

Dynamic-Droplet-Model Interpretation of Light-Scattering Experiments on Critical Fluids*

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Near the critical point of a fluid or fluid mixture, we postulate the existence of a size distribution of diffuse droplets or clusters of molecules. This distribution is combined with the Rayleigh-Debye scattering approximation and the theory of Brownian motion to describe the observed behavior of the intensity and the autocorrelation of light scattered by critical fluids.

Results of recent intensity autocorrelation experiments¹ for light scattering from a system of diffusing Brownian particles characterized by a finite-width size distribution (polydisperse system) indicate that a marked similarity exists between the k dependence of the observed diffusion rates of these systems and the diffusion rates of fluids near critical points. Here $k = (4\pi n/\lambda) \sin \frac{1}{2}\theta$, where n is the index of refraction of the medium, λ is the wavelength of the incident light, and θ is the scattering angle. This k dependence results from the strong sensitivity of the Mie scattering intensity² to particle size, when the scattering particles are comparable to, or smaller than, the wavelength of the light. As the scattered-light wave number is reduced, the larger particles scatter a greater portion of the light compared to the smaller particles. The diffusion constant, inferred from the intensity autocorrelation of the scattered light, represents an average over the diffusion rates of all the particles in the system weighted by the particle-size-dependent scattered-light intensity. The diffusion constant associated with a microsphere of radius l is given by the Stokes-Einstein relation $D = k_B T / 6\pi\eta l$, where k_B is Boltzmann's constant, T is the absolute temperature, and η is the shear viscosity of the medium. In an autocorrelation experiment on a polydisperse system, the dominant contribution of the larger particles at small k is reduced as the scattering angle is increased, and one would expect to measure an average diffusion rate which increases with increasing k .

Such a k dependence is indeed observed in a suitable polydisperse system of Brownian particles, and also in a fluid near its critical point. Specifically, a good experimental fit to the data for fluids in the critical region is given by the following diffusion rate D_f , or linewidth Γ_f ,^{3,4}

$$\Gamma_f = D_f k^2 = (k_B T / 16\bar{\eta}_s \xi) k^2 (1 + k^2 \xi^2)^{1/2}, \quad (1)$$

where ξ is the Ornstein-Zernike correlation length and $\bar{\eta}_s$ is a parameter determined by a best fit to the data.

In analogy with polydisperse systems we propose a new model to explain this k dependence of the Rayleigh linewidth near the critical point. We assume that the critical order-parameter fluctuations may be thought of as clusters of molecules diffusing like Brownian particles in a host fluid characterized by a *normal background viscosity*. These clusters are assumed to have a spherically symmetric density distribution which we take as Gaussian. By the Lorentz-Lorenz relation this implies that the index of refraction will also correspond to a Gaussian distribution. Finally we assume that the clusters are polydisperse in size because of the statistical nature of the fluid. This last assumption, along with the Mie theory, provides the k dependence. While the exact nature of the size distribution will affect the quantitative results of our model, it is important to realize that any reasonable size distribution will produce a qualitatively correct k dependence.

The particle-size distribution we use is given by

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

where B is an approximately temperature-independent factor related to the density of the fluid, ξ is a parameter which will be seen to be identical to the Ornstein-Zernike correlation length, and η is a variable exponent to be identified later and not to be confused with the symbol for shear viscosity. The general form of this distribution is similar to that used for static droplet models of critical phenomena.^{5,6}

For the Gaussian index-of-refraction distri-

bution of the diffuse spherical clusters we take

$$m^2(r, l) - 1 \cong 2[m(r, l) - 1] = A \exp(-r^2/l^2), \quad (3)$$

where $m(r, l)$ is the relative index of refraction of the cluster to the average background index of refraction, A is a measure of the deviation of the index of refraction and is the same for all cluster sizes, and r is the distance from the center of the cluster.

To calculate the scattered intensity, the Rayleigh-Debye theory² is employed because it has a simple analytic form and is a good approximation of the exact Mie theory for the range of cluster sizes and index of refraction differences expected in critical phenomena. Thus the light scattered at a given wave vector k by a single cluster with

index of refraction profile $m(r, l)$ is given by

$$I(l, k) = (k_0^4/32\pi^2 R^2) \left| \int d^3r [m^2(r, l) - 1] e^{ikr} \right|^2 \quad (4)$$

for incident light polarized perpendicular to the plane of incidence, where the incident intensity is unity, and R is the distance from the scatterer to the point of observation. Here $k_0 = 2\pi/\lambda$. For our choice of $m(r, l)$, Eq. (3), the scattered intensity from a cluster of size l becomes

$$I(l, k) = (A^2 k_0^4 l^6 \pi / 32 R^2) \exp(-k^2 l^2 / 2). \quad (5)$$

Assuming single scattering from clusters, the total light intensity scattered by our dispersion is found by using Eqs. (2) and (5) to be

$$I(k) = \int N(l) I(l, k) dl = (A^2 B k_0^4 \pi / 32 R^2) (k^2 + \xi^{-2})^{-1+\eta/2} \Gamma(2-\eta) D_{-2+\eta}(0), \quad (6)$$

where Γ is the gamma function and $D_{-2+\eta}$ is the parabolic cylinder function of order $2-\eta$. For small η , $\Gamma(2-\eta) D_{-2+\eta}(0) \simeq 1$. Thus, we write

$$I(k) = A^2 B k_0^4 \pi / [32 R^2 (k^2 + \xi^{-2})^{1-\eta/2}]. \quad (7)$$

This is the Fisher-corrected Ornstein-Zernike form⁷ for the light intensity scattered from a critical fluid. The critical exponent η comes in through our size distribution, Eq. (2). If the cluster-size distribution is cut off at atomic sizes, the value of B can be shown to be essentially constant as T_c is approached. Thus, the model correctly predicts this experimentally verified form.

To calculate the results for dynamical critical phenomena, we assume that in first approximation the droplets act as physically hard spheres of radius l and execute Brownian motion without growing or decaying appreciably during the *measured decay time*. The result for photon-correlation spectroscopy on a dispersion of single-sized hard spheres is given in the literature,⁸ and is easily generalized to encompass a size distribution¹:

$$\frac{\langle E(0)E^*(t) \rangle}{\langle E(0)E^*(0) \rangle} = \frac{\int_0^\infty dl N(l) I(l, k) \exp(-k_B T k^2 t / 6\pi\eta_b l)}{\int_0^\infty dl N(l) I(l, k)}, \quad (8)$$

where E is the scattered electric field, E^* is the complex conjugate of E , and $k_B T / 6\pi\eta_b l$ is the diffusion constant for a particle of size l moving through a background composed mostly of small or atomic-sized particles as indicated by the form of $N(l)$, with a background viscosity η_b .

Since the average correlation function is a sum of exponentials, it is not in general an exponential. However, experimental work¹ has shown that it is nearly exponential, and a reasonably good value for the diffusion rate can be determined by looking at the slope of the correlation function near $t=0$. To express this mathematically we write

$$\frac{\langle E(0)E^*(t) \rangle}{\langle E(0)E^*(0) \rangle} \cong \exp(-\bar{D}k^2 t), \quad (9)$$

where \bar{D} is the average diffusion constant. Evaluating the time derivative at $t=0$, we have

$$\frac{d}{dt} \frac{\langle E(0)E^*(t) \rangle}{\langle E(0)E^*(0) \rangle} = -\bar{D}k^2 = \bar{\Gamma}, \quad (10)$$

where $\bar{\Gamma}$ is the average linewidth. Applying Eq. (10) to Eq. (8) we have

$$\bar{D}k^2 = \frac{\int_0^\infty dl N(l) I(k, l) k^2 k_B T / 6\pi\eta_b l}{\int_0^\infty dl N(l) I(k, l)}. \quad (11)$$

From Eqs. (2) and (5)

$$\bar{D}k^2 = \frac{k_B T}{6\pi\eta_b} k^2 (k^2 + \xi^{-2})^{1/2} \frac{\Gamma(1-\eta) D_{-1+\eta}(0)}{\Gamma(2-\eta) D_{-2+\eta}(0)}. \quad (12)$$

When the coefficients are evaluated near $\eta=0$,

the average diffusion rate reduces to

$$\begin{aligned}\bar{D}k^2 = \bar{\Gamma} &= \left(\frac{\pi}{2}\right)^{1/2} \frac{k_B T}{6\pi\eta_b \xi} k^2 (1 + k^2 \xi^2)^{1/2} \\ &= \left(\frac{\pi}{2}\right)^{1/2} k^2 D(k, \xi).\end{aligned}\quad (13)$$

Except for a numerical factor of order unity, this is identical to the experimentally fitted result of Eq. (1).

$$S(\omega) = \frac{D(k, \xi)k^2}{\omega^2} \left[\frac{1}{\sqrt{\pi}} - \frac{D(k, \xi)k^2}{\omega} \exp\left(\frac{D^2(k, \xi)k^4}{\omega^2}\right) \operatorname{erfc}\left(\frac{D(k, \xi)k^2}{\omega}\right) \right], \quad (14)$$

where erfc is the complimentary error function⁷ and ω is the frequency. The half-width of this line-shape function is $\Gamma_{1/2} = (0.96)D(k, \xi)k^2$. Surprisingly this line-shape function can be fitted quite well by a Lorentzian except in the wings, where it decays more slowly. However, shot-noise corrections could have masked this non-Lorentzian behavior from experimenters.

In general the measured diffusion rate or linewidth will be given by $\Gamma = Dk^2 = \gamma D(k, \xi)k^2$, where γ is a number of order unity depending on the method of analysis used. For $\gamma = 1$ this diffusion rate or linewidth is identical to Eq. (1) if $\bar{\eta}_s/\eta_b = 1.18$. Data presented in the article by Swinney and Henry⁴ has been fitted by Eq. (1) and the ratio of $\bar{\eta}_s$ to the extrapolated background viscosity η_b is determined (a summary of results is included

In deriving Eq. (13) we have assumed that the experimental determination of the decay time of the scattered-light correlation function is a fit to the $t \rightarrow 0$ part of the spectrum. We have performed computer calculations of Eq. (8) and found the diffusion rate to be given approximately by $\bar{\Gamma}_{1/e} = \bar{D}_{1/e}k^2 = 0.88 D(k, \xi)k^2$ at the $1/e$ point of the normalized field correlation function.

For $\eta \rightarrow 0$ one can Fourier transform the time variable in the field correlation function. The resulting line shape, $S(\omega)$, can be determined exactly as

in Table VII of their article). An example of the theoretical fit to the data of Chang *et al.*¹⁰ is included in Fig. 1. The agreement between our theory and experiment is seen to be quite good, especially if we are not restricted to $\gamma = 1$. It should be noted, however, that a background subtraction,⁴ related to the Rayleigh line in the non-critical fluid, has been made for the pure fluids before fitting by Eq. (1).

In this Letter we have presented a simple model which is used to interpret light-scattering experiments on critical fluids. We have assumed that clusters of molecules exist in the fluid, that these clusters grow in size as the critical point is approached, and that they execute Brownian motion. The Rayleigh-Debye approximation is used to calculate the scattered intensity from a single cluster. This intensity is then combined with the cluster-size distribution and then with the theory of light scattered from a particle executing Brownian motion to find the scattered intensity and the Rayleigh linewidth. The agreement with experiment seems to be within experimental error limits.

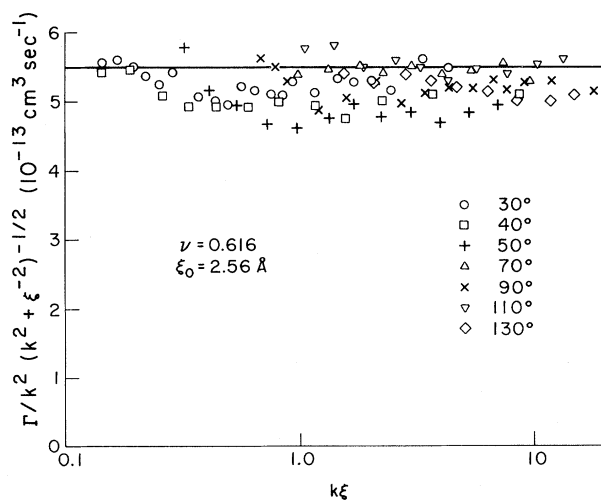


FIG. 1. Linewidth data for 3-methylpentane-nitroethane mixture (Ref. 10), divided by $k^2(k^2 + \xi^{-2})^{1/2}$ and plotted as a function of $k\xi$. The theoretical curve is for $\gamma = 1$ and $\eta_b = 0.400$ cP.

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¹C. M. Sorensen, B. J. Ackerson, R. C. Mockler, and W. J. O'Sullivan, to be published.

²M. Kerker, *The Scattering of Light* (Academic, New York, 1969).

³R. Perl and R. A. Ferrell, *Phys. Rev. Lett.* **29**, 51 (1972), and *Phys. Rev. A* **6**, 2358 (1972).

⁴H. L. Swinney and D. L. Henry, *Phys. Rev. A* **8**, 2586 (1973).

⁵M. E. Fisher, *Physics* (Long Is. City, N. Y.) **3**, 255 (1967).

⁶C. S. Kiang and D. Stauffer, *Z. Phys.* **235**, 130 (1970).

⁷M. E. Fisher, J. Math. Phys. (N. Y.) 5, 944 (1964).

⁸H. Z. Cummins and H. L. Swinney, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam,

1970), Vol. VIII.

⁹R. F. Chang, P. H. Keyes, J. V. Sengers, and C. O. Alley, Phys. Rev. Lett. 27, 1706 (1971).

Sum Rules and High-Frequency Behavior of Dynamic Structure Function of Quantum Fluids

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Using a novel diagrammatic perturbation-theory approach, it is found that the dynamic structure function of quantum fluids at high frequencies is independent of quantum statistics, depends only on the interparticle potential, and has a long tail as a function of frequency. In particular, it is found that the *fifth and higher frequency moments diverge in charged quantum systems*. This is demonstrated to hold in general by an investigation of the fifth-moment sum rule.

A function of central importance in the description of many-body systems is the dynamic structure function, $S(k, \omega)$, which represents the maximum information that can be obtained from the linear response of a system to a density probe, e.g., a neutron-scattering experiment.¹ At zero temperature, $S(k, \omega)$ is defined as the positive-frequency spectral function of the density response function $F(k, \omega)$ by²

$$S(k, \omega) = -\pi^{-1} \text{Im} F(k, \omega), \quad \omega \geq 0, \quad (1)$$

where

$$F(k, \omega) = -i \int dt e^{i\omega t} \langle [\rho_{\vec{k}}(t), \rho_{\vec{k}}^\dagger(0)] \rangle \theta(t). \quad (2)$$

In Eq. (2) the brackets $\langle \dots \rangle$ denote the ground-state average and $\rho_{\vec{k}}$ is the density operator. Inelastic scattering of neutrons on superfluid helium reveal¹ that in analogy to the classical fluids, $S(k, \omega)$, considered as a function of ω at fixed k , decreases continuously with a long smooth tail at large ω . Recently some progress has been made in calculating $S(k, \omega)$ in the high-frequency limit for classical systems,³ but there does not exist a general result for quantum fluids.

In this Letter I describe a *unified* diagrammatic approach for the calculation of the dynamic structure function of both Fermi and Bose fluids at zero temperature. It is based on an idea originally put forward by Brandow⁴ and extended by Lee,⁵ that a condensed Bose gas may be regarded as a fictitious Fermi gas with spin degeneracy equal to the total number of particles. This procedure

allows us to write down the same set of diagrams for any quantum many-particle system and to let the quantum statistics of the particles enter only in the final stage of the actual calculations. In contrast to the usual Green's-function formulations, my approach enables us to achieve perturbation approximations which obey local number conservation and related sum rules.

I find from examining low-order diagrams that in the high-frequency limit, the dynamic structure function of quantum fluids (1) is independent of quantum statistics of the particles, (2) depends only on the Fourier transform of the interparticle potential, and (3) can have a long smooth tail at fixed k as a function of ω . This high-frequency tail implies that the higher moments of $S(k, \omega)$ are divergent in certain quantum systems. I find that aside from the general result of Kleban⁶ for the divergence of the third frequency moment for hard-core potential, *the fifth and higher frequency moments diverge for charged quantum fluids*.⁷ I show that this result is general and independent of perturbation theory by presenting some arguments based on the fifth-moment sum rule.⁸

The density response function $F(k, \omega)$ can be expressed in terms of the proper polarization part $\Pi(k, \omega)$ by

$$F(k, \omega) = \Pi(k, \omega) / [1 - v(k)\Pi(k, \omega)], \quad (3)$$

where $v(k)$ is the Fourier transform of the interparticle potential. An exact calculation of the polarization part is clearly impossible at the mo-