We are then left with two equations to solve[7] for A and B:

$$1+\frac{2}{3\pi}\left(\frac{r_0}{r_c}\right)^3\int_0^\infty x\sin x\left\{\left[1+\left(\frac{r_c}{r_0}\right)^3\left(\frac{\alpha(x)A+\beta(x)B}{x^5}\right)\right]^{1/2}-1\right\}dx=0, \tag{5}$$

$$1+\frac{2}{3\pi}\left(\frac{r_0}{r_c}\right)^3\int_0^\infty x^2\cos x\left\{\left[1+\left(\frac{r_c}{r_0}\right)^3\left(\frac{\alpha(x)A+\beta(x)B}{x^5}\right)\right]^{1/2}-1\right\}dx=0, \tag{6}$$

where r_0 is the average particle distance and A and B are dimensionless parameters, linear in the unknown $\lambda g(r_c)$ and $g'(r_c)$ and $\lambda g'(r_c)$.

In order to find an analytic solution, we assume $r_c/r_0 \to 0$. Then Eqs. (5) and (6) can be solved exactly and we find $A=12$ and $B=-54$. With these values of A and B we calculate the excitation spectrum or, equivalently, the sound velocity which turns out to be[8]

$$C=(\hbar/\sqrt{2}mr_c)(r_c/r_0)^{3/2}\sqrt{3}. \tag{7}$$

The sound velocity we find in this simple calculation is very close to the exact result,[9] the only difference remaining being the factor $2^{-1/2}$ which does not occur in the exact result.

In conclusion, we show in this Letter that divergences in the potential can be consistently eliminated, and that linear response theory can be used to obtain the excitation spectrum of a hard-sphere Bose gas in a relatively simple way. We specialized for the case of extreme dilution in order to have an analytic solution but, in principle, Eqs. (5) and (6) can be solved for any density.

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[6] For the relations between $\psi(q)$, $S(q)$, and $g(r)$, see Ref. 2.

[7] We extended the form of $\psi(q)$, valid for low q's, for all q values. The argument is that the low-q part is the most important contribution to Eqs. (5) and (6).

[8] In the small-q region of the spectrum, $E(q)$ is linear with q, as can be easily checked in Eq. (3) since $\psi(q)$ is independent of q. We thus have a sound-wave spectrum where $c=E(q)/\hbar q$.

[9] See Huang, Ref. 5, pp. 409-434.

DECOUPLED-MODE DYNAMICAL SCALING THEORY OF THE BINARY-LIQUID PHASE TRANSITION*

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The critical slowing down of the diffusion in a binary liquid is calculated from the fluctuation-dissipation theorem. The fluctuating current is the product of the local fluctuations in concentration and velocity. Assuming statistical independence of these variables yields results identical to those found by Kawasaki using another method.

The central idea in the dynamical scaling theory[1,2] of phase transitions is that the correlation length is the same for static and dynamic properties. Calculations of the so-called "mode-mode mixing" type[3,4] have been carried out on the binary-liquid phase transition and give a concrete example of how the static correlation length enters the dynamical properties. The purpose of the present note is to point out an alternative approach to the dynamics of the binary-liquid phase transition, which is simply an application of the fluctuation-dissipation theorem to the fluctuations in particle current. By introducing a certain mode-decoupling approximation we obtain results identical to those found by Kawasaki[4] from his mode-coupling theory.

Throughout this paper we will be dealing only with the low-frequency end of the concentration-fluctuation spectrum, which results from the diffusion of one component, the "solute," through the other component, the "solvent." The transport coefficient determining the width of this Lorentzian line is the conductivity, which we can calculate from the fluctuation-dissipation theorem[5,6] (or so-called "Kubo formula")

$$\lambda = (6T)^{-1}\int d^4 21 \langle \vec{J}(2)\cdot\vec{J}(1)\rangle. \tag{1}$$

As there is only one critical concentration it is sufficient to deal only with the solute and leave the solvent in the background. The solute particle current at the space-time point $(\vec{x}, t)$ is the second-order product of the solute particle density fluctuation s times the local velocity $\vec{v}$,

$$\vec{J}(\vec{x}, t) = s(\vec{x}, t)\vec{v}(\vec{x}, t). \tag{2}$$

We will use the terms density and concentration interchangeably in referring to $s(\vec{x}, t)$. The scalar product of the particle currents at the two different space-time points is averaged over the equilibrium thermal ensemble, and integrated over all space-time differences. Equation (1) is essentially the same formula as that used by Mountain and Zwanzig[7] to study the critical divergence of the thermal conductivity in a single-component gas. In the latter case, the reduction of the heat current to the simple form of Eq. (2) is somewhat involved, and we therefore defer a discussion of the liquid-gas phase transition to another publication.[8] Equation (2) has a simple physical significance which is already familiar in the theory of acoustic radiation pressure. For example, if s is interpreted as the mass-density fluctuation in a fluid and $\vec{J}$ is the nonlinear contribution to the momentum density, then when a longitudinal sound wave is being propagated in the fluid, Eq. (2) yields a mean momentum density which is second order in the amplitude of the wave. This is found by using first-order linearized hydrodynamics to relate the density and velocity fluctuations. The average of $s\vec{v}$ then yields the familiar result that the momentum density in a propagating sound wave is the energy density divided by the velocity of propagation. In the present case, we are not dealing with a single propagating mode, but rather with a large collection of thermally excited nonpropagating diffusive modes. The essential point is, however, that any simultaneous fluctuations whatsoever in the density and velocity fields automatically lead to nonvanishing contributions to the current, according to Eq. (2). Such fluctuations in the current then necessarily in turn give a contribution to the conductivity in accordance with Eq. (1).

In order to demonstrate how Eq. (1) can be applied to the present problem, we need to introduce the equal-time density correlation function

$$G(\vec{x}_{21}) = \langle s(\vec{x}_2, 0)s(\vec{x}_1, 0)\rangle, \tag{3}$$

and the time-integrated velocity correlation tensor

$$F_{ij}(\vec{x}_{21}) = \int_0^\infty dt_{21}\langle v_i(\vec{x}_2, t_2)v_j(\vec{x}_1, t_1)\rangle. \tag{4}$$

At this point, we observe that the transverse fluctuations in velocity do not lead to density changes of the liquid and therefore have much lower frequencies than the longitudinal velocity fluctuations. They are consequently much more effective in contributing to Eq. (4). Therefore we neglect longitudinal velocity fluctuations, and furthermore make the additional assumption that the transverse modes are statistically independent of the density fluctuations. This assumption permits us to write the integrand of Eq. (1) in the factorized form (where F is the trace of F_{ij}

$$\lambda = (3T)^{-1}\int G(x)F(x)d^3x. \tag{5}$$

Because of the critical slowing down in the concentration fluctuations it has been possible to approximate their correlation function by the equal-time correlation function of Eq. (3). Now the frequency width of the concentration-fluctuation spectrum is determined by the diffusion coefficient. This is obtained by dividing the conductivity by an appropriate thermodynamic function, which in this case is $c(\partial c/\partial\pi)_T$, where c and π are the equilibrium concentration and osmotic pressure of the solute, respectively. This static response function is normalized by the equal-time concentration correlation function according to

$$c(\partial c/\partial\pi)_T = T^{-1}\int G(x)d^3x. \tag{6}$$

The ratio is the diffusion coefficient

$$D = \frac{\lambda}{c(\partial c/\partial\pi)_T} = \tfrac{1}{3}F_{\text{ave}}. \tag{7}$$

We note that the density fluctuations enter the problem as a weighting factor in determining a suitable average over the velocity correlation field, as defined by the ratio of the two integrals in Eqs. (5) and (6).

The time-integrated velocity correlation function, describing random thermal excitation of the transverse hydrodynamic modes, is

$$F_{ij}(\vec{x}) = \frac{T}{8\pi\eta}\left(\frac{\delta_{ij}}{x} + \frac{x_i x_j}{x^3}\right), \tag{8}$$

where T, η, and δ_{ij} are the temperature, coefficient of viscosity, and Kronecker delta function, respectively. (We use temperature units in which Boltzmann's constant is unity.) The trace of Eq. (8) is

$$F(x) = \frac{T}{2\pi\eta}\frac{1}{x}. \tag{9}$$

We now introduce the correlation length ξ by means of the Ornstein-Zernike function which, normalized according to Eq. (6), can be written in the form

$$G(x) = \frac{Tc}{4\pi\xi^2}\left(\frac{\partial c}{\partial \pi}\right)_T \frac{1}{x} e^{-x/\xi}. \tag{10}$$

The average required in Eq. (7) is readily found to be $(1/x)_{\text{ave}} = \xi^{-1}$ which, substituted into Eqs. (7) and (9), yields

$$D = T/6\pi\eta\xi = T\mu_\xi. \tag{11}$$

This result has already been obtained from the mode-mode coupling theory by Kawasaki[4] who has noted that $\mu_\xi = (6\pi\eta\xi)^{-1}$ is identical to the Stokes expression for the mobility of a sphere of radius ξ moving in a fluid of viscosity η.

This relationship of the Stokes formula to the present work can be elucidated by an approximate derivation of it, which also makes use of the fluctuation-dissipation theorem, or Einstein relation

$$T\mu_a = \tfrac{1}{3}\int_0^\infty dt_{21}\langle \vec{v}(t_2)\cdot\vec{v}(t_1)\rangle. \tag{12}$$

Here $\vec{v}(t)$ represents the velocity of a sphere of radius a at time t. The left-hand side of this equation is the temperature times the mobility of the sphere, while the right-hand side is the time-integrated autocorrelation function of the velocity of this sphere undergoing Brownian motion. Now we can imagine the sphere to be made up of the same kind of atoms as compose the surrounding fluid, and we can estimate its velocity by averaging over the velocities of all of the particles inside the sphere, disregarding the boundary. Thus we substitute into Eq. (13) the approximate expression

$$\vec{v}(t) \simeq (3/4\pi a^3)\int_{x<a} d^3x\, \vec{v}(\vec{x}, t), \tag{13}$$

where $\vec{v}(\vec{x}, t)$ is the unperturbed velocity field of the fluid in the absence of any boundary condition at $x = a$. This yields

$$T\mu_a \simeq \tfrac{1}{3}(3/4\pi a^3)^2 \iint_{x_1, x_2 < a} d^3x_1 d^3x_2 F(x_{21}) \simeq \frac{T}{6\pi\eta}\left(\frac{1}{x_{21}}\right)_{\text{ave}} \simeq \frac{T}{6\pi\eta a}, \tag{14}$$

It is not worthwhile to evaluate the numerical coefficient because the boundary condition at the surface of the sphere does perturb the velocity field of the surrounding fluid, so that the Brownian motion of the sphere is only qualitatively reflected by the velocity fluctuations of the unperturbed liquid. The purpose of this approximate derivation of Stokes law is to demonstrate that the velocity correlation function F plays qualitatively the same role in Stokes law as it does in the critical diffusion problem.

Equations (5) and (6) can be generalized[8,9] to finite wave number q by replacing one third of the trace of the velocity correlation tensor by its component in the $\vec{q}$ direction, which we indicate by the unit vector $\hat{q}$. Including a plane-wave factor of $\exp(i\vec{q}\cdot\vec{x})$ in the integrals gives then for the ratio, after a straightforward calculation, Fawasaki's result[4] for the q-dependent diffusion coefficient [where $g(q)$ is the Fourier transform of $G(x)$]

$$\begin{aligned} D(q) &= \lambda(q)/T^{-1}g(q) = (F_{\hat{q}\hat{q}})_q{}^{\text{ave}}, \\ &= \frac{T(1+z^2)}{8\pi\eta\xi}\left[\frac{1}{z^2} + \left(\frac{1}{z} - \frac{1}{z^3}\right)\tan^{-1}z\right], \\ &= \frac{T}{6\pi\eta}(q^2 + \xi^{-2})^{1/2}\sigma(z). \end{aligned} \tag{15}$$

Here we have introduced the dimensionless variable $z = q\xi$. The dynamical scaling function

$$\sigma(z) = \tfrac{3}{4}(1+z^2)^{1/2}\left[\frac{1}{z^2} + \left(\frac{1}{z} - \frac{1}{z^3}\right)\tan^{-1}z\right] \tag{16}$$

expresses quantitatively the deviation from the qualitative dynamical scaling rule[1,2] that ξ^{-1} is to be replaced by q in the short-wavelength limit ($z \to \infty$). The variation of $\sigma(z)$ between these two limits of $\sigma(0) = 1.0$ and $\sigma(\infty) = 3\pi/8 = 1.178$ is exhibited in Fig. 1 as a function of $\tan^{-1}z$. At intermediate values of z, the Fourier transform of the static correlation function $G(x)$, via the combination $(\xi^{-2} + q^2)^{1/2}$, gives a measure of the "distance" in the plane of the variables ξ^{-1} and q of an arbitrary point from the critical point $(\xi^{-1}, q) = (0, 0)$. $\sigma(z)$ expresses the slight difference in this measure between the dynamical and static properties. As noted by Kawasaki,[4] $\sigma(z)$ is sensitive to deviations of $G(x)$ from the Ornstein-

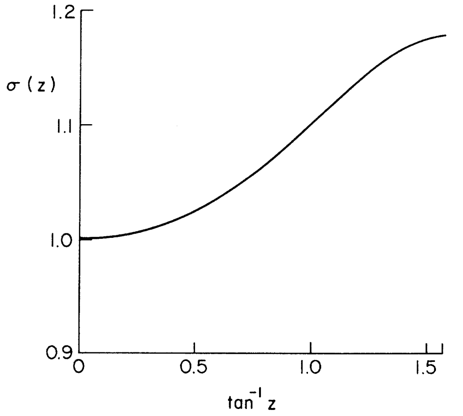

FIG. 1. Dynamical scaling function $\sigma(z)$ vs $\tan^{-1}q\xi$. The dimensionless variable $z = q\xi$ is 2π times the ratio of the correlation length ξ to the wavelength of a fluctuation $2\pi/q$. In the long-wavelength hydrodynamic limit $\sigma(0) = 1$, while $\sigma(\infty) = 3\pi/8$ gives the deviation between dynamic and static scaling in the extreme nonlocal limit.

Zernike form. It is worthwhile and straightforward to calculate this modification, but the results of the calculation are rather complicated and will therefore be relegated to a more detailed report.[8]

In summary, we have seen how the simple physical picture of the nonlinear mixing of density and velocity fluctuations, which is the basis of the conventional theory of acoustic radiation pressure, leads in the present case to fluctuations in the particle current. It is then a straightforward task to calculate by means of the fluctuation-dissipation theorem the conductivity corresponding to these fluctuations. Generalizing this approach to wave-number–dependent quantities gives results in complete agreement with the mode-mixing calculation of Kawasaki. The resulting dynamical scaling factor $\sigma(z)$ confirms the qualitative validity of the dynamical scaling theory,[1,2] putting it into a precise quantitative form. Exactly the same treatment can be given to the heat-current fluctuations in a single-component gas.[8] In this case Eqs. (16) and (17) describe the nonlocal critical slowing down at the liquid-gas critical point. It should further be noted that the decoupling approximation used here is similar to that employed in paraconductivity theory[10-12] where, however, its validity in the critical region is questionable because of the interaction of the modes. The neglect of mode interaction in the present problem is reasonable theoretically because of the presumably noncritical nature of the shear modes, and seems to have been confirmed experimentally.[13] Finally, it is a pleasure to acknowledge a helpful discussion with Professor R. Zwanzig.

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