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Diffusing droplet model for Rayleigh linewidth studies on critical fluids*

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Measurements of the intensity autocorrelation of light scattered from diffusing microspheres suspended in a normal fluid show that if the particle radii satisfy the condition $l \lesssim \lambda_0$, where λ_0 is the wavelength of the incident light, and if the suspension is polydisperse (a finite-width particle-size distribution), the experimental diffusion constant displays a dependence upon the scattered wave number k which is qualitatively the same as that for a critical fluid system in the nonhydrodynamic ($k\xi \gtrsim 1$) regime. These experimental observations have led us to propose a model of a *critical* fluid in which the order-parameter fluctuations are considered as spherical molecular clusters, or droplets, performing Brownian motion in a normal host fluid. The droplets are assumed to have a Gaussian index of refraction spacial profile, and a particle-size distribution $N(l)$ characterizing the suspension determined from the requirement that the scattered light intensity be of the modified Ornstein-Zernike form. In a first approximation, the droplets are assumed to diffuse without changing size for times of the order of the characteristic diffusion time. The intensity-autocorrelation function of light scattered by our model system of diffusing droplets is evaluated, and the effective Rayleigh linewidth is found to agree to within a constant factor of order 1 with the *ansatz* for the critical part of the Rayleigh linewidth chosen by Perl and Ferrell. The resulting line-shape function is nearly Lorentzian, except in the wings where experimental detection of a departure from Lorentzian behavior becomes extremely difficult. Our droplet-size distribution is very similar to that which results from the static droplet model of Fisher which has been applied successfully to describe static critical phenomena in fluids below the critical temperature. In the diffusing droplet model, the k dependence of the diffusion constant extracted from light-scattering measurements on critical fluids is seen to be an artifact introduced by the light-scattering process, and introduces no new physical information concerning the critical fluid behavior which is not contained in the droplet-size distribution function.

I. INTRODUCTION

The Rayleigh linewidth Γ of light scattered quasielastically from order-parameter fluctuations is the essential experimental parameter used to test the mode-mode[1-3] and decoupled-mode[4,5] theoretical descriptions of the dynamical behavior of critical fluids. The behavior of Γ for a specific fluid as a function of temperature for $T > T_c$ may be described simply. For finite wave number k, and for $T - T_c$ large enough that the *hydrodynamic* condition $k\xi \ll 1$ is satisfied, plots of Γ/k^2 as a function of $T - T_c$ all fall on the same straight line, for all scattering angles. [k is specified by the relation $k = (4\pi n/\lambda_0)\sin(\theta/2)$, where λ_0 is the light wavelength *in vacuo*, n is the index of refraction in the sample, and θ is the scattering angle; ξ is the Ornstein-Zernike correlation length.[6]] Thus the effective diffusion constant $D = \Gamma/k^2$ is independent of k in the hydrodynamic regime. As $T - T_c$ is reduced and $k\xi \gtrsim 1$, the *nonhydrodynamic*, or critical, regime is entered where conditions of local thermodynamic equilibrium no longer apply. In this regime, the experimental diffusion constant becomes a function of the wave number k, showing an *increase* with increasing scattering angle.

The mode-mode coupling theory of Kawasaki[1] and Kadanoff and Swift[2] and the decoupled-mode theory of Ferrell,[4] provide descriptions of the *critical*[7] part of the Rayleigh linewidth Γ^c which is valid for general values of $k\xi$. Although the two theoretical methods predict slightly different behavior for Γ^c for large values of $k\xi$, the essential form of the result is as given by Kawasaki,

$$\Gamma^c = (k_B T/6\pi\eta\xi^3)F(k, \xi), \tag{1}$$

where η is the macroscopic shear viscosity, T is the absolute temperature, and $F(k, \xi)$ is a function which describes the modification of Γ^c due to the nonlinear response of the fluid in the regime $k\xi \gtrsim 1$. In the limit as $k\xi \ll 1$, both the Kawasaki and Ferrell theories predict that the critical part of the diffusion constant becomes

$$D = k_B T/6\pi\eta\xi. \tag{2}$$

This is an extremely suggestive result, since it represents the Einstein-Stokes diffusion constant for microspheres of effective size ξ, diffusing through a host fluid characterized by a shear viscosity η. This correspondence between fluid order-parameter fluctuations *in the hydrodynamic regime* and a system of diffusing microspheres has been previously recognized.[8-10] In particular, it has been suggested[10] that the details of the structure of the diffusing units become important near the critical point, where the effective size of the fluctuations becomes larger than k^{-1}, and that the scaling function $F(k, \xi)$ might take this structure dependence into account. In other words, Eq. (1) represents a modified Einstein-Stokes equation which retains validity into the critical regime.

The purpose of this paper is twofold. In Sec. II we provide experimental evidence that the analogy implied in Eq. (2) between microspheres diffusing in a normal host fluid and order-parameter fluctuations of size ξ diffusing in a critical fluid under conditions such that $k\xi \ll 1$ can be extended into the critical regime. In particular, we show that if microspheres are selected whose sizes compare to ξ in a critical fluid near T_c, and if a polydisperse (finite-width size distribution) rather than a monodisperse (single-particle size) suspension in a normal fluid is studied, then the diffusion coefficient inferred from the intensity autocorrelation of visible light scattered by the microspheres shows a wave-number dependence which is qualitatively the same as that for a critical fluid in the nonhydrodynamic regime.

In Sec. III we discuss a very simple model of a critical fluid in which the order-parameter fluctuations are considered as a *particular* size distribution of diffuse microspheres with a time-independent structure, performing Brownian motion in a host fluid characterized by a *normal* background shear viscosity. This model is applied to the calculation of Γ^c for a critical fluid system. Section IV consists of a summary of conclusions, and discussion of the relation of this model to static droplet models of critical behavior in fluids.

II. INTENSITY-AUTOCORRELATION STUDIES ON POLYDISPERSE MICROSPHERE SUSPENSIONS

The intensity autocorrelation of light scattered at a particular scattering angle by a dilute monodisperse suspension of microspheres is[11, 12]

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

where N is the number of coherence areas incident on the detector, D is the particle diffusion constant, and k is the scattered wave number. If the constant background term can be successfully subtracted from the total signal, a decay rate $\Gamma = 2Dk^2$ will be determined. Thus, a wave-number-independent diffusion constant given by $D = \Gamma/2k^2$ results for a dilute *monodisperse* system of diffusing microspheres even if the microsphere size is not small compared to λ_0. This result is similar to that found for critical fluids in the hydrodynamic regime. However, in a critical fluid when the condition $k\xi \ll 1$ no longer is satisfied, Γ/k^2 increases with increasing k. In this section we show under what conditions the analogy between a system of diffusing microspheres and a critical fluid can be extended into the nonhydrodynamic regime. These observations on systems of diffusing microspheres will lead us to propose a diffusing droplet model for critical fluids.

There are two key factors involved in the extension of the correspondence suggested by Eq. (2) into the critical regime. The first is the effective particle *size*. The characteristic size of fluctuations in a critical fluid scales with temperature as $\xi = \xi_0\epsilon^{-\nu}$, where the critical exponent $\nu \simeq \frac{2}{3}$, $\epsilon \equiv (T - T_c)/T_c$, and where $\xi_0 \cong 3$ Å in a typical fluid or fluid mixture. For the case of visible light scattering which we are considering, if we are to attach a particle significance to the order-parameter fluctuations, then the effective particle size will not be negligible compared to λ_0 for small values of ϵ. As a result, the scattering process must be treated in terms of the general electromagnetic theory of scattering from dielectric particles, which we will refer to as Mie scattering.[13] The second key factor is *polydispersity*. Although ξ in some sense defines a characteristic cluster size for a critical fluid, since a fluid is a many-body system, statistical considerations dictate that there be a distribution of cluster sizes. Thus, in continuing the microsphere–critical-fluid analogy, the critical fluid must be considered to be a *polydisperse* suspension of effective Brownian particles.

To provide experimental evidence in support of the importance of these two factors in the continuation of the analogy into the critical regime, we measured the intensity-autocorrelation function of light scattered from two systems of polydisperse suspensions of microspheres of varying relative concentrations.

System I was made up of microspheres 0.109 μm and 0.234 μm in diameter; system II was made up of microspheres 0.234 and 0.500 μm in diameter. The microspheres were obtained from monodisperse samples of Dow polystyrene latex spheres. Their index of refraction is 1.59. They were suspended in distilled water which had been filtered with a 0.05-μm millipore filter. Three monodisperse suspensions were made, one for each microsphere size, each at a concentration of 1:10^5 by weight. The polydisperse systems were made by mixing various proportions of the monodisperse samples.

In the light-scattering experiment, the light source was an argon-ion laser operating at a wavelength of 5145 Å. The incident light power never exceeded 10 mW, and no effects due to small variations of the intensity about this figure were observed. The light was focused by a lens

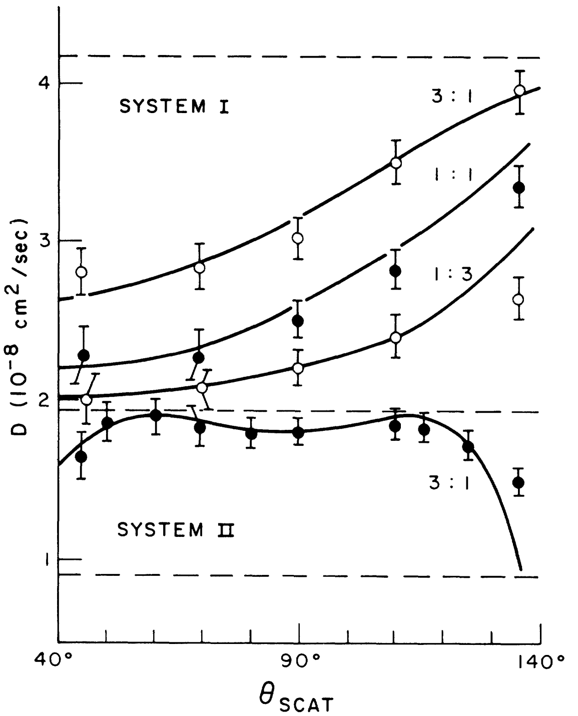

FIG. 1. Plot of the diffusion constant D as a function of scattering angle θ_{scat}. The theoretical lines are calculated from Eq. (6). Each set of data and theory is labeled with the concentration by weight of the smaller microsphere relative to the larger. The dashed lines represent the diffusion constants for monodisperse systems for sizes 0.109, 0.234, and 0.500 μm, for the top, middle, and bottom, respectively.

into the scattering cell, which consisted of a test tube 18 mm in diameter with a bubble blown in it of approximately 200° of arc horizontally around the circumference of the tube. This bubble eliminated the reflected image of the beam and backscattered light from the walls of the tube, thus eliminating spurious scattered light. Measurements on monodisperse samples using this system showed no k dependence in the diffusion constant to better than 1%. The cell temperature was measured before and after each experimental run, with a run taking about 15 min. The temperature was constant to within ±0.1 °C during a run. The scattered light was collected by a small aperture and pinhole. The pinhole diffracts one coherence area onto the cathode of an ITT FW 130 photomultiplier tube. The pulses from the photomultiplier tube were passed to an autocorrelator[12] which produced the intensity-intensity autocorrelation function of the scattered light. The autocorrelation functions for each run were analyzed by a least-squares fitting routine with an on-line computer to determine the diffusion constant. The experimental results, along with our theoretical curves, are given in Fig. 1, where the measured diffusion constant is plotted versus the scattering angle. The major sources of error were in defining the scattering angle and in the measurement of the diffusion constant by autocorrelation methods. A k-dependent diffusion constant is observed in both systems.

To understand the origin of the k dependence, one must examine the Mie scattering function for a dielectric sphere. The key to this understanding is to plot the relative light-scattering intensity against the particle size, using the scattering angle as the curve parameter as in Fig. 2. The Mie functions were obtained from standard tables.[14] In this way, it is easy to see how the relative light-scattering intensities for different sized particles change with scattering angle. For example, the ratio of the relative light-scattering intensity of a 0.20-μm particle to a 0.15-μm particle is 4.8:1 at a scattering angle of 45°, whereas at 135° this ratio is only 1.6:1. Thus for a system consisting of an equal number concentration of each size, one would expect the larger balls to dominate the spectrum at small scattering angles, but as we go to larger angles the smaller balls would begin to contribute more and more to the spectrum. The measured diffusion constant is some average, dependent on the relative Mie scattering intensities.

To derive the theoretical curves, we put these ideas into a more precise mathematical form. The field correlation function of the scattered light from a system of Brownian diffusing particles

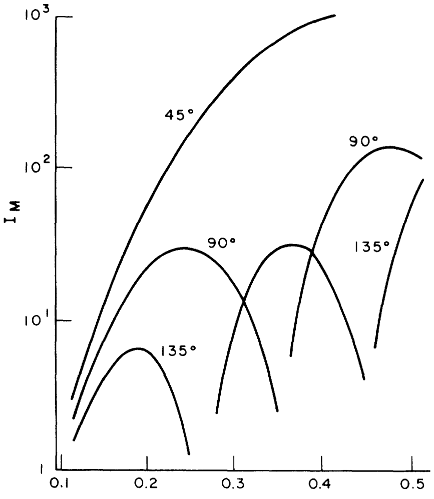

FIG. 2. Plot of the relative Mie scattering intensity I_m as a function of particle diameter in micrometers and parametrized by the scattering angle, for microspheres with a relative index of refraction of $m = 1.59/1.33 \simeq 1.20$, and for $\lambda_0 = 0.5145$ μm.

radius r and diffusion constant $D(r)$ is

$$\langle E^*E(t)\rangle = I_m(r)e^{-D(r)k^2t}. \tag{4}$$

We write the intensity of the scattered light from particles of radius r as the Mie scattering intensity, $I_m(r)$, times the probability density $N(r)$ for that particle size, $I(r)=N(r)I_m(r)$. The average field correlation function is then given by

$$\langle\langle E^*E(t)\rangle\rangle = \int dr\, N(r)I_m(r)e^{-D(r)k^2t}. \tag{5}$$

Here the second set of angular brackets indicates an average over r. We make the usual assumption of Gaussian scattering statistics[15] and find the intensity-intensity autocorrelation function of the scattered light to be

$$\langle\langle II(t)\rangle\rangle = \langle\langle |E|^2\rangle\rangle^2 + A\langle\langle E^*E(t)\rangle\rangle^2, \tag{6}$$

where A is a constant independent of the radius.

To compare theory and experiment, we use Eq. (6) to generate an average correlation function for the different experimental values of concentration and microsphere size. Because Eq. (6) predicts a nonexponential correlation function, we account for both the first and second cumulants in the experimental data and the simulated data from Eq. (6) by fitting to the form $\exp(-at+bt^2)$ using a least-squares routine. The details of this fitting scheme are given elsewhere.[16] This form fits the data and Eq. (6) quite well, and we find that both the experimental and theoretical autocorrelation functions are nearly exponential. That is, the ratio b/a^2 is $\lesssim 0.04$.

The agreement between experiment and theory is good for all the suspensions studied. In particular, the k dependence of D for system I, which consists of microspheres whose diameters are slightly smaller than λ_0, is qualitatively similar to the behavior shown by the diffusion constant for critical fluids in the nonhydrodynamic regime. That is, D increases with increasing k (increasing scattering angle). The k dependence for system II is more complicated due to interference effects from the larger (0.5 μm) microspheres (see Fig. 2). While this is consistent with theory, such effects are not observed in critical fluids. However, these strong interference effects can be shown to be markedly reduced for a microsphere whose index of refraction does not change discontinuously at its boundary.

We conclude that a polydisperse suspension of dielectric microspheres of size comparable to the incident light wavelength will produce a k-dependent diffusion constant when investigated by light-scattering techniques. This diffusion constant increases with increasing wave number just as does the diffusion constant for a critical fluid when $k\xi \gtrsim 1$.

We describe the origin of this wave-number dependence and its relation to particle size and polydispersity in the following way. When the particle radius l *does not* satisfy the condition $l \ll \lambda_0$, the scattered-light intensity becomes a very sensitive function of l (see Fig. 2). When light is scattered from a polydisperse suspension of particles, the diffusion constant inferred from the intensity autocorrelation of the light scattered by the particles represents an average over the diffusion rates of all the particles weighted by the particle-size-dependent light intensity, and the particle-size distribution. For small scattering angles (small k) the larger particles in the dispersion provide the dominant contribution to the scattered light. Since the diffusion constant for a specific particle size varies inversely with the particle diameter through the Einstein-Stokes relation, the D extracted for small k is small. As the scattering angle is increased, inspection of Fig. 2 confirms that the relative contribution of the *smaller* particles to the scattered intensity increases, leading to an average D which increases as k increases.

III. DYNAMIC DROPLET-MODEL INTERPRETATION OF LIGHT-SCATTERING EXPERIMENTS ON CRITICAL FLUIDS

In analogy with the polydisperse microsphere systems discussed in the previous section, we proposed[17] a new model to explain the k-dependent Rayleigh diffusion coefficient of a critical fluid. We assume that the order-parameter fluctuations in a critical fluid may be considered as a *polydisperse* suspension of molecular clusters diffusing like Brownian particles in a host fluid characterized by a normal background viscosity. These clusters are assumed to have a spherically symmetric Gaussian density distribution in a single-component fluid (a spherically symmetric Gaussian concentration distribution in a binary mixture). The Lorentz-Lorenz relation coupled with the assumption of a Gaussian cluster profile insures that the index of refraction will also correspond to a Gaussian distribution of the form

$$m^2(r,l) - 1 \simeq 2[m(r,l)-1] = A\exp(-r^2/l^2), \tag{7}$$

where $m(r,l)$ is the *relative* index of refraction of a cluster of size l, A is an amplitude factor which is taken to be the same for all cluster sizes, and r is the distance measured from the center of the cluster. The cluster size distribution we determine is

$$N(l) = B\exp(-l^2/2\xi^2)/l^{5+\eta} \tag{8}$$

where B is an approximately temperature-independent factor related to the density of the fluid, ξ will be identified with the Ornstein-Zernike correlation length, and η is a variable exponent which will be identified with the critical exponent introduced by Fisher.[18] The determination of our specific cluster size distribution was dictated by the requirement that the calculated expression for the scattered-light intensity agree with the Fisher-modified[18] Ornstein-Zernike form for light scattered from a critical fluid, $I(k) \sim (k^2 + \xi^{-2})^{-1+\eta/2}$. It is of interest that our resultant distribution function is very similar to that used in the *static droplet model* description of critical phenomena.[19,20]

We use the Rayleigh-Debye theory[13] to calculate an analytic expression for the scattered intensity. For the index-of-refraction profile assumed in Eq. (7), the cluster size distribution corresponding to Eq. (8), and assuming single scattering from clusters, the total scattered intensity at a specific scattering angle, for an incident intensity of unity is[17]

$$\begin{aligned} I(k) &= \int N(l) I(l, k)\, dl \\ &= (A^2 B k_0^4 \pi / 32R^2)(k^2 + \xi^{-2})^{-1+\eta/2}\, \Gamma(2 - \eta) D_{-2+\eta}(0). \end{aligned} \tag{9}$$

Here, $k_0 = 2\pi n/\lambda_0$, R is the distance from the scattering volume to the point of observation, Γ is the gamma function, and $D_{-2+\eta}$ is the parabolic cylinder function of order $2 - \eta$. For small η, Eq. (9) becomes

$$I(k) = \frac{A^2 B k_0^4 \pi}{32R^2 (k^2 + \xi^{-2})^{1-\eta/2}}, \tag{10}$$

which is the Fisher-Ornstein-Zernike result for the light intensity scattered from a critical fluid.

To this point we have shown that a model in which the order-parameter fluctuations in a critical fluid are considered as a polydisperse suspension of spherical clusters, each with a Gaussian index-of-refraction profile, and in which the degree of polydispersity is represented by Eq. (8), can reproduce the experimentally verified form for the scattered-light intensity. In this process we have identified the parameters ξ and η in Eq. (8), with the Ornstein-Zernike correlation length and the Fisher critical exponent η, respectively. We find that our size distribution function is very similar to that arising from the static droplet model,[19,20] as applied to critical fluids for $T < T_c$. In fact, by simply multiplying our form for $m^2(r, l)$ by $l^{1.6-\eta}$, a $N(l)$ would result which is in agreement with that for the static droplet model on the coexistence curve. This modification would amount to weighting the amplitude of the relative index of refraction for the larger droplets more heavily.

The extension of our model to cover the dynamic aspects of light scattering from critical fluids is direct. We assume, that in *first approximation* the order-parameter droplets act as physically hard spheres of radius l, and that they execute Brownian motion without growing or decaying appreciably for times of the order of the measured diffusion time.[21] The normalized field autocorrelation function for light scattered from a *monodisperse* system of hard spheres is given in Eq. (4), and is easily generalized to include a size distribution as shown in Eqs. (5) and (6). The correlation function which is weighted by $N(l)$ will in general not be an exponential, but for a dilute polydisperse suspension of noninteracting clusters it will be very nearly exponential. A reasonably good value for the diffusion rate can be determined by looking at the slope of the correlation function near $t = 0$, that is,

$$\left(-\frac{d}{dt} \frac{\langle\langle E(0) E^*(t) \rangle\rangle}{\langle\langle E(0) E^*(0) \rangle\rangle} \right)_{\lim t \to 0} = \bar{D} k^2 = \bar{\Gamma}, \tag{11}$$

where $\bar{\Gamma}$ is the effective Rayleigh linewidth. We find[17]

$$\bar{D} k^2 = \frac{\int_0^\infty dl\, N(l) I(k, l) k^2 k_B T / 6\pi\eta_b l}{\int_0^\infty dl\, N(l) I(k, l)}, \tag{12}$$

where $I(k, l)$ is the Rayleigh-Debye scattered intensity for spheres of size l and for a specific k. Equation (12) yields

$$\bar{D} k^2 = \frac{k_B T}{6\pi\eta_b} k^2 (k + \xi^{-2})^{1/2} \frac{\Gamma(1 - \eta)}{\Gamma(2 - \eta)} \frac{D_{-1+\eta}(0)}{D_{-2+\eta}(0)}. \tag{13}$$

When this expression is evaluated near $\eta = 0$, the effective diffusion rate reduces to

$$\begin{aligned} \bar{D} k^2 = \bar{\Gamma} &= \left(\frac{\pi}{2} \right)^{1/2} \frac{k_B T}{6\pi\eta_b \xi} k^2 (1 + k^2 \xi^2)^{1/2} \\ &= \left(\frac{\pi}{2} \right)^{1/2} k^2 D(k, \xi). \end{aligned} \tag{14}$$

In deriving Eq. (14) we assumed that the experimentally determined decay time of the scattered-light correlation function is a fit to the $t \to 0$ part of the spectrum. We have performed computer calculations on the resulting field autocorrelation function for $\eta = 0$ by evaluating the slope at the $1/e$ point and have found

$$\bar{\Gamma}_{1/e} = \bar{D}_{1/e} k^2 = (0.88)\, D(k, \xi)\, k^2. \tag{15}$$

In addition, for $\eta \to 0$, one can Fourier-transform the time variable in the field correlation function. The resulting line shape can be determined exactly as

$$S(\omega) = \frac{D(k,\xi)k^2}{\omega^2}\left[\frac{1}{\sqrt{\pi}} - \frac{D(k,\xi)k^2}{\omega} \exp\left(\frac{D^2(k,\xi)k^4}{\omega^2}\right) \times \operatorname{erfc}\left(\frac{D(k,\xi)k^2}{\omega}\right)\right], \qquad (16)$$

where erfc is the complementary error function. This line-shape function can be fitted by a Lorentzian except in the wings, where it decays more slowly, and where detection of such a departure would tend to be obscured by shot noise corrections and the requirement for a background signal subtraction to determine the *critical* part of the signal. The half-width of this line-shape function is found to be $\Gamma_{1/2} = (0.96)D(k,\xi)k^2$. Thus, in general, the measured diffusion rate seems to be given by

$$\bar{\Gamma} = \bar{D}k^2 = \gamma D(k,\xi)k^2, \qquad (17)$$

where γ is a number of order unity, the value of which depends upon the method of analysis used.

Our primary result, Eq. (14) is of some interest. In particular, it differs only by a numerical factor of order 1 from the *ansatz* for the critical part of the Rayleigh linewidth chosen by Perl and Ferrell[5] as a starting point for their theory of critical viscosity,

$$\Gamma = Dk^2 = (k_BT/16\eta_s\xi)k^2(1+k^2\xi^2)^{1/2}, \qquad (18)$$

where η_s was treated as an adjustable parameter. Equation (18) provided a good fit to the experimental linewidth data for a specific critical binary mixture[22] (3-methylpentane-nitroethane). In addition this expression has been used by Swinney and Henry[7] to fit linewidth data for a series of critical fluids and binary mixtures.

To compare our results with experiment, we convert the experimental linewidth data to a scaled linewidth with the equation

$$\Gamma_D^* = (6\pi\eta_b/k_BTk^3)\Gamma. \qquad (19)$$

This form is the same as that used by Swinney and Henry[7] except we use the background viscosity η_b instead of the critical viscosity η_s because our results indicate the background viscosity is the relevant parameter.

We are left with the single parameter γ which we consider adjustable in the process of fitting our theoretical result, Eq. (17), to experiment. An example of the agreement between our result and the raw Rayleigh linewidth data of Thiel *et al.*[23] for the binary fluid system carbon tetrachloride-perfluormethylcyclohexane is included in the lower half of Fig. 3. The results of measurements of the viscosity of this system performed by the above authors[23] was used to extract the background viscosity required to relate Γ_D^* to Γ through Eq. (19). Here we find the best fit of Eq. (17) to their data for $\gamma = 1.16$ The fit is better than that provided by the mode-mode theory shown in the upper half of Fig. 3.

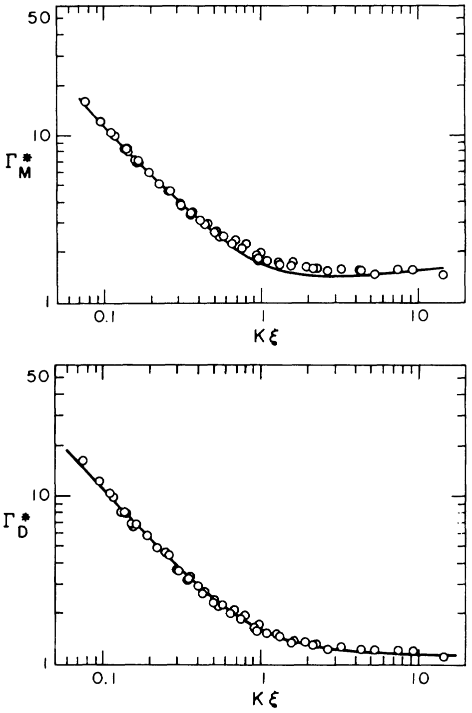

FIG. 3. Top: Comparison between the scaled linewidth, $\Gamma_M^* = 6\pi\Gamma\eta_s/k_BTk^3$, extracted from the Rayleigh linewidth data of Thiel *et al.* (Ref. 23) on carbon tetrachloride-perfluormethylcyclohexane and the mode-mode theory prediction. Bottom: Comparison of $\Gamma_D^* = 6\pi\Gamma\eta_b/k_BTk^3$ for the same system and the prediction of the diffusing droplet model, Eq. (17), for $\gamma = 1.16$.

At the present stage of development of our model, the physical significance of the parameter γ remains unclear. If $\gamma \equiv \eta_b/\eta_s$, our Eq. (17) could be reformulated into the form of Eq. (18). However, our model, with the static-droplet-size assumption, should be considered as a first approximation to a more realistic picture of fluid critical behavior. In its present form the model predicts a nonexponential autocorrelation function, with a departure from exponentiality large enough to enable it to be detected in a careful measurement. As a result, the value of γ depends upon the manner in which a decay time is extracted from the scattered field autocorrelation function. A preliminary attempt to relax the static-size-droplet restriction led to results which suggest that much of the deviation from exponentiality of the autocorrelation function may be an artifact following from the static assumption. Thus, until a more realistic treatment of droplet growth and decay is included in the model, and the question of the form of the line-shape function is settled, we will treat γ as a fitting parameter whose value should be constrained within a narrow range about unity.

IV. SUMMARY AND CONCLUSIONS

We have shown that polydisperse suspensions of dielectric microspheres in a *normal fluid* yield a k-dependent diffusion constant when studied by visible-light scattering techniques. If the spheres are of a typical size, $l \lesssim \lambda_0$, where λ_0 is the free-space wavelength of the incident light, the resultant k dependence of D is qualitatively similar to that observed in *critical* fluids. This observation led us to propose a very simple model of a critical fluid in which the order-parameter fluctuations are considered as independently[24] diffusing microspheres forming a polydisperse suspension in a *normal host fluid*. This model leads to an essential justification of the *ansatz* of Perl and Ferrell[5] for the critical part of the Rayleigh linewidth associated with light scattered quasielastically by the fluid. In its first-approximation form, the model assumes that the *effective microspheres* diffuse without changing size[21] or shape in a time corresponding to the characteristic diffusion time. A Gaussian index-of-refraction profile is assumed for the droplets, and this, along with the requirement that the scattered intensity be of the form given by Eq. (10), leads to a particular cluster-size distribution function. This function is essentially like that resulting from the static-droplet model of Fisher,[19,20] with the exception that our $N(l)$ varies as $l^{-(5+\eta)}$, while the Fisher distribution function, which is consistent with scaling requirements, varies as $l^{-6.6}$. The comparison between our size distribution and Fisher's could be made exact by adjusting the form for the index-of-refraction profile,[25] but there exists no physical justification for such an adjustment. It should be noted that essentially, any finite-width distribution of particle sizes will lead to a diffusion constant which shows a k dependence similar to that for a critical fluid in the nonhydrodynamic regime. Even a rectangular size distribution produces, qualitatively, the correct dependence upon k. The requirement placed on the behavior of the scattered intensity and the assumption of a Gaussian index-of-refraction distribution limits $N(l)$ to the form in Eq. (8).

It is of interest to compare the significance of the wave-number dependence of the Rayleigh linewidth as interpreted by the mode-mode theory, for example, and by the cluster model developed in this paper. From the mode-mode point of view, the divergent behavior of the response function of the fluid as the critical point is approached leads to a nonlinear coupling of the macroscopic normal-mode solutions of the linear hydrodynamic equations. The onset of wave-number dependence in the diffusion constant reflects, and in a sense is a probe of the nonlinearity of the fluid response to order-parameter fluctuations. In the cluster model, all of the physics which specifically pertains to the critical behavior of the fluid is contained in the cluster-size distribution $N(l)$. The clusters move through a normal host fluid, characterized by a background viscosity η_b. The onset of k-dependent diffusion behavior reflects the growth in average size of the clusters and the resulting sensitivity of the scattered-light intensity to particle size. In the cluster model, the k dependence of the effective diffusion constant is an artifact reflecting the prejudicial averaging with respect to particle size of the light-scattering process, and it provides no information about the fluid dynamical behavior that is not contained in $N(l)$.

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[1] K. Kawasaki, Phys. Rev. 150, 291 (1966); Ann. Phys. (N. Y.) 61, 1 (1970); Phys. Rev. A 1, 1750 (1970).

[2] L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968).

[3] S. M. Lo and K. Kawasaki, Phys. Rev. A 5, 421 (1972); A 8, 2176 (1973); and K. Kawasaki and S. M. Lo, Phys. Rev. Lett. 29, 48 (1972).

[4] R. A. Ferrell, Phys. Rev. Lett. 24, 1169 (1970).

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

[6] L. S. Ornstein and F. Zernike, Proc. Sect. Sci. K. Med. Akad. Wet. 17, 793 (1914).

[7] H. L. Swinney and D. L. Henry, Phys. Rev. A 8, 2586 (1973).

[8] B. Chu, S. P. Lee, and W. Tscharnuter, Phys. Rev. A 7, 353 (1973).

[9] G. Arcovito, G. Faloci, M. Roberti, and L. Mistura, Phys. Rev. Lett. 22, 1040 (1969).

[10] G. B. Benedek, J. B. Lastovka, M. Giglio, and D. Cannell, in *Critical Phenomena*, edited by R. E. Mills, E. Aschner, and R.I. Jaffery (McGraw-Hill, New York, 1971).

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

[12] K. B. Lyons, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. A 10, 393 (1974).

[13] M. Kerker, *The Scattering of Light* (Academic, New York, 1969).

[14] H. H. Renham, W. Heller, and W. J. Pangonis, *Angular Scattering Functions for Spheres* (Wayne State Univ. Press, Detroit, 1966).

[15] H. Z. Cummins and H. L. Swinney, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1970), Vol. VIII.

[16] K. B. Lyons, Ph. D. thesis (University of Colorado, 1973) (unpublished).

[17] B. J. Ackerson, C. M. Sorensen, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 34, 1371 (1975).

[18] M. E. Fisher, J. Math. Phys. 5, 944 (1964).

[19] M. E. Fisher, Physics (N. Y.) 3, 255 (1967).

[20] C. S. Kiang, and D. Stauffer, Z. Phys. 235, 130 (1970). From this article it can be inferred that the Fisher droplet-size distribution is identical to ours with the major exception that it varies as $\sim l^{-6.6}$, rather than as $l^{-(5+\eta)}$.

[21] If we associate the rate of change of droplet size with the *background* contribution to the Rayleigh linewidth, in the worst case, that of a pure-fluid system, the effective background diffusion constant in the critical regime is smaller by a factor of 10 than the diffusion constant we associate with the Brownian motion of the droplets. This difference becomes much larger in the case of a binary mixture, where the background term is still smaller.

[22] R. F. Chang, P. H. Keyes, J. V. Sengers, and C. O. Alley, Phys. Rev. Lett. 27, 1706 (1971).

[23] D. Thiel, B. Chu, A. Stein, and G. Allen, J. Chem. Phys. 62, 3689 (1975).

[24] To be valid, the assumption of independently diffusing droplets requires that in the critical limit the large droplets, which contribute most to the scattered intensity, remain spacially separated. The volume occupied by droplets with a radius greater than u is given approximately by $n_u = \int_u^\infty l^3 N(l)\,dl$. In the critical limit as $\xi \to \infty$, and for $\eta \to 0$, $n_u = B/u$, while the total volume occupied by droplets of all sizes is $n_T = B/u_{\min}$, where $u_{\min}$ is the cutoff radius chosen to be of atomic size. Then, $n_u/n_T = u_{\min}/u$. If we take $u_{\min} \sim 1$ Å and $u = 100$ Å, then $n_u/n_T \sim 0.01$, and the concentration of larger sized droplets is 1% by volume. This represents an extreme limiting case, and in general we conclude that as long as long-range forces are not involved, the *independent* droplet model is valid into the critical regime.

[25] Rather, it can be shown, by using simple diffusion theory and the Lorentz-Lorenz relation, that if the density fluctuations grow and decay by molecular diffusion, the index-of-refraction profile associated with a molecular cluster will be Gaussian. However, the growth and decay of such clusters near T_c is not simply governed by molecular diffusion, and we cannot generalize the above observation.