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Light scattering investigation of dense microemulsions above and below the percolation threshold

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Abstract. We performed an extensive series of dynamic light scattering measurements of a three-component water-in-oil microemulsion system, consisting of AOT/water/decane, throughout the isotropic one-phase region at water to AOT molar ratio $X = 40.8$, covering wide ranges of volume fraction φ and temperature T above and below the percolation threshold. The droplet density correlation function at long time has a non-exponential form for $\varphi > 0.4$ and below the percolation threshold. When fitted to a stretched exponential function, the apparent exponent β , starting at about 0.7 at the lowest temperatures, increases continuously and approaches unity at the percolation temperature and above. The initial and the average decay rates of the correlation function, as a function of temperature, show an abrupt change of slope at the percolation threshold.

1. Introduction

For a certain range of compositions, three-component mixtures of oil, water and surfactant may form a homogeneous, isotropic phase called microemulsions. In the case of a ternary system consisting of sodium-di-2-ethyl hexyl sulfosuccinate (AOT)/water/decane, the microemulsion phase contains water droplets coated by a monolayer of surfactant molecules dispersed in a continuous oil medium. Assuming that the solution is incompressible, we can calculate the volume fraction of the dispersed phase φ as $\varphi = \varphi_w + \varphi_s$ where φ_w and φ_s are respectively the volume fractions of water and surfactant. When the molar ratio $X = [\text{water}]/[\text{AOT}]$ is kept constant at say 40.8, the water core of the microemulsion droplet has a radius of about 50 Å [1]. The number density of the microemulsion droplet can be varied by adjusting the amount of decane while keeping X constant. This microemulsion system shows a wide variety of interesting physical phenomena upon varying the temperature T and volume fraction φ .

The phase diagram in the T - φ plane for the system with $X = 40.8$ is shown in figure 1. The cloud-point curve, separating the homogeneous microemulsion phase from the two-phase microemulsions, extends from $\varphi = 0.04$ to 0.40 and shows a highly asymmetric shape with a lower consolute point occurring at $\varphi_c = 0.098$ and $T_c = 39.960$ °C. The shape of the coexistence curve in the vicinity of the critical point can be

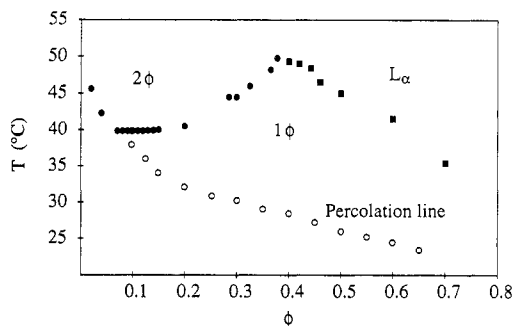


Figure 1. Phase diagram of AOT/water/decane microemulsions. The closed circles and squares denote respectively the phase boundary between the one- and two-phase microemulsions and between the one phase microemulsions and the lamellar L_α phase. Open circles are the percolation locus separating the non-conducting (below) and the conducting (above) one-phase microemulsions.

fitted to a power law [2] with an exponent 0.35, very close to the value for the three dimensional Ising universality class. The cloud-point curve ends abruptly in a cusp at $\phi = 0.40$, where it joins to a phase boundary separating the homogeneous microemulsion phase at lower temperatures and a lamellar phase L_α at higher temperatures. In a quite large domain of volume fractions and temperatures in the one-phase region below the critical point, the well established critical laws have been verified by means of neutron [3] and light scattering experiments [2], provided the effect of unusually large size of the droplets has been properly taken into account.

Very recently we have shown the existence of a percolation line, determined by electrical conductivity measurements, in the one-phase region [4]. The percolation locus extends from the low volume fraction side of the cloud point curve near $T = 40$ °C, down to 22 °C at $\phi = 0.7$ and is also shown in figure 1. The values of the electrical conductivity increase by six orders of magnitude when crossing the percolation line from below. The system passes from a very good insulator at low temperatures to a very good conductor at high temperatures. Percolation phenomena in microemulsions have been detected previously in some other more complex quaternary systems like sodium dodecylsulphate/water/toluene/butanol (or pentanol) [5]. In our case the behaviour of electrical conductivity along the percolation line, as a function of temperature, has been well understood [4]. A fluctuating charge model [6] is valid for small volume fractions over a large temperature interval, while a power law behaviour dominates above and below the percolation threshold. Values of the percolation indices are in agreement with that of a static percolation above the threshold, but with that of a dynamic percolation below [7]. In the dynamic percolation regime, transient fractal clusters are formed [8] and the droplets show an increased connectivity. The overall shape of the percolation line can be accounted for theoretically using a model of percolation in probability due to Xu and Stell [4, 9]. The model assumes an inter-droplet potential consisting of a hard core plus a small but long-ranged attractive Yukawa tail having temperature-dependent parameters.

Another remarkable feature of the three-component microemulsion is the occurrence of a glass-like transition in the dense region close to the volume fraction of 0.6. This phenomenon has been detected by means of a dynamic light scattering experiment measuring the droplet density time correlation function [10]. The droplet density correlation function decays like an exponential at short time, up to about 100 μ s, but gradually changes into a stretched exponential at long time. In a time window from 16 μ s up to about 1600 μ s, the apparent characteristic exponent β attains values as small as 0.65.

2. Experiment

In this paper we report a series of static and dynamic light scattering experiments performed throughout the one phase region of the AOT/water/decane microemulsion

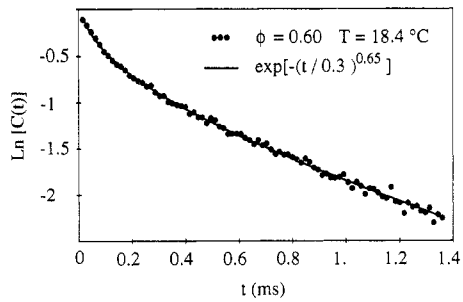


Figure 2. A droplet density correlation function for a non-percolating microemulsion at volume fraction of 0.6 and temperature of 18.4 °C. Notice the correlation function has a well defined first cumulant up to about 100 μs and has a long time stretched exponential decay with a characteristic exponent $\beta = 0.65$ and a relaxation time $T = 0.3$ ms.

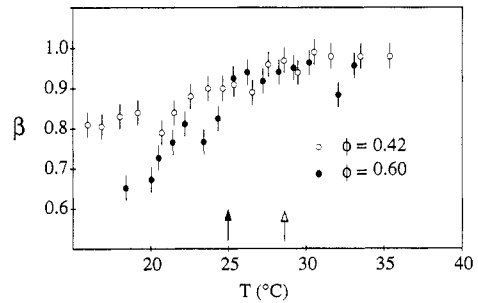


Figure 3. The apparent stretched exponential exponent β as a function of temperature for two dense microemulsions. Black circles represent the data for a volume fraction of 0.60 and open circles that of 0.42. The arrows indicate the locations of the percolation temperatures.

system at $X = 40.8$. We made a very accurate and extensive set of measurements of the total scattered intensity, turbidity and intensity–intensity time correlation function for different values of scattering wavevectors. Measurements we report here are confined to those with magnitude of wavevector q equal to $2 \times 10^5 \text{ cm}^{-1}$, corresponding to 90° scattering angle. The laser source was a 5 mW He–Ne laser operating at 632.8 nm. The turbidity is so low that there is no worry of multiple scattering. We measured the droplet density time correlation functions using a 100-channel clipped real-time correlator and repeating the measurements, under the same conditions, for increasing sampling times from 2 μs /channel up to 64 μs /channel in multiples of two. This procedure allows us to construct the correlation functions with good precision from 2 to 1600 μs . The fitting routine deals with at least 600 data points, taken at different sampling times. For the sake of illustration, we display in figure 2 a droplet density correlation function for a case corresponding to a volume fraction of 0.6 at the lowest temperature of 18.4 °C (below the percolation threshold). On the same graph is also shown a fit of this correlation function to a stretched exponential with the exponent $\beta = 0.65$ and the characteristic time $T = 0.3$ ms (defined in equation (2) of the next section).

3. Discussion

We shall discuss our experimental results in terms of the low and the high volume fraction regimes. Looking at the phase diagram given in figure 1, the natural dividing line for the two regimes is at the volume fraction of 0.4 corresponding to the cusp in the phase boundaries. For volume fractions $\varphi \leq 0.4$ and temperatures between 18 °C and the cloud-point curve, the density correlation functions can all be fitted, with good accuracy, to exponential functions. This indicates the existence of a single relaxation process in this regime. In fact as far as quasi-elastic light scattering is concerned, in this part of the phase diagram, the density fluctuation behaviour of the microemulsion is completely dominated by the presence of a consolute critical point [2].

The situation is totally different for volume fractions $\varphi \geq 0.4$. In this high volume fraction case, the long time decay of the normalized density correlation function $C(t)$ is

no longer a simple exponential at low temperatures. A very good fit to our data can be made by using the Kohlrausch–Williams–Watts formula

$$C(t) = \exp[-(t/T)^\beta] \quad (1)$$

with parameters T and β related to the average relaxation time and the width of the distribution of the relaxation times respectively. In figure 3 we show the apparent stretched exponent β as a function of temperature for a volume fraction $\varphi = 0.42$, at the beginning of the high temperature lamellar phase, and another one at $\varphi = 0.60$, close to the onset of the glass-like transition [10]. For the higher volume fraction case, we observe the lowest value $\beta = 0.65 \pm 0.05$ at 18 °C, and then β increases sharply with increasing temperature, reaching a maximum of unity at and beyond the percolation threshold (25 °C). The overall behaviour is similar for the case of $\varphi = 0.42$, with a higher starting value of β at the lowest temperature and reaching a maximum of unity again at the percolation threshold (28 °C). For both volume fractions $\varphi = 0.42$ and 0.60, we have compared our results, in the low temperature range, with the measurements of [10] at 22.6 °C, and find complete agreement.

One other important parameter describing the density correlation function is the average relaxation time τ defined as

$$\tau = \int_0^\infty dt \exp[-(t/T)^\beta] = \frac{1}{\beta} \Gamma\left(\frac{1}{\beta}\right) T \quad (2)$$

where $\Gamma(x)$ is the gamma function. For the two volume fractions we reported here, the average relaxation rate $1/\tau$ shows a sudden change of slope as a function of temperature when crossing the percolation line at constant volume fraction. Since the droplet density correlation function shows an initial exponential decay we can also extract reliably the first cumulant. We are surprised to find that the initial decay or the first cumulant $\bar{\Gamma}$ shows the same temperature variation as $1/\tau$. It is relevant therefore to note that the collective diffusion coefficient as measured by the average relaxation rate in dense microemulsions is sensitive to the percolation phenomenon.

4. Conclusion

We observe good evidence that at sufficiently high volume fractions and below the percolation threshold, the microemulsion droplets form transient fractal clusters due to mutual attraction among them. The scattering theory based on the existence of these polydispersed fractal clusters [11] can be shown to lead to a time correlation function which decays initially as an exponential function of time but evolves continuously into a stretched exponential at long time with $\beta = \frac{2}{3}$ [12]. As the temperature is raised towards the percolation threshold, the increased thermal motions probably weaken the strong inter-droplet correlations and the droplets begin to become more mobile much as in ordinary liquids. In this latter case the density correlation function should be a purely exponential function as indicated by our experiment. However, far above the percolation threshold, as the microemulsion approaches the lamellar phase boundary, the density fluctuation may be increasingly controlled by the pre-transitional ordering, and possibly by the change of the microemulsion structure from that of isolated spherical droplets. The precise time dependence of the density correlation function is hard to predict in this regime.

Finally we would like to mention that our recent measurements of ultrasonic propagation and attenuation [13] in the same microemulsion system show that in the high

volume fraction regime, there is clear evidence of a viscoelastic behaviour. The anomalous sound absorption, however, is not correlated with the precise location of the percolation threshold. It is more likely caused by a sort of pre-transitional ordering related to the presence of the lamellar phase at higher temperatures.

Acknowledgments

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