Surface polymer network model and effective membrane curvature elasticity

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(Received 12 October 1994)

A microscopic model of a surface polymer network–membrane system is introduced with contact polymer surface interactions that can be either repulsive or attractive and slip links of functionality 4 randomly distributed over the supporting membrane surface anchoring the polymers to it. For the supporting surface perturbed from a planar configuration and a small relative number of surface slip links we investigate an expansion of the free energy in terms of the local curvatures of the surface and the surface density of slip links, obtained through the application of the Balian-Bloch-Duplantier multiple surface scattering method. As a result, the dependence of the curvature elastic modulus, the Gaussian modulus as well as of the spontaneous curvature of the "dressed" membrane, i.e., polymer network plus membrane matrix, is obtained on the mean polymer bulk end-to-end separation and the surface density of slip links.

PACS number(s): 82.70.−y, 05.20.−y, 61.25.Hq

I. INTRODUCTION

Polymer networks often provide highly specialized elastic properties to biological systems. The structure of the red blood cell (RBC) membrane is typical in this respect [1] in the sense that it unites the lipid matrix and the (polymer) spectrin network into a single "dressed" membrane, where the polymer network not only interacts with the underlying lipid surface but is actually anchored to it via ankyrin molecules. The polymer network consists of negatively charged spectrin tetramers of ~ 200 nm contour length, with intrinsic persistence length of ~ 10 nm. The replicating network of spectrin tetramers has a junction functionality of between 4 and 6. The network junctions do not coincide with attachment points (ankyrin molecules). The contour length of the spectrin tetramers is between 2 and 6 times larger than the separation between anchoring points and the whole system thus looks like a cross-linked two-dimensional gel attached to the supporting lipid surface while the polymers are allowed to stretch into the cytoplasmic (polymer rich) solution and away from the lipid surface [2].

The problem of elastic properties of a "dressed" membrane, where the individual polymer molecules or their junctions are confined to lie on (or are embedded in) the supporting surface, motivated by our present understanding of the RBC spectrin network, received a lot of attention recently [3–5]. The method of choice in most of these investigations has been the Monte Carlo simulations that led to several important insights regarding surface-tethered polymers and/or surface polymer networks. The analytical limits for these systems have been

much harder to come by due to the complicated nature of the polymer network-surface interactions. In this paper we shall try to fill this gap and establish some approximate limiting analytical results for the elastic properties of a surface polymer network pinned to a supporting flexible membrane surface. More specifically, we shall investigate the modifications in the elastic energy parameters of a flexible membrane wrought by the presence of a surface polymer gel where the cross-links (in this case presumed to be slip links) are constrained to lie on the supporting membrane surface. The parts of the polymeric chains between the junctions are allowed to sample all the configurations on one side of the supporting membrane, i.e., are constrained to lie in the half space defined by the position of the membrane surface (see Fig. 1).

Several theoretical studies recently addressed the issues pertaining to the modifications of elastic properties of a membrane in contact with a polymer solution that interacts with it [6–8]. Though the problem in this case is simpler than in the surface polymer gel case, it appears that certain features of the approach employed [8] can be generalized to this case. Specifically, we shall derive the curvature expansion of the free energy of a surface polymer gel with deformed supporting surface and show that the spontaneous curvature as well as the elastic modulus of the "dressed" membrane become functions of the polymer parameters, most notably the monomer-surface interaction and the polymer bulk end-end separation.

We presume that the chains in between the junctions are Gaussian and that their interaction with the supporting membrane surface, aside from the slip links where they are pinned to the surface, is of a contact type, thus simulating the screened electrostatic or other short range interactions between polymer segments and the membrane surface (see Fig. 1). The proposed formulation of the surface gel on a nonplanar supporting surface problem is closely related to the formulation of similar polymer problems in the bulk introduced by Edwards and Freed [9] and is particularly suited for the application of

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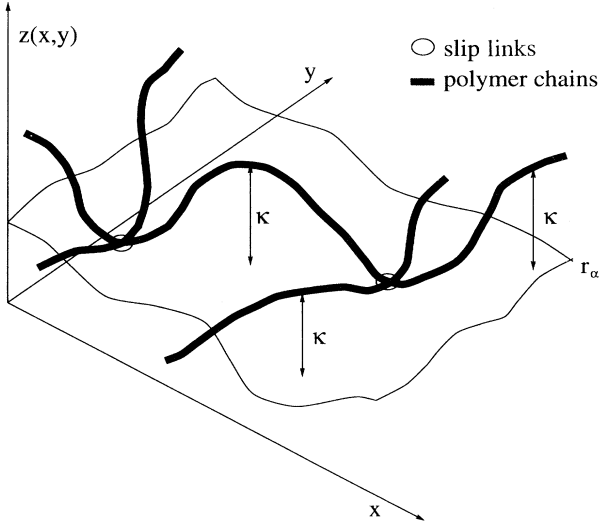
FIG. 1. Schematic representation of the model system. Polymers are pinned to the supporting surface $\mathbf{r}_\alpha$ with slip links of functionality 4 that are mobile along the surface. The interaction of the chains between the slip links with the surface is short ranged and described with the phenomenological parameter κ.

the Balian-Bloch-Duplantier [10] multiple surface scattering Green function formalism, which gives a local curvature expansion for a Helmholtz equation in a region with deformed boundaries.

A major drawback of this approach is that we have been unable to include volume interactions between polymer chains, extensively studied in [3,4], into the formulation in a consistent manner. However, this drawback is substantially counterbalanced by the facts that, first of all, analytic results are feasible in this approximation and that the effect of even very complicated polymer-surface interactions, as is the case in this model system, can be readily investigated within the developed formalism.

II. MODEL

We define our system as a statistical ensemble of freely mobile slip links confined to the supporting surface $\mathbf{r}_\alpha$ (here and below the greek indices stand for coordinates along the supporting surface) produced after N chains $\mathcal{N}$ monomers long are cross-linked M times with functionality 4. Following [9] the cross-links are taken to be introduced by an external auxiliary field $\phi(\mathbf{r})$ of a "coupling strength" $\sqrt{\mu}$ that produces polymer chains with Green function $\mathcal{G}_\phi(\mathbf{r}, \mathbf{r}'; \mathcal{N})$ if the chains are $\mathcal{N}$ segments long. One can show through a diagrammatic expansion of this Green function that if it is averaged over a Gaussian distribution of $\phi(\mathbf{r})$ this operation formally introduces an arbitrary number of cross-links of functionality 4, distributed randomly through space and along the chains, with the partition function

$$\Xi(N,\mathcal{N}) = \left\langle \left(\iint d^3\mathbf{r}\,\mathcal{G}_\phi(\mathbf{r}, \mathbf{r}'; \mathcal{N}) d^3\mathbf{r}' \right)^N \right\rangle_\phi, \qquad (1)$$

for N chains.

If one now expands the Green function in terms of $\sqrt{\mu}\phi(\mathbf{r})$ and then averages with $\langle\rangle_\phi$, the coefficient of μ^M contains all the terms with M cross-links randomly distributed across the space and along the chains. Thus the partition function of a system with M cross-links can be formally written as

$$\Xi(M, N, \mathcal{N})$$

$$= \frac{1}{2\pi\imath} \oint_C \frac{M!\, d\mu}{\mu^{M+1}} \left\langle \left(\iint d^3\mathbf{r}\,\mathcal{G}_\phi(\mathbf{r}, \mathbf{r}'; \mathcal{N}) d^3\mathbf{r}' \right)^N \right\rangle_\phi.$$

$$(2)$$

For the system discussed here the partition function can be obtained along the lines of [9], except that the auxiliary field should now be confined to the surface $\mathbf{r}_\alpha$. This would signify that it should affect not the equation defining the Green function itself, but rather its boundary condition at this surface. Also, if there exist other interactions between the polymers and the surface, they should also show up only in the boundary condition if their range is short enough.

Putting everything together now we derive the partition function of our model system in the following compact notation:

$$\Xi(M, N, \mathcal{N}) = \frac{M!}{2\pi\imath} \oint_C \frac{d\mu}{\mu^{M+1}}$$

$$\times \left\langle \left[\mathcal{L}^{-1} \iint d^3\mathbf{r}\,d^3\mathbf{r}'\,\mathcal{G}_\phi(\mathbf{r}, \mathbf{r}'; s) \right]^N \right\rangle_\phi$$

$$= \frac{M!}{2\pi\imath} \oint_C \frac{d\mu}{\mu^{M+1}} \left\langle \Xi_\phi(\mu, \mathcal{N})^N \right\rangle_\phi, \qquad (3)$$

where $\mathcal{G}_\phi(\mathbf{r}, \mathbf{r}'; s)$ is the Laplace transformed Green function of a free flight polymer, satisfying a Helmholtz-type equation [11]

$$\left[\nabla^2 - s \right] \mathcal{G}_\phi(\mathbf{r}, \mathbf{r}'; s) = -\delta^3(\mathbf{r} - \mathbf{r}'). \qquad (4)$$

Here we made a transformation $\mathbf{r} \to \frac{\sqrt{6}\mathbf{r}}{\ell}$, measuring the spatial dimensions in units of $\frac{\ell}{\sqrt{6}}$, where ℓ is the step length. $\mathcal{L}^{-1}$ stands for the inverse Laplace transform, i.e., $\mathcal{L}^{-1} f(s) = \oint_C e^{s\mathcal{N}} f(s) ds = f(\mathcal{N})$ and the definition of $\Xi_\phi(\mu, \mathcal{N})$ is obvious. At the supporting membrane surface $\mathbf{r}_\alpha$ the Green function satisfies [12]

$$\frac{\partial \mathcal{G}_\phi(\mathbf{r}_\alpha, \mathbf{r}'; s)}{\partial \mathbf{n}_\alpha} - \kappa \mathcal{G}_\phi(\mathbf{r}_\alpha, \mathbf{r}'; s)$$

$$+ \sqrt{\mu}\phi(\mathbf{r}_\alpha) \mathcal{G}_\phi(\mathbf{r}_\alpha, \mathbf{r}'; s) = 0, \quad (5)$$

where κ is the strength of the contact membrane surface-polymer interaction. It can be either repulsive ($\kappa > 0$) or attractive ($\kappa < 0$). The last term in the above equation, proportional to $\sqrt{\mu}$, creates at random positions along the supporting surface $\mathbf{r}_\alpha$ as well as along the polymer chains junctions of fourfold functionality (slip links), of "chemical potential" μ per single junction, after the

Green function is averaged over a Gaussian distribution of the auxiliary field $\phi(\mathbf{r}_\alpha)$ [9],

$$\langle\,\rangle_\phi = \int \mathcal{D}\phi(\mathbf{r}_\alpha)\,(\,)\,e^{-\frac{1}{2}\int \phi^2(\mathbf{r}_\alpha)d^2\mathbf{r}_\alpha} \Big/ \int \mathcal{D}\phi(\mathbf{r}_\alpha)$$
$$\times e^{-\frac{1}{2}\int \phi^2(\mathbf{r}_\alpha)d^2\mathbf{r}_\alpha}. \qquad (6)$$

The averaging over a Gaussian distribution of the auxiliary field preserves only terms with even powers of $\sqrt{\mu}$.

We shall now try to obtain an approximate solution of the above model in the limit of $\frac{M}{N} \ll 1$ while separately $N \gg 1$ and $M \gg 1$, with the additional proviso that the volume (or surface) density of chains $\frac{N}{V}$ (or $\frac{N}{S_\omega}$ depending on the sign of κ) and the surface density of slip links $\frac{M}{S_\omega}$ are finite (thermodynamic limit).

We first of all cast the model in a form that will be

appropriate for later formal developments. It is easiest to obtain a power series solution of Eq. (5) in terms of the free space solution $\mathcal{G}_0(\mathbf{r},\mathbf{r}';s)$, i.e.,

$$\mathcal{G}_0(\mathbf{r},\mathbf{r}';s) = \frac{e^{-\sqrt{s}|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}. \qquad (7)$$

This series has been derived already by Balian and Bloch in [10] and we merely quote their result. Introducing $\Gamma(\mathbf{r}_\gamma,\mathbf{r}_\epsilon;s)$ as

$$\Gamma(\mathbf{r}_\alpha,\mathbf{r}_\beta;s) + 2\kappa \int dS_\gamma \mathcal{G}_0(\mathbf{r}_\alpha,\mathbf{r}_\gamma;s)\Gamma(\mathbf{r}_\gamma,\mathbf{r}_\beta;s)$$
$$= \delta^2(\mathbf{r}_\alpha - \mathbf{r}_\beta), \qquad (8)$$

one obtains the following expansion for the Green function:

$$\mathcal{G}_\phi(\mathbf{r},\mathbf{r}';s) = \mathcal{G}_0(\mathbf{r},\mathbf{r};s) + 2\iint dS_\alpha dS_\beta \mathcal{G}_0(\mathbf{r},\mathbf{r}_\alpha;s)\Gamma(\mathbf{r}_\alpha,\mathbf{r}_\beta;s)\nabla_\beta \mathcal{G}_0(\mathbf{r}_\beta,\mathbf{r}';s)$$
$$+ 2^2 \iiiint dS_\alpha dS_\beta dS_\gamma dS_\delta \mathcal{G}_0(\mathbf{r},\mathbf{r}_\alpha;s)\Gamma(\mathbf{r}_\alpha,\mathbf{r}_\delta;s)\frac{\partial \mathcal{G}_0(\mathbf{r}_\delta,\mathbf{r}_\gamma;s)}{\partial \mathbf{n}_\delta}$$
$$\times \Gamma(\mathbf{r}_\delta,\mathbf{r}_\beta;s)\nabla_\beta \mathcal{G}_0(\mathbf{r}_\beta,\mathbf{r}';s) + \cdots, \qquad (9)$$

where

$$\nabla_\alpha = \frac{\partial}{\partial \mathbf{n}_\alpha} - \kappa + \sqrt{\mu}\phi(\mathbf{r}_\alpha). \qquad (10)$$

We might just add here that for a planar surface the normal derivative of the Green function, $\frac{\partial \mathcal{G}_0(\mathbf{r}_\delta,\mathbf{r}_\gamma;s)}{\partial \mathbf{n}_\delta}$, is zero and thus the expansion Eq. (9) is basically an expansion in the curvature of the bounding surface.

Combining now both Eqs. (8) and (9) we can derive the partition function in a rather transparent form:

$$\Xi_\phi(\mu,\mathcal{N}) = \Xi_b(\mathcal{N}) + 2\,\mathrm{Tr}\,U_\phi(\mathbf{r}_\alpha,\mathbf{r}_\beta;\mathcal{N})$$
$$= V + 2\int dS_\omega U_\phi(\mathbf{r}_\omega,\mathbf{r}_\omega;\mathcal{N}), \qquad (11)$$

where $\Xi_b(\mathcal{N}) = \iint d^3\mathbf{r}d^3\mathbf{r}'\mathcal{G}_0(\mathbf{r},\mathbf{r}';\mathcal{N}) = V$ is the volume of the polymer solution with unperturbed boundaries and the operator $U_\phi(\mathbf{r}_\alpha,\mathbf{r}_\beta;s)$ is obtained as a solution of

$$U_\phi(\mathbf{r}_\alpha,\mathbf{r}_\beta;s) - 2\int dS_\gamma U_\phi(\mathbf{r}_\alpha,\mathbf{r}_\gamma;s)\nabla_\gamma \mathcal{G}_0(\mathbf{r}_\gamma,\mathbf{r}_\beta;s)$$

$$= \nabla_\alpha F(\mathbf{r}_\alpha,\mathbf{r}_\beta;s), \qquad (12)$$

with dS_ω being the area element of the surface $\mathbf{r}_\alpha$, and

$$F(\mathbf{r}_\alpha,\mathbf{r}_\beta;s) = \iint d^3\mathbf{r}d^3\mathbf{r}'\mathcal{G}_0(\mathbf{r},\mathbf{r}_\alpha;s)\mathcal{G}_0(\mathbf{r}_\beta,\mathbf{r}';s). \qquad (13)$$

Equations (11) and (12) represent just a more compact formalization of the results already derived in [10] that is conveniently suited for our purposes.

Formally the above equations define our model system. Their solution is obviously nontrivial and additional ap-

proximations have to be introduced in order to make the problem tractable. First of all we shall introduce the approximation of low polymer density that will make the evaluation of $\langle\,\rangle_\phi$ fairly tractable in the form of a power series in the chemical potential of the slip links, μ. Next we shall resolve the integration over μ by reverting to the saddle-point ansatz and finally we shall use the approximation of the local tangential plane that explicitly introduces the surface curvature dependence of the Green functions to evaluate the different curvature terms in the final expression for the partition function.

III. ANALYSIS

Starting from Eq. (11), $\Xi_\phi(\mu,\mathcal{N})^N$ can be written in the form of a "virial" expansion in terms of the polymer volume density. If this density is small enough we can stop at the first order term, thus obtaining

$$\Xi(M,N,\mathcal{N}) \cong \frac{M!}{2\pi i}\oint_C \frac{d\mu}{\mu^{M+1}}\,e^{N\ln\langle\Xi_\phi(\mu,\mathcal{N})\rangle_\phi}$$

$$= \frac{M!}{2\pi i}\oint_C \frac{d\mu}{\mu^{M+1}}\,e^{N\ln\left(V+2\,\mathrm{Tr}\,\langle U_\phi(\mathbf{r}_\alpha,\mathbf{r}_\beta;\mathcal{N})\rangle_\phi\right)}. \qquad (14)$$

As we have done before [8] we now substantially reduce the tedious algebra proceeding from the above equations if we presume that $|\kappa| \gg \frac{\partial \ln \mathcal{G}_0(\mathbf{r}_\alpha,\mathbf{r}';s)}{\partial \mathbf{n}_\alpha}$. First of all we solve Eq. (12) in the form of a formal series in $\phi(\mathbf{r}_\alpha)$. This series solution of Eq. (12) for $U_\phi(\mathbf{r}_\alpha,\mathbf{r}_\beta;s)$ can be effectively resummed and averaged over the Gaussian distribution of the auxiliary field $\phi(\mathbf{r}_\alpha)$, Eq. (6). Only even

powers of $\phi(\mathbf{r}_\alpha)$ survive this averaging and we can re-group the remaining terms, obtaining a power series in μ. By defining

$$U_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s) = -\kappa \int dS_\gamma F(\mathbf{r}_\alpha, \mathbf{r}_\gamma; s) \Gamma(\mathbf{r}_\gamma, \mathbf{r}_\beta; s) ,$$

$$\Delta(\mathbf{r}_\alpha, \mathbf{r}_\beta; s) = \int dS_\gamma \mathcal{G}_0(\mathbf{r}_\alpha, \mathbf{r}_\gamma; s) \Gamma(\mathbf{r}_\gamma, \mathbf{r}_\beta; s) ,$$

$$W_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s) = \tfrac{1}{2} \iint dS_\gamma dS_\epsilon F(\mathbf{r}_\alpha, \mathbf{r}_\gamma; s)$$
$$\times \Gamma(\mathbf{r}_\gamma, \mathbf{r}_\epsilon; s) \mathcal{G}_0^{-1}(\mathbf{r}_\epsilon, \mathbf{r}_\beta; s) , \qquad (15)$$

we thus obtain the ϕ average of $U_\phi(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$ in the form of a series in the chemical potential of the pinning slip links, μ,

$$\langle U_\phi(\mathbf{r}_\alpha, \mathbf{r}_\beta; s) \rangle_\phi = U_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$$
$$+ 4\mu \int dS_\gamma \Delta(\mathbf{r}_\alpha, \mathbf{r}_\gamma; s) W_0(\mathbf{r}_\gamma, \mathbf{r}_\beta; s)$$
$$+ 16\mu^2 \iint dS_\gamma dS_\epsilon \Delta(\mathbf{r}_\alpha, \mathbf{r}_\epsilon; s)$$
$$\times \Delta(\mathbf{r}_\epsilon, \mathbf{r}_\gamma; s) W_0(\mathbf{r}_\gamma, \mathbf{r}_\beta; s) + \cdots , \qquad (16)$$

where we redefined the chemical potential $\mu \to \mu\Delta(\mathbf{r}_\alpha, \mathbf{r}_\alpha; \mathcal{N})$, with $\Delta(\mathbf{r}_\alpha, \mathbf{r}_\alpha; \mathcal{N}) \to \pi\sqrt{\mathcal{N}} V^{-\frac{1}{3}} \gg 1$. This relation stems from the conservation of the degrees of freedom of the chain [9]. At each order of the μ ex-

pansion we retain only the largest term while omitting all the additional powers of $\Delta^{-1}(\mathbf{r}_\alpha, \mathbf{r}_\alpha; \mathcal{N})$. The above expansion in terms of μ is convergent if $\frac{M}{N} \ll 1$, and we can stop at the second order term.

The zero order term in this expansion, Eq. (16), is exactly the one corresponding to the example treated previously [8], which corresponds to the case without any surface pinning of the polymers through the slip links.

The approximate form of $\langle \Xi_\phi(\mu, \mathcal{N}) \rangle_\phi$ is thus obtained as

$$\langle \Xi_\phi(\mu, \mathcal{N}) \rangle_\phi = V + 2 \int dS_\omega \langle U_\phi(\mathbf{r}_\omega, \mathbf{r}_\omega; \mathcal{N}) \rangle_\phi$$
$$\cong \Xi_0(\mathcal{N}) + \mu \Xi_1(\mathcal{N}) + \tfrac{1}{2}\mu^2 \Xi_2(\mathcal{N}) + \cdots , \qquad (17)$$

where aside from V all the other μ terms in the expansion can be obtained by comparison with Eq. (16) as

$$\Xi_0(\mathcal{N}) = \Xi_b(\mathcal{N}) + 2 \, \mathcal{L}^{-1} \left[\text{Tr} \, U_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s) \right] ,$$

$$\Xi_1(\mathcal{N}) = 8 \, \mathcal{L}^{-1} \left[\text{Tr} \int dS_\gamma \Delta(\mathbf{r}_\alpha, \mathbf{r}_\gamma; s) W_0(\mathbf{r}_\gamma, \mathbf{r}_\beta; s) \right] ,$$

$$\Xi_2(\mathcal{N}) = 64 \, \mathcal{L}^{-1} \left[\text{Tr} \iint dS_\gamma dS_\epsilon \Delta(\mathbf{r}_\alpha, \mathbf{r}_\gamma; s) \right.$$
$$\left. \times \Delta(\mathbf{r}_\gamma, \mathbf{r}_\epsilon; s) W_0(\mathbf{r}_\epsilon, \mathbf{r}_\beta; s) \right] , \qquad (18)$$

where $\Xi_b(\mathcal{N}) = \mathcal{L}^{-1} \left[\frac{1}{s} \int d^3\mathbf{r} \right] = V$.

The final μ integration in Eq. (14) is now of the form

$$\Xi(M, N, \mathcal{N}) \cong \frac{M!}{2\pi i} \oint_C d\mu e^{N \ln \left(\Xi_0(\mathcal{N}) + \mu \Xi_1(\mathcal{N}) + \frac{1}{2}\mu^2 \Xi_2(\mathcal{N}) + \cdots \right) - (M+1) \ln \mu} , \qquad (19)$$

which is amenable to an analytic treatment through the saddle-point approximation in the thermodynamic limit of $N \gg 1$ and $M \gg 1$, yielding an approximate result $\mu = \mu^*(\frac{M}{N})$, where to the lowest order we obtain $\mu^* \sim \frac{M}{N} \frac{\Xi_0(\mathcal{N})}{\Xi_1(\mathcal{N})} + \cdots$. The saddle-point free energy $\mathcal{F}$ is thus obtained as $[\beta = (kT)^{-1}]$

$$\beta\mathcal{F} = -\ln\Xi(M, N, \mathcal{N})$$
$$\cong -N\ln \left[\Xi_0(\mathcal{N}) + \mu^*\Xi_1(\mathcal{N}) + \tfrac{1}{2}\mu^{*2}\Xi_2(\mathcal{N}) \right]$$
$$+ (M + 1)\ln\mu^* . \qquad (20)$$

Following the expansion of the statistical sum in terms of the relative number of slip links, i.e., $\frac{M}{N}$, we now additionally presume that the supporting surface $\mathbf{r}_\alpha$ is deformed and we investigate the lowest order expansion of the free energy in terms of the local curvatures of the deformed surface. We approach this problem by the Balian-Bloch-Duplantier method [10] as was explained in detail for a somewhat simpler case of polymer-surface interactions [8].

The principle of the curvature expansion is simple. First of all we note that the partition function Eq. (18) contains different surface integrals of either $G_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$, $\Delta(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$, or $F(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$. Since all these quantities

depend only on the difference of the surface coordinates in the arguments we can expand them around the local tangential plane up to the second order in the deviations from that plane and then evaluate the surface integrals explicitly. This expansion in terms of the deviations from the local tangential plane is valid only as long as the Green function is of a range smaller than the local curvatures. Practically this would mean that one can always find a range of curvature values where the expansion of a Yukawa-type Green function Eq. (7) in the vicinity of a local tangential plane of a nonplanar surface is justified.

We write the equation of the bounding surface $\mathbf{r}_\alpha$ in the reference frame of the tangential plane at $\mathbf{r}_\omega$ as

$$z_\omega(x, y) \cong \tfrac{1}{2} \left(\frac{x^2}{R_{\omega_1}} + \frac{y^2}{R_{\omega_2}} \right) + \cdots , \qquad (21)$$

where R_{ω_1} and R_{ω_2} are the two principal radii of curvature at the point $\mathbf{r}_\omega$ on the bounding surface. We can now straightforwardly derive the form of the curvature dependence up to and including the second order of the Green function by expanding the coordinate dependence in the vicinity of the tangential plane for each point along the bounding surface. The only nonzero terms in the expansion of $G_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$ are the zero and the second order,

thus giving

$$G_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$$

$$\cong G_0^{(p)}(\mathbf{r}_\alpha, \mathbf{r}_\beta; s) + \tfrac{1}{2} z_\alpha^2(x, y) \frac{\partial^2 G_0^{(p)}(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)}{\partial z_\alpha^2} + \cdots ,$$

$$(22)$$

where the superscript p stands for the "planar" (i.e., zero curvature) approximation of the quantity to which it is affixed. Furthermore, $\frac{\partial G_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)}{\partial \mathbf{n}_\alpha}$ obviously has only odd terms in the expansion starting with

$$\frac{\partial G_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)}{\partial \mathbf{n}_\alpha} \cong -\left(\frac{\partial z_\alpha(x,y)}{\partial x} \frac{\partial}{\partial x} + \frac{\partial z_\alpha(x,y)}{\partial y} \frac{\partial}{\partial y} \right)$$
$$\times G_0^{(p)}(\mathbf{r}_\alpha, \mathbf{r}_\beta; s) + \cdots , \qquad (23)$$

$$F(\mathbf{r}_\alpha, \mathbf{r}_\beta; s) = \iint d^3\mathbf{r} d^3\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}_\alpha; s) G_0(\mathbf{r}_\beta, \mathbf{r}'; s)$$

$$= \frac{1}{s^2} \left[\frac{1}{4} - \int \frac{\partial G_0(\mathbf{r}_\gamma, \mathbf{r}_\alpha; s)}{\partial \mathbf{n}_\gamma} dS_\gamma + \iint \frac{\partial G_0(\mathbf{r}_\gamma, \mathbf{r}_\alpha; s)}{\partial \mathbf{n}_\gamma} \frac{\partial G_0(\mathbf{r}_{\gamma'}, \mathbf{r}_\beta; s)}{\partial \mathbf{n}_{\gamma'}} dS_\gamma dS_{\gamma'} \right] , \qquad (25)$$

where the curvature dependence transpires more directly. With all these provisos we can now evaluate the surface integrals in the defining equations Eq. (15) explicitly order by order in the inverse curvature [8]. Though this procedure is tedious it is nevertheless straightforward. The following relations are obtained:

$$\int U^{(0)}(\mathbf{r}_\omega, \mathbf{r}_\alpha; s) \, dS_\alpha^{(p)} = -\frac{\kappa}{4\sqrt{s}^3(\kappa + \sqrt{s})} ,$$

$$\int U^{(1)}(\mathbf{r}_\omega, \mathbf{r}_\alpha; s) \, dS_\alpha^{(p)} = \frac{\kappa}{2s^2(\kappa + \sqrt{s})} \frac{1}{R_\omega} ,$$

$$\int U^{(2)}(\mathbf{r}_\omega, \mathbf{r}_\alpha; s) \, dS_\alpha^{(p)}$$

$$= -\frac{\kappa}{4\sqrt{s}^5(\kappa + \sqrt{s})}$$
$$\times \left[\frac{1}{R_\omega^2} - \frac{\kappa}{2(\kappa + \sqrt{s})} \left(\frac{1}{R_\omega^2} - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) \right] ,$$

$$\int \Delta^{(0)}(\mathbf{r}_\omega, \mathbf{r}_\alpha; s) \, dS_\alpha^{(p)} = \frac{1}{2(\kappa + \sqrt{s})} ,$$

$$\int \Delta^{(2)}(\mathbf{r}_\omega, \mathbf{r}_\alpha; s) \, dS_\alpha^{(p)}$$

$$= \frac{1}{4\sqrt{s}(\kappa + \sqrt{s})} \left(\frac{1}{R_\omega^2} - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) ,$$

$$\int W_0^{(0)}(\mathbf{r}_\omega, \mathbf{r}_\alpha; s) \, dS_\alpha^{(p)} = \frac{1}{4s(\kappa + \sqrt{s})} ,$$

$$\int W_0^{(1)}(\mathbf{r}_\omega, \mathbf{r}_\alpha; s) \, dS_\alpha^{(p)} = -\frac{1}{2\sqrt{s}^3(\kappa + \sqrt{s})} \frac{1}{R_\omega} ,$$

since the local normal is defined as $\mathbf{n}_\alpha = (1, -\frac{\partial z_\alpha(x,y)}{\partial x}, -\frac{\partial z_\alpha(x,y)}{\partial y})$. The third origin of the curvature dependence is the surface area element dS_ω itself in Eqs. (8) and (15),

$$dS_\omega \cong dS_\omega^{(p)} + \tfrac{1}{2} \left[\nabla z_\omega(x, y) \right]^2 dS_\omega^{(p)}. \qquad (24)$$

Finally, Eqs. (22), (23), and (24) have to be averaged locally over all the directions of the principal curvature axes.

These fundamental dependencies of the Green function $G_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$ and its normal derivative on the local curvature now generate the corresponding functional dependence for the surface Green function $\Gamma(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$ through the defining equation Eq. (8), and for $F(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$ that can be written in an alternative form

$$\int W_0^{(2)}(\mathbf{r}_\omega, \mathbf{r}_\alpha; s) \, dS_\alpha^{(p)}$$

$$= \frac{1}{4s^2(\kappa + \sqrt{s})}$$
$$\times \left[\frac{1}{R_\omega^2} - \frac{(2\kappa + \sqrt{s})}{2(\kappa + \sqrt{s})} \left(\frac{1}{R_\omega^2} - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) \right] ,$$

$$(26)$$

which are, on the other hand the only quantities that we need in evaluation of the partition functions Eq. (18). This is so due to the fact that $F(\mathbf{r}_\alpha, \mathbf{r}_\beta; s)$ depends only on the difference between the coordinates and not on their absolute values. This property then reverberates through the defining equations all the way to the partition function Eq. (18).

We now follow the definitions Eqs. (16), (15), and (8) and thus as a result obtain a curvature expansion for $\Xi_0(\mathcal{N})$, $\Xi_1(\mathcal{N})$, and $\Xi_2(\mathcal{N})$. To the lowest order in the average curvature $\frac{1}{R_\omega} = \tfrac{1}{2} \left(\frac{1}{R_{\omega_1}} + \frac{1}{R_{\omega_2}} \right)$, and in the limit of long polymers, $\mathcal{N} \gg 1$, we derive the following curvature expansion for the case $\kappa > 0$:

$$\Xi_0(\mathcal{N}) = V - \frac{\sqrt{\mathcal{N}}}{\sqrt{\pi}} \int dS_\omega \left[1 - \sqrt{\pi}\sqrt{\mathcal{N}} \frac{1}{R_\omega} \right.$$

$$\left. + \frac{2\mathcal{N}}{3} \left(\frac{1}{R_\omega^2} + \frac{1}{R_{\omega_1} R_{\omega_2}} \right) \right] + \cdots ,$$

$$\Xi_1(\mathcal{N}) = \frac{1}{\kappa^2} \int dS_\omega \left[1 - \frac{4\sqrt{\mathcal{N}}}{\sqrt{\pi}} \frac{1}{R_\omega} + \frac{\sqrt{\mathcal{N}}}{\kappa\sqrt{\pi}} \left(\frac{1}{R_\omega^2} \right. \right.$$

$$\left. \left. - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) + \mathcal{N} \frac{1}{R_{\omega_1} R_{\omega_2}} \right] + \cdots ,$$

$$\Xi_2(\mathcal{N}) = \frac{4}{\kappa^3} \int dS_\omega \left[1 - \frac{4\sqrt{\mathcal{N}}}{\sqrt{\pi}} \frac{1}{R_\omega} + \frac{2\sqrt{\mathcal{N}}}{\kappa\sqrt{\pi}} \left(\frac{1}{R_\omega^2} \right. \right.$$

$$\left. \left. - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) + \mathcal{N} \frac{1}{R_{\omega_1} R_{\omega_2}} \right] + \cdots , \qquad (27)$$

where ω stands for the index of the coordinate over which the final integration of the Tr operation is carried out; see Eq. (17).

In the opposite case of $\kappa < 0$ the spectrum of $G_0(\mathbf{r}_\alpha, \mathbf{r}_\beta; \mathcal{N})$ has bound states leading to the following dependence on $\mathcal{N} \gg 1$ after the inverse Laplace transform:

$$\Xi_0(\mathcal{N}) = V + \frac{e^{\kappa^2 \mathcal{N}}}{\kappa} \int dS_\omega \left[1 - \frac{2}{\kappa} \frac{1}{R_\omega} \right.$$

$$\left. + \mathcal{N} \left(\frac{1}{R_\omega^2} - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) \right] + \cdots ,$$

$$\Xi_1(\mathcal{N}) = \frac{4(\kappa^2 \mathcal{N}) \, e^{\kappa^2 \mathcal{N}}}{\kappa^2} \int dS_\omega \left[1 - \frac{2}{\kappa} \frac{1}{R_\omega} + \frac{1}{\kappa^2} \frac{1}{R_\omega^2} \right.$$

$$\left. + \mathcal{N} \left(\frac{1}{R_\omega^2} - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) \right] + \cdots ,$$

$$\Xi_1(\mathcal{N}) = \frac{16(\kappa^2 \mathcal{N})^2 \, e^{\kappa^2 \mathcal{N}}}{\kappa^3} \int dS_\omega \left[1 - \frac{2}{\kappa} \frac{1}{R_\omega} + \frac{1}{\kappa^2} \frac{1}{R_\omega^2} \right.$$

$$\left. + \mathcal{N} \left(\frac{1}{R_\omega^2} - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) \right] + \cdots . \qquad (28)$$

One should not forget at this point that all the above relations were derived under the restriction that $|\kappa| \gg \frac{\partial \ln \mathcal{G}_0(\mathbf{r}_\alpha, \mathbf{r}'; s)}{\partial \mathbf{n}_\alpha}$. This restriction is not particularly stringent if one does not approach the region $\kappa \cong 0$.

IV. RESULTS AND DISCUSSION

Taking now equations Eqs. (20) and (27) and assuming that the surface density $\frac{M}{S_\omega}$ and the volume density $\frac{N}{V}$ are finite, we end up with the following form of the free energy in the limit of $\kappa > 0$:

$$\beta \mathcal{F} \cong \beta \mathcal{F}_0 - (N - M) \ln V - M \ln S_\omega$$

$$+ \left(\frac{N}{V} \right) \left[\frac{\sqrt{\mathcal{N}}}{\sqrt{\pi}} \int dS_\omega - \mathcal{N} \int dS_\omega \frac{1}{R_\omega} + \frac{2\sqrt{\mathcal{N}}^3}{3\sqrt{\pi}} \int dS_\omega \left(\frac{1}{R_\omega^2} + \frac{1}{R_{\omega 1} R_{\omega 2}} \right) \right]$$

$$+ \left(\frac{M}{S_\omega} \right) \left[\frac{4\sqrt{\mathcal{N}}}{\sqrt{\pi}} \int dS_\omega \frac{1}{R_\omega} - \frac{\sqrt{\mathcal{N}}}{\kappa\sqrt{\pi}} \int dS_\omega \left(\frac{1}{R_\omega^2} - \frac{1}{R_{\omega 1} R_{\omega 2}} \right) - \mathcal{N} \int dS_\omega \frac{1}{R_{\omega 1} R_{\omega 2}} \right]$$

$$- \frac{\kappa}{2} \left(\frac{M}{S_\omega} \right)^2 \left(\frac{N}{V} \right)^{-1} \left[\int dS_\omega + \frac{4\sqrt{\mathcal{N}}}{\sqrt{\pi}} \int dS_\omega \frac{1}{R_\omega} - \mathcal{N} \int dS_\omega \frac{1}{R_{\omega 1} R_{\omega 2}} \right] + \cdots . \qquad (29)$$

$\beta \mathcal{F}_0$ contains irrelevant constants and combinatorial terms, while the second and the third terms describe the removal of M out of a total of N volume translational degrees of freedom and the creation of M surface translational degrees of freedom due to the existence of mobile surface slip links. The nature of the other terms in the free energy is also straightforwardly discernible (see below).

In the opposite limit of $\kappa < 0$, assuming now that the two surface densities $\frac{M}{S_\omega}$ and $\frac{N}{S_\omega}$ are finite, we derive the following form of the free energy:

$$\beta \mathcal{F} \cong \beta \mathcal{F}_0 - N \ln S_\omega + \left(\frac{N}{S_\omega} \right) \left[-\kappa^2 \mathcal{N} \int dS_\omega + \frac{2}{\kappa} \int dS_\omega \frac{1}{R_\omega} - \mathcal{N} \int dS_\omega \left(\frac{1}{R_\omega^2} - \frac{1}{R_{\omega_1} R_{\omega_2}} \right) \right]$$

$$- \left(\frac{M}{S_\omega} \right) \frac{1}{\kappa^2} \int dS_\omega \frac{1}{R_\omega^2} - \frac{1}{2} \left(\frac{M}{S_\omega} \right)^2 \left(\frac{N}{S_\omega} \right)^{-1} \frac{1}{\kappa^2} \int dS_\omega \frac{1}{R_\omega^2} + \cdots , \qquad (30)$$

where the second term now simply signifies that in this limit the chains are mostly adsorbed to the surface as we assumed that there are no volume interactions between them.

The above two results should be compared with the canonical form of the membrane elastic energy [1],

$$\mathcal{F} = \frac{1}{2} K_c \int dS_\omega \left(\frac{1}{R_\omega} - \frac{1}{R_0} \right)^2 + K_G \int dS_\omega \frac{1}{R_{\omega 1} R_{\omega 2}}, \qquad (31)$$

from which one obtains the contribution of the polymer-surface interactions to the curvature modulus (K_c) and spontaneous curvature radius (R_0), as well as to the modulus of Gaussian curvature (K_G).

On comparison with the results of Ref. [8], it is clear that the fourth term in the free energy Eq. (29) corresponds to the statistically averaged contact excluded volume interaction of the polymer solution with the deformed boundary, as the limit $|\kappa| \gg 0$ assumed in deriving this result essentially reduces to the Dirichlet boundary condition. We shall refer to this term in the free energy as the contact term.

The term linear in $\frac{M}{S_\omega}$ is the only one that vanishes completely for a flat surface and is formally analogous to

an effective polymer adsorption term [8]. As it is non-zero only for a rough surface it stems from the "in plane bridging" (see Ref. [8]) provided by the segments of the polymers between different slip links. Obviously, it tends to curve the surface towards the polymer rich side and thus acts in opposition to the contact term.

The last term in Eq. (29), being of the second order in $\frac{M}{S_\omega}$, corresponds to the free energy of chain segments caught by the slip links and thus brought into the immediate vicinity of the repulsive surface. Its zero and first order curvature terms are both negative, reflecting the predominant influence of the diminished entropy over the interaction energy (2κ per link) of the chains meeting at the slip link confined to the supporting surface. This term acts to expose a larger area to the polymer rich side, thus tending to curve the supporting surface away from it in concert with the contact term. It is also the only term in the energy expansion that does not affect the curvature modulus at all.

The final rescaling of the curvature modulus and spontaneous curvature in this limit then assume the form

$$K_c \longrightarrow K_c + \tfrac{2}{3}kT\phi\frac{\mathcal{R}_G^3}{\sqrt{\pi}} - kT\left(\frac{M}{S_\omega}\right)\frac{\mathcal{R}_G}{\kappa\sqrt{\pi}} + \cdots \quad (32)$$

and

$$\frac{K_c}{R_0} \longrightarrow \frac{K_c}{R_0} + kT\phi\mathcal{R}_G^2\left[1 + 2\kappa\left(\frac{M}{S_\omega}\right)^2\frac{\phi^{-2}}{\mathcal{R}_G}\right]$$
$$-kT\left(\frac{M}{S_\omega}\right)\frac{4}{\sqrt{\pi}}\mathcal{R}_G + \cdots, \quad (33)$$

where we introduced the radius of gyration, which in appropriate units assumes the form $\mathcal{R}_G = \sqrt{\mathcal{N}}$, and the volume density of polymers $\phi = \frac{N}{V}$.

The free energy of the system in the limit of $\kappa \gg 0$ thus emerges as being composed of three decoupled terms: the surface energy of the bulk polymer solution due to the repulsive interaction of the polymers with the surface, the energy of those polymer chains that happen to join different slip links and lie in the plane of the unperturbed surface, and the surface energy of slip links themselves, since at the points of cross-linking different segments of the chains make contact with the (repulsive) surface. After relaxing the limit $\frac{M}{N} \ll 1$ we can presume that only the last two mechanisms will remain in making a substantial contribution to the total free energy. Unfortunately, the relaxing of this limit makes the whole calculation much more demanding, probably due to the fact that the system goes through a surface gelation transition.

In the case of attractive interactions between the chains and the surface the third term corresponds to the free energy of a polymer bound to a deformed surface with energy κ per surface area. The term in the square brackets is simply the adsorption energy [12]. The term linear in curvature prefers bending towards the polymer rich side and thus acts exactly in the opposite direction to the analogous term in the contact term Eq. (29). This is also the only term in the whole free energy expression that is linear in curvature.

The rescaling of the curvature modulus obviously stems in this case from three different mechanisms which, interestingly enough, all act in the direction of destabilizing the curvature modulus. The first contribution, being linear in $\frac{N}{S_\omega}$, comes from the adsorption energy and is of the same form as in the case when no pinning to slip links is present [8]. The second and third contributions, being linear and quadratic in $\frac{M}{S_\omega}$, respectively, are obviously due to the presence of surface-bound slip links. The linear term is due to the energy difference in the pinning at the slip link as compared to the "soft" adsorption, while the third term is due to the energy difference of an adsorbed portion of the chain when it is pinned by two slip links, at the beginning and at the end, and when it is "softly" adsorbed.

The final rescaling of the elastic properties of the "dressed" membrane can in this limit be cast into the form

$$K_c \longrightarrow K_c - 2\left(\frac{N}{S_\omega}\right)\mathcal{R}_G^2$$
$$-2\left(\frac{M}{S_\omega}\right)\kappa^{-2}\left[1 + \tfrac{1}{2}\left(\frac{M}{S_\omega}\right)^2\left(\frac{N}{S_\omega}\right)^{-2}\right] + \cdots \quad (34)$$

and

$$\frac{K_c}{R_0} \longrightarrow \frac{K_c}{R_0} + \left(\frac{N}{S_\omega}\right)\frac{2}{\kappa} + \cdots. \quad (35)$$

The modifications in the Gaussian modulus are important because they extend only over the area occupied by polymers and are thus position dependent (otherwise they would make no contribution to the equations determining the shape of the "dressed" membrane). In the case of repulsive polymer-membrane interactions, i.e., $\kappa > 0$, we obtain the following form for the change in the Gaussian curvature modulus:

$$K_G \longrightarrow K_G + \phi\frac{2\mathcal{R}_G^3}{3\sqrt{\pi}} - \left(\frac{M}{S_\omega}\right)\left[\mathcal{R}_G^2 - \frac{\mathcal{R}_G}{\kappa\sqrt{\pi}}\right]$$
$$+ \frac{\kappa}{2}\left(\frac{M}{S_\omega}\right)^2\phi^{-1}\mathcal{R}_G^2 + \cdots. \quad (36)$$

Since the signs of different contributions in this case are not uniform there is no general statement that one could make regarding the proliferation of handles.

In the opposite case of attractive polymer-membrane interactions, $\kappa < 0$, the Gaussian curvature modulus has a very simple dependence on the polymer parameters:

$$K_G \longrightarrow K_G + \left(\frac{N}{S_\omega}\right)\mathcal{R}_G^2 + \cdots \quad (37)$$

that in conjunction with Eq. (34) favors the proliferation of handles. The last result is interesting also from

the point of view of a recent analysis of the modifications in the Gaussian curvature modulus of partially polymerized surfactant membranes [5]. Clearly, for large negative values of κ our problem is isomorphous to the problem of polymers embedded in the membrane. In case there are no interactions between embedded polymer chains the result derived by Kozlov and Helfrich [5] for this particular model system reduces exactly to Eq. (37).

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