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Brownian motion in a critical mixture: K-dependent diffusion*

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A light-scattering investigation of Brownian motion in the critical mixture nitroethane-isooctane is reported, along with a theory to explain the results. The diffusion constant of 0.3-μ Teflon particles was measured by autocorrelation spectroscopy, at various values of scattering wave vector $\vec{K}$. The experimental results exhibit a K dependence stronger than can be accounted for by a simple dynamic scaling approach to the shear viscosity. The theory presented takes into account the nonlocality of the shear viscosity and its effect on the diffusion of small material particles. In addition, we develop a theory to explain the effect of a specific interaction between the particles and the two fluid components. Defining an effective viscosity as $\eta_{\text{eff}} \equiv k_B T/6\pi R D$, where D is the diffusion coefficient, the theoretical results may be expressed as $\eta_{\text{eff}} = \eta(\xi_1) + G\alpha^2\xi_2^2[1/2 - (R/\xi_2)K_1(2R/\xi_2)]$, $\xi_1^{-2} \equiv (0.94R)^{-2} + \xi^{-2} + a^2K^2$, $\xi_2^{-2} \equiv B\alpha + \xi^{-2} + a^2K^2$, where $\eta(\xi)$ is the viscosity expressed as a function of the correlation length ξ, a is the dynamic scaling parameter ($a = 1.12 \pm 0.1$), and $K_1(x)$ is the Bessel function of imaginary argument. The parameters G and B are nonadjustable and depend on the particle size R, the intermolecular spacing, and the Ornstein-Zernike parameter. The parameter α is a measure of the surface interaction between the particles and the fluids. The resulting expression fits the data within the experimental error of 1%.

I. BROWNIAN MOTION IN A CRITICAL MIXTURE: K-DEPENDENT DIFFUSION

The problem of Brownian motion in critical mixtures has received scant attention in the literature. The interactions between the critical fluctuations of average size ξ and small material particles of comparable size are important in this situation. To discuss the problem, let R be the radius of the spherical particles and D be their diffusion constant. Then we can define

$$\eta_{\text{eff}} \equiv k_B T/6\pi R D. \tag{1}$$

Equation (1) is written such that in a normal liquid we have Stokes's law with $\eta_{\text{eff}} = \eta_{\text{hyd}}$, where η_{hyd} is the hydrodynamic shear viscosity. In the critical region η_{hyd} exhibits an anomaly which is apparently logarithmic in character.[1] It has been found by other workers[2] that the anomaly may be described by

$$\Delta\eta/\eta_{\text{hyd}} \equiv (\eta_{\text{hyd}} - \eta_b)/\eta_{\text{hyd}} = A \ln Q_D \xi, \tag{2}$$

where η_b is a background viscosity extrapolated from temperatures well above T_c and A and Q_D are parameters.

In the critical region it has been found experimentally that Stokes's law is not obeyed. That is, η_{eff} is *not* the same as η_{hyd}. A tracer diffusion study[3] using isotopically labeled molecules of 3-methylpentane in the mixture nitroethane-3-methylpentane, that is, for the case $R \ll \xi$, found that the anomaly disappeared completely ($\eta_{\text{eff}} \sim \eta_b$). On the other hand, a microphotography study,[4] for the case $R \gtrsim \xi$, showed an enhancement of the anomaly $[(\eta_{\text{eff}} - \eta_b)/\Delta\eta \gg 1]$. If this effect is assumed to be because R/ξ is becoming small in the critical region, then the lack of an anomaly in the tracer diffusion study is an apparent contradiction. For this reason it was desirable to study an intermediate situation by the most accurate means available, namely light scattering.

We have recently studied Brownian motion of 0.3-μ Teflon particles in the mixture isooctane-nitroethane by a light-scattering technique.[5,6] The results have indicated a very strong dependence of the diffusion coefficient upon the scattering momentum transfer. Indeed, the observed K dependence cannot be accounted for by simply using a dynamic scaling approach to modify the *hydrodynamic viscosity*. We have previously outlined a theory[6] to account not only for this enhanced K dependence, but also for the enhanced temperature dependence of the viscosity anomaly observed in the earlier work.[4] The purpose of this paper is to expand on that theoretical treatment and to report the details of the experimental arrangement. In Sec. II, we describe the experimental apparatus. In Sec. III we present the results and the comparison with a simple dynamic scaling approach. In Sec. IV we develop in some detail the theory of the *two* contributions to the anomalous effective viscosity, and in Sec. V we compare our data to that theory. A discussion of the effects of dealing with a distribution of particle sizes is included in the Appendix.

II. EXPERIMENTAL ARRANGEMENT

The method of investigation is autocorrelation spectroscopy. The relationship of the correlation properties of the scattered light to the diffusion constant of the particles has been derived by Clark, Lunacek, and Benedek.[7] Their result is that the intensity autocorrelation function for light scattered at an angle θ is given by

$$\langle I(t)I(t+\tau)\rangle = I^2(1+N^{-1}e^{-2DK^2\tau}), \tag{3}$$

where N is the number of coherence areas incident on the detector, D is the diffusion constant, and K is the scattering momentum transfer

$$K=(4\pi n/\lambda)\sin\tfrac{1}{2}\theta. \tag{4}$$

From Eq. (3) it is apparent that analysis of the spectrum in terms of an exponential contribution superimposed on a constant background will yield a characteristic decay time or correlation time τ_c which will be interpreted as the average time required for a particle to move a distance $1/K$, and in terms of which the diffusion constant is obtained as

$$D=1/2K^2\tau_c. \tag{5}$$

Thus, the intensity autocorrelation of light scattered at a specific angle from Brownian particles is directly related to the motion of individual particles over a distance of roughly $1/K$. In the critical region of a binary mixture, the coherence length of the concentration fluctuations becomes larger than the range of characteristic lengths accessible in a light-scattering investigation. We would not expect that the character of the particle motion as manifested in the diffusion constant would be the same for motion over distances comparable to ξ and over distances much larger than ξ. In other words, we would expect to observe nonlocal or K-dependent diffusion behavior in the critical region.

The liquid system chosen for the investigation was nitroethane-isooctane. The reason for this choice was that the refractive indices of the two components are matched very closely,[8] differing only by $\Delta n = 0.0001$ at room temperature and by slightly more at the transition temperature (31 °C). The intensity of the opalescence scattering is thus much lower[9] than in the usual binary liquid system ($\Delta n \sim 0.2$). This allowed us to study the diffusion of the particles even very close to the transition without significant interference from light scattered by the concentration fluctuations themselves.

The liquids were both purified to 99.95+% before the mixture was made, and the final mixture was sealed in a glass vial with a tightly fitting, triply ribbed Teflon stopper. Outside the stopper was a glass cap, secured by a Teflon O-ring. This arrangement was thus similar to that used by Stein, Allegra, and Allen.[3] The purification of both liquids was carried out in a spinning-band distillation column, and the purity was checked by gas chromatography with an estimated sensitivity of 0.01%. All handling of the liquids after purification was done under a dry atmosphere.

The particles chosen for the investigation were 0.3-μ Teflon particles. They were obtained from a Teflon suspension manufactured by Dupont. The width of the size distribution, as estimated from the correlation spectrum, was 10% (see Appendix). After centrifugal fractionation in a sucrose gradient the sucrose was removed by dialysis. The particles were then evaporated from the pure water suspension to complete dryness in a mixing vial. Purified nitroethane was added and the vial was agitated in an ultrasonic bath to disperse the particles. This "doped" nitroethane was then used to make the final binary mixture. No correction was made for the weight of the particles in weighing the nitroethane, since the mass fraction occupied by the particles was negligible. We estimate the particle density to be 10^9 cm^{-3} as evidenced by the scattering cross section.

The critical concentration of the mixture has not previously been determined with good accuracy.[8-10] The reason for this is that the matched refractive indices of the components make meniscus observations very difficult. We were able to make use of a nucleation raining phenomenon[6] as an indicator of the transition. This method allowed accurate location of the meniscus even very close to the transition. If the homogeneous sample was cooled very slowly through the transition, all the Teflon particles would be carried up into the isooctane-rich phase. Using a laser beam it was then simple to locate the meniscus position, since there would be a very sharp change in the scattered intensity at the meniscus. In fact, the change as measured by our detector was several orders of magnitude, and easily visible to the eye. By this technique we located the critical concentration to be 47.6 ± 0.1-wt% nitroethane. In the final sample used for the work reported here it was 47.70 ± 0.01 wt%. While the transition could be located in a relative sense by this technique to an accuracy of 0.001 °C, the absolute accuracy of that determination was 0.2 °C, owing to thermometer calibration. The value found was (30.75 ± 0.2)°C, in good agreement with most previously reported values.[8-10]

The viscosity of the pure binary liquid was measured as a function of temperature by a standard capillary technique. It was found that the temperature dependence could be adequately described by Eq. (2) in agreement with the theory due to Perl and Ferrell.[1] This dependence has been found experimentally in other systems which were investigated more accurately.[3] Our interest in this measurement was simply to compare Eq. (2) to the results for the effective viscosity, defined in the in-

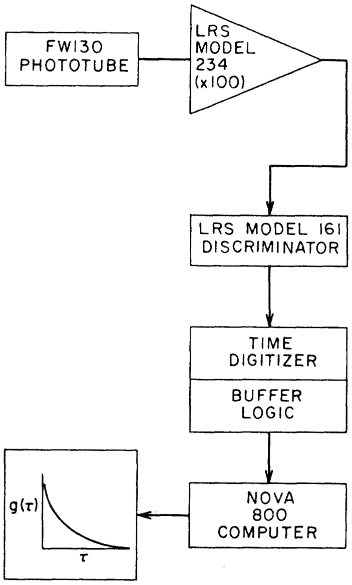

FIG. 1. Organization of the computer-controlled autocorrelation spectrometer.

troduction. The fit to our data gave $A = 0.0538$, in good agreement with the theoretical value of 0.054, if we estimate the correlation length to be given by

$$\xi = \xi_0[(T - T_c)/T_c]^{-0.62}. \tag{6}$$

Estimating $\xi_0 \approx 3A$, we obtain $Q_d = 6.36 \times 10^6\ \mathrm{cm}^{-1}$. These values are used in the later data analysis, in Secs. III and V.

The temperature control of our sample was accomplished by an ac double Kelvin bridge of rather standard design.[11] The use of ac control allowed the use of inductive ratio arms, which characteristically have very low temperature coefficients (~0.02 ppm/°C).[12] The effect of laboratory temperature fluctuations on the bridge was therefore negligible. The control achieved was typically ±0.0003 °C for periods of half a day or more.

The controlled bath was glycerin, and was *not* stirred. Stirring was avoided to preclude any possibility of transmittance of vibrations into the sample. This would have interfered with the correlation measurements of the scattered light. The temperature gradients were effectively removed by the addition of zone heaters at the top and bottom of the controlled bath, which were independently controlled. The temperature variation across the sample was less than 0.0003 °C.

The autocorrelation spectrometer was of rather unique design. As shown in Fig. 1, it utilized an on-line computer (Nova 800) to perform the data analysis. The external device, the time digitizer, counted time between photon pulses in units of 0.2 μsec. These sequential counts were transferred directly to the computer memory via a triple-buffer network. The computer was programmed to use those counts to construct the autocorrelation spectrum, in real time.

It was necessary to periodically agitate the sample to disperse the particles, which were slowly settling out during the course of the experiment. Apparently, owing to some amount of irreversible coagulation, it was found that the particle size distribution and average size were not exactly the same after every such agitation. Therefore, it was necessary to use a normalization procedure to relate the observed correlation times to an effective viscosity. After agitation, a period of 8–10 hours would be allowed, during which large particles (or conglomerations of particles) would settle out of the sample, and a certain amount of nonreproducible coagulation apparently took place. After that period it was found that the average particle size, as observed by the correlation spectrum, would undergo a steady drift downward, as the particles of slightly different sizes settled at different rates. That drift was slow enough, however, to allow an interpolation procedure to be used.

The procedure used consisted of several steps. The correlation time τ_c would be measured at a calibration temperature at least 1 °C above the transition. Several points could be taken over a period of 15–18 hours. Then the correlation time would again be measured at the calibration temperature. It was always observed to decrease slightly—never more than 2%. Defining the correlation time at the calibration temperature to be τ_1, we would then calculate the ratio τ_c/τ_1, using a value of τ_1 obtained by interpolating in real time between the initial and final values. The result of this procedure was a *relative* effective viscosity. This, in turn, was related to an absolute viscosity by multiplying by the known viscosity at the calibration temperature, as measured by the capillary viscometer. Using this technique we were able to get very reproducible results.

III. EXPERIMENTAL RESULTS

There are at least three things that might be expected of Brownian motion in the critical region. The diffusion constant should reflect the viscosity anomaly. It should also take on wave-vector dependence. Last, we might expect that the Einstein-Smoluchowski relation[13]

$$\langle \Delta z^2(\tau) \rangle = 2D\tau \tag{7}$$

might not hold for times τ on the order of the lifetime of the concentration fluctuations. The first thing we shall do in this section is show by a simple argument that the deviations from Eq. (7) should be small.

The relation (7) may be derived easily by writing the displacement of a particle in time τ as

$$\Delta z(\tau) = \int_0^\tau v(s)\,ds\,. \tag{8}$$

From Eq. (8) we can construct the mean-squared displacement in terms of the velocity autocorrelation function for the particle. Taking the time derivative of the resulting expression we obtain

$$\frac{d}{d\tau}\langle \Delta z^2(\tau)\rangle = 2\int_0^\tau \langle v(s)v(s+s')\rangle\,ds'\,. \tag{9}$$

Ignoring the long-time "tail" of the velocity correlation function which has recently been discovered (in normal liquids),[14] we can write that function as

$$\langle v(s)v(s+s')\rangle = v_0^2 e^{-\gamma t/m} \tag{10}$$

and, for times $\gg m/\gamma$, we see that the relation (7) is obtained. As mentioned, the expression (10) is not entirely correct. This is due to inertial effects in the liquid movement.[14] However, the value of the time integral of Eq. (10) remains unchanged when this effect is included. This can be understood intuitively since the time integral is related only to the $\omega \to 0$ component of the velocity fluctuation spectrum. It is reasonable that inertial effects should therefore disappear from the result. Moreover, for the same reason we should not expect the effect of the liquid inertia to become anomalous owing to critical fluctuations. Hence we can conclude that the result (7) should remain valid in the critical region, for the time regime $t \gg m/\gamma$. The important time in the problem is thus not the lifetime of the fluctuating force (which *is* related to the lifetime of the concentration fluctuations) but rather to the velocity correlation time of the particle. The latter should not display a large anomaly in the critical region, and even decreases as the viscosity increases. For our system we estimate $m/\gamma = 4\times10^{-9}$ sec. Since the time scale of the motion being studied is measured in milliseconds, any effect due to deviation from Eq. (7) may be ignored. We therefore do not expect any anomalous deviation from exponentiality of the correlation spectra in the critical region. None was observed.

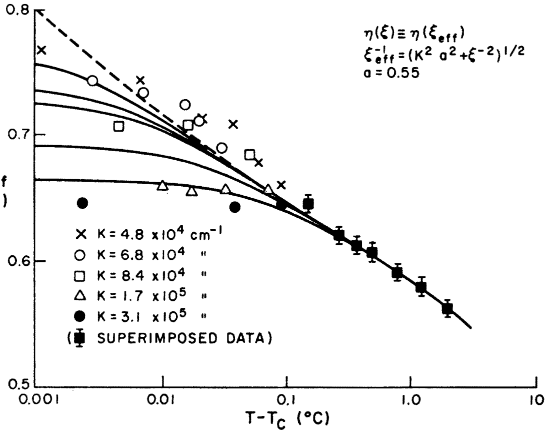

FIG. 2. Simple dynamic scaling approach to the effective viscosity data. The five solid lines are calculated by simply replacing the correlation length by an effective value, obtained by a dynamic scaling approach, in the theoretical expression for the anomalous viscosity.

The other two effects were observed, however. The data, taken at the five indicated values of K, are presented in Fig. 2.[6] The dashed line in that figure represents the hydrodynamic viscosity obtained in our capillary measurements. The solid lines are calculated by the dynamical scaling procedure indicated at upper right in the figure for the five experimental values of K. The value of the dynamic scaling parameter, $a = 0.55$, was chosen by a least-squares procedure. The fit to the data is poor and the value of the scaling parameter is approximately half that theoretically expected. If the scaling parameter were arbitrarily chosen as 1.0, the solid lines would all fall well *below* the relevant data points. We conclude that the effective viscosity as derived from the friction coefficient determined by measurement of the diffusion constant cannot be simply related to the K-dependent hydrodynamic shear viscosity. Further we note that there is an apparent extra anomaly in the effective viscosity which is evident in the region $0.01 < T - T_c < 0.1$, which would be even more obvious if $a = 1.0$ were chosen. Also, it is evident that the K dependence of the results is stronger than indicated by the simple dynamic scaling approach taken above. We interpret these facts as evidence of a contribution to the friction coefficient of a particle from some source other than the usual viscosity phenomenon.

IV. THEORY

There are two parts to the theory to be presented here. First, we shall derive the way in which the nonlocality of the viscosity enters into Stokes's law. Next we shall consider the additional anomaly indicated by our data in the last section, as well as by the data of others.

To see how the K dependence of the viscosity enters into Stokes's law, we use an approach originally due to Zwanzig.[15] In his treatment, he uses a theorem due to Faxen[16] which relates the force on a spherical particle to the *(steady state)* velocity field which exists in the absence of the particle. The velocity is simply averaged over the surface Σ of the sphere,

$$\vec{F} = 6\pi\eta R \frac{1}{4\pi} \oint_{\Sigma} d\Omega\, v(\Sigma). \tag{11}$$

For the case of a K-dependent viscosity we must modify this theorem. In this case, the Navier-Stokes equation, on which Eq. (11) is based, is valid only in an operator sense—that is, in k space. If the velocity field is a pure Fourier component, $v = v_k e^{i\vec{k}\cdot\vec{r}}$, the Navier-Stokes equation is valid by definition, provided we replace η by η_k. Thus, we see that the necessary modification of Faxen's theorem is to write

$$\begin{aligned}\vec{F} &= 6\pi R \int \frac{d^3k}{(2\pi)^3} \eta_k \vec{v}_k \frac{1}{4\pi} \int d\Omega\, e^{i\vec{k}\cdot\vec{R}} \\ &= 6\pi R \int \frac{d^3k}{(2\pi)^3} \eta_k \vec{v}_k \frac{\sin kR}{kR}\,.\end{aligned} \tag{12}$$

Using Zwanzig's treatment, it is easy to show that the velocity time correlation function is related to the time correlation function for the stress tensor as,

$$\begin{aligned}\langle \vec{v}_k(0)\cdot\vec{v}_{k'}(t)\rangle &= \frac{16\pi^3\delta(\vec{k}+\vec{k}')}{\eta_k^2 k^2} \\ &\quad\times \int d^3r\, e^{i\vec{k}\cdot\vec{r}} \langle S_{xy}(0,0) s_{xy}(r,t)\rangle\,.\end{aligned} \tag{13}$$

The time integral is then given, using the fluctuation-dissipation result[1] for the K-dependent viscosity, to be

$$\int_0^\infty \langle \vec{v}_k\cdot\vec{v}_{k'}(t)\rangle\, dt = 16\pi^3\delta(\vec{k}+\vec{k}')k_BT/k^2\eta_k\,. \tag{14}$$

Using Eq. (12) we construct the force autocorrelation function. The friction coefficient is related to that function by[17]

$$\gamma = \frac{1}{3k_BT}\int_0^\infty dt \langle \vec{F}(0)\cdot\vec{F}(t)\rangle\,. \tag{15}$$

We note that the effective viscosity is related to γ as $\eta_{\text{eff}} = \gamma/6\pi R$. The integral that results in Eq. (15) may be simplified considerably by use of Eq. (14) and we obtain, using $x = kR$,

$$\eta_{\text{eff}} = \frac{2}{\pi}\int_0^\infty dx \frac{\sin^2 x}{x^2}\eta_{x/R}\,. \tag{16}$$

In the limit as R becomes large, this reduces to just the hydrodynamic viscosity η_0, as it must. However, if R is small enough that there is significant k dependence for $k \lesssim 1/R$, then that k dependence must be taken into account in writing Stokes's law by replacing η by η_{eff} as given by Eq. (16). In a critical fluid, since the correlation length can be as long as about one micron, this effect must be considered in treating the motion of particles of the size used in our experiment, 0.3 μ.

It is possible to make a first-order approximation which can be evaluated exactly for a critical fluid. From the theory of Perl and Ferrell[1] we have for the first-order expression for the anomalous part of the k-dependent viscosity in the critical limit

$$\Delta\eta_k \approx \eta_b A \ln(Q_D/k), \tag{17}$$

where η_b is the "background" viscosity, $A = 0.054$, and Q_D is an empirical parameter. Substituting this into Eq. (16) we may perform the integral to obtain the anomalous part of η_{eff}

$$\begin{aligned}\Delta\eta_{\text{eff}} &= \frac{2}{\pi}\int_0^\infty \frac{\sin^2 x}{x^2}\eta_b A \ln\left(\frac{Q_D R}{x}\right) dx \\ &= A\eta_b\left(\ln Q_D R - \frac{2}{\pi}\int_0^\infty \frac{\sin^2 x}{x^2}\ln x\, dx\right) \\ &\cong A\eta_b \ln(1.31 Q_D R)\,.\end{aligned} \tag{18}$$

There is a correction which should be applied to this, however. We have used the expression of Eq. (17) for extremely low k (all the way to $k = 0$) where it does not apply. In fact, the entire negative contribution to the integral in the second line of Eq. (18) comes from this region. We can make a first-order correction for this fact by giving the integral a nonzero cutoff on the low side. That is, we must *add* to the above result the integral

$$A\eta_b \frac{2}{\pi}\int_0^{R/\xi_m} \ln x\, dx, \tag{19}$$

where ξ_m is the estimated maximum value of ξ which can occur (thus, $k_{\min} \sim 1/\xi_m$). It is likely that impurity effects, as well as breakdown of the Ornstein-Zernike theory,[18] would become important in the region of $T - T_c \lesssim 0.001\,°\text{C}$. For this value of temperature, we have $\xi_m \sim 0.75\ \mu$ from Eq. (6). Using this we obtain $R/\xi_m \sim \frac{1}{5}$, and the correction becomes $-0.33A\eta_b$. Adding this in gives the final result

$$\Delta\eta_{\text{eff}} \cong A\eta_b \ln(0.94 Q_D R)\,. \tag{20}$$

To extend this approximate result outside of the critical limit we use

$$\xi_1 = (\xi^{-2} + 0.94R^{-2})^{-0.5} \tag{21}$$

in place of ξ to calculate the viscosity to be used in Stokes's law to obtain the friction coefficient for the particles. This *ad hoc* "scaling law" assumption has simply been chosen to give the limiting behavior found in Eq. (20) as T_c is approached. This "first effective correlation length" ξ_1, then, gives a "Stokes's effective viscosity" which should describe the diffusion of the particles in the absence of any additional contribution to the friction coefficient. The approximation used in Eq. (17) as corrected in Eq. (20) is probably good to order

$A = 0.054$, or about 5% of the value of $\Delta\eta_{\text{eff}}$. The essential point is that we do obtain the intuitively expected result that in the critical limit the anomalous part of the effective viscosity is obtained by substituting R for ξ, within a factor of order unity.

As pointed out in Sec. III, however, it is apparent that there is an additional phenomenon leading to an *increase* in the effective viscosity over the hydrodynamic value [as opposed to the result of Eq. (21) which leads to a decrease]. Clearly, this must be related to the concentration fluctuations in the host mixture, and their interactions with the foreign particles under investigation. The above calculation has included only that part of the interaction that takes place via the velocity field of the fluid, and the modification of that field by the presence of the fluctuations. There is, however, the possibility of a direct interaction between the concentration gradients and the particles. Another way of describing this difference is to say that the above calculation has taken account of interactions between the two types of host molecules present, but has ignored the interaction of the surface of the particles with the host molecules.

To see what effect this might have on the motion of the particles, let us make the assumption that the energy of a surface element dA in contact with the fluid is proportional to the concentration fluctuation at the surface, if we subtract the constant energy due to the average concentration of the fluid. That is,

$$dE_s = \alpha dA, \tag{22}$$

where α is a surface tension derivative[19] with respect to concentration. Evaluating the total energy for a spherical particle located at r_0 due to the kth component of the concentration fluctuation $\delta C_k e^{i\vec{k}\cdot\vec{R}}$ we obtain

$$E_s = 4\pi(i/k)\alpha R\delta C_k \sin kR e^{i\vec{k}\cdot\vec{r}_0}. \tag{23}$$

The force exerted on the particle is then given by

$$\vec{F} = \frac{-dE_s}{d\vec{r}_0} = 4\pi\hat{k}\alpha R\delta C_k \sin kR e^{i\vec{k}\cdot\vec{r}_0}. \tag{24}$$

The force correlation function may be evaluated exactly in terms of the concentration correlation function. Using the Ornstein-Zernike result[18] the final expression is

$$\langle\vec{F}^*\cdot\vec{F}(t)\rangle = \frac{32R^2\alpha^2 Z}{3\pi}\int d^3k\,\eta_k \frac{\sin^2 kR}{k^2(k^2+\xi^{-2})^{3/2}}. \tag{25}$$

An approximate closed-form result may be obtained by ignoring the k dependence of the viscosity, and removing it from the integral, with the result (see Eq. 15)

$$\Delta\eta_{\text{eff}} \equiv \frac{\Delta\gamma}{6\pi R} = G\xi^2\alpha^2\left[\frac{1}{2} - \left(\frac{R}{\xi}\right)K_1\left(\frac{2R}{\xi}\right)\right]. \tag{26}$$

where $K_1(x)$ is the Bessel function of imaginary argument. The proportionality constant is $G = 16RZ\eta_{1/R}/9\pi k_B T$. For $R \gg \xi$, this effect goes as ξ^2, while in the critical limit where $R \ll \xi$, we obtain $\Delta\eta_{\text{eff}} = G\alpha^2R^2\ln\xi/R$. Hence, the character of the anomaly changes, but it does not approach a hard limit as $\xi \to \infty$.

One of the assumptions made above breaks down, however, in the critical limit. Namely, the use of the Ornstein-Zernike form for the concentration correlation function implied the assumption that the fluctuations at the surface of the particle are the same as in the bulk of the liquid. It is well known that the long-range fluctuations exist basically because $\partial\mu/\partial c \to 0$ at the critical point. However, if the particle has a specific surface interaction with the two components, as implied by Eq. (22), then $\partial\mu/\partial c$ approaches a limiting value given by $\alpha\sigma$, where σ is an area parameter. We would expect σ to be the square of an intermolecular distance d. In the usual Ornstein-Zernike derivation[18] the correlation length is given by $\xi^{-2} = (\partial\mu/\partial c)nZ$, where Z is the Ornstein-Zernike parameter and n is the molecular number density. Hence the correlation length ξ_s to be used in place of ξ in Eq. 26 is given by

$$\xi_s^{-2} = \xi^{-2} + \alpha\sigma nZ \equiv \xi^{-2} + \xi_m^{-2}. \tag{27}$$

If $\xi_m \ll R$ (strong interaction), the maximum value of the expression in Eq. (26) is $\Delta\eta_{\text{eff}} = (8Rd\alpha/9\pi k_B T)\eta$. For our case, using α in ergs/cm^2 this works out to about $6\alpha\eta$. The condition $\xi_m \ll R$ may be written

$$1 \ll \alpha\sigma ZnR^2 = \alpha ZR^2/d \sim 40\alpha \tag{28}$$

in the same units. It is thus obvious that for particles of the size used in our study, the strong interaction case would give a contribution to the effective viscosity at least comparable to the usual hydrodynamic viscosity anomaly (which is typically $\Delta\eta \sim \frac{1}{3}\eta$) in the critical limit.

It at first would seem that the cross correlation of the forces considered in Eqs. (12) and (24) above would also contribute. However, for a given $\vec{k}$, the force due to the surface energy is parallel to $\vec{k}$, while the force due to the stress tensor (velocity field) is perpendicular to $\vec{k}$ for an incompressible fluid. Hence the two force contributions are orthogonal and the cross term may be ignored.

Therefore, the final result is obtained by adding the two contributions calculated above for $\Delta\eta_{\text{eff}}$. In our case we shall find that neither the weak nor the strong interaction limit applies (see Sec. V), so the result of Eq. (26) cannot be simplified. Adding that to the simplified result of Eq. (21), we obtain

$$\Delta\eta_{\text{eff}} = A\eta_b \ln Q_d\xi_1 + G\alpha^2\xi_2^2[\tfrac{1}{2} - (R/\xi_2)K_1(2R/\xi_2)],$$
$$\xi_1^{-2} \equiv \xi_{\text{eff}}^{-2} + (0.94R)^{-2}, \quad \xi_2^{-2} \equiv \xi_{\text{eff}}^{-2} + B\alpha,$$
$$G \equiv 16RZ\eta_{1/R}/9\pi k_B T \sim 1.3\times10^{12}\ \text{cP cm}^2\,\text{erg}^{-2},$$
$$B = nZ\sigma \cong Z/d \sim 2\times10^{11}\ \text{erg}^{-1}. \tag{29}$$

The parameters have been estimated using the results given after Eq. (6), and an estimate of the Ornstein-Zernike parameter ($Z = 10^4$ cm/erg), derived from opalescence intensity measurements. The K dependence will be contained in the scaling hypothesis[1]

$$\xi_{\text{eff}}^{-2} = \xi^{-2} + a^2K^2. \tag{30}$$

V. DISCUSSION AND CONCLUSIONS

A preliminary effort was made to fit the data to Eq. (29) with $B = 0$ (i.e., without surface damping of the critical fluctuations). The results are shown in Fig. 3.[6] It is evident that the fit of the five solid curves to the five sets of data is a definite improvement over the results of Fig. 2. It can also be seen, however, that the dependence for low-k values close to the transition is still incorrect. This is related to the use of the Ornstein-Zernike correlation function at the surface of the particle (i.e., $B = 0$). If the damping of the fluctuations becomes significant then the effect would be to decrease the temperature dependence, and hence the low-k dependence, close to the transition. This would tend to improve the agreement with the data.

The value of the surface energy parameter obtained in the fit of Fig. 2 is 0.025 erg/cm^2 and the value of the dynamic scaling parameter found to give the best fit was $a = 1.15 \pm 0.2$. From Eq. (28) we see that we have $\xi_m \simeq R(40\alpha \simeq 1)$. Since we worked well into the region $\xi > R$, the damping effect should be quite significant, particularly for our lowest k value.

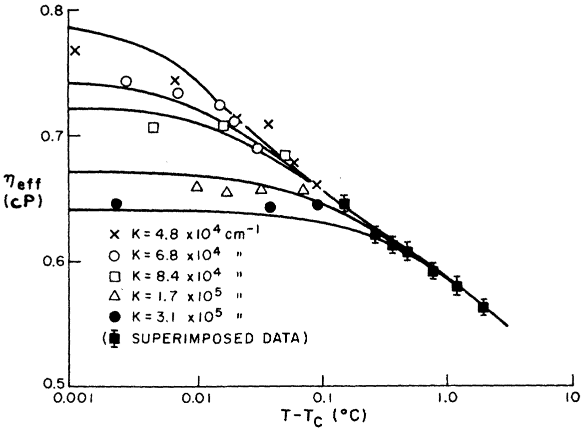

FIG. 3. Comparison of the data to the theory of the effective viscosity obtained by taking account of the nonlocality of the normal viscosity as well as the simple surface energy effect.

The full expression of Eqs. (29) and (30) was then used to fit the data. The resulting surface energy parameter was 0.0362 ± 0.0005 erg/cm^2, and the fit is shown in Fig. 4. (The accuracy of this number of course depends on the parameter Z, so its *absolute* accuracy may be trusted only to one significant figure.) Compared to typical surface energies at fluid-gas interfaces this parameter seems quite small. However, we did choose the Teflon particles with the aim of reducing any such interaction. It seems we were successful in this attempt.

The fit in Fig. 4 is again an improvement over the results shown in Fig. 3. In fact, it is now within experimental error for virtually all the points. The dynamic scaling parameter, again chosen by the least-squares technique, was found to be 1.12 ± 0.1. Moreover, the apparent paradox alluded to in the introduction may now be reconciled. Namely, the tracer diffusion results mentioned there are obviously consistent with the results of Eqs. (20) and (21), since no anomaly was observed in the diffusion coefficient of an isotopically labeled component.[3] No foreign material is introduced for such a measurement, so the surface-energy correction does not apply. Since ξ_1 in Eq. (21) is limited in this case to a molecular dimension, the absence of a critical anomaly is reasonable. The microphotography results of the Russian group,[4] on the other hand, showed an enhanced anomaly, far beyond that in the shear viscosity measured by other techniques. This can now be understood by assuming that they observed a surface-energy contribution far larger than in the Teflon-nitroethane-isooctane system used in our own investigation.

We see then that the existing data on Brownian motion in critical mixtures are amenable to a consistent interpretation in the light of the theory we have proposed. Not only the temperature dependence is explained, but also the k dependence, which was observed for the first time in the experiments described here.

All three types of experiments may be understood on the basis of two physically simple phenomena.

(i) For the "normal" viscosity effect, the zeroth approximation is to take account of critical fluctuations in calculating the shear viscosity.[1] For small particles, however, this must be modified

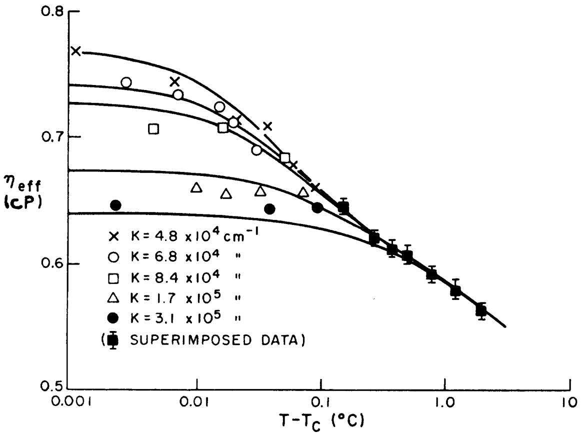

FIG. 4. As in Fig. 3, but with surface damping added to the theory of the surface-energy effect.

by the k dependence of that calculated viscosity. We found by this technique [see Eq. (20)] that the anomaly in the effective viscosity is strongly rounded in the critical region, approaching a limiting value given roughly by replacing ξ by R.

(ii) The surface interaction between the particles and the fluid molecules is a very important contribution to the friction coefficient of the particle. Using a very simple approach, and a correction based on surface damping of the Ornstein-Zernike concentration fluctuations, this contribution has also been calculated in Eq. (29), and was shown to approach a limiting value again, but this time depending on the strength of the surface-energy interaction.

The k dependence of the diffusion constant was then inserted by a simple scaling hypothesis which, for this case, must be considered an *ad hoc* assumption. The resulting theoretical expression explains the data obtained with the experimental error of 1%. The value of the scaling parameter was found to be 1.12 ± 0.1, in good agreement with theoretical expectations. The fact that the k dependence is found to obey Eq. (30) may be taken as another experimental verification of that scaling hypothesis.

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APPENDIX: EFFECT OF FINITE PARTICLE SIZE AND SIZE DISPERSION

Following the treatment of Clark, Lunacek, and Benedek[7] we consider the problem of calculating the intensity autocorrelation function for light scattered from N particles treated as point scatterers, moving independently of each other. We find that, for a specific scattering angle θ,

$$\langle I(t)I(t+\tau)\rangle = N^2|E'|^4 + |E'|^4 \sum_{mj}{}' \langle \exp[-i\vec{K}\cdot(\Delta\vec{r}_m - \Delta\vec{r}_j)]\rangle \;, \tag{A1}$$

where the primed summation indicates $m \neq j$, the displacement of the jth particle between time t and $t+\tau$ is Δr_j, and where we have assumed that all the particles are the same size so that the scattered field amplitudes are identical (i.e., $E'_j = E'$). Assuming that the particles move independently, the sum in Eq. (A1) may be written

$$N^2|\langle e^{i\vec{k}\cdot\Delta\vec{r}}\rangle|^2 \equiv N^2 g_1(\tau)^2 , \tag{A2}$$

where we dropped terms of order N. If we assume that the motion is a Gaussian process, this quantity is easily evaluated, and we find

$$\langle e^{i\vec{k}\cdot\Delta\vec{r}(\tau)}\rangle = \exp[-\tfrac{1}{2}K^2\langle\Delta\vec{r}(\tau)^2\rangle] . \tag{A3}$$

We use the Einstein-Smoluchowski relation to define the diffusion constant and the intensity autocorrelation function takes the form

$$\langle I(t)I(t+\tau)\rangle = N^2(1+e^{-2DK^2\tau}) , \tag{A4}$$

where we have not accounted for the effect of multiple-coherence areas in this expression. We see that in this case, analysis of the spectrum in terms of an exponential contribution superimposed on a constant background will yield a decay time τ_c.

Two of the assumptions made above can be relaxed without affecting the result greatly. Namely, the assumption of point scatterers and the assumption of no size dispersion can be changed.

Treating first the effect of finite particle size, we note that this will merely introduce an angular dependence of the scattered amplitude. If we are observing a small enough solid angle that the angular variation of the field over the detector is negligible, then that term is the same for all the particles and may be factored out of the sum in the expression for the scattered field. It enters only into the total cross section of the scattering, and not into the correlation properties of the light. The condition of small solid angle is always satisfied in our experiment.

The assumption of no size dispersion can be relaxed with a bit more difficulty, but the difficulties are merely algebraic, so long as the fractional width of the size distribution is small. We do not know the size distribution in our sample, so we can only hope to make a correction based on some assumed distribution, with a single parameter to represent the width, and expect that correction to be small. Taking this approach, we may define a size distribution which makes the mathematics particularly easy. We will define the distribution of inverse particle diameter to be

$$f(1/d)=d^{-6}\exp[-(1/d-1/d_0)^2w^2] \tag{A5}$$

for reasons that will become evident in the ensuing treatment.

It is clear from Eq. (A5) that the modification necessary in the quantity $g_1(\tau)$, defined in Eq. (A2) is merely to write it as

$$g_1(\tau)=N^{-2}\sum_d N_d V_d\langle\exp[-\vec{K}\cdot\Delta\vec{r}_d(\tau)]\rangle, \tag{A6}$$

where we have N_d particles of volume V_d, and d is the particle diameter. Following the procedure used to obtain Eq. (A3) we write, using the distribution function of Eq. (A5),

$$g_1(\tau)=\frac{\int f(x)x^{-6}\exp[-\frac{1}{2}K^2\langle z^2(\tau,x)\rangle]\,dx}{\int f(x)x^{-6}\,dx}, \tag{A7}$$

where the weighting factor $f(x)x^{-6}$ will be referred to as the intensity distribution function. The integral in the numerator becomes

$$\begin{aligned}\int_0^\infty dx\exp[-(x-d_0^{-1})^2w^2-K^2\tau\gamma x]&\\ =\exp[-(K^2\gamma/d_0)\tau+(K^2\gamma/2w)^2\tau^2]&\\ \times\int_0^\infty dx\exp\{-[x-(1/d_0-K^2\tau\gamma/2w^2)]^2w^2\},&\end{aligned} \tag{A8}$$

where

$$\gamma\equiv k_BT/6\pi\eta\,.$$

Now we put in the assumption that the width of the distribution is small, that is, $d_0/w\ll 1$. Since the maximum delay time τ_m involved in a typical spectrum is such that

$$K^2\gamma\tau_m/d_0\lesssim 5, \tag{A9}$$

we see that the location of the peak of the integrand in Eq. (A8), under the small-width assumption, can be written

$$(1/d_0)[1-(K^2\gamma\tau_m/d_0)(d_0/w)^2]\gtrsim(1/d_0)[1-5(d_0/w)^2]. \tag{A10}$$

This makes it obvious that the region of integration can be extended to $-\infty$ without significantly affecting the validity of the result. The remaining integral then cancels with the one in the denominator, which may similarly be extended to $-\infty$, and we obtain the final result for the spectrum

$$\begin{aligned}\langle I(t)I(t+\tau)\rangle&=N^2E'^4\{1+e^{-2K^2\gamma\tau/d_0}\\&\qquad\times\exp[2(K^2\gamma/2w)^2\tau^2]\}\\&=N^2E'^4[1+e^{-\tau/\tau_c}\exp(\tau^2/\tau_w^2)]\end{aligned} \tag{A11}$$

for $\tau\ll\tau_w$, where we define two correlation times

$$\tau_c=d_0/2K^2\gamma,\quad \tau_w=\sqrt{2}w/K^2\gamma \tag{A12}$$

and we see that the width is given by

$$d_0/w=2\sqrt{2}(\tau_c/\tau_w), \tag{A13}$$

which in our experiment was typically less than 0.1.

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[1] R. Perl and R. A. Ferrell, Phys. Rev. A 6, 2358 (1972).

[2] J. V. Sengers, Ber. Bunsenges, Phys. Chem. 76, 234 (1972).

[3] A. Stein, J. C. Allegra, and G. F. Allen, J. Chem. Phys. 55, 4265 (1971).

[4] Ya. A. Bal'tsevich, V. G. Martynets, and E. V. Matizen, Zh. Eksp. i Teor. Fiz. 51, 983 (1966) [Sov. Phys.-JETP 24, 654 (1967)].

[5] K. B. Lyons, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 30, 42 (1973).

[6] K. B. Lyons, R. C. Mockler, and W. J. O'Sullivan, Phys. Fluids 16, 2092 (1973); and K. B. Lyons, Ph.D. thesis (University of Colorado, 1973) (unpublished).

[7] N. A. Clark, J. H. Lunacek, and G. B. Benedek, Am. J. Phys. 38, 575 (1970).

[8] Yu. G. Shoroshev, M. I. Shakhparonov, and L. V. Lanshina, Vestnik. Mosk. Univ. Xim, 22, 147 (1967) [Moscow Univ. Chem. Bull. 22, 97 (1967)].

[9] M. A. Anisimov, I. M. Aref'ev, A. V. Voronel, V. P. Voronov, Yu. F. Kiyachenko, and I. L. Fabelinskii, Zh. Eksp. i Teor. Fiz. 61, 1524 (1971) [Sov. Phys.-JETP 34, 813 (1972)].

[10] M. I. Shakparonov, Yu. G. Shoroshev, S. S. Aliev, M. G. Khaliulin, and P. K. Khabibullaev, Zhur. Fiz. Khim. 43, 2543 (1969) [Russ. J. Phys. Chem. 43, 1425

(1969)].

[11] G. I. Rochlin, Rev. Sci. Instrum. 41, 73 (1970).

[12] J. Hill and A. P. Miller, Proc. IEEE 110, 453 (1963).

[13] A. Einstein, *Investigations on the Theory of the Brownian Movement*, edited by R. Furth, translated by A. D. Cowper (Methuen and Co., London, 1926).

[14] T. S. Chow and J. J. Hermans, J. Chem. Phys. 56, 3150 (1972).

[15] R. Zwanzig, J. Res. NBS 68B, 143 (1964).

[16] J. Peres, Compt. Rend. Acad. of Sci. Paris 188, 310 (1929).

[17] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, translated by J. B. Sykes and W. H. Reid (Addison-Wesley, Reading, Mass., 1959).

[18] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, translated by E. Peierls and R. F. Peierls (Addison-Wesley, Reading, Mass., 1958).

[19] This "surface tension" is *not* that at the meniscus between the two liquid phases, but rather at the surface of the particle. It is nonanomalous near T_c.