Snaky Conformations of Strongly Adsorbed (2D) Comblike Macromolecules

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ABSTRACT: We study the decay of orientational correlations between segments, the gyration radius, and the Kuhn segment length of a 2D comblike macromolecule (brush) with random distribution of the side chains with respect to the backbone. This distribution is assumed to be fixed and controlled by an initial conformation of the molecule in 3D. Both “frozen’’ (quenched) fluctuations of left−right positions of the side chains and the thermodynamic fluctuations of the whole molecule in 2D are taken into account. We show that extra bending of the brush due to the locally uneven number of left and right side chains promotes the decay of the orientational correlation function, and reduces the gyration radius. The correlation function has a nonmonotonous decay with one minimum.

1. Introduction

It is well-known that the Gaussian chain with a persistent flexibility mechanism has an exponential decay of orientational correlation function, i.e., a thermodynamic average of the cosine of the angle $\theta(s)$ between two tangents to the chain separated by contour length s is $\langle\cos\theta(s)\rangle = \exp(-s/\lambda_p)$.[1] Here λ_p is the persistence length which characterizes the length scale of the decay. Recently, it was shown that long range correlations in semidilute solutions and melts of linear chains are responsible for an unexpected, scale free power-law regime of the orientational correlation function, $\langle\cos\theta(s)\rangle \sim s^{-\omega}$, $\omega > 1$.[2] Furthermore, the nonexponential decay is predicted for linear chain in a Θ-solvent.[3]

In the present paper, we report about the unusual form of the correlation function of single comblike macromolecule strongly adsorbed on a plane surface (2D chain). This function has a nonmonotonous decay with one minimum corresponding to the negative value of the correlation function. Such behavior is a result of extra curvature of the macromolecule induced by its adsorption. The gyration radius and the Kuhn segment length are analyzed.

Comblike macromolecules, sometimes called bottle-brushes, are polymers consisting of a long flexible main chain (backbone) and densely grafted side chains.[4,5] The peculiarity of such molecules is an enhanced stiffness induced by interactions between the side chains.[6−9] Relying on the strong dependence of the induced stiffness on the length of the side chains and on their grafting density, conformation of the brush molecules in a good solvent can vary from a rodlike to the coiled one.

Strong adsorption of the brushes on a flat surface, when most of the side chains attain two-dimensional conformations, diversifies behavior of the molecules. In particular, stiffness of the brushes becomes more pronounced due to the stretching of the adsorbed side chains,[10−12] and the break of the local cylindrical symmetry of the macromolecule, i.e., formation of “left” and “right” (with respect to the backbone) side chains, is responsible for a number of effects. If the adsorbed side chains are allowed to be redistributed between left and right sides of the brush (usually this process requires strong external action[13,14]), spontaneous curvature of the molecule occurs.[15−19] This curvature is driven by locally uneven distribution of the side chains that reduces the total free energy of the molecule. If an excess of the side chains is formed only in one side of the brush and this asymmetry is fixed along the whole molecule (the so-called segregating side chains), various conformations, such as spirallike[10] or horseshoe,[20] can be stable.

It has been shown recently that conformations of strongly adsorbed brush molecules consisting of a poly(2-hydroxyethyl methacrylate) backbone and poly(*n*-butyl acrylate) (pBA) side chains strongly depend on the conditions of adsorption.[21] In particular, the molecules which are adsorbed on mica from a good solvent (chloroform), reveal elongated conformations whereas the spreading of the molecules on the surface from a 3D globular state gives much more compact conformations. In the present paper, we propose a theory which quantifies possible conformations of strongly adsorbed (2D) comblike macromolecules. For this purpose we use a model of the brush with random distribution of the side chains with respect to the backbone. This model is able to describe the observed variety of the molecular conformations.

2. Model

Once a comblike macromolecule is adsorbed on a flat surface, the thermodynamic fluctuations are not able to change the distribution of the side chains with respect to the backbone, if attraction of the chains to the surface is very high. Indeed, a flip of one side chain requires simultaneous desorption and further readsorption of all monomer units of the chain. The thermal energy is too small to overcome the high attraction energy. To do it, some external action is needed. For example, lateral compression of a monolayer of the brush molecules on a liquid surface[13] or treatment of the molecules on a solid surface by various vapors[14] are able to change the position of the side chains. On the other hand, the thermodynamic fluctuations of the side chains in 2D are not suppressed and provide an equilibrium conformation of the molecule (at the given left−right distribution of the side chains). It is this regime of adsorption that will be discussed below.

Let us assume that the local distribution of the side chains with respect to the backbone of strongly adsorbed brush mole-

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cule and, consequently, its 2D conformation is determined by initial conformation of the brush in solution (3D). If the molecule is adsorbed from a good solvent, where it possesses elongated rodlike or coiled conformation, one can expect that the distribution is close to the symmetric one, and local deviations of the fraction of the side chains from the symmetric case are small. If the molecule has a globular conformation in the solution, the strong adsorption may lead to the formation of pancakelike globule with a curved conformation of the molecule. This conformation is expected to have locally asymmetric distribution of the side chains, i.e., the fraction of left (right) side chains is highly fluctuating parameter. Below we will analyze the case of weakly asymmetric distribution of the side chains.

The 2D brush molecule is considered to be incompatible with the surrounding medium (solvent or air), i.e. attractive forces dominate between monomer units of the side chains and the backbone. Minimization of the area of polymer−solvent contacts results in a dense packing of monomer units of the brush (2D melt). N and M denote the numbers of the segments in the backbone and the side chain, respectively, $N \gg M \gg 1$; a is the size of the segment. We consider densely grafted polymer brushes, i.e., the side chains are attached to each segment of the backbone and their number is equal to N.

Local excess of the side chains in one side of the backbone induces bending of the brush molecule.[10] The free energy of the bent brush per unit length comprises the elastic free energy of the side chains,[17] whereas the bending energy of flexible backbone and the mixing entropy of the side chains can be neglected:[17]

$$f = \frac{\beta^2 R}{2a^2} \ln\left(1 + \frac{2aM\beta}{R}\right) - \frac{(1-\beta)^2 R}{2a^2} \ln\left(1 - \frac{2aM(1-\beta)}{R}\right) \tag{1}$$

Here the first and the second terms correspond to the elastic free energy of the side chains forming convex and concave sides of the brush, respectively ($k_BT \equiv 1$). β, $1/2 \le \beta \le 1$, is the fraction of the side chains of the convex side, and R is the radius of the curvature of the brush section. Denote by $\epsilon = \beta - 1/2$ the small excess of the side chains, $\epsilon \ll 1$. Then the bending of the brush segment induced by this asymmetry is also small, i.e., the curvature radius has to be much larger than the width of the brush (the end-to-end distance of the side chains),[17] $aM/R \ll 1$. Expansion of the free energy f in a series in powers of ϵ and aM/R gives

$$f = \frac{M}{4a} + \frac{aM^3}{12}\left(\frac{1}{R} - \frac{6\epsilon}{aM}\right)^2 + ... \tag{2}$$

where the first term corresponds to the elastic free energy of the side chains of rectilinear segment of the brush, and the second term is the energy of small bending. The multiplier before the brackets has a meaning of the bending modulus[10] κ:

$$\kappa = \frac{aM^3}{6} \tag{3}$$

The optimum curvature of the brush segment, $1/R_0$, is given by minimization of eq 2 with respect R, $1/R_0 = 6\epsilon/aM$.

In order to find the bending energy of the whole macromolecule, we need to summarize the contributions from all the segments. In doing so, we have to take into account that each segment has (in general) a different curvature radius and that the position of the contour of the brush can fluctuate around a "trajectory" which is determined by the optimum radii. Denote by $\mathbf{x}(s)$ a spatial coordinate of the brush contour located at contour distance s from the end of the chain, $0 < s < L$, $L = aN$. Then the curvature is defined as $\partial^2\mathbf{x}(s)/\partial s^2$ and the total bending energy takes the form

$$F_{\text{bend}} = \frac{\kappa}{2}\int_0^L \mathrm{d}s \left(\frac{\partial^2 \mathbf{x}(s)}{\partial s^2} - \frac{6\mathbf{n}(s)}{aM}\right)^2 \tag{4}$$

where the vector $\mathbf{n}(s)$ is directed along the radius of the optimum curvature at the point s and has the value $\epsilon(s)$. $\mathbf{n}(s)$ is a random parameter which describes "frozen" (quenched) fluctuations of the fraction of the side chains. To find correlation functions of this parameter, let us consider the discrete description of the molecule consisting of the finite number of segments, each of some given curvature. The signs of the curvatures of two different segments (ith and jth) are statistically independent (each segment has equal probability to be bent to left or to right), therefore the averaging gives $\overline{\mathbf{n}_i} = 0$ and $\overline{\mathbf{n}_i\mathbf{n}_j} = \Delta^2\delta_{ij}$. Here $\delta_{ij} = 1$ if $i = j$, and $\delta_{ij} = 0$ if $i \neq j$. The dimensionless parameter $\Delta \ll 1$ is a measure of the local asymmetry of the distribution of the side chains: the higher Δ, the higher the bending of the segments. Passing to the continual description of the molecule, the averages can be rewritten as follows:

$$\overline{\mathbf{n}(s)} = 0,\ \overline{\mathbf{n}(s)\mathbf{n}(s')} = \Delta^2 a\delta(s - s') \tag{5}$$

where $\delta(s - s')$ is the Dirac δ function and the upper line means the average with respect to the quenched fluctuations (in contrast to the thermodynamic fluctuations).

For calculation of the orientational correlation function of the brush molecule, let us use the Gaussian model which is restricted by the bending elasticity, eq 4, and by the condition that the average of the square of tangential unit vector of the bush contour, $\mathbf{u}(s)$, has to be equal to unity at any point, $\overline{\langle \mathbf{u}(s)^2\rangle} = 1$, $\mathbf{u}(s) = \partial\mathbf{x}(s)/\partial s$. Here the angle brackets mean the thermodynamic average. Then the total free energy of the molecule takes the form:

$$F = \frac{1}{\lambda}\int_0^L \mathrm{d}s \left(\frac{\partial \mathbf{x}(s)}{\partial s}\right)^2 + \frac{\kappa}{2}\int_0^L \mathrm{d}s \left(\frac{\partial^2 \mathbf{x}(s)}{\partial s^2} - \frac{6\mathbf{n}(s)}{aM}\right)^2 \tag{6}$$

where λ is the Kuhn segment length of the brush and calculation of the orientational correlation function

$$\overline{\langle \cos\theta\ (s, s')\rangle} = \overline{\langle \mathbf{u}(s)\mathbf{u}(s')\rangle} = \frac{\overline{\int \mathcal{D}\mathbf{x}(s)\dfrac{\partial \mathbf{x}(s)}{\partial s}\dfrac{\partial \mathbf{x}(s')}{\partial (s')}\exp(-F)}}{\int \mathcal{D}\mathbf{x}(s)\exp(-F)} \tag{7}$$

is done in the Appendix, eq 19:

$$\overline{\langle \cos\theta\ (s, s')\rangle} = \exp\left\{-\tau\left(\frac{1}{\kappa} + \frac{9\Delta^2}{aM^2}\right)\right\}\left(1 - \tau\frac{9\Delta^2}{aM^2}\right),\quad \tau = |s - s'| \tag{8}$$

and the Kuhn segment length is determined by eq 18:

$$\lambda = \frac{2\kappa}{\left(1 + \dfrac{9\Delta^2\kappa}{aM^2}\right)^2} \tag{9}$$

Taking into account that the end-to-end vector of the brush, $\mathbf{r}$, can be presented in the form $\mathbf{r} = \mathbf{x}(L) - \mathbf{x}(0) = \int_0^L \mathrm{d}s\mathbf{u}(s)$, we find

$$\overline{\langle \mathbf{r}^2 \rangle} = \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \overline{\langle \cos\theta\,(s, s')\rangle}$$
$$= \frac{2}{A^2}\,[AL - 1 + \exp\{-AL\}] + \frac{2B}{A^3}\,[2(1 - \exp\{-AL\}) - AL\,(1 + \exp\{-AL\})]$$
$$A = \frac{1}{\kappa} + \frac{9\Delta^2}{aM^2},\ B = \frac{9\Delta^2}{aM^2} \tag{10}$$

by integration of eq 8.

3. Discussions

The decay of the average cosine of the angle between two tangential vectors of the brush molecule, eq 8, is presented in Figure 1. If we deal with perfectly symmetric distribution of the side chains with respect to the backbone, $\Delta = 0$, the brush reveals exponential decay (solid curve) and we can define the persistence length, λ_p, which coincides with the bending modulus, $\lambda_p = \kappa$, and is twice less than the Kuhn segment length, $\lambda = 2\lambda_p$. The presence of local asymmetry of the distribution enhances the decay of the correlation function (dashed and dotted curves): the higher Δ is, the stronger the decay. Indeed, the local quenched bending of the brush to the left and to the right promotes the loss of the orientational correlations. Furthermore, the correlation function can be equal to zero at $\tau/\kappa = 1/\alpha$ and can have a negative minimal value, $-\exp(-2 - 1/\alpha)\ \alpha/(1 + \alpha)$, at $\tau/\kappa = (1 + 2\alpha)/\alpha(1 + \alpha)$, $\alpha = 3\Delta^2 M/2$. The parameter $\alpha \geq 0$ can attain high enough values, $\alpha \gg 1$, if the local asymmetry of the distribution of the side chains is not so small, $\Delta \leq 1$. Thus, in contrast to chains with persistent flexibility mechanism ($\kappa = \lambda_p$), the loss of the orientational correlations of the adsorbed brush, $\overline{\langle \cos\theta \rangle} = 0$, can be achieved at the contour lengths τ smaller than the bending modulus, $\tau = aM^2/9\Delta^2 = \kappa/\alpha \ll \kappa$, i.e., the quenched fluctuations of the side chains are responsible for this effect. In other words, an elementary length of the brush, where the thermodynamic fluctuations are suppressed, can be curved. If the contour length is slightly above the value where $\overline{\langle \cos\theta \rangle} = 0$, the correlation function has a minimum: the higher α, the deeper the minimum, Figure 1. Calculation of the characteristic size of the brush, $\sqrt{\overline{\langle \mathbf{r}^2 \rangle}}$, eq 10, whose contour length corresponds to the minimum of the correlation function, $L/\kappa = (1 + 2\alpha)/\alpha(1 + \alpha)$, leads to the value $\sqrt{\overline{\langle \mathbf{r}^2 \rangle}} \approx \kappa/\alpha$, $\alpha \gg 1$, i.e. $\sqrt{\overline{\langle \mathbf{r}^2 \rangle}} \approx L$. Therefore, despite of the local bending of a characteristic size aM/Δ (the curvature radius), the conformation of the brush is elongated and the average angle between the ends of the molecule belongs to the range 90° < θ < 270°.

The characteristic size of the molecule, $\sqrt{\overline{\langle \mathbf{r}^2 \rangle}}/\kappa$, as a function of L/κ is shown in Figure 2. One can see that the higher asymmetry of the local distribution of the side chains Δ (the higher α), the more compact conformation of the brush. If the contour length L is smaller than both length scales, κ and $aM^2/9\Delta^2$, $L(1/\kappa + 9\Delta^2/aM^2) \ll 1$, the brush has a rodlike conformation, $\overline{\langle \mathbf{r}^2 \rangle} \approx L^2$. Unusual behavior, comprising independence of the gyration radius of the brush on the contour length, is predicted in the range $aM^2/9\Delta^2 \ll L \ll \kappa$, $\alpha \gg 1$. Here $\overline{\langle \mathbf{r}^2 \rangle} \approx 2(aM^2/9\Delta^2)^2$. The physical picture of such behavior is the following. As we showed above, the brush of the contour length $\tau \sim aM^2/\Delta^2$ has a linear dependence of the end-to-end distance on τ, $\sqrt{\overline{\langle \mathbf{r}^2 \rangle}} \sim \tau$. It means that if we circumscribe such brush by a circle of the radius $\sim aM^2/\Delta^2$, there is a lot of "empty" (free of polymer) space within the circle, Figure 3a. The conformation of longer brush can be imagined as a "filling" of the circle, Figure 3b, that is why the size of the molecule is determined by the radius of the circle rather than the contour length of the molecule. Finally, if the length of the brush exceeds the bending modulus κ, $L \gg \kappa$, the thermodynamic fluctuations

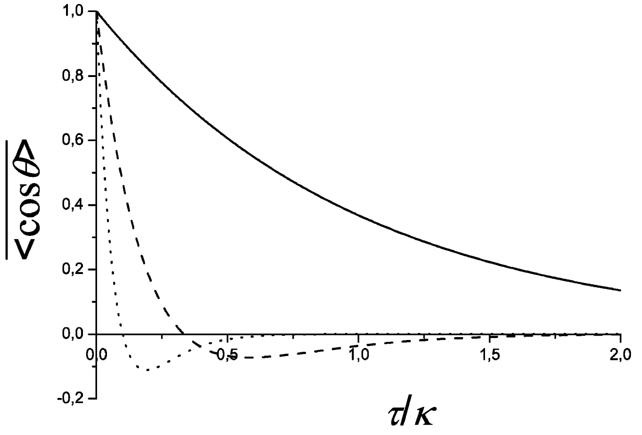

Figure 1. Average cosine of the angle between two tangential vectors of the brush separated by the contour length τ as a function of the dimensionless ratio τ/κ at different values of the parameter $\alpha = 9\Delta^2\kappa/aM^2 = 3\Delta^2 M/2$: $\alpha = 0$ (solid), 3 (dashed), 10 (dotted).

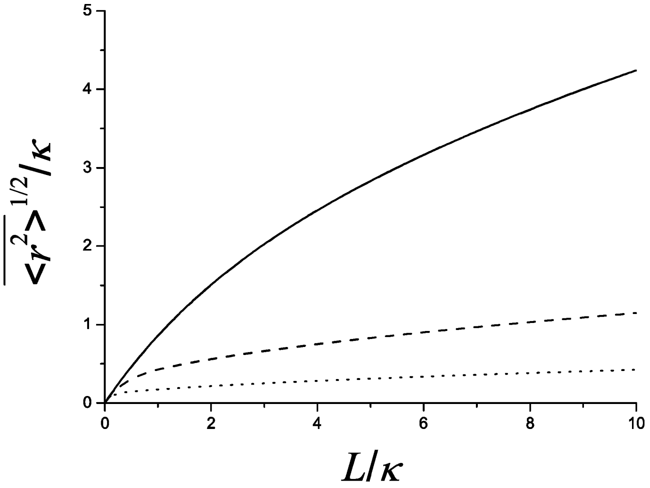

Figure 2. Ratio of the characteristic size of the molecule $\sqrt{\overline{\langle \mathbf{r}^2 \rangle}}$ to the bending modulus κ as a function of the dimensionless contour length L/κ at different values of the parameter $\alpha = 3\Delta^2 M/2$: $\alpha = 0$ (solid), 3 (dashed), 10 (dotted).

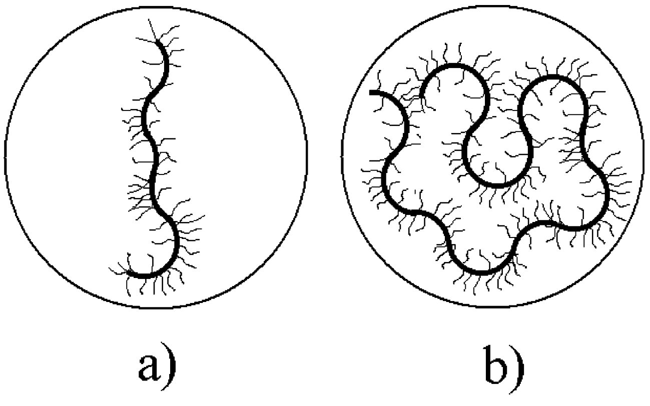

Figure 3. Schematic representation of 2D conformations of the brush molecule of the contour lengths $\tau \sim aM^2/\Delta^2$ (a) and $aM^2/\Delta^2 \ll \tau \ll \kappa$ (b). The radius of the circle is $\sim aM^2/\Delta^2$.

are responsible for conformation of the brush. The average of the squared end-to-end distance takes the Gaussian form, $\overline{\langle \mathbf{r}^2 \rangle} \approx \lambda L$. Here the Kuhn segment length λ is done by eq 9. Relying on attraction between uncorrelated (distant) segments of the brush because of the line tension (the monomer units of the side chains attract each other), the conformation can be imagined as a dense packing of L/λ blobs, each of the size λ. The Kuhn segment length has a very strong dependence on the distribution of the side chains. It takes the maximum value, $\lambda = aM^3/3$, at $\Delta = 0$, and the minimum value, $\lambda \approx 4aM/27\Delta^4$, at $\alpha \gg 1$. In the latter case, our theory can formally be applied to the regime of maximum bending of the segments, $\Delta \sim 1$, that corresponds to the densely packed 2D globule, $\overline{\langle \mathbf{r}^2 \rangle} \sim a^2MN$.

4. Concluding Remarks

We propose a theory of strongly adsorbed comblike macromolecules (brushes) with random distribution of the side chains with respect to the backbone. The decay of the orientational correlation function, the gyration radius, and the Kuhn segment length are analyzed. We show that local asymmetry in the left−right distribution of the side chains, which is controlled by the regime of adsorption (initial 3D conformation of the brush), (i) promotes the decay of the orientational correlation function and (ii) decreases the gyration radius. The correlation function is shown to have a nonmonotonous behavior with one minimum. In contrast to linear chain, the gyration radius of the brush can be independent of the contour length L in certain range of L values.

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5. Appendix

Calculation of the orientational correlation function of eq 7 can be done using Fourier transforms for the vector $\mathbf{x}(s)$:

$$\mathbf{x}(s) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \mathbf{x}_\omega \exp(i\omega s), \qquad \mathbf{x}_\omega = \int_{-L/2}^{L/2} \mathrm{d}s\, \mathbf{x}(s) \exp(-i\omega s), \quad L \to \infty \tag{11}$$

$$\overline{\langle \mathbf{u}(s)\mathbf{u}(s') \rangle} = \frac{1}{L} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \omega^2 \overline{\langle \mathbf{x}_\omega \mathbf{x}_{-\omega} \rangle} \exp\{i\omega(s - s')\} \tag{12}$$

The thermodynamic average of the left-hand side of eq 12 can be presented as

$$\langle \mathbf{x}_\omega \mathbf{x}_{-\omega} \rangle = \frac{\delta^2}{\delta \mathbf{h}_\omega \delta \mathbf{h}_{-\omega}} \frac{\int \mathscr{D}\mathbf{x} \exp(-F + \int_{-\infty}^{\infty} d\omega \mathbf{h}_\omega \mathbf{x}_{-\omega})}{\int \mathscr{D}\mathbf{x} \exp(-F)} \Bigg|_{\mathbf{h}=0} \tag{13}$$

$$F = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \left[\frac{\omega^2 \mathbf{x}_\omega \mathbf{x}_{-\omega}}{\lambda} + \frac{\kappa}{2} \left(\omega^4 \mathbf{x}_\omega \mathbf{x}_{-\omega} + \frac{12\omega^2}{aM} \mathbf{x}_\omega \mathbf{n}_{-\omega} + \frac{36 \mathbf{n}_\omega \mathbf{n}_{-\omega}}{a^2M^2} \right) \right] \tag{14}$$

where the symbol δ denotes variation derivative, $\delta \mathbf{h}_{\omega'}/\delta \mathbf{h}_\omega \equiv \delta(\omega - \omega')$; $\mathscr{D}\mathbf{x} \equiv \prod_\omega \mathrm{d}x_\omega$ is a product of differentials and the free energy of the brush molecule is rewritten using the Fourier transforms, eq 14. The Gaussian integrals of eq 13 are calculated by the following substitution of variables

$$\mathbf{x}_\omega \to \mathbf{x}_\omega + \frac{2\pi \mathbf{h}_\omega - \frac{6\kappa}{aM} \omega^2 \mathbf{n}_\omega}{\kappa\omega^4 + 2\omega^2/\lambda} \tag{15}$$

The result is

$$\langle \mathbf{x}_\omega \mathbf{x}_{-\omega} \rangle = \frac{\delta^2}{\delta \mathbf{h}_\omega \delta \mathbf{h}_{-\omega}} \exp\left(\int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\pi \mathbf{h}_{\omega'} \mathbf{h}_{-\omega'} - 6\kappa\omega^2 \mathbf{h}_\omega \mathbf{n}_{-\omega}/aM}{\kappa\omega^4 + 2\omega^2/\lambda} \right) \Bigg|_{\mathbf{h}=0} = \frac{2L}{\kappa\omega^4 + 2\omega^2/\lambda} + \frac{36\kappa^2 \mathbf{n}_\omega \mathbf{n}_{-\omega}}{a^2M^2(\kappa\omega^2 + 2/\lambda)^2} \tag{16}$$

where we used the condition $2\pi\delta(\omega = 0) = L$. The factor 2 in the first term of eq 16 comes from the dimension of the system. Taking into account that $\overline{\mathbf{n}_\omega \mathbf{n}_{-\omega}} = \Delta^2 aL$ (see eq 5), we get

$$\overline{\langle \mathbf{u}(s)\mathbf{u}(s') \rangle} = \sqrt{\frac{\lambda}{2\kappa}} \exp\left(-\tau\sqrt{\frac{2}{\lambda\kappa}}\right) + \frac{9\Delta^2}{aM^2} \sqrt{\frac{\lambda\kappa}{2}} \exp\left(-\tau\sqrt{\frac{2}{\lambda\kappa}}\right)\left(1 - \tau\sqrt{\frac{2}{\lambda\kappa}}\right), \qquad \tau = |s - s'| \tag{17}$$

by substitution of eq 16 into eq 12 and integration with respect to ω. The condition $\overline{\langle \mathbf{u}(s)^2 \rangle} = 1$ determines the Kuhn segment length λ by means of equating of the right-hand side of eq 17 to unity at $\tau = 0$:

$$\lambda = \frac{2\kappa}{\left(1 + \frac{9\Delta^2\kappa}{aM^2}\right)^2} \tag{18}$$

and ultimate expression of the correlation function takes the following form:

$$\overline{\langle \mathbf{u}(s)\mathbf{u}(s') \rangle} = \exp\left\{-\tau\left(\frac{1}{\kappa} + \frac{9\Delta^2}{aM^2}\right)\right\}\left(1 - \tau\frac{9\Delta^2}{aM^2}\right) \tag{19}$$

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