Interfacial properties of amphiphilic systems: The approach to Lifshitz points

G. Gompper

Sektion Physik der Ludwig-Maximilians-Universität München, 8000 München 2, Germany

Robert Hołyst*

Department of Physics FM-15, University of Washington, Seattle, Washington 98195

M. Schick†

Department of Physics, University of Oslo, P.O. Box 1048 Blindern, 0316 Oslo, 3 Norway

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Recent experiments on oil, water, and surfactant mixtures indicate that these systems can be brought close to a Lifshitz tricritical point. We investigate the interfacial properties of a system in the vicinity of such a point, based on a single-order-parameter Ginzburg-Landau model. We find that the microemulsion does not wet the oil-water interface all the way to the Lifshitz tricritical point. In addition, the scattering intensity shows a characteristic scaling form. The interfacial behavior near Lifshitz critical end points is also examined.

The interfacial properties of amphiphilic systems are interesting for several reasons. First, and most obvious, is that the interfacial tension between oil and water can, in the presence of amphiphile, be made several orders of magnitude smaller than in its absence. The possible reasons for this have been addressed by many authors.[1-5] Second, the middle phase of such systems, the microemulsion, is characterized by the presence of an extensive amount of internal interface. Hence the typical monotonic change in system properties at an interface between one phase and another, a form dictated by the energy cost in making spatial variations in bulk properties, need not necessarily be encountered here simply because the cost of making spatial variations seems not to be large at all. In fact, exponentially damped *oscillatory* profiles at the interfaces between microemulsion and the oil-rich or water-rich phases with which it can coexist have been predicted.[4,5] Recently, it has been shown[5] that the presence of these oscillations is intimately related to the observation[6,7] that the middle phase does not wet the oil-water interface when it is made from a good amphiphile, whereas it does wet the interface when the amphiphile is poor. It is natural to assume that this nonwetting behavior of a good amphiphilic system will change to a wetting one as the tricritical point is approached. This follows from the irrelevance, in the renormalization-group sense, of long-range forces at the tricritical point, and the inevitability of wetting at a tricritical point in a square gradient approximation applicable to short-range forces.[8] However, it must be remembered that there are lamellar phases in these systems, and that the transitions to them, which are usually weakly first order, can take place very close to the tricritical point of the system. This can be seen very clearly in the sequence of experiments[9] on water, n-decane, and $C_{2i}E_i$, in which a tricritical point was approached by increasing i from 3 to 6, and on water, n-octane, and C_iE_4 for which i was increased from 6 to 12.

As the concentrations of the coexisting water, oil, and middle phases became close to one another, they also approached that of the lamellar L_α phase. If all *four* phases were to become critical simultaneously, as opposed to only the first three, then they would do so at a Lifshitz tricritical point[10] as opposed to an ordinary tricritical point. If this system is indeed close to a Lifshitz tricritical point, it would be an extremely unusual situation,[11] one which undoubtedly would be reflected not only in the interfacial behaviors, but in bulk ones as well.

We consider here the interfacial properties of a system in the vincinity of such a point by means of the following functional for the free energy per unit area, which depends upon a scalar order parameter $\phi(z)$ representing the difference between water and oil concentrations, and varying only in one direction,

$$\sigma\{\phi\} = \int dz [c(\phi'')^2 + g(\phi)(\phi')^2 + f(\phi)] , \tag{1}$$

where a prime denotes differentiation with respect to the argument. As discussed in Ref. 5, scattering experiments show that $g(\phi)$ can be negative in the middle phase. [See Eq. (4) and subsequent discussion]. Therefore, the term $(\phi'')^2$ is required to provide stability of $\sigma\{\phi\}$. The function $f(\phi)$ is the bulk free-energy density that, to describe tricritical phenomena, we take to be

$$f(\phi) = w^2\phi^2(\phi^2 - M_b^2)^2 , \tag{2}$$

where the order parameter takes the values $\pm M_b$ in the bulk oil- and water-rich phases, and zero in the middle phase. The coefficient of the gradient square term, $g(\phi)$, depends on the order parameter because it is expected that the cost of making spatial variations in ϕ will be less in the middle phase, $\phi \approx 0$, than in either the oil- or water-rich phases. This variation emerges naturally from lattice models of amphiphilic systems.[12] The Euler-Lagrange equation for the function $M(z)$, which makes

$\sigma\{\phi\}$ an extremum, is

$$2cM'''' - 2g(M)M'' - 2g'(M)(M')^2 + f'(M) = 0 . \tag{3}$$

The structure function of the middle phase is, within the Gaussian approximation,

$$S(q) \propto [cq^4 + g(0)q^2 + w^2 M_b^4]^{-1} . \tag{4}$$

Its Fourier transform, the correlation function, decays monotonically with z for large distances in the middle phase provided that $g(0) \geq 2\sqrt{c}\, w M_b^2$, and oscillates with an exponentially decaying amplitude when the inequality is not fulfilled. We denote the fluid as being unstructured in the former case, and structured (a microemulsion) in the latter. The locus of points at which the equality is fulfilled defines the disorder line.[13] From the work of Ref. 5, which employed an $f(\phi)$ and $g(\phi)$ such that Eq. (3) was exactly soluble, we expect that the middle phase will not wet the oil-water interface when it is structured. For values of $g(0) < 0$, the structure function of the middle phase has a peak at nonzero wave vector.[14] Stability of the microemulsion with respect to the formation of a lamellar phase implies that $g(0)$ cannot be too negative; $-2\sqrt{c}\, w M_b^2 < g(0)$.

When a tricritical point is approached and the correlation length becomes large, the first term in the integrand of Eq. (1) becomes ignorable with respect to the second unless $g(\phi)$ vanishes there. If it does vanish, the point is denoted a Lifshitz tricritical point. In order to approach this point, we write g in the scaling form

$$g(\phi, M_b) = 2w\sqrt{c}\, M_b^2 \hat{g}(\phi/M_b) \tag{5}$$

and take

$$\hat{g}(m) = Am^2 - B . \tag{6}$$

With this form, $g(\phi, M_b)$, evaluated in any of the bulk phases, vanishes as the tricritical point is approached, $M_b \to 0$. The middle phase is a microemulsion when $-1 \leq B \leq 1$.

We have solved Eq. (3) numerically for the profiles $m(z) \equiv M(z)/M_b$ for $A = 2\sqrt{2}$ and $-1 \leq B \leq 1/\sqrt{2}$, and calculated the interfacial tensions between all phases from Eq. (1). These tensions can be written in a scaling form by measuring lengths in units of the correlation length $\xi_L \equiv (c/w^2 M_b^4)^{1/4}$,

$$\sigma_{if} = c^{1/4} w^{3/2} M_b^5 \hat{\sigma}_{if}(A, B) , \tag{7}$$

where $i, f = +, 0$ or $-$ denote the water-rich, middle, and oil-rich phases, respectively. For positive and small negative values of B, we find quite clearly that $\sigma_{-+} < \sigma_{-0} + \sigma_{0+}$, which means that the microemulsion does not wet the oil-water interface. From the scaling form of Eq. (7), all interfacial tensions decrease proportionally as the tricritical point is approached, hence the inequality remains *all the way to and including* the Lifshitz tricritical point. As we make B more negative in Eq. (6) making the middle phase less structured, it appears that σ_{-+} approaches the sum $\sigma_{-0} + \sigma_{0+}$ with common slope (Fig. 1) so that a continuous wetting transition takes place, as predicted in Ref. 5. Due to limited
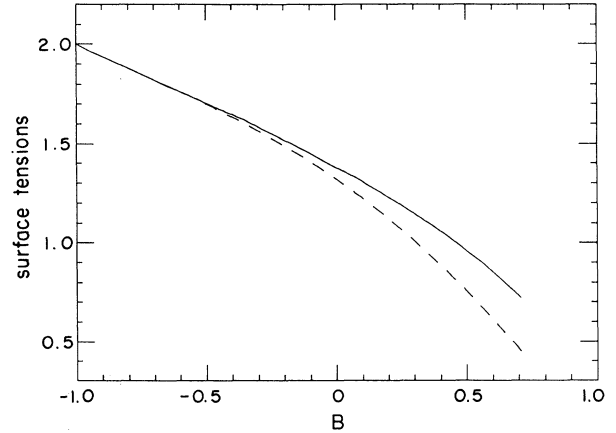

FIG. 1. Interfacial tension of the oil-water interface (dashed line) and sum of oil-middle phase and water-middle phase tensions (solid line) vs B.

numerical accuracy, we are not able to pinpoint if the transition occurs exactly at the disorder line, $B = -1$, and with the essential singularity predicted.

For the particular choice of Eq. (6) and $A = (1 + 2B^2)/B$, the Euler-Lagrange equation can be solved exactly for the interface profile between oil and water: $m(z) = \tanh(\sqrt{B}z/\sqrt{2}\xi)$. The interfacial energy of this nonwetting solution is $\hat{\sigma}_{-+} = \frac{8}{15}\sqrt{2}(1-B^2)/\sqrt{B}$. For $B = 1/\sqrt{2}$, we have compared this interfacial energy with those of the microemulsion-water and -oil interfacial energies obtained numerically, and have verified that it is indeed lower than that of a wetting solution.

The most direct means of determining the nature of the tricritical point that is being approached experimentally is to examine the structure function of the middle phase. This function is expected to take a scaling form,

$$S(q, T)/S(0, T) \to s(q\xi) , \tag{8}$$

a form that will be specific to the kind of tricritical point. Approaching an ordinary tricritical point at which $g(0)$ is a positive constant, the mean-field form of $s(x)$ is

$$s(x) = (x^2 + 1)^{-1} , \tag{9}$$

which shows a peak at zero wave vector. The correlation length in this case is $\xi_t = \sqrt{g(0)}/(wM_b^2)$. If the path of approach is within the plane of three-phase coexistence, then $\xi \propto (\bar{T} - T_{\text{tri}})^{-\nu}$, with $\bar{T}$ the average of the upper and lower critical end points. The mean-field exponent, $\nu = 1$, is exact in this case as the upper critical dimension $d_u = 3$. In contrast, approaching a Lifshitz tricritical point, the mean-field form of $s(x)$ is

$$s(x) = x^4 + 2\hat{g}(0)x^2 + 1 . \tag{10}$$

As $d_u = 6$ in this case,[10] neither the exponent ν nor the scaling form $s(x)$ are expected to show mean-field behavior. Depending on whether $\hat{g}(0)$ is smaller or greater than unity, the middle phase will or will not be structured. If $\hat{g}(0) < 0$, the scaling form of the structure func-

tion has a peak at nonzero wave vector $(q\xi)_{max}=\sqrt{-\hat{g}(0)}$. On an absolute scale of course, the peak moves towards zero as the Lifshitz tricritical point is approached. However, the ratio $S(q_{max})/S(0)$ remains unchanged. Observation of such a scaling form would be sufficient to identify the tricritical point as being of the Lifshitz kind. So also would be an observation of failure of the middle phase to wet the interface between the other two even as the tricritical point was approached.

The unusual properties of the interfacial tensions and structure functions at the Lifshitz tricritical point are a direct consequence of the lamellar phase becoming critical at the same time that the oil, water, and middle phases do. It would seem that to observe such properties, it would not be necessary that all three of these phases become critical simultaneously, but that it would be sufficient if the lamellar phase were to become critical at the same time that *two* of them did, as occurs at a critical end point. This circumstance would convert such a point into a Lifshitz critical end point. Such points are likely to be more common than Lifshitz tricritical points simply because critical end points are more common than tricritical points. To determine whether this expectation is correct, we study such end points by taking

$$f(\phi)=w^2\phi^2(\phi-M_-)^2(\phi-M_+)^2 , \qquad (11)$$

which is an asymmetric generalization of Eq. (2). To be definite, we shall approach a critical end point by letting $M_-\rightarrow0$. We write $g(\phi)$ in the scaling form

$$g(\phi,M_-,M_+)=2w\sqrt{c}M_-M_+\hat{g}(\phi/M_+,M_-/M_+) , \qquad (12)$$

which generalizes Eq. (5). By examining the structure factors of the three phases within the Gaussian approximation, it is seen that the value of the scaling function $\hat{g}$ in a given phase determines whether that phase is structured or not at the critical end point. It follows that of the two fluids that become critical at the end point, both, neither, or only one of them may be structured.

Of the several forms of $\hat{g}$ that we have studied, we present here the results for two of them. The first is a simple quadratic form

$$\hat{g}(m,m_-)=2\sqrt{2}m^2/m_- . \qquad (13)$$

With this choice, $g(\phi,M_-,M_+)\rightarrow0$ in both bulk phases, which become critical at the end point, $\phi=0$, and $\phi=M_-\rightarrow0$, so that it is a Lifshitz critical end point. Furthermore, both critical phases are structured. We find that no phase wets the interface between the other two all the way to the critical end point. The contact angle[15] characterizing a pendant drop of middle phase increases as the critical end point is approached, as shown in Fig. 2. Again, limited numerical accuracy prevents us from calculating the contact angle closer to the Lifshitz critical end point than shown.
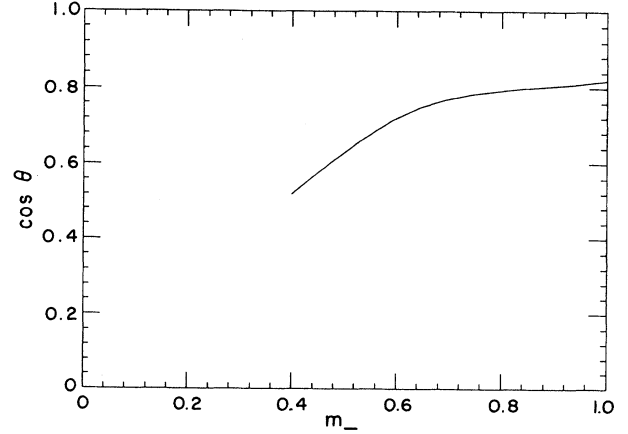

FIG. 2. Calculated cosine of the contact angle (Ref. 15) of a pendant drop of microemulsion at the oil-water interface vs order parameter in the oil-rich phase, $m_-\equiv M_-/M_+$. The system is characterized by $\hat{g}$ of Eq. (13). The Lifshitz critical end point is at $m_-=0$. For $m_-<0.4$, numerical limitations vitiated the calculation of contact angles.

The second form,

$$\hat{g}(m,m_-)=\frac{(1+2B^2)}{Bm_-}m^2-2B\left[\frac{1}{m_-}-1\right]m$$
$$+\left[\frac{1}{4}\left[\sqrt{m_-}-\frac{1}{\sqrt{m_-}}\right]^2-1\right]B , \qquad (14)$$

is a generalization of Eqs. (5) and (6) to the asymmetric case. Note that it is a second-order polynomial in m. The particular form of the coefficients is chosen because it again permits an exact solution of the profile between the M_- and M_+ phases; $M(z)=(M_+e^{kz}-M_-e^{-kz})/2\cosh(kz)$, with $k=(B^2w^2/64c)^{1/4}(M_++M_-)$. Clearly this is a profile in which the middle phase does not wet the interface between the two others. For the specific case $B=1/\sqrt{2}$, we have verified numerically that indeed $\sigma_{-+}<\sigma_{-0}+\sigma_{0+}$. This nonwetting behavior is expected as long as the middle phase is a microemulsion, i.e., $\hat{g}(0,m_-)$ is not too large. This is the case sufficiently far from the critical end point. As the end point is approached, however, $\hat{g}(0,m_-)$ increases, the middle phase crosses a disorder line, and it becomes unstructured as are the other two phases. Inspection of Eqs. (12) and (14) shows that $g(\phi,M_-,M_+)$ approaches a positive, nonzero, value in both bulk phases, which become critical, so that this critical end point is an ordinary, not a Lifshitz, one. We expect, therefore, that some interface will be wetted as the end point is approached, but know that it is not the $+-$ interface. In fact we find that it is the $+-0$ interface, between the middle phase and the spectator phase, which is wetted by the other critical $(-)$ phase. This can be seen from Fig. 3, in which all interfacial energies are shown. The wetting transition is first or-

der. This unusual behavior has been encountered previously, both theoretically[16] and experimentally.[17]

In sum, we have investigated the implications for both the interfacial and scattering behavior of the assumption that a system of oil, water, and amphiphile is close to a Lifshitz tricritical point[10] or a Lifshitz critical end point.[18] Experimental phase diagrams of at least two systems make plausible that they are close to the former, and we would naively expect the latter to be more common. We noted that the observation of certain scaling forms or the failure to observe the wetting of any interface would be diagnostic of such points. It would be useful to know the exponents governing the crossover from Lifshitz behavior in three-dimensional systems, in case experimental paths only take the system close to these points. However, only ϵ expansion results around $d_u = 6$ (Lifshitz tricritical point) or $d_u = 8$ (Lifshitz critical end point) are known.[19] Finally, it would be very interesting to understand how the parameters of the systems studied[9] are such as to lead it near so special a location in phase space as a Lifshitz tricritical point.
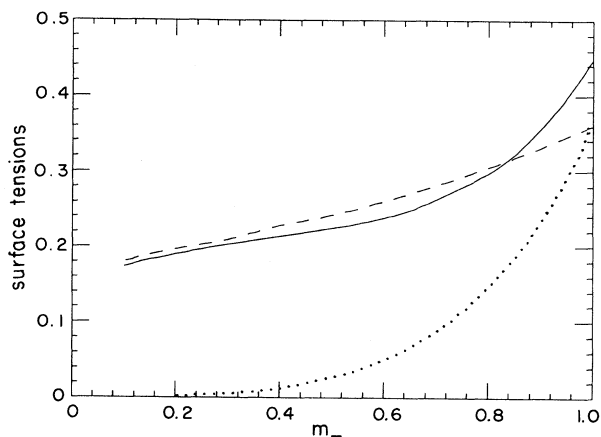
FIG. 3. For a system characterized by $\hat{g}$ of Eq. (14), the tensions of all interfaces are shown vs order parameter in the oil-rich phase, m_-. Dotted line, oil-middle phase (or $--0$) tension; dashed line, water-middle phase (or $+-0$) tension; solid line, water-oil (or $+--$) tension.

*Permanent address: Institute of Physical Chemistry of the Polish Academy of Sciences, Department III, Kasprzaka 44/52, 01224 Warsaw, Poland.

†Permanent address: Department of Physics FM-15, University of Washington, Seattle, WA 98195.

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