Magnetic-field-induced anisotropic curvature elasticity of a vesicle membrane containing magnetic polyions

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Interaction between a charged membrane and the electrolyte solution containing magnetic polyions is considered. A self-magnetic field, which arises due to the nonhomogeneous magnetic particle distribution near a charged membrane increases the effective charge screening length for the parts of a membrane normal to a magnetic field. The anisotropy of elastic properties of a membrane depending on the screening length is calculated on the basis of the curvature expansion. It is shown that due to diminishing of the spontaneous curvature for the parts of a membrane normal to a magnetic field there are two competing mechanisms of the ferrovesicle shape transformation under the influence of a magnetic field—the formation of a prolate shape orientated along a field due to the diminishing action of the demagnetizing field energy and the deformation to a oblate shape due to the decrease in the spontaneous curvature of the parts of a membrane normal to a field.

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I. INTRODUCTION

The interaction between colloidal particles and membranes is an active area of research. In [1,2] various aspects of those interactions in relation to steric effects are considered. On the other hand, an important role in behavior of lipid bilayers or membranes is played by electrostatic forces. The elastic properties of membranes due to electrostatic interactions have been considered in several papers [3–6]. A review of fascinating phenomena connected with the electrostatic interactions of the macroions has recently appeared [7]. A new object, ferrovesicle or vesicle containing dilute colloidal solution of single-domain ferromagnetic particles, is introduced in [8] and its behavior under the action of an external field is studied. It is found that thermal fluctuations of a membrane are flattened with increase in the tension of a membrane with an applied field and ferrovesicle elongates along the field direction forming a prolate shape [8]. By studying the ferrovesicles for different ionic strengths of the interior colloidal solution it has been established in [9] that the ferrovesicle depending on the ionic strength can take an oblate or prolate shape. Since magnetic colloidal particles are charged it is quite natural to assume that the transition to an oblate shape occurs due to modification of elastic properties of a membrane under the influence of a magnetic-field-caused change in the length of Debye screening of the internal electrolyte solution containing magnetic polyions [9]. Debye length calculation depending on the magnetic field strength for a planar membrane as well as existing theoretical relations for various electrostatic contributions to the elastic properties of membrane has supported this assumption [9,10]. Nevertheless, the approach based on application of an expression of the Debye length derived for a planar membrane for calculating the energy of a curved surface could be inconsistent in the sense that some terms arising due to the interaction of charged magnetic particles with a curved charged membrane could be omitted. Values of numerical coefficients obtained in such a way could serve only as rough estimates. Full analysis of interaction of charged magnetic particles with the charged curved membrane in an external magnetic field is carried out in this study. Although results obtained before in approximation of the planar membrane are confirmed with accuracy up to numerical coefficients, nevertheless, several new effects not mentioned before are demonstrated—the anisotropy of the bending elasticity in a tangential plane of a membrane and dependence of the Gaussian curvature elasticity constant on the magnetic field strength except its direction as well as others. In Sec. II, the free energy of a charged membrane surrounded by an electrolyte solution containing magnetic particles is introduced. Fundamental solution of equations describing the interaction between the charge and the electrolyte solution containing magnetic ions is obtained in Sec. III. On this basis the dependence of the Debye length on the magnetic field strength for a planar membrane is established. The curvature elasticity energy of the charged membrane interacting with an electrolyte solution containing the magnetic polyions depending on the magnetic field strength and its direction is derived in Sec. IV. Some conclusions concerning the ferrovesicle shape transformations according to the present model and comparison with available experimental data are given in Sec. V.

II. FREE ENERGY OF THE CHARGED MEMBRANE IN THE ELECTROLYTE SOLUTION WITH MAGNETIC POLYIONS

Due to the electrostatic interaction between a charged membrane and magnetic polyions their concentration near the membrane becomes nonhomogeneous. When a magnetic field is applied the perturbation of the magnetic field takes place. The energy of the magnetic field perturbation must be included when describing the interaction of magnetic polyions with a membrane. If accounted for the electrical field energy, the mixing entropy of ions and the self-magnetic field energy of the nonhomogeneous distribution of magnetic polyions within the framework of the linear Poisson-Boltzmann approach the free energy could be written as follows:

$$F=\frac{\epsilon}{8\pi}\int(\nabla\phi)^2dV+k_BT\int n_+\ln\frac{n_+}{n_{+0}}dV+k_BT\int n_-\ln\frac{n_-}{n_{-0}}dV+k_BT\int n_k\ln\frac{n_k}{n_{k0}}dV-k_BT\int(n_++n_-+n_k-n_{+0}-n_{-0}-n_{k0})dV+\frac{1}{8\pi}\int\mu_0(\delta\boldsymbol{H})^2dV \tag{1}$$

where n_+ and n_- are the concentrations of positive and negative ions, n_k is the concentration of magnetic polyions, and n_{+0}, n_{-0}, and n_{k0} are their values far away from a charged membrane. The potential of a electrostatic field ϕ and the field strength of the perturbed magnetic field $\delta\boldsymbol{H}$ shall satisfy the following equations:

$$\epsilon\Delta\phi=-4\pi\rho=-4\pi e(z_+n_+-z_-n_-+z_kn_k), \tag{2}$$

$$\mu_0\mathrm{div}(\delta\boldsymbol{H})=-4\pi\chi_0(\boldsymbol{H_0}\nabla)n_k, \tag{3}$$

where the density of electrical charges ρ is equal to $e(z_+n_+-z_-n_-+z_kn_k)$, e is the absolute value of an electron charge, $z_+$and z_- are valencies of cations and anions, z_ke is the charge of a magnetic polyion, ϵ is the dielectric permeability of a fluid, $\mu_0=1+4\pi\chi_0n_{k0}$ is the magnetic permeability of an initially homogeneous magnetic colloid, and χ_0 is the magnetic susceptibility of a single particle. Since the concentration of magnetic particles in a ferrovesicle is very small, the dependence of χ_0 on the concentration of magnetic polyions may be neglected. In the case when the magnetic polyions are absent the expression (1) coincides with the expression for the free energy of a electrolyte solution during its interaction with a charged membrane [11,12]. Let us calculate the variation of the free energy (1) accounting for Eqs. (2) and (3) and the boundary conditions on a charged membrane ($\boldsymbol{n}$ is the external normal to a membrane, σ is the surface charge density on a membrane):

$$-\epsilon\boldsymbol{n}\nabla\phi=4\pi\sigma, \tag{4}$$

$$\delta\psi^e=\delta\psi^v, \tag{5}$$

$$\boldsymbol{n}(\mu_0\delta\boldsymbol{H}^e+4\pi\chi_0\boldsymbol{H}_0n_k)=\boldsymbol{n}\delta\boldsymbol{H}^v, \tag{6}$$

where it is assumed that the exterior region of a vesicle surrounding a charged membrane contains magnetic particles. Quantities in the interior region of the vesicle are denoted by the index v, whereas on the outside by the index e. Since the dielectric permeability of water is much higher than that of a lipid bilayer, the so-called one-sided model with opaque boundary conditions is considered [Eq. (4)] when the electric field generated by the charges on an exterior side of a membrane does not penetrate the interior region [3,12]. Varying the free energy in relation to n_+, n_-, n_k and accounting for the electric and magnetic field equations (2), (3) and boundary conditions (4), (5), and (6) lead to

$$\delta F=\int\phi\delta\sigma dS+\int\delta n_+\left(k_BT\ln\frac{n_+}{n_{+0}}+ez_+\phi\right)dV\times\int\delta n_-\left(k_BT\ln\frac{n_-}{n_{-0}}-ez_-\phi\right)dV+\int\delta n_k\left(k_BT\ln\frac{n_k}{n_{k0}}+ez_k\phi-\chi_0\boldsymbol{H}_0\delta\boldsymbol{H}\right)dV \tag{7}$$

From relation (7) the following equilibrium conditions follow:

$$k_BT\ln\frac{n_+}{n_{+0}}+ez_+\phi=\text{const}, \tag{8}$$

$$k_BT\ln\frac{n_-}{n_{-0}}-ez_-\phi=\text{const}, \tag{9}$$

$$k_BT\ln\frac{n_k}{n_{k0}}+ez_k\phi-\chi_0\boldsymbol{H}_0\delta\boldsymbol{H}=\text{const}. \tag{10}$$

The last relation expresses the balance between thermal, electric, and magnetic forces acting on magnetic polyions. The concentrations of ions in an electrolyte solution and magnetic polyions can be expressed from relations (8), (9), and (10) as follows:

$$n_+=n_{+0}\exp\left(-\frac{ez_+\phi}{k_BT}\right), \tag{11}$$

$$n_-=n_{-0}\exp\left(\frac{ez_-\phi}{k_BT}\right), \tag{12}$$

$$n_k=n_{k0}\exp\left(-\frac{ez_k\phi}{k_BT}+\frac{\chi_0\boldsymbol{H}_0\delta\boldsymbol{H}}{k_BT}\right) \tag{13}$$

By linearizing the last relations with respect to the ratios of the electric and magnetic energies of particles to the thermal one we obtain the linear Poisson-Boltzmann model. Within the framework of this model the potential depends linearly on the charge density of a membrane. Thus, by carrying out the quasistatic charging process of a membrane in relation to its free energy in the surrounding electrolyte solution we obtain

$$F=\tfrac{1}{2}\int\phi\sigma dS \tag{14}$$

It should be pointed out that the obtained expression for the free energy of a membrane coincides with those used in different contexts previously, see, for example, [6,11,12].

III. FUNDAMENTAL SOLUTION OF COUPLED SET OF EQUATIONS FOR ELECTRIC AND MAGNETIC FIELDS

Introducing the potential of a magnetic field $\delta\boldsymbol{H}=\nabla\delta\psi$ and linearizing the relations (11)–(13) with respect to the energy ratios after substitution of the linearized expressions into equations (2) and (3), we arrive at the following set of coupled equations for the electric and magnetic field potentials

$$\left(\chi^2=\frac{4\pi e^2 z_+^2 n_{+0}}{\epsilon k_B T}+\frac{4\pi e^2 z_-^2 n_{-0}}{\epsilon k_B T}+\frac{4\pi e^2 z_k^2 n_{k0}}{\epsilon k_B T}\right),$$

$$\Delta\phi=\chi^2\phi-\frac{4\pi e z_k\chi_0 n_{k0}}{\epsilon k_B T}(\boldsymbol{H}_0\nabla)\,\delta\psi, \tag{15}$$

$$\mu_0\Delta\,\delta\psi=\frac{4\pi e z_k\chi_0 n_{k0}}{k_B T}(\boldsymbol{H}_0\nabla)\,\phi-\frac{4\pi\chi_0^2 n_{k0}}{k_B T}(\boldsymbol{H}_0\nabla)^2\,\delta\psi. \tag{16}$$

In the absence of a magnetic field the fundamental solution of the set (15), (16) reads

$$G_0=\frac{\exp\{-[\chi|(\boldsymbol{r}-\boldsymbol{r}')|]\}}{\epsilon|(\boldsymbol{r}-\boldsymbol{r}')|} \tag{17}$$

Since the concentration of magnetic particles is small in the expansion with respect to $\chi_0 H_0$ we will calculate the fundamental solution up to the first nonvanishing term. Thus, the first correction of the fundamental solution (17) will be found from the set of equations

$$\Delta\phi^1=\chi^2\phi^1-\frac{4\pi e z_k\chi_0 n_{k0}}{\epsilon k_B T}(\boldsymbol{H}_0\nabla)\,\delta\psi^1, \tag{18}$$

$$\mu_0\Delta\,\delta\psi^1=\frac{4\pi e z_k\chi_0 n_{k0}}{k_B T}(\boldsymbol{H}_0\nabla)\,\phi^0 \tag{19}$$

Accounting for the condition of the total electroneutrality according to which the total charge of the particles surrounding the fixed point charge is exactly equal to it whereas carries an opposite sign, the fundamental solution G up to the second-order term in $\chi_0 H_0$ as determined from set (18), (19) yields ($\boldsymbol{h}_0=\boldsymbol{H}_0/H_0$)

$$G=G_0+\frac{\lambda^2}{\mu_0\chi^2}\left[\frac{1}{\chi^2}(\boldsymbol{h}_0\nabla)^2\frac{\exp(-\chi r)}{r}+\frac{1}{2\chi}(\boldsymbol{h}_0\nabla)^2\exp(-\chi r)\right], \tag{20}$$

where

$$\lambda=\frac{4\pi e z_k\chi_0 n_{k0}}{\epsilon k_B T}H_0.$$

Since the fundamental solution G depends on the magnetic field strength and its orientation with the respect to the surface, the relation (20) allows to calculate the dependence of the curvature elasticity of a membrane on the magnetic field strength. The curvature expansion technique [6] will be used for this purpose in the next part of our work. To illustrate the physical meaning of the relations obtained here we shall calculate the fundamental solution in one-dimensional (1D) $G^{(1)}$ from the relation (20) for the case when a magnetic field is perpendicular to the charged plane. $G^{(1)}$ is expressed as follows:

$$G^{(1)}(z)=\int G(z\boldsymbol{e}_z,\boldsymbol{\rho})\,dS(\boldsymbol{\rho}), \tag{21}$$

where $\boldsymbol{\rho}$ is the radius vector to the point in a plane from the projection of the point at a distance z from the plane. By carrying out the integration we obtain

$$G^{(1)}(z)=\frac{2\pi}{\epsilon\chi}\exp(-\chi z)+\frac{2\pi\lambda^2}{\mu_0\chi^2}\frac{1}{2}\frac{1+\chi z}{\chi}\exp(-\chi z). \tag{22}$$

Of course, expression (22) for the fundamental solution in 1D case coincides with the expression of the fundamental solution found from Eqs. (15) and (16) which in that case reads

$$\frac{d^2\phi}{dz^2}=\chi^2\phi-\frac{4\pi e z_k\chi_0 n_{k0}H_0}{\epsilon k_B T}\frac{d\,\delta\psi}{dz}, \tag{23}$$

$$\frac{d}{dz}\left(\mu_0\frac{d\,\delta\psi}{dz}+\frac{4\pi n_{k0}\chi_0^2 H_0^2}{k_B T}\frac{d\,\delta\psi}{dz}-\frac{4\pi e z_k\chi_0 n_{k0}H_0}{k_B T}\phi\right)=0. \tag{24}$$

Solution of Eq. (24) gives

$$\frac{d\,\delta\psi}{dz}=\frac{\dfrac{4\pi e z_k\chi_0 n_{k0}H_0}{k_B T}}{\mu_0+\dfrac{4\pi n_{k0}\chi_0^2 H_0^2}{k_B T}}\phi$$

that as a result Eq. (23) can be rewritten as follows:

$$\frac{d^2\phi}{dz^2}=\left(\chi^2-\frac{\epsilon\lambda^2}{\mu_0+\dfrac{4\pi n_{k0}\chi_0^2 H_0^2}{k_B T}}\right)\phi. \tag{25}$$

Solution of Eq. (25) accounting for the corresponding boundary conditions yields

$$\phi=\frac{2\pi}{\epsilon\sqrt{\chi^2-\dfrac{\epsilon\lambda^2}{\mu_0+\dfrac{4\pi n_{k0}\chi_0^2H_0^2}{k_B T}}}}\times\exp\left(-z\sqrt{\chi^2-\dfrac{\epsilon\lambda^2}{\mu_0+\dfrac{4\pi n_{k0}\chi_0^2H_0^2}{k_B T}}}\right). \tag{26}$$

As it is possible to see from relation (26) at low magnetic-field values when the magnetodipolar interaction parameter $n_{k0}\chi_0^2H_0^2/k_BT$ determined by the mean distance between magnetic particles is small, the application of a magnetic field diminishes the effective screening parameter χ by the following value:

$$\frac{\epsilon\lambda^2}{2\mu_0\chi}, \tag{27}$$

which corresponds to the increase in the characteristic Debye screening length. Maximum diminution of the screening parameter is achieved at large magnetic-field values and equals $4\pi e^2 z_k^2 n_{k0}/\epsilon k_B T$, i.e., at large magnetic-field values screening is determined only by presence of ions in an electrolyte solution:

$$\chi^2 - \frac{4\pi e^2 z_k^2 n_{k0}}{\epsilon k_B T} = \frac{4\pi e^2 z_+^2 n_{+0}}{\epsilon k_B T} + \frac{4\pi e^2 z_-^2 n_{-0}}{\epsilon k_B T}$$

The last result can be explained in physical terms in the following way, the magnetic force acts on charged magnetic particles at their nonhomogeneous distribution near a charged membrane. The said force returns particles to a membrane, thus diminishing the contribution of polyions to the screening of the charge of a membrane. Since the strength of the interaction of charges on a membrane depends on the screening length, then due to its dependence on the magnetic field strength and its orientation the magnetic field will influence the elastic properties of a membrane as well. These effects are considered in the next part of the work. At the end of this part we would like to mention that expanding the fundamental solution for 1D [Eq. (26)] up to the first-order terms for λ^2 yields

$$G^{(1)} = \phi = \frac{2\pi}{\epsilon\chi}\exp(-\chi z) + \frac{\pi\lambda^2}{\mu_0\chi^2}\frac{1+\chi z}{\chi}\exp(-\chi z)$$

The last relation coincides with the result obtained by integration of the fundamental solution for three dimensions according to expression (21).

IV. CURVATURE ELASTICITY CONSTANTS DEPENDING ON THE MAGNETIC-FIELD STRENGTH

Above we have arbitrarily assumed that magnetic particles are located in the region surrounding a membrane. Other cases can be arrived at by simply rearranging algebraic signs. Calculation of the electrostatic energy of a membrane

$$F = \tfrac{1}{2}\int \sigma\phi\, dS$$

in the one-sided model can be reduced to the solution of the Neumann problem with the following boundary condition:

$$-\epsilon\frac{\partial\phi}{\partial n}\bigg|_+ = 4\pi\sigma \tag{28}$$

for a set of differential equations (15) and (16). Using the fundamental solution G this problem can be solved by writing the single-layer potential

$$\phi = \int G(\mathbf{r}-\mathbf{r}')\Sigma(\mathbf{r}')\,dS', \tag{29}$$

where the unknown function Σ using the theorem for the normal derivative of the single-layer potential

$$\epsilon\frac{\partial\phi}{\partial n}\bigg|_+ = -2\pi\Sigma + \epsilon P\int \frac{\partial G}{\partial n}(\mathbf{r}-\mathbf{r}')\Sigma(\mathbf{r}')\,dS'$$

can be found from the following boundary integral equation (P denotes the Cauchy principal value):

$$\Sigma = 2\sigma + \frac{1}{2\pi}\epsilon \mathrm{P}\int \frac{\partial G}{\partial n}(\mathbf{r}-\mathbf{r}')\Sigma(\mathbf{r}')\,dS'. \tag{30}$$

Equation (30) is useful for obtaining the expansion for the free energy in relation to the curvature of a surface [6]. Details of the calculation are given in the Appendix. Expression for the free energy up to the second-order terms in the curvature gives

$$\begin{aligned} F = F^0 &- \frac{2\pi\sigma^2\lambda^2 h_{0n}^2}{\mu_0\chi^2}\frac{1}{2\chi^2}\int\left(\frac{1}{R_1}+\frac{1}{R_2}\right)dS \\ &+ \int \frac{2\pi\sigma^2\lambda^2}{\mu_0\chi^2}\left[\frac{21 h_{0n}^2}{16\chi^3}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2 - \frac{3}{4\chi^3}\frac{1}{R_1R_2}\right. \\ &\left. - \frac{3}{4\chi^3}h_{0\xi}^2\frac{1}{R_1^2} - \frac{3}{4\chi^3}h_{0\eta}^2\frac{1}{R_2^2}\right]dS, \end{aligned} \tag{31}$$

where ξ,η axis of local Cartesian coordinates are directed along the principal directions of a curvature. The result given by expression (31) draws attention due to several interesting issues. The first one is the increase in the curvature elasticity constant depending on the angle between the normal to a membrane and a field. The value of the increase in the elasticity constant according to relation (31) equals

$$\Delta K_c = \frac{21}{4}\frac{\pi\sigma^2\lambda^2}{\mu_0\chi^2}\frac{h_{0n}^2}{\chi^3}. \tag{32}$$

The obtained result differs only by a numerical coefficient from the increase in the curvature elasticity constant that could be found from the expression of the electrical contribution to the curvature elasticity constant of the one-sided model [3,6]

$$\frac{3\pi\sigma^2}{2\epsilon\chi^3}$$

by substituting the effective value of the screening parameter found above when considering the charge screening of a planar membrane [9,10]:

$$\chi_e \simeq \chi - \frac{\epsilon\lambda^2 h_n^2}{2\mu_0\chi}, \tag{33}$$

which for the elasticity constant gives

$$\Delta K_c = \frac{9\pi\sigma^2\lambda^2 h_{0n}^2}{4\mu_0\chi^5}.$$

This value differs from the value found from the curvature expansion by a coefficient 7/3. It is interesting to note that the same procedure carried out for the Gaussian curvature elasticity constant gives exact result. Indeed, if, in the case when the field is normal to the membrane, we substitute χ by its effective value (33) in the expression for the Gaussian curvature elasticity constant [3,6] $\pi\sigma^2/\epsilon\chi^3$, we obtain the value decreased by $\Delta K_G = 3\pi\sigma^2\lambda^2/2\mu_0\chi^5$—the same that follows from the curvature expansion. It is important to remark that the decrease in the Gaussian curvature elasticity constant does not depend on the orientation of a field with respect to a membrane. The third effect that follows from our analysis is related to appearance of the anisotropy of the bending elasticity in a tangential plane of a membrane. The physical reason of this effect consists in the redistribution of magnetic polyions near a charged membrane due to the rise of magnetic forces at the bending of a membrane. We can derive the expression for the spontaneous curvature of a membrane from relation (31) accounting for the curvature elasticity constant $3\pi\sigma^2/2\epsilon\chi^3$ of a charged membrane in the one-sided model. By selecting a model in which the surface density of charges on either side of a membrane is identical, whereas the magnetic polyions are located only on the one side of a membrane, i.e., on the outside of the vesicle in the considered case, the total contribution to the surface density of the free energy of a membrane reads

$$\frac{1}{2}2\frac{3\pi\sigma^2}{2\epsilon\chi^3}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2+\frac{21\pi\sigma^2\lambda^2 h_{0n}^2}{8\mu_0\chi^5}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2 -\frac{\pi\sigma^2\lambda^2 h_{0n}^2}{\mu_0\chi^4}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)+\frac{2\pi\sigma^2\lambda^2}{\mu_0\chi^2} \times\left(-\frac{3}{4\chi^3}\frac{1}{R_1R_2}-\frac{3}{4\chi^3}h_{0\xi}^2\frac{1}{R_1^2}-\frac{3}{4\chi^3}h_{0\eta}^2\frac{1}{R_2^2}\right). \tag{34}$$

To interpret the conclusions following from relation (34) it should be taken into account that due to the presence of polyions only from one side of a membrane it already exhibits a spontaneous curvature, which could be expressed by the following relation [3,6] ($\chi_{e,i}$ are screening constants of the exterior and interior regions of a vesicle, respectively):

$$\frac{1}{R_0} = -\frac{2}{3}(\chi_e-\chi_i) \tag{35}$$

Accounting for expression of the screening constant of an electrolyte with magnetic polyions gives

$$\frac{1}{R_0} = -\frac{1}{3}\frac{z_k^2 n_{k0}}{z_+^2 n_{+0}+z_-^2 n_{-0}} \tag{36}$$

By introducing the spontaneous curvature according to relation (35), relation (34) can be written as follows

$$\frac{1}{2}K_c\left(\frac{1}{R_1}+\frac{1}{R_2}-\frac{1}{R_0}-\Delta\frac{1}{R_0}\right)^2+K_G\frac{1}{R_1R_2}-K_a h_{0\xi}^2\frac{1}{R_1^2} -K_a h_{0\eta}^2\frac{1}{R_2^2}, \tag{37}$$

where the anisotropic curvature elasticity modulus is defined as

$$K_a = \frac{3\pi\sigma^2\lambda^2}{2\mu_0\chi^5}, \tag{38}$$

$$K_c = 2\frac{3\pi\sigma^2}{2\epsilon\chi^3}+\Delta K_c, \tag{39}$$

$$K_G = 2\frac{\pi\sigma^2}{\epsilon\chi^3}-\Delta K_G, \tag{40}$$

but the change in the spontaneous curvature due to the action of a magnetic field can be expressed as follows:

$$\Delta\frac{1}{R_0} = \frac{\epsilon\lambda^2\epsilon^2 h_{0n}^2}{3\mu_0\chi} \tag{41}$$

Relation (41) gives the same result as obtained by substituting the effective value of the screening constant due the action of a magnetic field as calculated for a planar membrane (the small difference between χ and χ_i is neglected) in the relation (35):

$$\chi_e = \chi_i - \frac{\epsilon\lambda^2 h_n^2}{2\mu_0\chi_i}$$

Thus, the conclusions obtained within the framework of the planar model [9,10] concerning the influence of a magnetic field on the spontaneous curvature of a membrane coincides with that obtained from the curvature expansion. Relations for the spontaneous curvature of a membrane obtained for the case currently under our consideration when magnetic particles are located outside a vesicle just by the change in signs in relations (36) and (41) gives the corresponding relations for a more usual case when magnetic polyions lie inside a vesicle, i.e., in the absence of a magnetic field it is energetically more advantageous for a membrane to bend in the direction of the part that contains magnetic polyions due to stronger screening there. As an external field moves magnetic polyions against the membrane, the characteristic screening length for the sections of a membrane perpendicular to a field is increased and a membrane flattens. According to relation (41) respective diminishing in the spontaneous curvature can be calculated in accordance with the following relation:

$$\Delta\frac{1}{R_0}=-\frac{\epsilon\lambda^2h_{0n}^2}{3\mu_0\chi} \tag{42}$$

Since the change in the spontaneous curvature depends on the angle between a membrane and the direction of the magnetic field strength the spontaneous curvature of a membrane becomes anisotropic. Besides the anisotropy connected with the spontaneous curvature there is, as it follows from the relation (37), another anisotropy connected with the bending energy in the magnetic field having the components tangential to the membrane. The relation (37) shows that the energy of bending in the direction along the magnetic field lines is lower than that in perpendicular direction. Anisotropy of the bending energy is remarked also in DNA-cationic lipid complexes—the stacks of the membranes intercalated with DNA strands [13]. The simplest phenomenon by which the effects considered above could manifest themselves is connected with an oblate-prolate shape transition of a vesicle under the action of an external field reported in [9,10] and considered there within the framework of the planar approximation. Several simple relations for description of this effect follow in the next part. It should be noticed that due to the variation in the screening length in the presence of a field a change in the surface energy of a planar membrane takes place. Since the field effect depends on the angle between a field and the normal to a membrane it leads to the anisotropy of the surface tension. Since this effect is compensated by the local anisotropic deformation of a membrane it can be neglected in the following consideration of the prolate-oblate transition.

V. PROLATE-OBLATE TRANSITION IN EXTERNAL FIELD AND COMPARISON WITH EXPERIMENTAL DATA

A ferrovesicle with the membrane whose properties are not influenced by a magnetic field under the action of an external field elongates in the direction of a field [8]. In this case when a magnetic field modifies the interaction between a charged membrane and magnetic polyions situation becomes more complicated since the trend of elongation of a ferrovesicle along the field direction due to the diminishing demagnetizing-field effects now is competing with the trend of the flattening of a membrane near poles caused by the diminishing spontaneous curvature there. Additional contribution to the vesicle shape transformation can be attributed to the field-induced anisotropy of the bending modulus of a membrane. Complete analysis of the resulting phase diagram is quite complicated and will be the subject for further investigations. By using simple energetic arguments we intend to consider eventual competing mechanisms behind the ferrovesicle shape transformations. Let us assume that a ferrovesicle undergoes the axisymmetric shape transformation that in the spherical system of coordinates with the polar axis running along the field direction may be described by the following equation (r is the modulus of the radius-vector to a point on a vesicle, θ is the angle in the spherical system of coordinates):

$$r=R+\Delta\zeta=R+\frac{Re^2(3\cos^2\theta-1)}{6}, \tag{43}$$

where e^2 is positive if deformation leads to a prolate shape and negative for the case of the oblate deformation. The magnetic energy of a ferrovesicle assuming its ellipsoidal shape reads $(N(e)=[(1-e^2)/2e^3][\ln(1-e)/(1+e)-2e]$, which is the demagnetizing field coefficient, e is the eccentricity of a prolate ellipsoid)

$$E_m=-\frac{1}{2}\frac{\chi_0 n_{k0}H_0^2}{[1+(\mu_0-1)N(e)]}V \tag{44}$$

and for small deviations from the spherical shape $(e^2\ll 1)$ gives

$$E_m=-\frac{(\mu_0-1)H_0^2}{8\pi}V-\frac{(\mu_0-1)^2H_0^2}{4\pi}\frac{e^2}{15}V, \tag{45}$$

which describes the trend of the prolate deformation under the action of a field. It is possible to show that the contribution of the anisotropic part of the curvature elasticity modulus determined by relation (32) up to the first order in e^2 exactly equals zero. Another mechanism that induces the shape transformation in a ferrovesicle is related to the part of anisotropy of the curvature energy that is described by the last two terms in relation (31). This part of the curvature energy up to the first order in e^2 gives

$$E_a=\frac{16\pi^2}{5}\frac{\sigma^2\lambda^2}{\mu_0\chi^5}e^2 \tag{46}$$

and by introducing the parameter $a=z_k^2n_{k0}/(z_+^2n_{+0}+z_-^2n_{-0})$ characterizing the contribution of magnetic polyions to the screening constant and electrostatic contribution to the curvature elasticity modulus $K_c^e=3\pi\sigma^2/\epsilon\chi^3$ can be rewritten as follows:

$$E_a=\frac{16\pi}{15}K_c^e a Mo e^2. \tag{47}$$

The parameter $Mo=4\pi n_{k0}^2\chi_0^2H_0^2/\mu_0 n_{k0}k_BT$ characterizes the ratio of the magnetic and osmotic pressures and thus describes importance of magnetic forces in bringing about the change in the membrane charge screening under the action of a magnetic field. From relation (47) one could see that the anisotropy of the bending modulus favors an oblate shape $(e^2<0)$ and thus competes with the magnetic energy causing elongation of a ferrovesicle along the direction of a magnetic field. Even a more important contribution favoring an oblate shape arises from the anisotropy of the spontaneous curvature of a membrane. The curvature elasticity energy

$$\frac{1}{2}K_c^e\int\left(\frac{1}{R_1}+\frac{1}{R_2}-\frac{1}{R_0}-\Delta\frac{1}{R_0}\right)^2 dS \tag{48}$$

accounting for the following relations (χ_s is the screening constant of an outer electrolyte solution without magnetic polyions) yields

$$\frac{1}{R_0}=\frac{\chi_s a}{3}$$

and

$$\Delta\frac{1}{R_0}=-\frac{\epsilon\lambda^2 h_{0n}^2}{3\mu_0\chi_s}$$

up to the first-order terms for e^2 at shape deformation described by relation (43) when

$$h_n^2=\cos^2\theta-2e^2\cos^2\theta\sin^2\theta$$

at $\chi_s a\gg R^{-1}$ gives

$$E_c^{spon}=\text{const}+\pi K_c^e Moa^2(\chi_s R)^2\frac{32}{405}e^2. \tag{49}$$

Since $\chi_s R\gg 1$, the contribution of the anisotropy of the spontaneous curvature to the formation of oblate shape is more important than anisotropy of the bending modulus. As it follows from relations (45) and (49) there are two competing mechanisms leading in dependence on the physical conditions to the prolate or oblate vesicle deformation. By the comparison of the energy of magnetic interactions (45) with the energy value due to the variation in the spontaneous curvature [Eq. (49)] the following equation for the prolate-oblate transition line is obtained

$$\pi K_c^e Moa^2(\chi_s R)^2\frac{32}{405}=\frac{(\mu_0-1)^2}{4\pi}\frac{H_0^2 V}{15}. \tag{50}$$

Inserting the values of the physical parameters the last relation transforms into

$$R=\frac{8\pi\sigma^2}{3e\sqrt{4\pi\epsilon k_B T}\mu_0}\frac{z_k^4 n_{k0}}{(z_+^2 n_{+0}+z_-^2 n_{-0})^{5/2}} \tag{51}$$

In experiments described in [9,10] trisodium citrate is used as electrolyte. By introducing the notation for the electrolyte concentration $c=n_{-0}$ the condition of the electroneutrality $z_+n_{+0}=z_-n_{-0}$ allows one to express the critical radius of the oblate-prolate transition in dependence on the electrolyte concentration as follows:

$$R=\frac{8\pi\sigma^2}{3e\sqrt{4\pi\epsilon k_B T}\mu_0}\frac{z_k^4 n_{k0}}{[z_+(z_++z_-)]^{5/2}c^{5/2}}. \tag{52}$$

Several physical parameters are introduced in Eq. (52), surface charge density σ on the membrane, n_{k0} is concentration of the colloidal particles in the membrane. Since due to uncertainties of the colloidal particle entrapment at the vesicle preparation process n_{k0} varies considerably from a vesicle to vesicle, it must be determined for each vesicle separately. For this purpose magnetophoretic mobility of each ferrovesicle in the magnetic field of the given gradient was determined in [9,10] and magnetic susceptibility of the colloidal solution obtained. Due to the very low concentration

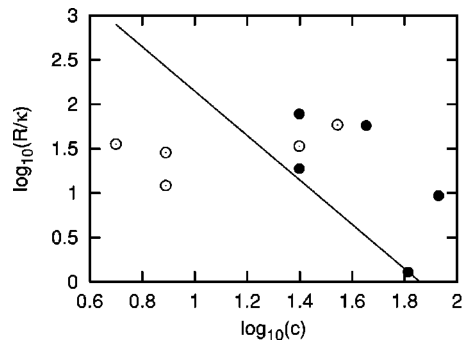

FIG. 1. Dependence of oblate-prolate transition upon electrolyte concentration. Open circles correspond to oblate shapes, filled circles to prolate shapes. Electrolyte concentration c in mmol/l.

of the ferroparticles the magnetic susceptibility can be expressed by the Langevin formula

$$\kappa=\frac{n_{k0}M_s^2 V_p^2}{3k_B T}, \tag{53}$$

where M_s is the saturation magnetization of ferromagnetic colloidal particles but V_p is the volume of a colloidal particle. Thus relation (52) reads

$$\frac{R}{\kappa}=\frac{8\pi\sigma^2 k_B T}{e\sqrt{4\pi\epsilon k_B T}M_s^2 V_p^2}\frac{z_k^4}{[z_+(z_++z_-)]^{5/2}c^{5/2}}. \tag{54}$$

Values for R/κ in electrolyte concentration dependence in logarithmic coordinates are given in Fig. 1. The following values of the physical parameters are used [9,10]: $M_s=360$ G, diameter of the particles $d=1.2$ nm, the colloidal particles have $z_k=25$ elementary charges and $\sigma=400$ esu/cm^2. The last value corresponds to the surface area per elementary charge $\Sigma=1.2\times10^{-12}$ cm^2, which means that about 1% of all lipids are charged. Experimentally measured values of R and κ tabulated in [9,10] are shown in Fig. 1 by filled (the prolate shape) and open (the oblate shape) circles. Although the data shown in Fig. 1 are rather scarce, nevertheless, they give the clear indication that the proposed model of the oblate-prolate transition is reasonable since the magnetic and electrostatic energies of the deformed vesicle corresponding to the measured values of R and κ are of the same order of magnitude in the range of the electrolyte concentration where oblate-prolate transition takes place. Accounting for many factors influencing the behavior of magnetic vesicles that does not seem to be trivial result. As it is possible to conclude from Fig. 1 that the data points reflect the trend of the prolate deformation if the electrolyte concentration or the radius of a vesicle grows. Besides we should remark that many more nontabulated data points given in [9,10], for example, in Fig. 11.6 of [9], correspond to that conclusion reasonably well. It should be remarked as well that for considered case of weak magnetic fields the condition of the prolate-oblate transition does not depend on magnetic field strength. Existing experimental results [9,10] are given for a single fixed value of the magnetic field strength 400 Oe.

VI. CONCLUSION

The influence of a magnetic field on the membrane charge screening by an electrolyte solution with magnetic polyions is considered by taking into account the magnetic field nonhomogenity arising due to the repulsion of charged magnetic particles from a charged membrane. It is shown that a magnetic field increases the effective screening distance for those parts of the membrane that are noncollinear to the magnetic field direction; maximum increase takes place for the parts that are normal to a magnetic field. It is demonstrated that due to the anisotropy of the effective charge screening distance, the elastic properties of a membrane become anisotropic. The curvature elasticity modulus due to increase in the screening length grows to reach the maximum value for those parts of a membrane that are normal to a field. The spontaneous curvature too becomes anisotropic, taking the minimum value for these parts of a membrane that are normal to a magnetic field. Thus, deformation of a ferrovesicle under the action of a magnetic field is determined by two competing mechanisms—elongation of a ferrovesicle along the magnetic field direction due to the tendency to diminish the demagnetization-field energy and to transform into an oblate shape due to the decrease in the spontaneous curvature for these parts of a membrane which are normal to an external field. The boundary in the parameter space between prolate and oblate shapes is found from the elastic properties of a membrane in a field, which are calculated by the curvature expansion of the free energy. The conclusions from the theoretical model are in qualitative and quantitative agreement with the available experimental results.

APPENDIX

Solving integral equation (30) by the iterative procedure we obtain the following curvature expansion for the function $\boldsymbol{\Sigma}$

$$\Sigma = 2\sigma + \epsilon \mathrm{P}\frac{1}{2\pi}\int \frac{\partial G}{\partial n}(\boldsymbol{r}-\boldsymbol{r}')2\sigma dS' + \frac{1}{2\pi}\epsilon \mathrm{P}\int \frac{\partial G}{\partial n}(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\epsilon \mathrm{P}\int \frac{\partial G}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')2\sigma dS''. \tag{A1}$$

As a result the free energy reads

$$F = \sigma^2\Bigg[\int dS\int G(\boldsymbol{r}-\boldsymbol{r}')dS' + \epsilon\int dS\int G(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS'' + \epsilon^2\int dS\int G(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G}{\partial n'} \times(\boldsymbol{r}'-\boldsymbol{r}'')dS''\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G}{\partial n''}(\boldsymbol{r}''-\boldsymbol{r}''')dS'''\Bigg]. \tag{A2}$$

The fundamental solution (20) can be expressed as follows:

$$G = G_0 + G_1,$$

where

$$G_1(\boldsymbol{r}) = (\boldsymbol{h}_0\nabla)^2 H(r) \tag{A3}$$

and the following expression is valid for the function $H(r)$

$$H = \frac{\lambda^2}{\mu_0\chi^2}\left[\frac{\exp(-\chi r)}{\chi^2 r} + \frac{1}{2\chi}\exp(-\chi r)\right]. \tag{A4}$$

By introducing the Cartesian set of coordinates with ζ axis along the external normal of a surface in the point with radius-vector $\boldsymbol{r}$ and ξ,η axes along the principal directions of the curvature, the surface equation near the point with the radius-vector $\boldsymbol{r}$ reads

$$\boldsymbol{r}' = \boldsymbol{r} + (\xi,\eta,\zeta),$$

where

$$\zeta = -\frac{\xi^2}{2R_1} - \frac{\eta^2}{2R_2}$$

(R_1, R_2 are the principal radiuses of the curvature). Expression (A3) for G_1 gives (H' denotes H derivative with respect to r)

$$G_1 = \frac{H'}{|\boldsymbol{r}-\boldsymbol{r}'|} - \frac{[\boldsymbol{h}_0(\boldsymbol{r}-\boldsymbol{r}')]^2}{|\boldsymbol{r}-\boldsymbol{r}'|^3}H' + \left(\frac{\boldsymbol{h}_0(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)^2 H''.$$

As a result the following expression of the fundamental solution up to the terms of the second order in the curvature is obtained ($\rho = \sqrt{\xi^2+\eta^2}$):

$$\begin{aligned} G_1 = {} & \frac{H'}{\rho} + \left(H'' - \frac{H'}{\rho}\right)\frac{(h_{0\xi}\xi + h_{0\eta}\eta)^2}{\rho^2} \\ & + \left(H'' - \frac{H'}{\rho}\right)\frac{2h_{0n}\zeta(h_{0\xi}\xi + h_{0\eta}\eta)}{\rho^2} \\ & + \left(\frac{H'}{\rho}\right)'\frac{1}{2}\frac{\zeta^2}{\rho} - \left(H'' - \frac{H'}{\rho}\right)\frac{(h_{0\xi}\xi + h_{0\eta}\eta)^2\zeta^2}{\rho^4} \\ & + \left(H'' - \frac{H'}{\rho}\right)\frac{h_{0n}^2\zeta^2}{\rho^2} + \left(H'' - \frac{H'}{\rho}\right)' \\ & \times\frac{1}{2}\frac{\zeta^2}{\rho}\frac{(h_{0\xi}\xi + h_{0\eta}\eta)^2}{\rho^2}. \end{aligned} \tag{A5}$$

Now, on the basis of expression for the free energy [Eq. (A2)] and relation (A4) the curvature expansion of the free energy may be obtained. Since the concentration of magnetic particles in a ferrovesicle is small, we will find this expansion up to the first-order terms in λ^2 ($d\Sigma$ denotes integration along the plane tangential to a membrane)

Up to the λ^2 the first-order terms in the curvature expansion are

$$F^{(1)}=\epsilon\sigma^2\int dS\int G_0(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_1}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS''$$
$$+\epsilon\sigma^2\int dS\int G_1(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_0}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS''. \tag{A6}$$

The first term in the last relation is readily transformed into

$$\int dS\int G_0(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_1}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS''$$
$$=\int dS\frac{1}{2}\left(\int dS'\frac{1}{2\pi}\mathrm{P}\int G_0(\boldsymbol{r}-\boldsymbol{r}')\frac{\partial G_1}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS''\right.$$
$$\left.+\int dS''\frac{1}{2\pi}\mathrm{P}\int G_0(\boldsymbol{r}-\boldsymbol{r}')\frac{\partial G_1}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS'\right)$$
$$=\int dS\frac{1}{2}\int G_0(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}$$
$$\times\int\left(\frac{\xi}{R_1}\frac{\partial G_1}{\partial\xi}+\frac{\eta}{R_2}\frac{\partial G_1}{\partial\eta}\right)dS''$$
$$=-\int dS\frac{1}{2}\int G_0(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)\int G_1 dS''. \tag{A7}$$

Then using the relations

$$\int d\Sigma\, G_0(\boldsymbol{r}-\boldsymbol{r}')=\frac{2\pi}{\chi},$$

$$\int d\Sigma''\frac{\partial G_0}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')=-\frac{\pi}{\chi}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)(\boldsymbol{r}'),$$

and

$$\frac{1}{2\pi}\int d\Sigma\, G_1=\frac{1}{2\chi}h_{0n}^2\frac{\lambda^2}{\mu_0\chi^2} \tag{A8}$$

as found for calculation of the fundamental solution for 1D case for the first-order contribution to the free energy we obtain

$$F^{(1)}=-\frac{2\pi\sigma^2\lambda^2h_{0n}^2}{\mu_0\chi^2}\frac{1}{2\chi^2}\int\left(\frac{1}{R_1}+\frac{1}{R_2}\right)dS'. \tag{A9}$$

In a similar way the next-order terms are calculated. Second-order terms read

$$I_1+\sigma^2\int dS\int G_1\left(\frac{1}{2}\frac{\xi^2}{R_1^2}+\frac{1}{2}\frac{\eta^2}{R_2^2}\right)d\Sigma$$
$$+\epsilon^2\sigma^2\int dS\left[\frac{1}{2\pi}\mathrm{P}\int G_0(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}\right.$$
$$\times\int\frac{\partial G_1}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS''\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_0}{\partial n''}(\boldsymbol{r}''-\boldsymbol{r}''')dS'''$$
$$+\frac{1}{2\pi}\mathrm{P}\int G_0(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_0}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS''$$
$$\left.\times\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_1}{\partial n''}(\boldsymbol{r}''-\boldsymbol{r}''')dS'''\right]+\epsilon^2\sigma^2\int dS\frac{1}{2\pi}\mathrm{P}$$
$$\times\int G_1(\boldsymbol{r}-\boldsymbol{r}')dS'\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_0}{\partial n'}(\boldsymbol{r}'-\boldsymbol{r}'')dS''$$
$$\times\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_0}{\partial n''}(\boldsymbol{r}''-\boldsymbol{r}''')dS''', \tag{A10}$$

where

$$I_1=\sigma^2\int dS\int d\Sigma\left[\frac{1}{2}\left(\frac{H'}{\rho}\right)'\frac{\zeta^2}{\rho}-\left(H''-\frac{H'}{\rho}\right)\right.$$
$$\times\frac{(h_{0\xi}\xi+h_{0\eta}\eta)^2\zeta^2}{\rho^4}+\left(H''-\frac{H'}{\rho}\right)\frac{h_{0n}^2\zeta^2}{\rho^2}$$
$$\left.+\left(H''-\frac{H'}{\rho}\right)'\frac{\zeta^2}{2\rho}\frac{(h_{0\xi}\xi+h_{0\eta}\eta)^2}{\rho^2}\right]. \tag{A11}$$

The third term in the last expression using the relations

$$\int\frac{\partial G_0}{\partial n''}(\boldsymbol{r}-\boldsymbol{r})dS'''=-\frac{\pi}{\epsilon\chi}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)(\boldsymbol{r}),$$

$$\int\frac{\partial G_0}{\partial n'}(\boldsymbol{r}-\boldsymbol{r})dS'=-\frac{\pi}{\epsilon\chi}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)(\boldsymbol{r}),$$

$$\int d\Sigma\, G_0(\boldsymbol{r}-\boldsymbol{r})=\frac{2\pi}{\epsilon\chi}$$

can be transformed into

$$-\sigma^2\epsilon^2\int dS\, G_0(\boldsymbol{r}-\boldsymbol{r})\int\left[\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_1}{\partial n''}(\boldsymbol{r}-\boldsymbol{r})dS'''\right.$$
$$\left.+\frac{1}{2\pi}\mathrm{P}\int\frac{\partial G_1}{\partial n'}(\boldsymbol{r}-\boldsymbol{r})dS'\right]\frac{1}{2\epsilon\chi}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)(\boldsymbol{r})dS''. \tag{A12}$$

By applying the relations

$$\frac{\partial G_1}{\partial n'} = \frac{\partial G_1}{\partial \zeta} + \frac{\xi}{R_1}\frac{\partial G_1}{\partial \xi} + \frac{\eta}{R_2}\frac{\partial G_1}{\partial \eta},$$

$$\frac{\partial G_1}{\partial n''} = -\frac{\partial G_1}{\partial \zeta},$$

the last expression can be rewritten as

$$\sigma^2 \int \frac{2\pi}{2\chi^2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2 dS'' \frac{1}{2\pi}\int G_1 d\Sigma.$$

To arrive at the contribution of the second-order terms in the curvature expansion, $(1/2\pi)\int G_1 d\Sigma$ from the expression (A8) and the following relations:

$$\begin{aligned}\int G_1\left(\frac{1}{2}\frac{\xi^2}{R_1^2}+\frac{1}{2}\frac{\eta^2}{R_2^2}\right)d\Sigma &= \frac{\pi}{R_1^2}\int_0^\infty \rho^2 H' d\rho + \frac{\pi}{R_2^2}\int_0^\infty \rho^2 H' d\rho + \pi h_{0\xi}^2 \\ &\quad \times \int_0^\infty \rho^2\left(H''-\frac{H'}{\rho}\right)\left(\frac{3\rho^3}{8R_1^2}+\frac{\rho^3}{8R_2^2}\right)d\rho + \pi h_{0\eta}^2 \\ &\quad \times \int_0^\infty \left(H''-\frac{H'}{\rho}\right)\left(\frac{\rho^3}{8R_2^2}+\frac{\rho^3}{8R_1^2}\right)d\rho, \end{aligned} \tag{A13}$$

$$\begin{aligned} I_1 &= \frac{2\pi}{64}\int_0^\infty\left(\frac{3}{R_1^2}+\frac{3}{R_2^2}+\frac{2}{R_1R_2}\right)\left(\frac{H'}{\rho}\right)'\rho^4 d\rho + \frac{2\pi}{4}h_{0n}^2 \\ &\quad \times \int_0^\infty\left(H''-\frac{H'}{\rho}\right)\rho^3\left(\frac{3}{8R_1^2}+\frac{3}{8R_2^2}+\frac{2}{8R_1R_2}\right)d\rho - 6\pi h_{0\xi}^2 \\ &\quad \times \int_0^\infty\left(H''-\frac{H'}{\rho}\right)\rho^3\left(\frac{5}{64}\frac{1}{R_1^2}+\frac{1}{64}\frac{1}{R_2^2}+\frac{2}{64}\frac{1}{R_1R_2}\right)d\rho \\ &\quad - 6\pi h_{0\eta}^2\int_0^\infty\left(H''-\frac{H'}{\rho}\right) \\ &\quad \times \rho^3\left(\frac{5}{64}\frac{1}{R_2^2}+\frac{1}{64}\frac{1}{R_1^2}+\frac{2}{64}\frac{1}{R_1R_2}\right)d\rho \end{aligned} \tag{A14}$$

are used. The following integrals appear in relations (A13) and (A14):

$$\int_0^\infty \left(\frac{H'}{\rho}\right)'\rho^4 d\rho = \frac{12}{\chi^3},$$

$$\int_0^\infty \left(H''-\frac{H'}{\rho}\right)d\rho = \frac{12}{\chi^3}.$$

After regrouping of terms the contribution of the second-order terms to the free energy reads

$$\int \frac{2\pi\sigma^2\lambda^2}{\mu_0\chi^2}\left[\frac{21h_{0n}^2}{16\chi^3}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2 - \frac{3}{4\chi^3}\frac{1}{R_1R_2} - \frac{3}{4\chi^3}h_{0\xi}^2\frac{1}{R_1^2} - \frac{3}{4\chi^3}h_{0\eta}^2\frac{1}{R_2^2}\right]dS.$$

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