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LETTER TO THE EDITOR

Experimental evidence of a crossover in critical behaviour of water-in-oil microemulsions

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Abstract. An extensive static and dynamic light-scattering experiment on a water-in-oil microemulsion system (water/n-decane/AOT) showed that the critical dynamics of this three-component microemulsion is completely governed by a Debye cut-off wavenumber q_D , which is equal to the inverse diameter of the microemulsion droplet. Furthermore, we found occurrence of a crossover phenomenon for the statics and dynamics, at a correlation length ξ_c such that $q_D \xi_c = 1$, the crossover temperature being at about 10 °C below the critical temperature.

In the vicinity of room temperature certain three-component mixtures of water, n-decane (oil) and a surfactant, sodium di-2-ethylhexylsulphosuccinate (AOT), form water-in-oil microemulsions of well defined droplet size determined by the molar ratio ω of water to AOT (see [1], [2] and references therein, [3]). For a solution with $\omega = 40$, having a volume fraction of the droplets, $\varphi_c = 0.098$, and on raising the temperature, one observes a lower consolute point at $T_c = 39.860$ °C. Above T_c the solution separates into two microemulsion phases of different composition but with the same ω -ratio [2, 4]. Keeping ω constant and changing the amount of n-decane, allow us to vary the volume fraction of the droplets but not their radii [2, 3]. In this respect ω can be considered [4], at least to a first approximation, as a field variable in the sense of Griffiths and Wheeler [5], i.e. a quantity that has the same value in the ordered and the disordered phase. Therefore a water-in-oil microemulsion can be regarded, when close to the phase transition temperature, as a pseudo-binary system with the droplet volume fraction as the order parameter [2] (at least for small values of φ), having a Widom–Fisher [6, 7] type renormalisation of the critical indices, since in reality it is a ternary system [8].

In this Letter we will briefly summarise a new and extensive static and dynamic light-scattering experiment including intensity, turbidity and relaxation rate measurements along the critical iso-volume fraction line, and off-critical paths of approach to the critical point, over a wide temperature range. The full set of data will be reported in a forthcoming paper [9], but we shall here focus on the most important new results obtained for the sample with the critical volume fraction. We have found an experimental

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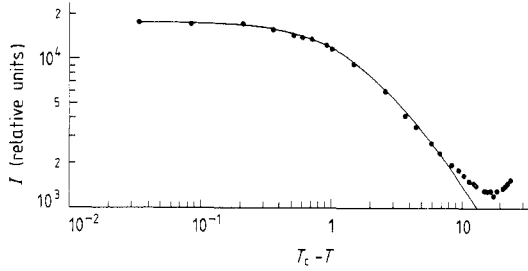


Figure 1. A log–log plot of the total scattered intensity versus $T_c - T$. The full circles are the experimental results whereas the full curve is the best fit to the data according to equation (1).

evidence of a very low value for the Debye cut-off wavenumber q_D , which turns out to be equal to the inverse of the diameter of microemulsion droplets [10]. Moreover, a crossover temperature $\tau_c = 29^\circ\text{C}$ exists at which $q_D \xi_c = 1$, where ξ_c is the crossover correlation length. In the vicinity and below τ_c , the static light-scattering intensity no longer follows the well known Ornstein–Zernike behaviour, but is dominated by the single-particle scattering of the microemulsion droplets. The situation is similar for the dynamic light scattering for which there is a crossover of the order parameter relaxation rate from the critical slowing-down regime to the Brownian dynamics regime.

The scattered intensity I_s in a critical pseudo-binary mixture, whose order parameter correlation function obeys the Ornstein–Zernike–Fisher relation, can be written as $I_s = KS(q)$, where K is a constant factor depending on the wavelength of the incident light, the index of refraction of the microemulsion and the scattering geometry. The interdroplet structure factor $S(q)$ in the small- q region is given by

$$S(q) = \rho k_B T \chi_T / (1 + q^2 \xi^2)^{1 - \eta/2} \quad (1)$$

where ρ is the number density of the microemulsion droplets, χ_T is the diverging response function of the order parameter (isothermal osmotic compressibility) whose constant amplitude is χ_0 , q the magnitude of the transfer wavevector, $q = (4\pi n/\lambda)\sin(\theta/2)$, $n = 1.410$ is the refractive index of the critical sample at the laser wavelength $\lambda = 632.8$ nm and θ is the scattering angle, usually 90° in our experiment. We assume the Fisher index $\eta \approx 0$. The correlation length ξ behaves like $\xi = \xi_0 \varepsilon^{-\nu^*}$ with $\varepsilon = |T - T_c|/T_c$ and $\nu^* = \nu/(1 - \alpha) \approx 0.70$ is a renormalised critical exponent obtained from a renormalisation group calculation of the critical indices, α being the specific heat anomaly index. In an analogous way, χ_T diverges like $\chi_T = \chi_0 \varepsilon^{-\gamma^*}$, where $\gamma^* = \gamma/(1 - \alpha) \approx 1.40$, also from renormalisation group calculation [9]. In fitting the intensity data, we first subtract from the measured intensity a constant background which amounts to 4% of the total scattering. Physically this background corresponds to the non-critical scattering from the individual droplets which is present in the solution at all temperatures. Figure 1 shows the scattered intensity as a function of $T_c - T$ in a log–log scale. The full circles are the experimental points and the full curve is the calculation based on equation (1). In using this equation we employed the renormalised values of the critical exponents γ^* and ν^* and chose $\xi_0 = (13.5 \pm 1.5) \text{ \AA}$. It is seen that the fit between theory and experiment is excellent up to $T_c - T = 6^\circ\text{C}$. If we take the exponents to be the unrenormalised values, then the fit is much worse for any choice of ξ_0 . The value of ξ_0 is considerably larger than 2–3 Å, the range usually found for pure fluids or binary molecular liquid

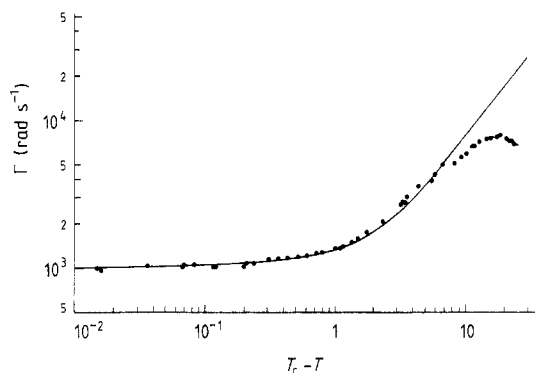


Figure 2. A log–log plot of the relaxation rate versus $T_c - T$. The full circles are the experimental results, whereas the full curve is the best fit to the data according to equations (2) and (3).

solutions [8, 11, 12]. However, it is of the same order of magnitude as values found for non-ionic critical micellar solutions (see [13] and references therein) and also as given by Huang and Kim [14] for the same mixture, i.e. $(12.2 \pm 2.0) \text{ \AA}$. When $T_c - T$ is larger than $6 \text{ }^\circ\text{C}$ the experimental points deviate from equation (1), signifying a transition to a non-critical behaviour in which the osmotic compressibility as a function of temperature follows the behaviour of a non-ideal solution.

The relaxation rate Γ , which is the inverse of the correlation time of the order parameter fluctuations, has also been measured from $15 \text{ }^\circ\text{C}$ up to T_c by photon correlation spectroscopy. Figure 2 depicts Γ as a function of $T_c - T$ in a log–log plot; the full circles are the experimental data. When far from T_c , for T ranging from $15 \text{ }^\circ\text{C}$ to $30 \text{ }^\circ\text{C}$, we observe first an increase then a decrease of the linewidth that reaches a maximum around $22 \text{ }^\circ\text{C}$ for a wavevector $q = 1.98 \times 10^5 \text{ cm}^{-1}$ ($\theta = 90^\circ$). The same phenomenon appears by changing the scattering angle to 33° , corresponding to $q = 8.1 \times 10^4 \text{ cm}^{-1}$. This behaviour exactly mirrors the behaviour of the scattered intensity in this temperature range. SANS [1, 2] measurements show that one can expect to observe in this temperature range Brownian motion of the quasi-monodisperse microemulsion droplets. Under such circumstances it is known [15] that the relaxation rate for a system of interacting particles behaves like $\Gamma = q^2 D_0 / S(q)$ where D_0 is the Stokes–Einstein diffusion coefficient of particles of hydrodynamic radius R_H given by $D_0 = k_B T / 6\pi\eta R_H$, η being the shear viscosity of the sample. The shear viscosity has been very accurately measured [16] for this microemulsion system in the whole concentration and temperature range, including the critical region. We therefore deduced from the data away from the critical point, $R_H S(0) = (83 \pm 5) \text{ \AA}$ independent of temperature and concentration. From SANS [1, 2] measurements it is known that the mean droplet radius is about $(68 \pm 5) \text{ \AA}$ and thus the hydrodynamic radius R_H obtained from light scattering is consistent with SANS values.

When close to the critical point, the viscosity data from [16] can be written in the form $\eta = \eta_B (q_D \xi)^\psi$ where η_B is the background shear viscosity, ψ a universal exponent and q_D the Debye cut-off of the largest wavevector. When written in terms of ε the viscosity power-law exponent was found experimentally to be 0.03, whereas its theoretical value is around 0.04. These two values are sufficiently close to each other that one can expect to apply mode-coupling theories [17–20]. Such an attempt has already been made [21] but, in order to fit their data in the critical regime, $x \equiv q\xi > 1$, these authors

were obliged to use an amplitude factor (see equations (3) and (4) below) $R = 1.2$, whereas in mode-coupling theories it has a universal value $R = 1.027$ [11]. The choice of $R = 1.2$ leads further to a rather large discrepancy between theory and experiment in the hydrodynamic regime where $x < 1$.

We have been able to fit our data, and also those of [21], from the critical and on off-critical constant volume fraction lines [9], by using a more complete mode-coupling theory including background effects on the transport coefficients [19] in conjunction with a linear model equation of state for the calculation of the correlation length for the off-critical lines [22]. In this model the transport coefficients, like the shear viscosity and the relaxation rate, can be written as a sum of a background and a critical part

$$\Gamma(q, T) = \Gamma_C(q, T) + \Gamma_B(q, T). \quad (2)$$

As we showed in [8] and [9], these quantities are given by

$$\Gamma_B(q, T) = R(k_B T q^3 / 6\pi\eta) 0.675(q/q_D)^{1-\psi} (1 + 1/x^2)x^\psi \quad (3)$$

$$\Gamma_C(q, T) = R(k_B T q^3 / 6\pi\eta) K(x) / x^3 \quad (4)$$

where $K(x) = \frac{3}{4} [1 + x^2 + (x^3 - 1/x)\tan^{-1}x]$ is the Kawasaki universal scaling function for the relaxation rate [18]. Equations (2) and (4) can be compared with the experimental results provided that the Debye cut-off wavenumber q_D is known. This can be obtained using the argument [10] that the size of the microemulsion droplet sets the microscopic length scale and determines the reciprocal of the wavenumber cut-off entering in the mode-coupling theory. Let us therefore put $2R_H = q_D^{-1}$. Since $2R_H \approx (166 \pm 10)\text{\AA}$ we get $q_D = 0.60 \times 10^6 \text{ cm}^{-1}$. This value is very small compared to what is obtained in the case of simple fluids and binary or ternary molecular mixtures [8, 11], i.e. $q_D \approx 2 \times 10^7 \text{ cm}^{-1}$. Using the theoretical estimate $2R_H = q_D^{-1}$ in equation (3) we get a very nice agreement between the theory and the experimental results both in the deep critical and in the hydrodynamic regime, for x ranging from 0.2 to 30. This is indicated in figure 2 by a full curve. We also note that the best fit to the data in [14] by this method leads to $q_D = (0.65 \pm 0.05) \times 10^6 \text{ cm}^{-1}$. To demonstrate more vividly the extent of agreement between the mode-coupling theory and the experimental results we plot in figure 3 the reduced relaxation rate, defined as $\Gamma^* \equiv (\Gamma - \Gamma_B)(Rk_B T q^3 / 6\pi\eta)^{-1}$ against x for all the data on this system. The symbols represent the experimental data and the full curve is the theoretical prediction given by $x^{-3}K(x)$. The details of the analyses of the data of the off-critical lines will be reported in [9].

Let us now make some comments on the analyses of the experimental results. Since q_D is small, the background relaxation rate Γ_B calculated from equation (3) is very large even in the deep critical regime, $x = 30$, where it accounts for roughly 20% of the total relaxation rate. This explains the fact that when Γ_B is not properly taken into account it is necessary to set $R = 1.2$. It is worth stressing that the mode-coupling theoretical value of the amplitude factor is $R = 1.027$ [20], and this is the value that has been used throughout this paper. In critical pure fluids or multicomponent systems [8, 12] consisting of small molecules, q_D^{-1} is of the order of the range of the interatomic potential, say a few \AA . Then even far from the critical point one has always $q_D \xi \gg 1$. In critical water-in-oil microemulsions we have shown that the prediction $q_D^{-1} = 2R_H$ is very well satisfied, and since $2R_H$ is large we found $\xi_c \approx 2R_H$ rather close to the critical point. This crossover appears, in the case of our critical sample, only 10°C below the lower consolute point. We can therefore fix the crossover temperature at $\tau_c = 29^\circ\text{C}$. Above τ_c the water-in-oil microemulsion obeys very accurately the universal critical laws with renormalised critical

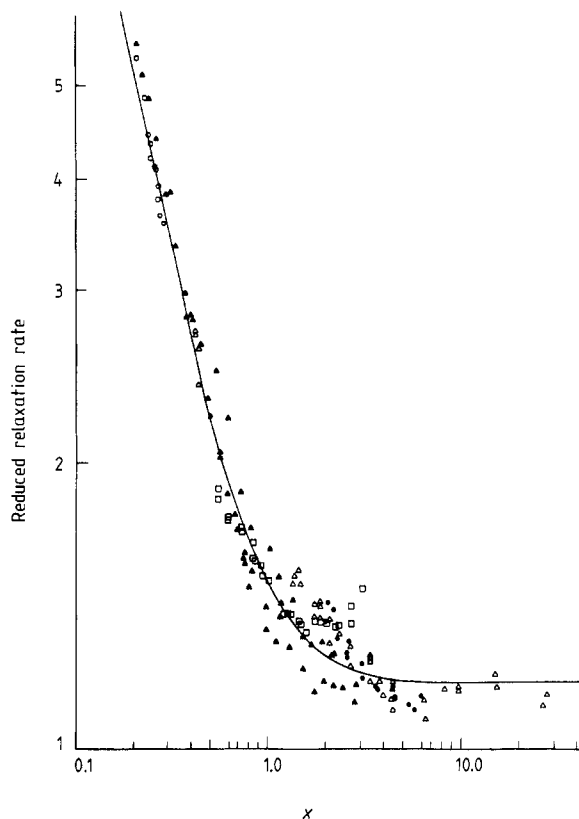


Figure 3. A log-log plot of the reduced relaxation rate Γ^* as a function of $x = q\xi$. Open triangles: critical volume fraction $\varphi_c = 0.098$; open circles: $\varphi = 0.22$; full circles: $\varphi = 0.064$; squares: $\varphi = 0.192$; full triangles: data from [21]. The full curve is the prediction of the mode-coupling theory.

indices. Below τ_c we observe the Brownian motion of spherical quasi-monodisperse droplets. Around and below τ_c the behaviour of strongly divergent quantities such as the osmotic compressibility or the relaxation rate changes completely, and they no longer can be treated using the conventional critical phenomena theories. As a final comment it is worth noting that the parameter $q_D^{-1} = 2R_H$ which can be measured only very far from T_c in the single-particle scattering regime, in fact governs the critical dynamics of the mixture close to T_c in a decisive way, via its influence to the shear viscosity and the order parameter relaxation rate.

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