

Second-Order Symmetric-Asymmetric Phase Transition of Randomly Connected Membranes

C. Coulon, D. Roux, and A. M. Bellocq

Centre de Recherche P. Pascal, Avenue du Dr. Schweitzer, 33600 Pessac, France

(Received 30 October 1990)

Static light-scattering experiments on pseudoternary systems of salted water, pentanol, and sodium dodecyl sulfate are presented. The results show evidence for a second-order phase transition between two isotropic phases which is not a classical liquid-liquid phase separation. We discuss these results in the frame of the sponge-asymmetric phase transition which has been described for systems of self-avoiding connected membranes. Both the correlation function and the critical behavior of the scattered intensity are analyzed and are shown to be in agreement with theory.

PACS numbers: 64.70.Ja, 64.60.Fr, 78.35.+c

The problem of self-avoiding random liquid surfaces has recently received a lot of attention, mainly because of its equivalence with lattice gauge theories used in elementary-particle physics.^{1,2} The deduced theoretical diagrams reveal the possibility of a phase transition between two isotropic liquid phases.¹⁻⁴ One of these phases consists of a randomly connected surface separating two equivalent volumes. This symmetry can be spontaneously broken, leading to a phase of surfaces where an inside can be unambiguously defined from an outside. As a consequence, a line of critical points (i.e., a second-order line) between the symmetric and the asymmetric phase is predicted theoretically.¹⁻⁴

In the context of condensed matter, such a description has been used to predict the phase behavior and thermodynamical properties of surfactants in solution.³⁻⁵ Indeed, among other organizations surfactant molecules can form monolayers or bilayers. For example, it is well known^{5,6} that in certain cases microemulsions can be described as two continuous domains (oil and water) separated with a monolayer surfactant film. As far as bilayers are concerned, these membranes can also form isotropic phases of self-avoiding connected membranes, the main difference with microemulsions being that the chemical nature of the two continuous domains is the same. One can arbitrarily define an inside from an outside domain corresponding, for example, to oil and water in the microemulsion case. Because of the equivalence between the domains, the bilayer system can exist in two different states: a symmetric state (the sponge phase) corresponding to a perfect symmetry between the two domains (the inside and outside volumes are the same) and an asymmetric state where this symmetry is broken (there is less inside than outside). The structure of these phases has been clearly established by neutron-scattering experiments.⁷ Moreover, the symmetric (or asymmetric) nature can be demonstrated by light-scattering experiments⁸ (as discussed in the following) and these phases are experimental realizations of phases of randomly connected membranes.⁹

From theoretical grounds,^{4,9} when diluting a symmet-

ric (sponge) phase, one expects a sponge-to-asymmetric (*S-A*) phase transition. In fact, such a transition has been observed.⁸ However, up to now only first-order transitions were described. We report in this Letter the first evidence for a line of second-order *S-A* transitions. The corresponding critical behavior is analyzed by static light-scattering experiments which are shown to discriminate between the symmetric and asymmetric phases. The divergence of $I(0)$ (scattered intensity extrapolated at $q=0$) and ξ (correlation length of the critical fluctuations) are deduced from the fit of the experimental data and compared with the theoretical predictions. In particular, the critical exponent $\varepsilon \sim 0.5-0.6$ deduced for the divergence of $I(0)$ is shown to be in agreement with the theory.

The phases of interest in this study are obtained with pseudoternary systems of salted water (20 g/liter of NaCl), sodium dodecyl sulfate (SDS), and pentanol when a large proportion of water is present.¹⁰ Figure 1 shows the relevant part of the phase diagram. Two monophasic domains are present corresponding respec-

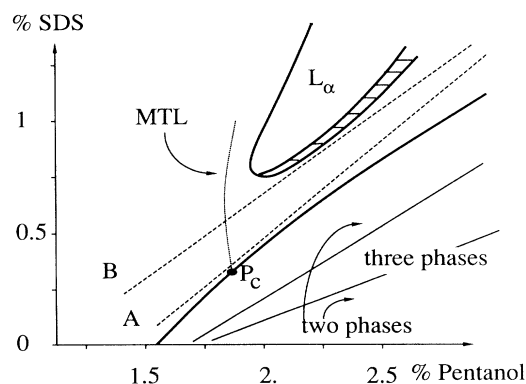


FIG. 1. Schematic view of the phase diagram. L_α stands for the lamellar phase (expressed in wt%). P_c is the critical point. The dashed lines give the experimental dilution lines. MTL is the line of maxima of turbidity.

tively to a lamellar (L_α) and an isotropic domain. The phase separation between these two phases corresponds in the right part of the figure to a weak first-order transition. The exact topology of the phase diagram on the left side of the L_α domain is presently under investigation. In the right part of Fig. 1, below the demixing line a complex polyphasic region is observed. In particular, a phase separation between two isotropic phases is present with a critical point P_c . In the isotropic monophasic region, a line of maximum of turbidity (MTL) is found experimentally which seems to end very close to P_c (because of the extreme dilution the exact topology of the phase diagram is not known). The isotropic phase located on the right (concentrated) side of the MTL has already been identified as a sponge phase of connected membranes.^{7,8} The characteristic size of the sponge ξ_0 increases continuously as the MTL line is approached. Therefore this line is a good candidate for a second-order S - A line. To check this assumption, two series of samples were prepared along the dilution lines given in Fig. 1. To discuss the influence of P_c , one of these lines is very close to the two-phase region (line A), the other one being as far from P_c as allowed by the presence of the lamellar domain (line B). Intermediate shorter lines were also prepared to confirm the results.

Static light scattering was used to characterize the different samples. This method gives the density correlation function. This function has been recently calculated in both the S and the A phases using perturbation theory.^{8,9,11} To describe the correlation functions at the level of a Landau-Ginzburg approximation, two order parameters are necessary. Introducing ϕ the volume fraction of membrane, one can define the density order parameter $\rho = \phi - \langle \phi \rangle$. In addition, another order parameter η associated with the S - A transition should be introduced. It can be defined as the difference between the outside and inside volumes. The free energy density reads as follows:

$$\Delta f = (A/2)\eta^2 + (B/4)\eta^4 + (a/2)\rho^2 + (b/4)\rho^4 + \lambda\rho\eta^2 + (C/2)(\nabla\eta)^2 + (c/2)(\nabla\rho)^2.$$

This free energy is valid in both phases. In the asymmetric phase, the nonzero value of η gives an extra coupling term (with $\delta\eta = \eta - \langle \eta \rangle$) $2\lambda\rho\delta\eta$.

The Fourier transform of the density correlation function $\langle \rho(0)\rho(r) \rangle$ has been estimated in both cases.^{8,9,11} The result is

$$\langle |\rho_q|^2 \rangle = \frac{\Gamma_\rho}{1 + \xi_\rho^2 q^2} + \frac{B_{S,A}}{(1 + \xi_\rho^2 q^2)^2} F(q\xi_\eta),$$

with $B_S = K\Gamma_\eta^2 \Gamma_\rho^2 \xi_\eta^{-3}$, $B_A = K'\Gamma_\eta \Gamma_\rho^2$, and

$$F_S(q\xi_\eta) = \frac{\tan^{-1}(q\xi_\eta/2)}{q\xi_\eta/2}, \quad F_A(q\xi_\eta) = \frac{1}{1 + \xi_\eta^2 q^2},$$

where S and A stand for sponge and asymmetric, respec-

tively. $\Gamma_\rho = 1/a$ and $\Gamma_\eta = 1/A$ are the susceptibilities for ρ and η . $\xi_\rho = (c/a)^{1/2}$ and $\xi_\eta = (C/A)^{1/2}$ are the corresponding correlation lengths. K and K' are proportional to the square of the coupling constant λ . Close to the S - A transition, the expected behavior is more complex (a crossover between the two formulas should indeed be observed). In both cases the first term gives the well-known Ornstein-Zernike law. However, when the η fluctuations dominate, the q dependence of the correlation function becomes original and the result is different for the symmetric and asymmetric phases.

The experimental data obtained can always be fitted using one of the above formulas depending upon the location of the sample compared to the line of maxima of turbidity. Indeed, for the most concentrated samples, only the symmetric formula gives a reasonable fit. On the contrary, only an asymmetric fit is possible for the most dilute samples. As expected both formulas give a reasonable fit very close to the maximum of turbidity. Figure 2 gives examples of these three situations with a plot of $1/I(q)$ vs q^2 which is an easy way to discriminate between the different cases. Indeed, in the symmetric case the data are curved downward while they are curved upward in the asymmetric case.

For all the measured samples Γ_ρ remains small and the first term can be ignored. This means that direct density fluctuations remain small. In the same way the correlation length ξ_ρ remains smaller than a few 100 Å with no critical behavior. On the other hand, $I(0)$ and ξ_η show

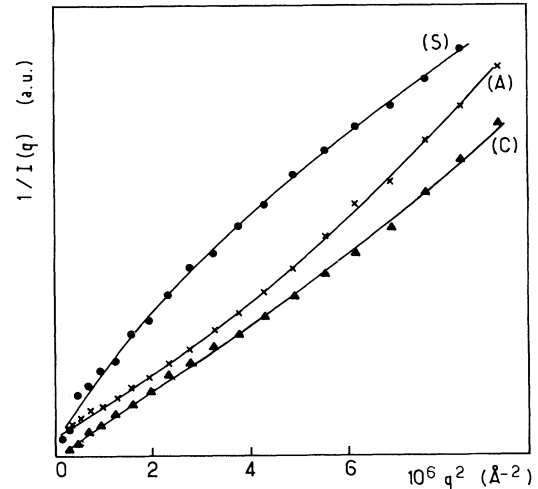


FIG. 2. Plot of the inverse of the scattered intensity against the square of q to show the different regimes. The points give the experimental results. The solid lines give the fits using the theory. S , A , and C are typical curves in the sponge, asymmetric phase, and close to the phase transition. They correspond to samples of dilution line B with $\phi = 3.5\%$, 1.9% , and 2.8% , respectively (ϕ_c is 2.25% for this line). ϕ is the membrane volume fraction (SDS plus alcohol volume fraction).

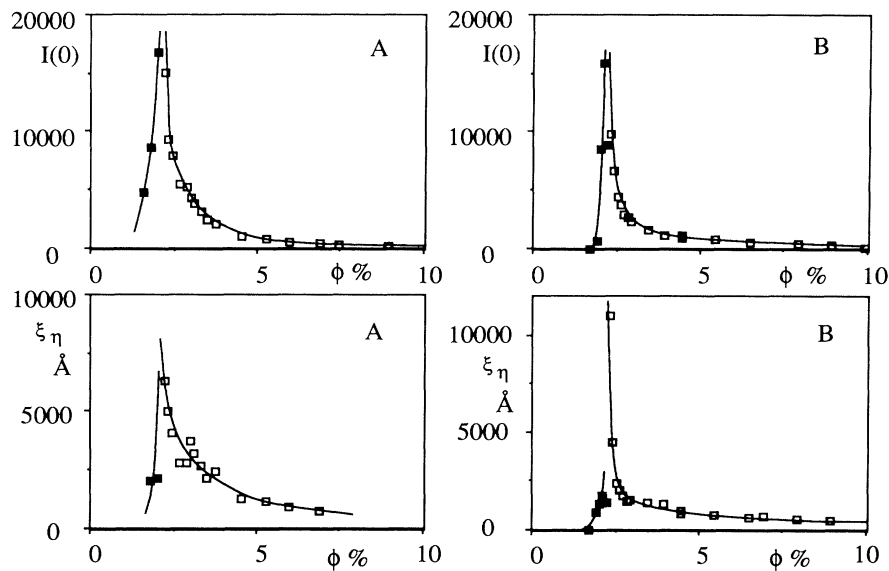


FIG. 3. Light-scattering results for dilution lines *A* and *B*. $I(0)$ is the intensity extrapolated at $q=0$; ξ is the correlation length for the order parameter η as introduced in the text. Open and solid symbols stand for the *S* and *A* fits, respectively.

for both dilution lines a sharp increase close to the maximum of turbidity as seen in Fig. 3. The comparison of Figs. 3(a) and 3(b) shows that the vicinity of the critical point P_c for one of the lines does not enhance the observed divergence. The comparison with intermediate shorter lines shows the same divergence all along the line of maxima of turbidity. This demonstrates that this line is a line of second-order *S-A* phase transitions corresponding to the divergence of the η fluctuations.

We now analyze in more detail the critical behavior at the transition. Both $I(0)$ and ξ_η determined from the fit show a divergence close to the transition. However, only $I(0)$ is insensitive to the details of the fit and is accurate enough to allow the determination of a critical exponent. Because of the sharpness on the *A* side only the divergence on the symmetric (sponge) side will be analyzed.

Since the approach of the second-order line follows a concentration path, in order to extract the singular part from the thermodynamical quantities, one needs to take into account the regular volume-fraction dependence. In the case of the sponge phase, the characteristic length ξ_0 (cell size) which gives the length scale below which the membrane is flat is proportional to $1/\phi$, where ϕ is the volume fraction of membrane.^{4,7} This comes from the invariance of the sponge under the transformation $\phi' = a\phi$, $x' = x/a$ (where x is a length). The same argument predicts $f' = a^3 f$ for the free energy per unit volume.¹² The experimental estimation of ξ_0 is given by the position of the bilayer correlation peak and shows the expected $1/\phi$ behavior.⁷ With similar arguments one can deduce that the regular part of B_s [$I(0)$ when η fluctuations are dominant] scales like the compressibility, i.e., like $1/\phi$.

Thus to extract the critical behavior, one should plot $\ln(\phi I)$ against $\ln(\phi - \phi_c)$, where ϕ_c is the volume fraction of membrane at the transition (we have estimated $\phi_c \approx 2.05\%$ and 2.25% for dilution lines *A* and *B*, respectively). This plot for the line *B* is given in Fig. 4. We obtain a linear plot with an exponent of $\varepsilon = 0.5 - 0.6$. Considering the expression for Γ_η and ξ_η with exponents γ and ν , respectively, we expect to find $\varepsilon = 2\gamma - 3\nu = \nu(1 - 2\eta)$. The corresponding mean-field and Ising values are respectively 0.50 and 0.58, both in agreement with our result. It is remarkable that this exponent is far from the one expected for a compressibility usually deduced from $I(0)$ in a light-scattering experiment ($\gamma = 1 - 1.2$). This clearly supports the theoretical analysis of the *S-A* phase transition in terms of a two-order-parameter problem. A

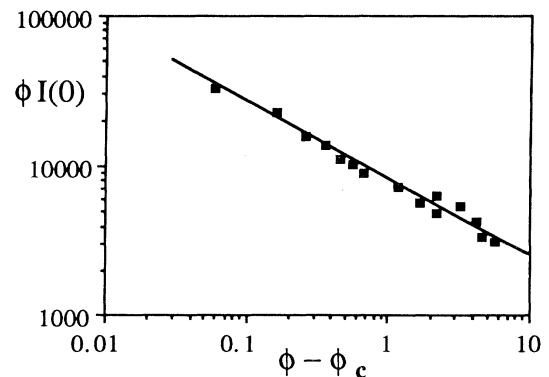


FIG. 4. Log-log plot of ϕI_0 vs $\phi - \phi_c$ for dilution line *B* to show the critical behavior. The straight line has a slope of 0.5.

similar value of ε is found very close to ϕ_c for line A . However, the log-log plot shows in this case some curvature for larger values of ϕ . The vicinity of P_c (i.e., a possible influence of ρ fluctuations) is probably at the origin of this result.

Finally, the dissymmetry of the data shown in Fig. 3 is quite remarkable: The domain where critical effects are important is more narrow on the asymmetric side. As far as B is concerned, this figure is not surprising: The expected critical behavior from the formula given previously should be different, in particular, with different critical exponents on the S and A sides. The accuracy for ξ_η is not good enough for a detailed discussion. In any case, the observed asymmetry may result at least partially from the vicinity of a tricritical point.^{9,11}

In summary, we have presented static light-scattering experiments to show the existence of a continuous sponge-asymmetric phase transition. The critical behavior close to the transition has been shown to originate from fluctuations of the η order parameter revealed by light scattering through its coupling with the density. Because of this peculiar situation the divergence of $I(q=0)$ is quite dissymmetric. In the symmetric phase the expected critical exponent is about 0.5, in agreement with experiment. Further studies, such as dynamic light scattering, are in progress for a better understanding of the critical behavior.

It is a pleasure to thank F. Nallet, M. Cates, and S. Ramaswamy for fruitful discussions and M. Maugey for

technical help.

¹F. David, Europhys. Lett. **9**, 575 (1989).

²M. Karowski and H. J. Thun, Phys. Rev. Lett. **54**, 2556 (1985).

³D. A. Huse and S. Leibler, J. Phys. (Paris) **49**, 605 (1988); (to be published).

⁴M. E. Cates, D. Roux, D. Andelman, S. T. Milner, and S. A. Safran, Europhys. Lett. **5**, 733 (1988).

⁵D. Andelman, M. E. Cates, D. Roux, and S. A. Safran, J. Chem. Phys. **87**, 7229 (1987); L. Golubovic and T. Lubensky, Europhys. Lett. **10**, 513 (1989).

⁶L. E. Scriven, Nature (London) **263**, 123 (1976).

⁷G. Porte, T. Marignan, P. Bassereau, and R. May, J. Phys. (Paris) **49**, 511 (1988); D. Gazeau, A. M. Bellocq, D. Roux, and T. Zemb, Europhys. Lett. **9**, 447 (1989).

⁸D. Roux, M. E. Cates, U. Olsson, R. C. Ball, F. Nallet, and A. M. Bellocq, Europhys. Lett. **11**, 229 (1990).

⁹D. Roux and M. E. Cates, in *Dynamics and Patterns in Complex Fluids*, edited by A. Onuki and K. Kawasaki, Springer Proceedings in Physics Vol. 52 (Springer, Berlin, 1990), p. 19.

¹⁰G. Guerin and A. M. Bellocq, J. Phys. Chem. **92**, 2550 (1988).

¹¹The Fourier transform of the density correlation function given in the text differs slightly from the one given in the previous references. This is the result of a more general perturbation theory: D. Roux, C. Coulon, and M. E. Cates (to be published).

¹²G. Porte, J. Appell, P. Bassereau, and J. Marignan, J. Phys. (Paris) **50**, 1335 (1989).