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► **To cite this version:**

P. Pieruschka, S. Marčelja. Statistical mechanics of random bicontinuous phases. *Journal de Physique II*, 1992, 2 (2), pp.235-247. 10.1051/jp2:1992127 . jpa-00247627

**HAL Id: jpa-00247627**

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Submitted on 4 Feb 2008

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Classification

Physics Abstracts

05.40 — 62.20D — 82.65D

## Statistical mechanics of random bicontinuous phases

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(Received 10 July 1991, accepted 22 October 1991)

**Abstract.** — We consider a random wave description of bicontinuous microemulsions, where the structure is specified by a correlation length  $\xi$  and a preferred wave vector  $k_0$ . The entropy of the system is calculated as the information content of a random field with an experimentally determined spectral distribution. Together with the elastic energy which has been previously derived by Teubner, we can minimise the free energy of the system and thus estimate the value of the elastic modulus  $\kappa$  of the film. For example, in water — toluene — SDS/butanol microemulsions the parameters  $\xi$  and  $k_0$  obtained from fits to the neutron scattering data lead to values for  $\kappa$  of about two units of  $kT$ .

### 1. Introduction.

Bicontinuous disordered phases of oil — surfactant (and cosurfactant) — water mixtures can be conveniently studied on a phenomenological level, where an elastic surfactant film divides the system volume into two distinct phases. A particularly useful model of such systems is provided by the formal adaptation of Cahn's random wave model of spinodal decomposition [1, 2]. As shown by Teubner [3], the superposition of random waves results in a random Gaussian field with a given spectral density, which allows the calculation of statistical averages over the film surface.

In the following we wish to expand the random wave model to calculate the system entropy, free energy and bending modulus.

The physical system consisting of the surfactant film dividing the volume into two phases is defined as a level crossing of the generating random Gaussian field. Under specific conditions there are theorems which indicate that the information content of a two dimensional surface obtained by level crossing is equivalent to the information content of the generating three dimensional field [4]. The information content of a random process with a given spectral density was evaluated in a classical work of Shannon [5], and this can consequently be applied to disordered bicontinuous phases.

The evaluation of the entropy is dependent on the unique correspondence between each spatial configuration of the surfactant film and the corresponding realisation of the random Gaussian field with a known spectral density. Away from the isometric composition, the assumption of a random surface geometry becomes progressively less accurate. But even if

this problem is disregarded, homogeneous regions of oil or water become larger and the reconstruction of the corresponding random field from such a configuration may require unphysically high accuracy in specifying the position of the surfactant film.

The class of random fields under consideration, which is associated with random bicontinuous structures, is specified by two physical parameters, the preferred wave vector  $k_0$  and the correlation length  $\xi$ . As an example for such a field we will adopt in the following section a particular localised random wave model [6] and apply it to a SDS based microemulsions system studied by Auvray *et al.* [7, 8]. Having obtained  $\xi$  and  $k_0$  from the experimental bulk neutron scattering data and having checked those values by means of the film scattering data, we will evaluate the free energy of the model as a function of  $\xi$  and  $k_0$ . The free energy must be minimal for the measured values of  $\xi$  and  $k_0$ , and this provides a route for the calculation of the bending elasticity modulus of the film from the scattering data.

## 2. Geometry : correlation functions, spectral densities, scattering curves.

The original model of Berk [2] bases the spatial distribution of two phase media on a superposition of random waves in  $R^3$  with uniformly distributed phases and wave vector directions and a certain probability distribution for the magnitude of the wave vector

$$S(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{i=1}^N A_i \cos(\mathbf{k}_i \cdot \mathbf{r} + \phi_i). \quad (1)$$

In order to obtain realistic small angle neutron and X-ray scattering (SANS, SAXS) intensities, Berk assumed for the magnitudes of  $\mathbf{k}_i$  a Gaussian distribution around some preferred value  $k_0$ . Other authors [3, 9] used differently broadened distributions  $f(k)$ .

An alternative to *a priori* assumptions about the probability density  $f(k)$  is a natural probability spread in  $k$ -space obtained as a consequence of physical localisation of the constituent waves in real space [6]. The form of the localisation is given by an envelope  $u(r)$  with a characteristic decay length  $\xi$ .

The modified random field  $S$  has the form

$$S(\mathbf{r}; \xi, k_0) = \frac{1}{\sqrt{N}} \sum_{i=1}^N u(|\mathbf{r} - \mathbf{r}_i|; \xi) \cos(\mathbf{k}_i \cdot (\mathbf{r} - \mathbf{r}_i)), \quad \text{with } \mathbf{k}_i = k_0 \cdot \mathbf{e}_i. \quad (2)$$

The directions of  $\mathbf{k}_i$  and the positions  $\mathbf{r}_i$  are again uniformly distributed. We emphasise the fact that the class of random fields discussed throughout this paper is the class dependent on two length scales given by  $\xi$  and  $k_0$  which have obvious experimental meaning in bicontinuous microemulsion systems [10, 11]. The particular functional form in which the two parameters are later introduced is only an illustrative example and is of no importance for the major results.

Equation (2) is, as pointed out by Teubner [3], in the limit of an infinite number of constituent waves a Gaussian process. This opens a relatively simple access to the statistical properties of the system, using the well-known fact [3] that a Gaussian field is completely determined by its mean and covariance functions,  $m(\mathbf{r}) = \langle S(\mathbf{r}) \rangle$  and  $g(\mathbf{r}_1, \mathbf{r}_2) = \langle S(\mathbf{r}_1) S(\mathbf{r}_2) \rangle$ , in either real or Fourier space. Further simplification arises from the fact that  $S$  is homogeneous and isotropic [12]. The covariance function simplifies then to  $g(r) = \langle S(0) S(r) \rangle$  with momentum representation  $f(k)$ .

It is a physical constraint that only modes down to a certain wavelength  $\lambda_c$  are to be represented by the random wavelets of the model [11, 13]. The shortest possible wavelength is determined by the film — oil — film — water sequence, at least about four monolayer

thicknesses. Our estimate of  $\lambda_c$  can be refined, by exploiting the fact [2, 14] that the experimental surface to volume fraction  $S/V$  is proportional to the square root of the second moment  $\langle k^2 \rangle$  of the spectral density  $f(k)$ , and  $\langle k^2 \rangle$  is in turn dependent on the cut-off  $k_c = 2\pi/\lambda_c$ . This relation delivers an upper limit for  $\lambda_c$ ; we will return to this point when treating a specific example of a localised field in Appendix A.

**2.1 CORRELATION FUNCTION AFTER LEVELLING.** — In describing SANS or SAXS experiments the original three phase system oil — surfactant — water is usually represented as a two phase system, by either « black-white coloring » of the two bulk partitions (where the surfactant layer is normally split and assigned to the two bulk partitions) or, alternatively, by contrasting the entire bulk with the film, when experimental water and oil scattering length densities are matched.

If  $\alpha, \beta, \dots$  are the cutting levels specifying the layer system, the clipped correlation function  $\Gamma^{\alpha\beta\dots}(r)$  can be gained from the knowledge of  $g(r)$  and the Gaussian bivariate by representation of the clipping process as a product of the appropriate linear combinations of Heaviside step functions. The number of steps is identical to the number of levelling parameters.

For two phase contrasts we use  $\Theta_{\alpha\beta}$ , where  $\Theta_{\alpha\beta} = 1$  for  $\alpha \leq x \leq \beta$  and zero otherwise. Although a two phase contrast modelling meets experimental situations, three and higher phase terms may have some minor impact on the behaviour of scattering curves due to slight, involuntary mismatches. Those corrections can be easily included, but two phase terms will be sufficient to demonstrate the general idea.

The clipped correlation function

$$\Gamma^{\alpha\beta}(r) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{1}{2\pi \sqrt{1-g(r)^2}} e^{-\frac{x^2+y^2-2g(r)xy}{2(1-g(r)^2)}} \Theta_{\alpha\beta}(x) \Theta_{\alpha\beta}(y) dx dy,$$

can be simplified to

$$\Gamma^{\alpha\beta}(r) = \Gamma^{\alpha\beta}(0) - \frac{1}{2\pi} \int_{g(r)}^1 \frac{1}{\sqrt{1-t^2}} \left( e^{-\frac{\alpha^2}{1+t}} + e^{-\frac{\beta^2}{1+t}} - 2e^{-\frac{1}{2} \frac{1}{1-t^2} (\alpha^2 - 2\alpha\beta t + \beta^2)} \right) dt. \quad (3)$$

A numerically useful transformation  $t = \sin \phi$  that avoids the artificial singularity of the integrand at the upper limit leads to

$$\begin{aligned} \Gamma^{\alpha\beta}(r) &= \\ &= \Gamma^{\alpha\beta}(0) - \frac{1}{2\pi} \int_{\arcsin(g(r))}^{\pi/2} \left( e^{-\frac{\alpha^2}{1+\sin\phi}} + e^{-\frac{\beta^2}{1+\sin\phi}} - 2e^{-\frac{1}{2} \frac{1}{\cos^2\phi} (\alpha^2 - 2\alpha\beta \sin\phi + \beta^2)} \right) d\phi. \quad (4) \end{aligned}$$

We can normalise with respect to the correlation at  $r = 0$

$$\gamma^{\alpha\beta}(r) = \frac{\Gamma^{\alpha\beta}(r) - \Gamma^{\alpha\beta}(\infty)}{\phi_s(1 - \phi_s)} = \frac{\Gamma^{\alpha\beta}(r) - \phi_s^2}{\phi_s(1 - \phi_s)}, \quad (5)$$

where  $\phi_s$  is the surfactant volume fraction.

Teubner's more specialised result for one-step levelling is immediately recovered by taking  $\beta \rightarrow \infty$   $\left( \lim_{\beta \rightarrow \infty} \gamma^{\alpha\beta} = \gamma^\alpha \right)$ . Berk's  $2/\pi \arcsin(g(r))$  term [2] is the obvious limit of equation (4) for  $\beta \rightarrow \infty$ ,  $\alpha = 0$ . It was used to check the numerical stability of equation (4).

Despite the attractive simplicity of expression (4) it should be noted that (4) is only an approximation not valid for too small values of  $r$  (or too high values of  $k$  in momentum space). The problem arises from the nonuniform thickness of the film created by two level cuts of a three dimensional field. In order to obtain correct asymptotic behaviour for high  $k$  a more tedious approach is available [3], but as we will see in the following subsection our approximation serves well for practical purposes.

Signal clipping has long been used in communication theory and the relation between clipped and unclipped spectral densities are well known [15]. The shape of the clipped spectrum largely resembles the unclipped one, but decays slower — it is smeared out.

**2.2 FITS TO FILM AND BULK SANS DATA.** — To our knowledge only Auvray *et al.* [8] have published suitable pairs of corresponding bulk and film SANS intensity data. We used a specific example of localised random waves described in Appendix A to fit the scattering data of reference [8] and to obtain the experimental parameters  $\xi$  and  $k_0$ . The fits to the bulk scattering data easily delivered the relevant  $\xi$ ,  $k_0$  pairs and comparisons to the film scattering were performed to verify those model parameters.

We were making use of the standard relation for isotropic scatterers

$$I(k) = 4 \pi \langle \eta^2 \rangle \int_0^\infty \gamma(r) r^2 j_0(kr) dr, \quad (6)$$

where  $\gamma(r) = \gamma^\alpha(r)$  for two-phase scattering and  $\gamma(r) = \gamma^{\alpha\beta}(r)$  for film scattering, and actual evaluation of the expressions was done with the sample functions of Appendix A.

Values for  $\langle \eta^2 \rangle$  (essentially the scattering length densities) and other experimental parameters were taken from references [7, 8]. The volume fraction of the surfactant was estimated by the weight densities and molecular weights for SDS heads and tails [7]. We followed the advice of reference [8] to ignore the influence of cosurfactant on the scattering length profile and to count the surfactant layer in the case of bulk scattering entirely as a part of the oil domain. We are therefore shifted by a few percent from the phase symmetry. The cutoff wavelength was taken to be about  $\lambda_c \approx 55 \text{ \AA}$  (Appendix A).

Figures 1 and 2 give the results and fit parameters for the cases of SDS weight fractions of 7 % and 10 % respectively. (Note that the relative experimental error for weight fractions is about 5 % [7].) All intermediate cases can be done analogously. Taking into account that the model is only varying the two natural scales  $\xi$  and  $k_0$ , and that no adjustment of  $\xi$  and  $k_0$  was performed when fitting the film scattering, the agreement with the experimental data is very satisfactory. The  $\xi$ ,  $k_0$  parameters obtained from the fits are close to those used for the same system by Teubner and Strey [10], as one would expect from the conceptual similarity (note, however, that the Teubner-Strey theory is a three parameter theory).

In the case of 10 % SDS film scattering the « hump » pattern of the scattering curve is not reproduced. The hump may be a genuine effect or an artefact due to a slight mismatch in the two bulk scattering length densities. As the bulk intensities are about a factor of 100 greater than film intensities, even minute discrepancies in the scattering length densities will have a visible effect.

Figures 3 and 4 verify correct asymptotic behaviour of the model as far as the experimental data are given. With respect to figure 3 it should be noted that the standard  $k^4 I(k)$  vs.  $k$  plot in practice cannot fully match the experimental data. Due to the different decay behaviour of bulk ( $I(k) \propto k^{-4}$ ) and film ( $I(k) \propto k^{-2}$ ) scattering intensity, the experimental asymptotic behaviour in the bulk case will be sensitive to a weak film component in the scattering length profile, and is likely to be overridden by the slowly decaying film tail. This has been verified experimentally [7]. Figure 4 is a  $k^2 I(k)$  vs.  $k^2$  plot as used in reference [8] to demonstrate the

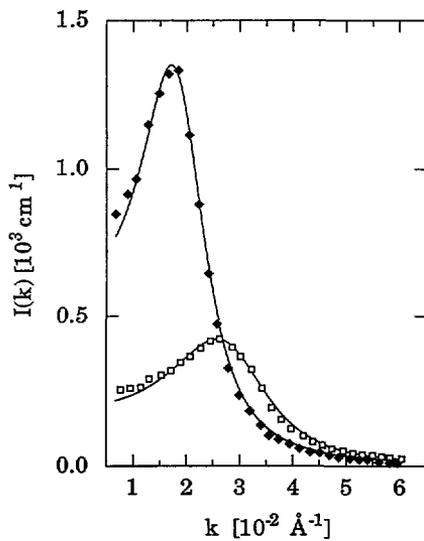


Fig. 1.

Fig. 1. — Symbols : SANS bulk intensity for 7 % ( $\blacklozenge$ , upper curve) and 10 % ( $\square$ , lower curve) SDS microemulsion systems (taken from Ref. [8]). Lines : localised random wave fit to the data. Model parameters : for 7 % SDS :  $\xi = 133 \text{ \AA}$ ,  $k_0 = 1.87 \times 10^{-2} \text{ \AA}^{-1}$  For 10 % SDS :  $\xi = 87 \text{ \AA}$ ,  $k_0 = 2.822 \times 10^{-2} \text{ \AA}^{-1}$  For both systems the cut-off values were  $r_m = 10 \text{ \AA}$  and  $\lambda_c = 55 \text{ \AA}$  while  $\langle \eta^2 \rangle$  had the experimental value of  $3.32 \times 10^{21} \text{ cm}^{-4}$ . The experimental surfactant volume fractions were  $\phi_s(7\% \text{ SDS}) = 5.5\%$  and  $\phi_s(10\% \text{ SDS}) = 7.5\%$ .

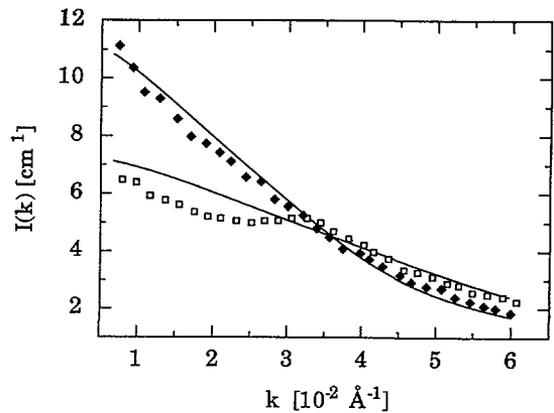


Fig. 2.

Fig. 2. — Symbols : SANS film intensity for 7 % ( $\circ$ , upper curve) and 10 % ( $\square$ , lower curve) SDS microemulsion systems (taken from Ref. [8]). Lines : localised random wave fit to the film scattering data ; all parameters are the same as in figure 1 (with the exception of  $\langle \eta^2 \rangle = 2.79 \times 10^{21} \text{ cm}^{-4}$ ).

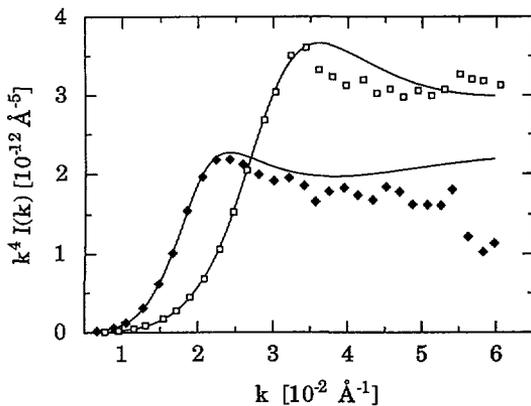


Fig. 3.

Fig. 3. —  $k^4 I(k)$  vs.  $k$  for 7 % ( $\circ$ ) and 10 % ( $\square$ ) SDS. All parameters are the same as in figure 1. Theoretical fits are again shown as solid lines.

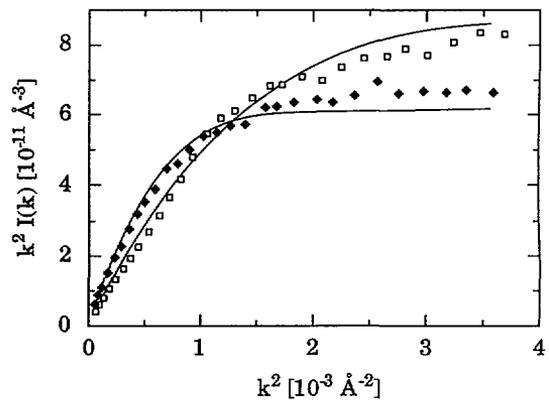


Fig. 4.

Fig. 4. —  $k^2 I(k)$  vs.  $k^2$  for 7 % ( $\circ$ ) and 10 % ( $\square$ ) SDS. All parameters are the same as in figure 2. Theoretical fits are again shown as solid lines.

typical  $k^{-2}$  asymptotic behaviour. Quantitative agreement is good, and qualitatively the shapes of our curves and figure 2 of reference [8] show strong resemblance. As mentioned above the mathematical asymptotic analysis of our film scattering prediction will eventually obey Porod's  $k^{-4}$  law. In an intermediate range, however, which goes far beyond the experimentally accessible  $k$  range, the  $k^{-2}$  law is obeyed and we conclude that approximation (4) comes close enough to reality to successfully match experiments. Nevertheless a detailed comparison between equation (4) and the method used in [3] is a sensible task.

Finally in figure 5 we present two dimensional cuts through the spatial structures which correspond to the model fits of figure 1. As expected they show a higher degree of disorder than the comparable images of references [2, 6].

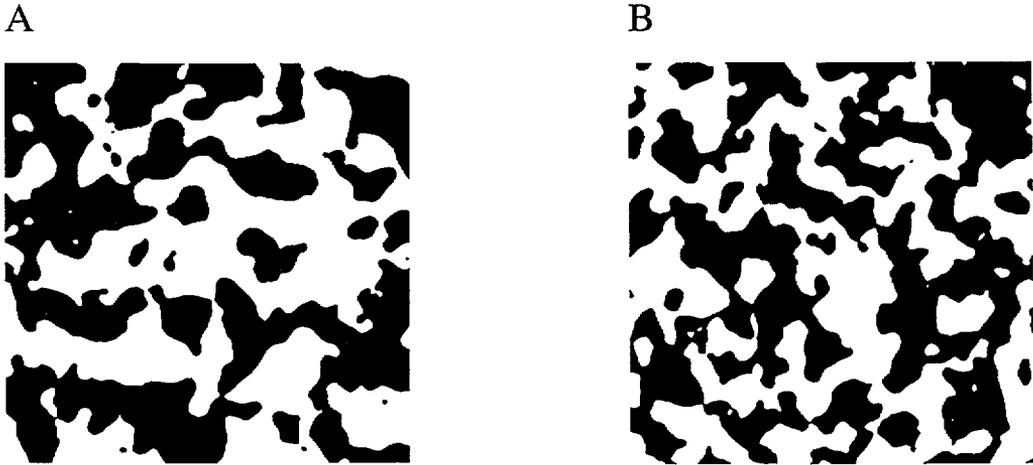


Fig. 5. — Spatial structures corresponding to the model fits in figure 1. The white-black interfaces are the sets  $S = 0$  of equation (2) (picture A : 7 % SDS, picture B : 10 % SDS). The image sizes are five characteristic wavelengths of the 7 % SDS system ( $\approx 1\,680 \text{ \AA}$ ). The images were obtained from a superposition of  $N = 10\,000$  localised random waves, distributed throughout a volume somewhat larger than the actual size of the figures.

### 3. Entropy and free energy.

In previous work on the question of the entropy of random bicontinuous phases, e.g. references [16, 17], a subdivision of the system was applied in order to discretise the number of possible states and thus make them accessible to counting. Safran *et al.* [17] achieved this by introducing a structural length scale (similar to de Gennes' persistence length [11], or our correlation length). To follow those lines would for our model mean estimating the order of magnitude of the system entropy by counting the number of « degrees of freedom », « modes » etc. and assigning equal energy or equal probability to each kind of excitation. Such an estimate is essentially equivalent to measuring the volume of the phase space available to the system.

We can calculate the normalised standard deviation in Fourier space for localised waves described by the decay length  $\xi$  [18] and arrive at

$$\Delta k \propto \frac{1}{\xi}. \quad (7)$$

In a very rough estimate, the number of states should go like  $4 \pi k_0^2 \Delta k \propto 1/\xi^3$ , consistent with the result of Safran *et al.* [17]. We used the fact that for the bicontinuous microemulsions under consideration the product  $k_0 \xi$  always has a small value of about 2-3.

Although we will suggest in the following section a more accurate entropy evaluation which does not depend on discretisation, the above procedure can at least be used to estimate the number  $N$  of constituent waves in equation (2) as  $N \approx V \cdot 4 \pi k_0^2 \Delta k$ .

**3.1 ENTROPY OF A BAND-LIMITED RANDOM FIELD.** — A truly continuous estimate of the entropy is obtained if the rms amplitude or energy associated with each degree of freedom varies with the position in  $k$ -space. For non-interacting models in planar geometry, this variation can be obtained from the equipartition theorem [13]. Alternatively, if the amplitude variation can be deduced from experimental data the equivalence of physical and informational entropy [19] opens a way to the calculation of the system free energy.

We will use the three dimensional version of Shannon's classical derivation of the entropy change in linear, band-limited filters in the time/frequency domain [5] to derive an expression for the entropy differences between all possible wave fields with filter characteristic  $f(k; \xi, k_0)$  associated with a given random physical bicontinuous system.

Consider a band-limited signal  $Y$  which is given by its sampling representation in  $k$ -space, i.e. as a  $N$ -dimensional vector  $\mathbf{y} = (y(\mathbf{k}_1), \dots, y(\mathbf{k}_N)) = (y_1, \dots, y_N)$ , where the  $y$  are continuously variable in the band-limited domain. Each of the components  $y_i$  has a given probability distribution  $p_i(y_i)$  and the joint distribution associated with  $\mathbf{y}$  can be denoted as  $p = p(p_1(y_1), \dots, p_N(y_N)) = p(\mathbf{y})$ . The signal  $Y$  can then be treated as a random variable with a probability distribution  $p(\mathbf{y})$ .

The difference between a reference signal  $Y$  and a signal  $Y'$  with spectral density  $f(k)$  can be easily expressed by a simple weighting procedure or linear transformation  $y'(\mathbf{k}_i) = f(\mathbf{k}_i) \cdot y(\mathbf{k}_i)$  and with Shannon's entropy of a continuous random field  $Y$  given as [5, 20]

$$H = \int p(\mathbf{y}) \ln p(\mathbf{y}) d\mathbf{y},$$

a linear transformation of the above kind will result in the modified entropy

$$\begin{aligned} H' &= \int p(\mathbf{y}') \ln p(\mathbf{y}') d\mathbf{y}' \\ &= \int J p(\mathbf{y}) \ln (J p(\mathbf{y})) J^{-1} d\mathbf{y} \\ &= H + \int p(\mathbf{y}) \ln J d\mathbf{y} \\ &= H + \ln J. \end{aligned}$$

The entropy change due to a certain spectral density is therefore just  $(\ln J)$ , the logarithm of the Jacobi determinant assigned to the transformation process. With

$$\begin{aligned} \ln J &= \ln \left( \prod_{i=1}^N f_i(\mathbf{k}) \right) \\ &= \sum \ln f_i(\mathbf{k}) \\ &\approx \frac{V}{(2\pi)^3} \int_0^{k_c} \ln f(\mathbf{k}) d\mathbf{k}, \end{aligned}$$

an expression for the entropy of isotropic random fields relative to some reference field can be written as

$$H = \frac{V}{(2\pi)^3} \int_0^{k_c} 4\pi k^2 \ln f(k; \xi, k_0) dk. \quad (8)$$

The remaining task is to establish that the information in the unlevelled random process with a spectrum  $f(k)$  is the same as the information contained in the corresponding levelled field. This problem has been recently considered by Curtis and Oppenheim [4]. Their Theorem 4 states that for band-limited, Fourier expandable, multidimensional signals the level surfaces contain the same information as the unlevelled field (up to an overall intensity factor). The equivalence has been illustrated by examples of recovering two dimensional images from level crossings.

However, the link has to be considered with care, as it does not take into account the thermal fluctuations or the finite sharpness of the level surface. Until we have fully examined this problem, we shall take the informational correspondence between the surfaces and the field as exact.

**3.2 EVALUATION OF THE FREE ENERGY, BENDING MODULUS.** — Having determined the experimental parameters  $(\xi, k_0)$ , we can perform the free energy minimisation which will yield the elastic modulus  $\kappa$  of a given experimental surfactant system. Note that in a particular surfactant system  $S/V \propto \sqrt{\langle k^2 \rangle}$  can only weakly vary with  $\xi$  and  $k_0$ , and we therefore consider the surface to volume ratio as constant. This effectively reduces the problem to the dependence on one free variable, chosen here as the coherence length  $\xi$ .

The bending energy will in general comprise Gaussian and mean square curvature terms. The Gaussian curvature (cf. Appendix A) is proportional to  $\langle k^2 \rangle$  and thus constant in a given surfactant system with a constant  $S/V$  ratio [3]. If we are interested in free energy differences only, the Gaussian curvature term can be discarded.

Adding Teubner's result for the mean square curvature [3] to the informational entropy equation (8) completes the expression for the free energy difference between two surface systems  $\Delta F = \Delta U - T \Delta H$ . We compare two random fields characterised by two distinct pairs of parameters  $(\xi, k_0)_1, (\xi, k_0)_2$  denoted in the following by the subscripts 1 and 2.

$$\begin{aligned} \Delta F &= (U_1 - U_2) - kT(H_1 - H_2) \\ &= \frac{2\kappa}{5\langle k^2 \rangle} S(\langle k^4 \rangle_1 - \langle k^4 \rangle_2) - \frac{V}{(2\pi)^3} \int_0^{k_c} 4\pi k^2 \ln \frac{f_1(k)}{f_2(k)} dk \end{aligned}$$

and thus for the free energy density

$$\frac{\Delta F}{V} = \frac{4\kappa}{5\sqrt{3}\pi} \langle k^2 \rangle^{-\frac{1}{2}} (\langle k^4 \rangle_1 - \langle k^4 \rangle_2) - \frac{1}{2\pi^2} \int_0^{k_c} k^2 \ln \frac{f_1(k)}{f_2(k)} dk. \quad (9)$$

In a self-consistent theory, variation (with respect to  $f$ ) of the free energy terms in equation (9) with an additional Gaussian curvature term and with the two conditions on the norm and the second moment should determine the functional form of  $f(k)$ . Restricting the consideration to the set of functions compatible with the usual boundary conditions we find that with the appropriate functional  $L = F + \lambda k^2 f + \mu k^4 f$  (where  $\lambda, \mu$  are Lagrange multipliers [25]) the extremal requirement  $dL/df = 0$  is fulfilled by spectral densities of the form

$$f(k) \propto \frac{1}{Ak^4 + Bk^2 + C}, \quad (10)$$

which are formally equivalent to the phenomenological Teubner-Strey scattering intensity function [10] or the first term in equation (12) of Appendix A.

Figure 6 shows bending energy, entropy and the resulting free energy curves for the model parameter pairs which we obtained for the 7% and 10% SDS systems from a fit to the scattering data in the previous section. The physical requirement of finding a free energy minimum for the experimental parameter pairs yields the value of the bending moduli  $\kappa = 2.0 kT$  for 10% SDS and  $\kappa = 2.6 kT$  for 7% SDS. The bending moduli show a certain dependence on the cut-off length  $\lambda_c$ , and vary in the cut-off range (cf. Appendix A) by a factor of less than two.

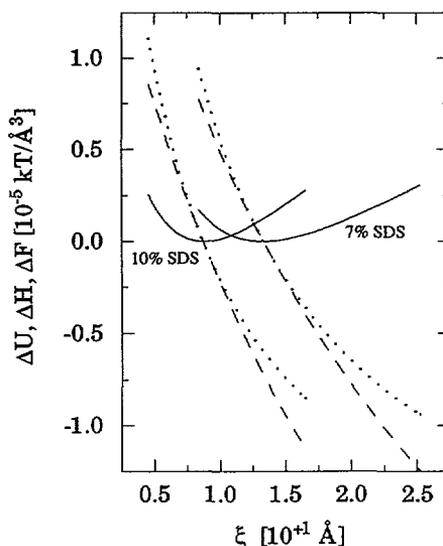


Fig. 6. — Bending energy (dotted), entropy (broken) and resulting free energy (solid) for the 7% SDS and 10% SDS systems as a function of the coherence length  $\xi$ . The bending moduli were  $\kappa = 2.02 kT$  for 10% SDS and  $\kappa = 2.64 kT$  for 7% SDS. Surface to volume fraction was kept constant in both cases. The functional forms of the spectral densities  $f(k; k_0, \xi)$  in figures 5 and 6 were assumed to be the same as to the ones used in figures 1-4.

Measurements of the bending constant of membrane systems in ordered phases have been performed by several authors (see [21] for a summary of results). On SDS and cosurfactant systems Safinya *et al.* [22] found  $\kappa$  values between 1 and 3  $kT$ , if the cosurfactant tails is 5-6 carbons long and much higher values for longer tails. Our system consisting of SDS monolayers is different and several factors could have influenced the results. The SDS and cosurfactant monolayer between oil and water is not symmetrical, and spontaneous curvature is likely to be different from zero. As a result, the monolayer is on average under some bending stress, which could lead to a higher value of  $\kappa$ .

The entropy term given in the work of Safran *et al.*, which corresponds to our expression (7) is in general lower than the entropy of equation (8), and the quantitative difference depends on the magnitude of  $\xi$ . The Safran *et al.* entropy contains no contributions from the region of the phase space where  $|k| > 2\pi/\xi$ . When entropy is evaluated in the range of  $\pm 10\%$  around the experimental values of  $\xi$ , we find that the two entropies differ in the case of 7% SDS by about a factor of 10 and in the case of 10% SDS by a factor of 5.

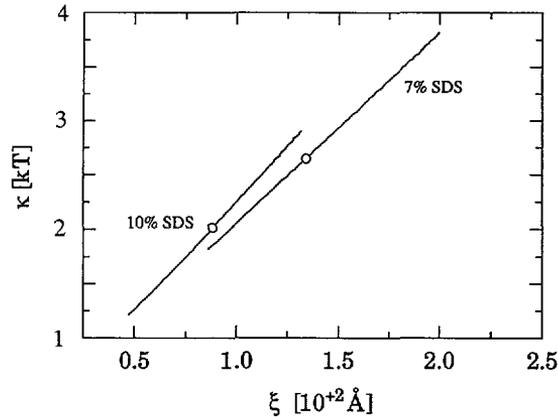


Fig. 7. — The coherence length  $\xi$  as a function of the bending modulus  $\kappa$  for 7 % SDS and 10 % SDS systems. The experimental values of  $\xi$  are highlighted by circles. The lack of smoothness in the curves is due to numerical noise.

Figure 7 concludes our considerations of the bending modulus  $\kappa$  in a two parameter  $\xi$ ,  $k_0$  (with boundary condition) system. We draw the functional dependence of  $\kappa$  on the coherence length  $\xi$  for the 7 % and 10 % SDS systems. A stiffer system is predicted to have a larger coherence length, as it should.

#### 4. Discussion.

The degree of disorder in a physical system is always indicated by the broadening of its X-ray, neutron, light... scattering spectrum. But the link between the scattering spectrum and the system entropy is straightforward only in very simple geometries. With liquid state type of order, the link is very complicated even in the case of simple constituents (e.g. in the hard sphere fluid).

Within a given phase of an amphiphilic system, the degree of disorder is dependent on the elastic restoring force and the temperature. In a lamellar system, given the elastic constants, one can determine from the equipartition theorem the spectrum of the excited modes, the entropy, the correlation function and the broadening of the scattering peak [13, 23].

In the irregular geometry of random bicontinuous phases the physical principles are the same but the path is not straightforward. In the preceding sections we have argued that a similar program is feasible in the simple case of a system of random bicontinuous surfaces. It is based on a geometrical assumption of an ensemble of surfaces described by the associated Gaussian random field (instead of the surfaces in a planar multilayer system). The experimental scattering spectrum then uniquely determines the spectrum of the underlying random field, and the entropy associated with the latter can be calculated from its information content. To obtain a link to the elastic modulus of the film we need to include the fundamental laws of statistical mechanics (equivalent to the use of the equipartition theorem in the earlier work on multilayers). As we do not have an explicit equation linking the spectrum to the elastic properties, we achieve the same result by adjusting the values of the elastic constant until the known physical state corresponds to the minimum of the calculated free energy.

Many of the concepts and results presented in this paper are generalisations of similar earlier work for planar multilayer systems. Disordered bicontinuous systems described by

random Gaussian fields provide another interesting geometry where a relatively simple formalism can be used to study the statistical mechanics of surface configurations.

### Acknowledgments.

The authors would like to thank Drs. M. Teubner and T. Zemb for helpful discussions and suggestions.

One of the authors (P. P.) was supported in part by the *Deutscher Akademischer Austauschdienst* (Bonn, Germany) under grant 315/901/504/1. The other author was supported in part by the National Science Foundation Grant No. PHY82-17853, supplemented by funds from the National Aeronautics and Space Administration and administered by the Institute of Theoretical Physics, University of California, Santa Barbara where this work was initiated.

### A Appendix.

#### Correlation function, spectral density and curvatures of a localised random field.

Localised waves as suggested in reference [6] will after averaging over the « grain » positions  $r_i$  and the directions of  $\mathbf{k}$ , give the two point function  $g(r)$  and the corresponding spectral density  $f(k) = \frac{1}{(2\pi)^3} \int_0^\infty 4\pi r^2 j_0(kr) g(r) dr$ . To give an example of the procedure, and to prove the basic utility of the model a Yukawa-like localisation for  $u(r; \xi)$  has been chosen for the constituent wavelets

$$s(\mathbf{r}) = \left( \frac{e^{-|\mathbf{r}|/\xi} - e^{-|\mathbf{r}|/r_m}}{|\mathbf{r}|} \right) \cos(\mathbf{k}_0 \mathbf{r}). \quad (11)$$

We stress that there is nothing unique about this function, and other functions (possibly Bessel functions or functions derived from experimental scattering intensity curves) might be used just as well.  $r_m$  is necessary in equation (11) to avoid the singularity at  $r = 0$  and will be taken as constant of the size of the monolayer thickness minus headgroup length for SDS systems (given by Auvray *et al.* [7] as about 10 Å). The two point function is then [6]

$$g(r) = \frac{a(a+1)}{(a-1)^2} \left( e^{-r/\xi} + \frac{1}{a} e^{-ar/\xi} - \frac{4\xi(e^{-r/\xi} - e^{-ar/\xi})}{r(a^2-1)} \right) \frac{\sin k_0 r}{k_0 r},$$

with  $a = \xi/r_m$  and the spectral density

$$f(k) = \frac{1}{2\pi^2} \frac{a(a+1)}{(a-1)^2} \left\{ \frac{4/\xi}{[1/\xi^2 + (k-k_0)^2][1/\xi^2 + (k+k_0)^2]} + \frac{4/\xi}{[a^2/\xi^2 + (k-k_0)^2][a^2/\xi^2 + (k+k_0)^2]} + \frac{2\xi}{(a^2-1)kk_0} \ln \left( \frac{[a^2/\xi^2 + (k+k_0)^2][1/\xi^2 + (k-k_0)^2]}{[a^2/\xi^2 + (k-k_0)^2][1/\xi^2 + (k+k_0)^2]} \right) \right\}. \quad (12)$$

For experimental parameters the first term dominates for reasonably low values of  $k$  the other terms by at least one order of magnitude. Over the physical range our test function  $f(k)$  is thus consistent with the result equation (10) of the variational procedure carried out in subsection 3.2. Nevertheless we note that the minor deviation might indicate that the localisation is in reality a slightly different one.

The small  $r$  expansion of  $g(r)$  is

$$\begin{aligned} g(r) &= g(0) - 1/2 g''(0) r^2 + 1/24 g^{(4)}(0) r^4 + O(r^5) \\ g''(0) &= \frac{a + k_0^2 \xi^2}{3 \xi^2} \\ g^{(4)}(0) &= \frac{3 a + 9 a^2 + 3 a^3 + 10 a k_0^2 \xi^2 + 3 k_0^4 \xi^4}{15 \xi^4} \end{aligned}$$

The well-known rule for the large  $k$  expansion of any rotational Fourier transform  $F(k)$  of some correlation function  $G(r)$  [26, 27]

$$F(k) = -\frac{1}{2 \pi^2} \left( \frac{2 G'(0)}{k^4} + \frac{4 G'''(0)}{k^6} + \frac{6 G^{(5)}(0)}{k^8} + \dots \right)$$

yields that  $f(k)$  has here a  $k^{-8}$  asymptotic term, hence it's second and it's fourth moment will exist asymptotically.

The relationship between the even spectral moments and the behaviour of the correlation function at  $r = 0$  is  $\langle k^{2n} \rangle \propto \lim_{r \rightarrow 0} (-1)^n \Delta^{2n} g(r)$  [12]. It can be used to derive the useful relations  $\langle k^2 \rangle = 3 g''(0)$  and  $\langle k^4 \rangle = 5 g^{(4)}(0)$ .

With those rules we obtain easily by application of Teubner's results [3]:

*The Gaussian curvature*

$$\langle K \rangle = \frac{1}{6} \langle k^2 \rangle (\alpha^2 - 1) \rightarrow \frac{1}{6} \frac{a + k_0^2 \xi^2}{\xi^2} (\alpha^2 - 1).$$

*The mean curvature*

$$\langle H \rangle = \frac{1}{2} \sqrt{\frac{\pi}{6} \langle k^2 \rangle} \alpha \rightarrow \frac{1}{2} \sqrt{\frac{\pi}{6} \frac{a + k_0^2 \xi^2}{\xi^2}} \alpha.$$

*The mean square curvature*

$$\begin{aligned} \langle H^2 \rangle &= \frac{1}{6} \langle k^2 \rangle \left( \alpha^2 + \frac{6 \langle k^4 \rangle}{5 \langle k^2 \rangle^2} - 1 \right) = \langle K \rangle + \frac{1}{5} \frac{\langle k^4 \rangle}{\langle k^2 \rangle} \\ &\rightarrow \frac{1}{6} \frac{a + k_0^2 \xi^2}{\xi^2} \left( \alpha^2 - 1 + \frac{6}{15} \frac{3 a + 9 a^2 + 10 a k_0^2 \xi^2 + 3 k_0^4 \xi^4}{(a + k_0^2 \xi^2)^2} \right). \end{aligned}$$

For our specific  $g(r)$ ,  $f(k)$  of localised random fields the Gaussian curvature is a factor 5-10 smaller than the mean square curvature for the cases of 7% and 10% SDS.

The surface to volume fraction is well-known [14] to be

$$\frac{S}{V} = -4 \cdot \phi_s (1 - \phi_s) \frac{d\gamma^\alpha}{dr} (0) = \frac{2}{\pi} \sqrt{\frac{\langle k^2 \rangle}{3}} e^{-\alpha^2/2}$$

The above simple analytic expressions for the curvatures are asymptotic cases when no wavelength cut-off is taken into account,  $\lambda_c \rightarrow \infty$ . They were used as good cross checks for the bandlimited case that was constructed by  $f_c(k) = f(k)$  for  $k \leq k_c$  and  $f_c(k) = 0$  for  $k > k_c$ . For band limitation, too, the integrals can be done analytically, yielding far more complex expressions.

Hence our construction prescription for  $g_c(r)$  will be  $g_c(r) = \int 4 \pi k^2 j_0(kr) f_c(k) dk$  with normalisation factor  $\int 4 \pi k^2 f_c(k) dk$ .

For the specific case of the SDS surfactant systems studied in section 2, the upper and lower limits, as discussed in section 2, of  $\lambda_c$  turn out to be 50-70 Å. The lower limit is four times the monolayer thickness of about 12 Å [7], the upper limit can be estimated when analysing the dependence of  $S/V$  on the cut-off scale. Although  $S/V$  is given experimentally only roughly (for 7 % SDS :  $S/V \approx 1.0 \times 10^{-2} \text{ \AA}^{-1}$  ; for 10 % SDS :  $S/V \approx 1.5 \times 10^{-2} \text{ \AA}^{-1}$ ), with the fast convergence of the theoretical  $S/V$  a limit of  $\lambda_c$  can be identified beyond which agreement with  $S/V$  can not be possibly reached. It has to be remarked, that the situation is complicated by the fact that the theoretical bulk scattering curve is also influenced by  $\lambda_c$  and some interrelation with  $\xi$  and  $k_0$  arises. But the effect on the scattering (before  $k_c$ ) is of the magnitude of some 1 % only, and so our estimate for the cut-off remains valid. The values of  $k_c$  determined by this technique are for SDS 7 %  $\approx 6 k_0$  and for SDS 10 %  $\approx 4 k_0$ . This is in agreement with de Gennes and Taupin's [11] estimate  $k_c \approx 10/\xi_k$ .

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