). \tag{3.13}$$

With the Jacobian of the transformation equaling one-half, Eq. (3.11) becomes

$$\frac{\Delta\eta(0, q, \gamma)}{\eta(q)} = \frac{1}{\pi^2} \int_{-1}^{+1} dx' \int_1^{(2q_c/q)^2} d(x^2) \times \frac{x'^2 (1 - x'^2)(x^2 - 1)}{(x^2 - x'^2)[x^2 + 3x'^2 + (4/x)\gamma^3]} \ . \tag{3.14}$$

Let us now consider the limiting case of static nonlocality, $\gamma = 0$. This simplifies the integration sufficiently that it can be carried out by elementary means, giving the nonlocal static result

$$\begin{aligned} \frac{\Delta\eta(0, q, 0)}{\eta(q)} &= \frac{8}{15\pi^2} \left(\ln \frac{q_c}{q} + \frac{13}{15} - \frac{4\pi}{9\sqrt{3}} \right) \\ &= \frac{8}{15\pi^2} \left(\ln \frac{q_D}{q} + \frac{11}{5} - \ln 2 - \frac{4\pi}{9\sqrt{3}} \right) \ . \end{aligned} \tag{3.15}$$

[Here we have substituted Eq. (2.12)]. This result is plotted as the dashed line in Fig. 1 labeled "N.L." One might be tempted to assume that this nonlocal result could be used as the effective q-dependent viscosity for the critical diffusion problem. As is apparent in Fig. 1, the comparison between the theory and the experimental data shown by the circles and error bars would then not be very satisfactory. As we will see in Sec. V, such an identification is not justified, because of the time dependence of the critical concentration fluctuations. For this reason it is necessary to include the effect of time dependence or "retardation" in studying the critical diffusion of the concentration fluctuations. But before proceeding to the study of retardation in the following sections, we would like first to characterize the result of Eq. (3.15) in the language of Eq. (1.10). There we saw that the passage from the hydrodynamic limit to the completely nonlocal limit can generally be expressed by means of a numerical factor, which in this case we denote by $a_{\text{eff}}^{\text{N.L.}}$. This means that we should be able to write Eq. (3.15) in the form

$$\frac{\Delta\eta(0,q,0)}{\eta(q)}=\frac{\Delta\eta(\kappa_{\text{eff}})}{\eta(\kappa_{\text{eff}})}=\frac{8}{15\pi^2}\ln\frac{q_D}{\kappa_{\text{eff}}}$$

$$=\frac{8}{15\pi^2}\left(\ln\frac{q_D}{q}-\ln a_{\text{eff}}^{\text{N.L.}}\right). \tag{3.16}$$

This result[14] follows from substituting Eq. (1.10) into Eq. (1.1). Identification of Eq. (3.16) with Eq. (3.15) fixes the numerical factor[16] by

$$-\ln a_{\text{eff}}^{\text{N.L.}}=\tfrac{11}{5}-\ln 2-4\pi/9\sqrt{3}=0.701 \tag{3.17}$$

or

$$a_{\text{eff}}^{\text{N.L.}}=2e^{4\pi/9\sqrt{3}-11/5}=0.496\ . \tag{3.18}$$

IV. FREQUENCY-DEPENDENT VISCOSITY

In this section we study the frequency dependence of the generalized viscosity function. It is convenient to separate out the frequency dependence by subtracting from Eq. (3.14) its static limit $\gamma=0$. The resulting function is independent of q and permits us to define a normalized dynamical scaling function $\sigma(\gamma)$ by

$$\frac{\eta(0,q,\gamma)-\eta(0,q,0)}{\eta(q,0,0)}=\frac{8}{15\pi^2}\,\sigma(\gamma)\ , \tag{4.1}$$

where we have substituted $\eta(q,0,0)$ for $\eta(q)$ in the denominator. In taking the difference within the integral sign, we obtain an integral which converges at the upper limit; consequently the upper limit can be set equal to infinity, $q_c\to\infty$. In other words, the cutoff parameter disappears at this point and will no longer occur in the subsequent work. The resulting expression for the dynamical scaling function is the double integral

$$\sigma(\gamma)=-30\gamma^3\int_0^1 dx'\int_1^\infty dx$$

$$\times\frac{x'^2(1-x'^2)\,(x^2-1)}{(x^2-x'^2)(x^2+3x'^2)[x^2+3x'^2+(4/x)\gamma^3]}\ . \tag{4.2}$$

For low frequencies, $\gamma\ll 1$, we can approximate the integral by setting $\gamma=0$ in the denominator of the integrand. Evaluating the resulting double integral yields the low-frequency expression

$$\sigma(\gamma)=-0.316\gamma^3. \tag{4.3}$$

In the opposite range of $\gamma\gg 1$ we can neglect x' compared to x in the denominator of the integrand. The remaining dependence upon x' factors out and we readily obtain

$$\sigma(\gamma)\simeq-30\gamma^3\int_0^1 dx'\,x'^2(1-x'^2)\int_1^\infty\frac{dx}{x(4\gamma^3+x^3)}$$

$$=-4\gamma^3\int_1^\infty\frac{dx}{x(x^3+4\gamma^3)}$$

$$\sim-\int_1^\gamma\frac{dx}{x}=-\ln\gamma\ . \tag{4.4}$$

The last line is an asymptotic expression which is valid only to logarithmic accuracy. In this extreme nonstatic limit the wave-number dependence disappears and $\eta(0,q,\gamma)$ depends only on the frequency through $(q\gamma)^3$. (We recall that γ is defined as proportional to the cube root of the frequency divided by q.) With more careful treatment of the integral we obtain the improved high-frequency expression

$$\sigma(\gamma)=\ln\frac{2^{1/3}}{\gamma}-\frac{\frac{1}{3}\pi}{\sin\frac{1}{3}\pi}\;(2^{2/3}\gamma)^{-2}-\tfrac{13}{15}+\frac{\frac{2}{3}\pi}{3\sin\frac{1}{3}\pi}$$

$$=0.171-\ln\gamma-0.480\gamma^{-2}\ . \tag{4.5}$$

The intermediate region $\gamma\simeq 1$ can be calculated by first carrying out the integration with respect to x'. The resulting one-dimensional integral over x has been computed numerically. We have noted that the above low-frequency and high-frequency expressions, Eqs. (4.3) and (4.5), are in fact quite accurate in the ranges $\gamma<0.5$ and $\gamma>1.5$, respectively. Interpolation between these two ranges is provided by the numerical computations and results[14] in the curve for $\sigma(\gamma)$ vs γ shown in Fig. 3. We now proceed in Sec. V to make use of this scaling function in the computation of the critical diffusion.

V. NONLOCAL DIFFUSION

The rate at which a concentration fluctuation of wave number q relaxes is connected by Eqs. (1.3) and (1.4) to $\lambda(q)$, the q-dependent conductivity of Eq. (1.5). To calculate $\lambda(q)$ we substitute for the current from Eq. (1.6) in terms of concentration and velocity fluctuations. Applying the decoupling approximation to the time correlation function for the current gives

$$\langle J_{\vec q}(2) J_{\vec q}(1)\rangle \simeq \langle S(2)S(1)\rangle \langle v_{\vec q}(2) v_{\vec q}(1)\rangle \,. \tag{5.1}$$

Denoting the mass density of the fluid by ρ, we can normalize the Fourier components of the equal-time velocity correlation function by their equipartition value T/ρ. For $t_{21} \neq 0$ the $\vec k$ Fourier component contains the relaxation factor $\exp(-\eta\rho^{-1}k^2 |t_{21}|)$. Because of the frequency dependence of η, the time dependence is not a simple exponential function and has to be understood in an operator sense, i.e., in terms of the Fourier transform. This point is discussed more completely in Appendix B. Denoting now the angle between $\vec q$ and $\vec k$ by θ and keeping in mind that only the shear modes contribute to the critical behavior of Eq. (5.1), we have the velocity time correlation function

$$\langle v_{\vec q}(2) v_{\vec q}(1)\rangle = \frac{T/\rho}{(2\pi)^3} \int d^3k \sin^2\theta \exp\left(i\vec k \cdot \vec x_{21} - \frac{\eta}{\rho} k^2 |t_{21}| \right) \,. \tag{5.2}$$

Substituting from Eqs. (5.2), (5.1), and (2.2) into Eq. (1.5) and carrying out the integration gives the convolution integral

$$\lambda(q) = \frac{1}{(2\pi)^3} \int \frac{d^3k}{k^2} \frac{\sin^2\theta\, g(k')}{\eta(0,k,k'/k)} \,, \tag{5.3}$$

where $\vec k' = \vec q - \vec k$. In Appendix B we show in detail how the finite relaxation rate $\Gamma_{k'}$ of the concentration fluctuations results in the viscosity-retardation correction appearing via k'/k in Eq. (5.3).

The remainder of this section consists of the computation of the effective average viscosity defined by

$$\begin{aligned}\lambda_c(q) &= \frac{ZT}{(2\pi)^3} \int \frac{d^3k}{k^2 k'^2} \frac{\sin^2\theta}{\eta(0,k,k'/k)} \\ &\equiv \frac{ZT}{\eta_{\text{eff}}(q)} \frac{1}{(2\pi)^3} \int \frac{d^3k}{k^2 k'^2} \sin^2\theta \\ &= \frac{ZT}{\eta_{\text{eff}}(q)} \frac{q^{-1}}{4\pi^2} \int_0^\pi d\theta \sin^3\theta \int_0^\infty \frac{du}{u^2+1-2u\cos\theta} \,.\end{aligned} \tag{5.4}$$

Here, and throughout the rest of this paper, we are concentrating on the critical limit $\kappa \to 0$, which is indicated by the subscript c on the conductivity and other related functions. As in the preceding sections, u and u' denote k/q and k'/q, respectively. The radial and angular integrations are readily carried out,

$$\int_0^\infty \frac{du}{u^2+1-2u\cos\theta} = \frac{\pi-\theta}{\sin\theta} \,, \tag{5.5}$$

$$\int_0^\pi d\theta\, (\pi-\theta) \sin^2\theta = \tfrac{1}{4}\pi^2 \,, \tag{5.6}$$

resulting in

$$\lambda^c(q) = [ZT/16\eta_{\text{eff}}(q)]\, q^{-1} \,. \tag{5.7}$$

Substituting Eqs. (5.7) and (1.4) into Eq. (1.3) yields for the critical linewidth

$$\Gamma_q^c = q^2 D_c(q) = q^2 \frac{\lambda_c(q)}{\chi_c(q)} = Z^{-1} q^4 \lambda_c(q) = \frac{Tq^3}{16\eta_{\text{eff}}(q)} \,. \tag{5.8}$$

Although Eq. (5.8) is of familiar form, it is of no use without an explicit expression for $\eta_{\text{eff}}(q)$. This we now proceed to obtain by carrying out the necessary averaging process. Because of the small value of the coefficient $A = 8/15\pi^2$, we are permitted to expand η^{-1} to first order in the nonlocal and retardation corrections. Thus we obtain

$$\begin{aligned}\frac{\eta(q)}{\eta_{\text{eff}}(q)} &= \left\langle \frac{\eta(q)}{\eta(0,k,k'/k)} \right\rangle_{\text{AVE}} = \left\langle \left(1 + \frac{\eta(0,k,k'/k) - \eta(q,0,0)}{\eta(q)} \right)^{-1} \right\rangle_{\text{AVE}} \simeq \left\langle 1 - \eta(q)^{-1} \left[\eta\left(0, k, \frac{k'}{k}\right) - \eta(q,0,0) \right] \right\rangle_{\text{AVE}} \\ &= 1 - \eta(q)^{-1} \left\{ [\eta(0,q,0) - \eta(q,0,0)] + \langle [\eta(0,k,0) - \eta(0,q,0)] \rangle_{\text{AVE}} + \left\langle \left[\eta\left(0,k,\frac{k'}{k}\right) - \eta(0,k,0) \right] \right\rangle_{\text{AVE}} \right\} \,.\end{aligned} \tag{5.9}$$

The first term in brackets is the nonlocal correction to the hydrodynamic viscosity, $-\ln a_{\text{eff}}^{\text{N.L.}}$, while the second term determines the effective value of k which should be used in the nonlocal static viscosity. The latter requires averaging over

$$\begin{aligned}\eta(q)^{-1}[\eta(0,k,0) - \eta(0,q,0)] &= -\frac{8}{15\pi^2} \ln\frac{k}{q} \\ &= -\frac{8}{15\pi^2} \ln u \,.\end{aligned} \tag{5.10}$$

Now we note that the integral in Eq. (5.5) is invariant with respect to the substitution $u \to u^{-1}$, while $\ln u$ changes sign under this substitution. Therefore

$$\langle \ln u \rangle_{\text{AVE}} = 0 \,. \tag{5.11}$$

This leaves the third term in the braces in Eq. (5.9), which according to Eq. (4.1) can be written

$$\eta(q)^{-1} \left\langle \left[\eta\left(0,k,\frac{k'}{k}\right) - \eta(0,k,0) \right] \right\rangle_{\text{AVE}}$$

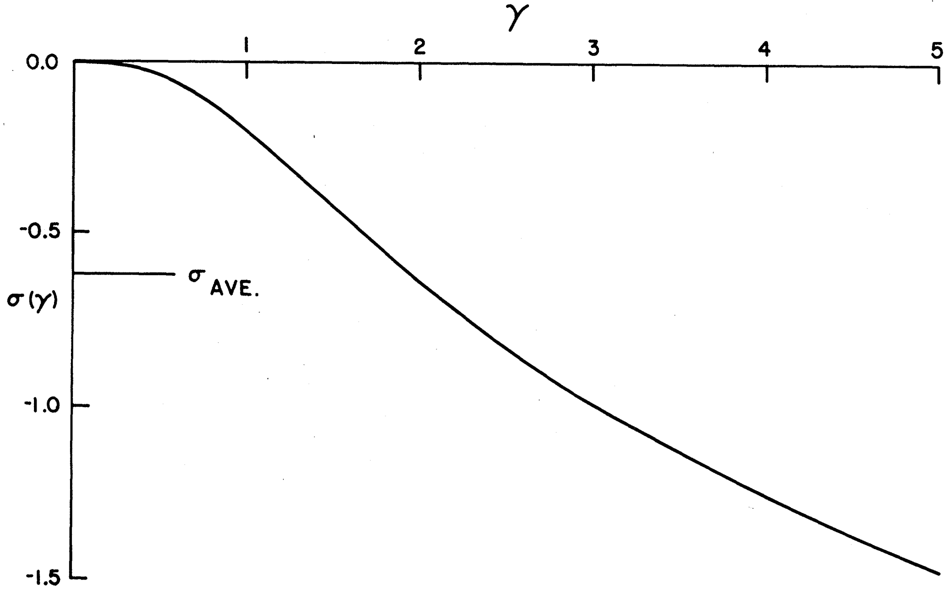

FIG. 3. Viscosity dynamical scaling function $\sigma(\gamma)$ vs (frequency)$^{1/3}$. γ^3 is the frequency in units of Γ_q^c, the critical diffusive linewidth at wave number q. $\sigma_{\text{AVE}} = -0.60$ is the weighted mean of $\sigma(\gamma)$ which expresses the retardation correction in the critical diffusion.

$$= \frac{8}{15\pi^2} \left\langle \frac{\eta(k,0,0)}{\eta(q,0,0)}\; \sigma\left(\frac{k'}{k}\right)_{\text{AVE}} \right\rangle$$

$$\simeq \frac{8}{15\pi^2} \left\langle \sigma\left(\frac{k'}{k}\right)\right\rangle_{\text{AVE}} \equiv \frac{8}{15\pi^2}\, \sigma_{\text{AVE}}\ , \qquad (5.12)$$

where we ignore the higher-order effect of the difference between k and q inside the angular brackets. Substituting Eq. (5.12) into Eq. (5.9) and then inserting Eq. (3.16) gives

$$\eta_{\text{eff}}(q) = \eta(0,q,0) + \frac{8\eta(q)}{15\pi^2}\, \sigma_{\text{AVE}}$$

$$= \eta(q,0,0) + \frac{8\eta(q)}{15\pi^2}\left(-\ln a_{\text{eff}}^{\text{N.L.}} + \sigma_{\text{AVE}}\right)\ . \qquad (5.13)$$

In the same way as we wrote $a_{\text{eff}} = a_{\text{eff}}^{\text{N.L.}}$ in Eq. (3.16) for the effect of nonlocality alone, we can here introduce a new numerical coefficient $a_{\text{eff}}^{\text{visc}}$ to describe the total effect of the critical viscosity on the diffusion. This coefficient combines both of the effects of nonlocality and retardation. The effective viscosity can be written in terms of it as

$$\frac{\eta_{\text{eff}}(q)}{\eta(q)} = \frac{\eta(a_{\text{eff}}^{\text{visc}}\, q)}{\eta(q)} = 1 + \frac{8}{15\pi^2}\left(-\ln a_{\text{eff}}^{\text{visc}}\right)\ . \qquad (5.14)$$

Identifying Eq. (5.14) with (5.13) yields

$$-\ln a_{\text{eff}}^{\text{visc}} = -\ln a_{\text{eff}}^{\text{N.L.}} + \sigma_{\text{AVE}} \qquad (5.15)$$

or

$$a_{\text{eff}}^{\text{visc}} = a_{\text{eff}}^{\text{N.L.}}\, e^{-\sigma_{\text{AVE}}}\ . \qquad (5.16)$$

Since $\sigma(\gamma)$ is a negative definite function, as is evident from Fig. 3, $a_{\text{eff}}^{\text{visc}}$ is necessarily greater than $a_{\text{eff}}^{\text{N.L.}}$.

We now turn to the evaluation of σ_{AVE}. As $\sigma(\gamma)$ depends only upon the ratio $\gamma = k'/k = u'/u$, it is convenient to introduce into the plane of the bipolar coordinates u, u' of Fig. 4 the polar coordinates

$$\phi = \tan^{-1}\gamma = \tan^{-1} u'/u \qquad (5.17\text{a})$$

and

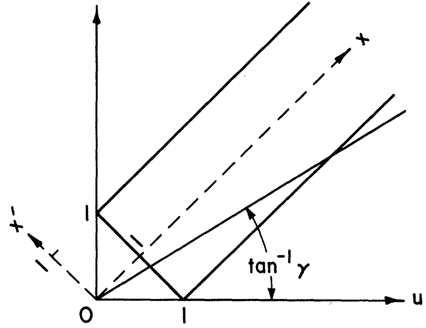

FIG. 4. Plane of the bipolar coordinates $u = k/q$ and $u' = k'/q$. k and k' are the wave numbers in the convolution integrals of Eqs. (3.5) and (5.3) and add vectorially to q. The rotation of coordinates to the new Cartesian variables $x = u' + u$ and $x' = u' - u$, whose axes are shown by the dashed lines, facilitates the integration. The physical region is contained within the semi-infinite strip $x \geq 1$, $|x'| \leq 1$. In calculating the effect of retardation, it is useful to make the further change to polar coordinates, shown by the line at angle $\phi = \tan^{-1}\gamma = \tan^{-1} u'/u$. The radial integration can then be carried out analytically, leaving numerical integration of the dynamical scaling function only over the angle variable, as described in Eq. (5.21).

$$v=(u'^2+u^2)^{1/2}\ . \tag{5.17b}$$

In this coordinate system we can immediately integrate out the radial variable v along a line of constant ϕ (see Fig. 4) to obtain for the integral of Eq. (5.4),

$$S(\phi)=\csc\phi\,\sec^3\phi\,\frac{1}{\pi^2}\int_{(1/\sqrt{2})\sec(\pi/4-\phi)}^{(1/\sqrt{2})|\sec(\pi/4+\phi)|}\frac{dv}{v^3}\times(2v^3-1-v^4\cos^2 2\phi\,),$$

$$S(\phi)=\frac{4}{\pi^2}\sec^2\phi\left(\frac{\ln|\tan(\frac{1}{4}\pi+\phi)|}{\sin 2\phi}-1\right). \tag{5.18}$$

This angle-weighting function has the limiting value $S(\frac{1}{2}\pi)=16/3\pi^2$ and behaves as $S(\phi)\simeq 16\phi^2/3\pi^2$ for $\phi\ll 1$. It is normalized to unity,

$$1=\int_0^{\pi/2}d\phi\,S(\phi)\ , \tag{5.19}$$

so that the required average is to be obtained simply by multiplying by $\sigma(\tan\phi)$ and integrating over the quadrant. The numerical work is facilitated, however, by using Eq. (5.19) to subtract from $\sigma(\gamma)$ its value at $\gamma=1$, $\sigma(1)=-0.19$. This serves to suppress the logarithmic singularity of $S(\phi)$ at $\phi=\frac{1}{4}\pi$. The remaining singularity in the vicinity of $\phi=\frac{1}{2}\pi$ originates from the logarithmic divergence of Eq. (4.4), and can be represented asymptotically by

$$S(\tfrac{1}{2}\pi)[\sigma(\tan\phi)-\sigma(1)]\simeq-(16/3\pi^2)\ln\tan\phi$$

$$\simeq(16/3\pi^2)\ln(2-4\phi/\pi)\ . \tag{5.20}$$

In addition to having the correct asymptotic behavior, this expression also vanishes at $\phi=\frac{1}{4}\pi$. The integration thus splits up into several portions:

$$\sigma_{\text{AVE}}=\int_0^{\pi/2}d\phi\,S(\phi)\sigma(\tan\phi)=\sigma(1)+\int_0^{\pi/2}d\phi\,S(\phi)[\sigma(\tan\phi)-\sigma(1)]=\sigma(1)+\int_{\pi/4}^{\pi/2}d\phi\,(16/3\pi^2)\ln(2-4\phi/\pi)$$
$$+\int_{\pi/4}^{\pi/2}d\phi\,\{S(\phi)[\sigma(\tan\phi)-\sigma(1)]-(16/3\pi^2)\ln(2-4\phi/\pi)\}+\int_0^{\pi/4}d\phi\,S(\phi)[\sigma(\tan\phi)-\sigma(1)]\ . \tag{5.21}$$

The second term in Eq. (5.21) is readily found to be

$$(16/3\pi^2)\int_{\pi/4}^{\pi/2}d\phi\ln(2-4\phi/\pi)=-4/3\pi=-0.42\ . \tag{5.22}$$

The remaining two integrals are devoid of divergences and are relatively small. Simpson's rule gives $+0.01$ for their total contribution, so we find

$$\sigma_{\text{AVE}}=-0.19-0.42+0.01=-0.60\ . \tag{5.23}$$

Substitution into Eq. (5.16) yields

$$a_{\text{eff}}^{\text{visc}}=a_{\text{eff}}^{\text{N.L.}}\,e^{-\sigma_{\text{AVE}}}$$
$$=0.496e^{0.60}=0.90\quad, \tag{5.24}$$

in satisfactory agreement with the experimental value of

$$a_{\text{eff}}^{\text{visc}}(\text{EXPT})=2\pm1. \tag{5.25}$$

The fact that the theoretical value for this coefficient comes out so close to unity is a consequence of two competing physical effects, the nonlocality and the retardation, which tend to cancel one another. Equation (5.24) is so close to unity that we can summarize the outcome of the calculation by $\eta_{\text{eff}}(q)\simeq\eta(q)$. For this reason it is not worthwhile to draw another line on Fig. 1. The straight line labeled "HYD." is a sufficiently accurate representation of the theoretical result. Since it corresponds to the ansatz of Eq. (2.6), with which we began the calculation, we can regard our treatment as being self-consistent.

VI. SUMMARY

We began this calculation with the empirical fit Eq. (2.6) to the linewidth data of Chang *et al.*[4] shown in Fig. 2. Simple application of the fluctuation-dissipation theorem along the lines indicated by Deutch and Zwanzig[6] yields a logarithmically diverging hydrodynamic viscosity. The coefficient of the logarithm is $A=8/15\pi^2=0.054$, in good agreement with experimental data.[2,3]

Generalizing the theory to include space and time dependence, we calculate the special case of static nonlocality in Sec. III. Here we find that the dependence on wave number q is to be obtained from the dependence of the hydrodynamic viscosity on the inverse correlation length ξ^{-1} by replacing ξ^{-1} by q and adding $-\ln a_{\text{eff}}^{\text{N.L.}}=0.70$ to the logarithm.

The static q-dependent viscosity cannot, however, be used in the critical diffusion problem. This is because the critical viscosity is attributable, by virtue of the fluctuation-dissipation theorem, to concentration fluctuations. The characteristic frequency for the viscosity is consequently of the same order of magnitude as the concentration relaxation rates. The frequency dependence of the viscosity is thus unavoidable and is determined in Sec. IV in terms of the dynamical scaling function shown in Fig. 3.

In Sec. V we study in detail the critical diffusion process and find that the effective viscosity is affected by both nonlocal and retardation corrections. Our result is that to the logarithm has to be added −0.60 from retardation, as well as 0.70 from nonlocality. Thus the two corrections practically cancel one another. Physical reasons for this cancellation are cited following Eq. (5.16) and in Ref. 16. The net correction of 0.10 is only 2% of the value of the logarithm in the range of the light scattering measurements.[4] To this accuracy we can claim that our calculation is self-consistent and can be summarized by the following simple rule: *To obtain the effective viscosity from the hydrodynamic viscosity, replace* ξ^{-1} *by* q*—no further numerical adjustment is required.*

This rule is in satisfactory agreement with the linewidth data[4] as is evident in Fig. 1 from a comparison of the solid line with the circles and error bars. A more quantitative comparison is provided by citing the values of the net addition to the logarithm $-\ln a_{\mathrm{eff}}^{\mathrm{visc}}$. We find $a_{\mathrm{eff}}^{\mathrm{visc}} = 0.90$, whereas the experimental value is $a_{\mathrm{eff}}^{\mathrm{visc}}(\mathrm{EXPT}) = 2 \pm 1$.

A further outcome of the theory, which we mention only in passing, is that the retardation produces some non-Lorentzian distortion[17] in the diffusion line shapes.

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APPENDIX A: CANONICAL STRESS TENSOR IN GINZBURG–LANDAU THEORY

In this Appendix we establish Eq. (2.1), the connection between the familiar Ginzburg–Landau free-energy density F and the less familiar expression for the stress tensor. This connection is essential for all of our work, where we calculate the critical viscosity from fluctuations in the off-diagonal component of the stress tensor T_{ij}. (Here we denote the Cartesian components by the indices i, $j = 1, 2, 3$, rather than by the letters x, y, etc.). For the specific purpose, however, of finding the general formula for T_{ij} in terms of the spatial derivatives of the concentration s_i we do not have to deal with fluctuations. Instead, we consider that the liquid is well away from the critical point, so that the fluctuations are weak and can be ignored. In order to set up an arbitrary spatial variation in $s(\vec{x})$, we imagine that we apply an external potential $V(\vec{x})$ to the system so that the energy density of interaction is $s(\vec{x})V(\vec{x})$. $V(\vec{x})$ is imagined to have a suitable spatial dependence so as to set up the desired configuration in the field $s(\vec{x})$. Thus the total free-energy density has an explicit linear dependence on $V(\vec{x})$ in the form

$$F(s, s_i, V) = F(s, s_i, 0) + sV. \tag{A1}$$

Because of the assumed spatial variation in the input potential $V(\vec{x})$, and because of the resulting spatial dependence of $s(\vec{x})$, F will have an implicit dependence on $\vec{x}$. Each element of the fluid has a tendency to move so as to reduce its free energy. The corresponding body-force density is the gradient

$$\vec{K} = -\nabla F = -\frac{\partial F}{\partial s}\nabla s - \sum_i \frac{\partial F}{\partial s_i}\nabla s_i - s\nabla V. \tag{A2}$$

Note that the gradient operator acts on the free-energy density only via its dependence on s, s_i, and V. We now proceed to simplify Eq. (A2) by applying the strict Ginzburg–Landau mean-field theory, completely neglecting fluctuations. This requires that we minimize the total free energy of the system in the presence of the given function $V(\vec{x})$, according to

$$\delta \int d^3x\, F(s, s_i, V) = 0. \tag{A3}$$

The resulting optimal configuration is determined by the Euler–Lagrange equation

$$\frac{\partial F}{\partial s} = \sum_i \frac{\partial}{\partial x_i}\frac{\partial F}{\partial s_i}. \tag{A4}$$

Selecting the jth component of Eq. (A2) and substituting Eq. (A4) yields

$$K_j = -\sum_i \frac{\partial}{\partial x_i}\left(\frac{\partial F}{\partial s_i}s_j\right) - sV_j = -\sum_i \frac{\partial}{\partial x_i}T_{ij} - sV_j, \tag{A5}$$

where

$$T_{ij} = \frac{\partial F}{\partial s_i}s_j \tag{A6}$$

is the desired canonical expression for the stress tensor which is used in Eq. (2.1).

The second term in the right-hand member of Eq. (A6) is the body force coming directly from the external potential. The first term is the body force resulting from the net sum of the intermolecular forces to the extent that this depends upon the gross distribution of the molecules through the derivatives of the macroscopic field variable $s(\vec{x})$. Although we have derived this result in the mean-field region, its validity is obviously not restricted to this case. The intermolecular forces described by Eq. (A6) are the same for a given configuration $s(\vec{x})$, regardless of how this configuration happens to occur. Therefore Eq. (A6) should be expected to be true even if the values of s_i refer to a fluctuation rather than to a steady mean-field situation.

APPENDIX B: ROLE OF VISCOSITY FREQUENCY DEPENDENCE IN DIFFUSION PROCESS

The critical diffusion process has been studied in Sec. V. We supply here more of the details relevant to the velocity correlation function of Eq. (5.2). We are particularly interested in the effect of the frequency dependence of the viscosity, which is evident in the denominator of the integrand of Eq. (5.3). Let us denote the Fourier component of the transverse velocity field associated with wave number $\vec{k}$ by $v_{\vec{k}\mu}(t)$. The subscript μ denumerates the two independent shear modes belonging to each value of $\vec{k}$. Aside from the trivial trigonometric factor $\sin^2\theta$, the time-correlation function of $v_{\vec{k}\mu}(t)$ is simply the Fourier transform of Eq. (5.2):

$$\langle v_{\vec{k}\mu}(t_2)v^*_{\vec{k}\mu}(t_1)\rangle = \frac{T}{\rho}\, e^{-(\eta k^2/\rho)|t_{21}|}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, f(k,\omega)e^{-i\omega t_{21}}. \tag{B1}$$

Taking the Fourier transform also with respect to time, we have

$$f(k,\omega) = \mathrm{Re}\,\frac{2T/\rho}{(\eta/\rho)k^2 - i\omega}\quad . \tag{B2}$$

This is written in the general form which follows from the fluctuation-dissipation theorem. η is analytic in the upper half of the complex frequency plane, corresponding to a causal response function.

But before taking up the frequency dependence of η let us simplify Eq. (B2) by noting that the frequency ω will be of the order of magnitude of the relaxation rate Γ^c_k. It is useful to introduce a characteristic wave number k_0 at which the shear relaxation rate equals the longitudinal diffusion rate. This requires, from Eq. (3.9),

$$(\eta/\rho)k_0^2 = \Gamma^c_{k_0} = (T/16\eta)k_0^3 \tag{B3}$$

or

$$k_0 = 16\eta^2/\rho T\ . \tag{B4}$$

It is convenient to evaluate Eq. (B4) by observing in Fig. 2 that $\Gamma^c_k/k^3 = T/16\eta = 5\times10^{-13}\ \mathrm{cm}^3\,\mathrm{sec}^{-1}$. With $\rho \simeq 1\ \mathrm{g\,cm}^{-3}$ and $T = 4\times10^{-14}$ erg, we find

$$k_0 = (16\eta/T)^2\,(T/16\rho) = 10^{10}\ \mathrm{cm}^{-1}\ . \tag{B5}$$

This is, of course, only a dimensional parameter of the fluid. There are no actual fluctuation modes corresponding to a wavelength of such small subatomic dimensions. Because of the different power-law dependence on wave number, the diffusion rate will be smaller than the shear relaxation rate, for physically realizable values of k, by the ratio k/k_0. Thus in the range of optical wavelengths,

$$\frac{\Gamma^c_k}{(\eta/\rho)k^2} = \frac{k}{k_0} \simeq \frac{10^5\ \mathrm{cm}^{-1}}{10^{10}\ \mathrm{cm}^{-1}} = 10^{-5}\quad . \tag{B6}$$

It is therefore apparent that ω is completely negligible in the denominator of Eq. (B2), and to a very high degree of accuracy we have

$$f(k,\omega) = (2T/k^2)\,\mathrm{Re}\,(1/\eta)\ . \tag{B7}$$

We now need to examine the frequency dependence of η. In order to distinguish this function clearly from the Laplace transform defined in Eq. (3.1), we denote it by $\eta(k\,|\,\omega)$. The fluctuation-dissipation theorem expresses the real part of this function as the Fourier integral

$$\mathrm{Re}\,\eta(k\,|\,\omega) = \frac{1}{2T}\int_{-\infty}^{+\infty} dt_{21}\,\langle T_{xy}(2)\,T_{xy}(1)\rangle_{\vec{k}}\, e^{i\omega t_{21}}\quad , \tag{B8}$$

where the spatial Fourier transform is

$$\langle T_{xy}(2)\,T_{xy}(1)\rangle_{\vec{k}} \equiv \int d^3x_{21}\,\langle T_{xy}(2)\,T_{xy}(1)\rangle\, e^{i\vec{k}\cdot\vec{x}_{21}}\ . \tag{B9}$$

It is awkward to deal with the frequency dependence in the denominator of Eq. (B7). Fortunately, this is a relatively small portion of $\eta(k\,|\,\omega)$, and we are therefore permitted to expand it in powers of the difference $\eta(k\,|\,\omega) - \eta(k\,|\,0)$, and to work only to first order. This gives us

$$\eta(k\,|\,\omega)^{-1} = [\eta(k\,|\,0) + \eta(k\,|\,\omega) - \eta(k\,|\,0)]^{-1}$$

$$\simeq \eta(k\,|\,0)^{-1} - \eta(k\,|\,0)^{-2}\,[\eta(k\,|\,\omega) - \eta(k\,|\,0)]\ . \tag{B10}$$

Substituting Eqs. (B10) and (B8) into Eq. (B7) yields

$$f(k,\omega) = \frac{2T}{k^2\eta(k\,|\,0)} - k^{-2}\,\eta(k\,|\,0)^{-2}$$

$$\times\int_{-\infty}^{+\infty} dt_{21}\,\langle T_{xy}(2)\,T_{xy}(1)\rangle_{\vec{k}}\,(e^{i\omega t_{21}} - 1)\ . \tag{B11}$$

Substituting this result into Eq. (B1) and carrying out the integration over the frequency, we note that the terms in Eq. (B11) which are not explicitly frequency independent yield Dirac δ functions in the relative time variable t_{21}. Thus we find

$$\langle v_{\vec{k}\mu}(t_2)\,v^*_{\vec{k}\mu}(t_1)\rangle = \frac{2T}{k^2\eta(k\,|\,0)}\,\delta(t_{21})$$

$$- k^{-2}\eta(k\,|\,0)^{-2}[\,\langle T_{xy}(2)\,T_{xy}(1)\rangle_{\vec{k}} - \delta(t_{21})$$

$$\times\int_{-\infty}^{+\infty} dt'_{21}\langle T_{xy}(2')\,T_{xy}(1')\rangle_{\vec{k}}\,].$$

Equation (B12) is the required more precise form of Eq. (5.2). As explained in Sec. V, Eq. (5.2) as written there has only a formal symbolic meaning. At this point we can identify the two nonlocal static functions $\eta(k\,|\,0) \equiv \eta(0,k,0)$. With Eq. (B12), we can substitute Eq. (5.1) into Eq. (1.5) and carry out the required space and time integrations. The former leads to the convolution integral shown in Eq. (5.3), while in the time integration over the velocity correlation function we have to include the diffusion relaxation factor $e^{-\Gamma^c_{k'}|t_{21}|}$ for the concentration fluctuation of wave number k'. This brings in the ratio $\gamma = k'/k$, in the notation of Eq. (3.1). The resulting integral is

$$\int_{-\infty}^{+\infty} dt_{21}\, e^{-\Gamma^c_{k'}|t_{21}|} \langle v_{\vec{k}\mu}(t_2) v^*_{\vec{k}\mu}(t_1)\rangle$$

$$= \frac{2T}{k^2}\left\{\frac{1}{\eta(0,k,0)} - \frac{1}{\eta(0,k,0)^2} \times \left[\eta\left(0,k,\frac{k'}{k}\right) - \eta(0,k,0)\right]\right\}$$

$$\simeq \frac{2T}{k^2\eta(0,k,k'/k)} \qquad \text{(B13)}$$

and appears in the integrand of Eq. (5.3).

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[16] It is interesting to note that Eq. (12) confirms the general rule of thumb [R. A. Ferrell, J. Phys. 32, 85 (1971)] that when the factorization brings in the correlation length twice (via the equal-time Green's function), $a_{\text{eff}} \approx \frac{1}{2}$.

[17] We plan to deal with this application of the theory in a later paper.

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Electron Gas at Metallic Densities*

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The ground-state properties of an electron gas at metallic densities are investigated using the Wu–Feenberg theory of Fermi liquids. The correlation energy, the low-temperature specific heat, and the spin susceptibility are computed, and the ground state is found to be paramagnetic. The perturbative correction to the correlation energy owing to the particle-hole excitations in a correlated-basis-function formulation is found to be insignificant.

I. INTRODUCTION

The problem of a quantum electron gas in its ground and low excited states has been a subject of interest for many years. The study was initiated by Wigner[1] in a calculation of the correlation energy which he defined to be the difference between the true ground-state energy and that given by the Hartree-Fock approximation. The correlation energy is a function of the electron density which is