Film orientational correlations from random planar sections

Oleg V. Vasil'ev, Alexander V. Gorelov,* and Kenneth A. Dawson†

Theory Group and Complex Fluids Group, Centre for Soft Condensed Matter and Biomaterials, Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

(Received 30 September 1994)

We reveal how various film orientational correlations are related to the correlations of the curves which are the intersections of the film with a random plane. We suggest that the relations we have found can be used for recovery of film orientational correlations by analyzing planar sections of bulk material. The relation of the film orientational correlations with the density-density correlations is also discussed.

PACS number(s): 61.20.Qg, 61.90.+d, 68.10.−m

The structure of a three-dimensional system with a quasi-two-dimensional subsystem is a problem relevant to a wide area of studies of membranes and surfaces [1]. Examples range from cell tissue, foams, sponge phase to microemulsion. For example, in cell tissue the tight contacts between the cell walls determine the short range order, but correlations on somewhat larger distances are not well understood. In the present paper, we describe how the film orientational correlations may be related to the correlations of the curves arising from the intersections of the film with a randomly selected plane. The relation we derive may, therefore, be used for the recovery of the film orientational correlations by analysis of random planar sections of the material. Examples of such planar sections include sectioned cell tissue, or, perhaps, freeze-fractured microemulsion.

The curves we discuss on the planar section correspond to those places where the plane crosses the film. Let us denote by $\mathbf{e}(\mathbf{r})$ the normal to the film at the point $\mathbf{r}$. The projection of the vector $\mathbf{e}$ onto the plane is $\mathbf{e}^{\parallel}=\mathbf{e}-(\mathbf{e}\cdot\mathbf{n})\mathbf{n}$, where $\mathbf{n}$ is a normal to the plane. If the sectioning plane crosses the film at the point $\mathbf{r}$, $\mathbf{e}^{\parallel}(\mathbf{r})/|\mathbf{e}^{\parallel}(\mathbf{r})|$ is just the normal in the plane to the curve at the point $\mathbf{r}$. Let us consider all pairs of such intersection points separated by distance r. We seek a relation between the correlations of $\mathbf{r}$, $\mathbf{e}^{\parallel}(0)$, and $\mathbf{e}^{\parallel}(\mathbf{r})$ and the correlations of $\mathbf{r},\mathbf{e}(0)$, and $\mathbf{e}(\mathbf{r})$. The orientational randomness of a section plane implies a distribution of angles β and β_a between the vector $\mathbf{r}$, which necessarily lies on the plane, and the vectors $\mathbf{e}^{\parallel}(0)$ and $\mathbf{e}^{\parallel}(\mathbf{r})$, respectively. Let us choose a suitable cartesian system of coordinates. Let the Z axes be along $\mathbf{r}$, $\mathbf{r}=r(0;0;1)$, $\mathbf{e}(0)$ is in the XZ plane, and $\mathbf{e}(0)=(\sin\alpha;0;\cos\alpha)$. Let ξ be the polar angle in the XY plane, so that $\mathbf{e}(\mathbf{r})=(\sin\alpha_1\cos\xi;\sin\alpha_1\sin\xi;\cos\alpha_1)$. The angles α and α_1 are the angles between $\mathbf{r}$ and $\mathbf{e}(0)$ and $\mathbf{e}(\mathbf{r})$, respectively, and $\alpha,\alpha_1\in[0;\pi];\xi\in[0;2\pi]$. The orientation of the plane is given by the angle ϕ:$\mathbf{n}=(\cos\phi;\sin\phi;0)$. The angles β and β_1 depend on the orientation of the plane, so that

$$\beta(\alpha,\phi)=\mathrm{sgn}(\sin\phi)\arccos\left[\frac{\cos\alpha}{\sqrt{1-\sin^2\alpha\cos^2\phi}}\right] \qquad (1)$$

and $\beta_1=\beta(\alpha,\phi-\xi)$. By $\mathrm{sgn}(x)$, we mean the sign of x; $\mathrm{sgn}(x)=1$ at $x>0$ and $\mathrm{sgn}(x)=-1$ at $x\le 0$. Notice that in (1) we have chosen the interval $\beta\in[-\pi;\pi]$. These results are direct results only of three-dimensional geometry.

The average $\langle\ \rangle_p$ of a function $\Phi(\beta,\beta_1)$ in the plane may be derived by the averaging of the Φ over all the possible plane orientations:

$$\langle\Phi(\beta,\beta_1)\rangle_p=\langle\Phi^{\dagger}(\alpha,\alpha_1,\xi)\rangle_{0,\mathbf{r}}\ , \qquad (2)$$

$$\Phi^{\dagger}(\alpha,\alpha_1,\xi)=\frac{1}{2\pi}\int_0^{2\pi}d\phi\,\Phi[\beta(\alpha,\phi),\beta(\alpha_1,\phi-\xi)]\ , \qquad (3)$$

where the averaging $\langle\ \rangle_{0,\mathbf{r}}$ is defined to be carried out over only those film configurations in which the film passes through the points 0 and $\mathbf{r}$. Thus, statistics from planar sections can provide $\langle\Phi^{\dagger}(\alpha,\alpha_1,\xi)\rangle_{0,\mathbf{r}}$ for any function $\Phi^{\dagger}$ that is obtained via the transformation [which is defined by Eqs. (3) and (1)] of some function Φ. The complete class of functions that can be obtained by this transformation is not clear in advance. Fortunately, simple geometrical arguments help us to find some examples of functions Φ, which transform into representative functions $\Phi^{\dagger}$. In fact, we can readily determine $\langle\Upsilon(\alpha,\alpha_1,\xi)\rangle_{0,\mathbf{r}}$, where Υ is an angle between any two vectors we are interested in [any pair of $\mathbf{e}(0)$, $\mathbf{e}(\mathbf{r})$, $\mathbf{r}$ or their linear combinations]. To see this, let us imagine that we can obtain the projections of two vectors (call them $\mathbf{v}_1$ and $\mathbf{v}_2$) onto any vector $\mathbf{a}$. The projections can be collinear $(\mathbf{a}\cdot\mathbf{v}_1)(\mathbf{a}\cdot\mathbf{v}_2)>0$ or anticollinear, $(\mathbf{a}\cdot\mathbf{v}_1)(\mathbf{a}\cdot\mathbf{v}_2)<0$. It is easy to prove that if we gather the statistics of both cases for a random choice of vector $\mathbf{a}$ in three-dimensional space, we would find

$$\pi\frac{N_a}{N}\rightarrow\langle\Upsilon(\mathbf{r})\rangle_0\ , \qquad (4)$$

*Permanent address: Institute of Theoretical and Experimental Biophysics, Russian Academy of Science, Pushchino, Moscow Region 142292, Russia.

†Also at the Institute of Theoretical and Experimental Biophysics, Russian Academy of Science, Pushchino, Moscow Region 142292, Russia.

where N_a is the number of the anticollinear cases, and N is the total number. In fact, we may take the vector **a** to be in our section plane, but then we must include the weight sin[**ar**] [where $\angle(\mathbf{a},\mathbf{r})$ is the angle between **a** and **r**] to our statistics. We can also use the projections $\mathbf{v}_1^{\parallel}$ and $\mathbf{v}_2^{\parallel}$ of the vectors $\mathbf{v}_1$ and $\mathbf{v}_2$ onto the plane instead of the vectors $\mathbf{v}_1$ and $\mathbf{v}_2$ themselves, and the result will be the same. It is now convenient to rewrite all of this in terms of the statistics of angles, rather than statistics of signs. Thus, it is straightforward to evaluate $1/2\pi\int_A d\varphi \sin\angle(\mathbf{a},\mathbf{r})$, where φ is the polar angle on the section plane, and $A=A(\beta,\beta_1)$ is that region of φ which correspond to anticollinear cases. In this manner, we have expressed the relation (4) in terms of β and β_1. We present here two such examples:

$$\Phi_1(\beta,\beta_1)=\Phi_0(\beta)\equiv\begin{cases}\frac{\pi}{2}\sin|\beta| & \text{when } |\beta|\in\left[0;\frac{\pi}{2}\right]\\ \frac{\pi}{2}(2-\sin|\beta|) & \text{when } |\beta|\in\left[\frac{\pi}{2};\pi\right]\end{cases}. \tag{5}$$

$$\Phi_2(\beta,\beta_1)=\begin{cases}|\Phi_0(\beta)-\Phi_0(\beta_1)| & \text{when } \beta\beta_1>0\\ \Phi_0(\beta)+\Phi_0(\beta_1) & \text{when } \beta\beta_1<0;|\beta-\beta_1|<\pi\\ 2\pi-\Phi_0(\beta)-\Phi_0(\beta_1) & \text{when } \beta\beta_1<0;|\beta-\beta_1|>\pi\end{cases}. \tag{6}$$

$$\Phi_1^{\dagger}(\alpha,\alpha_1,\xi)=\alpha; \tag{7}$$

$$\begin{aligned}\Phi_2^{\dagger}(\alpha,\alpha_1,\xi)&=\angle(\mathbf{e}(\mathbf{0}),\mathbf{e}(\mathbf{r}))\\ &=\arccos(\sin\alpha\sin\alpha_1\cos\xi+\cos\alpha\cos\alpha_1)\ .\end{aligned} \tag{8}$$

The integrals (3) of (5) and (6) [along with (1)] are not well known and so we have checked numerically the results (7) and (8).

Both $\langle\Phi_1^{\dagger}\rangle_{0,\mathbf{r}}$ and $\langle\Phi_2^{\dagger}\rangle_{0,\mathbf{r}}$ represent the orientational structure of the film. We have now shown that they correspond [by the Eqs. (2) and (3)] to the averages $\langle\Phi_1\rangle_p$ and $\langle\Phi_2\rangle_p$, respectively.

We now wish to present some other examples that may be of interest. It is instructive to consider the transformation (3) of the function $\cos^{2n}\beta, n=1,2,3,\ldots,$ which leads to the integral,

$$\begin{aligned}(\cos^{2n}\beta)^{\dagger}&=\frac{1}{\pi}\cot^{2n}\alpha\int_0^1\frac{dx}{\sqrt{x(1-x)}\left[\frac{1}{\sin^2\alpha}-x\right]^n}\\ &=|\cos\alpha|^n P_{n-1}\left[\frac{1+\cos^2\alpha}{2|\cos\alpha|}\right]\ .\end{aligned} \tag{9}$$

$$\begin{aligned}\frac{(\cos^{2n+2}\beta)^{\dagger}}{|\cos\alpha|}&=\frac{(2n-1)!!}{2^n n!}+\frac{(2n-3)!!}{2^{n-1}(n-1)!}\frac{1!!}{2^1 1!}\cos^2\alpha\\ &+\frac{(2n-5)!!}{2^{n-2}(n-2)!}\frac{3!!}{2^2 2!}\cos^4\alpha\\ &+\frac{(2n-7)!!}{2^{n-3}(n-3)!}\frac{5!!}{2^3 3!}\cos^6\alpha\\ &+\cdots+\frac{(2n-1)!!}{2^n n!}\cos^{2n}\alpha\ .\end{aligned} \tag{10}$$

Here, P_n is the Legendre polynomial of order n.

Thus, $(\cos^{2n}\beta)^{\dagger}$ is just a polynomial of odd powers of $|\cos\alpha|$, up to $(2n-1)$ power. The simplest example is $(\cos^2\beta)^{\dagger}=|\cos\alpha|$. Conversely, inverting the system of polynomials (10), one may obtain that $|\cos^{2n-1}\alpha|$ for any $n=1,2,3,\ldots$ is the result of the transformation (3) of a polynomial of even powers of $\cos\beta$, up to the $2n$ power. However, we can obtain more. The result for a function $(\text{sgn}\beta\cos^{2n}\beta)^{\dagger}$ is just the right hand side of Eqs. (9) and (10) multiplied by $\text{sgn}(\cos\alpha)$. This means that one may also obtain $\cos^{2n-1}\alpha$ for any $n=1,2,3\ldots$ as a transformation (3) of a product of $\text{sgn}\beta$ and a polynomial of even powers of $\cos\beta$, up to the $2n$ power. A particularly interesting example is

$$\cos\alpha=(\text{sgn}\beta\cos^2\beta)^{\dagger}\ . \tag{11}$$

The corresponding average $\langle\cos\alpha\rangle_{0,\mathbf{r}}$ is related also to some film density correlation functions, as we will explain below.

So far, we argue, we have established how a range of film orientational correlations may be related to the correlations of the intersections of the film with a random plane. For a comparison, we wish to list here all the possible orientational correlations, which are related to the film density correlation functions. The density correlation functions had been intensively investigated in the microemulsion physics [2], and one possible application of our work is in that field.

The usual bulk-bulk correlation function is $G(r)\equiv\langle\phi(0)\phi(\mathbf{r})\rangle$, where $\phi(\mathbf{r})$ is the density of the bulk material (i.e., the interfilm medium) at a point **r**. (In case of a microemulsion the Fourier transform $\tilde{G}$ may be determined by bulk-contrast neutron scattering [3,4].) We wish to consider the tensor [5],

$$\begin{aligned}\partial_{\mathbf{r}_1}\otimes\partial_{\mathbf{r}_2}G(|\mathbf{r}_1-\mathbf{r}_2|)&=\langle\nabla\phi(\mathbf{r}_1)\otimes\nabla\phi(\mathbf{r}_2)\rangle\\ &\approx\chi^2\langle\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\mathbf{e}(\mathbf{r}_1)\otimes\mathbf{e}(\mathbf{r}_2)\rangle\ ,\end{aligned} \tag{12}$$

where ρ is the film material density. The coefficient

$$\chi = \frac{\langle |\nabla\phi| \rangle_f}{\rho_0} = \frac{\phi_0}{b\rho_0} , \tag{13}$$

where $\langle |\nabla\phi| \rangle_f$ is $|\nabla\phi|$, averaged (only) over the film, ϕ_0 is the average density of the bulk material, ρ_0 is the density of the film and b is the width of the film. The approximation in (12) assumes that the density and width of the film are not correlated with its curvature and approximately constant throughout the film. The width of the film is supposed to be small in comparison with the interfilm distances; the boundary between the film and the bulk material is supposed to be sharp, so either $\rho(\mathbf{r})$ is neglected if the film does not pass the point $\mathbf{r}$, or $\rho(\mathbf{r})=\rho_0$ if the film passes the point $\mathbf{r}$ (see the analogous consideration in [5]). The last point is essentially used in the next step.

Let us denote by $\mathcal{S}_0$ the subset of configurations, c, in which the film passes through the points 0 and $\mathbf{r}$ and note that for these configurations $\rho(0)=\rho(\mathbf{r})=\rho_0$. The entire set of configurations is denoted by $\mathcal{S}$, and we have the following simple relation:

$$\langle \rho(0)\rho(\mathbf{r})\mathbf{e}(0)\otimes\mathbf{e}(\mathbf{r}) \rangle = \frac{\rho_0^2 \Sigma_{c\in\mathcal{S}_0} \mathbf{e}(0)\otimes\mathbf{e}(\mathbf{r})\exp(-H(c))}{\Sigma_{c\in\mathcal{S}}\exp(-H(c))}$$

$$= g(r)\langle \mathbf{e}(0)\otimes\mathbf{e}(\mathbf{r}) \rangle_{0,\mathbf{r}} . \tag{14}$$

Here $g(r)\equiv\langle \rho(0)\rho(\mathbf{r}) \rangle$ is the film-film correlation function. The tensor

$$\langle \mathbf{e}(0)\otimes\mathbf{e}(\mathbf{r}) \rangle_{0,\mathbf{r}} \equiv \frac{\Sigma_{c\in\mathcal{S}_0} \mathbf{e}(0)\otimes\mathbf{e}(\mathbf{r})\exp(-H(c))}{\Sigma_{c\in\mathcal{S}_0}\exp(-H(c))} \tag{15}$$

represents the orientational correlations of the film.

The normal-normal tensor $\langle \mathbf{e}(0)\otimes\mathbf{e}(\mathbf{r}) \rangle_{0,\mathbf{r}}$ may be contracted with vectors to produce averages with scalar values. We may obtain a scalar result from (15) by two independent methods: Either we take the trace of the tensor or the double scalar product with $\mathbf{r}$ [5]. Thus, from the bulk-bulk (G) and film-film (g) density correlation functions, and using the result (15), one may obtain any linear combination of the averages:

$$\langle \cos\alpha \cos\alpha_1 \rangle_{0,\mathbf{r}} \approx -\frac{1}{\chi^2}\frac{G''(r)}{g(r)} ; \tag{16}$$

$$\langle \sin\alpha \sin\alpha_1 \cos\xi \rangle_{0,\mathbf{r}} \approx -\frac{2}{\chi^2}\frac{G''(r)}{rg(r)} . \tag{17}$$

The bulk-film correlation function $E(r)=\langle \phi(0)\rho(\mathbf{r}) \rangle$. (In the case of a bicontinuous microemulsion, it may be determined experimentally from contrast matching experiments [6]. One can derive, analogously to (12) and (14),

$$\partial_{\mathbf{r}_1} E(|\mathbf{r}_1-\mathbf{r}_2|) = \langle \nabla\phi(\mathbf{r}_1)\rho(\mathbf{r}_2) \rangle$$

$$\approx \chi g(|\mathbf{r}_1-\mathbf{r}_2|)\langle \mathbf{e}(\mathbf{r}_1) \rangle_{\mathbf{r}_1,\mathbf{r}_2} . \tag{18}$$

Thus, from bulk-film (E) and film-film (g) density correlation functions one can obtain

$$\langle \cos\alpha \rangle_{0,\mathbf{r}} \approx -\frac{1}{\chi}\frac{E'(r)}{g(r)} . \tag{19}$$

Before proceeding further, let us notice that the relations (16), (17), and (19) are relatively model independent and yield orientational correlations, which are of a geometrical nature, in terms of the density-density correlations.

Notice also the important Porod's limit [7]. For small r (approximately flat film) we have, in particular, $\langle \cos\alpha \cos\alpha_1 \rangle_{0,\mathbf{r}} \approx 1$ and $\langle \sin\alpha \sin\alpha_1 \cos\xi \rangle_{0,\mathbf{r}} \approx 0$, and so [see (16), (17), and (13)]

$$\left[\frac{\phi_0}{b\rho_0}\right]^2 = \chi^2 \approx \frac{k^2\tilde{G}(k)}{\tilde{g}(k)}, \quad \text{for } \langle |k_{\mathrm{pr}}| \rangle \ll k \ll \frac{1}{b} . \tag{20}$$

This relates the width, b, of the film to the Porod's slopes of the Fourier transforms $\tilde{G}(k)\sim k^{-4}$ and $\tilde{g}(k)\sim k^{-2}$. The restriction in Eq. (20) is the usual one, and k_{pr} is the principal curvature [8,5,7].

We have now provided a link between film orientational correlations and bulk or bulk-film density correlations, thereby providing a potential means of relating statistical analysis of fractures samples to more conventional experimental approaches. One remarkable result is that the orientational correlation function $\langle \cos\alpha \rangle_{0,\mathbf{r}}$ may be determined in two independent manners [see (19) and (11)]. This would permit one to compare our approach to the recovery of orientational correlations from the planar sections, with the alternative using the density-density correlations.

For the use of a microemulsion, however, the main weakness in the argument is that the fractured surface may be nonplanar. Thus, though there are suitable freeze-fracture electron microscopy images [9,10], there may be difficulties with local correlations between the section "plane," possibly curved, and the film. In this case, the comparison mentioned above would be rather a test on the planarity of the section "plane."

Finally, we believe that the present work establishes good means of studying film orientational correlations and might be applied to two-dimensional cuts of cell tissue and similar systems that contains a two-dimensional subsystem, thereby revealing the implicit three-dimensional correlations. This might be an interesting field of study in the biological sciences.

The work was supported, in part, by the Higher Education Authority of Ireland, and the Digital Equipment Company.

[1] *Statistical Mechanics of Membranes and Surfaces,* edited by D. Nelson, T. Piran, and S. Weinberg (World Scientific, Singapore, 1989).
[2] G. Gompper and M. Schick, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebowitz (Academic, London, in press), and references therein; K. A. Dawson, in *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution,* edited by S.-H. Chen *et al.* (Kluwer Academic Publishers, Netherlands, 1992), and references there made to other models.
[3] L. Auvray, J.-P. Cotton, R. Ober, and C. Taupin, J. Phys. Chem. **88**, 4586 (1984).
[4] M. Teubner and R. Strey, J. Chem. Phys. **87**, 3195 (1987).
[5] M. Teubner, J. Chem. Phys. **92**, 4501 (1990).
[6] L. Auvray, J.-P. Cotton, R. Ober, and C. Taupin, Physica **136B**, 281 (1986).
[7] G. Porod, Kolloid Z. Z. Polym. **124**, 83 (1951); **125**, 21 (1952); **125**, 108 (1952).
[8] R. Strey, J. Winkler, and L. Magid, J. Phys. Chem. **95**, 7502 (1991).
[9] W. Jahn and R. Strey, J. Phys. Chem. **92**, 2294 (1988).
[10] R. Strey, W. Jahn, G. Porte, and P. Bassereau, Langmuir **6**, 1635 (1990).