Entropically-Stabilized Self-compactification in Model Colloidal Systems

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We discuss the phenomenon of spontaneous self-compactification in a model colloidal system, proposed in a recent work on DNA-mediated self-assembly. We focus on the effect of thermal fluctuations on the stability of membrane-like self-assembled phase with in-plane square order. Surprisingly, the fluctuations are shown to enhance the stability of this quasi-2D phase with respect to transition to alternative 3D structures.

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I. INTRODUCTION

Effects of physical dimensionality on crystallization are among the most important problems in Condensed Matter Physics. As was established by Landau and Pierls [1], the long-range crystalline order in 2D is universally destroyed by thermal fluctuations. The problem has been revisited in 1970s by Kosterlitz and Thouless [2], who have shown that crystals do exist in 2D, within a new topological definition. Nevertheless, their melting temperature is believed to be always lower than in 3D systems (assuming the same interparticle potential). One of the manifestations of this effect is the phenomenon of surface melting: a microscopic liquid layer normally appear at the interface of a crystalline solid well below its bulk melting temperature.

In this paper, we describe a remarkable example in which the thermal fluctuation stabilize a 2D crystalline solid, embedded in 3D physical space, with respect to transition to an alternative 3D structure. The model system discussed below has been introduced in the recent work by one of us [3], in order to describe DNA-assisted self-assembly of colloids. Its essential ingredients are cohesive interparticle interactions and medium-range soft core repulsion. The binary system of same-size spheres (A and B) discussed in Ref. [3], combines the repulsive potential $U(r)$ acting between same-type particles, with A–B attraction. As was shown at that work, both interactions may be induced by properly designed DNA. It was found that this colloid–DNA mixture may exhibit an unusually diverse phase diagram as a function of two control parameter: the relative strength of attraction and repulsion, and aspect ratio $\xi/a$ ($\xi$ is the range of repulsive potential $U(r)$, and $a$ is the particle diameter).

Among various self-assembled phases expected for that system, it was especially striking to find quasi-2D membrane with the in-plane square order (SQ). In other words, according to our calculations, this 3D system may prefer to self-assemble into a lower-dimensional structure. We will refer to this phenomenon as spontaneous self-compactification. Of course, there are other known examples of self-compactified structures in condensed matter, such as lipid membranes [4]. However, our case is quite unique because it is based on isotropic pair potentials (in contrast to anisotropic interactions between lipids, or covalent bonding of carbon atoms in graphite). Note also that at the found SQ phase is not a stacking of weakly coupled layers (lamella-like), but rather an isolated membrane-like structure.

In our early calculations, we have only accounted for the interplay of repulsive and attractive energies, while the thermal fluctuations were totally ignored. Even though this approximation is applicable when the characteristic energies considerably exceed $k_B T$, the entropic effects are expected to be significant in any realistic case. Given that fluctuations are known to strongly affect 2D crystals, one might wonder whether the phenomenon of self-compactification will still be present if the fluctuations are introduced. Below we present the detailed study of this question.

II. THE MODEL AND ITS GENERIC FEATURES

Before going into a specific example, we describe our model and its generic features. We start with particles packed into ideal crystalline lattices, whose fluctuation free energies are to be compared. The interparticle potentials will be replaced with linear springs, whose spring constants correspond to the second derivatives of the corresponding potentials. The first derivatives of the potentials will give rise to a pre-existing stresses in those springs. We consider only very short-range interactions, so that any connections beyond second nearest neighbors will be neglected.

Let $\kappa$ and $\tilde{\kappa}$ be spring constants for the first and second nearest neighbor bonds, respectively. Repulsion between the second nearest neighbors induces tension $\tilde{\tau}$ in $\kappa$–springs, which should be balanced by an appropriate compressive force $-\tau$ in $\tilde{\kappa}$–springs. If the interaction range $\xi$ is much shorter than nearest neighbors distance $a$, one expects $\kappa \gg \tilde{\kappa}$, and $\tau \sim \tilde{\tau} \sim \kappa/\xi$. This gives rise to a hierarchy of elastic constants in this system: $\kappa \gg \tilde{\kappa} \gg \tau/a$. Below, we will use harmonic analysis to diagonalize the phonon Hamiltonian and find the fluctational contributions to Free Energies of the competing phases. As an example, we compare 2D square lattice (SQ) (embedded in 3D physical space) to an
alternative three-dimensional phase with a very similar local structure. Figure 1 shows this 3D counterpart of SQ (referred below as "dual phase"), which also has four nearest neighbors lying in one plane around each particle. The difference from SQ is that now there are eight, rather than four second nearest neighbors for each site. Because of this difference in the number of repulsive bonds, SQ phase is generally preferred energetically over its 3D dual, at the zero temperature limit. Below, we will see whether the free energy balance between the two phases may be reversed by the thermal fluctuations.

Before we present the exact results for SQ, and its 3D-dual phase, we discuss certain general features of this problem. Given the hierarchy of the spring constants, one can distinguish between several kinds of phonon modes. Namely, there are hard modes, which involve deformations of strong $\kappa$-springs, and soft modes which only depend on spring constant $\tilde{\kappa}$. There are 3 degrees of freedom per particle, and 2 of them correspond to hard modes, both for 2D lattice and its 3D dual phase. In 3D structure, the third mode is the soft one ($\tilde{\kappa}$-mode). However, if there were no stresses $\tau$ and $\tilde{\tau}$, within harmonic approximation there would be no restoring force for the out-of-plane fluctuations in the 2D structure. This means that in 2D lattice the effective spring constant for the transverse modes should be of the order of $\tau/a$ (since $k \gg \tilde{\kappa} \gg \tau/a$, we may justifiably call these modes of 2D lattice supersoft). Because of the replacement of the soft modes with the supersoft ones, we do expect the entropy of the quasi-2D structure to be higher, which will further shift the free energy balance to its favor. In addition, in small-$q$ limit, the out-of-plane modes in 2D structure will universally have dispersion $\sim q^4$ (associated with bending rigidity). This will give another negative correction to free energy compared to dispersion $\sim q^2$ of regular acoustic phonons. Note that these arguments are quite universal, and can be applied beyond the particular case of SQ lattice.

III. EXAMPLE: SQUARE VS. ITS 3D-DUAL

We now proceed with the discussion of the specific example, 2D SQ vs. its 3D-dual phase. The latter 3D structure may be obtained from a simple cubic lattice, by removing the particles occupying sites $(2m, 2l, 2k + 1)$ and $(2m + 1, 2n + 1, 2k)$. In this geometry, the equilibrium condition requires $\tau = -2\sqrt{2}\tilde{\tau}$, compared to $\tau = -\sqrt{2}\tilde{\tau}$ for SQ. Note that it is tension $\tilde{\tau}$, not $\tau$ which is expected to be nearly identical for the two competing structures, since it is given by derivative of the potential, $-\partial_r U(r)$ (taken at the distance of the second nearest neighbor). In contrast, $\tau$ can be considerably varied by relatively small deformation of the strong $\kappa$-spring.

An obvious choice of unit cell for 2D lattice is a square containing one atom. For the 3D structure, consider a cube containing eight smaller cubes, as shown on Figure 1(b). The particles are located at $(2m, 2l, 2k) + \vec{x}$, where $\vec{x}$ is $(1,0,0)$, $(1,0,0)$, $(0,0,1)$, $(1,0,1)$, $(1,1,1)$, $(1,1,1)$, $(1,1,0)$. The translational symmetry in this structure is generated by vectors $(2,0,0)$, $(0,2,0)$ and $(1,1,1)$, i.e. the cube on the picture corresponds to two unit cells. Given the translational symmetry, the particle at $(1,1,1)$ is equivalent to $(0,0,0)$ (we label them as type 'a' particles), $(0,1,1)$ to $(1,0,0)$ (type 'b') and $(1,0,1)$ to $(0,1,0)$ (type 'c'). We can now obtain Hamiltonian $H$ and calculate the phonon contribution to free energy.

The number of particles per a unit cell is, $n = 1$ for SQ and $n = 3$ for its 3D-dual. For the 2D phase, displacement of a particle at $(m,n)$ is $\vec{u}(m,n) = \sum_q \vec{u}(q) e^{i(q_1 m + q_2 n)}$. For the 3D phase, the displacements there are three families of modes, corresponding to the three types of non-equivalent particles, 'a', 'b', and 'c':
By performing the Gaussian integration over $u$, the phonon free energy has a general form:

$$F^{(fl)} = -k_B T \log \int D[u_i(q)] \exp \left( -\frac{H}{k_B T} \right)$$

Here index $i = 1, ..., 3n$ parameterizes all the modes for a given wave vector $q$, and Hamiltonian $H$ is given by

$$H = \sum_q \gamma_{ij}(q) u_i(q) u_j(-q)$$

By performing the Gaussian integration over $u_i(q)$, one can transform Eq. (2) into:

$$F^{(fl)} = \frac{k_B T N}{2n} \int \frac{dq}{(2\pi)^d} \log \left( \det \left[ \frac{\hat{\gamma}(q)}{\pi k_B T} \right] \right)$$

The integration here is performed over a single Brillouin zone, i.e. each component of the wave vector runs from $-\pi$ to $\pi$.

Note that in our regime ($\kappa \gg \tilde{\kappa}$ and $\kappa \gg \tau/\alpha$), one can neglect the coupling between hard and soft modes, which allows one to represent the determinants entering Eq. (3) in factorized form: $\det[\hat{\gamma}(q)] \approx \det[\hat{\gamma}^{(hard)}(q)] \det[\hat{\gamma}^{(soft)}(q)]$. Furthermore, the hard modes have essentially identical spectra in both structures (corresponding to one-dimensional chain of $\kappa$-springs). Therefore, the difference of the fluctuational free energies is mainly due to the soft mode contributions. In the case of SQ phase, there is only one soft mode:

$$\det[\hat{\gamma}^{(soft)}_{2D}(q)] = \gamma_{zz}(q) = \frac{4\sqrt{2} \pi}{a} \sin^2 \left( \frac{q_1}{2} \right) \sin^2 \left( \frac{q_2}{2} \right)$$

For the 3D–dual phase, 3 out of 9 modes are soft, namely $(u_{ax}, u_{by}, u_{cz})$:

$$\hat{\gamma}^{(soft)}_{3D}(q) = 2\tilde{\kappa} (1 + 3\alpha) \delta_{ij} + \frac{\tilde{\kappa} (1 + \alpha)}{4} \begin{bmatrix} 0 & \chi(q_1, q_2) & \chi(q_1, \tilde{q}_3) \\ \chi(q_1, q_2) & 0 & \chi(q_2, \tilde{q}_3) \\ \chi(q_1, \tilde{q}_3) & \chi(q_2, \tilde{q}_3) & 0 \end{bmatrix}$$

Here $\alpha = \tilde{\tau}/(2\tilde{\kappa} a)$, $\chi(q, q') = [1 + \cos(q + q') - \cos(q) - \cos(q')]$, and $\tilde{q}_3 = 2q_3 - q_2 - q_1$. Thus,

$$\det[\hat{\gamma}^{(soft)}_{3D}] \approx 8\kappa^3 (1 + 3\alpha)^3 \left[ 1 - \varpi_1 \left( \frac{1 + \alpha}{8(1 + 3\alpha)} \right)^2 + \varpi_2 \left( \frac{1 + \alpha}{8(1 + 3\alpha)} \right)^3 \right]$$

Here $\varpi_1 = \chi^2(q_1, q_2) + \chi^2(q_1, \tilde{q}_3) + \chi^2(\tilde{q}_3, q_2)$, and $\varpi_2 = 2\chi(q_1, q_2) \chi(q_1, \tilde{q}_3) \chi(\tilde{q}_3, q_2)$. Now we can calculate the fluctuational contribution into the free energy difference between the two structures:

$$\Delta F^{(fl)} = F^{(fl)}_{2D} - F^{(fl)}_{3D} \approx -\frac{N k_B T}{2} \left[ \log \left( \frac{1}{\alpha} + 3 \right) + 2 \log 2 - \frac{15}{132} \left( \frac{1 + \alpha}{1 + 3\alpha} \right)^2 \right]$$

Consistent with the above general arguments, we obtain $F^{(fl)}_{2D} - F^{(fl)}_{3D} < 0$, i.e. the entropic effects enhance the stability of the self-compactified phase. One can identify the physical origin of each of the three contributions at the above result. The first logarithmic term is due to an entropic gain of a single fluctuation particle with all of its neighbors fixed. One can see that these fluctuations are enhanced in 2D case (for an arbitrary value of parameter $\alpha$), mainly due to the smaller number of second nearest neighbors there. The second term, $-N k_B T \log 2$ represent an additional gain due to $q^4$ dispersion of the soft acoustic phonon in SQ phase. In contrast, the soft modes in 3D phase correspond to optical phonons, whose dispersion gives rise to the negligible third term in Eq. (7).
IV. DISCUSSION

Since the effects responsible for the dominant contributions to our result, Eq. (7), are not specific for the above example, we expect our conclusions to be rather universal, and applicable to other self-compactified phases. In fact, the very same binary system introduced in Ref. [3], provides other examples of such phases, e.g. honeycomb lattice. This structure has several 3D counterparts [5], some of which are shown on Fig. 2. We expect the thermal fluctuations to enhance the stability of honeycomb with respect to transition to alternative 3D structures, as in the case of SQ.

Another aspect of our observation is that the region of the phase diagram corresponding to quasi-2D structures (like SQ or honeycomb), should expand when thermal fluctuations are introduced. However, in this study we have not discuss the transition between solid and liquid phases. In fact, the strong fluctuations in 2D structures indicate that they should melt earlier than 3D solid phases, which is consistent with the classical picture. In other words, the thermal fluctuations enhance the stability of quasi-2D latices with respect to transition to 3D crystalline structures, but not to the disordered liquid phase.

Note also that the self-compactified structure need not to be an ideal crystal, even topologically. Introduction of defects such as disclination or dislocation, normally associated with 2D melting, is not expected affect our arguments, as long as the systems remains effectively two-dimensional. That is because the dominant contribution to the free energy is associated with length scales of the order of the interparticle distance. Hence, the macroscopic properties and conformation of these lattices are not relevant for the discussed phenomenon. As long at the large-scale behavior is concern, one might expect their properties to be similar to those of tethered (solid-like) membranes [6]. It should be noted that the non-zero bending rigidity is known to stabilize such a membrane with respect to crumpling transition.

One may give a simple qualitative interpretation to the obtained results. The self-compactification in zero-fluctuation limit corresponds to the regime of the interparticle repulsion which is too weak to destabilize the 2D structure, yet strong enough to cause an overall repulsion between two such layers. Introduction of thermal fluctuations results in an additional effective repulsion between these 2D layers, an effect very similar to Helfrich interaction between conventional membranes [4], [7].

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