

# Fluctuations in a crystalline monolayer on the surface of water

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The structure factor of a crystalline monolayer on the surface of a liquid is calculated. It is shown that the finite rigidity of the monolayer remains in the main approximation of the power-law profile of the quasi-Bragg peaks typical of 2D systems, but leads to the reduction of the x-ray scattering intensity. It was found that this effective Debye–Waller factor depends strongly on the length ( $h$ ) of the chains that form the monolayer. Specifically, it is proportional to  $\exp(-h^3/\xi a^2)$ , where  $\xi$  is a chain persistent length, and  $a$  is the characteristic atomic scale.

1. A large variety of properties related to the surface crystallization of different substances at the surface of a liquid have recently been studied.<sup>1–3</sup> In particular, we would like to mention the highly systematic x-ray diffraction and the thermodynamic measurements of the crystalline monolayers of fatty alcohols on the surface of water.<sup>4,5</sup> It was shown in those experiments<sup>4,5</sup> that almost all of the internal degrees of freedom are frozen in the monolayer (especially in short chain monolayers). However, even in 2D crystalline monolayers there are nonetheless some internal degrees of freedom (which are related to conformational and elastical fluctuations of the chains).

In this paper we will formulate a simple model which describes the role of these internal degrees of freedom for the fluctuations of the displacements in the two-dimensional lattice constructed from finite-length chains. Our aim here is not to claim that our oversimplified phenomenological description necessarily holds for real systems investigated in Refs. 4 and 5, but rather to explore the consequences of this simple model.

2. Let us consider a crystalline monolayer formed by chains. We believe that these chains are rather stiff, and therefore the configurations with the so-called hairpin defects are forbidden. The crystalline order in a system occurs only in a plane which is orthogonal (on the average) to the chains. For simplicity, we consider only the hexagonal crystalline structure (i.e., there is no cooperative tilt of the chains).

Thus the elastic energy of such a monolayer can be written as follows:

$$E = \frac{1}{2} \int_{-h/2}^{h/2} dz \int d^2r \left( B_l (\nabla_\alpha u_\alpha)^2 + B_t \varepsilon_{\alpha\beta} (\nabla_\alpha u_\beta)^2 + K \left( \frac{\partial^2 u_\alpha}{\partial z^2} \right)^2 \right), \quad (1)$$

where the Greek subscripts designate the coordinates in the plane orthogonal to the

chains,  $u_\alpha$  is a displacement vector in this plane which describes the elastic energy of a two-dimensional hexagonal lattice,  $B_l$  and  $B_t$  are elastic moduli of this lattice (longitudinal and transverse with respect to the wave vector),  $\varepsilon_{\alpha\beta}$  is a two-dimensional antisymmetric, second-order tensor and  $K$  is a bending elastic module which describe elasticity of the chains, and  $z$  is a coordinate orthogonal to the surface of the monolayer.

Note that there is no term proportional to  $(\partial_z u_\alpha)^2$  in (1), which makes it possible for chains to glide with respect to each other in a liquid-like manner. Note also that the last term in (1) is relevant only for wave vectors  $p_z \gg p_\perp$ . We must therefore disregard, together with the last term, the terms proportional to  $(\partial_z \nabla_\alpha u_\alpha)^2$  or to  $(\partial_z \varepsilon_{\alpha\beta} \nabla_\alpha u_\beta)^2$ .

We believe that our system has a large number (the area  $S$ ) of crystalline domains (as in the case of the systems investigated in Refs. 4 and 5). Therefore, we can use Fourier transformation over the coordinates along the monolayer ( $x$  and  $y$ ). Thus, instead of the energy  $E$ , (1), it is convenient to use the form

$$E(q) = \frac{S}{2} \int_{-h/2}^{h/2} dz \left( A_{\alpha\beta} u_{q\alpha} u_{-q\beta} + K \left| \frac{\partial^2 u_{q\alpha}}{\partial z^2} \right|^2 \right), \quad (2)$$

where

$$A_{\alpha\beta} = B_l q^2 \delta_{\alpha\beta} + B_t q^2 \left( \delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2} \right).$$

Our ultimate aim in this paper is to find the static correlator of the displacements  $\langle u_{q\alpha} u_{-q\beta} \rangle$  for the crystalline monolayer. This correlator can be represented as a sum of longitudinal and transverse parts:

$$\langle u_{q\alpha} u_{-q\beta} \rangle = \frac{T}{\Lambda_l(q)} \frac{q_\alpha q_\beta}{q^2} + \frac{T}{\Lambda_t(q)} \left( \delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2} \right). \quad (3)$$

To find this correlator, we must know two functions,  $\Lambda_l(q)$  and  $\Lambda_t(q)$ .

To calculate the functions  $\Lambda_l(q)$  and  $\Lambda_t(q)$ , we must diagonalize the energy (2). In other words, we must solve the Euler–Lagrange equations that follow from (2). It is convenient to introduce the longitudinal and transverse components of the displacement

$$u_\alpha = u_l \frac{q_\alpha}{q} + u_t \varepsilon_{\alpha\beta} \frac{q_\beta}{q}.$$

In our harmonic approximation there is no coupling between the longitudinal and transverse components and the two Euler–Lagrange equations have a similar form:

$$K \frac{\partial^4 u_{l,t}}{\partial z^4} + A_{l,t} u_{l,t} = 0. \quad (4)$$

Here  $A_{l,t}$  are correspondingly the longitudinal and transverse components of the matrix  $A_{\alpha\beta}$ .

To solve these equations, we must know the boundary conditions. The so-called natural boundary conditions correspond to the surface contributions which come from the bulk energy (1). In our case these contributions lead to the conditions

$$\left(\frac{\partial^2 u_{l,t}}{\partial z^2}\right)_{z=\pm h/2} = \left(\frac{\partial^3 u_{l,t}}{\partial z^3}\right)_{z=\pm h/2} = 0. \quad (5)$$

If there is a specific surface energy  $E_s$  on the right side of the second of these conditions, we must add the terms  $(\delta E_s / \delta u_{l,t})_{z=\pm h/2}$  which describe the surface elasticity. In the simplest approximation this surface elasticity can be represented in the following way:

$$E_s = \int d^2r \delta(z \pm h/2) \epsilon_s^{(\pm)} (\nabla u_{l,t})^2,$$

where  $\epsilon_s^{(\pm)} = -n_s \partial \gamma^{(\pm)} / \partial n_s$  is the modulus of the surface elasticity,  $\gamma^{(\pm)}$  is the surface tension,  $n_s$  is the concentration of molecules constituting the monolayer, and the superscripts  $(\pm)$  represent the corresponding quantities of the boundaries ( $z = \pm h/2$ ).

These surface contributions modify the quantitative results. Qualitatively (as we will see) the correlation functions  $\langle u_\alpha u_\beta \rangle$ , which only we are interested in, are very similar. Therefore, in what follows we ignore these surface contributions. Note that these surface contributions are extremely small. All the corrections are proportional to the parameter

$$\epsilon_s q^2 h^3 / K \ll 1,$$

which for real systems investigated in Refs. 4 and 5 is on the order of  $10^{-6}$ .

Diagonalization of the functional (2) is reduced to solving of the following equation for the eigenfunctions  $\psi_{l,t}$  and eigenvalues  $\Lambda_{l,t}$ :

$$K \frac{\partial^4 \psi_{l,t}}{\partial z^4} + A_{l,t}(q) \psi_{l,t} = \Lambda_{l,t} \psi_{l,t} \quad (6)$$

with the boundary conditions (5). There are symmetrical and antisymmetrical solutions

$$\psi_{l,t}^{(s)} = A \cosh(p_{l,t} z) + B \cos(p_{l,t} z),$$

and

$$\psi_{l,t}^{(\alpha)} = C \sinh(p_{l,t} z) + D \sin(p_{l,t} z),$$

where

$$p_{l,t}^4 = \frac{\Lambda_{l,t} - A_{l,t}(q)}{K}.$$

It is easy to see that there are solutions of Eq. (6) which satisfy the boundary conditions (5) only at  $p_{l,t}^4 > 0$  and when the quantities  $p_{l,t}$  are solutions of the following equations:

(i) for the symmetrical case

$$\tanh\left(\frac{p_m h}{2}\right) = -\tan\left(\frac{p_m h}{2}\right),$$

(ii) for the antisymmetrical case

$$\tanh\left(\frac{p_m h}{2}\right) = \tan\left(\frac{p_m h}{2}\right).$$

Each equation has the set of solutions

$$p_0 = 0; \quad p_1^{(s)} h/2 = \pm 2.36502; \quad p_2^{(s)} h/2 = \pm 5.4978; \quad p_3^{(s)} h/2 = \pm 8.6394\dots$$

and

$$p_1^{(a)} h/2 = \pm 3/9266; \quad p_2^{(a)} h/2 = \pm 7.06858; \quad p_3^{(a)} h/2 = \pm 10.2102\dots$$

Finally, we find the normalized eigenfunctions

$$\psi_s = \frac{1}{\sqrt{h}} \sum \sqrt{(1 + \tanh^2(p_m h/2))} \left( -\frac{\sin(p_m h/2)}{\sinh(p_m h/2)} \cosh(p_m z) + \cos(p_m z) \right),$$

and

$$\psi_a = \frac{1}{\sqrt{h}} \sum \sqrt{(1 + \tanh^2(p_m h/2))} \left( \frac{\sin(p_m h/2)}{\sinh(p_m h/2)} \sinh(p_m z) + \sin(p_m z) \right).$$

The eigenvalues are

$$\Lambda_{(l,i),m}^{(s,a)} = (K p_{(l,i),m}^{(s,a)4} + A_{(l,i)}(q)) h. \quad (7)$$

3. We have solved the problem of the static fluctuations in the crystalline monolayer on the surface of a liquid. Let us discuss now the qualitative physical consequences of this solution.

First, let us estimate the contributions of the different values of  $p_m$  which enter the static correlation function of the displacements (3) or, more exactly, the eigenvalues (7). The contribution  $p_0 = 0$  gives us the pure 2D result:

$$\langle u_0^2 \rangle \approx \frac{T}{Bh} \ln\left(\frac{R}{a}\right),$$

where  $R$  is the characteristic size of a single-domain region of the crystalline monolayer, and  $a$  is the characteristic atomic scale.

For the systems investigated in Refs. 4 and 5 the chains are rather short ( $h \propto 10a$ ) and stiff ( $K/B > h^4 a^2$ ). This means that the persistence length  $\xi$  (see, e.g., Ref. 6 is larger than  $h$ .<sup>1)</sup>

The contributions from the higher-order terms in  $p_m$  decrease as  $p_m^{-4}$ , i.e., very rapidly. In a first approximation we can therefore restrict the analysis to only two terms with the smallest values of  $p_m$ . It gives us the following corrections to the 2D result, (8):

$$\langle u_1^2 \rangle \approx \theta \frac{T}{K} \frac{h^3}{a^2}, \quad (9)$$

where the numerical factor  $\theta$  is on the order of  $10^{-3}$ .

Physically interesting and measurable property is not the static correlator (3), but the structure factor which is directly related to the x-ray scattering intensity:

$$S(Q) \approx h \int d^2r \int_{-h/2}^{h/2} dz G(r, z) \exp(iQR), \quad (10)$$

where the wave vector  $\mathbf{Q} = \mathbf{b} + \mathbf{k}$ ,  $b$  is the reciprocal lattice vector,  $k \ll b$ , and the function  $G(r, z)$  can be represented in the form<sup>6</sup>

$$G(r, z) = \exp(-\frac{1}{2}H(r, z)b^2),$$

where

$$H(r, z) = \frac{Tb^2}{Bh} \int \frac{dq}{q} (J_0(qr) - 1) + \theta \frac{Th^3b^2}{K} \int q dq (J_0(qr) \cos(p_1z) - 1), \quad (11)$$

where  $J_0$  is a zero-order Bessel function. Note that we have retained in (10) explicitly only those factors which depend on  $h$ .

Let us consider the case in which  $Q_z = 0$  (which corresponds to a very interesting situation). From (11) and (10) we find

$$S(Q) \approx \frac{h^2}{|\mathbf{b} - \mathbf{Q}|^{2-\eta}} \exp\left(-\frac{\theta Th^3b^2}{Ka^2}\right), \quad (12)$$

where  $\eta = Tb^2/(Bh)$ .

In our approximation the role of the finite length of the chain thus reduces to an effective Debye-Waller factor, which does not change the shape of the peaks which correspond to the well-known power-law behavior typical of 2D systems. Note that this factor strongly reduces the intensity of high-order peaks in the x-ray scattering.

We have used expression (12) to adjust the data<sup>5</sup> for the x-ray intensity for four compounds, whose  $h$  varies from  $8a$  to  $14a$ . It gives us a rather reasonable estimate  $\xi \approx 2h$ .

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<sup>1</sup>Here we use the conventional definition of the persistence length  $\xi = C_{\text{eff}}/T$ , where the effective elastic modulus of a chain is related to our modulus,  $K = T^2/2C_{\text{eff}}$ .

<sup>1</sup>A. M. Bibo, C. M. Knobler, and I. R. Peterson, *J. Phys. Chem.* **95**, 5591 (1991).

<sup>2</sup>H. Mohwald, *Rep. Prog. Phys.* **56**, 653 (1993).

<sup>3</sup>B. Berge and A. Renault, *Europhys. Lett.* **21** (1993).

<sup>4</sup>B. Berge, O. Konovalov, J. Lajzerowicz *et al.*, *Phys. Rev. Lett.* **73**, 1652 (1994).

<sup>5</sup>J. F. Legrand, A. Renault, O. Konovalov *et al.*, *Thin Solid Films* **248**, 95 (1994).

<sup>6</sup>L. D. Landau and E.M. Lifshitz, *Statistical Physics, Part 1*, Pergamon Press, Oxford (1980).

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