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Double-exponential relaxation near the critical point of an ionic micellar system

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The system dodecylammonium chloride+water+KCl $(0.30M)$ has been studied using dynamic light scattering near the liquid-liquid critical point. The correlation functions have been found to be single-exponential for temperatures well above the critical one, while a new decay process at longer times becomes evident at $|T-T_c|<4$ K. The correlation functions can be well fitted either with the sum of two exponentials or with a double-exponential distribution using Laplace inversion methods. The decay rate associated with the fast relaxation mode has a diffusive character over the whole temperature range, while the decay rate of the slow mode is diffusive in the long-wavelength limit; and at higher wave vectors q shows a crossover from a q^2 to a q^3 dependence. The relative weight of the amplitude of the slow relaxation mode decreases as the temperature and the angle of observation increase. The diffusion coefficient associated with concentration fluctuations has been calculated from both relaxation modes using the characteristics of the matrix equation that relates the transport coefficient matrix and the susceptibility matrix for asymmetric binary fluids. It has been analyzed in terms of the predictions of the mode-coupling theory, and good agreement is found when experimental shear viscosity data are used together with correlation lengths obtained from static light-scattering measurements. The apparent relaxation rate associated with the background contribution has a clear diffusive character, i.e., q^2 dependence. It shows a smooth temperature change and far from T_c it agrees with the values expected for the micellar dynamic. [S1063-651X(96)00711-8]

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I. INTRODUCTION

The behavior of micellar systems near a critical point has attracted much attention in the last few years [1]. Although some experiments lead to critical exponents different from those of the three-dimensional (3D) Ising model, recent work has clearly established that this is not the case [2]. However, there exist some specificities linked to the fact that micelles seem to act as units through the critical region. As discussed by Fisher [3], the hydrodynamic radius of the micelles sets a microscopic scale in the system that can lead to apparent critical exponents different from the 3D Ising ones. On the other hand, the value of the critical amplitude of the correlation length ξ_0 is frequently an order of magnitude larger than in simple binary mixtures [4]. According to the Ginzburg criterion [5], this may reduce significantly the size of the critical region, thus making it more difficult to analyze some of the experimental results, and making it necessary to perform the measurements rather close to the critical point. Similar conclusions, related to the apparent nonuniversal values of the critical exponents and to the shrunken size of the asymptotic critical region, are arrived at from a theoretical model developed by Martinez-Meckler *et al.* [6].

Contrary to the relatively well understood critical behavior of the static properties in micellar systems, the situation is less satisfactory with respect to the critical dynamics. The critical dynamics of simple binary mixtures has been studied in detail [7], and the experimental results show a remarkable agreement with the predictions of mode-coupling and renormalization-group theories of dynamic critical phenomena [8–10]. As described by Hohenberg and Halperin [11], the key factor for the critical slowing down of the order-parameter fluctuations is the nondissipative coupling between the order parameter and the transverse part of the momentum density. For a real binary fluid, for which the coexistence curve is asymmetric with respect to the composition axis, the concentration fluctuations are described by the order parameter [11]

$$c(\overline{x})=[\langle\rho_A\rangle\rho_B(\overline{x})-\langle\rho_B\rangle\rho_A(\overline{x})]/\langle\rho\rangle^2, \tag{1}$$

where ρ_A and ρ_B are the mass densities of the two species. The binary fluid has an additional long-wavelength diffusive mode $u(\overline{x})$ that in mixtures plays a role analogous to the thermal fluctuation density in binary fluids near the vapor-liquid critical line. It is a linear combination of ρ_A and ρ_B and the energy density $e(\overline{x})$, chosen such that $u(\overline{x})$ and $c(\overline{x})$ are orthogonal to each other in the sense that their cross-correlation functions vanish at long wavelengths in equilibrium. Note that $c(\overline{x})=[\rho_B(\overline{x})/\rho_A(\overline{x})]-\rho_B/\rho$ for small deviations from equilibrium, and $c(\overline{x})$ is loosely referred to as the concentration fluctuation. The binary fluid has two long-wavelength (i.e., $q\to 0$) diffusive modes. These two normal modes are the eigenvalues of the matrix equation

$$\overline{D}q^2=\overline{\Lambda}\,\overline{S}^{-1}q^2 \tag{2}$$

that can be explicitly written as

$$\begin{vmatrix} D_c & D_1 \\ D_2 & D_u \end{vmatrix} = \begin{vmatrix} \Lambda_{cc} & \Lambda' \\ \Lambda' & \Lambda_{uu} \end{vmatrix} \begin{vmatrix} S_{cc}^{-1} & 0 \\ 0 & S_{uu}^{-1} \end{vmatrix}, \tag{3}$$

with the elements of the transport matrix defined according to

$$\Lambda_{i,j}=\lim_{q,\omega\to 0}\frac{\omega}{iq^2}S_{i,j}(q,\omega), \tag{4}$$

and the $S_{i,j}$ are the elements of the static susceptibilities matrix. The indices i and j are either c or u, thus making S diagonal. In the vicinity of the consolute point only S_{cc} diverges strongly, while S_{uu} does not. On the basis of the mode-coupling theories, it has been found that one of the eigenvalues of Λ diverges at T_c, while the other one remains finite [12]. Furthermore, the diverging part of Λ is simply Λ_{cc}, so that in the asymptotic critical region Λ and S may be simultaneously diagonalized.

For binary liquid mixtures, the decay of the order-parameter fluctuations $\Gamma(q)$ is most frequently obtained from photon correlation spectroscopy experiments. Despite the fact that the theory predicts the existence of two relaxation modes near a consolute point [11], there is a very limited number of experiments reporting nonsingle exponential correlation functions $g^1(q,t)$. Ackerson and Hanley [13] studied a mixture of methane+ethane near the vapor-liquid critical point, and found two exponential decays for $g^1(q,t)$. Similar results were reported by Miura *et al.* [14] for mixtures of ^{3}He+^{4}He. Also the scattering data of Hair *et al.* [15] and Yajima *et al.* [16] on polymer blends near the critical point have revealed bimodal correlation functions. The authors have analyzed their results in terms of Eqs. (1)–(4), concluding that their systems were still outside the asymptotic scaling regime for the critical dynamics, and therefore a detailed study of the applicability of the predictions of the mode-coupling theory for their Λ_{cc} data was not possible. Gallagher *et al.* [17] have reported bimodal autocorrelation functions in a study of polystyrene suspensions in a near-critical binary liquid mixture. The low time process (fast mode) was attributed to the concentration fluctuations, while the long-time process (slow mode) was attributed to the Brownian motion of the latex spheres. Finally, Rouch *et al.* [18] and Hamano *et al.* [19] have reported nonexponential correlation functions for a microemulsion. They found that in order to describe the long-time behavior of the correlation function it was necessary to use a stretched exponential function: $\exp[-(\Gamma t)^{\beta}]$ with $0<\beta<1$.

We have recently studied the critical behavior of an ionic micellar system: dodecylammonium chloride (DAC) +water+KCl, for different salt concentrations. Both the coexistence curve [20] and the static light-scattering data [21] confirm that the system can be described with 3D Ising critical exponents. Preliminary dynamical experiments revealed correlation functions that depart from a single-exponential behavior. Therefore we considered it interesting to carry out a detailed study of the decay rate $\Gamma(q,T)$ for the DAC +water+KCl system near the liquid-liquid critical point, and a comparison with the mode-coupling predictions for Γ_c.

The rest of the paper is organized as follows. Section II gives some details of the experimental procedure. The data and the methods followed from the data analysis are summarized in Sec. III, and the discussion of the results is made in Sec. IV. Finally, Sec. V summarizes the conclusions.

II. EXPERIMENT

Dodecylammonium chloride (DAC) was synthesized, from previously distilled dodecylamine (Aldrich RPE) dissolved in benzene, by bubbling ‘‘*in situ*’’ prepared HCl, under continuous stirring. The product was recrystallized in benzene until no amine was found, and the purity was checked by spectroscopic methods and differential scanning calorimetry. Also the critical micellar concentration in pure deionized water (Millipore Milli-Q) was determined by conductivity and surface tension, giving a value of $1.5\times10^{-2}\ M$, in agreement with previously reported data [22]. Potassium chloride, KCl, was Carlo Erba RPE, purity >99%, and was dried under vacuum at 100 °C shortly before use.

Dynamic light-scattering measurements were performed on a modified temperature controlled Malvern Model 7032 apparatus, with a Coherent Model 300 Ar$^+$ laser operating at 514.5 nm, with an angular range of 10°–150° [23]. The wave vector is defined as $q=(4\pi n/\lambda)\sin(\Theta/2)$, where λ is the light wavelength in vacuum, n is the refraction index of the medium, and Θ the scattering angle. The sample cell was thermostated using a Tronac PTC-41 proportional controller with a TCP-25-s probe, and the temperature was measured *in situ* with a calibrated platinum resistance thermometer. The long-term temperature stability was better than 3 mK. The measuring cell was placed in an isorefractive index bath.

The performance of the light-scattering apparatus was tested every week using a toluene sample (afterpulsing effects appear always well below the time window of interest for our experiments) and poly(styrene) latex samples of well-defined radius. For temperatures close to the critical one, the influence of multiple scattering was checked by repeating measurements with three cells of different path lengths: 3, 10, and 25 mm. Only measurements with negligible contributions from turbidity were retained.

The mixtures were prepared by weight just before use, with a precision of ±0.01 mg. The critical coordinates for a DAC+water+KCl, with [KCl]=0.30M, were $w_c=(0.95\pm0.02)\%$ and $T_c=299\,450\pm0.005$ K, w_c being the weight fraction of DAC in the solution. These values are in very good agreement with those reported previously [20]. The samples were filtered using 0.2-μm polycarbonate membranes just before use.

The viscosity measurements were carried out using an Ubbelhode viscometer, and the data were corrected to zero shear. The precision in composition and the temperature stability were the same as for the static light-scattering experiments [21].

III. RESULTS

The second-order or normalized intensity correlation function $g^{(2)}(t)$ has been calculated from the experimental temporal correlation function $G(t)$ through [24]

$$g^{(2)}(t)=\frac{G(t)}{B}, \tag{5}$$

where B is the experimental base line. For photocurrents obeying Gaussian statistics, the normalized first order or field, $g^{(1)}(t)$, and intensity correlation functions are related by

$$g^{(2)}(t)-1=\beta|g^{(1)}(t)|^2, \tag{6}$$

where the coherence factor β is a t-independent constant, usually treated as an adjustable parameter for each $G(t)$ set of data [25]. Figure 1 shows the normalized $(g^{(2)}-1)$ (here-

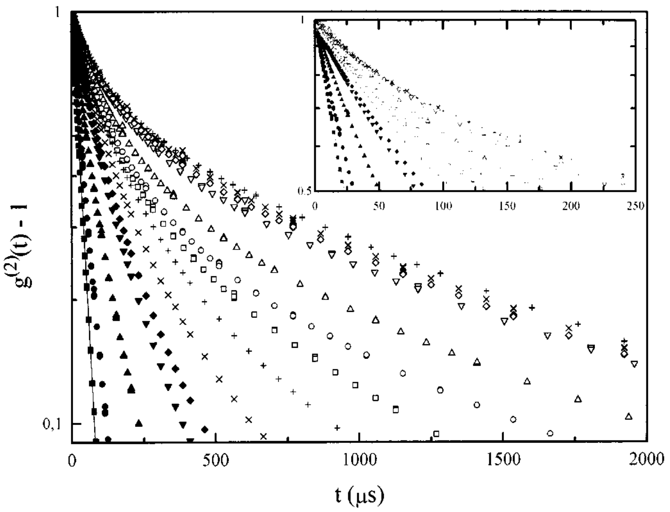

FIG. 1. Experimental correlation functions for the DAC+water +KCl(0.3M) system at different temperatures and fixed scattering angle of 90°. Only part of the experimental data is shown for the sake of clarity. Note that for temperatures far from the critical one the correlation function shows a single-exponential decay, while near T_c there are two decays. The inset shows the short-time behavior in detail. The line corresponds to the fit to Eq. (7) for $\Delta T = 18.28$ K. Symbols correspond to ΔT (K): ■, 18.28; ●, 13.41; ▲, 8.53; □, 3.83; ○, 2.92; △, 2.46; ▽, 0.98; ◇, 0.60, ×, 0.40; +, 0.29. The data shown for ΔT (K): ▼, 12.618; ◆, 7.63, ×, 7.09; and +, 6.01 are those obtained at the laboratory of Professor D. Woermann (Cologne, Germany).

inafter the correlation function) for some of the temperatures studied, far and near T_c. In all the cases the decay of the $g^{(2)} - 1$ was followed up to times long enough as to reach the base line (e.g., up to 1 s for $\Delta T = |T - T_c = 0.42$ K).

Far from the critical point, micellar systems usually show single-exponential correlation functions, and the data are analyzed using the cumulants method [24–26], which to a second order takes the form:

$$\ln[g^{(2)}(t) - 1] = \ln\beta - 2k_1 t + k_2 t^2. \tag{7}$$

The first cumulant k_1 is related to the z-average diffusion coefficient by $k_1 = \langle D_m(q)\rangle_z q^2$, and the variance $v = k_1/k_2^2$ is related to the polydispersity of the system. Figure 1 shows the correlation function for $\Delta T = 18.28$ K, and the fit to Eq. (7) with $\langle D_m\rangle_z = (3.17 \pm 0.04) \times 10^{-7}$ cm^2 s^{-1}, $v = 0.197$, and $\beta = 0.575 \pm 0.001$. Fits of similar quality are found for temperatures $|T - T_c| \geqslant 4$ K. Fitting $[g^{(2)}(t) - 1]$ to a single exponential leads to similar results; e.g., for the same data as above, this procedure leads to $\beta = 0.569 \pm 0.002$ and $D_m = (2.95 \pm 0.03) \times 10^{-7}$ cm^2 s^{-1}, which, as expected for a moderately broad distribution, is smaller than the z average.

However, as T approaches T_c, the correlation functions can no longer be described by a single-exponential function as is clearly seen in Fig. 2 for $\Delta T = 0.42$ K. Following the procedure of Rouch *et al.* [18] we have tried to fit the results using a stretched exponential, but, as it can be observed, the residuals still show systematic trends. Therefore we used a double exponential as did Ackerson and Hanley [13] and Hair *et al.* [15] and Onuki [27]:

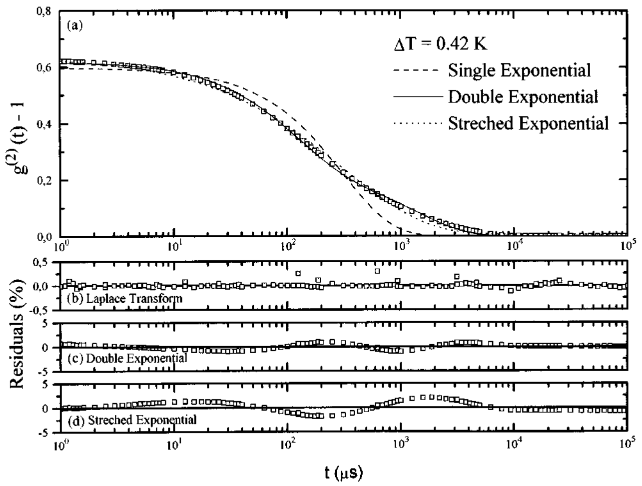

FIG. 2. (a) Experimental correlation function for a near critical temperature ($\Delta T = 0.42$ K). The curves are the best fits to a single exponential decay (– – –), a stretched exponential (···), and a double exponential (——). (b) Residuals of the best fits corresponding to a stretched exponential and to a double exponential. Note that the fits to a stretched exponential lead to systematic trends in the residuals.

$$g^{(2)}(t) - 1 = \beta[A_{\text{fast}} e^{-\Gamma_{\text{fast}} t} + A_{\text{slow}} e^{-\Gamma_{\text{slow}} t}]^2, \tag{8}$$

where Γ_{fast} and Γ_{slow} are the decay rates and A_{fast} and A_{slow} the corresponding amplitudes. As can be observed in Fig. 2 the residuals still show systematic trends, although for large values of t, they are smaller than for a stretched exponential. Similar results are obtained for the other correlation functions within $|T - T_c| \leqslant 4$ K.

In a study of nonionic micellar systems near the critical point, Dietler and Cannell [2] found a significant contribution from multiple scattering for $|T - T_c| < 0.1$ K. In some systems, multiple scattering appears as a high frequency shoulder in the contribution corresponding to concentration fluctuations [28], and shows a diffusive behavior, and therefore its decay rate should have a q^2 behavior [2,29]. In order to rule out the fact that the fast contribution appearing in our results near T_c [and therefore the inability of Eq. (17) to describe our correlation functions] is due to multiple scattering, we have carried out measurements for $|T - T_c| < 0.3$ K using cells of 25 mm and of 3-mm path length instead of the standard 10-mm cell used for the measurements shown in Fig. 1. We have found that within experimental uncertainty there was no significant change in the relative weights of the two relaxation processes.

Since the time scales of the two relaxations are rather different (for $\theta = 90°$ and $\Delta T = 0.42$ K the corresponding decay rates are $\Gamma_{\text{fast}} = 7.3 \times 10^{-3}$, and $\Gamma_{\text{slow}} = 4.1 \times 10^{-4}$ μs^{-1}), an alternative method of data analysis can be used. In effect the correlation function can be expressed as a continuous distribution of decay rates, $\Gamma = 1/\tau$:

$$g^{(2)}(t) - 1 = \beta \left| \int_0^\infty A(\Gamma) e^{-\Gamma t} d\Gamma \right|^2, \tag{9}$$

where $A(\Gamma)$ is the distribution function [26] that can be obtained from $g^{(2)}(t)$ by Laplace inversion. We have used two different algorithms to obtain $A(\Gamma)$: one was the CONTIN algorithm developed by Provencher [30], and the other is based on the regularization method described by Jakes (REPES algorithm) [31,32]. Both algorithms lead to almost identical results, and are able to accurately reproduce the experimental correlation functions, as can be observed in Fig. 2. There is a fundamental difference between describing the correlation function with Eq. (8) or with Eq. (9). In effect, while in the first case two relaxation processes are assumed, in the second one, two distributions of relaxation times are taken into account. However, it must be remarked that the Laplace inversion method leads, in our results, to distributions of relaxation times that are centered at the values of Γ obtained when using Eq. (8). Therefore, for the sake of simplicity, hereafter we will refer to the results obtained from Eq. (8).

Either type of analysis leads to single-exponential correlation functions for $|T-T_c|\geqslant 4$ K, while a second process appears as T_c is approached. The slow component becomes dominant near T_c. The decay rates are shown in Fig. 3. It can be observed that the fast mode has a diffusive character through the whole (T,q) experimental range for which two processes are observed. For the sake of comparison, Fig. 3(a) also shows the decay rate for the temperature farthest away from T_c. The q^2 dependence of Γ_{fast} allows one to define a diffusion coefficient $D_{\text{fast}}(T)=\Gamma_{\text{fast}}(T,q)/q^2$ that decreases with T, as shown in Fig. 4. It must be remarked that there is a smooth transition between the diffusion coefficient D^0 obtained from the single-exponential correlation function measured at temperatures far away from the critical one and $D_{\text{fast}}(T)$ for the temperature interval in which two processes can be separated. Figure 4 shows also the correlation length ξ results, previously reported for this system [21]. It can be observed that for $|T-T_c|>8$ K ξ changes very little, indicating that the diffusion coefficient obtained from the single-exponential correlation functions at the six highest temperatures may be attributed to the diffusion of the micellar entities, with a small contribution from critical fluctuations.

Figure 3(b) shows that Γ_{slow} presents a diffusive character only for low q's. The maximum value of q for which a q^2 behavior is observed decreases as T approaches T_c. For high values of q, Γ_{slow} shows a q^3 dependence. This kind of crossover has been extensively discussed in the literature for the decay rate of critical fluctuations [26]. Onuki [27] has also discussed a q^2 to q^3 crossover for $^3\text{He}+^4\text{He}$ mixtures. There is no contradiction with the results found by Hair *et al.* [15] and Yajima *et al.* [16] since, as they concluded, their systems were outside the asymptotic critical region, and therefore they have not reached the crossover region.

It should also be mentioned that the values of the decay rates corresponding to the fast peaks are similar to those corresponding to the dynamics of micelles in noncritical mixtures, i.e., far from T_c [33]. On the other hand, the values of Γ of the slow peaks are of the same order of those usually assigned to the concentration fluctuations in near critical micellar systems.

In order to study the critical fluctuations in Sec. IV, it is useful to introduce an apparent diffusion coefficient associated with the slow process $D_{\text{slow}}(T,q)=\Gamma_{\text{slow}}(T,q)/q^2$. D_{slow} will become independent of q only for low q; i.e., outside the crossover region. Our data lead to a ratio $D_{\text{fast}}(T)/D_{\text{slow}}(T,q)$ that ranges from 10^2 near T_c to 10 for temperatures far from T_c for the correlation functions obtained at $\theta=40°$. In general, for a given temperature the above ratio is larger for larger observation angles. Similar results of $D_{\text{fast}}(T)/D_{\text{slow}}(T)$ were reported in Refs. [15] and [16]. Figure 5 shows the ratio of the amplitudes $A_{\text{slow}}(T,q)/[A_{\text{slow}}(T,q)+A_{\text{fast}}(T,q)]$. These results will be discussed in Sec. IV.

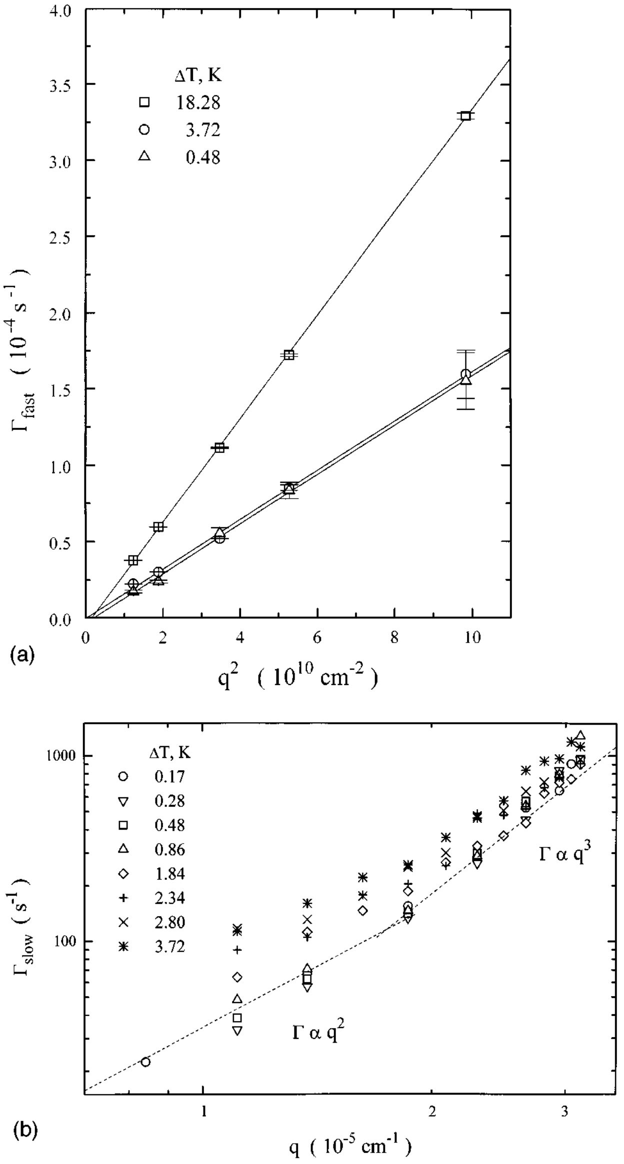

FIG. 3. (a) Decay rate corresponding to the fast relaxation mode for two temperatures within the interval for which two modes can be resolved. For the sake of comparison the results for a far from critical temperature (where single-exponential behavior is found) are also included. (b) Decay rate corresponding to the slow relaxation mode. Note that, within the experimental range, there is a crossover from a q^2 to a q^3 behavior. Lines are an aid to the eye.

IV. DISCUSSION

In order to check the predictions of the mode-coupling theory we must calculate $D_c=\Lambda_{cc}/S_{cc}$ from the two contributions to the correlation function. We have followed the

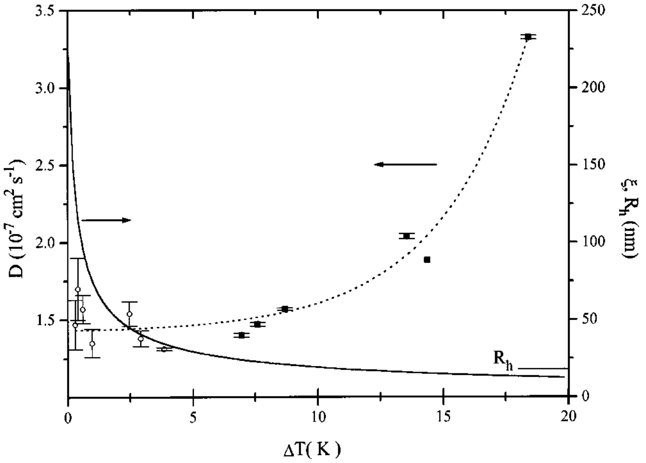

FIG. 4. Diffusion coefficient D^0 obtained from the single-exponential correlation functions at temperatures far from the critical one (■). The values $D_{\rm fast}=\Gamma_{\rm fast}/q^2$ are also plotted for the sake of comparison (○). The bar labeled R_h represents the value of the apparent hydrodynamic value calculated from $D_u(T_c,q=0)$. The dashed line represents the values of $D_u(T)$ calculated from Eq. (13) under the assumptions mentioned in the text, and using the value of R_h mentioned above. Note that, as expected, $D_u(T)$ smoothly changes from the values of D^0 far from T_c to the value $D_u(T_c,q=0)$. Also notice that to a good approximation $D_u \approx D_{\rm fast}$. The continuous line represents the correlation length ξ obtained from Ref. [21]. Notice that R_h is approximately the value of ξ for temperatures well above the critical one.

same procedure of Hair *et al.* [15], and Yajima *et al.* [16]. The eigenvalues of matrix D in Eq. (3) are given by

$$\lambda^2-(D_c+D_u)\lambda+D_cD_u-D_1D_2=0 \qquad (10)$$

with solutions $\lambda_1=D_{\rm fast}(T)$ and $\lambda_2=D_{\rm slow}(T,q)$. Since the trace of D is invariant under a change of basis, it follows that

$$D_c(q,T)=D_{\rm fast}(T)+D_{\rm slow}(q,T)-D_u(q,T), \qquad (11)$$

which relates the diffusion coefficient D_c to the measured fast and slow modes and to a background D_u [14]. As extensively discussed in the literature [34–36], the background corresponds to the value that the diffusion coefficient would have in the absence of any critical anomaly, whence, a smooth continuation is expected for the background contribution from the noncritical region to the critical point. The knowledge of the background contribution to any dynamic property near a critical point is fundamental since it is an important part of the total value of such property [36]. An approximate method for estimating $D_u(q,T)$ in our system follows.

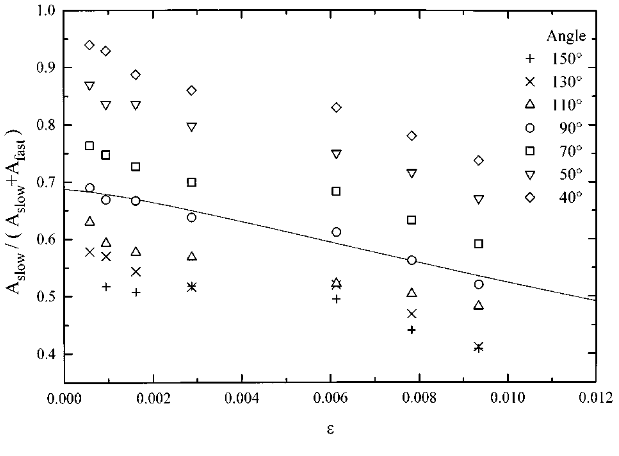

FIG. 5. Relative weights of the amplitudes of the slow and fast relaxation modes [Eq. (8)] for different values of T and q.

It is well known that

$$\lim_{q,\varepsilon\to 0} D_c(q,\varepsilon)=0, \qquad (12)$$

where $\varepsilon=|T-T_c|/T_c$, and as a consequence $D_u(T_c,q=0)=D_{\rm fast}(T_c)+D_{\rm slow}(T_c,q=0)$. As already mentioned, for low values of q both $\Gamma_{\rm fast}$ and $\Gamma_{\rm slow}$ are diffusive, which greatly facilitates the calculation of the $D_u(T_c,q=0)=1.35\times10^{-7}$ cm^2 s^{-1}. Hair *et al.* [15] and Yajima *et al.* [16] have assumed that D_u is constant through their experimental temperature interval, despite the strong change in viscosity of one of their systems (in Ref. [15] the viscosity η changes from 15 P at 80 °C to 1500 P at 41 °C). Such an approach does not seem acceptable in our system. In effect, as stated above, one must expect that far from the critical point the background contribution will account for the whole diffusion coefficient. This means that in our system it should essentially coincide with the value of Γ/q^2 obtained from the single-exponential correlation functions. As T approaches T_c, the background contribution D_u should smoothly link the q-independent $D(T \gg T_c)$ with the value $D_u(T_c,q=0)$. As shown in Fig. 4, for the six temperatures farthest away from T_c the diffusion coefficient decreases with T and is substantially larger than $D_u(T_c,q=0)$. We still need to specify the q and T dependences of D_u. In order to do so we again turn to the physical meaning of the background contribution, and remember that the diffusion coefficient for noncritical micellar systems D^0 has been most frequently written as

$$D^0=\frac{k_BT}{6\pi\eta R_h S(q=0)}, \qquad (13)$$

where η is the shear viscosity of the solution and R_h the hydrodynamic radius of the micelles [34]. For dilute micellar systems and relatively high salt concentration, as in our case, it is usually found that $S(q=0)\approx 1$ [37], thus allowing the description of D^0 in terms of an apparent hydrodynamic radius. Ducros *et al.* [38] have reviewed some of the experiments that suggest that R_h remains approximately constant as the critical point is approached in several micellar systems. This assumption has been frequently made in calculating the background contribution to the total scattering intensity in the critical region [35,38,39]. Under these assumptions the value $D_u(T_c,q=0)$ and Eq. (13) lead to $R_h=18.3$ nm. This value is shown in Fig. 4, and essentially agrees with the value of the correlation length for $\Delta T\approx 20$ K. Using Eq. (13) with this hydrodynamic radius and the experimental viscosity data we have calculated $D_u(T)$, which is shown in Fig. 4 as a line. Obviously this approach implicitly assumes a diffusive character for D_u [Eq. (13)].

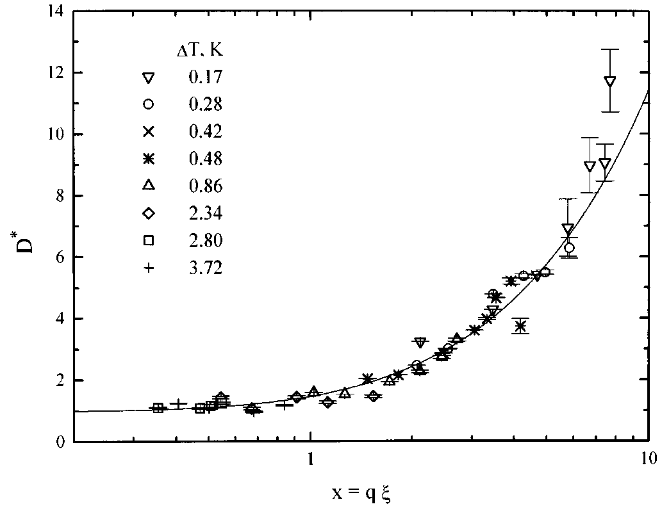

FIG. 6. Reduced diffusion coefficient associated with the concentration fluctuations. The continuous line corresponds to the Kawasaki function arising from the mode-coupling theory. Note that the D_c^* have been calculated using independent experimental values of the viscosity and of the static correlation length.

Now the calculated values of D_c can be compared with the predictions of the mode-coupling theory. If the weak divergence of the shear viscosity η_c is neglected in solving the coupled integral equations that describe the diffusional mobility and the viscosity, Γ_c is given by

$$\Gamma_c(q,T)=q^2D_cK(x)/x \tag{14}$$

to lowest order in the solution of the mode-coupling equations. In Eq. (14) $D_c=R_ck_BT/(6\pi\eta\xi)$, and $K(x)=(3/4)[1+x^2+(x^3-x^{-1})\tan^{-1}(x)]$ is the Kawasaki universal function with $x=\xi q$. In the preceding expressions $R_c=1.027$.

In order to compare more easily the theoretical predictions with the experimental results, it is customary to reduce the diffusion coefficient associated with the decay rate as

$$D^*=D_c(6\pi\eta\xi/k_BTR_c)=K(x)/x^2. \tag{15}$$

Figure 6 shows the results obtained as well as the predictions given by Kawasaki's function. The agreement is remarkable, considering that we have used for ξ the experimental values previously obtained from static light scattering [21] and that the uncertainty for large values of $q\xi$ increases due to the small relative weight of one of the relaxation modes that makes their separation more difficult.

It is worth noting that, as in Refs. [15] and [16] we have found that D_{fast} is much larger than D_{slow}. As a consequence, and taking into account Eq. (11), over most of the T and q values, we have $D_u \approx D_{\text{fast}}$, and therefore $D_c \approx D_{\text{slow}}$ [this is so from a numerical point of view, but from the physical point of view Eqs. (3) and (11) indicate that both modes contain part of the critical fluctuations]. A complete decoupling of the hydrodynamic modes would allow us to interpret the two contributions in Eq. (18) directly in terms of critical and noncritical contributions, a result similar to that of Onuki [27] for ^{3}He+^{4}He mixtures. Figure 4 makes this rather clear, since one can observe that the values of D_{fast} are almost coincident with the calculated values of D_u. This figure also points out that for $|T-T_c|<5$ K, D_u changes very little.

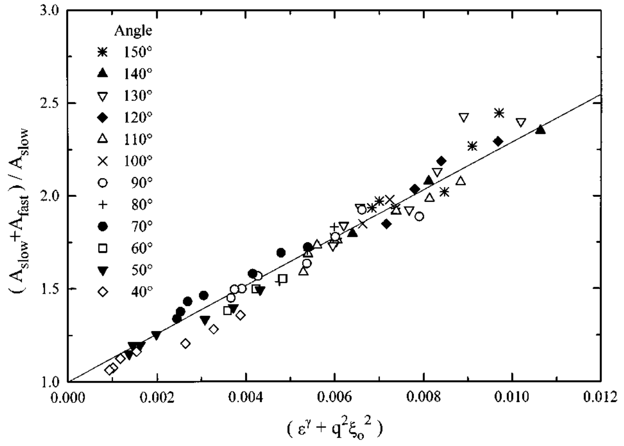

FIG. 7. Comparison of the relative weights of the amplitudes of the two relaxation modes with the predictions of Onuki's theory, Eq. (16). The line corresponds to a least-squares fit constrained to intercept the point (0,1).

These facts are interesting, since within Onuki's formalism [27] it is possible to find a relatively simple equation that relates the amplitudes of the two exponentials in Eq. (8). In effect, Onuki predicts

$$(A_{\text{slow}}+A_{\text{fast}})/A_{\text{slow}}=1+C(\varepsilon^\gamma+q^2\xi_0^2), \tag{16}$$

with $\gamma=2\nu=1.24$, $\xi_0=2.6$ nm is again taken from the static light-scattering experiments, and C is a system-dependent constant that in our system was found to be $C=135$. Figure 7 shows that the amplitudes already shown in Fig. 5 can be very well described by Eq. (16), thus reinforcing the idea that, despite the general formalism outlined, in our system there is a high degree of decoupling between the critical and noncritical contributions to the experimental correlation functions.

V. CONCLUSIONS

The dynamics of the DAC+water+KCl(0.30M) system has been studied using light scattering. The intensity correlation functions show one decay process for $|T-T_c|>4$ K, while closer to the consolute point a second decay process appears at larger times. The correlation function has been fitted to a double exponential, and also the distribution of decay rates has been calculated by Laplace inversion of the correlation functions. The diffusion coefficient associated with the concentration fluctuations D_c has been calculated from their contributions to both relaxation processes, assuming that the hydrodynamic radius of the micelles does not change in the critical region. Using the experimental values of the viscosity and the correlation length obtained from static light scattering, the values of D_c can be well described by the Kawasaki function arising from mode-coupling theory using the 3D Ising values for the critical exponents.

Despite the fact that the theory predicts that both relaxation modes contain critical and noncritical contributions, the coupling seems to be small in our system. As a consequence, the ratio of the amplitudes of the two relaxation modes can be described quite well with the theory of Onuki.

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