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Dynamic Slowing-Down and Nonexponential Decay of the Density Correlation Function in Dense Microemulsions

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Quasielastic-light-scattering measurements were made on microemulsions in which the apparent volume fraction ϕ of the microemulsion droplets was varied from 0.1 to 0.75. The density correlation function shows an exponential decay at short time but deviates from it at long time especially for intermediate ϕ. The initial decay rates of the correlation functions decrease steadily as a function of ϕ, reaching a minimum at $\phi_c = 0.62$, and increase thereafter. The overall time dependence of the correlation functions can be fitted by the function $\exp[-(t/T)^\alpha]$; the exponent α varies from 1 down to 0.66 and back up again to 0.9 over the range of ϕ.

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It is common knowledge that oil and water do not mix, and if a mixture is mechanically agitated it usually forms a thermodynamically unstable macroemulsion phase which separates eventually in time. However, with the addition of a certain amount of surfactant to the oil and water, frequently the mixture can form a "microemulsion" which is a transparent and thermodynamically stable system. The microscopic structure of microemulsions in general can be quite complicated and varied from system to system. But for a three-component system formed by mixtures of surfactant di-2-ethylhexylsulfosuccinate (AOT), water, and oil (in this case decane) we have previously shown unambiguously by small-angle neutron scattering that the microemulsion consists of droplets of water dispersed in oil.[1-3] Furthermore, this water-in-oil droplet structure persists into the region of the phase diagram where the oil and water volume fractions are one to one and the so-called bi-continuous structure[4] apparently never sets in. The picture we arrived at from analysis of this experiment[3] was that for dense microemulsions of volume fractions ϕ ranging from 0.50 to 0.71, the droplets were basically spherical with a polydispersity of about 25%. These spheres are packed locally with a face-centered-cubic structure which gives rise to a prominent peak in the neutron structure factor. However, because of the polydispersity, the ordering is expected to be short ranged[5] and glasslike. We have also attempted to detect the second and third peaks of the structure factor which would be indicative of the glasslike ordering,[6,7] but were unsuccessful. This may be because of the effects of polydispersity on the structure factor and on the form factor of the spheres which tends to wash out the weaker structures at large-wave-vector transfer Q. We have therefore turned to a dynamic study which is considerably more sensitive to the onset of a glasslike transition at high packing fractions.[8-12] The microemulsion is an attractive system for the study of dynamics of the glass transition experimentally because the packing fraction of the spheres can easily be changed simply by adding more surfactant and water to the oil.

Microemulsions were prepared by dissolving appropriate amounts of AOT in decane and then D_2O was added and the sample tube put on a high-frequency mixer for emulsification. The sample was then allowed to age for a day before the measurements. The same sample is usually measured repeatedly over a period of a month to ensure its equilibrium. This is essential for highly viscous samples where relaxation rates are slow.

The photon correlator was a Malvern model K-7025 with 128 delay channels and monitor channels. The enhancement time is typically 4000 sec and photocounts of about 10^7 were registered in the first channel. The uncorrelated dc "backgrounds" were computed from outputs of the monitor channels and subtracted from the signal at each channel. Logarithms of these signals are then plotted as a function of the delay time t and fitted by a polynomial $K_0 - K_1 t + \frac{1}{2} K_2 t^2$, from which the first cumulant K_1 was extracted. This procedure was usually repeated two or three times, varying the channel width of the correlator by large factors in order to make sure a correct initial slope K_1 was extracted. We shall henceforth call $K_1 = \Gamma_1$ the initial decay rate of the density correlation function. The scattering angle was varied over a range between 45° to 135° and an approximate Q^2 dependence of Γ_1 was verified. For the subsequent discussion we refer only to Γ_1 values measured at 90°. All measurements were made at a temperature 23.5 ± 0.1 °C.

In this series of measurements we would like to keep the average size of the microemulsion droplets identical. This can be achieved by keeping the molar ratio of water and surfactant, $X = [D_2O]/[AOT]$, constant.[1] We choose a value $X = 40.8$, which, according to our previous experiment,[2] gives an average radius of the water droplets $\bar{R} = 50$ Å. The apparent volume fraction of the microemulsion droplets was calculated from the sum of the volume fractions of water (D_2O) and surfactant (AOT) added to the oil. The specific volume of dry AOT was taken to be 0.8789 cm^3/g.

The base-line-subtracted photon correlation function at a typical value of the apparent volume fraction $\phi = 0.50$ is plotted in Fig. 1. The ordinate is $C + 2\ln F_N(Q,t)$, where C is a constant depending only on the light-collecting optics in front of the detector and the scattering wave number Q.[13] $F_N(Q,t)$ is the normalized density autocorrelation function of the droplets.

When $\phi \leqslant 0.10$ the plot is essentially linear in t and one can easily extract the decay rate Γ_1. For $\phi \geqslant 0.20$ the plots start linear but gradually bend upward and tend to a tail at long times. This trend continues to higher volume fractions and the linear range of the plots becomes somewhat smaller, but always exists. One can, if necessary, extract it by operating the photon correlator at shorter channel widths. The Γ_1 we extract this way represents the average decay rate of a continuous distribution of decay rates exhibited by the density autocorrelation function.

We plot in Fig. 2 Γ_1 vs ϕ for many series of measurements, including some repeated measurements of the same samples at different times. Γ_1 is seen to vary between 4.0 and 6.8 kHz at $Q = 1.70 \times 10^5$ cm^{-1}. The striking feature of this plot is that Γ_1 shows a minimum at $\phi_c = 0.62$. This means that the average damping of the nonpropagating modes of the density fluctuation decreases to a minimum value at a certain critical packing fraction ϕ_c of the spheres and increases again thereafter. If the droplets were to maintain a dense liquidlike structure in the whole range of ϕ this minimum would be difficult to understand. However, if the droplets were to undergo a structural transition similar to the glass transition in supercooled liquids[6] or in dense polymer solutions,[14] then the recent mode-mode coupling theories[8-10] can be used qualitatively explain the result. According to the mode-mode coupling theory of Leutheusser,[8] in dense liquids near the glass transition the nonpropagating part of the dynamic structure factor $S(Q,\omega)$, which is a Fourier transform of the density autocorrelation function, consists of two components: a broad component representing the normal longitudinal density fluctuation in liquids (or solids), and a sharp component representing the local structural-relaxation mode of a highly viscous liquid. The two modes are strongly coupled near the glass transition and as a result both modes narrow as the fluid is compressed toward ϕ_c. At ϕ_c the structural relaxation mode is frozen and becomes a delta function due to the structural arrest in the glassy state. The freezing out of the structural relaxation mode after the glassy transition effectively decouples the two modes and the longitudinal density-fluctuation mode broadens again to the normal width as before the glass transition. The shape of our graph looks similar to a result of a recent computer simulation on truncated Lennard-Jones fluid done by Ullo and Yip[11] (see their Fig. 4). The structural-relaxation mode predicted by

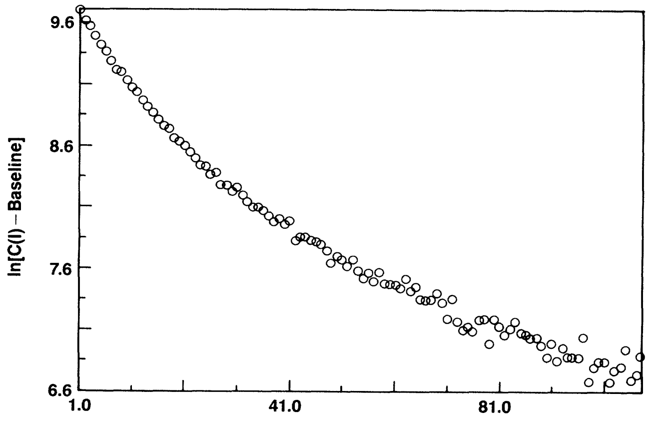

FIG. 1. Logarithm of a photon correlation function with base line subtracted. The base line is computed from counts registered in the monitor channels of the correlator. The abscissa is the channel number I with a channel width 7.5 msec. The apparent volume fraction of the microemulsion droplets is 0.5. The existence of a well-defined initial decay rate together with a nonexponential tail at longer time are clearly seen.

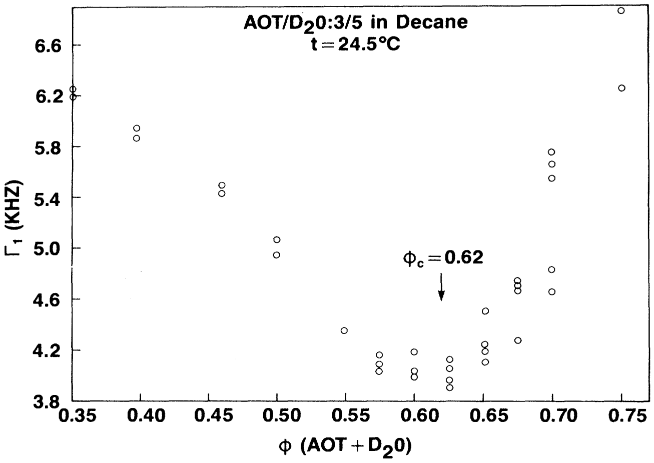

FIG. 2. The extracted initial decay rate Γ_1, plotted as a function of the apparent droplet volume fraction ϕ. There is a minimum decay rate at $\phi_c = 0.62$. All the photon correlation functions are taken at 90° scattering angle with a helium-neon laser.

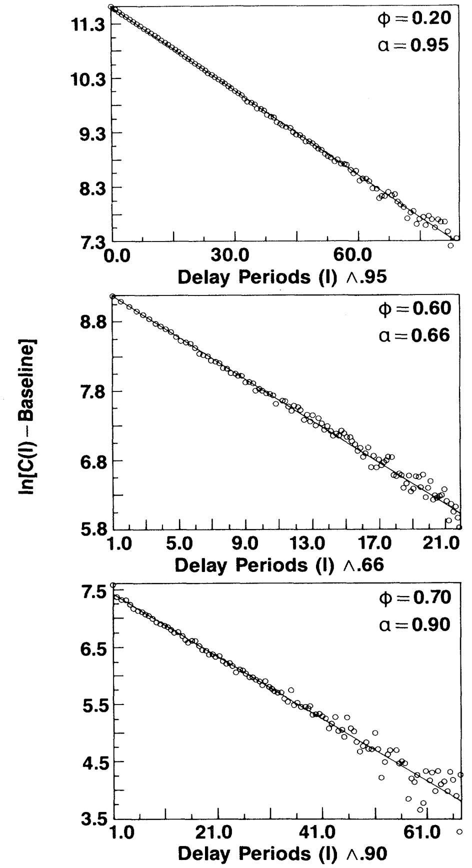

FIG. 3. Test of the stretched exponential form of the photon correlation function. The ordinate is proportional to $C + 2\ln F_N(Q,t)$. The abscissa is proportional to t^α where t is the delay time to the correlator. It is seen that with an appropriate choice of values of α the plots can be made into good straight lines. Note also the abnormally high value of the first channel in the lowest graph with $\phi = 0.70$. This phenomenon is universal for all systems with $\phi \geqslant 0.62$. We suspect that this is due to the Brillouin scattering in the glass phase.

TABLE I. Fitted parameters for the stretched exponential function.

ϕ	α	$\langle T \rangle$ (msec)
0.05	1.0	56
0.10	0.98	61
0.20	0.95	70
0.30	0.89	79
0.40	0.80	98
0.50	0.75	133
0.60	0.66	237
0.65	0.85	122
0.70	0.90	94
0.73	0.90	80

theory[8] would correspond to the nonexponential long-time tail in our photon correlation functions. The freezing out of a mode, or of a multiple of modes, would produce a constant tail in the photon correlation function, which is difficult to distinguish from the uncorrelated dc background.

As a second approach to analyses of the global time behavior of the density autocorrelation function, we tried a stretched exponential function of the form

$$F_N(Q,t) = \exp[-(t/T)^\alpha].$$

This form is known to represent well the asymptotic behavior of nonexponential relaxations of various nonequilibrium parameters of macroscopic systems.[15,16] The advantage of this functional form is that it could represent the entire multiple-relaxation-time behavior of the correlation function by only two parameters, namely, an exponent α satisfying $0 < \alpha \leqslant 1$, and an average correlation time $\langle T \rangle$,[14]

$$\langle T \rangle = \int_0^\infty \exp[-(t/T)^\alpha]dt = (1/\alpha)\Gamma(1/\alpha)T,$$

where $\Gamma(x)$ is the gamma function.

Microscopic theories[17] of this relaxation function are usually formulated for some single-particle properties of a system. For example, in our case, consider motions of a typical microemulsion droplet in a cage of other neighboring droplets. At high packing fractions, diffusion of the central particle is controlled by the opening up of a vacancy in the nearest-neighbor shell so that it can move out. When the opening of these "relaxation channels" is blocked in a random way by motion of the neighbors and also when the time between the opening and closing of these channels is long compared to the vibrational period of the central particle in the cage, this relaxation function can be shown to hold asymptotically.[15] Small α means longer pausing times between diffusional jumps.[16]

Figure 3 illustrates that the stretched exponential form fits the overall time dependence of the density correlation functions reasonably well. When logarithms of the base-line-subtracted photon-correlation functions are plotted against t^α, they can be put into straight lines by an appropriate choice of values of α. At low ϕ, α is near unity, signifying a good exponential decay of the correlation functions. As ϕ increases α decreases initially to 0.95 at $\phi = 0.20$ and to 0.70 at $\phi = 0.50$ and reaches a lowest value 0.66 at $\phi_c = 0.62$. However, α seems to gradually recover to about 0.9 as ϕ increases beyond ϕ_c.[18] In Table I we list values of α and $\langle T \rangle$ extracted at each volume fraction. One can show that $\langle T \rangle = \langle 1/\Gamma \rangle$, the average of the inverse decay rates, which shows more or less similar behavior to Γ_1 which is $\langle \Gamma \rangle$.

We have made a systematic study of the droplet density autocorrelation functions in dense microemulsions as a function of the droplet volume fraction when the microemulsion droplet size is kept constant. The initial decay rates of the correlation functions show a minimum at a hypothetical glass transition point $\phi_c = 0.62$. We argued that this dynamic slowing down near ϕ_c is in qualitative agreement with the recent mode-mode coupling theory predictions. In a polydispersed system a steady decrease of the initial decay rate Γ_1 as a function of ϕ can also be expected due to the effect of the mixing of single-particle scattering into the light-scattering spectra.[19] This effect, however, would not produce a minimum of Γ_1 at ϕ_c. The overall time dependence of the correlation functions can also be fitted well by the stretched exponential function with a lowest exponent $\alpha_c = 0.66$ at $\phi = \phi_c$.

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