COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Fluctuating interfaces in microemulsion and sponge phases"

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In a recent paper Gompper and Goos [Phys. Rev. E **50**, 1325 (1994)] use the random-interface approach to discuss film scattering from sponge and microemulsion phases. We show that their calculations of the film scattering lack the integration measure so that subsequent conclusions about the random-level-surface model have to be revised. Furthermore we find in contrast to that paper that a sponge-lamellar transition in the random-interface approach is possible.

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In a recent paper Gompper and Goos discuss level surfaces in random fields and their applicability as models for fluctuating amphiphilic systems such as sponge and microemulsion phases [1]. The authors claim that their calculations show that the variational model which is the basis for the random-interface model of microemulsions and sponge phases [2,3] (a) does not produce a peak in the film scattering signal at nonzero wave vector k and is therefore a doubtful description of bicontinuous phases ["...the variational approach is unable to produce a peak of the scattering intensity in film contrast at finite wave vector k. This is a serious deficiency of the Gaussian model. It shows that *level surfaces of Gaussian random fields do not accurately describe the structure of bicontinuous microemulsions.*" (italics by the authors of [1])], (b) does not lead to a sponge to lamellar transition ("...the variational approach fails ... for the phase transition between microemulsion and lamellar phase.").

We believe (as will be shown in this Comment) that these points and the subsequent conclusions are in error. Point (a) is based on an inconsistent approximation for the film scattering. The correct calculation of the film scattering results in the arctangent form for the scattering at small wave vector and indicates that a peak at finite wave vector can emerge, in agreement with experiment. The lack of a spinodal, (b), is not an indication of the correctness of a given theory; it merely indicates that the transition is first order, again, in agreement with experiment. As a matter of fact, the variational formulation of the random surface model which has a clear energetic basis (the bending Hamiltonian) and is not based on a purely phenomenological low wave vector free energy expansion predicts a first order sponge-lamellar transition without adjustable parameters.

First, Gompper and Goos adopt an analytic method to calculate the film-film correlation function for a continuous bulk order parameter field, $\phi(\vec{r})$, by the correlation of different regions of the film around level surfaces at $\phi(\vec{r})=0$. This concept is due to Berk [4] and was further elaborated by Teubner [5], Berk [6], Pieruschka and Marčelja [2], and Chen, Lee, and Chang [7] in the context of the effective interface description of amphiphilic systems which assumes that all the surfactant is located at the water-oil (inside-outside) interface. Gompper and Goos base their calculation on the film-film correlation function

$$G_{\text{film}}(r)\sim\langle\delta(\phi(0))\delta(\phi(r))\rangle\ . \tag{1}$$

The correct formula, however, should read

$$G_{\text{film}}(r)\sim\langle\,|\nabla\phi(0)|\delta(\phi(0))|\nabla\phi(r)|\delta(\phi(r))\rangle\ . \tag{2}$$

The gradient terms in Eq. (2) are necessary for the correct integration measure. It is possible to see the necessity of gradient terms, if one considers the correct formula for the area of the interface which was derived by Teubner [5]

$$S/V=\langle\,|\nabla\phi|\delta(\phi)\rangle\ . \tag{3}$$

As a matter of fact, the authors used this formula for the area, S/V, correctly incorporating the area measure but did not include the area factor in the film correlation function—which is thus inconsistent.

While in Eq. (1) the correlation matrix in the Gaussian exponent is of order 2×2 and contains the bulk correlation function $g(r)$ only, so that $G_{\text{film}}(r)=G_{\text{film}}(g(r))$, the correct correlation matrix is of order 8×8 and involves major contributions from the gradient terms so that $G_{\text{film}}(r)=G_{\text{film}}(g(r),\partial g(r)/\partial r,\partial^2 g(r)/\partial r^2,r^{-1}\partial g(r)/\partial r)$. The correct calculation of the film scattering is rather

complex [5,8,9] and results in the limit of large r and bulk symmetry in a linear combination of terms [9] $g^2(r), g_1^2(r), g_2^2(r)$ where approximately

$$g(r) \approx e^{-r\xi^{-1}} \frac{\sin k_0 r}{k_0 r} ,$$

$$g_1(r) \approx e^{-r\xi^{-1}} \frac{1}{k_0 r} [k_0 \cos k_0 r - \xi^{-1} \sin k_0 r] ,$$

$$g_2(r) \approx e^{-r\xi^{-1}} \frac{1}{k_0 r} [k_0^2 \sin k_0 r + 2k_0 \xi^{-1} \cos k_0 r - \xi^{-2} \sin k_0 r] .$$

This leads (for real k_0) to contributions which are proportional to $\exp[-2\xi^{-1}r]/(k_0 r)^2$, $\exp[-2\xi^{-1}r]/(k_0 r)^2 \sin[2k_0 r]$, and $\exp[-2\xi^{-1}r]/(k_0 r)^2 \cos[2k_0 r]$. The Fourier transform of the first term leads approximately to

$$G_{\text{film}}(k) \sim \text{const} + k^{-1} \arctan \frac{\xi k}{2} \tag{4}$$

in the low-k regime. The functional arctangent form at low k is well established in experiments and Ginzburg-Landau theory of L_3 phases [10]. (The Fourier transforms of the second and third term are insignificant at low k. For intermediate k they show a step and peak shape, respectively, for sufficiently large $k_0\xi$ at $k \approx 2k_0$. For small $k_0\xi$ or imaginary k_0 these irregularities at $2k_0$ vanish.) For intermediate k no simple analytical approximation exists. Scattering can then be either calculated by numerical evaluation of Eq. (2) or by approximate numerical treatment based on real-space representations, Eq. (7) (cf. below). The latter indicates in the limit of large correlation length $\xi^{-1} \to 0$ a peak at $2k_0$ in the film scattering. While we do not argue here that the film scattering structure factor given by the random-interface model can provide perfect fits to experimental data it is clear from the above that the film scattering calculated in [1] is based on an unsatisfactory formulation of the correlation function. The subsequent conclusions about the validity of the random surface model are therefore unwarranted.

In their numerical evaluation of the film scattering signal Gompper and Goos assume that the film-film correlation function is given by the average [Eq. (6) in [1]]

$$G_{\text{film}}(r) \sim \langle \delta_\epsilon(\phi(0)) \delta_\epsilon(\phi(r)) \rangle , \tag{5}$$

where $\delta_\epsilon = \epsilon^{-1}$ for $-\epsilon/2 \le x \le \epsilon/2$ and zero otherwise. They assume that the level cuts at $\pm\epsilon/2$ delineate a "...thin layer of [physical] thickness ϵ around the $\phi=0$ surface." This, however, is not quite correct, because Gaussian random fields do not support a parallel family of surfaces [2]. Equation (5) describes scattering from a film with nonuniform thickness. Gradient terms account for the fact that the value of ϕ located at a distance $\pm\epsilon/2$ along the normal from the surface of $\phi=0$ varies in space. Taylor series expansion about the surface at $\phi=0$ shows that the film enclosed by the surface at a distance $\epsilon/2$ from $\phi=0$ is given by

$$\phi(r) \le \frac{\epsilon}{2} |\nabla \phi(r)| \tag{6}$$

and the correlation function should read [8]

$$G_{\text{film}}(r) \sim \text{Prob} \left[|\phi(0)| \le \frac{\epsilon}{2} |\nabla \phi(0)|, |\phi(r)| \le \frac{\epsilon}{2} |\nabla \phi(r)| \right] , \tag{7}$$

where the gradient terms correct nonuniform film thickness in first order. [We have to emphasize, however, that while Eq. (7) comes much closer to a correct description of a film with constant physical thickness than the method used in [1], Eq. (7) still does not implement a *perfect* description of such a film. However, in the limit $\epsilon \to 0$ the rigorous result Eq. (2) in retrieved.] Hence all numerical results concerning film scattering (even concerning Ginzburg-Landau simulations) in [1] are done for films of nonuniform thickness and should be revised, if they are to give reliable information on film scattering from uniformly thick films (as erroneously stated in [1]). A justification for using Eq. (5) can only be given by arguing that in Ginzburg-Landau models the surfactant does not have to be concentrated on a sharp interface [11]. This, however, was not discussed in [1].

Second, the statement concerning the failure of the variational approximation to yield a sponge-lamellar transition has no formal basis ("Much to our surprise no such spinodal exists."). In fact, the lamellar to sponge transition is first order in microemulsions and L_3 phases. There is no requirement for a second order transition or spinodal between the sponge and lamellar phase. Hence the absence of a spinodal is by no means a proof of the failure of a model to predict a phase transition. Indeed, we have recently shown that the variational formalism leads to a first order sponge-lamellar transition upon increase (decrease) in bending (saddle-splay) modulus or surfactant concentration [12].

We believe (as shown in this Comment) that two of the major conclusions of the paper [1] by Gompper and Goos are based on erroneous assumptions and calculations. In fact, one can show that the random-interface model correctly predicts the arctangent form of the film scattering for small wave vector as seen in many experiments [10]. Approximate numerical calculations [based on Eq. (7)] also indicate a peak at finite wave vector for large, scaled correlation length $k_0\xi$. Finally, the random-interface model is able to consistently predict a sponge-lamellar transition in agreement with experiment.

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[1] G. Gompper, and J. Goos, Phys. Rev. E **50**, 1325 (1994).
[2] P. Pieruschka and S. Marčelja, J. Phys. (France) II **2**, 235 (1992).
[3] P. Pieruschka and S. A. Safran, Europhys. Lett. **22**, 625 (1993).
[4] N. F. Berk, Phys. Rev. Lett. **58**, 2718 (1987).
[5] M. Teubner, Europhys. Lett. **14**, 403 (1991).
[6] N. F. Berk, Phys. Rev. A **44**, 5069 (1991).
[7] S.-H. Chen, D. Lee, and S.-L, Chang, J. Mol. Struct. **296**, 259 (1993).
[8] M. Teubner (unpublished).
[9] P. Pieruschka and S. A. Safran (unpublished).
[10] D. Roux, *et al.*, Europhys. Lett. **11**, 229 (1990); C. Coulton, D. Roux, and A. M. Bellocq, Phys. Rev. Lett. **66**, 1709 (1991); C. Coulon, D. Roux, and M. E. Cates, *ibid.* **67**, 3194 (1991); R. Granek, and M. E. Cates, Phys. Rev. A **46**, 3319 (1992); D. Roux, C. Coulon, and M. E. Cates, J. Phys. Chem. **96**, 4174 (1992).
[11] G. Gompper (private communication).
[12] P. Pieruschka, Ph.D. thesis, Australian National University, Canberra, 1994 (unpublished).