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Scattering from two-phase random media

Max Teubner

Max-Planck-Institut für biophysikalische Chemie, Postfach 2841, D-3400 Göttingen,
Federal Republic of Germany

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A unified exposition is given of the known exact results for the scattering from random two-phase isotropic media with a smooth interface. For the bulk-bulk scattering a new and simple derivation is given for the next to leading term (Porod-Kirste). The corresponding term for the film-film scattering is calculated. It is pointed out that from careful contrast matching experiments it may be possible to measure the average squared mean curvature $\langle H^2 \rangle$ and the average Gaussian curvature $\langle K \rangle$.

INTRODUCTION

In this paper we study the scattering from a random two-phase medium. We do not assume a definite structure of the system. Rather our basic hypothesis is that there is some length l_0 much longer than atomic distances, such that all the interfaces are flat on the scale of l_0 . In this case a continuum description is adequate and the interface can be modeled by a smooth surface S . Thus we deliberately exclude random structures that are fractal down to molecular dimensions.¹ For microemulsions, for example, a finite bending energy^{2,3} assures the existence of such a length. Other examples are furnished by colloidal aggregates of small particles.⁴

We are particularly interested in microemulsions and in extracting exact structural information from the scattering curves. For bicontinuous microemulsions, one is especially interested in geometric quantities like the mean curvature $\langle H \rangle$ and the Gaussian curvature $\langle K \rangle$. For symmetric microemulsions, where $\langle H \rangle = 0$, one is also interested in $\langle H^2 \rangle$, which is proportional to the bending energy. While there has been some effort⁵ to determine the mean curvature $\langle H \rangle$, no methods are known to measure $\langle K \rangle$ or $\langle H^2 \rangle$. It will be shown in this paper, that in favorable cases it may be possible to obtain these quantities from neutron scattering.

The paper is organized into two parts. In the first part the finite thickness of the interface is neglected. The results are then applied in the second part to realistic systems with a thin but finite interface.

I. THE TWO-PHASE MEDIUM WITH AN INFINITELY THIN INTERFACE

We shall give a new and concise derivation of the relations due to Porod^{6,7} and Kirste and Porod⁸ and indicate a systematic procedure to obtain still higher terms in q^{-2} . Analogous and mostly new results are obtained for the surface-surface correlation function. We also show that the bulk correlation function can be expressed in terms of statistical properties of the interface.

A. Scattering intensity, correlation function, and large- q expansion

Consider a two-phase medium in a volume V , let the volumes occupied by the two phases be V_1 and V_2 , respectively, and let S be the interface. Then

$$\varphi = \frac{V_1}{V}, \quad 1 - \varphi = \frac{V_2}{V} \quad (1)$$

are the volume fractions. Let $\phi(\mathbf{r})$ be the characteristic function of phase 1. $\phi(\mathbf{r})$ is equal to 1 if $\mathbf{r} \in V_1$ and 0 if $\mathbf{r} \in V_2$. Then for a statistically homogeneous medium

$$\langle \phi(\mathbf{r}) \rangle = \varphi. \quad (2)$$

The bulk correlation function defined by

$$g_{bb}(\mathbf{r}) = \langle \phi(\mathbf{r}') \phi(\mathbf{r}' + \mathbf{r}) \rangle \quad (3)$$

depends only upon $|\mathbf{r}|$ and tends to φ^2 for $|\mathbf{r}| \rightarrow \infty$. $[g_{bb}(\mathbf{r}) - \varphi^2]/\varphi(1 - \varphi)$ is the normalized correlation function γ introduced by Debye.^{9,10}

In the following we study various correlation functions g and their Fourier transforms

$$\chi(q) = \int_0^\infty 4\pi r^2 \frac{\sin qr}{qr} g(r) dr. \quad (4)$$

We are especially interested in the large- q behavior. Partially integrating, we find

$$\begin{aligned} \chi(q) = 4\pi \left[q^{-2} \lim_{r \rightarrow 0} (rg) - q^{-4} \lim_{r \rightarrow 0} (rg)'' \right. \\ \left. - q^{-5} \int_0^\infty \cos qr (rg)''' dr \right]. \end{aligned} \quad (5)$$

If $g(0)$ is finite and $g''(r)$ is continuous, $\chi(q)$ decays like the inverse fourth power of q (Porod^{6,7}):

$$\chi(q) = -8\pi g'(0) q^{-4} + O(q^{-5}). \quad (6)$$

A finite discontinuity of g'' gives rise to additional oscillatory terms. Such a discontinuity presupposes a special geometrical arrangement of the interface.¹¹ Monodisperse spheres belong to this class of surfaces, but any finite-size distribution washes out the discontinuity and restores (6). In the following we assume that rg is at least four times differentiable for $r > 0$. Then $\chi(q)$ has the asymptotic expansion

$$\begin{aligned} \chi(q) = 4\pi \left[q^{-2} \lim_{r \rightarrow 0} (rg) - q^{-4} \lim_{r \rightarrow 0} (rg)'' \right. \\ \left. + q^{-6} \lim_{r \rightarrow 0} (rg)'''' - \dots \right]. \end{aligned} \quad (7)$$

B. The correlation tensor for the normals

In this section we derive a relation between the correlation function g_{bb} and the correlation tensor T_{ij} for the nor-

mals on the interface S . T_{ij} is defined by

$$T_{ij}(\mathbf{r}, \mathbf{r}') \equiv \langle n_i(\mathbf{r}) n_j(\mathbf{r}') \delta_s(\mathbf{r}) \delta_s(\mathbf{r}') \rangle. \quad (8)$$

This relation is easily obtained from the formula

$$\nabla \phi(\mathbf{r}) = -\mathbf{n}(\mathbf{r}) \delta_s(\mathbf{r}), \quad (9)$$

where δ_s is the δ function concentrated on S . Using (9), we obtain from (3)

$$\begin{aligned} \frac{\partial g_{bb}}{\partial x_i}(\mathbf{r}) &= -\langle \phi(\mathbf{r}') n_i(\mathbf{r}' + \mathbf{r}) \delta_s(\mathbf{r}' + \mathbf{r}) \rangle \\ &= -\langle \phi(\mathbf{r}' - \mathbf{r}) n_i(\mathbf{r}') \delta_s(\mathbf{r}') \rangle \end{aligned} \quad (10)$$

and

$$\frac{\partial^2 g_{bb}}{\partial x_i \partial x_j}(\mathbf{r}) = -\langle n_j(\mathbf{r}' - \mathbf{r}) \delta_s(\mathbf{r}' - \mathbf{r}) n_i(\mathbf{r}') \delta_s(\mathbf{r}') \rangle, \quad (11)$$

and we find the simple result

$$T_{ij} = -\frac{\partial^2 g_{bb}}{\partial x_i \partial x_j}. \quad (12)$$

For an isotropic medium we obtain

$$\text{Tr } T = -g''_{bb}(r) - \frac{2}{r} g'_{bb}(r), \quad (13)$$

$$\frac{\mathbf{r} \cdot T \cdot \mathbf{r}}{r^2} = -g''_{bb}(r). \quad (14)$$

C. Surface-surface and surface-bulk correlation functions

Let $\delta_s^\epsilon(\mathbf{r})$ be the characteristic function for a thin sheet S^ϵ of uniform thickness ϵ approximating S . For small ϵ , $\epsilon^{-1} \delta_s^\epsilon$ is an approximation to δ_s . Then

$$\lim_{\epsilon \rightarrow 0} \epsilon^{-1} \langle \delta_s^\epsilon(\mathbf{r}) \rangle \equiv \langle \delta_s(\mathbf{r}) \rangle = \frac{S}{V}. \quad (15)$$

We define the surface-surface correlation function by

$$\begin{aligned} g_{ss}(r) &\equiv \lim_{\epsilon \rightarrow 0} \epsilon^{-2} \langle \delta_s^\epsilon(\mathbf{r}') \delta_s^\epsilon(\mathbf{r}' + \mathbf{r}) \rangle \\ &\equiv \langle \delta_s(\mathbf{r}') \delta_s(\mathbf{r}' + \mathbf{r}) \rangle. \end{aligned} \quad (16)$$

g_{ss} is the correlation function for the mass concentrated on S . It determines the scattering from the interface which we study in Sec. II. For large r we have

$$\lim_{r \rightarrow \infty} g_{ss}(r) = (S/V)^2 \quad (17)$$

An equivalent definition is the following: Let $p_s^\epsilon(\mathbf{r}, \mathbf{r}')$ be the conditional probability, that \mathbf{r}' is located in the sheet S^ϵ provided \mathbf{r} is on S . Then

$$g_{ss}(\mathbf{r}, \mathbf{r}') = \frac{S}{V} \lim_{\epsilon \rightarrow 0} p_s^\epsilon(\mathbf{r}, \mathbf{r}'). \quad (18)$$

For very small r the surface is locally flat, and p_s^ϵ is just the circumference of a circle divided by the surface of a sphere with the same radius r . Therefore

$$g_{ss}(r) = \frac{S}{V} \cdot \frac{1}{2r} + O(r). \quad (19)$$

The next term is calculated in Sec. I E.

The surface-bulk correlation function is defined by

$$g_{sb}(\mathbf{r}) = \langle \phi(\mathbf{r}') \delta_s(\mathbf{r}' + \mathbf{r}) \rangle. \quad (20)$$

For large r we have

$$\lim_{r \rightarrow \infty} g_{sb}(r) = \phi \frac{S}{V} \quad (21)$$

and, since the surface is locally flat,

$$g_{sb}(0) = \frac{1}{2} \frac{S}{V}. \quad (22)$$

For a symmetric medium (which implies $\phi = 1/2$) $g_{sb}(r) \equiv (1/2)(S/V)$ identically.

D. An integral representation for the correlation functions

We now construct a representation for the correlation functions that will be very useful in the next section where we study the correlation functions for small r .

We start with g_{ss} and $p_s^\epsilon(\mathbf{r}, \mathbf{r}')$. Let \mathbf{r} be a point on S and consider the sphere about \mathbf{r} with radius $|\mathbf{r}' - \mathbf{r}|$. It intersects S in a certain curve $C_{r,r'}$ (this curve may consist of several pieces). Let F_ϵ be that part of the sphere's surface, that is common to S^ϵ , and let $|F_\epsilon|$ be its area. Then, by definition of p_s^ϵ , we have

$$\epsilon p_s^\epsilon(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi |\mathbf{r}' - \mathbf{r}|^2} \langle |F_\epsilon| \rangle. \quad (23)$$

F_ϵ consists of one or several narrow bands on the sphere. These bands have the curve $C_{r,r'}$ at their center, and their width w at a typical point $\mathbf{r}' \in C_{r,r'}$ is given by

$$w = \frac{\epsilon}{|\hat{\mathbf{r}} \times \mathbf{n}'|}, \quad (24)$$

where \mathbf{n}' is the unit normal on S at \mathbf{r}' , and

$$\hat{\mathbf{r}} \equiv \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \quad (25)$$

If $C_{r,r'}$ is parametrized by arclength s' , $|F_\epsilon|$ is given by

$$|F_\epsilon| = \epsilon \int_{C_{r,r'}} \frac{ds'}{|\hat{\mathbf{r}} \times \mathbf{n}'|}. \quad (26)$$

Setting (18), (23), and (26) together, we obtain the desired representation for g_{ss}

$$g_{ss}(\mathbf{r}, \mathbf{r}') = \frac{S}{V} \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|^2} \left\langle \int_{C_{r,r'}} \frac{ds'}{|\hat{\mathbf{r}} \times \mathbf{n}'|} \right\rangle. \quad (27)$$

For very small $|\mathbf{r} - \mathbf{r}'|$ the surface is flat, $|\hat{\mathbf{r}} \times \mathbf{n}'| = 1$, $C_{r,r'}$ is a circle, and we recover (19) as we should. The analogous expression for the tensor T is

$$T_{ij}(\mathbf{r}, \mathbf{r}') = \frac{S}{V} \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|^2} \left\langle n_i(\mathbf{r}) \int_{C_{r,r'}} \frac{n_j(\mathbf{r}')}{|\hat{\mathbf{r}} \times \mathbf{n}'|} ds' \right\rangle. \quad (28)$$

In particular,

$$\begin{aligned} g''_{bb}(|\mathbf{r} - \mathbf{r}'|) &= -\frac{S}{V} \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|^2} \\ &\quad \times \left\langle \int_{C_{r,r'}} \frac{\hat{\mathbf{r}} \cdot \mathbf{n}(\mathbf{r}) \hat{\mathbf{r}} \cdot \mathbf{n}(\mathbf{r}')}{|\hat{\mathbf{r}} \times \mathbf{n}'|} ds' \right\rangle. \end{aligned} \quad (29)$$

This relation has been obtained previously by a rigorous but somewhat complicated analysis by Ciccariello *et al.*¹² For $|\mathbf{r} - \mathbf{r}'| \rightarrow 0$, $\hat{\mathbf{r}} \cdot \mathbf{n}$ and $\hat{\mathbf{r}} \cdot \mathbf{n}'$ both converge to zero. This yields immediately⁸

$$g''_{bb}(0) = 0. \quad (30)$$

Similarly, since $\mathbf{n} \cdot \mathbf{n}' \rightarrow 1$ for $|\mathbf{r} - \mathbf{r}'| \rightarrow 0$ it follows from (13) and the remark after (27) that⁹

$$g'_{bb}(0) = -\frac{1}{4} \frac{S}{V}. \quad (31)$$

Differentiating the surface-bulk correlation function g_{sb} and using (9), we obtain

$$g'_{sb}(|\mathbf{r} - \mathbf{r}'|) = \langle \delta_s(\mathbf{r}) \mathbf{r} \cdot \mathbf{n}(\mathbf{r}') \delta_s(\mathbf{r}') \rangle, \quad (32)$$

where \mathbf{n} points into phase 2. The corresponding representation is

$$g'_{sb}(|\mathbf{r} - \mathbf{r}'|) = \frac{S}{V} \frac{1}{4\pi|\mathbf{r} - \mathbf{r}'|^2} \left\langle \int_{C_{r,r'}} \frac{\hat{\mathbf{r}} \cdot \mathbf{n}'}{|\hat{\mathbf{r}} \times \mathbf{n}'|} ds' \right\rangle. \quad (33)$$

E. Small- r expansion of the correlation functions

The next term in the small- r expansion of g_{bb} , namely $\bar{g}_{bb}(0)$, has been determined by Kirste and Porod⁸ by a rather complicated analysis. We will utilize the representation (29) to obtain a concise derivation of this result. Furthermore, we will obtain the corresponding term for the surface correlation function $g_{ss}(r)$.

To do this we need the curve $C_{r,r'}$ which is the intersection of S with the sphere of radius $|\mathbf{r} - \mathbf{r}'|$ about \mathbf{r} . We translate the origin to \mathbf{r} , and rotate the coordinates to represent the surface locally by

$$z = \frac{k_1}{2}x^2 + \frac{k_2}{2}y^2 + O(r^3), \quad (34)$$

where k_1 and k_2 are the two principal curvatures. The normal is

$$\mathbf{n}(\mathbf{r}) = (1 + k_1^2 x^2 + k_2^2 y^2)^{-1/2} \begin{bmatrix} k_1 x \\ k_2 y \\ -1 \end{bmatrix}, \quad (35)$$

and one finds easily

$$|\hat{\mathbf{r}} \times \mathbf{n}'| = \frac{1}{r} (x^2 + y^2)^{1/2} [1 + O(r^3)]. \quad (36)$$

It is convenient to introduce cylindrical coordinates. Then the projection of the curve $C_{0,r}$ onto the x - y plane is given by

$$x = p(\varphi) \cos \varphi, \quad y = p(\varphi) \sin \varphi \quad (37)$$

with

$$p^2(\varphi) = r^2 - \frac{1}{4} r^4 (k_1 \cos^2 \varphi + k_2 \sin^2 \varphi)^2 + O(r^5). \quad (38)$$

The arclength s is given by

$$ds = (x'^2 + y'^2 + z'^2)^{1/2} d\varphi, \quad (39)$$

where the prime denotes differentiation with respect to φ . Since $p'(\varphi) = O(r^3)$, we have

$$x'^2 + y'^2 = p^2 + p'^2 = p^2 + O(r^6). \quad (40)$$

Since

$$z' = r^2 (k_2 - k_1) \cos \varphi \sin \varphi + O(r^3), \quad (41)$$

we have

$$ds = p(1 + \frac{1}{2} r^2 (k_1 - k_2)^2 \cos^2 \varphi \sin^2 \varphi + O(r^3)) d\varphi, \quad (42)$$

and therefore

$$\frac{ds}{|\hat{\mathbf{r}} \times \mathbf{n}'|} = \left[r + \frac{r^3}{2} (k_1 - k_2)^2 \cos^2 \varphi \sin^2 \varphi + O(r^4) \right] d\varphi. \quad (43)$$

Inserting into (27), we obtain

$$g_{ss}(r) = \frac{S}{V} \left[\frac{1}{2r} + \frac{r}{32} \langle (k_1 - k_2)^2 \rangle + O(r^2) \right]. \quad (44)$$

Similarly, using

$$\hat{\mathbf{r}} \cdot \mathbf{n}(0) \hat{\mathbf{r}} \cdot \mathbf{n}(\mathbf{r}) = -\frac{1}{4} r^2 (k_1 \cos^2 \varphi + k_2 \sin^2 \varphi)^2 + O(r^3), \quad (45)$$

we find

$$\int_{C_{0,r}} \frac{\hat{\mathbf{r}} \cdot \mathbf{n}(0) \hat{\mathbf{r}} \cdot \mathbf{n}(\mathbf{r})}{|\hat{\mathbf{r}} \times \mathbf{n}|} ds = -\frac{\pi r^3}{2} \left(\frac{3}{8} k_1^2 + \frac{3}{8} k_2^2 + \frac{1}{4} k_1 k_2 \right), \quad (46)$$

and therefore

$$\bar{g}_{bb}(0) = \frac{S}{V} \frac{1}{64} (3 \langle k_1^2 \rangle + 3 \langle k_2^2 \rangle + 2 \langle k_1 k_2 \rangle), \quad (47)$$

which is the result of Kirste and Porod.⁸

Finally, for the surface-bulk correlation function we find¹³

$$g'_{sb}(0) = \frac{1}{4} \frac{S}{V} \langle H \rangle. \quad (48)$$

In principle, it is straightforward to determine by this method still higher coefficients in the small- r expansion. However, these higher terms [corresponding to q^{-8} and higher terms in the expansion of $i(q)$] are probably impossible to determine experimentally. Furthermore, they depend upon third-order derivatives of the surface which have no simple geometrical meaning. Finally, the small- r expansion probably does not, in general, converge, and is only asymptotic. An explicit example of random two-phase structures with nonanalytic correlation function is the structure introduced by Cahn¹⁴ in the context of spinodal decomposition. The correlation function of this model has been calculated by Berk¹⁵ and Teubner.¹⁶ It is nonanalytic at the origin.

F. Test for smoothness

In deriving our main results (44) and (47) we have assumed that the surface is sufficiently regular and possesses no singularities. These results, as well as (48), are only valid for surfaces that are everywhere regular.¹⁷ It is interesting that this assumption of regularity can be tested experimentally.^{16,18,19} For smooth surfaces we have

$$\lim_{r \rightarrow 0} \left[g_{ss}(r) - \frac{S}{V} \frac{1}{2r} \right] = 0 \quad (49)$$

and

$$g''_{bb}(0) = 0. \quad (50)$$

In q space these relations are equivalent to

$$\int_0^\infty \left[q^2 \chi_{ss}(q) - 2\pi \frac{S}{V} \right] dq = 0 \quad (51)$$

and to

$$\int_0^\infty \left(q^4 \chi_{bb} - 2\pi \frac{S}{V} \right) dq = 0. \quad (52)$$

While (51) and (52) clearly are necessary for regularity, each one alone is also sufficient; it has in fact been proved^{16,20} that the left side of Eq. (51) [Eq. (52)] is always positive [negative] for surfaces with edges or contact points.

II. THE TWO-PHASE MEDIUM WITH A THIN INTERFACE

We now study the scattering from a two-phase medium with a thin but finite interface composed of a third component. We have in mind a microemulsion consisting of domains of water and oil separated by an amphiphilic layer of constant thickness d . As in Sec. I we do not make any assumptions about the structure of the system, except that the system is statistically homogeneous and isotropic, and that the interface is smooth. Later we will also assume that the thickness of the interface is small compared to the local radius of curvature. We assume that the scattering length densities of the water and the oil are constant in the respective volumes; the scattering length density n_f of the film, however, may vary in the direction normal to the film.

A. Geometry of the surfactant film

Let S_{WF} and S_{OF} be the water-film and oil-film interfaces, respectively. We assume that S_{WF} and S_{OF} are parallel surfaces of constant distance d . If S is the surface situated halfway between, S_{WF} and S_{OF} can be represented as

$$S_{WF} = \left\{ \mathbf{r} - \frac{d}{2} \mathbf{n}(\mathbf{r}) : \mathbf{r} \in S \right\}, \quad (53a)$$

$$S_{OF} = \left\{ \mathbf{r} + \frac{d}{2} \mathbf{n}(\mathbf{r}) : \mathbf{r} \in S \right\}. \quad (53b)$$

Here \mathbf{n} is the unit normal on S pointing from water to oil. It can be shown²¹ that the area of the surface element on S_{WF} and S_{OF} is given by

$$dS_{WF} = \left(1 + dH + \frac{d^2}{4} K \right) dS, \quad (54a)$$

$$dS_{OF} = \left(1 - dH + \frac{d^2}{4} K \right) dS, \quad (54b)$$

where H is the mean and K the Gaussian curvature²¹ of S . H and K can be expressed in terms of the principal curvatures introduced in Sec. I E:

$$H = \frac{1}{2}(k_1 + k_2), \quad (55)$$

$$K = k_1 k_2. \quad (56)$$

Any point in the interior of the film can be uniquely represented as $\mathbf{r} + \rho \mathbf{n}(\mathbf{r})$ where $\mathbf{r} \in S$ and $|\rho| \leq (d/2)$. $\{\mathbf{r}, \rho\}$ constitutes a natural curvilinear system of coordinates for the film, and it can be shown that the volume element in these coordinates is²¹

$$dV = (1 - 2H\rho + K\rho^2) d\rho dS. \quad (57)$$

B. The scattering intensity

Let V_w , V_o , and V_f be the volumes occupied by the water, the oil, and the interfacial film, respectively, and let n_w , n_o , and n_f be the corresponding scattering length densities. n_w and n_o are constants while n_f may depend upon the position in the film. Then the scattering intensity is given by

$$i(q) = \frac{1}{V} \langle |\mathfrak{U}|^2 \rangle, \quad (58)$$

where the amplitude \mathfrak{U} is

$$\mathfrak{U}(q) = n_w \int_{V_w} e^{iq \cdot r} d\mathbf{r}^3 + n_o \int_{V_o} e^{iq \cdot r} d\mathbf{r}^3 + \int_{V_f} n_f e^{iq \cdot r} d\mathbf{r}^3. \quad (59)$$

Since a constant background does not contribute to the scattering, we can eliminate the first or the second term and obtain

$$\mathfrak{U}(q) = (n_w - n_o) \int_{V_w} e^{iq \cdot r} d\mathbf{r}^3 + \int_{V_f} (n_f - n_o) e^{iq \cdot r} d\mathbf{r}^3. \quad (60)$$

Squaring and averaging, we find that $i(q)$ is a sum of three terms

$$i(q) = i_{ww}(q) + i_{ff}(q) + 2i_{wf}(q). \quad (61)$$

The first term is

$$i_{ww}(q) = (n_w - n_o)^2 \chi_{ww}(q), \quad (62)$$

where

$$\chi_{ww}(q) = \int \langle \phi_w(0) \phi_w(r) \rangle e^{iq \cdot r} d\mathbf{r}^3, \quad (63)$$

and ϕ_w is the characteristic function of the water phase. The second term is due to the film alone

$$i_{ff}(q) = \frac{1}{V} \langle |\mathfrak{U}_f|^2 \rangle, \quad (64)$$

where

$$\mathfrak{U}_f(q) = \int_{V_f} (n_f - n_o) e^{iq \cdot r} d\mathbf{r}^3, \quad (65)$$

and the third term is the cross-correlation term

$$i_{wf}(q) = (n_w - n_o) \frac{1}{V} \text{Re} \left(\mathfrak{U}_f(q) \int_{V_w} e^{-iq \cdot r} d\mathbf{r}^3 \right). \quad (66)$$

C. Scattering by the water phase

Obviously, $i_{ww}(q)$ is the scattering from a hypothetical two-phase medium, where the second phase is composed of oil and the surfactant film (it corresponds to a situation where the scattering length densities of the oil and the film are matched):

$$\chi_{ww}(q) = \int_0^\infty 4\pi r^2 g_{ww}(r) \frac{\sin qr}{qr} dr, \quad (67)$$

where

$$g_{ww}(r) = \langle \phi_w(r') \phi_w(r' + r) \rangle.$$

For large q we employ (7) in connection with (31) and (47) to obtain

$$\chi_{ww}(q) = 2\pi \frac{S}{V} \left[q^{-4} + q^{-6} \left(\frac{3}{2} \langle H^2 \rangle - \frac{1}{2} \langle K \rangle \right) \right] + O(q^{-8}), \quad (68)$$

where k_1 and k_2 have been replaced by H and K . This is valid

for q so large that the film appears nearly flat on this scale. Quantitatively, we may define a correlation length ξ_s by

$$\xi_s \equiv (\langle k_1^2 + k_2^2 \rangle)^{-1/2}. \quad (69)$$

Then (68) is an asymptotic expansion in $(q\xi_s)^{-2}$.

D. Scattering by the film

$i_{ff}(q)$ is the scattering intensity of a system where the scattering length densities of the water and the oil have been matched, and only the film scatters. Using (57), the amplitude is written as

$$\mathcal{A}_f = \int_{-d/2}^{d/2} [n_f(\rho) - n_o] \int_S e^{iq \cdot (r + \rho n)} \times (1 - 2Hp + K\rho^2) d\rho dS. \quad (70)$$

Now we employ our assumption that the thickness of the film is small compared to the correlation length ξ_s ,

$$\frac{d}{\xi_s} \ll 1. \quad (71)$$

Then (70) can be replaced by

$$\mathcal{A}_f = \int_{-d/2}^{d/2} \Delta n(\rho) \int_S e^{iq \cdot (r + \rho n)} d\rho dS, \quad (72)$$

where

$$\Delta n(\rho) \equiv n_f(\rho) - n_o. \quad (73)$$

Averaging, we find

$$i_{ff}(q) = \frac{1}{V} \int_{-d/2}^{d/2} d\rho_1 \int_{-d/2}^{d/2} d\rho_2 \Delta n(\rho_1) \Delta n(\rho_2) \times \int_S \int_S \frac{\sin|q||r_1 - r_2 + \rho_1 n_1 - \rho_2 n_2|}{|q||r_1 - r_2 + \rho_1 n_1 - \rho_2 n_2|} dS_1 dS_2. \quad (74)$$

Now we note that a good approximation to this is

$$i_{ff}(q) = \int_{-d/2}^{d/2} d\rho_1 \int_{-d/2}^{d/2} d\rho_2 \Delta n(\rho_1) \Delta n(\rho_2) \times \int_0^\infty 4\pi r^2 g_{ss}(r) \frac{\sin|q|[r^2 + (\rho_1 - \rho_2)^2]^{1/2}}{|q|[r^2 + (\rho_1 - \rho_2)^2]^{1/2}} dr. \quad (75)$$

Indeed, for $qd \ll 1$ both expressions reduce to

$$i_{ff}(q) = d^2 (\Delta n)^2_f \chi_{ss}(q), \quad (76)$$

where

$$(\Delta n)_f \equiv \frac{1}{d} \int_{-d/2}^{d/2} \Delta n(\rho) d\rho \quad (77)$$

and

$$\chi_{ss}(q) \equiv \int_0^\infty 4\pi r^2 g_{ss}(r) \frac{\sin|q|r}{|q|r} dr. \quad (78)$$

On the other hand, for $qd \gg 1$ we have $q\xi_s \gg 1$ and the film is effectively flat on this scale. Then

$$|r_1 - r_2 + \rho_1 n_1 - \rho_2 n_2| = [r^2 + (\rho_1 - \rho_2)^2]^{1/2}, \quad (79)$$

and (75) is generally valid.

Let us take a closer look at the two regimes $qd \ll 1$, $qd \gg 1$.

1. $qd \ll 1$

In this region the interface is infinitely thin. Experimentally, it is the region of the scattering peak.²² Equation (78) contains information about the average size and shape of the water-oil domains. For large q , while remaining in this regime, we can employ (7) and (44) to obtain

$$\chi_{ss}(q) = 2\pi \frac{S}{V} \left[q^{-2} - q^{-4} \left(\frac{1}{2} \langle H^2 \rangle - \frac{1}{2} \langle K \rangle \right) \right] + O(q^{-6}). \quad (80)$$

This is valid for

$$d \ll q^{-1} \ll \xi_s. \quad (81)$$

2. $qd \gg 1$

In this regime the film is flat and we find by partial integration and using (19), that the inner integral in (75) is

$$\frac{2\pi}{q^2} \frac{S}{V} \cos|q||\rho_1 - \rho_2|. \quad (82)$$

Therefore,¹³

$$i_{ff}(q) = 2\pi \frac{S}{V} q^{-2} \int_{-d/2}^{d/2} d\rho_1 \int_{-d/2}^{d/2} d\rho_2 \Delta n(\rho_1) \Delta n(\rho_2) \times \cos|q||\rho_1 - \rho_2|. \quad (83)$$

For $q \rightarrow 0$, while remaining in this regime, we recover the first term in (80) as we should.

E. The cross term i_{wf}

In the symmetric case i_{wf} is very small and, in general, an upper bound is given by the Schwarz inequality

$$|i_{wf}(q)| \leq [i_{ww}(q) i_{ff}(q)]^{1/2}. \quad (84)$$

If it can be measured¹³ by contrast matching, it yields valuable information about the structure of the system.

1. $qd \gg 1$

For the flat film, and where terms of the order d/ξ are neglected, i_{wf} has been calculated by Auvray,¹³

$$i_{wf}(q) = - (n_w - n_o) 2\pi \frac{S}{V} |q|^{-3} \times \int_{-d/2}^{d/2} \Delta n(\rho) \sin|q|(\rho + d/2) d\rho. \quad (85)$$

In the range $d \ll q^{-1} \ll \xi_s$,

$$i_{wf}(q) = - (n_w - n_o) 2\pi \frac{S}{V} |q|^{-2} \times \int_{-d/2}^{d/2} (\rho + d/2) \Delta n(\rho) d\rho. \quad (86)$$

2. $qd \ll 1$

Here the thickness of the film is negligible and

$$i_{wf}(q) = d(n_w - n_o) (\Delta n)_f \chi_{ws}(q) \quad (87)$$

with

$$\chi_{ws}(q) = \int_0^\infty 4\pi r^2 g_{ws}(r) \frac{\sin|q|r}{|q|r} dr, \quad (88)$$

where again terms of order d/ξ_s and qd have been neglected. For $d \ll q^{-1}$,

$$\chi_{ws}(q) = 2\pi \frac{S}{V} \langle H \rangle q^{-4} \quad (89)$$

(note that the sign of H depends upon the orientation of S . We have oriented S in such a way that it points from water to oil. Water spheres in oil then have $H = -1/R$ and oil spheres in water $H = +1/R$).

3. Possibility of measuring $\langle H \rangle$

In the region $d \ll q^{-1} \ll \xi_s$ the two expressions (86) and (89) are superimposed and

$$i_{wf}(q) = (n_w - n_o) 2\pi \frac{S}{V} d \left[q^{-4} \langle H \rangle (\Delta n)_f - q^{-2} d^{-1} \times \int_{-d/2}^{d/2} (\rho + d/2) \Delta n(\rho) d\rho \right]. \quad (90)$$

The first term can be discriminated from the second in the region

$$q \ll \left(\frac{|\langle H \rangle|}{d} \right)^{1/2}. \quad (91)$$

4. Structure and i_w

We have already obtained, in terms of $i_{wf}(q)$, a criterion for perfect water-oil symmetry. Defining a dimensionless function ν by

$$\nu(q) \equiv \frac{i_{wf}(q)}{[i_{ww}(q)i_{ff}(q)]^{1/2}}, \quad (92)$$

this criterion was simply

$$\nu(q) \equiv 0 \quad (93)$$

(here and in the following we concentrate on the region $qd \ll 1$). From Schwarz's inequality (84)

$$|\nu(q)| \leq 1 \quad (94)$$

for all q . Consider now a system composed of monodisperse water spheres in oil. Then the fluctuations of water and oil are perfectly correlated, and

$$\nu(q) \equiv 1. \quad (95)$$

Similarly, for monodisperse oil spheres in water

$$\nu(q) \equiv -1. \quad (96)$$

These relations are only valid, if the particles are monodisperse spheres. For monodisperse particles of arbitrary shape only

$$\nu(0) = \pm 1 \quad (97)$$

survives.

It is interesting to note that the condition $\nu^2(q) = 1$ is easily tested in neutron scattering experiments. In the region $qd \ll 1$ the intensity is given by

$$i(q) = (n_w - n_o)^2 \chi_{ww} + d^2 (n_f - n_o)^2 \chi_{ff} + 2d(n_w - n_o)(n_f - n_o) \chi_{wf}. \quad (98)$$

For fixed q , i is a quadratic function of the n_i . Varying n_o , for example, yields a parabola with minimum

$$i_{\min}(q) = (n_w - n_o)^2 d^2 \frac{\chi_{ww}(q) \chi_{ff}(q) - \chi_{wf}^2(q)}{\chi_{ww}(q) + d^2 \chi_{ff}(q) + 2d \chi_{wf}(q)}. \quad (99)$$

Therefore, the minimal scattering intensity vanishes for those q for which $\nu(q) = \pm 1$. The condition

$$i_{\min}(q) \ll i_{ff}(q) \quad (100)$$

provides conclusive evidence that one of the phases is composed of nearly monodisperse spheres. For spheres with a finite-size distribution $\sigma \ll R$, ν will be near ± 1 only for $q\sigma \ll 1$. Near $q\sigma \sim 1$ there is a crossover to the asymptotic behavior $|\nu| \sim 1/qR$ for $q\sigma \gg 1$.

F. Possibility of measuring $\langle H^2 \rangle$ and $\langle K \rangle$

We consider a system where the two relevant length scales ξ_s and d are widely separated. This is the case for microemulsions with long-chain surfactants, where d is of the order of 1 nm, while ξ_s 's of the order of several hundred nm can be achieved. It is the range $d \ll q^{-1} \ll \xi_s$ where rigorous statements can be made independently of any model, and where the film is almost (but not quite) flat and its thickness negligible. In this region we have

$$i(q) = i_{ww} + i_{ff} + 2i_{wf}, \quad (101)$$

$$i_{ww} = 2\pi \frac{S}{V} (n_w - n_o)^2 \left[q^{-4} + q^{-6} \left(\frac{3}{2} \langle H^2 \rangle - \frac{1}{2} \langle K \rangle \right) \right], \quad (102)$$

$$i_{ff} = 2\pi \frac{S}{V} (\Delta n)_f^2 d^2 \left[q^{-2} - q^{-4} \left(\frac{1}{2} \langle H^2 \rangle - \frac{1}{2} \langle K \rangle \right) \right], \quad (103)$$

$$i_{wf} = 2\pi \frac{S}{V} (n_w - n_o) (\Delta n)_f d q^{-4} \langle H \rangle, \quad (104)$$

where the ratio of the neglected terms to the last terms written down is $(q\xi_s)^{-2}$. The Porod-Kirste term overwhelms the other contributions to q^{-6} , if

$$\left| \frac{n_w - n_o}{(\Delta n)_f} \right| \gg \frac{d}{\xi_s}. \quad (105)$$

On the other hand, $(1/2) \langle H^2 \rangle - (1/2) \langle K \rangle$ can be isolated only in the region

$$\left| \frac{n_w - n_o}{(\Delta n)_f} \right| \leq \frac{d}{\xi_s}. \quad (106)$$

In neutron-scattering experiments, contrast variation is done by substituting protonated water or oil by the respectively deuterated compounds. An experiment is meaningful only if the structure of the system is not modified by such a substitution. For the system considered, where $d/\xi_s \sim 10^{-2}$, $|n_w - n_o|$ has only to be varied from 0 to a few percent to separate the three contributions i_{ww} , i_{ff} , i_{wf} . Such a small contrast variation is unlikely to induce any significant changes in the structure.

We conclude that it should be possible, in principle, to measure $\langle H^2 \rangle$ and $\langle K \rangle$ separately utilizing the next to leading terms of i_{ww} and i_{ff} . This, however, requires an appropriate system and very precise measurements.

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