

Isotropic-nematic transition of surface embedded polymers and the associated tubulization transition of the embedding surface

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A self-interacting polymer can undergo an orientational ordering transition, depending on the magnitude of the nematic interaction. The effect of embedding such a polymer into a flexible surface on this transition is studied on the mean-field level. Renormalized values of the elastic constants of the “dressed” surface are derived as functions of the orientational order parameter of the polymer chain. In the disordered state the surface tension and curvature modulus remain scalars, but depend on the surface coverage of the embedded polymer. In the nematic state there is a symmetry-breaking transition leading to anisotropic elastic constants. At a sufficiently large nematic order parameter the effective surface tension in the direction perpendicular to the nematic axis can become negative, leading to tubulization of the embedding surface. [S1063-651X(96)03210-2]

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I. INTRODUCTION

Usually the adsorption of polymers onto surfaces is discussed in terms of more or less diffuse adsorption layers, composed of trains, loops, and dangling ends. There is enough corroborating evidence that in many cases this simplified picture correctly captures the salient features of the polymer adsorption phenomena [1].

However, some recent results on adsorption of highly charged polyelectrolytes onto oppositely charged molecular surfaces give evidence to much stronger bonding of the adsorbing polymer to the surface [2,3]. It seems that the polymer adsorbs flat onto the surface without any observable loops, dangling ends, and even a very restricted number of crossings among the different segments of the chain, as the strong electrostatic attraction can apparently override any entropy driven tendency for less tightly bound configurations.

In this respect one can envision the adsorption process more as an embedding of polymer chains into (or onto) the adsorbing (supporting) surface. The theoretical significance of this observation would be that an analysis of the adsorption phenomenon could be carried out without taking into consideration the extremely improbable configurations with local desorption of the polymers (loops and dangling ends). In a certain sense this simplifies the analysis because the chains can be treated as embedded into the supporting matrix. However, the embedding also signifies that there is a strong coupling between the polymer and the surface configurations and thus the pertaining degrees of freedom cannot be decoupled and treated separately.

In this contribution we shall address the interplay of the polymer and surface degrees of freedom in connection with the nematic ordering transition of a polymer chain embedded (i.e., tightly adsorbed) onto a flexible, fluid surface. It will be

established that there can be no effective decoupling of the tight adsorption problem (embedding) into a separate polymer and surface parts. The influence of the surface degrees of freedom on the polymer ordering transition, as well as of the polymer degrees of freedom on the effective elastic constants of the “dressed” (meaning surface plus polymer) surface, will be derived and discussed. The renormalized form of the surface elastic constants will be shown to lead to a tubulization transition of the embedding surface.

II. OVERVIEW

I first present a sketchy overview of the main results and conclusions reached in the paper. Starting from an orientationally (nematically) interacting polymer chain embedded into a soft (membrane) surface, conditions for a second-order symmetry-breaking orientational ordering transition are derived. The presence of surface shape fluctuations only marginally influences the critical point of the transition. The nematic orientational order parameter, defined in a standard way [4] as $S = \frac{1}{2}(3\langle \cos^2 \Theta \rangle - 1)$, where Θ is the angle between the local direction and the nematic axis, is obtained as a solution of

$$S = \sqrt{1 - \sqrt{\frac{1}{2(\beta\epsilon\bar{\rho})\beta u'_a}}}} \quad (1)$$

where ϵ is the elastic modulus of the polymer chain, $\bar{\rho}$ is the polymer surface density (surface coverage), and u'_a is proportional to the excluded volume of the nematic interaction u_a , renormalized due to the presence of the embedding surface shape fluctuations

$$\beta u'_a \rightarrow \beta u_a - \frac{1}{2} \frac{\beta\epsilon}{\bar{\rho}} \langle (c_i - c_k)^2 \rangle_0, \quad (2)$$

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where c_i is the embedding surface curvature in the direction i , with $i=x,y$. The average in the above equation is with respect to the bare surface, i.e., with no embedded polymers.

Tied to this transition are also changes in the overall (dressed) elastic constants of the membrane. A closed expression is derived for the renormalized elastic constants, surface tension (γ) and the elastic modulus (K_c), of the dressed membrane

$$\begin{aligned} \gamma &\rightarrow \gamma + 2\frac{\lambda}{\beta}\bar{\sigma}_\alpha + \epsilon\bar{c}_\alpha, \\ K_c &\rightarrow K_c + \frac{\epsilon}{\rho}\bar{\sigma}_\alpha\bar{\sigma}_\beta, \end{aligned} \quad (3)$$

where the index α describes the components of the indexed quantities in the reference frame of their eigencoordinate system. Thus α can be either n , signifying a component parallel to the nematic axis, or \perp , signifying a component perpendicular to the nematic axis. $\bar{\sigma}_\alpha$ is the mean-field orientational tensor of the embedded polymer and \bar{c}_α its mean-field squared curvature tensor. λ is a scalar depending on the orientational order parameter.

Following from the above expression for the renormalized values of the elastic constants, we show that the renormalized surface tension can change sign in the direction perpendicular to the nematic axis for a sufficiently large nematic order parameter. Basing our analysis on the recent general investigation of the tubulization transition of polymerized membranes by Radzihovsky and Toner [5], we show, in the framework of Landau theory, that the preferred conformation of the surface is a tubule with the long axis perpendicular to the nematic direction of the embedded polymers. The tubulization transition of the membrane does not coincide with the isotropic-nematic transition of the embedded polymers.

III. ANALYSIS

A. Outline

The formalities of the derivation are a bit convoluted so I will give a short guided tour before actually developing them. The point of departure is the usual flexible chain Hamiltonian together with the ‘‘embedding ansatz,’’ constraining the chain to lie on the supporting surface. The expression for the partition function following from these premises is developed in Sec. III B. A closed form of the partition function can be obtained by introducing collective variables of the polymer chain: density, orientational tensor, and tensor of the squared curvature. This is developed in Sec. III C together with the final form of the partition function in collective coordinates in Sec. III D. This partition function has a simple closed-form solution if the collective variables are treated in a mean-field manner, ignoring local fluctuations in their values along the surface. This is done in Sec. III E, leading to the final derivation of effective elastic constants of the dressed membrane in Sec. III F. Once these are derived the tubulization transition can be described by means of the formalism set forth by Radzihovsky and Toner [5], as is done in Sec. III G.

B. Theory and formalism

The position of the n th bead along the polymer contour is described by a position vector $\vec{\mathbf{r}}(n) = (x(n), y(n), z(n))$, which is a continuous, differentiable function of arc length n , while the total length of the polymer is N . I limit myself to a single polymer chain case, but a generalization to many chains is quite straightforward. Let the embedding surface be represented in the Monge parametrization as $z = \zeta(x, y) = \zeta(\vec{\boldsymbol{\rho}})$, where $\vec{\boldsymbol{\rho}}$ is the two-dimensional radius vector. In this notation the partition function of a flexible, but otherwise noninteracting, polymer chain embedded into the surface $\zeta(\vec{\boldsymbol{\rho}})$ can be written as [6]

$$\begin{aligned} \Xi(\zeta(\vec{\boldsymbol{\rho}}(n))) &= \int \dots \int \mathcal{D}\vec{\mathbf{r}}(n) \prod_n \delta(z(n) - \zeta(\vec{\boldsymbol{\rho}}(n))) \\ &\times \prod_n \delta(\dot{\vec{\mathbf{r}}}(n)^2 - 1) e^{-\beta\mathcal{H}_0(\vec{\mathbf{r}}(n))}, \end{aligned} \quad (4)$$

where

$$\begin{aligned} \beta\mathcal{H}_0(\vec{\mathbf{r}}(n)) &= \frac{1}{2}\beta\epsilon \int_0^N \left(\frac{d^2\vec{\mathbf{r}}(n)}{dn^2} \right)^2 \\ &= \frac{1}{2}\beta\epsilon \int_0^N [\ddot{\vec{\mathbf{r}}}(n)]^2 dn. \end{aligned} \quad (5)$$

$\beta\epsilon$ is the energy associated with polymer bending and can be related to the persistence length [6]. By integrating out the $z(n)$ variable and enforcing the continuity condition $\dot{\vec{\mathbf{r}}}(n)^2 = 1$ only globally [7], i.e.,

$$\langle \dot{\vec{\mathbf{r}}}(n)^2 \rangle = \langle \dot{\vec{\boldsymbol{\rho}}}(n)^2 + \dot{\zeta}(\vec{\boldsymbol{\rho}}(n))^2 \rangle = 1, \quad (6)$$

one is led to the following form of the corresponding partition function:

$$\Xi(\zeta(\vec{\boldsymbol{\rho}})) = \int \dots \int \mathcal{D}\vec{\boldsymbol{\rho}}(n) \exp[-\beta\mathcal{H}_0(\vec{\boldsymbol{\rho}}(n))], \quad (7)$$

where some irrelevant constant terms have been omitted. The effective Hamiltonian $\mathcal{H}_0(\vec{\boldsymbol{\rho}}(n))$ has been obtained [6] as

$$\begin{aligned} \beta\mathcal{H}_0(\vec{\boldsymbol{\rho}}(n)) &= \frac{1}{2}\beta\epsilon \int_0^N \left[\ddot{\vec{\boldsymbol{\rho}}}(n)^2 + \ddot{\zeta}(n)^2 dn + \lambda \int_0^N [\dot{\vec{\boldsymbol{\rho}}}(n)^2 \right. \\ &\quad \left. + \dot{\zeta}(n)^2] dn \right. \\ &= \frac{1}{2}\beta\epsilon \int_0^N \left[\ddot{\vec{\boldsymbol{\rho}}}(n)^2 + \left(\frac{\partial\dot{\zeta}(\vec{\boldsymbol{\rho}})}{\partial\vec{\boldsymbol{\rho}}_i} \ddot{\vec{\boldsymbol{\rho}}}_i(n) \right. \right. \\ &\quad \left. \left. + \frac{\partial^2\dot{\zeta}(\vec{\boldsymbol{\rho}})}{\partial\vec{\boldsymbol{\rho}}_i\partial\vec{\boldsymbol{\rho}}_k} \ddot{\vec{\boldsymbol{\rho}}}_i(n)\ddot{\vec{\boldsymbol{\rho}}}_k(n) \right)^2 \right] dn + \lambda \int_0^N \left(\dot{\vec{\boldsymbol{\rho}}}(n)^2 \right. \\ &\quad \left. + \frac{\partial\dot{\zeta}(\vec{\boldsymbol{\rho}})}{\partial\vec{\boldsymbol{\rho}}_i} \frac{\partial\dot{\zeta}(\vec{\boldsymbol{\rho}})}{\partial\vec{\boldsymbol{\rho}}_k} \dot{\vec{\boldsymbol{\rho}}}_i(n)\dot{\vec{\boldsymbol{\rho}}}_k(n) \right) dn, \end{aligned} \quad (8)$$

where the constant λ is the Lagrange multiplier, ensuring the global condition Eq. (6), to be determined later. The validity of the above Hamiltonian is restricted to the case of a global continuity constraint Eq. (6) (for details of this transformation see [6] and [8]).

In the case of a self-interacting polymer chain the Hamiltonian has two additional terms corresponding to the interactions between different segments

$$\begin{aligned} \beta \mathcal{H}_0(\vec{\mathbf{r}}(n)) \rightarrow & \frac{1}{2} \beta \epsilon \int_0^N \ddot{\vec{\mathbf{r}}}(n)^2 dn + \frac{1}{2} \beta \int_0^N \int_0^N dndm V_{\text{iso}}[\vec{\mathbf{r}}(n) \\ & - \vec{\mathbf{r}}(m)] + \frac{1}{2} \beta \int_0^N \int_0^N dndm [\dot{\vec{\mathbf{r}}}(n) \times \dot{\vec{\mathbf{r}}}(m)]^2 \\ & \times V_{\text{an-iso}}(\vec{\mathbf{r}}(n) - \vec{\mathbf{r}}(m)), \end{aligned} \quad (9)$$

where the interaction has been split into an isotropic part and an anisotropic part, of a general nematic form [7]. After integrating out the variable $z(n)$ and taking into account the fact that the chain is embedded into the surface $\zeta(\vec{\rho})$ one obtains for the interaction part

$$\begin{aligned} & \frac{1}{2} \beta \int_0^N \int_0^N dndm V_{\text{iso}}(\vec{\rho}(n) - \vec{\rho}(m)) \\ & + \frac{1}{2} \beta \int_0^N \int_0^N dndm \mathcal{F}(\vec{\rho}(n), \vec{\rho}(m)) V_{\text{an-iso}}(\vec{\rho}(n) - \vec{\rho}(m)) \end{aligned} \quad (10)$$

where I used the shorthand $V(\vec{\rho}(n) - \vec{\rho}(m)) = V(\vec{\rho}(n) - \vec{\rho}(m); \zeta(\vec{\rho}(n)) - \zeta(\vec{\rho}(m)))$ and defined

$$\begin{aligned} \mathcal{F}(\vec{\rho}(n), \vec{\rho}(m)) = & [\dot{\vec{\rho}}(n)^2 + \dot{\zeta}^2(\vec{\rho}(n))] [\dot{\vec{\rho}}(m)^2 + \dot{\zeta}^2(\vec{\rho}(m))] - [\dot{\vec{\rho}}(n) \dot{\vec{\rho}}(m) + \dot{\zeta}(\vec{\rho}(n)) \dot{\zeta}(\vec{\rho}(m))]^2 \\ = & \dot{\rho}_i^2(n) \dot{\rho}_k^2(m) - \dot{\rho}_i(n) \dot{\rho}_i(m) \dot{\rho}_k(n) \dot{\rho}_k(m) + [\dot{\rho}_i^2(m) \dot{\rho}_k(n) \dot{\rho}_l(n) \\ & + \dot{\rho}_i^2(n) \dot{\rho}_k(m) \dot{\rho}_l(m) - 2 \dot{\rho}_i(n) \dot{\rho}_i(m) \dot{\rho}_k(n) \dot{\rho}_l(m)] \frac{\partial \zeta}{\partial \rho_k} \frac{\partial \zeta}{\partial \rho_l} + \dots \end{aligned} \quad (11)$$

In the definition of $\mathcal{F}(\vec{\rho}(n), \vec{\rho}(m))$ I limited myself only to terms up to and including second order in the derivatives of $\zeta(\vec{\rho})$, in order to be consistent with the harmonic approximation assumed later for the bare surface Hamiltonian.

The final integration in the partition function has to be over the surface degrees of freedom $\zeta(\vec{\rho})$. Assuming that in the absence of the embedded polymer the surface energy is given by $V(\zeta(\vec{\rho}))$, the partition function can be cast into the form

$$\Xi(N) = \int \dots \int \mathcal{D}\zeta(\vec{\rho}) \Xi(\zeta(\vec{\rho})) \exp[-\beta V(\zeta(\vec{\rho}))]. \quad (12)$$

In what follows I start from the assumption that $V(\zeta(\vec{\rho}))$ is a quadratic functional of the form

$$\begin{aligned} V(\zeta(\vec{\rho})) = & \frac{1}{2} \gamma \int [\nabla_{\perp} \zeta(\vec{\rho})]^2 d^2 \vec{\rho} + \frac{1}{2} K_c \int [\nabla_{\perp}^2 \zeta(\vec{\rho})]^2 d^2 \vec{\rho} \\ = & \frac{1}{2} \int \gamma_{ik} \frac{\partial \zeta(\vec{\rho})}{\partial \rho_i} \frac{\partial \zeta(\vec{\rho})}{\partial \rho_k} d^2 \vec{\rho} \\ & + \frac{1}{2} \int K_{iklm} \frac{\partial^2 \zeta(\vec{\rho})}{\partial \rho_i \partial \rho_k} \frac{\partial^2 \zeta(\vec{\rho})}{\partial \rho_l \partial \rho_m} d^2 \vec{\rho}, \end{aligned} \quad (13)$$

where γ is the bare surface tension and K_c is the bare curvature elastic modulus. In order to facilitate later computa-

tions the surface energy and the curvature modulus tensors are introduced, which for a bare isotropic membrane assume the straightforward form $\gamma_{ik} = \gamma \delta_{ik}$ and $K_{iklm} = K_c \delta_{ik} \delta_{lm}$. By gathering all the terms in $\ln \Xi(\zeta(\vec{\rho}))$ that contribute to quadratic order in $\zeta(\vec{\rho})$ one will be in position to evaluate the rescaled values of the elastic modulus and the surface tension, which is the aim of this computation.

Also conveniently for later developments we introduce $S_0(\vec{\mathbf{Q}})$ through Fourier decomposed $\zeta(\vec{\rho})$

$$V(\zeta(\vec{\mathbf{Q}})) = \sum_{\vec{\mathbf{Q}}} S_0(\vec{\mathbf{Q}}) |\zeta(\vec{\mathbf{Q}})|^2, \quad (14)$$

with

$$S_0(\vec{\mathbf{Q}}) = \frac{1}{2} \gamma Q^2 + \frac{1}{2} K_c Q^4. \quad (15)$$

$S_0(\vec{\mathbf{Q}})$ is of course connected with the structure function of the bare membrane.

C. Collective variables

One proceeds by defining collective variables in terms of which the partition function Eq. (7) assumes the form that allows an explicit introduction of mean fields. The three collective variables introduced to this effect are density, orientational tensor, and the tensor of the squared curvature

$$\begin{aligned}
\rho(\vec{\rho}) &= \int_0^N dn \delta(\vec{\rho} - \vec{\rho}(n)), \\
\sigma_{ik}(\vec{\rho}) &= \int_0^N dn \dot{\vec{\rho}}_i(n) \dot{\vec{\rho}}_k(n) \delta(\vec{\rho} - \vec{\rho}(n)), \\
c_{ik}(\vec{\rho}) &= \int_0^N dn \ddot{\vec{\rho}}_i(n) \ddot{\vec{\rho}}_k(n) \delta(\vec{\rho} - \vec{\rho}(n)). \quad (16)
\end{aligned}$$

It should be noted here that since all the above collective variables are defined on a two-dimensional surface, they do not share the same properties with their three-dimensional counterparts. For instance, the orientational tensor does not satisfy the equality $\text{Tr}\sigma_{ik}(\vec{\rho}) = \rho(\vec{\rho})$ [7]. Later on an analogous relation valid in two dimensions will be derived in detail. Furthermore, the squared curvature tensor is not connected with the torsion of the polymer chain, but can be simplified by means of the Frenet equation for a planar curve into

$$\begin{aligned}
c_{ik}(\vec{\rho}) &= \int_0^N dn \kappa^2(n) \vec{n}_i(n) \vec{n}_k(n) \delta(\vec{\rho} - \vec{\rho}(n)) \\
&= \langle \kappa^2(n) \vec{n}_i(n) \vec{n}_k(n) \rangle_{\text{chain}}, \quad (17)
\end{aligned}$$

where $\kappa(n)$ is the (planar) curvature and $\vec{n}_i(n)$ is the normal vector of the chain.

With collective variables the partition function Eq. (7) can be cast into the form

$$\begin{aligned}
\Xi(\zeta(\vec{\rho})) &= \int \cdots \int \mathcal{D}\vec{\rho}(n) \mathcal{D}\rho(\vec{\rho}) \mathcal{D}\sigma_{ik}(\vec{\rho}) \mathcal{D}c_{ik}(\vec{\rho}) \\
&\times \delta\left(\rho(\vec{\rho}) - \int_0^N dn \delta(\vec{\rho} - \vec{\rho}(n))\right) \\
&\times \delta\left(\sigma_{ik}(\vec{\rho}) - \int_0^N dn \dot{\vec{\rho}}_i(n) \dot{\vec{\rho}}_k(n) \delta(\vec{\rho} - \vec{\rho}(n))\right) \\
&\times \delta\left(c_{ik}(\vec{\rho}) - \int_0^N dn \ddot{\vec{\rho}}_i(n) \ddot{\vec{\rho}}_k(n) \delta(\vec{\rho} - \vec{\rho}(n))\right) \\
&\times \exp[-\beta H(\vec{\rho}(n), \rho(\vec{\rho}), \sigma_{ik}(\vec{\rho}), c_{ik}(\vec{\rho}))]. \quad (18)
\end{aligned}$$

The Hamiltonian $H(\vec{\rho}(n), \rho(\vec{\rho}), \sigma_{ik}(\vec{\rho}), c_{ik}(\vec{\rho}))$ is obtained by

substituting the collective variables into $\mathcal{H}_0(\vec{\rho})$. Assuming, furthermore (for the sake of convenience), that both the isotropic as well as the anisotropic parts of the interaction potential have the form of contact interaction $V_{\text{iso}}(\vec{\rho}, \vec{\rho}') = u_i \delta^2(\vec{\rho} - \vec{\rho}')$ and $V_{\text{an-iso}}(\vec{\rho}, \vec{\rho}') = u_a \delta^2(\vec{\rho} - \vec{\rho}')$, one remains with the following form of the interaction Hamiltonian:

$$\begin{aligned}
&\beta H(\vec{\rho}(n), \rho(\vec{\rho}), \sigma_{ik}(\vec{\rho}), c_{ik}(\vec{\rho})) \\
&= \frac{1}{2} \beta \epsilon \int_0^N dn \ddot{\vec{\rho}}(n)^2 + \lambda \int_0^N dn \dot{\vec{\rho}}(n)^2 \\
&+ \frac{1}{2} \beta \epsilon \int d^2 \vec{\rho} \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_i} \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_k} c_{ik}(\vec{\rho}) \\
&+ \lambda \int d^2 \vec{\rho} \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_i} \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_k} \sigma_{ik}(\vec{\rho}) \\
&+ \frac{1}{2} \beta \epsilon \int d^2 \vec{\rho} \rho^{-1}(\vec{\rho}) \frac{\partial^2 \zeta(\vec{\rho})}{\partial \vec{\rho}_i \partial \vec{\rho}_k} \frac{\partial^2 \zeta(\vec{\rho})}{\partial \vec{\rho}_l \partial \vec{\rho}_m} \sigma_{ik}(\vec{\rho}) \sigma_{lm}(\vec{\rho}) \\
&+ \beta u_a \int d^2 \vec{\rho} [\sigma_{ii}(\vec{\rho}) \sigma_{kk}(\vec{\rho}) - \sigma_{ik}(\vec{\rho}) \sigma_{il}(\vec{\rho})] \frac{\partial \zeta}{\partial \vec{\rho}_k} \frac{\partial \zeta}{\partial \vec{\rho}_l} \\
&+ \frac{1}{2} \beta u_i \int d^2 \vec{\rho} \rho^2(\vec{\rho}) + \frac{1}{2} \beta u_a \int d^2 \vec{\rho} \{\sigma_{ii}^2(\vec{\rho}) \\
&- \text{Tr}[\sigma_{ik}(\vec{\rho})]^2\}. \quad (19)
\end{aligned}$$

Here only terms up to and including second order in $\zeta(\vec{\rho})$ and its derivatives have been retained. A higher-order term can be derived from the $\ddot{\vec{\rho}}_i(n) \dot{\vec{\rho}}_k(n) \dot{\vec{\rho}}_l(n)$ term in Eq. (8) after the $\vec{\rho}(n)$ integration and has been consequently omitted.

D. Partition function

The next step is to introduce functional Fourier transform representations for δ functions appearing in Eq. (18). For each δ function we thus obtain an auxiliary field, the integration over which ensures that the definitions in Eq. (16) are satisfied. Calling the auxiliary fields $\phi(\vec{\rho})$ for $\rho(\vec{\rho})$, $\psi_{ik}(\vec{\rho})$ for $\sigma_{ik}(\vec{\rho})$, and $t_{ik}(\vec{\rho})$ for $c_{ik}(\vec{\rho})$, we obtain the relation

$$\begin{aligned}
\Xi(\zeta(\vec{\rho})) &= \int \cdots \int \mathcal{D}\rho(\vec{\rho}) \mathcal{D}\sigma_{ik}(\vec{\rho}) \mathcal{D}c_{ik}(\vec{\rho}) \mathcal{D}\phi(\vec{\rho}) \mathcal{D}\psi_{ik}(\vec{\rho}) \mathcal{D}t_{ik}(\vec{\rho}) \times \Xi(\phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho})) \\
&\times \exp[-\beta \mathcal{H}(\zeta(\vec{\rho}); \phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho}); \rho(\vec{\rho}), \sigma_{ik}(\vec{\rho}), c_{ik}(\vec{\rho}))], \quad (20)
\end{aligned}$$

where

$$\Xi(\phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho})) = \int \cdots \int \mathcal{D}\vec{\rho}(n) \exp[-\beta \mathcal{H}_0(\vec{\rho}(n); \phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho}))]. \quad (21)$$

The definitions employed in the above two formulas were

$$\begin{aligned} \beta\mathcal{H}_0(\vec{\rho}(n); \phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho})) &= \frac{1}{2} \beta \epsilon \int_0^N dn \vec{\rho}(n)^2 + \lambda \int_0^N dn \dot{\vec{\rho}}(n)^2 - \lambda \int_0^N dn + i \int_0^N dn \phi(\vec{\rho}(n)) \\ &+ i \int_0^N dn \psi_{ik}(\vec{\rho}(n)) \dot{\vec{\rho}}_i(n) \dot{\vec{\rho}}_k(n) + i \int_0^N dn t_{ik}(\vec{\rho}(n)) \ddot{\vec{\rho}}_i(n) \ddot{\vec{\rho}}_k(n), \end{aligned} \quad (22)$$

while

$$\begin{aligned} \beta\mathcal{H}(\zeta(\vec{\rho}); \phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho}); \rho(\vec{\rho}), \sigma_{ik}(\vec{\rho}), c_{ik}(\vec{\rho})) &= \frac{1}{2} \beta \epsilon \int d^2 \vec{\rho} c_{ik}(\vec{\rho}) \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_i} \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_k} + \lambda \int d^2 \vec{\rho} \sigma_{ik}(\vec{\rho}) \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_i} \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_k} \\ &+ \frac{1}{2} \beta \epsilon \int d^2 \vec{\rho} \rho^{-1}(\vec{\rho}) \sigma_{ik}(\vec{\rho}) \sigma_{lm}(\vec{\rho}) \frac{\partial^2 \zeta(\vec{\rho})}{\partial \vec{\rho}_i \partial \vec{\rho}_k} \frac{\partial^2 \zeta(\vec{\rho})}{\partial \vec{\rho}_l \partial \vec{\rho}_m} \\ &+ \beta u_a \int d^2 \vec{\rho} [\sigma_{ii}(\vec{\rho}) \sigma_{kl}(\vec{\rho}) - \sigma_{ik}(\vec{\rho}) \sigma_{il}(\vec{\rho})] \frac{\partial \zeta}{\partial \vec{\rho}_k} \frac{\partial \zeta}{\partial \vec{\rho}_l} \\ &+ \frac{1}{2} \beta u_i \int d^2 \vec{\rho} \rho^2(\vec{\rho}) + \frac{1}{2} \beta u_a \int d^2 \vec{\rho} \{ \sigma_{ii}^2(\vec{\rho}) - \text{Tr}[\sigma_{ik}(\vec{\rho})]^2 \} \\ &- i \int d^2 \vec{\rho} \rho(\vec{\rho}) \phi(\vec{\rho}) - i \int d^2 \vec{\rho} \sigma_{ik}(\vec{\rho}) \psi_{ik}(\vec{\rho}) - i \int d^2 \vec{\rho} c_{ik}(\vec{\rho}) t_{ik}(\vec{\rho}). \end{aligned} \quad (23)$$

The partition function of the membrane with an embedded flexible polymer chain can now be obtained in several straightforward steps. Let us first of all introduce the renormalized potential $\tilde{V}(\zeta(\vec{\rho}))$ which, is of the same form as Eq. (13) but with renormalized values of γ_{ik} and K_{iklm} ,

$$\begin{aligned} \gamma_{ik}(\vec{\rho}) &\rightarrow \gamma \delta_{ik} + \epsilon c_{ik}(\vec{\rho}) + 2 \frac{\lambda}{\beta} \sigma_{ik}(\vec{\rho}) + 2 u_a [\sigma_{ll}(\vec{\rho}) \sigma_{ik}(\vec{\rho}) \\ &- \sigma_{li}(\vec{\rho}) \sigma_{lk}(\vec{\rho})], \end{aligned}$$

$$K_{iklm}(\vec{\rho}) \rightarrow K_c \delta_{ik} \delta_{lm} + \frac{\epsilon}{\rho(\vec{\rho})} \sigma_{ik}(\vec{\rho}) \sigma_{lm}(\vec{\rho}). \quad (24)$$

The renormalized values of γ_{ik} and K_{iklm} thus depend on the set $\rho(\vec{\rho})$, $\sigma_{ik}(\vec{\rho})$, and $c_{ik}(\vec{\rho})$. The corresponding Fourier representation would ensue as

$$\begin{aligned} \tilde{V}(\zeta(\vec{Q})) &= \frac{1}{2} \sum_{\vec{Q}} [\gamma_{ik}(\vec{Q}) Q_i Q_k + K_{iklm}(\vec{Q}) Q_i Q_k Q_l Q_m] \\ &\times |\zeta(\vec{Q})|^2. \end{aligned} \quad (25)$$

Now we construct a generating functional (functional Fourier transform) of $\exp[-\beta \tilde{V}(\zeta(\vec{\rho}), \rho(\vec{\rho}), \sigma_{ik}(\vec{\rho}), c_{ik}(\vec{\rho}))]$ at some quenched value of the membrane shape $\zeta(\vec{\rho})$. By definition one has

$$\begin{aligned} \exp[-\beta \tilde{V}(\zeta(\vec{\rho}), \phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho}))] \\ = \mathcal{Z}_{\zeta(\vec{\rho})}(\phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho})) \end{aligned}$$

$$\begin{aligned} &= \int \cdots \int \mathcal{D}\rho(\vec{\rho}) \mathcal{D}\sigma_{ik}(\vec{\rho}) \mathcal{D}c_{ik}(\vec{\rho}) \\ &\times \exp(-\beta \tilde{V}(\zeta(\vec{\rho}), \rho(\vec{\rho}), \sigma_{ik}(\vec{\rho}), c_{ik}(\vec{\rho}))) \\ &- i \int d^2 \vec{\rho} \rho(\vec{\rho}) \phi(\vec{\rho}) - i \int d^2 \vec{\rho} \sigma_{ik}(\vec{\rho}) \psi_{ik}(\vec{\rho}) \\ &- i \int d^2 \vec{\rho} c_{ik}(\vec{\rho}) t_{ik}(\vec{\rho}), \end{aligned} \quad (26)$$

where the left-hand side should be read symbolically as a shorthand for the functional Fourier transform.

Finally, the partition function can be expressed as an average of the product of the generating functional with variables $\phi(\vec{\rho})$, $\psi_{ik}(\vec{\rho})$, $t_{ik}(\vec{\rho})$ and the partition function of a single polymer chain in the orienting field of external sources $\phi(\vec{\rho})$, $\psi_{ik}(\vec{\rho})$, and $t_{ik}(\vec{\rho})$, averaged over all the conformations of the membrane, i.e.,

$$\Xi(N) = \int \mathcal{D}\zeta(\vec{\rho}) \mathcal{Z}(\zeta(\vec{\rho})), \quad (27)$$

with

$$\begin{aligned} \mathcal{Z}(\zeta(\vec{\rho})) &= \int \cdots \int \mathcal{D}\phi(\vec{\rho}) \mathcal{D}\psi_{ik}(\vec{\rho}) \mathcal{D}t_{ik}(\vec{\rho}) \\ &\times \exp[-\beta \tilde{V}(\zeta(\vec{\rho}), \phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho}))] \\ &\times \Xi(\phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho})). \end{aligned} \quad (28)$$

Obviously the general form of the partition function is untractable and additional approximations have to be considered to get a closed-form solution.

E. Mean-field approximation

It was recently shown [6] that a similar partition function can be evaluated explicitly by introducing a mean-field description of the polymer collective coordinates $\rho(\vec{\rho}), \sigma_{ik}(\vec{\rho}), c_{ik}(\vec{\rho})$ as well as their auxiliary fields $\phi(\vec{\rho}), \psi_{ik}(\vec{\rho}), t_{ik}(\vec{\rho})$ by suppressing their $\vec{\rho}$ dependence and treating them as constants. Thus, by introducing $\rho(\vec{\rho}) \rightarrow \bar{\rho}$, $\sigma_{ik}(\vec{\rho}) \rightarrow \bar{\sigma}_{ik}$, and $c_{ik}(\vec{\rho}) \rightarrow \bar{c}_{ik}$ as well as $i\phi(\vec{\rho}) \rightarrow \bar{\phi}$, $i\psi_{ik}(\vec{\rho}) \rightarrow \bar{\psi}_{ik}$, and $it_{ik}(\vec{\rho}) \rightarrow \bar{t}_{ik}$ one can first of all explicitly evaluate the partition function of a single chain with external sources $\Xi(\bar{\phi}, \bar{\psi}_{ik}, \bar{t}_{ik})$. This calculation will not

be repeated as it has been already detailed in [6]. The final result valid in the limit $N \gg 1$ can be obtained as

$$\begin{aligned} & -kT \ln \Xi(\bar{\phi}, \bar{\psi}_{ik}, \bar{t}_{ik}) \\ &= \frac{N}{2} \sum_{\alpha} \left(\frac{(\lambda + \bar{\psi}_{\alpha})}{\left(\frac{\beta\epsilon}{2} + \bar{t}_{\alpha}\right)} \right)^{1/2} + \frac{N}{2\pi} q_{\max} \sum_{\alpha} \ln \left(1 + \frac{2\bar{t}_{\alpha}}{\beta\epsilon} \right) \\ & - N\lambda + N\bar{\phi}, \end{aligned} \quad (29)$$

where the index α refers to the eigenvalues so that $\bar{\psi}_{\alpha}, \bar{t}_{\alpha}$ are the indexed eigenvalues of $\bar{\psi}_{ik}$ and \bar{t}_{ik} . The next step now is to evaluate $\mathcal{Z}_{\zeta(\vec{\rho})}(\bar{\phi}, \bar{\psi}_{ik}, \bar{t}_{ik})$ on the mean-field level. In complete analogy with the calculations in [6] I obtain

$$\begin{aligned} -kT \ln \mathcal{Z}_{\zeta(\vec{\rho})}(\bar{\phi}, \bar{\psi}_{ik}, \bar{t}_{ik}) &= \frac{1}{2} \beta\epsilon \bar{c}_{\alpha} \int d^2\vec{\rho} \left(\frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_{\alpha}} \right)^2 + \lambda \bar{\sigma}_{\alpha} \int d^2\vec{\rho} \left(\frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_{\alpha}} \right)^2 + \frac{1}{2} \beta\epsilon \bar{\rho}^{-1} \bar{\sigma}_{\alpha} \bar{\sigma}_{\beta} \int d^2\vec{\rho} \frac{\partial^2 \zeta(\vec{\rho})}{\partial \vec{\rho}_{\alpha}^2} \frac{\partial^2 \zeta(\vec{\rho})}{\partial \vec{\rho}_{\beta}^2} \\ & + \beta u_a (\text{Tr} \bar{\sigma}_{\alpha}) \bar{\sigma}_{\beta} \int d^2\vec{\rho} \left(\frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_{\beta}} \right)^2 - \beta u_a \bar{\sigma}_{\alpha} \bar{\sigma}_{\beta} \int d^2\vec{\rho} \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_{\alpha}} \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_{\beta}} + \frac{1}{2} \beta u_i S \bar{\rho}^2 \\ & + \frac{1}{2} \beta u_a S [(\text{Tr} \bar{\sigma}_{\alpha})^2 - \text{Tr}(\bar{\sigma}_{\alpha}^2)] - S \bar{\rho} \bar{\phi} - S \bar{\sigma}_{\alpha} \bar{\psi}_{\alpha} - S \bar{c}_{\alpha} \bar{t}_{\alpha}. \end{aligned} \quad (30)$$

What remains now is the final integration over the membrane modes $\zeta(\vec{\rho})$ or equivalently over their Fourier components $\zeta(\vec{Q})$. It is performed in such a way that all the terms describing the bare membrane and thus depending only on $\mathcal{S}_0(\vec{Q})$ are discarded as they do not enter the mean-field evaluation of collective variables or their auxiliary fields. The final expression obtained in this way for $\Xi(N)$ thus assumes the form

$$\begin{aligned} kT \ln \Xi(N) &\cong \frac{N}{2} \sum_{\alpha} \left(\frac{(\lambda + \bar{\psi}_{\alpha})}{\left(\frac{\beta\epsilon}{2} + \bar{t}_{\alpha}\right)} \right)^{1/2} \\ & + \frac{N}{2\pi} q_{\max} \sum_{\alpha} \ln \left(1 + \frac{2\bar{t}_{\alpha}}{\beta\epsilon} \right) - N\lambda + N\bar{\phi} \\ & - S \bar{\rho} \bar{\phi} - S \sum_{\alpha} \bar{\sigma}_{\alpha} \bar{\psi}_{\alpha} - S \sum_{\alpha} \bar{c}_{\alpha} \bar{t}_{\alpha} \\ & + \frac{1}{2} \beta u_i S \bar{\rho}^2 + \frac{1}{2} \beta u_a S [(\text{Tr} \bar{\sigma}_{\alpha})^2 - \text{Tr}(\bar{\sigma}_{\alpha}^2)] \\ & + \frac{1}{2} \sum_{\vec{Q}} \ln \left(1 + \beta\epsilon \sum_{\alpha} \bar{c}_{\alpha} \frac{Q_{\alpha}^2}{\beta \mathcal{S}_0(\vec{Q})} \right) \\ & + 2\lambda \sum_{\alpha} \bar{\sigma}_{\alpha} \frac{Q_{\alpha}^2}{\beta \mathcal{S}_0(\vec{Q})} \end{aligned}$$

$$\left. + \frac{\beta\epsilon}{\bar{\rho}} \sum_{\alpha, \beta} \bar{\sigma}_{\alpha} \bar{\sigma}_{\beta} \frac{Q_{\alpha}^2 Q_{\beta}^2}{\beta \mathcal{S}_0(\vec{Q})} \right). \quad (31)$$

In the above equation I have limited myself to the lowest orders in \bar{c}_{α} and $\bar{\sigma}_{\alpha}$, meaning to first order in Q^2 terms and to second order in $\bar{\sigma}_{\alpha}$ for Q^4 terms, all the higher orders have been discarded. This essentially limits the validity of conclusion derived from Eq. (31) to the regime of low surface coverage of the membrane, i.e., to small $\bar{\rho}$.

Introducing now

$$\begin{aligned} \beta \mathcal{S}(\vec{Q}) &= \beta \mathcal{S}_0(\vec{Q}) + \beta\epsilon \sum_{\alpha} \bar{c}_{\alpha} Q_{\alpha}^2 + 2\lambda \sum_{\alpha} \bar{\sigma}_{\alpha} Q_{\alpha}^2 \\ & + \frac{\beta\epsilon}{\bar{\rho}} \sum_{\alpha, \beta} \bar{\sigma}_{\alpha} \bar{\sigma}_{\beta} Q_{\alpha}^2 Q_{\beta}^2, \end{aligned} \quad (32)$$

I obtain the set of mean-field equations (the leftmost quantity stands for the minimizing variable)

$$\bar{c}_{\alpha} : \bar{t}_{\alpha} = \frac{\beta\epsilon}{2} \sum_{\vec{Q}} \frac{Q_{\alpha}^2}{\beta \mathcal{S}(\vec{Q})},$$

$$\begin{aligned}
\bar{t}_\alpha: \bar{c}_\alpha &= -\frac{N/S}{4} \left(\frac{(\lambda + \bar{\psi}_\alpha)}{\left(\frac{\beta\epsilon}{2} + \bar{t}_\alpha\right)} \right)^{1/2} \left(\frac{\beta\epsilon}{2} + \bar{t}_\alpha \right)^{-1} \\
&+ \frac{N/S}{\pi} \frac{q_{\max}}{\beta\epsilon} \left(1 + \frac{2\bar{t}_\alpha}{\beta\epsilon} \right)^{-1}, \\
\bar{\sigma}_\alpha: \bar{\psi}_\alpha &= \beta u_a [(\text{Tr} \bar{\sigma}_\alpha) - \bar{\sigma}_\alpha] + \lambda \sum_{\mathbf{Q}} \frac{Q_\alpha^2}{\beta S(\mathbf{Q})} \\
&+ \frac{\beta\epsilon}{\bar{\rho}} \sum_{\beta} \bar{\sigma}_\beta \sum_{\mathbf{Q}} \frac{Q_\alpha^2 Q_\beta^2}{\beta S(\mathbf{Q})}, \\
\bar{\psi}_\alpha: \bar{\sigma}_\alpha &= \frac{N/S}{4} \frac{1}{\sqrt{(\lambda + \bar{\psi}_\alpha) \left(\frac{\beta\epsilon}{2} + \bar{t}_\alpha\right)}}, \\
\bar{\rho}: \bar{\phi} &= \beta u_i \bar{\rho} - \frac{\beta\epsilon}{2\bar{\rho}^2} \sum_{\alpha,\beta} \sum_{\mathbf{Q}} \bar{\sigma}_\alpha \bar{\sigma}_\beta \frac{Q_\alpha^2 Q_\beta^2}{\beta S(\mathbf{Q})}, \\
\bar{\phi}: \bar{\rho} &= N/S, \\
\lambda: \frac{N/S}{4} \sum_{\alpha} \frac{1}{\sqrt{(\lambda + \bar{\psi}_\alpha) \left(\frac{\beta\epsilon}{2} + \bar{t}_\alpha\right)}} \\
&= (N/S) - \sum_{\alpha} \bar{\sigma}_\alpha \sum_{\mathbf{Q}} \frac{Q_\alpha^2}{\beta S(\mathbf{Q})}. \quad (33)
\end{aligned}$$

The appearance of the wave vector q_{\max} is a consequence of the limit of the continuous description of a polymer chain and should be inversely proportional to the Kuhn length.

At this point a perturbation expansion in terms of the surface coverage of the polymers $\bar{\rho}$ is introduced and only the lowest order is taken into account, essentially making the approximation $\mathcal{S}(\mathbf{Q}) \rightarrow \mathcal{S}_0(Q)$. Since $\mathcal{S}_0(Q)$ is by assumption isotropic, one has

$$\begin{aligned}
\sum_{\mathbf{Q}} \frac{Q_\alpha^2}{\beta S(\mathbf{Q})} &\cong \sum_{\mathbf{Q}} \frac{Q_\alpha^2}{\beta S_0(Q)} = \lim_{\vec{\rho} \rightarrow \vec{\rho}'} \left\langle \frac{\partial \zeta(\vec{\rho})}{\partial \vec{\rho}_\alpha} \frac{\partial \zeta(\vec{\rho}')}{\partial \vec{\rho}'_\alpha} \right\rangle_0 = F, \\
\sum_{\mathbf{Q}} \frac{Q_\alpha^2 Q_\beta^2}{\beta S(\mathbf{Q})} &\cong \sum_{\mathbf{Q}} \frac{Q_\alpha^2 Q_\beta^2}{\beta S_0(Q)} = \lim_{\vec{\rho} \rightarrow \vec{\rho}'} \left\langle \frac{\partial^2 \zeta(\vec{\rho})}{\partial \vec{\rho}_\alpha^2} \frac{\partial^2 \zeta(\vec{\rho}')}{\partial \vec{\rho}'_\beta^2} \right\rangle_0 \\
&= F_{\parallel} \delta_{\alpha\beta} + F_{\perp} (1 - \delta_{\alpha\beta}). \quad (34)
\end{aligned}$$

The index 0 signifies that the averages are taken with respect to a bare membrane. Obviously F is the strength of the surface normal fluctuations and F_{\parallel} and F_{\perp} are the strengths of the surface curvature fluctuations.

At this point the calculation performed here substantially deviates from [6]. Since in that case the polymer was ideal, i.e., noninteracting, the orientational ordering was due to

higher-order expansion terms in $\mathcal{S}(\mathbf{Q})$, omitted here, as they would only rescale the already existing transition point but not its qualitative characteristics.

The mean-field equations can now be solved by means of the ansatz

$$\bar{\sigma}_\alpha = \frac{\bar{\rho}}{2(1+F)} (1 \pm S), \quad (35)$$

where S is the orientational order parameter $S = \frac{1}{2}(3\langle \cos^2 \Theta \rangle - 1)$ [4] with Θ being the angle between the local direction and the nematic axis. It thus follows that in this case $\text{Tr} \bar{\sigma}_{ik} = \bar{\rho}/(1+F)$ and as announced, thus differs from the three-dimensional equivalent $\text{Tr} \bar{\sigma}_{ik} = \bar{\rho}$. The difference is due to the projection of the continuity condition Eq. (8) onto a fluctuating surface [6].

Putting this ansatz into the minimization conditions, we are left with the results

$$\begin{aligned}
S \left[(1-S^2)^2 - \frac{1}{2(\beta\epsilon\bar{\rho}) \left[\beta u_a - \frac{\beta\epsilon}{\bar{\rho}} (F_{\parallel} - F_{\perp}) \right]} \right] &= 0, \\
\lambda &= \frac{1}{2(\beta\epsilon)} \frac{2(1+S^2)}{(1-S^2)^2} - \frac{\bar{\rho}}{(1+F)^2} \left(\beta u_a + \frac{\beta\epsilon}{\bar{\rho}} (F_{\parallel} + F_{\perp}) \right) \\
\bar{c}_\alpha &= -\frac{\bar{\rho}}{2(\beta\epsilon)^2(1+F)} \frac{(1 \mp S)}{(1-S^2)} + \frac{2\bar{\rho}}{\beta\epsilon} \frac{q_{\max}}{2\pi(1+F)}. \quad (36)
\end{aligned}$$

Clearly the solution of the above equations describes a second-order surface orientational transition characterized by $S=0$ and $S \neq 0$. The critical point of the transition is given as a solution of

$$2\beta\epsilon\bar{\rho} = \frac{1}{\left[\beta u_a - \frac{\beta\epsilon}{\bar{\rho}} (F_{\parallel} - F_{\perp}) \right]}. \quad (37)$$

The transition involves only the variables β , ϵ , and $\bar{\rho}$ and can thus be achieved by either a variation in temperature, polymer stiffness, or polymer surface coverage.

F. Effective elastic constants

The corresponding renormalization of the effective membrane elastic constants can be obtained on this level of approximations from

$$\begin{aligned}
\beta S(\tilde{\mathbf{Q}}) &\rightarrow \beta S_0(Q) + \beta \epsilon \sum_{\alpha} \bar{c}_{\alpha} Q_{\alpha}^2 + 2\lambda \sum_{\alpha} \bar{\sigma}_{\alpha} Q_{\alpha}^2 \\
&+ \frac{\beta \epsilon}{\bar{\rho}} \sum_{\alpha, \beta} \bar{\sigma}_{\alpha} \bar{\sigma}_{\beta} Q_{\alpha}^2 Q_{\beta}^2 \\
&= \frac{1}{2} \beta \gamma Q^2 + \frac{1}{2} \beta K_c Q^4 + \frac{1}{2} \beta \epsilon \sum_{\alpha} \bar{c}_{\alpha} Q_{\alpha}^2 \\
&+ \lambda \sum_{\alpha} \bar{\sigma}_{\alpha} Q_{\alpha}^2 + \frac{1}{2} \frac{\beta \epsilon}{\bar{\rho}} \sum_{\alpha, \beta} \bar{\sigma}_{\alpha} \bar{\sigma}_{\beta} Q_{\alpha}^2 Q_{\beta}^2. \quad (38)
\end{aligned}$$

The renormalized values of the elastic constants can be read off as

$$\begin{aligned}
\gamma &\rightarrow \gamma + \epsilon \bar{c}_{\alpha} + 2 \frac{\lambda}{\beta} \bar{\sigma}_{\alpha}, \\
K_c &\rightarrow K_c + \frac{\epsilon}{\bar{\rho}} \bar{\sigma}_{\alpha} \bar{\sigma}_{\beta}. \quad (39)
\end{aligned}$$

One observes first of all that the elastic modulus of the dressed membrane changes because of the elasticity of the embedded polymer, while the surface tension changes because of two distinct contributions: one stemming from the fact that polymer is embedded into the surface and thus scales linearly with λ , the other one stemming from the coupling between the curvature of the surface and curvature of the embedded chain.

If I now write

$$\begin{aligned}
\beta S(Q) &= \frac{1}{2} \Sigma_{\parallel} (Q_x^2 + Q_y^2) + \frac{1}{2} \Sigma_{\perp} S (Q_x^2 - Q_y^2) \\
&+ \frac{1}{2} \beta K_c (Q_x^2 + Q_y^2)^2 + \frac{1}{2} \frac{\beta \epsilon}{\bar{\rho}} [\sigma_{\parallel} (Q_x^2 + Q_y^2) \\
&+ \sigma_{\perp} S (Q_x^2 - Q_y^2)]^2, \quad (40)
\end{aligned}$$

thus defining the quantities σ_{\parallel} and σ_{\perp} as well as Σ_{\parallel} and Σ_{\perp} , I obtain

$$\begin{aligned}
\Sigma_{\parallel} &= \beta \gamma + 2 \beta \epsilon c_{\parallel} + 2 \left(2\lambda + \beta u_a \frac{\bar{\rho}}{(1+F)} \right) \sigma_{\parallel}, \\
\Sigma_{\perp} &= 2 \beta \epsilon c_{\perp} + 2 \left(2\lambda + \beta u_a \frac{\bar{\rho}}{(1+F)} \right) \sigma_{\perp}, \quad (41)
\end{aligned}$$

while

$$\begin{aligned}
\sigma_{\parallel} &= \sigma_{\perp} = \frac{\bar{\rho}}{2(1+F)}, \\
c_{\parallel} &= \left(\frac{2\bar{\rho}}{\beta \epsilon} \frac{q_{\max}}{2\pi(1+F)} - c_{\perp} \right), \\
c_{\perp} &= \frac{\bar{\rho}}{2(\beta \epsilon)^2 (1+F)(1-S^2)}. \quad (42)
\end{aligned}$$

It is clear from Eq. (40) that, depending on the orientational order parameter in the nematic phase, the elastic energy will be destabilized if $\Sigma_{\parallel} - \Sigma_{\perp} S < 0$. This destabilization of the surface energy is due to the existence of an easy axis, in the direction perpendicular to the nematic axis, characterized by a much smaller surface energy than in the direction parallel to the nematic axis. This effect follows directly from the anisotropic packing of the polymer on the embedding surface.

G. Tubulization transition

Renormalized elastic constants are now taken as a point of departure for the general analysis of the effective elastic energy. The recent quite general formalism developed by Radzihovsky and Toner [5] is taken as a lead.

Instead of choosing the Monge parametrization for the surface $\mathbf{r}(x, y) = (x, y, \zeta(x, y))$ one can write down the elastic energy Eq. (40) directly in terms of $\mathbf{r}(x_i)$ with $x_1 = x$, and $x_2 = y$. Also in order to ensure stability, in view of the discussion preceding this section, appropriate fourth-order terms [9] have to be added to the expansion Eq. (40). In the spirit of the Landau theory, we assume that the fourth-order displacement terms do not change sign as a function of the nematic order parameter and thus assume them as constant.

The total elastic energy, meaning the sum of Eq. (40) and the fourth-order terms, can now be written in terms of the gradients of local displacements as [5]

$$\begin{aligned}
\mathcal{F}(\mathbf{r}(x_i)) &= \frac{1}{2} \int dx_{\perp} dx_n \left\{ K_{\perp\perp} [\partial_{\perp}^2 \mathbf{r}(x_i)]^2 + K_{nn} [\partial_n^2 \mathbf{r}(x_i)]^2 \right. \\
&+ K_{n\perp} [\partial_{\perp}^2 \mathbf{r}(x_i)] [\partial_n^2 \mathbf{r}(x_i)] + t_{\perp} [\partial_{\perp} \mathbf{r}(x_i)]^2 \\
&+ t_n [\partial_n \mathbf{r}(x_i)]^2 + \frac{1}{2} u_{\perp\perp} [\partial_{\perp} \mathbf{r}(x_i) \partial_{\perp} \mathbf{r}(x_i)]^2 \\
&+ \frac{1}{2} u_{nn} [\partial_n \mathbf{r}(x_i) \partial_n \mathbf{r}(x_i)]^2 + u_{n\perp} [\partial_n \mathbf{r}(x_i) \partial_{\perp} \mathbf{r}(x_i)]^2 \\
&+ \frac{1}{2} v_{\perp\perp} [\partial_{\perp} \mathbf{r}(x_i) \partial_{\perp} \mathbf{r}(x_i)]^2 \\
&\left. + v_{n\perp} [\partial_n \mathbf{r}(x_i)]^2 [\partial_{\perp} \mathbf{r}(x_i)]^2 \right\}, \quad (43)
\end{aligned}$$

where we have chosen the nematic direction to be n . In order for the system to be stable the fourth-order constants have to be positive $u, v > 0$. The second-order constants can be obtained by comparison with Eq. (40). The effective elastic moduli are obtained as

$$\begin{aligned}
K_{\perp\perp} &= K_c + \frac{\beta \epsilon}{\bar{\rho}} (\sigma_n^2 - \sigma_n \sigma_{\perp} S + \sigma_{\perp}^2 S^2), \\
K_{nn} &= K_c + \frac{\beta \epsilon}{\bar{\rho}} (\sigma_n^2 + \sigma_n \sigma_{\perp} S + \sigma_{\perp}^2 S^2), \\
K_{n\perp} &= 2K_c + 2 \frac{\beta \epsilon}{\bar{\rho}} (\sigma_n^2 - \sigma_{\perp}^2 S^2), \quad (44)
\end{aligned}$$

and, as can be easily deduced from the definitions Eq. (42), are all positive. The effective surface tension can be cast into the form

$$\begin{aligned} t_n &= \Sigma_n + \Sigma_{\perp} S, \\ t_{\perp} &= \Sigma_n - \Sigma_{\perp} S, \end{aligned} \quad (45)$$

where t_{\perp} can be either positive or negative. The zero of t_{\perp} does not coincide with the isotropic-nematic transition of the polymers, i.e., with $S=0$.

This free energy is now treated in analogy with the usual ϕ^4 theories of the critical phenomena, identifying the tangent vectors $\mathbf{t}_\alpha = \partial_\alpha \mathbf{r}(x_i)$ as order parameters [9]. In what follows we will delimit the analysis to the mean-field approximation where we take the ansatz $\mathbf{r}_{\text{MF}} = (\zeta_{\perp} x, \zeta_n y)$, where the symmetry-breaking nematic axis has been oriented in the y (parallel) direction. The prefactors ζ_{\perp}, ζ_n are order parameters that measure the shrinkage of the membrane due to undulations [10]. With this ansatz one obtains for the free energy

$$\begin{aligned} \mathcal{F} = \frac{1}{2} L_{\perp} L_n \left[t_n \zeta_n^2 + t_{\perp} \zeta_{\perp}^2 + \frac{1}{2} (u_{\perp\perp} + v_{\perp\perp}) \zeta_{\perp}^4 + \frac{1}{2} u_{nn} \zeta_n^4 \right. \\ \left. + v_{n\perp} \zeta_n^2 \zeta_{\perp}^2 \right]. \end{aligned} \quad (46)$$

Following Radzihovsky and Toner [5], by minimizing the above free energy one obtains the following phase diagram topology for $(u_{\perp\perp} + v_{\perp\perp}) u_{nn} > v_{n\perp}^2$. There exists a crumpled phase with $\zeta_n = \zeta_{\perp} = 0$ for $t_n, t_{\perp} > 0$. As t_{\perp} changes sign a tubular phase sets in with $\zeta_{\perp} = \sqrt{|t_{\perp}|/u_{\perp\perp}}$ and $\zeta_n = 0$. This transition is second order. A transition to the flat phase, which can be expected on general grounds [5], never sets in as t_n cannot change sign due solely to the orientational ordering of the polymers. We shall refrain from discussing other mechanisms, not connected with polymer ordering, that might nevertheless lead to a change of sign of t_n .

That t_{\perp} is indeed bound to change sign somewhere within the polymer surface nematic phase is evident from the fact that $\lim_{S \rightarrow 0} t_{\perp} = \Sigma_n \sim \text{const} > 0$, while in the opposite limit $\lim_{S \rightarrow 1} t_{\perp} = \Sigma_n - \Sigma_{\perp} \sim -(1 - S^2)^{-1} < 0$. The exact position of the change of sign does not coincide with the isotropic-nematic transition of the embedded polymer chain, i.e., with $S=0$. Thus a sufficient ordering of the polymer chain has to be present before the tubulization transition of the whole embedding membrane can take place.

A second-order orientational transition of the embedded polymer chain thus drives an associated shape transition of the membrane, corresponding to a tubulization of the membrane in the direction perpendicular to the nematic axis or parallel to the easy axis of the surface energy. The two transitions (i.e., the nematic to isotropic transition of the polymer and the symmetry-breaking shape transition of the dressed membrane) do not, however, happen at the same value of the temperature (surface coverage or polymer stiffness).

IV. DISCUSSION

Strong adsorption of polymers onto soft supporting surfaces has different characteristics from ordinary polymer ad-

sorption where the adsorption phenomenon results from a competition between adsorption energy and entropically driven tendency for less tightly bound configurations. Recent experimental work [2,3] shows that in the strong adsorption case the polymer chains are basically confined to lie on the adsorbing surface, without any dangling end or train configurations. In this case, with polymer chains effectively embedded (onto) into the supporting surface, the main source of entropy is limited to either polymer conformational degrees of freedom along the embedding surface or to thermally driven fluctuations of the supporting surface.

Because of this tight coupling of the polymer with the supporting surface, polymer statistics is strongly influenced by local surface configurations. Furthermore, if the polymer is nonideal, i.e., self-interacting, the supporting surface fluctuations renormalize the interactions between polymer segments as has been amply demonstrated in a slightly different context by Goulian *et al.* [11]. This effect depends on the nature of the polymer self-interactions as well as on the magnitude of the supporting surface fluctuations. We have investigated the properties and phenomena connected with an orientational ordering transition of surface-embedded polymers exhibiting an orientational (nematic) interaction potential and have shown explicitly the nature of the renormalization of the polymer self-interaction due to the supporting surface fluctuations. The conclusion reached in this connection is that for a sufficiently stiff membrane this effect tends to be small since it depends on the equilibrium fluctuations of the bare surface curvature.

It is, however, not only true that thermally driven undulations of the supporting surface affect the polymer ordering transition, but this transition in its turn manifestly modifies the properties of the compound (bare membrane plus embedded polymers) membrane. The reverse effect, of polymer modified membrane properties, appears to be much more important both in qualitative and quantitative terms. Polymer orientational ordering spawns an associated symmetry-breaking transition in the mean shape of the compound membrane that prefers membrane configurations with most of the surface area in the direction of the easy (low energy) axis of the surface energy. This is achieved through a tubulization transition [5] where the long axis of the tubule is perpendicular to the nematic axis of the polymer ordering.

Though it is understandable that nematic ordering of a surface embedded polymer should have some consequences on the properties of the dressed surface, the drastic change in the mean shape of the compound membrane does come as a surprise.

One can foresee several effects that are beyond the presently formulated mean-field solution to the tight adsorption model. First of all, the coupling between local curvatures and the nematic order parameter of the polymer S is missing. It is intuitively plausible and indeed probable that local curvature should affect local ordering of the polymer segments tending to concentrate aligned polymers in regions with large local curvature. This effect could also introduce additional ordered phases [12] into the phase diagram of the dressed membrane. As is clear from a comparison with the general analysis [5],

the phase diagram of the polymer embedding surface covers only one part of the phase diagram expected on general grounds. The tubulization transition, if indeed present in the systems with strong adsorption of polymers to soft flexible

surfaces, would be of particular importance for understanding the DNA-cationic lipid aggregation [2,3], where the colloidal state of the aggregate is crucial for transfection of the DNA-lipid complex across the cellular membrane.

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