Green function approach to fluctuation-induced interaction between polymer chains on membranes

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Abstract

This paper investigates the fluctuation-induced interaction between flexible ideal polymer chains on membranes. Tiny fluctuations happen in the vicinity of the curved surface of the membrane where the potential energy is in the lowest value. The fluctuations are governed by the Helfrich effective surface energy and the effective interaction energy. Under this viewpoint, the energy and the entropy corresponds to one-point and two-point Green function, respectively. The variations of surface energy and the leading-term interaction between chains are calculated with chains anchored to a membrane and strongly confined between two planar membranes in the three dimensional space.

1. Introduction

The Casimir force was originally discussed by Casimir in his pioneering work about quantum electrodynamics in 1948 [1]. Nowadays, there are more general extensions [2]. In fact, these forces are induced by fluctuations. There are two basic ingredients for fluctuation-induced interaction: (i) fluctuating medium; and (ii) external objects whose presence suppresses or modifies the fluctuations [3].

The membrane is a fluctuating medium. Some constraints imposed upon the fluctuations induce forces. In the previous studies, the constraints are introduced by rigid bodies, such as rods [4], colloids [5], or anisotropic particles [6].

The main aim of this paper is to investigate the constraints caused by a kind of non-rigid bodies, i.e. polymer chains, which constitutes an interesting problem in soft matter physics. At biologically-relevant length scales, many physicists think such interactions can play an important role in illuminating the structure and function of surfaces. There have been studies on the effect of flexible polymers on the shapes of the fluctuating membranes and fluctuation spectra [7, 8]. The theoretical description of membrane deformation caused by polymer chains is obtained and the finite-element numerical approach is developed. This kind of discrete-element theory and processing should be universal and valid. To test this method, two models are considered in the paper where chains are anchored to a membrane and strongly confined between two planar membranes in the three dimensional space. To obtain the scaling relationship between induced interaction potential and some physical factors to compare with further experimental results or observation phenomenon in biologically system, the polymer chains must be considered as Gaussian chains and the leading-term approximation is performed. Further, we adopt the free-particle assumption where the interactions only result from the collisions between membrane molecules and polymer monomers.

These interactions can be approximated by the effective field theory based on the effective interaction energy [9]. Taking into account the Helfrich surface energy, one can at least obtain a stationary phase approximation. The surface equation that satisfies stationary-phase condition can be derived from the principle of minimum potential energy through functional variation. This topic about membrane deformation caused by polymer chains or other soft matter has been addressed extensively, with Green function theory [10–13].

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2. The energy and one-point green function

The interaction between the i-th membrane molecule with position $\vec{z}_i$ and the k-th polymer monomer with position $\vec{r}_k$ is $U(|\vec{r}_k - \vec{z}_i|)$. $U(|\vec{r}_k - \vec{z}_i|)$ can be the collisional $\delta$-potential, the van der Waals potential, or the Coulomb potential. Hence, the effective potential from which the membrane molecule subjects reads

$$U_{\text{eff}}(\vec{z}_i) = \sum_{k=1}^{N} U(|\vec{r}_k - \vec{z}_i|).$$

(1)

Here, $N$ is the total number of polymer monomers. $(\cdots)_r$ denotes the conformational average (ensemble or thermal average). Since the position of polymer monomers are not fixed, the effective potential has to be calculated with all possible polymer conformations.

Generally, in the continuous Monge representation [14], $\vec{z} \equiv (x, y, z^z + h(x, y))$, $z^z$ is related to the choice of the coordinate system. $U_{\text{eff}}(\vec{z}_i) \equiv U'_{\text{eff}}(h_i)$. The continuous form of the total effective potential reads

$$U_{\text{eff}}(h(x, y)) \equiv \lim_{M \to \infty} U'_{\text{eff}}(h_1, \ldots, h_M).$$

(2)

Here, $M$ is the total number of membrane molecules, with $M$ being sufficiently large.

The Helfrich effective surface Hamiltonian is given by [15]

$$H_0 = \int_A \left[ \sigma_0 + \frac{\kappa_0}{2}(\kappa_1 + \kappa_2 - 2\kappa_0) + \kappa_0\langle \kappa_1 \kappa_2 \rangle \right] \sqrt{1 + (h_x)^2 + (h_y)^2} \, dx \, dy.$$  

(3)

For symmetric bilayer membranes, the spontaneous curvature $\kappa_0 = 0$, $\kappa_1$ and $\kappa_2$ are the local principle curvatures. For membranes, $h_x \equiv \frac{\partial h}{\partial x} \ll 1$, $h_y \equiv \frac{\partial h}{\partial y} \ll 1$, $\kappa_1 + \kappa_2 \approx \kappa_{xx} + \kappa_{yy}$. Ignoring the term with saddle-splay modulus $\kappa_0$, one obtains the quadratic approximation of the surface Hamiltonian, which reads

$$H_0[h(x, y)] \approx \sigma_0 A + \frac{1}{2} \int_A \left[ \sigma_0 ([h_x]^2 + [h_y]^2) + \kappa_0 ([h_{xx} + h_{yy}]^2) \right] \, dx \, dy.$$  

(4)

Here, $\sigma_0$ is the surface tension, and $\kappa_0$ is the bending modulus. $A$ is the frame (projected) area of the membrane.

Generally speaking, $A/M \to 0$, to make the functional differential, one can re-write the functional form of the total effective potential which reads,

$$U'_{\text{eff}}(h(x, y)) = \int U'_{\text{eff}}(h(x', y')) \delta(h(x, y) - h(x', y')) \, dx \, dy.$$  

(5)

The total effective potential reads

$$H[h(x, y)] \equiv U[h(x, y)] \equiv H_0[h(x, y)] + U'_{\text{eff}}[h(x, y)].$$  

(6)

Based on the principle of minimum potential energy, which means

$$\frac{\delta U}[h(x, y)] = 0,$$  

(7)

one obtains the Euler equation which reads

$$\{\sigma_0(h_{xx} + h_{yy}) - \kappa_0(h_{xxxx} + 2h_{xyy} + h_{yyyy})\} = \frac{\partial U'_{\text{eff}}(h(x', y'))}{\partial h(x', y')} \delta(x - x') \delta(y - y').$$  

(8)

The solution $h_0(x, y)$ of equation (8) is the surface equations satisfying the stationary-phase condition. The variation of surface energy caused by polymer chains is characterized by the physical quantity

$$\Delta H \equiv H_0[h_0(x, y)] - H_0[h(x, y)] \equiv 0.$$  

(9)

Considering the ensemble theory, one can require

$$h_0(x, y) = \langle h \rangle \equiv \int Dh \left[ \exp \left[ - \frac{H_0}{k_B T} \right] \exp \left[ - \frac{U'_{\text{eff}}(h)}{k_B T} \right] \right].$$  

(10)

$h_0(x, y)$ is a one-point Green function, which corresponds to the energy.

To solve equation (8), one has to make the discretization with $\Delta x = \Delta y \approx D$. The density of membrane molecules is $\frac{1}{A} \equiv \frac{M}{A}$. For the sake of convenience one can introduce a force function $f(h) \equiv \frac{\partial U'_{\text{eff}}(h)}{\partial h}$. On the other hand, one also must know the force function $f(h)$ which is dependent of the polymer conformations. Thus solving equation (8) is bound to self-consistence as long as there exists the interaction between the polymer chains with the membrane, even though in the simplest case the surface described by the function $h(x, y)$ only plays a role of the boundary condition constraining the polymer conformations. The self-consistent field equation reads
\[
\{\sigma_0(h^{[0]}_{xx} + h^{[0]}_{yy}) - \kappa_0(h^{[0]}_{xxx} + 2h^{[0]}_{xyy} + h^{[0]}_{yyy})\} = f(h(\mathbf{x}', \mathbf{y}')) \delta(\mathbf{x} - \mathbf{x}') \delta(\mathbf{y} - \mathbf{y}') .
\] (11)

One can think \(h^{[0]}_{i} = 0\). If \(h^{[n]}_{i} = h^{[n]}\), namely \(h^{[n]}_{i} = h_{0i}\), here the index \([n]\) refers to the order of the iteration. One can obtain the solution of equation (8). The iteration provides a numerical method to seek for the more precise solution in the further research.

In many cases, the deflection terms, including \(h_{xxx}, h_{xyy}, h_{yyy}\), can be ignored, the Euler equation is further simplified to
\[
\sigma_0(h_{xx} + h_{yy}) = \frac{\partial U'_\text{eff}(h(\mathbf{x}', \mathbf{y}')))}{\partial h(\mathbf{x}', \mathbf{y}')} \delta(\mathbf{x} - \mathbf{x}') \delta(\mathbf{y} - \mathbf{y}') \approx \frac{f(h)}{D^2} .
\] (12)

The equation can be interpreted as a Young-Laplace equation which is
\[
\Delta P = \sigma_0(\zeta_1 + \zeta_2) .
\] (13)

Here, \(\Delta P\) is the difference of pressure, which is equivalent to \(\frac{d}{dx} \frac{\partial f(h)}{\partial h}\). Based on the local force equilibrium, one obtains the discrete-element equation:
\[
\sigma_0(\{h_{0}^{i+1,j} + h_{0}^{i-1,j} - 2h_{0}^{ij} + (h_{0}^{i+1,j} + h_{0}^{ij} - 2h_{0}^{ij})\}) = f(h_{0}^{ij}) ,
\] (14)
if \(h_x \ll 1, h_y \ll 1\). Hence, the relative surface energy \(\Delta H\) reads
\[
\Delta H \approx \frac{\kappa_0}{2} \int (h_{xx} + h_{yy})^2 dx dy = \frac{\kappa_0}{2\sigma_0 D^4} \int f(h) dx dy .
\] (15)

Because of \(f(h)|_{h = h_0} = f(h)|_{h=0} + O(h_0) \approx f(0)\), one obtains the surface energy of the membrane described as
\[
\Delta H \approx \frac{\kappa_0 M^2 f(0)^2}{2\sigma_0 A} .
\] (16)

In this paper, the interactions between polymer monomers are ignored. Further, the possibility distribution \(p(x_0, y_0)\) at \(x, y\)-orientation is a uniform distribution. As a demonstration, we only consider the case of \(\delta\)-potential. \(U[|\mathbf{r} - \mathbf{z}_i|] = \lambda \delta(|\mathbf{r} - \mathbf{z}_i|)\), where \(\lambda\) is the intensity \([\lambda] = [\text{energy}] [\text{length}]^3\). \(U'_\text{eff}(h(\mathbf{x}, \mathbf{y}))\) satisfies
\[
U'_\text{eff}(h_i) = \int p(z_0)[\lambda \sum_{k=1}^{N} \delta(|z_i^N + h_i - z_i|) P_{z_0}(z_{i1}, z_{i2}, \cdots, z_{IN})] d\mathbf{z}_0 \int_{-\infty}^{\infty} \frac{dz_{i0}}{b} .
\] (17)

Here, \(b\) denotes the statistical segment length between two nearest monomers. A derivation of \(U'_\text{eff}(h_i)\) will be shown in the appendix. Generally speaking, \(U'_\text{eff}(h(\mathbf{x}, \mathbf{y}))\) is a power series in \(h(\mathbf{x}, \mathbf{y})\) with some coefficients in a specific model. Because the zero point of energy is not important, we have
\[
U'_\text{eff}(h_i) = f(0) h_i + o(h) .
\] (18)

## 3. The entropy and two-point Green function

Based on the above Hamiltonian \(H[h(\mathbf{x}, \mathbf{y})]\), the free energy of fluctuation-induced interaction of two monomers(A, B) on membrane \([9]\) reads
\[
\mathcal{H} = -k_\text{B} T \log \int Dh \exp \left[ -\frac{H_0}{k_\text{B} T} \right] \exp \left[ \frac{U'_\text{eff}}{k_\text{B} T} \right] = -k_\text{B} T \log \langle \exp \left[ \frac{U'_\text{eff}}{k_\text{B} T} \right] \rangle .
\] (19)

Here, \(\langle (\cdots) \rangle\) denotes the associated Gaussian average. \(U'_\text{eff}\) is a function of \(h_i\), which usually could be expanded into power series of \(h_i\) in order to take advantage of Green-function theory. The free energy is related to entropy which can describes the fluctuation. \(N\)-point Green function can be expressed into one-point and two point Green functions. The two-point Green function satisfies
\[
g(\tilde{\mathbf{z}}_{i0} - \tilde{\mathbf{z}}_{j0}) = \langle h(\tilde{\mathbf{z}}_{i0}) h(\tilde{\mathbf{z}}_{j0}) \rangle \approx \langle h(\tilde{\mathbf{z}}_{i0}) h(\tilde{\mathbf{z}}_{j0}) \rangle ,
\] (20)
here \(\tilde{\mathbf{z}} \equiv (\mathbf{\tilde{z}}, \mathbf{\tilde{z}})\), \(\mathbf{\tilde{z}}_i\) and \(\mathbf{\tilde{z}}_j\) correspond to the projected coordinates of the monomer A and B on the membrane. In the paper, only considering the collision interaction and ignoring the influence of other monomers, one can have the effective potential between the monomer A and B that reads
\[
U'_\text{eff} = U'_A + U'_B \approx f(0) h(\tilde{\mathbf{z}}_{i0}) + f(0) h(\tilde{\mathbf{z}}_{j0}) .
\] (21)
Therefore, one can obtain the leading-term approximation of the fluctuation-induced interaction \(V^{AB}\) between the monomer A and B only when both are contacted with the membrane \([9]\). It reads
To adopt the method in [9], one must know the probability of the \( k \)th monomer at the position \( \tilde{\rho}_k \) on the membrane

\[
P_k(\tilde{\rho}) \equiv \int_{\rho_k}^{\rho_k+b} \int_{\rho_{k'}}^{\rho_{k'}+b} \int_{h_0(\rho_k, \rho_{k'})}^{h_0(\rho_k, \rho_{k'})-b} Q_k(T) \frac{d^3\rho}{b^3}.
\]

Therefore, one could obtain the fluctuation-induced interaction between two chains which reads

\[
V_{12} = \int_A \frac{d^2\tilde{\rho}_1}{D^2} \int_A \frac{d^2\tilde{\rho}_2}{D^2} \{ \sum_{k=1}^{N} \sum_{k'=1}^{N} V^{AB}(\tilde{\rho}_k, \tilde{\rho}_{k'}) \}
\]

In the case of a tension dominated surface \((\kappa_0 \approx 0)\), the two-point Green function reads

\[
g(\tilde{\rho}_k - \tilde{\rho}_{k'}) = \frac{k_b T}{4\pi\kappa_0} \ln[(\tilde{\rho}_k - \tilde{\rho}_{k'})^2/D^2],
\]

In the general case of a bending dominated surface \((\sigma_0 \approx 0)\), the two-point Green function reads

\[
g(\tilde{\rho}_k - \tilde{\rho}_{k'}) = \frac{k_b T}{16\pi\kappa_0} \ln[(\tilde{\rho}_k - \tilde{\rho}_{k'})^2/D^2].
\]

The applications of above formulas will be shown in the next section.

4. Applications

4.1. Case I: anchored to a membrane

Substantially, as shown in figure 1, the case is equivalent to the problem of diffusion in a half-space [16],

\[
h_0(x, y) \approx 0, \quad p(z_0) = \delta(z_0).
\]

Assuming the \( z > 0 \) or the \( z < 0 \) half-space diffusion and \( z^* = 0 \), one obtains the probability distribution \( Q^*_k(z) \), that reads

\[
Q^*_k(z) = \frac{|z|}{2Nb} \exp\left\{-\frac{z^2}{2Nb^2}\right\}.
\]
Considering $\sum_{k=1}^{N} \frac{1}{N} \approx \ln N$ and $|h(\kappa, \rho)|$ being tiny, one gets

$$U^{\text{eff}}(h) \approx \frac{\kappa h_0}{2b^4} \ln N,$$

and

$$f^I(0) = \pm \frac{\lambda \ln N}{2b^4}.$$

The variation of surface energy caused by polymer chains anchored to a membrane reads

$$\Delta H^I = \frac{\kappa_0^2 M D^3 \ln^2 N}{8 \sigma_0^2 b^8}.$$

The probability of the $k$th monomer at the position $\rho(\kappa, \rho)$ on the membrane reads

$$P^I_k(\rho) \approx \frac{1}{4MK}.$$

The interaction of polymer chains anchored to a membrane reads

$$V_{12} = - \text{Sign}(Ch_1Ch_2) \frac{\lambda^2 \ln^2 N}{64k_B T M^2 b^8} \left( \int_{A} d^2 \rho_1 \int_{A} d^2 \rho_2 G(\rho_1 - \rho_2) \right).$$

Here, if the two chains are on the same side of the membrane, $\text{Sign}(Ch_1Ch_2) = +1$. If the two chains are on different sides of the membrane, $\text{Sign}(Ch_1Ch_2) = -1$.

(i) In the case of $\kappa_0 = 0$, the mean potential of polymer chains anchored to a membrane reads

$$V_{12} = \text{Sign}(Ch_1Ch_2) \frac{\lambda^2 \ln^2 N \ln M}{512 \sigma_0 b^8}.$$

(ii) In the case of $\sigma_0 = 0$, the mean potential of polymer chains anchored to a membrane reads

$$V_{12} = - \text{Sign}(Ch_1Ch_2) \frac{\lambda^2 MD^2 \ln^2 N \ln M}{4096 \kappa_0 b^8}.$$

### 4.2. Case II: strongly confined between two planar membranes

As shown in figure 2, assuming the separate distance of two planar membranes $L < 2\pi R_g$ and $L > 2b$, one can think the polymer strongly confined by the membranes [17]. Here, $R_g^2 = \frac{NZ^2}{6}$ is the mean square radius of gyration for a Gaussian chain in bulk. This assumption is usually reasonable in the bio-membrane systems.

Considering $z^* = \pm \frac{\pi}{2}$, and $p(z_0) = \frac{1}{\pi}$, one gets the probability distribution that reads [17]
membranes from above analyses, although the leading-term approximation is made, where the interactions between polymer chains are very different from that between rigid bodies \[4 - 6\]. There are some natural features listed as follows: (i) The Euler equation is non-linear. (ii) It is a nonlocal and long range interaction. Besides, it strongly depends on the boundaries which are closely related to the behavior of chains. (iii) There may not exist a superposition principle, even if the potential between membrane molecules and polymer monomers possesses the superposition property. (iv) The interaction between polymer chains may be an attractive potential \(V_{12} < 0\) or a repulsive potential \(V_{12} > 0\). Moreover, it is independent of the attraction \(\lambda < 0\) or repulsion \(\lambda > 0\) between membrane molecules and polymer monomers, owing to existence of \(f(0)^2\).

The interaction originated in the variation of entropy, which is closely related to fluctuations. In the paper, only the leading-term approximation is made, where the fluctuations are averaged and described as deformation of surface. Beyond mean field theory, higher order resulting from the interaction between the polymers needs further investigation.

The polymer-membrane problem is important and complex. In biological systems, the membranes are almost everywhere. Biological membranes are complex entities formed by several kinds of biochemical molecules. Their basic structure is a lipid bilayer. Such a purely lipidic membrane can have phase-separated domains, some of them being liquid disordered, some of them being in the more condensed liquid-order phase, and some others being in a solid like gel phase. Moreover, bio-membranes include different kinds of associated DNA and proteins. These DNA and proteins are not only functional in order to communicate with other cells or cell organelles, but they are also involved in membrane shaping. On the other hand, how the structures and the functions of some DNA and protein macromolecules, as the polymer chains on membranes, are affected by the membranes? It keeps an open problem. The conformational behaviour of membranes continues to provide many challenging problems. As far as the shape fluctuations are concerned, there is no clear understanding of the large-scale behaviour of polymer chains on membranes. In the soft matter physics, the fluctuation-induced

\[
Q_N^L(\varepsilon) = \frac{\pi b}{2L} \cos \frac{\pi \varepsilon}{L}.
\]

For \(\varepsilon^* = -\frac{L}{2}\), one has

\[
U_{\text{eff}}^{0ii}(\eta_i) = \frac{\pi \lambda N}{2Lb^2} \sin \frac{\eta_i}{L} \approx \frac{\pi^2 \lambda N}{2L^2 b^2} \eta_i.
\]

\[
f^{ii}(0) = \frac{\pi^2 \lambda N}{2L^2 b^2}.
\]

For \(\varepsilon^* = \frac{L}{2}\), one has the same result.

The variation of the surface energy caused by polymer chains strongly confined between two planar membranes

\[
\Delta H^{ii} = \kappa_0 \lambda^2 \pi^4 MD^2 N^2 \frac{1}{4\sigma^2 L^4 b^4}.
\]

The probability of the \(k\)-th monomer at the position \(\vec{\rho}(\rho_1, \rho_2)\) on the membrane reads

\[
p^{ii}(\vec{\rho}) \approx \frac{\pi b}{2ML}.
\]

The interaction of polymer chains strongly confined between two planar membranes reads

\[
V_{12} = -2 \times \frac{\pi^6 \lambda^2 N^4}{16k_0 T M^2 L^4 b^2} \left( \int \frac{d^2 \hat{\rho}_1}{D^2} \int \frac{d^2 \hat{\rho}_2}{D^2} G(\hat{\rho}_1 - \hat{\rho}_2) \right).
\]

(i) In the case of \(\kappa_0 = 0\), the mean potential of polymer chains strongly confined between two planar membranes reads

\[
V_{12} = \frac{\pi^6 \lambda^2 N^4 \ln M}{64\sigma^2 L^4 b^2}.
\]

(ii) In the case of \(\sigma_0 = 0\), the mean potential of polymer chains strongly confined between two planar membranes reads

\[
V_{12} = -\frac{\pi^6 \lambda^2 MD^2 N^4 \ln M}{512\kappa_0 L^4 b^2}.
\]

5. Conclusion and discussion

From above analyses, although the leading-term fluctuation-induced interaction has only been calculated by the Green function method, one can understand that the interactions between polymer chains are very different from that between rigid bodies \(4-6\). There are some natural features listed as follows: (i) The Euler equation is non-linear. (ii) It is a nonlocal and long range interaction. Besides, it strongly depends on the boundaries which are closely related to the behavior of chains. (iii) There may not exist a superposition principle, even if the potential between membrane molecules and polymer monomers possesses the superposition property. (iv) The interaction between polymer chains may be an attractive potential \((V_{12} < 0)\) or a repulsive potential \((V_{12} > 0)\). Moreover, it is independent of the attraction \((\lambda < 0)\) or repulsion \((\lambda > 0)\) between membrane molecules and polymer monomers, owing to existence of \(f(0)^2\).

The interaction originated in the variation of entropy, which is closely related to fluctuations. In the paper, only the leading-term approximation is made, where the fluctuations are averaged and described as deformation of surface. Beyond mean field theory, higher order resulting from the interaction between the polymers needs further investigation.
interaction will play a fundamental role in deciding the phase structure of these polymer chains which can decode some life behaviors. However, because of its many-body property, this kind of interaction is hard to evaluate.

The interactions between the polymer monomers and membrane molecules simultaneously affect the conformations of the polymer chains and the fluctuation of the membranes. The behaviors have to be self-consistent. The aim of this paper is to review the theoretical approaches to study the polymer dynamics in different circumstances due to the membrane surface. Based on the Euler equation and the Fokker-Planck equation, a set of self-consistent equations is provided in this paper. The important bridge—the force function is explained and calculated. Further, the relations between the surface energy with the one-point Green function and the fluctuation-induced interaction with two-point Green function are discussed. As some demonstrations, this paper applies these methods to two common simplified models where the polymer chains are anchored on a membrane and strongly confined between two planar membranes. We focus on the explanation of chain interactions for interface fluctuations, which have been used to study polymer dynamics.

We look forward to the confirmations of these theories and results. This work sets the first step to understand the polymer dynamics on the membranes. In the future, one can contribute to the realization of the numerical method and higher order approximations. From a physical point of view, to understand the life deserves exploring.

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Appendix. Behavior of chains and the effective potential

Based on the random walk theory of 3-dimensional space [18], one obtains the number of possible paths (number of microstates) $W(\bar{r}_0; \bar{r})$, that reads

$$W(\bar{r}_0; \bar{r}) = 3^N G_s(\bar{r}_0; \bar{r}).$$

(A.1)

Here, $G_s(\bar{r}_0; \bar{r})$ satisfies the Fokker-Planck equation [19]:

$$-\frac{\partial G_s(\bar{r}_0; \bar{r})}{\partial \bar{r}} = \frac{b^2}{6} \nabla^2 G_s(\bar{r}_0; \bar{r}) + \frac{U(\bar{r})}{k_B T} G_s(\bar{r}_0; \bar{r}).$$

(A.2)

Here, $b$ is the distance of nearest polymer monomers, $k_B$ the Boltzmann constant, $T$ the temperature. For any fluctuation $h(x, y)$, $U(\bar{r}) = \sum_{i=1}^{M} U(|\bar{r} - \bar{z}_i|)$, the initial condition reads

$$G_s(\bar{r}_0; \bar{r}) = b^2 e^{b^2(|\bar{r} - \bar{r}_0|)} \to \delta_{\bar{r}_0, \bar{r}}.$$  

(A.3)

Here, $\delta_{\bar{r}_0, \bar{r}}$ satisfies a certain probability distribution $p(\bar{r}_0)$. The boundary condition (Dirichlet) reads

$$G_s(\bar{r}_0; \bar{r} \in S_{h(x,y)}) = 0.$$  

(A.4)

Here, $S_{h(x,y)}$ is the boundary established by the surface equation $h(x, y)$.

The fluctuation $h_0(x, y)$ most possibly happens. Obviously, solving $h_0(x, y)$ is a self-consistent procedure. At the beginning, $h_0^{(0)}(x, y) = 0$ is usually utilized to solve the Fokker-Planck equation in these iterations. $h_0^{(n)}(x, y) = h_0(x, y)$.

Therefore, the probability distribution $Q_N(\bar{r})$ reads

$$Q_N(\bar{r}) = \frac{W(\bar{r})}{Z} = \frac{\int_{\Omega_0} G_s(\bar{r}_0; \bar{r}) p(\bar{r}_0) d^3\bar{r}_0}{\int_{\Omega} \int_{\Omega_0} G(\bar{r}_0; \bar{r}) p(\bar{r}_0) d^3\bar{r}_0 d^3\bar{r}}.$$  

(A.5)

The transition probability $Q_{n+1}(\bar{r}'; \bar{r})$ satisfies

$$Q_{n+1}(\bar{r}') = \int Q_n(\bar{r}') Q_{n+1}(\bar{r}'; \bar{r}) \frac{1}{b^2} d^3\bar{r}' .$$

(A.6)

One only needs to take into account the conformational probability of the $z$-orientation $P_{z}(\{z_1, z_2, \ldots, z_N\})$, that reads
\[ P_{z_0}([z_1, z_2, \cdots, z_N]) = Q_{z_0;1}(z_1) \prod_{\alpha=1}^{N-1} Q_{z_0;1}(z_{\alpha+1}). \]  

(A.7)

Hence, the conformational average reads

\[ \langle X \rangle_2 \equiv \int p(z_0) X P_z([z_1, z_2, \cdots, z_N]) dz_0 \prod_{\alpha=1}^{N} \frac{dz_\alpha}{b}. \]  

Therefore, \( U_{\text{eff}}^*(h(x,y)) \) satisfies

\[ U_{\text{eff}}^*(h_i) = \int p(z_0) \left\{ \lambda \sum_{k=1}^{N} \delta(|z_k^* + h_i - z_k|) \right\} P_z([z_1, z_2, \cdots, z_N]) dz_0 \prod_{\alpha=1}^{N} \frac{dz_\alpha}{b}. \]  

(A.9)

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