

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 the power-law profile of quasi-Bragg peaks typical for 2d-systems but leads to the reduction of the X-ray scattering intensity. It is found that this effective Debye-Waller factor has very strong dependence on the length (h) of chains constructing the monolayer. Namely it is proportional to $\exp(-h^3/\xi a^2)$, where ξ is a chain persistent length and a is a characteristic atomic scale.

1. Recently a large variety of properties related to the surface crystallization of different substances at the surface of a liquid have been studied [1-3]. In particular we would like to mention the very systematical X-ray diffraction and thermodynamic measurements of the crystalline monolayers of fatty-alcohols on a water surface [4-5]. It has been shown in these experiments [4-5] that almost all internal degrees of freedom are frozen in the monolayer (especially for short chain monolayers) but nevertheless even for 2d crystalline monolayers there are some internal degrees of freedom (related to conformational and elastical fluctuations of chains).

In this paper we are going to formulate a simple model describing the role of these internal degrees of freedom for the fluctuations of the displacements in 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 [4-5] but rather to explore the consequences of this simplest model.

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

Thus the elastic energy of a such monolayer can be written in the following form:

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

where the Greek subscripts designate coordinates in the plane orthogonal to chains, u_α is a displacement vector in this plane, describing the elastic energy of a two-dimensional hexagonal lattice, B_l and B_t are elastic modules of this

lattice (longitudinal and transversal (with respect to a wave vector) ones), $\varepsilon_{\alpha\beta}$ is a two-dimensional antisymmetric second order tensor and K is a bending elastic module, describing the chains elasticity 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 $p_x \gg p_\perp$. Therefore we must not take into account, 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 our system has a large size (the area S) of crystalline domains (it is just the case for the systems investigated in [4-5]). Therefore one can use Fourier transformation over coordinates along the monolayer (x and y). Thus instead of the energy E (1) it is convenient to use the following 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 final aim in this paper to find the static correlator of displacements $\langle u_{q\alpha} u_{-q\beta} \rangle$ for the crystalline monolayer. This correlator can be represented as a sum of longitudinal and transversal parts

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

And therefore to find it we have to know two functions $\Lambda_l(q)$ and $\Lambda_t(q)$.

To calculate these functions $\Lambda_l(q)$, $\Lambda_t(q)$ one must diagonalize the energy (2), or by other words to solve Euler - Lagrange equations following from (2). It is convenient to introduce longitudinal and transversal 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 longitudinal and transversal components and both 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 longitudinal and transversal components of the matrix $A_{\alpha\beta}$.

To solve these equations we have to know boundary conditions. There are so-called natural boundary conditions which correspond to the surface contributions coming from the bulk energy (1). For our case these contributions lead to the following 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 are specific surface energy E_s in the r.h.s. of the second from these conditions equality one have to add 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 by the following way:

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

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

Accounting these surface contributions modify quantitative results, but qualitatively (as we will see) correlation functions $\langle u_\alpha u_\beta \rangle$ which only we are interesting in, are very similar. Therefore in what follows we neglect these surface contributions. Note also that even quantitative these surface contributions are extremely small. All corrections are proportional to the parameter

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

which for real systems investigated in [4-5] is of the order of 10^{-6} .

Diagonalization of the functional (2) is reduced to solving of the following equation for eigen-functions $\psi_{i,t}$ and eigen-values $\Lambda_{i,t}$

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

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

$$\psi_{i,t}^{(s)} = A \operatorname{ch}(p_{i,t} z) + B \cos(p_{i,t} z) \quad ,$$

and

$$\psi_{i,t}^{(a)} = C \operatorname{sh}(p_{i,t} z) + D \sin(p_{i,t} z) \quad ,$$

where

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

It is easy to see that there are solutions of the equation (6), satisfying the boundary conditions (5) only at $p_{i,t}^4 > 0$ and in this case quantities $p_{i,t}$ are solutions of the following equations:

(i) for the symmetrical case

$$\operatorname{th}\left(\frac{p_m h}{2}\right) = -\operatorname{tg}\left(\frac{p_m h}{2}\right),$$

(ii) for the antisymmetrical case

$$\operatorname{th}\left(\frac{p_m h}{2}\right) = \operatorname{tg}\left(\frac{p_m h}{2}\right).$$

Both equations have 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

$$p_1^{(a)} h/2 = \pm 3.9266; \quad p_2^{(a)} h/2 = \pm 7.06858; \quad p_3^{(a)} h/2 = \pm 10.2102\dots$$

And finally one can find the normalized eigen-functions:

$$\psi_s = \frac{1}{\sqrt{h}} \Sigma \sqrt{(1 + th^2(p_m h/2))} \left(-\frac{\sin(p_m h/2)}{\text{sh}(p_m h/2)} \text{ch}(p_m z) + \cos(p_m z) \right) ,$$

and

$$\psi_a = \frac{1}{\sqrt{h}} \Sigma \sqrt{(1 + th^2(p_m h/2))} \left(\frac{\sin(p_m h/2)}{\text{sh}(p_m h/2)} \text{sh}(p_m z) + \sin(p_m z) \right) .$$

Eigen-values are

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

3. We have solved the problem of investigations of 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 from different values of p_m entering the static correlation function of displacements (3) or more exactly the eigen - values (7). The contribution $p_0 = 0$ gives us the pure 2d result

$$\langle u_0^2 \rangle \simeq \frac{T}{Bh} \ln \left(\frac{R}{a} \right) , \quad (8)$$

where R is a characteristic size of a monodomain region for the crystalline monolayer, a is a characteristic atomic scale.

For the systems investigated in [4-5] the chains are rather short ($h \propto 10a$) and stiff ($K/B > h^4/a^2$). It means that the persistence length ξ (see e.g. [6]) is larger than h .¹⁾

Besides the contributions from the higher order terms in p_m decrease as p_m^{-4} , i.e. very rapidly. So in the first approximation one can restrict oneself to only the two terms with the smallest values of p_m . It gives us the following corrections to the 2d result (8)

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

where the numerical factor θ is of the order of 10^{-3} .

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

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

where the wave vector $Q = b + k$, b is the reciprocal lattice vector and $k \ll b$, and the function $G(r, z)$ can be represented in the following form [6]

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

¹⁾We use the conventional definition of the persistence length here $\xi = C_{eff}/T$, where the effective elastic module for a chain is related to our module $K = T^2/2C_{eff}$.

where

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

where J_0 is the zero order Bessel function. Note that we keep in (10) explicitly only all factors depending on h .

Let us consider the case when $Q_z = 0$ (which corresponds the really interesting situation). From (11) and (10) one can get

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

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

Thus in our approximation the role of the finite chain length is reduced to some effective Debye-Waller factor, which does not change the shape of the peaks which correspond to the well known power-law behaviour typical for 2d systems. Note that this factor reduces strongly the intensity of higher order peaks in the X-ray scattering.

We have used the expression (12) to adjust the data by [5] for the x-ray intensity for 4 compounds with h varying from 8a to 14a. It gives us a rather reasonable estimation $\xi \simeq 2h$.

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