

Experimental Evidence of Nonexponential Relaxation near the Critical Point of a Supramolecular Liquid Mixture

J. Rouch

*Centre de Physique Moléculaire Optique et Hertzienne, Université Bordeaux I,
351 Cours de la Libération, 33405 Talence Cedex, France*

P. Tartaglia

Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185 Roma, Italy

S. H. Chen

*Department of Nuclear Engineering and Center for Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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We report precise measurements of the time correlation function in a pseudo two-component water-in-oil microemulsion system made of surfactant AOT, water, and decane close to its consolute critical point and percolation threshold. Systematic studies of the intensity correlation functions using a correlator with a logarithmic sampling time show sizable deviations from a single exponential decay. It is shown that an extension of the dynamic droplet model is able to account for the nonexponential behavior at intermediate and long times. The linewidth is in satisfactory agreement with the model, which also takes into account the finite size of the microemulsion droplets.

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During the last decade great interest has been devoted to critical phenomena in supramolecular systems such as binary mixtures of water and nonionic surfactant [1] and multicomponent microemulsion systems [2]. In particular, critical dynamics of the AOT/water/decane microemulsion system has been analyzed in detail by us using a combination of the mode-coupling theory and the linear model equation of state [3]. One of the most striking features, as far as critical phenomena in supramolecular systems are concerned, is the presence of large dynamical background effects in the relaxation rate Γ of the order parameter fluctuations, when analyzed in terms of standard mode-coupling theories [4] of the transport coefficients. Using the Oxtoby and Gelbart model [5] we have been able to account phenomenologically for these effects by introducing an upper Debye cutoff wave number $q_D^{-1} = 2R_H$, where R_H is the hydrodynamic radius of the microemulsion droplet. This approach is appropriate when the correlation function shows a single exponential decay, which is probably accurate in the case of molecular fluids. The situation is different in the case of supramolecular fluids where the quasimacroscopic size of the aggregates provides a natural small length in the problem. For this latter case some phenomena far from the critical point have not been well explained. In particular, we observed experimentally a crossover phenomenon at temperature distances ΔT from the critical point around 5°C . In the regime $\Delta T \geq 5^\circ\text{C}$, the relaxation rate of the order parameter levels off and even decreases while the theory predicts a continuous increase. On the other hand, the behavior of the osmotic compressibility deduced from scattered intensity measurements shows a mirror image.

In the same AOT microemulsion system, we have recently shown that the behavior of the low frequency electrical conductivity and the droplet density correlation function are governed by a percolation phenomenon in the region of the phase diagram where the droplet volume fraction is large [6]. Static and dynamic light scattering experiments [7] performed in the vicinity of the well defined percolation locus have been accurately accounted for by assuming that the microemulsion droplets are forming transient polydispersed fractal aggregates of fractal dimension $D = 2.5$ and polydispersity index $\tau = 2.2$, these values being typical of percolation [8]. In the high volume fraction and low temperature regime, the droplet density time correlation function shows marked deviations from a single exponential decay. It evolves continuously from a single exponential decay $\exp[-\Gamma t]$ at short times to a stretched exponential $\exp[-(\Gamma t)^\beta]$ at long times with the exponent given by $\beta = D/(D + 1)$. This behavior is characteristic of strongly interacting systems with many degrees of freedom, involving different relaxation channels [9]. A very important feature of the percolation loci in this system is that it extends from low temperatures but very large volume fractions to the vicinity of the critical point at low volume fractions. The percolation point at the critical volume fraction occurs only 0.2°C below the critical consolute point. In practical terms percolation for this system occurs in the critical regime. This suggests that the behavior of the microemulsion may be governed, even in the vicinity of the critical point, by clustering phenomena characterized by the indices D and τ . This is indeed the case since a theoretical argument due to Coniglio and Klein [10] proves that the polydispersed physical clusters can

be defined close to the thermal critical point and are identified with the correlated regions of the order parameter. D and τ are given by $D = d - \beta/\nu$ and $D(\tau - 1) = d$ which become, using the known critical scaling relations, $D = (d + 2 - \eta)/2$ and $\tau = (3d + 2 - \eta)/(d + 2 - \eta)$. $\eta = 0.03$ is the Fisher's exponent, $d = 3$ is the space dimensionality, and $\beta = 0.33$ and $\nu = 0.63$ are, respectively, the critical indices for the coexistence curve and for the long range correlation length ξ . An experimental test of this theory has been made by Beysens *et al.* [11], who used an image processing technique to visualize the clusters very close to the critical point in a molecular binary liquid mixture. These authors report the value $D = 2.8$ for $d = 3$.

The aim of this paper is to report new experimental studies of the intensity correlation functions for the pseudobinary AOT/water/decane water-in-oil microemulsion system near the critical consolute point, both at short and long times. A careful analysis of the experimental data, based on a very accurate determination of the uncorrelated background, shows sizable departure of the correlation function from a single exponential decay. In order to interpret our experimental results we propose an extended version of the droplet model, which takes into account the numerical values of the exponents proposed by Coniglio and Klein [10] and the finite size effect of the microemulsion droplets. In this model both the deviation from a single exponential decay and the dynamical background of the relaxation rate of the order parameter are accounted for in a satisfactory way.

The AOT/water/decane microemulsions were prepared using the procedure previously described [3]. The critical temperature for the microemulsion, having a water to AOT molar ratio of 40.8, is $T_c = 39.85^\circ\text{C}$, and the critical volume fraction of the dispersed phase is $\phi_c = 0.10$. These values are close to those we reported for the same system [3]. For this new experiment use has been made of an ALV5000 multiple tau digital correlator having 256 channels. This correlator allows us to measure, with a very good accuracy, both the short time and long time behaviors of the intensity correlation function. While the time delay between the first sixteen channels is $0.2 \mu\text{s}$, as the delay time increases there is a progressive increase of the channel widths. As a result, the signal to noise ratio is kept constant at both short and long times. This allows a precise determination of the uncorrelated background [12] to an accuracy of the order of 1 part in 10^4 . It is essential that the background be determined to this degree of accuracy before one can quantitatively assess the deviation of the intensity correlation function from an exponential, which is rather small. We have used both a He-Ne laser having a wavelength of 632.8 nm and a solid state YAG laser pumped by diodes with frequency doubling and emitting a radiation of 532.0 nm. The temperature of the sample is kept constant with an accuracy of 1 mK for period of hours. It has to be stressed that the

scattering by this microemulsion is very weak, even very close to the critical point, because of the good refractive index matching of the microemulsion droplets and the solvent. Therefore multiple scattering is not a limitation of the experiment.

Two scattered intensity correlation functions $C^2(t)$ obtained at $\Delta T = 2.53^\circ\text{C}$ and $\Delta T = 0.05^\circ\text{C}$ are shown in Fig. 1 for the sake of illustration. The error bars are uniform and are smaller than 0.005. From this figure one can see the logarithmic spacing of the correlator channels. The background, which is not shown in the graphs, spans approximately 100 channels and can be measured on a very large time interval from 100 ms up to 100 s. It is constant in this time interval and equal to 1.0000 ± 0.0004 .

Different types of analyses can be made of the experimental results. One can first try to fit the experimental data points by a single exponential decay as was done in our previous work on the same system. In this experiment we have the possibility of calculating accurately the uncorrelated background, and we obtain results that are very similar to those reported previously [3]. However, with the increased accuracy of the measured correlation function at long times, we find some small but systematic deviations between the single exponential decay and the measured correlation function when $\Gamma t > 2$, a seldom explored time domain. The second possibility is to use the uncorrelated background as a free parameter. In this case a better fit is obtained but the fitted value of the uncorrelated background is largely outside the statistical error. These types of results have been reproduced many times for distances from the critical point ranging from $\Delta T = 0.05^\circ\text{C}$ up to $\Delta T = 10^\circ\text{C}$, and are independent of the sample and the type of laser we used. Furthermore, as we mentioned before, since the scattered intensity is very weak even close to the critical point, the correlation functions cannot be affected by multiple scattering effects. Therefore we believe that $C^2(t)$ deviates at long times from a single exponential decay, much as in the

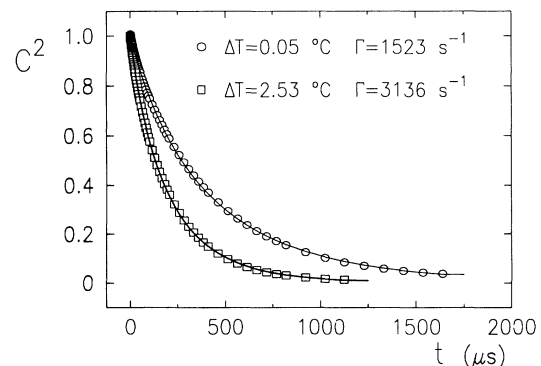


FIG. 1. The measured squared correlation functions at two temperatures, both at a scattering angle of 90° . Note the logarithmic spacing of the correlator channels. The full lines are given by Eq. (3).

case of dense systems. This effect was not noticed before in supramolecular systems because of the low accuracy of the experiments in the long time domain [13].

In order to account for these deviations we use an extended version of the so-called dynamic droplet model previously proposed by Ackerson and co-workers [14–16]. We shall treat the critical microemulsion system as made of physical polydispersed fractal clusters whose fractal dimension and polydispersity index are given by D and τ [10]. With this hypothesis we can calculate both the scattered intensity and the order parameter time correlation function using the procedure described below.

The static structure factor $S_k(q)$ of a fractal cluster containing k particles has been proposed by Chen and Teixeira [17]. It can be approximated at low values of the Bragg wave number q as $S_k(q) \approx \exp[-(qR_k)^2]$, where R_k is the radius of gyration of the cluster. Extension to polydispersed fractal clusters can be easily performed by assuming that the radius of gyration is given by $R_k = R_1 k^{1/D}$, where R_1 is the average radius of a droplet. The total structure factor is then computed by averaging $S_k(q)$ over the cluster size distribution function kc_k . For physical clusters near the critical point we assume a scaling cluster size distribution similar to the one of percolation distribution,

$$kc_k = \frac{k^{1-\tau} e^{-k/s}}{s^{2-\tau} \Gamma(2-\tau, \frac{1}{s})}, \quad (1)$$

where $\Gamma(a, z)$ is the incomplete Euler gamma function. s is the average cluster size that can be defined through the long range correlation length $\xi = R_1 s^{1/D} = \xi_0 (1 - T/T_c)^{-\nu}$, where ξ_0 is the system-dependent short range correlation length. By assuming that the physical clusters are independent scatterers, one can calculate the q -dependent scattered intensity $I(x)$ as a function of the scaling variable $x = q\xi$,

$$I(x) = \frac{\Gamma(3-\tau, u)}{\Gamma(2-\tau, (R_1/\xi)^D)} \left(\frac{\xi}{R_1} \right)^D (1+x^2)^{-D(3-\tau)/2}, \quad (2)$$

where $u = (R_1/\xi)^D (1+x^2)^{D/2}$ is related to the reduced radius of the monomer. The scattered intensity turns out to be not only a function of the scaling variable x but also of the size R_1 of the droplet. When R_1 becomes small compared to ξ this form reduces to the Ornstein-Zernike relation since $D(3-\tau)/2 = 1 - \eta/2$.

If we assume that the physical clusters are rigid, we can calculate the density time correlation function

$$C(x, u, w) = \frac{1}{\Gamma(3-\tau, u)} \int_u^\infty dz z^{2-\tau} e^{-z-w} z^{-1/D}, \quad (3)$$

where $w = D_1 R_1 q^3 t (1+x^2)^{1/2}$ is the reduced time. This quantity also explicitly depends on the nature of the sample via both R_1 and the diffusion coefficient of the microemulsion droplet D_1 . We express the latter as

$D_1 = RK_B T / 6\pi\eta R_1$, where R is a fitting parameter. From these equations it is easy to calculate the reduced first cumulant $\Gamma^*(x, x_1) = \Gamma/D_1 R_1 q^3$, with $x_1 = qR_1$,

$$\Gamma^* = \frac{3\pi}{8} \frac{\Gamma(3-\tau, x_1^D) \Gamma(3-\tau - \frac{1}{D}, u)}{\Gamma(3-\tau - \frac{1}{D}, x_1^D) \Gamma(3-\tau, u)} \left(1 + \frac{1}{x^2}\right)^{1/2}, \quad (4)$$

which explicitly depends on the droplet size. The results we obtain bear striking differences with those previously deduced from the mode-coupling [4] or decoupling [18] theories, since they contain a cutoff related to the size of the droplets. However, in the limit where R_1 is small compared to the long range correlation length ξ , the results reduce to the known mode-coupling results.

In Figs. 1 and 2 we report two samples of the measured $C^2(t)$ and the very good fits to the experimental data, spanning three decades from a delay time of 1 μ s up to more than 1 ms. The dashed lines in Fig. 2 refer to an exponential fit. We use realistic values of the parameters, namely, $\xi_0 = 10 \pm 2$ \AA , $R_1 = 40 \pm 10$ \AA , and $R = 1.2 \pm 0.1$ in the temperature range we studied. We use the renormalized critical exponent $\nu = 0.71$ [3] since in reality the AOT/water/decane microemulsion is a ternary system. These values are in agreement, within the error bars, with previous measurements [3,19,20].

The theoretical model we propose for describing $C^2(t)$ accounts well for the small but sizable deviation from a single exponential decay we observed experimentally in the long time domain $\Gamma t > 2$. We also deduce the reduced linewidth, Eq. (4), and plot it as a function of the scaling variable x in Fig. 3. Since it explicitly depends on the size of the droplets, we plot it for different values of the parameter x_1 . The lines, which are the theoretical predictions, correspond to different values of x_1 , the one for $x_1 = 0$ being very close to Kawasaki's result [4]. A very good agreement between the theoretical model we propose and the experiment is obtained in the critical regime, the hydrodynamic regime, and even in the

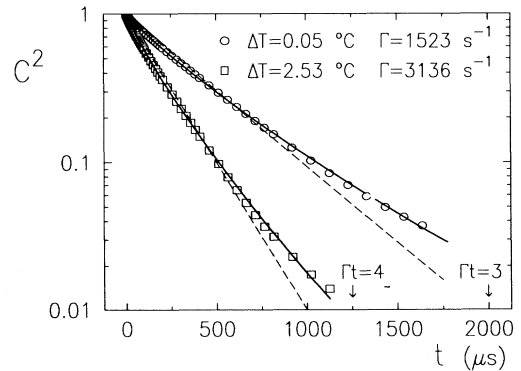


FIG. 2. Measured squared correlation functions showing deviations from the exponential behavior. The dashed lines represent the fit by an exponential; full lines are obtained from Eq. (3).

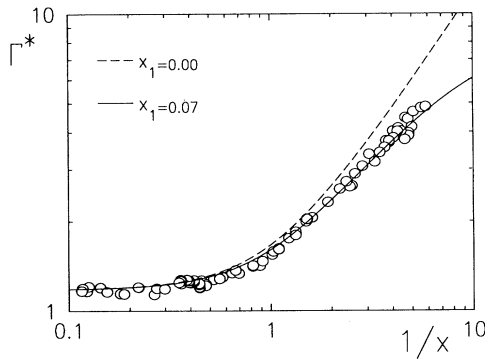


FIG. 3. The reduced linewidth as a function of the scaled variable x . The dashed and solid lines are obtained from Eq. (4), respectively, for $x_1 = 0$ and $x_1 = 0.07$, appropriate for the AOT microemulsion. Circles are the measurements taken at a constant 90° scattering angle but at a variable temperature distance from the critical point $\Delta T = 0.01$ K to 10 K.

crossover regime corresponding to temperatures 10°C far away from the critical point. This can be achieved with the same values of ξ_0 and R_1 reported above. We remark that in the previous analyses of critical phenomena in supramolecular aggregates the relaxation rate Γ is taken to be the sum of a critical part, which can be calculated using the mode-coupling theory, and a system-dependent background part which depends explicitly on the Debye cutoff parameter q_D . We have shown phenomenologically that the dynamical background was roughly proportional to the size of the aggregates, leading to a correction of the order of 10% of the total linewidth when close to the critical point. In the present model the dynamical background term enters in a natural way into the theory and it is physically provided by the lower bound of the integral defining the correlation function. However, the price we have to pay is the introduction of the multiplicative constant $R = 1.2 \pm 0.1$ in the definition of D_1 , in a way similar to the renormalization group [21] or mode-coupling theories [4].

In summary, the order parameter time correlation function is shown experimentally to deviate significantly from a single exponential function in a time range $\Gamma t < 4$. This is achieved through a much better accuracy of the measurements of the time correlation function at large times and a more accurate determination of the uncorrelated background. In the range of delay times from $3 \mu\text{s}$ to $2000 \mu\text{s}$ the correlation function can be fitted with the function given in Eq. (3). The parameters contained in this expression are D , τ , u , and Γ . The first two parameters are fixed by the values of the critical indices, while u is related to the size of the droplets and the correlation length. As a result, one obtains a unique average relaxation rate Γ from the fitting of the correlation func-

tion. We have shown for the first time that the dynamic droplet model, which identifies the clusters of droplets and the correlated order parameter regions, as suggested by the vicinity of the critical point and the percolation threshold, gives in a satisfactory way $\Gamma(q\xi)$, taking also into account the finite size of the microemulsion droplets.

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