SIMULATION OF CRITICAL FLUID RAYLEIGH LINEWIDTH BEHAVIOR BY A NORMAL FLUID SYSTEM☆

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The dynamic droplet model of a critical fluid provides a simple physical model of a critical fluid. We use this to model an emulsion which mimics the Rayleigh linewidth behavior of a critical fluid in the nonhydrodynamic regime.

The key experimental quantity extracted from laser light scattering studies on critical fluids is the Rayleigh linewidth, Γ. The behavior of Γ near a critical point has been described with reasonable success by the mode theories of Kawasaki [1] and Ferrell [2]. In addition, an empirical relation for Γ which is consistent with scaling requirements and which provides an excellent fit to linewidth data is [3],

$$\Gamma = \frac{k_B T}{6\pi\eta\xi}\, k^2(1+\xi^2k^2)^{1/2} \qquad (1)$$

where ξ is the Ornstein-Zernike correlation length, η a shear viscosity, usually treated as an adjustable parameter, and k is the scattered light wavenumber. For $|T - T_{crit}|$ large enough that the hydrodynamic condition $k\xi \ll 1$ is satisfied, the Rayleigh linewidth becomes $\Gamma = (k_B T/6\pi\eta\xi)\, k^2$, which is equivalent to the Rayleigh linewidth of light scattered from a suspension of microspheres of mean radius ξ, diffusing through a host fluid characterized by a shear viscosity η. A physical model of a critical fluid, based on a picture in which the fluid fluctuations can be considered as diffusing spherical droplets, has an obvious conceptual attraction.

Recently [4] we demonstrated how this picture of a critical fluid in the hydrodynamic regime could be generalized to provide a description of such a system into the non hydrodynamic regime where $k\xi \gtrsim 1$, and where, in the limit as $k\xi$ becomes large, Γ becomes proportional to k^3 and independent of ξ. In this model the order parameter fluctuations are considered as constituting a *polydisperse* suspension of droplets, or molecular clusters, diffusing as Brownian particles in a normal background fluid. The model successfully predicts the correct Rayleigh linewidth behavior in a critical fluid system, although, in its present form it overestimates the departure from exponentiality of the intensity autocorrelation function [5].

In this note we show, that by taking advantage of the physical picture contained in the droplet model, it is possible to construct a *normal* fluid system so as to simulate the Rayleigh linewidth behavior of a *critical* fluid in the non hydrodynamic regime. The requirements that must be satisfied by our mock critical fluid are that it must consist of a polydisperse system of diffusing particles characterized by a mean size parameter $\bar{R}$ such that $k\bar{R} \gtrsim 1$, just as $k\xi \gtrsim 1$ for a critical fluid in the non hydrodynamic regime. The number density of particles must be high to simulate the high number density of fluctuations in a critical fluid, and finally, the diffusing particle and the host fluid must have closely matched indices of refraction in order to reduce the complicating effects of multiple scattering [6]. To this end we set up an emulsion consisting of octane dispersed in a 38.72 % by wt. sucrose/H_2O solution. The specific sucrose concentration was chosen because, for it, the index of refraction of the sucrose-water solution is 1.3974, equal to that of the octane. The emulsion was formed by adding a small amount of wetting agent to disperse the fluids, and subjecting the mixture to ultrasonic agitation for a period of 5 minutes. After a few hours of settling the resultant emulsion proved to be reasonably stable for about 24 hours.

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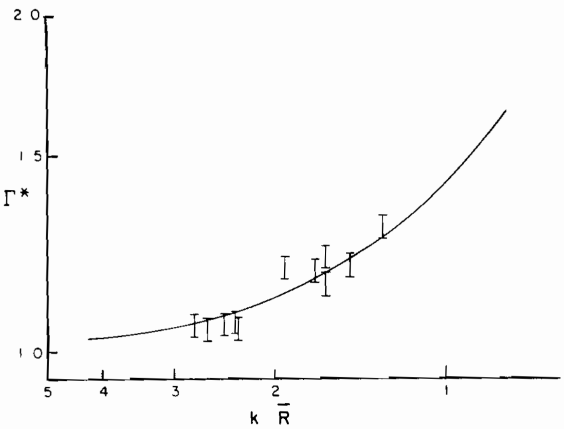

Fig. 1. The experimental scaled linewidth as a function of $k\bar{R}$ for $k\bar{R} \gtrsim 1$, where $k = (4\pi n/\lambda) \sin(\theta_{\mathrm{scat}}/2)$. The solid line is the empirical scaled linewidth given by eq. (3).

The basic light scattering experiment and autocorrelation spectrometer has been described elsewhere [4]. The observed intensity-intensity autocorrelation functions were slightly non exponential, but the least squares fitting routine we used extracted the first cumulant K_1 which equals the average value of Γ for $t \to 0$.

In fig. 1 we show a log-log plot of the experimental scaled linewidth Γ^* as a function of $k\bar{R}$, where

$$\Gamma^* = \Gamma\left(\frac{6\pi\eta\bar{R}}{k_{\mathrm{B}}Tk^3}\right). \tag{2}$$

Here Γ is the measured linewidth equal to the reciprocal of the correlation time, η is the viscosity of the "background" sucrose solution and $\bar{R}$ is the average radius determined from our measurements to be 0.088 μm. In addition we include the theoretical scaled linewidth analogous to that for critical fluids given by eq. (1),

$$\Gamma^*_{\mathrm{Theory}} = (1 + \bar{R}^2k^2)^{1/2}/k. \tag{3}$$

We see that there is good agreement between our experiment and the theory. (The "hydrodynamic regime" is easily simulated by all suspended particle systems with average particle radius such that $k\bar{R} \ll 1$.) In fig. 2 we show a log-log plot of the correlation time versus $\sin(\theta_{\mathrm{scat}}/2)$ which clearly reveals the onset of a k^3 dependence consistent with the scaling prediction for critical fluids in contrast to the typical k^2 dependence

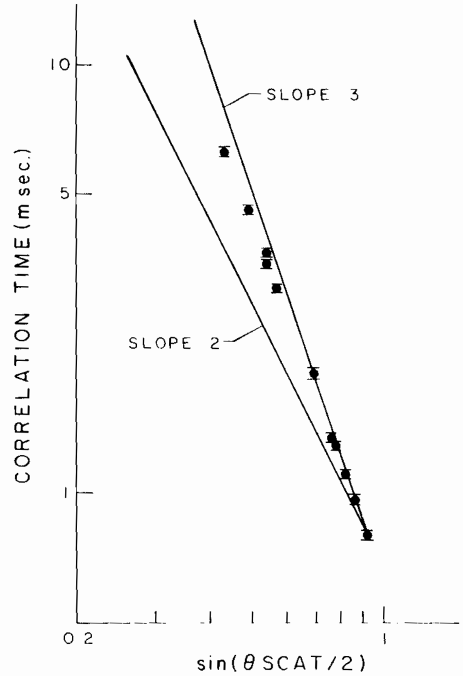

Fig. 2. A log-log plot of the experimental correlation time Γ^{-1} as a function of $\sin(\theta_{\mathrm{scat}}/2)$.

of Γ for a monodisperse system of Brownian particles.

In the Dynamic Droplet model of a critical fluid, the order parameter fluctuations are considered as *behaving like* diffuse droplets or clusters undergoing Brownian motion in a normal (as opposed to critical) background fluid. In this letter we have demonstrated that one can devise a fluid system, containing real droplets diffusing in a normal host fluid, whose Rayleigh linewidth shows a dependence upon scattered wavenumber which is the same as that for a critical fluid in the non hydrodynamic regime.

[1] K. Kawasaki, Phys. Rev. 150 (1966) 291; Ann. Phys. (N.Y.) 61 (1970) 1; Phys. Rev. A1 (1970) 1750.
[2] R.A. Ferrell, Phys. Rev. Lett. 24 (1970) 1169.
[3] R. Perl and R.A. Ferrell, Phys. Rev. A6 (1972) 2358.
[4] B.J. Ackerson, C.M. Sorensen, R.C. Mockler and W.J. O'Sullivan, Phys. Rev. Lett. 34 (1975) 1371; C.M. Sorensen, B.J. Ackerson, R.C. Mockler and W.J. O'Sullivan, Phys. Rev. A13 (1976) 1593.
[5] D. Wonica, H.L. Swinney and H.Z. Cummins, Phys. Rev. Lett. 37 (1976) 66.
[6] C.M. Sorensen, R.C. Mockler and W.J. O'Sullivan, Phys. Rev., to be published.