# A Green's-function perturbation theory for nonuniform semiflexible polymers: Phases and their transitions near attracting surfaces

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The chain stiffness is an important characteristic that affects the properties of many biological and synthetic polymers. We develop a perturbation theory in the framework of a Green's-function approach to treat the chain stiffness effects systematically. This scheme incorporates the standard flexible-chain Edwards equation in the zeroth order. When applied to the chains on the surface, the theory predicts novel features in adsorption–desorption transitions coupled with types of isotropic to nematic ordering transitions, giving a rigorous quantitative basis for our previous scaling theory results. We analyze the phase diagrams, and various quantities that detail the chain distribution including orientation-order-parameter distribution of the adsorbed semiflexible polymers. © *1997 American Institute of Physics.* [S0021-9606(97)50636-2]

## I. INTRODUCTION

There exists a multitude of models for polymer chain descriptions depending upon the length scales (see, for instance, Refs. 1 and 2). Some models, which we may call chemical, are concerned with the microscopic details of macromolecular structures. However, in many physical and biophysical problems, the macroscopic or mesoscopic scales of the polymer structure play a leading role.[1] There exists a wide class of the polymer-physical problems (so-called universality class), where general macroscopic polymer properties do not depend on any details of the small-scale polymer structure.

Among the nonmicroscopic models the Gaussian chain of ''beads'' represents the most frequently studied model for different problems. This chain is characterized by bead diameter $d$, average distance $a$ between nearest beads along the polymer chain (the Kuhn segment), and total number of the beads $N$. It is usually supposed that the chain is very long, i.e., $N \gg 1$. Already in the frameworks of this model we can separate three main length scales for the polymer properties: (i) the microscopic scales characterized by the size $d$ of a single bead; (ii) the mesoscopic scales described by the Kuhn-segment length $a$ larger than $d$; and (iii) the macroscopic scales determined by whole macromolecule dimensions (for instance, polymer radius of gyration or average end-to-end distance of the polymer). For an ideal Gaussian chain (in the absence of external fields and interchain interactions other than chain connectivity) the mean-square radius of gyration is equal to $R_g^2 = Na^2/6$ and $R_g \gg a$ for $N \gg 1$. Certainly, this model is very far from reality on microscopic and mesoscopic levels. In this model the backbone stiffness is neglected entirely and only the formal stiffness parameter $d/a$ can be used ($d/a \ll 1$ for the stiff chains and $d/a \sim 1$ for the flexible ones). Nevertheless the model leads to fine macromolecule descriptions on the macroscopic scales as many theoretical studies of polymer properties (see, for instance, Refs. 1 and 2) are shown to be in a good agreement with experiments and computer simulations.

Often it is necessary to study some polymer properties arising just from the mesoscopic level of chain structure, for instance, nematic liquid-crystalline ordering in long semiflexible polymer chains.[1,3] On mesoscopic scales the wormlike chain model (or the Kratky–Porod model) serves as a representative model that can describe the many polymer physical and biological problems. For example, the DNA double helix can be considered as a persistent wormlike chain of the very hight stiffness.[1] A semiflexible polymer is a polymer with chain stiffness intermediate between the absolutely flexible and rigid-rod-like structures. The orientation memory range along semiflexible chain given by the chain persistence length $l$ is much smaller than its total polymer contour length $L$, but much larger than the chain diameter $d$. As well as above for the Gaussian chain, three length scales are involved in the wormlike polymer description: (i) microscopic (the chain diameter $d$); (ii) mesoscopic (the stiffness scale $l$); and (iii) macroscopic scales (the whole macromolecule dimensions as the root-mean-square radius of gyration $R_g$ is, for a chain without volume interactions, $R_g^2 = Ll/3$).

The polymer-stiffness effects play an essential role for semiflexible polymers near attracting surfaces.[4] The adsorption–desorption problem and the properties of adsorbed polymers have been studied intensively for several years (see, for instance, Refs. 2,5–7 and references in Ref. 4), mainly for ideally flexible polymer chains. In many practical problems, however, the range of adsorbing forces is smaller or equal to the polymer stiffness-scale and therefore it is essential to consider these mesoscopic scale effects. The polymer stiffness effects in the adsorption problem were theoretically analyzed only in a few studies which involve only the very short-range surface attracting forces. These studies were carried out in the frameworks of lattice models[8–10] and by means of computer simulations.[10–12]

We have recently analyzed[4] semiflexible polymers near attracting surface for the case of semiflexible macromolecules, developing a scaling theory. The cases of flexible

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polymers and the short-range surface forces were incorporated as the particular limiting cases of this general description. Our scaling theory gave a qualitative picture of the various polymer phases, i.e., the desorbed phase, the adsorbed phases with isotropic and nematic-type segmental distributions, and their transitions that occur as competition between the thermal fluctuations, surface interaction, and chain stiffness.

In the present paper we develop an approximation scheme in the frameworks of the Green's-function description of semiflexible, wormlike polymers, which treats the polymer stiffness and persistence systematically (Sec. II). After describing briefly the general formulation of semiflexible chains in terms of the Green's function, we present a perturbation theory scheme, which considers the relative segmental density change over a persistence length as a small parameter. We develop a means of systematically incorporating the perturbation at any orders, which yields the standard flexible-chain Edwards equation as the zeroth-order approximation. We then develop an interpolation method, which incorporates asymptotically infinitely many orders of our perturbation scheme, to be used for analysis of polymer properties in the region where fast convergence of the perturbation expansion cannot be guaranteed. In Sec. III we apply this scheme to the semiflexible polymer properties near the surface and to the adsorption–desorption transition coupled with the isotropic to nematic-type one. We first formulate our perturbation theory specific to this problem and then analyze in detail its results in the first order and the interpolation approximations. The results confirm the qualitative pictures found in scaling theory and predict many new features in phase diagrams, order parameters, and segmental distributions.

## II. THE SEMIFLEXIBLE-POLYMER GREEN'S FUNCTION PERTURBATION THEORY

### A. General formulation

The conformation of a polymer chain can be described in analogy with Brownian motion. The Green's function $G_N(\mathbf{q}_N, \mathbf{q}_0)$ is the conditional probability that the segment of number $N$ (or the Brownian particle at time $N$) is placed at the point $\mathbf{q}_N$ provided the initial segment was at the point $\mathbf{q}_0$. While for flexible polymers the $\mathbf{q}$ is the three-dimensianal (3-D) coordinate $\mathbf{r}$, for wormlike polymers it is considered as the generalized coordinate $\mathbf{q}=(\mathbf{r},\mathbf{u})$, which includes 3-D position $\mathbf{r}$ and 2-D orientation $\mathbf{u}$. (In terms of the Brownian motion $\mathbf{u}$ corresponds to particle velocity with magnitude $|\mathbf{u}|=1$.)

The Green's function $G_{N+1}(\mathbf{q}_{N+1}, \mathbf{q}_0)$ has the recurrence relation

$$G_{N+1}(\mathbf{q}_{N+1}, \mathbf{q}_0) = \int G_1(\mathbf{q}_{N+1}, \mathbf{q}_N) G_N(\mathbf{q}_N, \mathbf{q}_0) d\mathbf{q}_N \quad (1)$$

or

$$G_{N+1} = \hat{Q} G_N, \quad (2)$$

where $\hat{Q}$ is the transfer operator written as

$$\hat{Q} = \exp(-\beta W)\hat{g}. \quad (3)$$

The $W(\mathbf{q})$ stands for an external field, $\beta \equiv 1/T$ (with $k_B = 1$), $\hat{g}$ is the so-called "linear memory operator":[1,13]

$$\hat{g}\psi(\mathbf{q}) = \int g(\mathbf{q},\mathbf{q}')\psi(\mathbf{q}')d\mathbf{q}'.$$

The function $g(\mathbf{q},\mathbf{q}')$ describes the connection of neighboring links along the chain in terms of the conditional probability in the absence of external fields.

If we are interested in the macroscopic polymer properties only, we could use the simplest Gaussian model, for which[1]

$$\hat{g} \simeq 1 + \frac{a^2}{6} \nabla_{\mathbf{r}}^2, \quad (4)$$

where $\nabla_{\mathbf{r}}^2$ is the Laplacian operator in the usual 3-D position space. As we are interested in the study of mesoscopic effects for the polymer chain with arbitrary persistence, we should at first appeal to a discrete model. Consider a discrete basic model of chain formed by a linear array of rigid-rod segments of the fixed length $\tilde{l}$ ($l \gg \tilde{l} \gg d$) connected at a fixed angle $\tilde{\theta}$. The operator $\hat{g}$ then takes the form[14]

$$\hat{g} \simeq 1 - \tilde{l}(\mathbf{u}\cdot\nabla_{\mathbf{r}}) + \frac{\tilde{\theta}^2}{4} \nabla_{\mathbf{u}}^2, \quad (5)$$

where $\nabla_{\mathbf{r}}$ is the gradient operator in the 3-D $\mathbf{r}$ space and $\nabla_{\mathbf{u}}^2$ is the Laplacian operator in the 2-D orientation $\mathbf{u}$ space (on the unit sphere $|\mathbf{u}|=1$). A semiflexible, wormlike chain can be viewed as the continuum limit $\tilde{l} \to 0$ and $\tilde{\theta} \to 0$ with a fixed finite value of the polymer persistence length $l \equiv 2\tilde{l}/\tilde{\theta}^2$.[1]

We should emphasize that Eqs. (3)–(5) are valid for a smooth variation of the external field $W(\mathbf{q})$ on the scale of the segmental length for each model,

$$\beta a|\nabla_{\mathbf{r}}W_a| \ll 1, \quad (6)$$

$$\beta\tilde{l}|\nabla_{\mathbf{r}}W_{\tilde{l}}| \ll 1. \quad (7)$$

The reason is that for these cases we can consider the interval between two neighboring links as unperturbed by external fields and identify Eq. (2) as the Chapman–Kolmogorov equation for transitional probabilities. Neglecting the part of the potential, if any, which is high, but constant over the relevant length scale and therefore nonessential, we can write this condition as

$$|\beta W| \ll 1. \quad (8)$$

Because the polymer segments have the length $a$ for the Gaussian chain and the length $\tilde{l}$ for the discrete one, the potential energy $W$, which is acquired by a single segment in the external field, can be written as $W_a = a\mathcal{U}$ or $W_{\tilde{l}} = \tilde{l}\mathcal{U}$ for these models, respectively. Here $\mathcal{U}$ is the potential energy per unit polymer contour length. Thus the condition (8) takes the forms

$$|\beta\mathcal{U}| \ll \frac{1}{a} \quad \text{or} \quad |\beta\mathcal{U}| \ll \frac{1}{\tilde{l}}. \quad (9)$$

For both cases of flexible and semiflexible wormlike chains the number of polymer segments is a large number $N \gg 1$, therefore we can rewrite Eq. (2) as

$$-\frac{\partial G_N}{\partial N} = (1-\hat{Q})G_N. \tag{10}$$

The Green's function can be expanded as

$$G_N(\mathbf{q}_N, \mathbf{q}_0) = \sum_j \Lambda_{(j)}^N \psi_{(j)}(\mathbf{q}_N)\psi_{(j)}(\mathbf{q}_0)$$

$$\simeq \Lambda_{(0)}^N \psi_{(0)}(\mathbf{q}_N)\psi_{(0)}(\mathbf{q}_0), \tag{11}$$

where $\Lambda_{(j)}$ and $\psi_{(j)}$ are, respectively, the eigenvalues and eigenfunctions of $\hat{Q}$:

$$\hat{Q}\psi_{(j)} = \Lambda_{(j)}\psi_{(j)}. \tag{12}$$

Since the partition function of a chain with $N$ segments is given by $\int\int G_N(\mathbf{q}_N, \mathbf{q}_0)d\mathbf{q}_N\, d\mathbf{q}_0$, in the ground-state dominance approximation (11) the equilibrium free energy per segment for a bound polymer is given by $F/(NT) = -\ln \Lambda_{(0)} \equiv \epsilon$, where $\Lambda_{(0)}$ is the ground-state eigenvalue.

For flexible chains, Eq. (12) for the ground state is reduced to the standard Gaussian-model equation:[1]

$$\frac{a^2}{6}\nabla_{\mathbf{r}}^2\psi(\mathbf{r}) = [\Lambda_a e^{\beta W_a(\mathbf{r})} - 1]\psi(\mathbf{r}) \tag{13}$$

and to the more complicated one for the discrete model:[14]

$$-\widetilde{l}(\mathbf{u}\cdot\nabla_{\mathbf{r}})\psi + \frac{\widetilde{\theta}^2}{4}\nabla_{\mathbf{u}}^2\psi = [\Lambda_{\widetilde{l}} e^{\beta W_{\widetilde{l}}(\mathbf{r},\mathbf{u})} - 1]\psi(\mathbf{r},\mathbf{u}). \tag{14}$$

Naturally, taking into account the smallness [Eq. (9)] of potential energy acquired by polymer segments in an external field, we can use the series expansions for the exponential terms in Eqs. (13) and (14). Using this expansion with the persistence length definition $l \equiv 2\widetilde{l}/\widetilde{\theta}^2$ and denoting $W_{2l} \equiv 2l\mathcal{U}$ and $\epsilon_{2l} \equiv -(4/\widetilde{\theta}^2)\ln \Lambda_{\widetilde{l}}$ we can rewrite Eq. (14) in terms of the continuous wormlike polymer:

$$-2l(\mathbf{u}\cdot\nabla_{\mathbf{r}})\psi + \nabla_{\mathbf{u}}^2\psi = [\beta W_{2l}(\mathbf{r},\mathbf{u}) - \epsilon_{2l}]\psi(\mathbf{r},\mathbf{u}). \tag{15}$$

It is the main equation for description of the semiflexible polymer properties at $L \gg l \gg d$. The eigenfunction $\psi$ determines the space and orientation density distribution of polymer segments:[1]

$$n(\mathbf{r},\mathbf{u}) = \psi^2(\mathbf{r},\mathbf{u}), \tag{16}$$

where $\int n(\mathbf{r},\mathbf{u})d^3r\, d^2u = N$, $N = L/(2l)$. It should be remarked here that although Eq. (15) is valid for $|\beta W_{\widetilde{l}}| \ll 1$ only, the value

$$|\beta W_{2l}| = 2l|\beta\mathcal{U}| = \frac{4}{\widetilde{\theta}^2}|\beta W_{\widetilde{l}}| \tag{17}$$

in Eq. (15) can go far beyond the same restriction because of the continuum limit $\widetilde{\theta}^2 \ll 1$.

## B. A perturbation scheme

The universality of the macroscopic properties means that on the large macroscopic scales and for small values of the external field $W_{2l}$ [i.e., at $|\beta W_{2l}| \ll 1$ in Eq. (17)] Eq. (15) for the wormlike polymer has to reduce to the standard Edwards equation[15] [compare with Eq. (13) for $\epsilon_a \equiv -\ln \Lambda_a$],

$$\frac{a^2}{6}\nabla_{\mathbf{r}}^2\psi(\mathbf{r}) = [\beta W_a(\mathbf{r}) - \epsilon_a]\psi(\mathbf{r}), \tag{18}$$

which is a Schrödinger-type equation. On the smaller length scales or for the larger values of external field $W_{2l}$ the corrections arising from the polymer stiffness should be taken into account. In this section we will consider: (i) a mathematical reduction of the semiflexible-persistent-chain description [Eq. (15)] to the flexible one [Eq. (18)]; (ii) the perturbation corrections to the flexible chain description, which will give a possibility to incorporate polymer stiffness without having to solve the much more difficult Eq. (15).

In Ref. 16 a similar problem was described for the homopolymer globule under isotropic volume interactions between segments without external fields, where the smallness of a self-consistent field at small concentrations of polymer segments was used. Here we will not suppose a priori the smallness of fields, but consider the corrections given by the small (mesoscopic) length scale description.

From now on we will concern ourselves only to the case, where, because of axial symmetry that can exist in the system, the polymer segments orientation $\mathbf{u}$ can be characterized by the single angle $\theta$ with respect to the symmetry axis. This axis coincides with the axis of density gradient $\nabla_{\mathbf{r}}\psi$. A wide class of the problems, including the problem of polymer adsorption on a flat surface discussed in this paper, belongs to this category.

Under the assumption

$$\psi(\mathbf{r},\mathbf{u}) = \psi(z,\theta) \tag{19}$$

we have

$$\nabla_{\mathbf{u}}^2\psi = (1-\gamma^2)\frac{\partial^2\psi}{\partial\gamma^2} - 2\gamma\frac{\partial\psi}{\partial\gamma}$$

and

$$(\mathbf{u}\cdot\nabla_{\mathbf{r}})\psi = \gamma\frac{\partial\psi}{\partial z},$$

where $\gamma \equiv \cos\theta$ and $z$ is the component of $\mathbf{r}$ parallel to $\nabla_{\mathbf{r}}\psi$. (Note that $z$ can be any component, for example a Cartesian or a radial component depending upon the geometry.) Using the dimensionless coordinate

$$\mathcal{Z} \equiv \frac{z}{2l} \tag{20}$$

and $\phi \equiv (\beta W_{2l} - \epsilon_{2l})$ we can rewrite Eq. (15) as

$$-\gamma\frac{\partial\psi}{\partial\mathcal{Z}} + \nabla_{\mathbf{u}}^2\psi = \phi\psi. \tag{21}$$

Here it is convenient to use the series expansions of the function $\psi$ and the external field $W$ with respect to the Legendre polynomials $P_i(\cos \theta)$:

$$\psi(z,\theta) = \sum_{i=0}^{\infty} \psi_i(z) P_i(\gamma), \qquad (22)$$

$$W_{2l}(z,\theta) = \sum_{i=0}^{\infty} W_{2l,i}(z) P_i(\gamma). \qquad (23)$$

In the present paper we will describe in details the perturbation approach for an isotropic external field where $W_{2l,i}(z) \equiv 0$ for $i \geq 1$. Using the following relations for the Legendre polynomials:

$$\Delta_u P_i(\cos \theta) = -i(i+1) P_i(\cos \theta)$$

and

$$P_1 P_i = \frac{(i+1) P_{i+1} + i P_{i-1}}{2i+1},$$

we can transform Eq. (21) into

$$\psi_i[i(i+1) + \phi] = -\frac{i}{2i-1} \frac{d\psi_{i-1}}{d\mathcal{Z}} - \frac{i+1}{2i+3} \frac{d\psi_{i+1}}{d\mathcal{Z}}, \quad (24)$$

where $i \geq 0$, or alternatively into

$$\psi_i = \hat{b}_{i-1} \psi_{i-1} + \hat{a}_{i+1} \psi_{i+1}, \qquad (25)$$

where

$$\hat{a}_i = -\frac{i}{(2i+1)[i(i-1)+\phi]} \frac{d}{d\mathcal{Z}} \qquad (26)$$

and

$$\hat{b}_i = -\frac{i+1}{(2i+1)[(i+1)(i+2)+\phi]} \frac{d}{d\mathcal{Z}}. \qquad (27)$$

Suppose that a length scale $\xi$, called the correlation length, characterizes the segmental density variation. As it was mentioned above, for the $\xi$ much larger than $l$ (on macroscopic scales) the properties of semiflexible and flexible polymers should be similar. Therefore it is natural to consider the ratio $l/\xi$ as a small parameter of the flexible chain perturbation theory. In general as will be seen below the relative curvature

$$\frac{1}{\psi_0} \left| \frac{d^2 \psi_0}{d\mathcal{Z}^2} \right| = \frac{(2l)^2}{\psi_0} \left| \frac{d^2 \psi_0}{dz^2} \right| \qquad (28)$$

is regarded as a small parameter.

Now let us express explicitly Eqs. (24) or (25) in low orders,

$$\psi_0 = -\frac{1}{3\phi} \frac{d\psi_1}{d\mathcal{Z}} \quad (i=0), \qquad (29)$$

$$\psi_1 = -\frac{1}{2+\phi} \frac{d\psi_0}{d\mathcal{Z}} - \frac{2}{5(2+\phi)} \frac{d\psi_2}{d\mathcal{Z}} \quad (i=1), \qquad (30)$$

$$\psi_2 = -\frac{2}{3(6+\phi)} \frac{d\psi_1}{d\mathcal{Z}} - \frac{3}{7(6+\phi)} \frac{d\psi_3}{d\mathcal{Z}} \quad (i=2), \qquad (31)$$

and so on. In determining $\psi_0(\mathcal{Z})$, our primary function, we will first calculate $\psi_1(\mathcal{Z})$ as a function of $\psi_0(\mathcal{Z})$ only, which will be substituted in Eq. (29). The function $\psi_1$ is described by Eq. (30), where the second term is determined by the function $\psi_2$, and is [in view of Eqs. (30) and (31)] of the order of $d^3 \psi_0 / d\mathcal{Z}^3$. Neglecting this order for a small parameter

$$\frac{1}{\psi_0} \left| \frac{d^2 \psi_0}{d\mathcal{Z}^2} \right| \ll 1$$

and retaining the first (leading) term of (30) only we obtain

$$\psi_1 \simeq -\frac{1}{2+\phi} \frac{d\psi_0}{d\mathcal{Z}}, \qquad (32)$$

which, when inserted into Eq. (29), yields the zeroth-order approximation

$$\frac{1}{6} \frac{d}{d\mathcal{Z}} \left[ \frac{1}{1+(\phi/2)} \frac{d\psi_0}{d\mathcal{Z}} \right] = \phi \psi_0. \qquad (33)$$

In terms of the space coordinate $\mathcal{Z}$ [see Eq. (20)] and the Kuhn segment length defined by $a = 2l$ in this order, the above equation is

$$\frac{a^2}{6} \frac{d}{dz} \left[ \frac{1}{1+(\beta W_{2l} - \epsilon)/2} \frac{d\psi_0}{dz} \right] = (\beta W_{2l} - \epsilon) \psi_0. \qquad (34)$$

At small values of $\beta W_{2l}$ and its gradient over $a$ [Eqs. (6)–(8)] the zeroth-order perturbation equation (34) is reduced to

$$\frac{a^2}{6} \frac{d^2 \psi_0}{dz^2} = (\beta W_{2l} - \epsilon) \psi_0, \qquad (35)$$

which is the standard flexible-chain Edwards equation (18) in 1-D.

Including the second term of Eq. (30), where $\psi_2$ is given by the first term of Eq. (31) and by Eq. (32), we have the first-order perturbation approximation for the function $\psi_1$:

$$\psi_1 \simeq -\frac{1}{2+\phi} \frac{d\psi_0}{d\mathcal{Z}}$$
$$-\frac{2}{5(2+\phi)} \frac{d}{d\mathcal{Z}} \left[ \frac{2}{3(6+\phi)} \frac{d}{d\mathcal{Z}} \left( \frac{1}{2+\phi} \frac{d\psi_0}{d\mathcal{Z}} \right) \right]. \qquad (36)$$

If we substitute it again into the basic Eq. (29), then we will have the first-order perturbation equation for the function $\psi_0$.

To clarify the $\psi_1$ calculations for any $k$ order of the perturbation approach, it is convenient to consider the solution process of Eqs. (25) at $i \geq 1$ as a move on a ladder (see Fig. 1). We start from the step 1 [Eq. (30)], then we can move up [second term of Eq. (30)] or down (first term). If the move reaches step 0, it will be stopped and it can resume a new one from step 1. On every step we can move up [the second term in Eq. (25)] and down (the first one). To carry out the calculations in the frameworks of $k$-order perturbation approximation it is necessary to sum up all the possible moves from step 1 to step 0, which consist of $(2k+1)$ steps or shorter. Every move up (from the step $i-1$ to the step $i$)
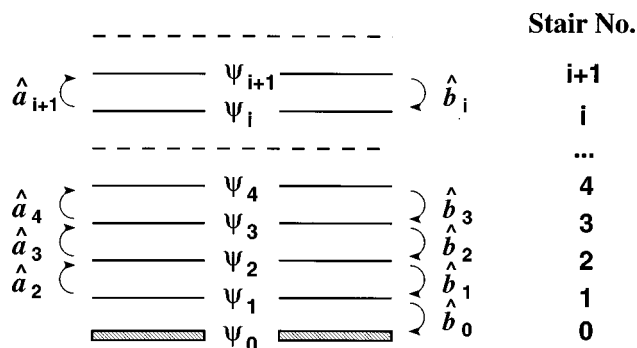
FIG. 1. The scheme of perturbation theory calculations as a move on the ladder (see the text).

is described by the raising operator $\hat{a}_i$, the move down (from the step $i+1$ to the step $i$) is described by the lowering operator $\hat{b}_i$ [see Fig. 1 and Eqs. (26) and (27)].

Now we can write expressions for $\psi_1$ function in any-order perturbation in terms of the operators $\hat{a}_i$ and $\hat{b}_i$ [compare two first expressions with Eqs. (32) and (36)]:

$$\psi_1 = \hat{b}_0 \psi_0 \quad \text{(0th order)}, \tag{37}$$

$$\psi_1 = (1 + \hat{a}_2 \hat{b}_1) \hat{b}_0 \psi_0 \quad \text{(1st order)}, \tag{38}$$

$$\psi_1 = [1 + \hat{a}_2(1 + \hat{a}_3 \hat{b}_2 + \hat{b}_1 \hat{a}_2) \hat{b}_1] \hat{b}_0 \psi_0 \quad \text{(2nd order)}, \tag{39}$$

$$\psi_1 = \{1 + \hat{a}_2[1 + \hat{a}_3(\hat{b}_2(1 + \hat{b}_1 \hat{a}_2) + (\hat{a}_4 \hat{b}_3 + \hat{b}_2 \hat{a}_3)\hat{b}_2) + \hat{b}_1 \hat{a}_2(1 + \hat{a}_3 \hat{b}_2 + \hat{b}_1 \hat{a}_2)]\hat{b}_1\} \hat{b}_0 \psi_0 \quad \text{(3rd order)}, \tag{40}$$

and so on. These last equations together with Eq. (29) describe a semiflexible polymer in the frameworks of perturbation approach of a given order with the relative curvature (28) as a small parameter. A smallness of the external field $\beta W_{2l}$ is not assumed here.

## C. An interpolation solution

In the previous section we considered the relative curvature as the small parameter of the perturbation approach. But in many situations, this parameter is not small enough to assure the convergence of low-order perturbation expansions. In the present section we develop an interpolation method, which incorporates the infinitely many orders asymptotically. Equations (29) and (30) lead to the following exact equation for the function $\psi_0$:

$$\psi_0 = \frac{1}{3\phi} \frac{d}{d\mathscr{Z}} \left[ \frac{1}{2+\phi} \frac{d\psi_0}{d\mathscr{Z}} + \frac{2}{5(2+\phi)} \frac{d\psi_2}{d\mathscr{Z}} \right]. \tag{41}$$

Here the second term in the right side, which is determined by the function $\psi_2(\mathscr{Z})$, is a correction to the zeroth-order equation (33). In this section we construct a scheme to calculate $\psi_2(\mathscr{Z})$ in an explicit form.

Equation (24) in the limit $i \to \infty$ is reduced to

$$i^2 \psi_i \simeq -\frac{d\psi_i}{d\mathscr{Z}}, \tag{42}$$

whose solution is

$$\psi_i = \Omega_i e^{-i^2 \mathscr{Z}} \quad (\Omega_i = \text{const}). \tag{43}$$

In our scheme, the solution of the type Eq. (43) is applied for $i=2$ and substituted into Eq. (41), which then becomes a closed equation for $\psi_0$. The choice of $\Omega_2$ is made in the manner that the resulting free energy, i.e., the ground-state eigenvalue $\epsilon$, is minimized. This is essentially a variational method to interpolate the flexible chain behavior with that of a stiff chain. This approach can be applied to the region, where a convergence of the perturbation theory is not guaranteed. As is shown below in application to surface adsorption–desorption transitions, the interpolation method indeed yields a good semiflexible chain description that is approached more closely by the higher perturbation approximation, while incorporating the flexible chain limit.

## III. SEMIFLEXIBLE POLYMER PROPERTIES NEAR SURFACE

### A. Perturbation theory

Now let us apply the perturbation scheme developed above to a particular problem of very long semiflexible polymers in a dilute solution near a planar surface. The attracting potential will be modeled by the hard square potential well: The potential energy acquired by a polymer link of unit length in the external field is given by

$$\mathscr{U} = \begin{cases} \infty, & z \leq 0, \\ -U, & 0 < z \leq b, \\ 0, & z > b, \end{cases} \tag{44}$$

where $z$ is the vertical distance from the surface.

Thus $b$ is the range of attracting forces and $U$ is the depth of the potential well. It is convenient to consider the twice persistent lengths $2l$, which is equal to the Kuhn segment in the limit of the standard flexible Gaussian-chain model,[1] as the length of polymer segments. Then $N = L/(2l)$ is the total number of segments in the chain and $2l\mathscr{U}$ is the potential energy per segment. We can characterize the segmental position by a single coordinate $z$ along the axis perpendicular to the surface, due to system symmetry. Also the segmental orientation can be characterized by a single polar angle $\theta$ with respect to the $z$ axis. In the framework of the scaling approach[4] we previously used the characteristic length scale $\xi$ of segments-density change as a single characteristic of the segments distribution. In the present paper we will describe the space and orientation density distributions in details in terms of the $\psi$ function.

It is convenient here to rewrite the operators $\hat{a}_i$ and $\hat{b}_i$ [see their definitions (26) and (27)] in terms of the functions $a_i(\phi)$ and $b_i(\phi)$:

$$\hat{a}_i = a_i(\phi) \frac{d}{d\mathscr{Z}} \quad \text{and} \quad \hat{b}_i = b_i(\phi) \frac{d}{d\mathscr{Z}}, \tag{45}$$

where $\phi \equiv (\beta 2l\mathscr{U} - \epsilon)$ and

$$a_i(\phi) = -\frac{i}{(2i+1)[i(i-1)+\phi]}$$

and

$$b_i(\phi) = -\frac{i+1}{(2i+1)[(i+1)(i+2)+\phi]}. \tag{46}$$

In these terms, Eq. (29) combined with Eq. (40), which incorporate the perturbation corrections up to the 3rd order, can be written, except at $z = b$, as

$$-3\phi\psi_0 = b_0 \frac{d^2\psi_0}{d\mathscr{Z}^2} + a_2 b_1 b_0 \frac{d^4\psi_0}{d\mathscr{Z}^4} + a_2 b_1 b_0 (a_3 b_2 + b_1 a_2)$$

$$\times \frac{d^6\psi_0}{d\mathscr{Z}^6} + a_2 b_1 b_0 [a_3 b_2 (a_4 b_3 + b_2 a_3 + 2b_1 a_2)$$

$$+ (b_1 a_2)^2] \frac{d^8\psi_0}{d\mathscr{Z}^8}. \tag{47}$$

For adsorbed state the physical solutions of the last (3rd order) equation as well as the corresponding solutions of lower- and higher-order ones should satisfy (i) boundary conditions:

$$\psi_0(0) = 0, \quad \left.\frac{d^i\psi_0}{d\mathscr{Z}^i}\right|_{\mathscr{Z}\to\infty} \to 0 \quad (i \geq 0) \tag{48}$$

(the last condition means that $\psi_0$ decays exponentially at $\mathscr{Z}\to\infty$); (ii) two conditions of continuity at $z = b$, i.e., at $\mathscr{Z} = b/(2l)$:

$$\psi_0\left(\frac{b}{2l} - 0\right) = \psi_0\left(\frac{b}{2l} + 0\right),$$

$$\left.\frac{d\psi_0}{d\mathscr{Z}}\right|_{\mathscr{Z}=b/(2l)-0} = \left.\frac{d\psi_0}{d\mathscr{Z}}\right|_{\mathscr{Z}=b/(2l)+0} \tag{49}$$

(as it follows even from the Edwards equation (18) the higher-order derivatives of $\psi_0$ with respect to position $\mathscr{Z}$ can have jumps at the edge of square-well potential); and (iii) the normalization condition

$$\int \psi^2(\mathbf{x},\mathbf{u})d^3x \, d^2u = N. \tag{50}$$

A solution of the $k$-order equation can be written as

$$\psi_0 = \sum_{i=0}^{k} \left[ C_{1,i}^{\text{in}} \sin(\sqrt{m_i^{\text{in}}}\mathscr{Z}) + C_{2,i}^{\text{in}} \cos(\sqrt{m_i^{\text{in}}}\mathscr{Z}) \right] \tag{51}$$

inside the potential well, where $\phi = \phi_{\text{in}} = -\beta 2lU - \epsilon < 0$, and as

$$\psi_0 = C_{1,0}^{\text{out}} \exp(-\sqrt{m_0^{\text{out}}}\mathscr{Z}) + C_{2,0}^{\text{out}} \exp(+\sqrt{m_0^{\text{out}}}\mathscr{Z})$$

$$+ \sum_{i=1}^{k} \left[ C_{1,i}^{\text{out}} \sin(\sqrt{m_i^{\text{out}}}\mathscr{Z}) + C_{2,i}^{\text{out}} \cos(\sqrt{m_i^{\text{out}}}\mathscr{Z}) \right] \tag{52}$$

outside it, where $\phi = \phi_{\text{out}} = -\epsilon > 0$. The boundary conditions (48) mean that in the solutions (51) and (52) $C_{1,i}^{\text{out}} = 0$ for $i \geq 1$, $C_{2,i}^{\text{out}} = 0$ for $i \geq 0$, and $\Sigma_{i=0}^{k} C_{2,i}^{\text{in}} = 0$.

For an example, let us analyze in detail the first-order perturbation equation by keeping two first terms in the right side of Eq. (47):

$$3\phi(2+\phi)\psi_0 = \frac{d^2\psi_0}{d\mathscr{Z}^2} + \frac{4}{15(2+\phi)(6+\phi)} \frac{d^4\psi_0}{d\mathscr{Z}^4}. \tag{53}$$

The solution of Eq. (53) subject to the boundary conditions is

$$\psi_0 = C_1 \sin(\sqrt{m_-}\mathscr{Z}) + C_2 \sin(\sqrt{m_+}\mathscr{Z})$$

$$+ C_3 [\cos(\sqrt{m_-}\mathscr{Z}) - \cos(\sqrt{m_+}\mathscr{Z})] \tag{54}$$

at $\mathscr{Z} \leq b/(2l)$ and

$$\psi_0 = C_0 \exp(-\sqrt{k}\mathscr{Z}) \tag{55}$$

at $\mathscr{Z} \geq b/(2l)$, where

$$m_{\mp} = \frac{15}{8}(2+\phi_{\text{in}})(6+\phi_{\text{in}})\left[1 \mp \left(1 + \frac{48}{15}\frac{\phi_{in}}{6+\phi_{in}}\right)^{1/2}\right], \tag{56}$$

$$k = \frac{15}{8}(2-\epsilon)(6-\epsilon)\left[-1 + \left(1 - \frac{48}{15}\frac{\epsilon}{6-\epsilon}\right)^{1/2}\right]. \tag{57}$$

It is clear that by using two continuity conditions and the normalization, we can determine the equilibrium free energy $\epsilon$ and constants $C_0$ and one of $C_1$, $C_2$, or $C_3$. The two free constants are to be chosen such that a minimum value of the equilibrium free energy $\epsilon$ is obtained. As can be seen, the minimal free energy corresponds to one of two following states: (i) $C_1 > 0$ and $C_2 = C_3 = 0$ (the state with $m_I \equiv m_- < m_+$, which we call an isotropic type because it has nearly zero orientation order parameter inside the surface potential well, as we shall see below) and (ii) $C_2 > 0$ and $C_1 = C_3 = 0$ (state with $m_N \equiv m_+$, which we call as nematic-type because of the higher orientation order that results).

From the conditions of continuity (49),

$$\sqrt{m_\mp} \cot[\sqrt{m_\mp} b/(2l)] = -\sqrt{k}. \tag{58}$$

Hence the condition of desorption–adsorption (D–A) transition, i.e., the condition of forming a bound state with $\epsilon = 0$ ($k = 0$), can be written as $\sqrt{m_\mp} b/(2l) = \pi/2$ or

$$\frac{15}{8}(2-\beta 2lU)(6-\beta 2lU)\left[1 \mp \left(1 - \frac{48}{15}\frac{\beta 2lU}{6-\beta 2lU}\right)^{1/2}\right]$$

$$= \left(\frac{\pi l}{b}\right)^2, \tag{59}$$

where negative and positive signs refer to isotropic and nematic-type phases. Equation (59) yields the phase boundary between desorbed and adsorbed states shown in Fig. 2. For $\beta 2lU \ll 1$, it coincides with the result obtained from the standard Edwards Eq. (18):[17]

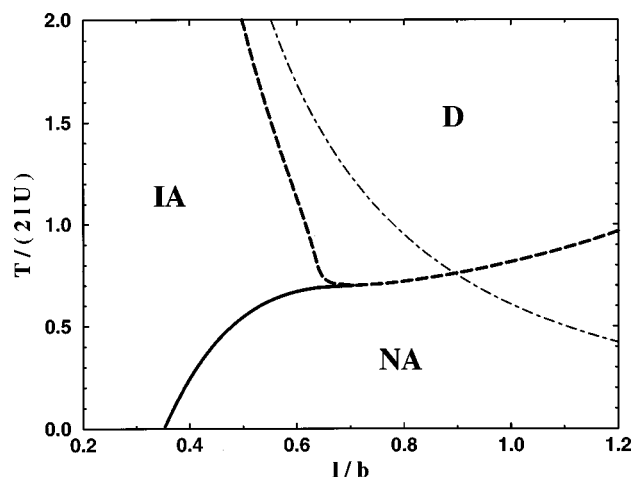$$\beta 2lU = \frac{1}{6}\left(\frac{\pi l}{b}\right)^2. \tag{60}$$

FIG. 2. The phase diagram obtained by the Green's-function first-order perturbation theory. The region (D) corresponds to the desorbed phase, the regions (IA) and (NA) are the isotropic and nematic-type adsorbed phases. The solid and dashed lines correspond to the first- and second-order phase transitions, respectively. The dot-dashed line describes desorption–adsorption boundary in the zeroth-order perturbation theory, i.e., the Edwards equation for flexible polymers.

From Eqs. (56)–(58) we find the derivatives of the free energy with respect to the reduced temperature $T/U$ or the stiffness ratio $l/b$ near the D–A transition:

$$\frac{d\epsilon}{d(T/U)}\bigg|_{l/b=\text{const},\epsilon\to0} \sim |\epsilon|^{1/2}$$

or

$$\frac{d\epsilon}{d(l/b)}\bigg|_{T/U=\text{const},\epsilon\to0} \sim |\epsilon|^{1/2}. \tag{61}$$

It means that

$$\epsilon \sim -\tau_T^2 \quad \text{or} \quad \epsilon \sim -\tau_{(l/b)}^2, \tag{62}$$

where $\tau_T \equiv (T-T_{D-A})/T_{D-A}$ and $\tau_{(l/b)} \equiv [(l/b)-(l/b)_{D-A}]/(l/b)_{D-A}$ are the relative distances of the phase from the transition points in terms of the temperature or the ratio $l/b$, respectively. In any case we obtain the proportionality to the second power of $\tau$ as $\tau\to0$. Thus within the first-order perturbation theory the D–A transition is the second-order phase transition, whether the adsorbed phase is isotropic or nematic. For flexible chains, for which the isotropic structure is the only possibility, this is a well-known result (see, for instance, Ref. 1). As it follows also from Eqs. (55), (57), and (62) in an adsorbed state near the D–A transition (at $\epsilon\to0$) the characteristic scale $\xi$ of adsorbed polymer density, or the bulk correlation length, goes like

$$\xi \equiv k^{-1/2} = (-6\epsilon)^{-1/2} \sim \tau^{-1}, \tag{63}$$

where $\tau$ is either $\tau_T$ or $\tau_{(l/b)}$.

The orientation ordering of polymer segments can be characterized by the standard orientation order parameter,

$$\eta(\mathscr{Z}) = \frac{\int_{-1}^{1}\psi^2(\mathscr{Z},\gamma)P_2(\gamma)d\gamma}{\int_{-1}^{1}\psi^2(\mathscr{Z},\gamma)d\gamma}, \tag{64}$$

where $\gamma\equiv\cos\theta$ and $P_2(\gamma)=(3\gamma^2-1)/2$ is the second Legendre polynomial. Using Eqs. (22), (30), (31), and the Legendre polynomial properties we can rewrite the last equation as

$$\eta(\mathscr{Z}) \simeq \frac{4}{15}\left[\psi_1^2(\mathscr{Z})+3\psi_0(\mathscr{Z})\psi_2(\mathscr{Z})\right]\left(\sum_{i=0}^{\infty}\frac{2\psi_i^2(\mathscr{Z})}{2i+1}\right)^{-1}$$

$$\simeq \frac{4}{15(2+\phi)^2}\left[\left(\frac{d\psi_0}{d\mathscr{Z}}\right)^2+\frac{2(2+\phi)}{6+\phi}\psi_0\frac{d^2\psi_0}{d\mathscr{Z}^2}\right]$$

$$\times\left(\sum_{i=0}^{\infty}\frac{2\psi_i^2}{2i+1}\right)^{-1}.$$

Inside the range $b$ of surface potential, where

$$\frac{d\psi_0}{d\mathscr{Z}}=2l\frac{d\psi_0}{dz}\sim\frac{l}{b}\psi_0,$$

so that

$$\eta(\mathscr{Z})\sim(l/b)^2, \tag{65}$$

and, for absolutely flexible chains ($l/b\to0$), the order parameter $\eta(\mathscr{Z})\to0$, i.e., we have isotropic chain conformation. If $l/b$ increases (stiffness increases) the polymer segment orientation order tends to increase because of the surface attraction that confines the segments within the well. This ordering increases monotonically as $l/b$ increases in the phase which we called conventionally isotropic-type phase.

As shown above in the first-order perturbation theory the adsorbed polymer states can be described by two different sets of parameters $C_i$ ($i=1,2,3,$ and 4) with the corresponding different values of $m_-$ or $m_+$ in Eqs. (54), (58), and (59). These two different states correspond to two phases of adsorbed polymers. The phase with higher values of the ratio $l/b$, i.e., the order parameter, is called nematic-type. The transition between isotropic ($I$)-type and nematic ($N$)-type phases can occur when the corresponding eigenvalues are identical, i.e., $\epsilon_I=\epsilon_N$. As it follows from Eqs. (58) and (57) this is possible at $m_I=m_N$. The condition is met [see Eq. (56)] at $\phi_{in}=-(\beta2lU+\epsilon)=-10/7$ at the temperatures below the bicritical point $T/(2lU)=0.7$, and, together with Eq. (58), determines the boundary between isotropic- and nematic-type phases (see Fig. 2).

Near the transition between isotropic-type adsorbed (IA) and nematic-type adsorbed phase (NA) Eqs. (56)–(58) lead to the following equations for derivatives of the equilibrium free energy:

$$\frac{d\epsilon_I}{d(T/U)}\bigg|_{l/b=\text{const},\epsilon\to0} \simeq 4l\left(\frac{T}{U}\right)^{-2}$$

$$-\frac{d\epsilon_N}{d(T/U)}\bigg|_{l/b=\text{const},\epsilon\to0}, \tag{66}$$

$$\frac{d\epsilon_I}{dl}\bigg|_{T/U,b=\text{const};\epsilon\to0} \simeq -4\beta U-\frac{d\epsilon_N}{dl}\bigg|_{T/U,b=\text{const};\epsilon\to0}, \tag{67}$$

$$\left.\frac{d\epsilon_I}{db}\right|_{T/U,l=\text{const};\epsilon\to0} \simeq -\left.\frac{d\epsilon_N}{db}\right|_{T/U,l=\text{const};\epsilon\to0}. \tag{68}$$

In any case we obtain

$$\epsilon_N - \epsilon_I \sim \tau_T \quad \text{or} \quad \epsilon_N - \epsilon_I \sim -\tau_{(l/b)}, \tag{69}$$

where $\tau_T \equiv (T - T_{\text{IA-NA}})/T_{\text{IA-NA}}$ and $\tau_{(l/b)} \equiv [(l/b) - (l/b)_{\text{IA-NA}}]/(l/b)_{\text{IA-NA}}$ are the relative distances of the phase from the transition point. Since the free energy is proportional to the first power of $\tau$ as $\tau\to0$, we can conclude that in the frameworks of first-order perturbation theory the IA–NA transition is the first-order phase transition as is usual for nematic ordering transitions in three-dimensional polymer systems.[1]

Figure 2 is the phase diagram that results from the first-order perturbation theory. It predicts that the semiflexible chain with persistence length larger than the range of the attraction adsorbs more easily (desorption temperature is higher) than is given by the Edwards equation for flexible chains. This fact is due to the emergence of nematic phase induced by stiffness. However, for the persistence length much smaller than the range, the D–A transition line tends to converge to that of Edwards equation. Also the first-order perturbation calculations show that the above desorption–adsorption, isotropic–nematic transitions are, respectively, the second and first order. The phase diagram (Fig. 2) is qualitatively in accord with our scaling theory prediction.[4] The first-order perturbation theory is limited by the condition of small curvature $[(2l)^2/\psi]|d^2\psi/dz^2|$ however. Therefore in describing the situations involving rapid segmental variation and high chain stiffness, one should turn to high-order perturbation theory. In the next section we apply the interpolation solution to the adsorption problem, which describes the weak-to-strong adsorption transitions, as well as the effect of chain stiffness in more details for $(l/b)>1$.

## B. Interpolation solution of the adsorption problem

Since for $l\gg b$ a rapid convergence of the perturbation scheme cannot be guaranteed, we resort to the interpolation solution. First Eqs. (41) and (43) for $i=2$ lead to

$$3\phi(2+\phi)\psi_0 = \frac{d^2\psi_0}{d\mathscr{Z}^2} + \Omega e^{-4\mathscr{Z}}, \tag{70}$$

where $\Omega=\text{const}$. Inside the potential well $[\mathscr{Z}<b/(2l), W_{2l} = -2lU<0]$ at $-2<\phi_{\text{in}}<0$ $(\phi_{\text{in}}\equiv -\beta2lU-\epsilon)$ the solution of the equation can be written as

$$\psi_0 = C_1 \sin(\sqrt{m}\mathscr{Z}) + C_2 \cos(\sqrt{m}\mathscr{Z}) - \frac{\Omega}{16+m}e^{-4\mathscr{Z}}, \tag{71}$$

where $m\equiv -3\phi(2+\phi)$. Outside the potential well $[\mathscr{Z}>b/(2l), W_{2l}=0]$, $\phi_{\text{out}}=-\epsilon>0$, and the solution of Eq. (70) has the form

$$\psi_0 = C_3 \exp(-\sqrt{k}\mathscr{Z}) + C_4 \exp(\sqrt{k}\mathscr{Z}) - \frac{\Omega}{16-k}e^{-4\mathscr{Z}}, \tag{72}$$

here $k\equiv -3\epsilon(2-\epsilon)$. The constants $C_i$ $(i=1,2,3,4)$ and the equilibrium free energy $\epsilon$ are determined by the conditions (48)–(50). In particular, the boundary conditions (48) yields $C_2=\Omega/(16+m)$ and $C_4=0$.

Equations (71) and (72) together with the boundary and continuity conditions lead to

$$\frac{C_1}{\Omega}\left[\sqrt{k}\,\sin\left(\sqrt{m}\,\frac{b}{2l}\right) + \sqrt{m}\,\cos\left(\sqrt{m}\,\frac{b}{2l}\right)\right]$$
$$+ \frac{1}{16+m}\left[\sqrt{k}\,\cos\left(\sqrt{m}\,\frac{b}{2l}\right) - \sqrt{m}\,\sin\left(\sqrt{m}\,\frac{b}{2l}\right)\right.$$
$$\left. + (4-\sqrt{k})\exp\left(-4\frac{b}{2l}\right)\right] = \frac{1}{4+\sqrt{k}}\exp\left(-4\frac{b}{2l}\right). \tag{73}$$

The $\Omega$ value (or the ratio $C_1/\Omega$) has to be chosen in such a way that a minimum value of the equilibrium free energy $\epsilon$ is obtained. In the case $l\ll b$ (flexible polymer limit), on the basis of direct calculations the free-energy minimum takes place at $|C_1/\Omega|\gg1$, and Eq. (73) transforms to

$$\sqrt{m}\,\cot[\sqrt{m}b/(2l)] = -\sqrt{k}, \tag{74}$$

which is identical with the first-order perturbation Eq. (58), where $m_- \simeq m$ at $\phi_{\text{in}} = -\beta2lU-\epsilon\ll1$. Moreover in the limits $l\ll b$ and $T\gg lU$ it coincides with the zeroth-order result for small fields,[17] i.e., with the result which follows from the Edwards equation. In the case $l\sim b$ of a nematic-type weakly adsorbed (NWA) state, we find that from direct calculation the minimal free energy corresponds to $|C_1/\Omega|\ll1$ in Eq. (73). For $l\gg b$ of a nematic-type strongly adsorbed (NSA) state the free-energy minimum is reached at finite values of the ratio $C_1/\Omega$.

For the adsorption–desorption transition conditions with the free-energy minimum set to zero ($\epsilon=0$ and thus $k=0$) Eq. (73) is transformed to

$$\frac{C_1}{\Omega}(16+m)\sqrt{m}\,\cos\left(\sqrt{m}\,\frac{b}{2l}\right) - \sqrt{m}\,\sin\left(\sqrt{m}\,\frac{b}{2l}\right)$$
$$= \frac{m}{4}\exp\left(-4\frac{b}{2l}\right). \tag{75}$$

The corresponding phase boundary is shown in Fig. 4. For $l\ll b$ the D–A transition curve of the interpolation approach coincides with the zeroth- [Eq. (60)], first- [Eq. (59)], and higher-order perturbation ones. At large $l$ (or at smaller $b$) values, i.e., at $l\sim b$, but still in the isotropic phase, evidently (Fig. 3) the D–IA transition curves for the third- and higher-order perturbations approach closely to that of the interpolation approximation (Fig. 4). As shown from direct calculations, the relations (61), (62), and (63), and thus the conclusion that the D–IA transition is the second-order phase transition are retained for all orders of the perturbation and the interpolation approximation.

For $l\sim b$ of a NA state with $|C_1/\Omega|\ll1$, Eq. (75) for D–A transition conditions is reduced to

$$-\sin\left(\sqrt{m}\,\frac{b}{2l}\right) = \frac{\sqrt{m}}{4}\exp\left(-4\frac{b}{2l}\right). \tag{76}$$
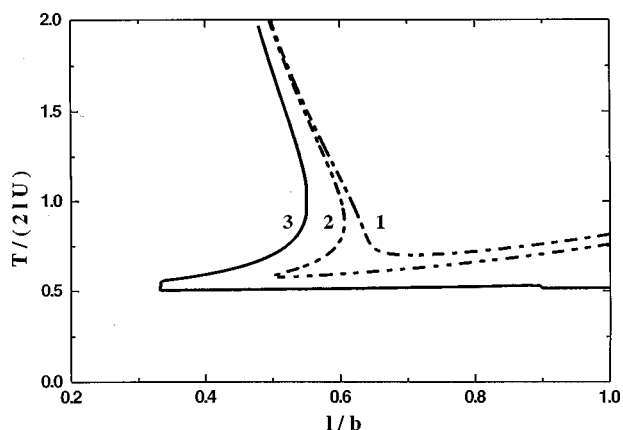
FIG. 3. The D–A transition curves obtained by the present Green's-function perturbation theory (PT). Here the dot-dashed line (1), which coincides with the dashed line in Fig. 2, is described by the first-order PT; the dotted line (2) was obtained by the third-order PT, while the solid one is a result of the interpolation approach (see the text). The last curve can be considered as an asymptotic limit of the PT.

while at $l \gg b$ the condition leads to

$$m = 0 \quad \left( \text{i.e., } \frac{T}{2lU} \simeq 0.5 \right). \tag{77}$$

For $l > b$ the differences between all the approximations are most pronounced (Fig. 3). While the Edwards equation (zeroth-order approximation) leads to a monotonic decrease of the D–A transition reduced temperature $T/(2lU)$ as a function of $l/b$ [Eq. (60)], all the higher-order and interpolation approximations do not abide by this behavior. As it has been shown in Fig. 2 the first-order result demonstrates a slight increase of the transition temperature as $l/b$ increases near the bicritical point $T/(2lU) = 0.7$, and $l/b \simeq 0.7045$. The similar increase, although tending to be reduced, is demonstrated in all the higher-order perturbation theories. Again the high-order perturbation results tend to approach that of
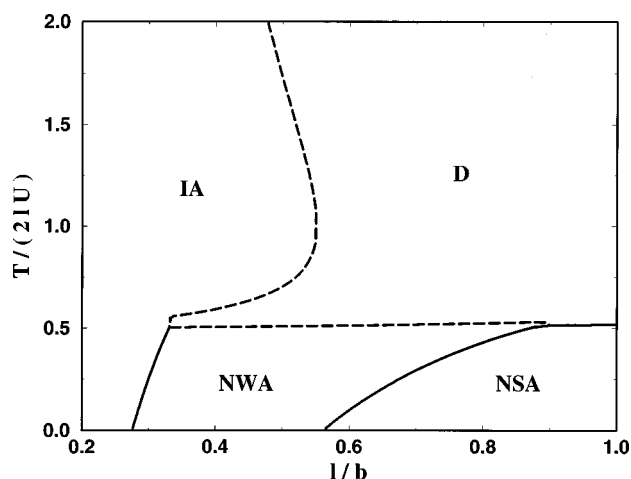


FIG. 4. The phase diagram obtained by the interpolation approximation of the Green's-function theory. The regions (D), (IA), (NWA), and (NSA) correspond to desorbed, isotropic adsorbed, nematic-type weakly and strongly adsorbed phases, respectively. The solid and dashed lines correspond to the first- and second-order phase transitions, respectively.

the interpolation approximation: the D–A transition reduced temperature is constant at $l \gg b$, $T/(2lU) \simeq 0.5$ (Fig. 4). Our scaling theory prediction[4] is consistent with this result.

For high polymer stiffness we obtain a nematic-type ordering in the adsorbed phase, which is impossible in the frameworks of flexible-chain description (Edwards or zeroth-order equations). The curve of isotropic to nematic-type ordering transition in the interpolation approximation (Fig. 4) is in a qualitative agreement with the corresponding scaling theory[4] and first-order perturbation curves and presumably close quantitatively to the exact one. The calculation in any of these approximations shows that the I–N transition is the first-order one as it usually is in any 3D system.

Now we analyze the weak-to-strong adsorption transition that appeared in our scaling theory study.[4] In the frameworks of our present analysis, which is valid for the very long chains only, we arrive at the same conclusion as in the scaling theory, that in isotropic adsorbed state the infinitely long flexible polymers undergo a crossover between the isotropic-type weakly adsorbed (IWA) and isotropic-type strongly adsorbed (ISA) states, not a phase transition. We should notice, however, that as it was shown in the scaling theory for finite chains, at finite temperatures the second-order transition to ISA phase, where all the polymer links are adsorbed, takes place, as it was also observed in the numerical simulation of Ref. 18. However, the transition temperature tends to be zero along with the increase of polymer length to infinity.

It is found that in the nematic-type adsorbed state the weak to strong adsorption transition occurs as the ratio $l/b$ increases in finite temperatures. The corresponding transition line is shown in Fig. 4, which shows the complete phase diagram derived from the interpolation approximation. This transition is the first order. At high polymer stiffness the transition curve merges with the D–A transition one. It means that in this region we have direct transition from the desorbed phase to the strongly adsorbed nematic-type one, which is the first order. The result on the order of NWA–NSA transition is the same as it was predicted in the frameworks of our scaling theory.[4] But the present approach makes it possible to obtain quantitatively the convergence of the D–NA and NWA–NSA transition lines and to discover the first-order nature of the D–A (D–NSA, more exactly) transition at high polymer stiffness. Indeed, near the D–NA transition the free-energy derivative is given by

$$\frac{d\epsilon}{d(T/2lU)} \sim \left( \frac{|\epsilon|}{m} \right)^{1/2}. \tag{78}$$

For $l \gg b$, $m \sim |\epsilon|$, and thus Eq. (78) leads to $\epsilon \sim \tau$, while for $l \sim b$ the value $m$ is finite, $d\epsilon/d(T/2lU) \sim |\epsilon|^{1/2}$ and $\epsilon \sim \tau^2$.

Figures 5(a) and 5(b) depict the dependence of dimensionless free energy per segment $\epsilon = (F/T)(2l/L)$ on the ratio $l/b$ and the reduced temperature $T/(2lU)$, respectively, for different regions of the adsorbed states. The curves 1–4 (ordered so that the higher number represents lower temperature) in Fig. 5(a) show the smooth change of equilibrium free energy in the isotropic adsorbed phase before it undergoes the desorption transition of the second order. The curve 5 in
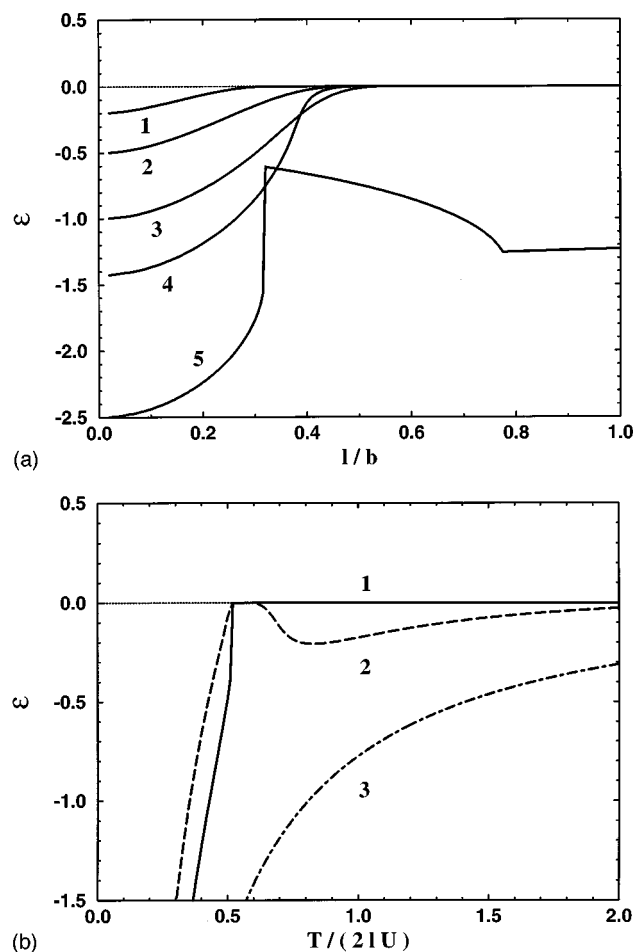
(a)



(b)

FIG. 5. The dimensionless free energy per segment versus (a) the ratio $l/b$ for different values of the reduced temperature: $T/(2lU) = 5.0$ (1), 2.0 (2), 1.0 (3), 0.7 (4), and 0.4 (5) versus (b) the reduced temperature $T/(2lU)$ for different values of the stiffness ratio: $l/b = 1.0$ (1), 0.4 (2), and 0.2 (3).

the same figure describes the free-energy behavior in the adsorbed state at a temperature below the minimum D–A transition temperature or the bicritical point (see Fig. 4). The discontinuities of derivatives of the free energy with respect to the ratio $l/b$ corresponds to the first-order phase transitions from IA (small $l/b$) to NWA phase (larger $l/b$), and then from NWA to NSA phase (largest $l/b$).

In Fig. 5(b) curve 1 (solid line) describes the free energy at fixed large polymer stiffness ($l/b = 1$), which leads to the first-order phase transition from the nematic-type strongly adsorbed phase (low temperatures) to the desorbed one (higher temperatures). The curve 3 (dot-dashed) shows the free-energy increase in the IA phase (lowest value of $l/b$) as the reduced temperature increases. This leads to the second-order IA–D phase transition eventually at a very high temperature. Curve 2 (dashed) describes an intermediate case of polymer stiffness where three different phases, the NWA phase, the desorbed phase (over the $\epsilon = 0$ region), then the IA and again desorbed ones can be reached by a temperature increase. All these transitions are the second order.

To analyze orientation and position distributions of the polymer segments it is convenient to use the standard orien-
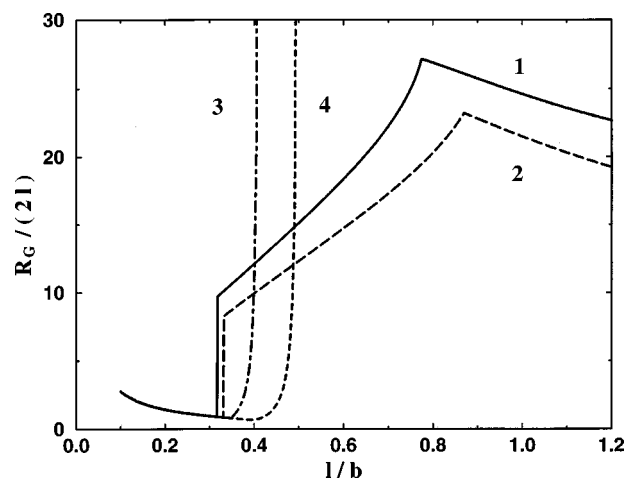


FIG. 6. The root-mean-square polymer dimension $R_G = \langle z^2 \rangle^{1/2}$ versus the ratio $l/b$ for $T/(2lU) = 0.4$ (1), 0.5 (2), 0.6 (3), and 0.7 (4).

tation order parameter (Eq. 64) and the mean-square dimension of polymer vertical to surface:

$$
\langle z^2 \rangle = \frac{\int z^2 n(x,\mathbf{u}) dz \, d^2 u}{\int n(z,\mathbf{u}) dz \, d^2 u}
$$

$$
= \frac{(2l)^2}{N_\perp} \int_0^\infty \int_{-1}^1 \mathscr{Z}^2 \psi^2(\mathscr{Z}, \gamma) d\mathscr{Z} \, d\gamma, \tag{79}
$$

where $N_\perp = \int_0^\infty \int_{-1}^1 \psi^2(\mathscr{Z}, \gamma) d\mathscr{Z} \, d\gamma$. Using Eqs. (22), (30), (43), and the Legendre polynomial properties we can rewrite Eqs. (79) and (64) for the interpolation approximation as

$$
\frac{\langle z^2 \rangle}{(2l)^2} N_\perp \simeq \int_0^\infty \left\{ 2\mathscr{Z}^2 \psi_0^2 + \frac{2\mathscr{Z}^2}{3(2+\phi)^2} \right.
$$

$$
\left. \times \left[ \frac{\Omega}{4} e^{-4\mathscr{Z}} - \frac{d\psi_0}{d\mathscr{Z}} \right]^2 \right\} d\mathscr{Z} + \frac{5\Omega}{2^{17}}, \tag{80}
$$

where

$$
N_\perp \simeq \int_0^\infty \left\{ 2\psi_0^2 + \frac{2}{3(2+\phi)^2} \left[ \frac{\Omega}{4} e^{-4\mathscr{Z}} - \frac{d\psi_0}{d\mathscr{Z}} \right]^2 \right\} d\mathscr{Z}
$$

$$
+ \frac{5\Omega}{2^{12}}
$$

and

$$
\eta(\mathscr{Z}) \simeq \left\{ \frac{4}{15} \left[ \psi_1^2(\mathscr{Z}) + 3\psi_0(\mathscr{Z})\psi_2(\mathscr{Z}) \right] + \frac{4}{35} \left[ \psi_2^2(\mathscr{Z}) \right. \right.
$$

$$
\left. \left. + 3\psi_1(\mathscr{Z})\psi_3(\mathscr{Z}) \right] \right\} \left( \sum_{i=0}^\infty \frac{2\psi_i^2(\mathscr{Z})}{2i+1} \right)^{-1}. \tag{81}
$$

The calculated values of $\langle \mathscr{Z}^2 \rangle^{1/2} = \langle z^2 \rangle^{1/2}/2l$ versus $l/b$ are shown in Fig. 6. The curves 1 and 2, representative of the two lowest temperatures below the bicritical point, manifest the discontinuous changes arising from the first-order IA–NWA and NWA–NSA transitions. On the other hand the curves 3 and 4 represent the continuous but drastic changes of $\langle \mathscr{Z}^2 \rangle^{1/2}$ as the second-order IA–D transitions are ap-
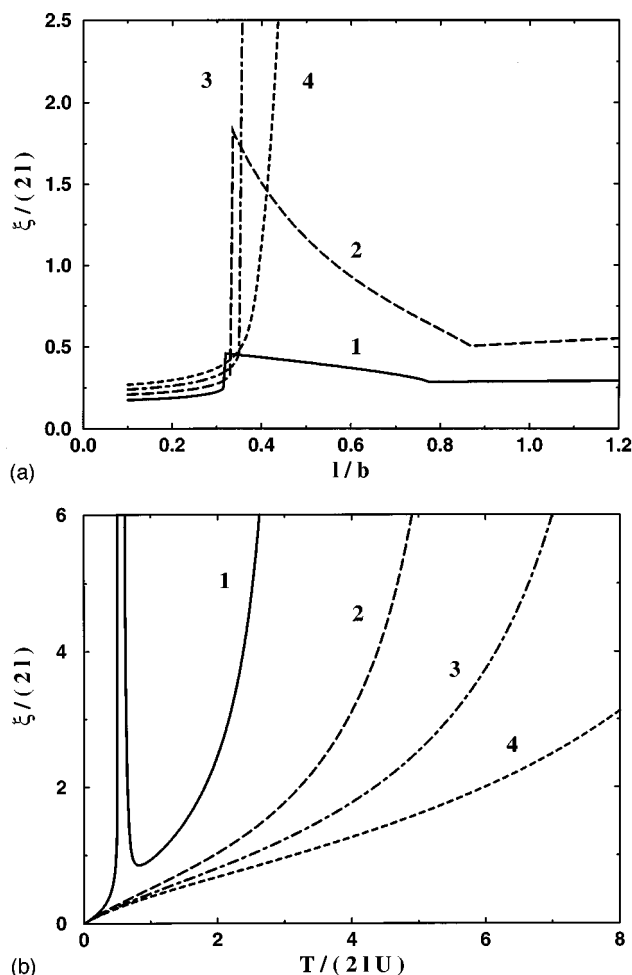
(a)



(b)

FIG. 7. The characteristic scale of density changing $\xi = 2lk^{-1/2}$ versus (a) the ratio $l/b$ for $T/(2lU) = 0.4$ (1), 0.5 (2), 0.6 (3), and 0.7 (4); (b) the reduced temperature for $l/b = 0.4$ (1), 0.3 (2), 0.25 (3), and 0.2 (4).

proached. The similar properties can be observed in the behaviors of the calculated values of the bulk correlation length $\xi \equiv 2lk^{-1/2}$ as shown in Fig. 7(a). It should be noted, however, that, in contrast to $\langle \mathscr{Z}^2 \rangle^{1/2}$, $\xi$ tends to be reduced as the temperature is decreased within the NA region.

Figure 7(b) shows the reduced correlation length $\xi/2l$ versus temperature for fixed stiffness in IA phases. The curve 1 represents the changes associated with the transitions NWA–D–IA–D. On the other hand, in curves 2–4, $\xi$ increases monotonically as temperature increases in the adsorbed phases below the IA–D transition.

The position distributions of the orientation order parameter $\eta(\mathscr{Z})$ inside the range of potential well for different polymer stiffness at the temperature below the bicritical point are depicted in Fig. 8 as $\eta$ versus $z/b \equiv \mathscr{Z}2l/b$ [see definition (20)]. Curve 1 demonstrates a slight perturbation of the isotropic segments distribution ($\eta = 0$) due to the small but finite value of polymer backbone stiffness, the so-called isotropic-type adsorbed structure. Curve 2 shows the orientation order parameter in IA phase for the segment with stiffness close to the IA–NWA transition. Curves 3 and 4 show
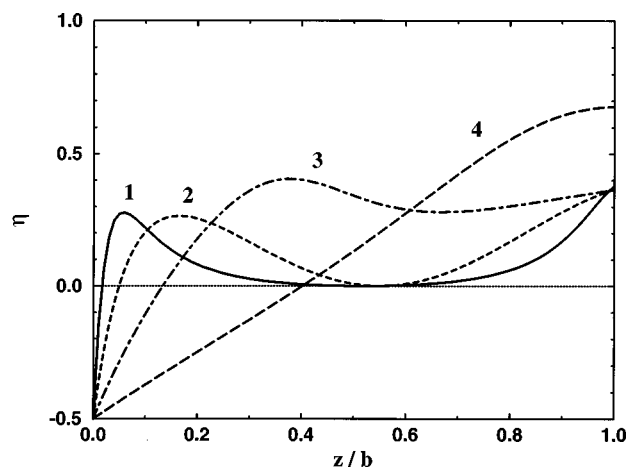


FIG. 8. The orientation order parameter $\eta$ inside the near-surface potential well for $T/(2lU) = 0.3$ and (1) $l/b = 0.1$, isotropic region; (2) $l/b = 0.3$, isotropic region near the IA–NA transition; (3) $l/b = 0.6$, weak adsorption region, and (4) $l/b = 2.0$, strong adsorption region.

the overall change of $\eta(\mathscr{Z})$ in the NWA and NSA phases, respectively.

In Figs. 9 and 10 the position dependence of the function $\psi_0(\mathscr{Z})$ and the segments density $n(\mathscr{Z}) = \int_{-1}^{1} \psi^2(\mathscr{Z}, \gamma) d\gamma$ are drawn for different adsorbed phases at the same values of reduced temperature and polymer stiffness, and using the same abscissa argument as in Fig. 8. We should emphasize here that the hard surface boundary condition $n(\mathscr{Z}) = 0$ for $\mathscr{Z} \leq 0$ is manifested explicitly in the Fig. 9 for $\psi_0(\mathscr{Z})$ only, which corresponds to the orientation-independent part of $\psi(\mathscr{Z}, \gamma)$ [Eq. (22)] descriptive of the polymer-ends density distribution:

$$\psi_0(\mathscr{Z}) = \frac{1}{2} \int_{-1}^{1} \psi(\mathscr{Z}, \gamma) d\gamma.$$

For absolutely flexible chains $n(\mathscr{Z}) = \psi_0^2(\mathscr{Z})$ (close to the case of curve 1 in Fig. 10) the polymer segments have no reason to align along the surface and the polymer density
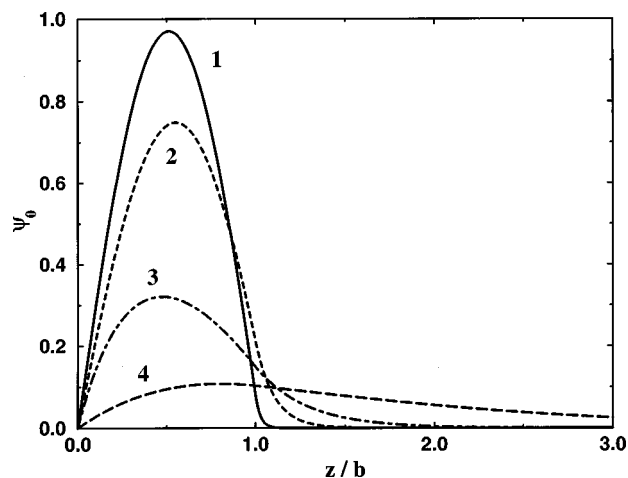


FIG. 9. The characteristic dependencies of $\psi_0(r)$ function at the same regions and the same values of the reduced temperature $T/(2lU)$ and the ratio $l/b$ as it was shown in Fig. 8.
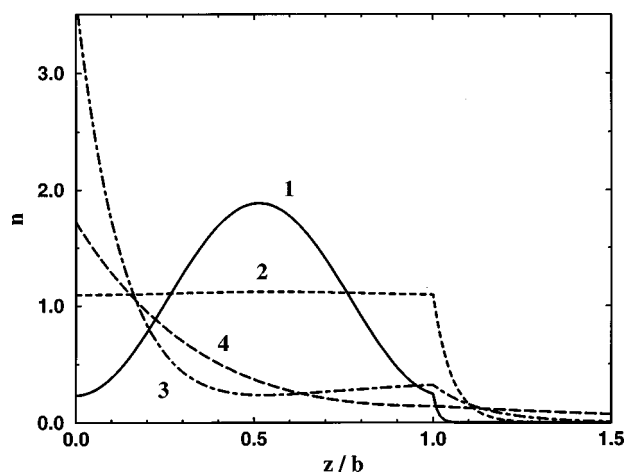
FIG. 10. The characteristic distributions of segments density $n(z)$ $= \int_{-1}^{1} \psi^2(z, \gamma) d\gamma$ for the same values of the reduced temperature $T/(2lU)$ and the ratio $l/b$ as in Fig. 8.

increases monotonically on the length scales of $b$. Due to finite stiffness, a polymer cannot drastically change an orientation along the chain near the surface. If a segment reaches the surface then the following segments at least within the range of persistence length sustain their position just near the surface. For semiflexible polymers it leads to a dramatic segmental density increase on the short length scales of the monomer diameter $d$. In the absence of excluded volume effects, as is the case with the present paper, we consider the limit $d \rightarrow 0$, which leads to a jump of the density at $\mathscr{Z} = 0$ even for rather flexible chains. The similar jumps take place for relatively small polymer stiffness on the other border of the potential well, $z = b$, and they reflect a similar orientation order of polymer segments along the attractive potential border to maximally attain negative potential energy for adsorption.

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