



ELSEVIER

Colloids and Surfaces

A: Physicochemical and Engineering Aspects 140 (1998) 289–293

COLLOIDS
AND
SURFACES

A

Relaxation phenomena in critical microemulsion systems

L. Letamendia ^{a,*}, E. Louisor ^a, E. Pru-Lestret ^a, J. Rouch ^a, F. Sciortino ^b,
P. Tartaglia ^b, H. Ushiki ^c

^a *Centre de Physique Moléculaire Optique et Hertzienne, URA 283 du CNRS, Université Bordeaux,
1351 Cours de la Libération, 333405 Talence, France*

^b *Dipartimento di Fisica, Università di Roma La Sapienza and Istituto Nazionale di Fisica della Materia,
Unità di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185 Rome, Italy*

^c *Laboratory of Transport and Transformation in Bio-systems Department of Biomechanics and Intelligent Systems,
Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu-shi, Tokyo 183, Japan*

Abstract

We discuss extensive sets of experimental data including static and dynamic light scattering, ultrasonic velocity measurements and high and low frequency dielectric relaxation, taken in the vicinity the critical point of a ternary microemulsion system. Upon approaching the critical point we observed a slowing down of the dielectric relaxation time and of the first cumulant of the time-dependent droplet density correlation function $C^2(t)$ which shows a non-exponential behavior at long time. These features can be well accounted for by assuming that the microemulsion system is made of polydispersed transient fractal aggregates having a fractal dimension $d_f=2.5$ and a polydispersity index $\tau=2.2$. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Ternary mixtures of AOT (sodium diethylhexyl sulfosuccinate), water, and decane can create self-assembling microstructures, the nature of which depends on the volume fraction ϕ of the water + surfactant dispersed phase. At low or moderate volume fraction ϕ and not too high temperature and for a value of the molar ratio $X = [\text{Water}]/[\text{AOT}] = 40.8$, one observes quasi-spherical rather monodispersed inverse water-in-oil microemulsion droplets having a radius of the order of 80 Å. This mixtures may show a cloud point curve with a lower critical point located at $\phi_c = 0.098$ and $T_c = 39.9^\circ\text{C}$. For temperatures above T_c , the microemulsion phase separates, the two phases being made with droplets having the

same diameter, but different volume fractions [1,2]. In this respect the critical sample can be considered as a binary mixture and should behave as a three-dimensional Ising system. An electrical conductivity percolation point has been evidenced [3] in the immediate vicinity of the critical point. Below the percolation threshold the exponent characterizing the divergence of the electrical conductivity σ is the one related to stirred percolation [4], whereas above the percolation threshold, experimental data are consistent with the picture of static percolation. The presence of a critical and of a percolation point is mediated by attractive interactions among droplets which do not behave as purely hard spheres. Dynamical light-scattering measurements have shown strong deviations [5] from the universal behavior described by Kawasaki's mode-coupling theory [6,7], like for non-ionic amphiphile-water binary mixtures [8,9].

* Corresponding author.

In this paper we will briefly summarize experimental results obtained by using different techniques, namely dielectric relaxation, static and dynamic light scattering, ultrasonic measurements. Our experimental data will be analyzed by using an extended version of the dynamical droplet model, first proposed Sorensen et al. [10] and Martin et al. [11–13] and recently rephrased [14–16] using Coniglio and Klein results [17].

2. Experimental results

Let us first discuss dynamical light scattering results. The scattered light intensity correlation function $C^2(t)$ has been measured in a very wide range of temperature and wave vectors [18], for different systems. Typical normalized intensity correlation functions $C^2(t)$ obtained with an ALV5000 multiple tau correlator at different values of $T_c - T$ are depicted in Fig. 1 in semi-log units. On such a plot, an exponential decay would correspond to a straight line. It can be seen from the graph that it is indeed the case at short time. At long time, however small but significant systematic deviations from the exponential decay are observed, the decay being well described by a stretched exponential.

From the initial slope of $C^2(t)$, one can deduce the first cumulant Γ which is the relaxation rate of the order parameter fluctuations. In reduced

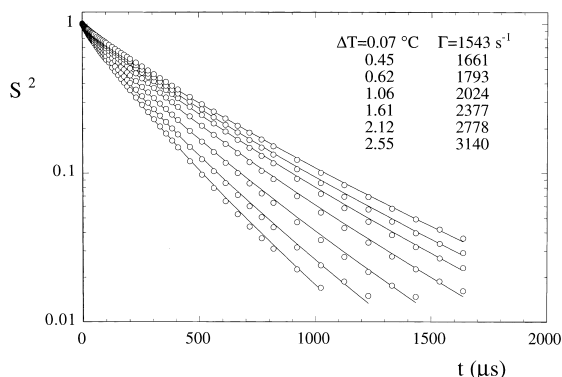


Fig. 1. The normalized scattered intensity correlation function as a function of time. The symbols are experimental data, while the curves are best fits to the extended version of the droplet model.

units (to be explained below) Γ^* is plotted as a function of the scaling variable $x = q\zeta$ on Fig. 2. It can be seen on the graphs that the overall behavior is similar to that observed for simple or molecular binary mixtures. However, far from T_c significant deviations occur. In particular one observes a levelling-off of Γ^* and even at high temperatures (not shown on the plot) a decrease of the line width. We also measured the Rayleigh–Brillouin spectrum of the critical mixture by using a multipass high resolution Fabry–Pérot interferometer. From these experiments one can deduce the very high frequency (typically 5 GHz) sound velocity and sound absorption. These data have to be compared with those inferred from ultrasonic measurements taken for frequency ranging from 1 kHz to 300 MHz. The sound velocity is plotted as a function of temperature for different frequencies on Fig. 3 quite similar [19], a very strong decrease of v close to T_c is observed in the kHz range. This result is in sharp contrast to the one reported in critical molecular binary fluids where only a small dispersion of the order of few m s⁻¹ is evidenced. The sound absorption measured close to T_c is plotted on Fig. 4 as a function of frequency. Two relaxation domains are clearly evidenced, one at low frequency, in the MHz range, and one at high frequency, the relaxation frequency ranging

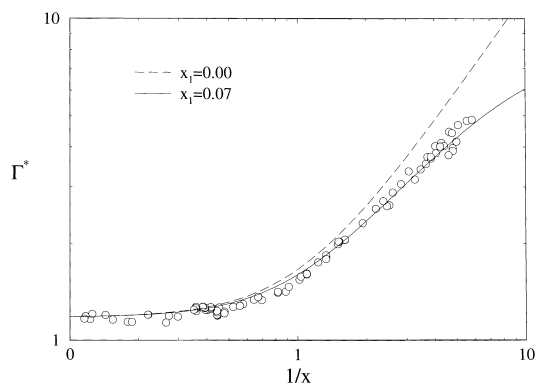


Fig. 2. The reduced first cumulant Γ^* plotted as a function of $x = q\zeta$ in a double log plot. The symbols are experimental data, the dashed curve which refers to droplet model with $X_1 = 0$ is identical to Kawasaki's mode coupling result the solid curve is the best fit of the data to droplet model with $X_1 = 0.07$.

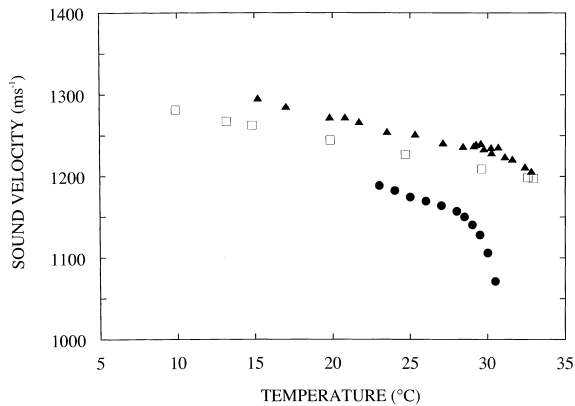


Fig. 3. The sound velocity as a function of the temperature. The triangles are Brillouin scattering data, the squares are ultrasonic data at 25 MHz while the circles are ultrasonic data at 1 kHz taken from ref. [14].

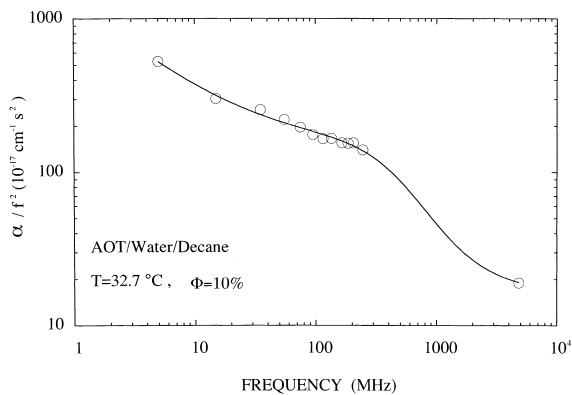


Fig. 4. The sound absorption as a function of frequency at $T = 32^\circ\text{C}$. The full line is the best fit to two Debye-like relaxation domains.

from 700 MHz far from T_c to 100 MHz close to T_c .

Using the time domain reflectometry technique, we also measured the electrical properties of the same system, as a function of both temperature and frequency. On Fig. 5 we have plotted the static dielectric constant as a function of the reduced temperature in a double log plot. The straight line we obtained, indicates a power law dependence. The characteristic exponent is -0.40 ± 0.04 . We also measured the frequency relaxation of the dielectric constant. Far from T_c , a Debye-type relaxation characterized by a single relaxation time is

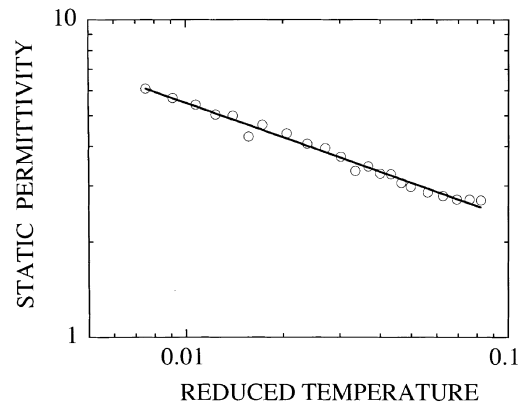


Fig. 5. The static permittivity measured as a function of the reduced temperature. The symbols are experimental data, while the full line is the best fit to a power law.

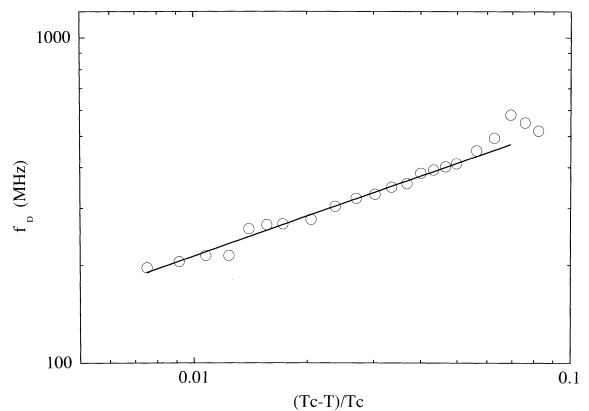


Fig. 6. The relaxation frequency as a function of the reduced temperature. The symbols are experimental data, while the full line is the best fit to a power law.

observed. On approaching the critical or percolation point¹, deviations from a Debye relaxation are evidenced. In the time domain, the time dependence of the dipole moment correlation function evolves from a single exponential to a complex curve: exponential decay at short time, followed by a power law, then at long time by a stretched exponential. In this respect, the correlation function bears strong similarities with the one characteristic of the slow dynamics in glassy systems.

¹ For more details, see papers by P. Tartaglia and by Y. Feldman, this volume.

The inverse of the first cumulant (relaxation frequency) is plotted as a function of the reduced temperature on Fig. 6. Here also we observe a power law with an exponent, $+0.40 \pm 0.04$. Thus experimentally the exponents, respectively, related to the temperature dependence of the dielectric constant and of the relaxation frequency are of opposite sign, but of equal absolute value. It is interesting to note that the dielectric relaxation frequency is very similar to the one characterizing the high frequency sound dispersion.

3. Discussion

The main features of all the experimental results described in the previous section are deviations from the quasi-exponential relaxation phenomena observed in simple fluids or in molecular binary mixture close to a critical consolute point. Also the percolation point of the critical microemulsion is extremely close to the critical point. The charge transport is mediated by interactions among droplets which form polydispersed transient fractal aggregates. Therefore, we are tempted to apply continuous percolation theory to explain our experimental results. In what follows, we will limit ourselves to a brief theoretical description of dynamical light scattering, the application of the model to dielectric relaxation will be given elsewhere.

A model to explain dynamic light scattering in terms of droplets has been first proposed by Sorensen et al. [10], and Martin et al. [11–13]. A modified version of this dynamical droplet model rephrased using Coniglio and Klein results [17] has been proposed recently [14–16]. In this model, it is assumed that the critical mixture is made of dilute polydispersed dynamical fractal clusters having a fractal dimension $d_f=2.5$ and a polydispersity index $\tau=2.2$. The static structure factor $S_k(q)$ of a fractal cluster containing k particles has been calculated by Chen and Teixeira [20]. Extension to polydispersed fractal clusters can be easily performed by averaging $S_k(q)$ over the cluster size distribution function assumed to be similar to the one relevant for percolation. The result is a

non-universal function of the scaling variable $x=q\xi$, where ξ is the long range correlation length, since it involves explicitly $x_1=qR_1$, the reduced size of the monomers.

We can also calculate the density–density time correlation function which reads

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

where

$$w = D_1 R_1 q^3 t (1+x^{-2})^{1/2} \quad (2)$$

is the reduced time. This quantity is also system-dependent via both R_1 and the translational diffusion coefficient of the monomer D_1 . Calculated correlation functions are depicted Fig. 1 assuming $d_f=2.5$ and $\tau=2.2$. It can be seen that a very good agreement with the experimental determination is achieved, in particular the long time tail is very well described. From these equations it is easy to infer the reduced first cumulant Γ^* which is given by

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

This quantity which also explicitly depends on the droplet size, bears striking differences to the predictions of the mode coupling theories, since it contains a system-dependent cut-off parameter x_1 .

The relaxation rate we obtain is plotted as a function of $x=q\xi$ for different values of x_1 on Fig. 2. Also a very good agreement is achieved when comparing the experimental determination and the model.

4. Conclusion

In the case of critical OAT–water–decane microemulsion systems we observed strong deviations

from the usually reported exponential relaxation phenomena in critical simple fluids or in molecular binary mixture close to a critical consolute point. In particular, both the scattered intensity correlation function and the dipolar correlation function show a long time tail which behaves in a similar way to the one observed for slow dynamics in glassy systems. The critical behavior of the system can be accurately described by using an improved version of the dynamical droplet model, which assumes the existence of polydispersed transient fractal aggregates. Most of the features we observed experimentally are well reproduced. In particular, the strong deviation of $C^2(q, t)$ from a single exponential decay is very well accounted for. At this point, however, one has to make an important remark. Most of the dynamical light scattering data are taken in a crossover regime, i.e. in a regime where $\Gamma \times t$ is not very large compared to unity. Therefore, it is not possible to infer from our experiments the fractal dimension and the polydispersity index. These quantities are input parameters of the model.

Acknowledgment

The authors would like to thank Professor C. Cametti for his very useful comments. CPMOH is Unité Associée 283 du C.N.R.S.

References

- [1] M. Kotlarchyck, S.H. Chen, J.S. Huang, M.W. Kim, *Phys. Rev. A* 28 (1983) 508.
- [2] M. Kotlarchyck, S.H. Chen, J.S. Huang, M.W. Kim, *Phys. Rev. A* 295 (1984) 2054.
- [3] C. Cametti, F. Sciortino, P. Tartaglia, J. Rouch, S.H. Chen, *Phys. Rev. Lett.* 75 (1995) 569.
- [4] M. Lagues, R. Ober, C. Taupin, *J. Phys. Lett. (Paris)* 39 (1978) L487.
- [5] A.M. Belloq, P. Honorat, D. Roux, *J. Phys. (Paris)* 46 (1985) 743.
- [6] K. Kawasaki, *Ann. Phys. (N.Y.)* 61 (1970) 1.
- [7] K. Kawasaki, in: C. Domb, M.S. Green (Eds.), *Phase Transitions and Critical Phenomena*, vol. 5A, Academic, New York, 1976, p.165.
- [8] M. Corti, V. Degiorgio, *Phys. Rev. Lett.* 55 (1985) 2005.
- [9] V. Degiorgio, in: V. Degiorgio, M. Corti (Eds.), *Physics of Amphiphiles, Micelles, Vesicles and Microemulsions*, North-Holland, Amsterdam, 1985.
- [10] C.M. Sorensen, B.J. Ackerson, R.C. Mockler, W.J. O'Sullivan, *Phys. Rev. A* 13 (1976) 1593.
- [11] J.E. Martin, B.J. Ackerson, *Phys. Rev. A* 31 (1985) 1180.
- [12] J.E. Martin, J. Wilkoson, D. Adolf, *Phys. Rev. A* 36 (1987) 1803.
- [13] J.E. Martin, J. Wilkoson, J. Odinek, *Phys. Rev. A* 43 (1991) 585.
- [14] P. Tartaglia, J. Rouch, S.H. Chen, *Phys. Rev. A* 45 (1992) 7275.
- [15] E. Ducros, J. Roucli, K. Hamano, P. Tartaglia, S.H. Chen, *J. Phys.: Condens. Matter.* 6 (1994) A293.
- [16] E. Ducros, S. Haouache, J. Rouch, K. Hamano, K. Fukuhara, P. Tartaglia, *Phys. Rev. E* 50 (1994) 1291.
- [17] A. Coniglio, W. Klein, *J. Phys. A: Math. Gen.* 13 (1980) 2775.
- [18] J. Rouch, P. Tartaglia, S.H. Chen, *Phys. Rev. Lett.* 71 (1993) 1947.
- [19] Y. Harada, M. Tabuchi, in: *Slow Dynamics in condensed Matter*, AIP, New York, 1992, pp. 320–321.
- [20] S.H. Chen, J. Teixeira, *Phys. Rev. Lett.* 57 (1986) 2583.