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Dynamic scaling in a critical microemulsion system

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We have used light scattering to study the dynamics of fluctuations in a water-in-oil microemulsion near a critical phase transition point and found excellent agreement with the mode-mode coupling theory of Kawasaki as modified by renormalization-group calculations. An alternative origin of the modification of the Kawasaki expression is also suggested by consideration of the effects of the internal current of a liquid droplet moving through another liquid.

We have previously studied the dynamic scaling behavior in a pure three-component water-in-oil microemulsion system which consists of a small amount of sodium di-2-ethylhexylsulfosuccinate (a surfactant commonly known at AOT), water and decane.[1,2] We have found that the average hydrodynamic radius, R_H, of the droplet phase as determined by dynamic light scattering, plays a similar role as that of the correlation length in an ordinary multicomponent system near a critical (or multicritical) point.[3,4] This average hydrodynamic radius appears to characterize the apparently monodispersed water droplets in oil reasonably well.

The surfactant-stabilized microdroplets are thought to behave like hard spheres.[5] But very near the transition temperature, it is observed that the single-exponential fit to the scattered intensity correlation function deteriorates, especially at large scattering angles. It is also known that as the average droplet size increases, the interfacial tension between the water and oil phases decreases.[6] Thus we suspect that the monodispersed hard-sphere droplet picture may not be an adequate representation of the minority water phase. In the neighborhood of the transition point, one might question the usefulness of a model-dependent hydrodynamic length as measured by the best single-exponential fit to the real time correlation function of the scattered light. A more serious drawback of using R_H to describe the characteristic length of the critical system is that this value as obtained via Stokes-Einstein relation depends on the viscosity of continuous-oil phase, which has a very different temperature dependence compared to that of the solution viscosity (Fig. 1). Since R_H is only an approximate measure of the static correlation length in the critical regime, we were satisfied in our previous publication[2] to have observed a qualitative fit of our R_H data to the mode-mode coupling theory.[7,8]

We have now removed this somewhat troublesome choice of viscosities by study of the static correlation length obtained by the angular asymmetry in the scattering intensity data. This characteristic length of the system (which we shall call ξ_I) can be calculated from the slope and the intercept of the inverse scattering intensity versus k^2 plot. [k is the photon momentum transfer: $k = (4\pi/\lambda)\sin\theta/2$, where λ is the wavelength of light in the scattering medium and θ is the scattering angle.] Since we have observed the Debye-Ornstein-Zernike behavior[9,10] of our intensity data we can identify ξ_I, some sort of "averaged" radius of gyration of the droplets, with that of the static correlation length.

In order to study the nature of the critical phase transition in a pure three-component microemulsion, we have carefully measured the static correlation length in a system containing 3 g of AOT surfactant in a 100-cm^3 of 5.8/94.2 mixture (by volume) of double distilled water and decane. The resultant microemulsion is a clear homogeneous fluid at room temperature. The sample was passed through a 0.2-μm filter into a 9.00-mm-i.d. precision bored NMR tube, which was later permanently sealed by a torch. A 15-mW He-Ne laser, a computer controlled 128 channel multibit Malvern correlator, and a temperature stabilized spectrometer (temperature was regulated to within ±0.002° C) were employed for our ex-

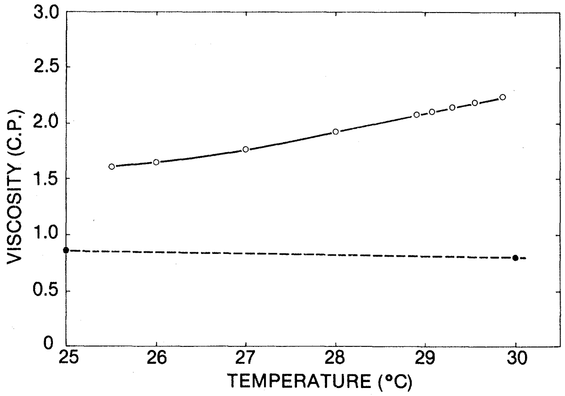

FIG. 1. Viscosity measurements of the microemulsion system are shown by the open circles, ○. The filled circles and the dotted line represent the solvent viscosity of the continuous phase.

periment.

Our data are summarized in Table I. ξ_l was calculated from angular asymmetry in the scattering intensity data, and the linewidth Γ was obtained from the method of cumulants[11] fitted to the intensity-intensity correlation function. The critical temperature of this system was determined to be 30.200° C. In this Communication, we discuss only the relation of static correlation length (ξ_l) and a dynamic linewidth (Γ) near the critical temperature.

The mode-mode coupling theory of Kawasaki[7,8] gives a relation between the dynamics of the fluctuations as measured by the linewidth Γ and the scaled correlation length $k\xi_l$:

$$\Gamma/Ak^2 = H_0(k\xi_l) \quad , \tag{1}$$

TABLE I. Values of the Kawasaki function Γ/Ak^2 [Eq. (1)] are listed at various temperature and $k\xi_l$. Γ is measured by dynamic light scattering, $k\xi_l$ is obtained from the angular asymmetry scattering intensity and $k = 4\pi/\lambda \sin(\theta/2)$ is the scattering wave number. The critical temperature is 30.200° C.

Temperature ($^{\circ}$C)	ξ_l (cm)	$k\xi_l$	$\frac{\Gamma}{Ak^2}$
29.841	1.175×10^{-5}	1.187	1.892
		2.195	3.251
		2.867	4.135
29.828	1.145×10^{-5}	1.160	1.891
		2.146	3.188
		2.804	4.036
29.802	1.140×10^{-5}	1.151	1.946
		2.129	3.155
		2.781	3.990
29.724	1.014×10^{-5}	1.024	1.856
		1.894	2.905
		2.474	3.575
29.669	8.949×10^{-6}	0.904	1.596
		1.672	2.579
		2.183	3.187
29.589	8.004×10^{-6}	0.808	1.579
		1.495	2.360
		1.953	2.900
29.472	7.184×10^{-6}	0.726	1.561
		1.342	2.310
		1.753	2.575
29.309	6.181×10^{-6}	0.624	1.613
		1.155	1.963
		1.508	2.353
29.071	5.309×10^{-6}	0.536	1.580
		0.992	1.854
		1.295	2.152
28.905	4.448×10^{-6}	0.449	1.459
		0.831	1.649
		1.085	1.889
28.695	4.023×10^{-6}	0.406	1.433
		0.751	1.586
		0.982	1.787
28.354	3.621×10^{-6}	0.366	1.464
		0.676	1.584
		0.884	1.727
28.048	3.298×10^{-6}	0.226	1.472
		0.262	1.465
		0.298	1.460
		0.330	1.442
		0.369	1.451
		0.436	1.495
		0.500	1.486
		0.560	1.534
		0.616	1.547
		0.691	1.606
		0.754	1.638
		0.805	1.675
27.360	3.045×10^{-6}	0.208	1.486
		0.242	1.514
		0.308	1.536
		0.402	1.520
		0.490	1.538
		0.569	1.572
		0.743	1.669
27.034	2.258×10^{-6}	0.154	1.259
		0.228	1.279
		0.298	1.289
		0.363	1.289
		0.422	1.289
		0.551	1.349
26.67	1.898×10^{-6}	0.130	1.142
		0.192	1.134
		0.251	1.148
		0.305	1.152
		0.355	1.158
		0.398	1.165
		0.434	1.176
		0.463	1.216
25.92	1.750×10^{-6}	0.177	1.170
		0.327	1.181

where $H_0(x)=\frac{3}{4}x[1/x^3+1/x+(1-1/x^4)\arctan x]$, and $A=k_BT/6\pi\eta\xi_l$. η_s, is the shear viscosity of the microemulsion and k_B is the Boltzmann constant. If we should take $\eta_s=\eta$, and plot our linewidth data $\Gamma/(Ak^2)$ vs $k\xi_l$, we see a systematic deviation of our data with the Kawasaki's function $H_0(k\xi_l)$, represented by the dashed curve in Fig. 2. The scattering of data points of small $k\xi_l$ values are primarily due to inaccuracy inherent of the weak scattering intensity at temperatures far away from the critical point. However, the fit can be made almost perfect by multiplying $H_0(k\xi_l)$ by a constant factor of 1.2 (solid curve in Fig. 2). This result, which is probably reliable to 10%, is in good agreement with the renormalization-group calculation of Siggia *et al.*[12] They have shown that, for the Rayleigh linewidth in the one-phase region above T_c, the Kawasaki function is modified by a coefficient Γ_0 which they estimated to be equal to 1.20:

$$\Gamma/Ak^2=\Gamma_0H_0(k\xi_l) \quad . \tag{2}$$

We feel the agreement between our data and Eq. (2) is significant despite the fact that there are still uncertainties in substituting η_s, the measured shear viscosity, for the frequency-dependent η in Eqs. (1) and (2). It is known from studies on the dynamics of concentration fluctuations in binary mixtures in the hydrodynamical and nonhydrodynamical regimes by Bêrge *et al.*[13] and by Chang *et al.*[14] that the error introduced by this approximation is probably quite small.

An alternative origin of the factor of 1.2 for Γ_0 in Eq. (2) may also be found in the hydrodynamic properties of the liquid droplets diffusing in a second liquid phase. The Einstein-Stokes relation with a nonslip boundary condition is appropriate to describe the Brownian motion of a solid sphere:

$$D=k_BT/f \quad , \tag{3}$$

where D is the diffusion constant, $f=6\pi\eta a$, and a is the radius of the sphere. The corresponding linewidth, Γ, as measured by light scattering is related to D by

$$\Gamma=Dk^2 \quad . \tag{4}$$

However, if we should consider the possible internal current in a moving liquid droplet, the Einstein-Stokes expression for the resistance f should be modified[15,16] with a factor

$$C=(\eta+\tfrac{2}{3}\eta')/(\eta+\eta') \quad , \tag{5}$$

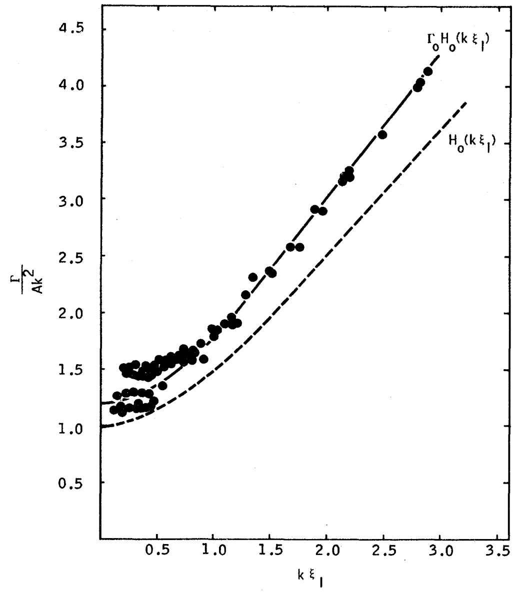

FIG. 2. Measured values of Γ/Ak^2 vs $k\xi_l$ are represented by the filled circles. The dotted line represents the Kawasaki function $H_0(k\xi_l)$ [Eq. (1)]. The solid line represents the best-fit function $\Gamma_0H_0(k\xi_l)$ with $\Gamma_0=1.20$.

where η as η' are the external and internal viscosities, respectively. For our microemulsion system, $\eta\simeq\eta'$, substituting this result into Eq. (5), we get $C\simeq\frac{5}{6}$, effectively changing the nonslip boundary condition for a rigid sphere into a nonstick condition for a liquid droplet. Equation (3) now reads

$$D=k_BT/Cf=1.20k_BT/f \tag{3'}$$

and Eq. (1) becomes

$$\Gamma/Ak^2=1.20H_0(k\xi_l) \quad , \tag{1'}$$

which gives the same result as Eq. (2).

The microdroplets of the dispersed phase in microemulsions in a certain sense behave like macromolecules in solutions. The nature of the critical phase transition is certainly similar to that observed in binary fluids.[2] The important difference between the two systems is that unlike the true macromolecular solutions, the number of droplets in microemulsion is not conserved due to the growing size of the droplets near the transition. A detailed theoretical treatment of the phase transition in this system should be of great interest.

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