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2000 J. Phys.: Condens. Matter 12 A459

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Critical behaviour of complex systems

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Received 12 August 1999

Abstract. An overview of recent results of the critical behaviour of micellar systems is given. It is found that it is possible to define a master curve for the effective critical exponent β_{eff} for systems that show a monotonic crossover. It is also shown that the critical behaviour of the osmotic susceptibility of a metastable critical system is the same as that of stable systems. Finally the two-exponential decay of the fluctuations of the order parameter is discussed.

1. Introduction

The range of universal critical behaviour in complex fluids (micelles, polymers, ionic fluids etc) is so small that it may not be experimentally accessible. In some cases, they exhibit a complex non-monotonic crossover from Ising to mean field behaviour [1]. Due to the limited extent of the asymptotic (Ising) regime, understanding the thermodynamic behaviour in the crossover region is extremely relevant from an experimental point of view in order to avoid puzzling results with respect to the experimental values of the critical exponents [2].

Ionic micellar systems are interesting since depending on the salt content their phase diagram may present an intersection between a critical line and a surface of first order phase transitions [3]. On one hand, this makes them useful for testing some of the theoretical predictions for systems near a critical end point (CEP) [4]. On the other hand, in driving the system below the CEP, they offer the possibility of studying the critical behaviour of systems in a metastable state.

In recent years, it has been found that for some systems the decay of the order parameter fluctuations is more complex than for simple fluids [5–7]. Although such a behaviour was already predicted by the asymmetric H model many years ago [8], two-exponential correlation functions had only been reported for a mixture near its vapour–liquid critical line [9].

In this work we will report some experimental results for an ionic micellar system: dodecylammonium chloride (DAC) + water + KCl. Since the salt content is the same in the two coexisting phases, the system can be considered as pseudobinary. The system shows an upper critical solution temperature. At low values of [KCl] the critical line intercepts the Krafft line, i.e. the line at which the a solid phase of pure surfactant is in equilibrium with the liquid.

In section 2 we will discuss the behaviour of the order parameter for three different values of [KCl], and compare it with other systems previously measured. In section 3 we present the results of the osmotic compressibility χ for a metastable critical sample. Finally, in section 4 we comment on the decay of the order parameter fluctuations for the same sample.

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2. Coexistence curves and order parameter

We have obtained detailed coexistence curve data for the poly(oxyethylene) (C_7E_5) + water and the DAC + water + KCl system at the three values of $[KCl]/M$: 0.305, 0.280, 0.265. The order parameter is well described by the Wegner expansion [10]:

$$\Delta w = B_0 t^\beta (1 + B_1 t^\Delta + B_2 t^{2\Delta} + \dots) \quad (1)$$

where $\beta = 0.325 \pm 0.001$ and $\Delta = 0.51 \pm 0.02$ are critical exponents; $t = (T - T_c)/T_c$; and the B_i are critical amplitudes. Both in the C_7E_5 and the DAC systems, the range of validity of the simple scaling is small ($t < 10^{-4}$) when compared to mixtures of simple fluids [10]. In the DAC systems this range decreases as the CEP is approached. Also, for the above systems $B_1 > 0$, which means that the effective exponent $\beta_{eff} = d \log(\Delta w) / d \log t$ presents a monotonic crossover from the Ising value ($\beta = 0.325$) to the mean-field value ($\beta = 0.5$) upon increasing t [1]. According to Fisher [2] and Bagnuls and Bervillier [11], the crossover will depend upon the internal scale length Λ characteristic of each system. As a consequence, it should be possible to define a universal crossover curve β_{eff} against t_r , where $t_r = t a_t$, where a_t is related to Λ [11]. Figure 1 shows the crossover master curve for β_{eff} for the micellar systems studied in this work, and for other systems previously studied and for which $B_1 > 0$. We have considered $a_t = 1$ for the methanol + *n*-heptane system since $\beta_{eff} \approx 0.325$ over the whole experimental range. In order to make a more strict test of this theoretical prediction, we have included in figure 2 the systems polystyrene + acetone and 2-butanol + water which are not too far from a double critical point. In these two cases the field t is defined according to Malomuzh and Veytsman [12]. The quality of the crossover curve is very good. When values of β_{eff} for some ionic fluids are considered they deviate from the master curve. This reflects the need of using two crossover parameters for each system, as pointed out by Anisimov *et al* [1].

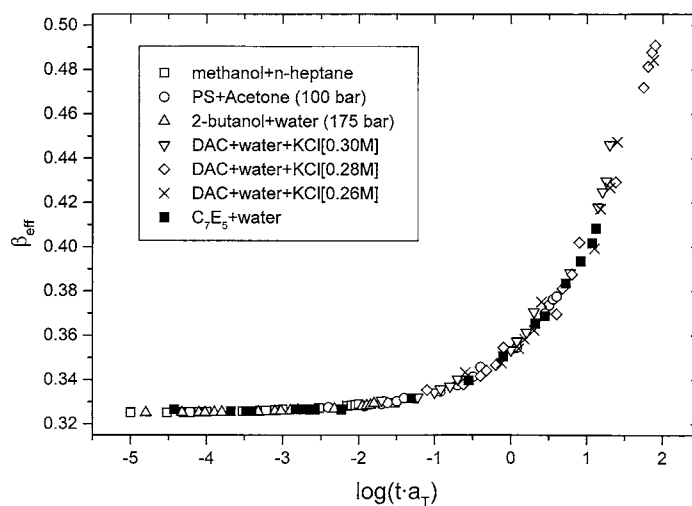


Figure 1. Master curve for the effective critical exponent of the order parameter in different systems. The shift factor a_T has been calculated with respect to the methanol + *n*-heptane system. The field t for the systems polystyrene + acetone and 2-butanol + water has been calculated according to [12].

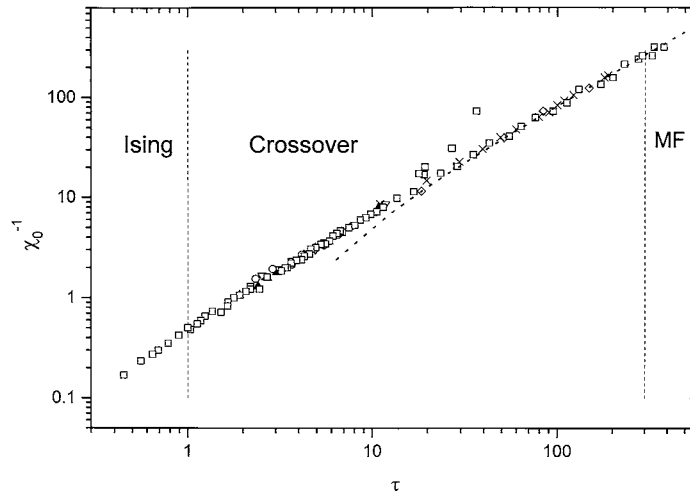


Figure 2. Universal crossover function for the reduced susceptibility χ_0 as a function of the reduced temperature $\tau = t/Gi$. The dashed line represents the mean-field (MF) behaviour. The empty squares correspond to the DAC + water + KCl system at the four values of [KCl] studied in this work. The crosses, circles and full triangles correspond to the microemulsion of Seto *et al* [15].

3. Static critical behaviour of a micellar system in a metastable state

In previous works we have studied the correlation length ξ and the osmotic compressibility χ for the DAC system with the three values of [KCl] mentioned above [13]. It is possible to undercool the system below the Krafft line, which opens the possibility of exploring the critical behaviour of a metastable system. In this work, we have chosen the value [KCl] = 0.205 M.

From the q and T dependences of the intensity of the scattered light, we have obtained the critical exponents ν associated with ξ , and γ associated with χ . As for the systems above the Krafft line, their values agree with the Ising ones within the experimental error when one correction term is used in the Wegner expansion. As in the case of the coexistence curves, the amplitude of the first correction term is positive, thus one may expect a monotonic crossover from the Ising to the mean-field values of ν and γ . Also, the range of validity of simple scaling for ξ and χ is almost one order of magnitude larger than for the order parameter.

Belyakov and Kiselev have proposed a phenomenological extension of the crossover process as described by the ε -expansion theory [14]. They arrived at the following expression for the susceptibility

$$\tau = (1 + 2.333\chi_0^{\Delta/\gamma})^{(\gamma-1)/\Delta} [\chi_0^{-1} + (1.2333\chi_0^{\Delta/\gamma})^{-\gamma/\Delta}]$$

$$\tau = t/Gi \quad \chi_0 = \chi a_0 Gi \quad (2)$$

where a_0 is related to the bare mass term of the free energy, and Gi is the Ginzburg number. As observed in figure 2, equation (2) is able to describe the susceptibility data of the DAC systems for the four salt concentrations considered in the present work. Figure 2 also includes the results of Seto *et al* for a three-component microemulsion [15]. The present set of results covers the whole crossover region from the asymptotic Ising region ($\tau < 1$) to the mean-field one ($\tau > 300$), and points out that the critical metastable system behaves like the stable ones. Similar conclusions can be drawn from the ξ data.

4. Two-exponential decay of dynamic light scattering

In a previous work [7] we found that the intensity correlation functions obtained for the DAC + water + KCl systems could not be described by a single exponential decay except far from the critical temperature. We have carried out a similar study for the metastable system with $[\text{KCl}] = 0.205 \text{ M}$. Figure 3 shows that the relaxation time τ distributions are monomodal far from T_c , while they are bimodal near the critical point. The mode corresponding to smaller τ (fast mode) presents a diffusive ($\sim q^2$) behaviour, and there is a smooth continuity with the single mode found far from T_c . The behaviour of the diffusion coefficient corresponding to the fast mode $D_f = \Gamma_f/q^2$ (Γ_f being the decay rate characteristic of the fast mode) for the metastable sample was found to be the same as for other samples above the Krafft temperature. In contrast, for the slow mode Γ_s shows a crossover from a q^2 to a q^3 dependence, as shown in figure 4. Since for this system $\text{Gi} = 6 \times 10^{-5}$, all the data shown in figure 4 are in the crossover and MF regimes (see figure 3).

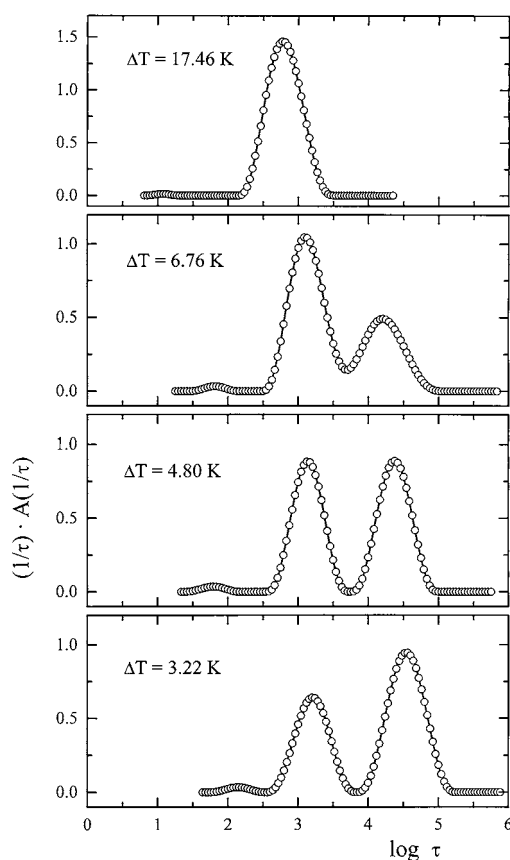


Figure 3. Relaxation time distribution functions for the metastable system DAC + water + KCl (0.205 M) corresponding to a scattering angle of 90° and for different values of $\Delta T = |T - T_c|$.

In order to obtain the critical D_c and background D_u contributions from Γ_f and Γ_s we have followed the same method as in [7]. The results lead to two main conclusions: first, the two modes are essentially decoupled, thus the fast mode contains mainly the background contribution to the diffusion coefficient, and the slow mode the critical contribution. Second,

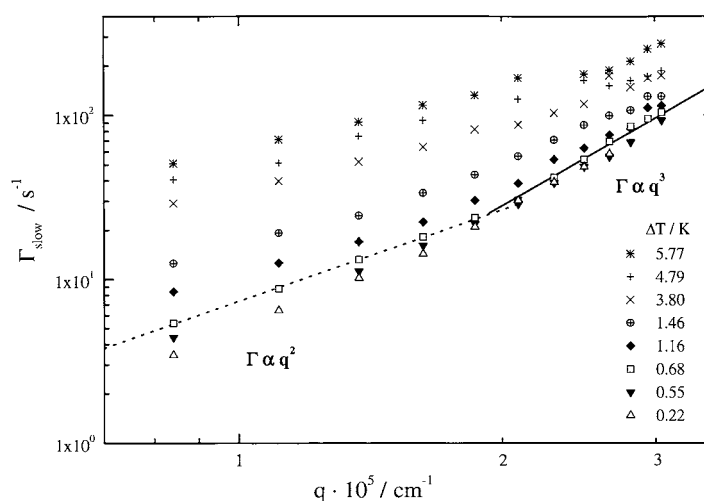


Figure 4. Temperature and wavevector (q) dependence of the decay rate of the slow-relaxation mode (Γ_{slow}) for the metastable system with $[KCl] = 0.205$ M. Notice the crossover from a q^2 to a q^3 regime. $\Delta T = |T - T_c|$.

the critical reduced diffusion coefficient is well described by the Kawasaki function derived from the mode coupling theory. This is in agreement with recent predictions of Anisimov *et al* [16], and with the findings for the DAC systems above the Krafft line [10].

Acknowledgments

This work was supported in part by DGES under grant 96/609 and by Fundación Ramón Areces.

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