Influence of surface interaction and chain stiffness on polymer-induced entropic forces and the dimensions of confined polymers

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The theories of Dolan and Edwards [Proc. R. Soc. London Ser. A **337**, 509 (1974)] and Eisenriegler *et al.* [J. Chem. Phys. **77**, 6296 (1982)] for Gaussian chains confined between parallel plates and to a half-space are generalized to chains having arbitrary stiffness. The generalized theory exploits a recently discovered relation between semiflexible polymers and Euclidean-type Dirac fermions in which "flexible" and "stiff" polymers correspond to the nonrelativistic (massive) and relativistic (massless) limits of the Dirac propagator, respectively. We show that half-space and parallel-plate problems are interrelated and this allows for a simplified and unified treatment of confined semiflexible polymers. The properties of confined semiflexible chains exhibit a complicated dependence on the polymer-surface interaction and chain stiffness. Results for polymer dimensions and entropic Casimir-like forces between plates are consistent with those obtained previously for flexible chains and corresponding results are obtained for semiflexible polymers. The new results for the forces between plates, having a semiflexible polymer in the gap, exhibit qualitative agreement with experimental data on confined chains at nonvanishing concentrations.

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I. INTRODUCTION

The statistical mechanics of bulk polymer solutions at various concentrations is rather well understood [1] for fully flexible chains with excluded volume interactions. However, the statistical mechanical description of partially flexible chain solutions is still relatively undeveloped. Recently, we introduced a new formalism which allows the extension of known results for flexible polymers to chains having arbitrary stiffness [2–8]. At the level of an isolated polymer chain, this approach reproduced known conformational properties of semiflexible chains and some new basic results were also obtained, e.g., an exact closed form for the scattering function $S(\mathbf{k})$ [8] for chains of arbitrary stiffness, etc. At the level of many chains, the classical results of Onsager [9] and Flory [10] for nematic order in solutions of rigid rods were also reproduced using an extension of a formalism applied earlier [11] to flexible polymer solutions. This approach allows for the treatment of fluctuation corrections for solutions of chains having arbitrary flexibility and this task will be developed in separate publications.

There are many physical problems involving polymer solutions in confined geometries which can be described by our new formalism. Examples include adsorption of polymer chains by surfaces [12], polymer stabilization of colloids [13], study of surface tension changes by polymers at interfaces [14], partitioning of polymers between the bulk and porous medium [15], shifts in the critical temperatures of phase separating solutions in confined geometries [16], etc.

To study the above problems analytically, two complementary approaches have been traditionally followed. One approach involves a continuum theory extension of bulk results to the case of restricted geometries [12,17,18], while the other approach employs lattice model of random walks in the presence of boundary constraints [19]. The latter approach is important, for example, for the study of polymer-induced entropic "Casimir-like" (since they derive from medium fluctuations) forces between parallel plates and has contributed significantly to our understanding of polymer colloid stabilization. For this geometry, Casimir-like forces were first considered by Meier [20], Cassasa and Tagami [21], and Dolan and Edwards [18], based on a continuum model for flexible polymer chains, and by DiMarzio and Rubin [19] for lattice random-walk chains. From the standpoint of the present work, it is notable that the continuum model calculations have been restricted to infinitely strong *repulsive* polymer-surface interactions while the DiMarzio and Rubin calculations have not been restricted in this fashion. Limited results related to semiflexible chains have been obtained by this approach, however. The continuum models are sometimes more advantageous because they admit an easy generalization to finite polymer concentrations, the presence of excluded volume, etc. [22], while the discrete lattice calculations are usually limited to chains in the absence of excluded volume effects [19]. For the half-space problem, the situation is similar. Following the discrete chain formulation of Privman and Svrakič [23] and earlier work, Ref. [19], the fraction of absorbed monomers is readily considered. The same quantity is much harder to define in the continuum approach (see Fig. 1 and discussion given in Sec. VII B below). The choice of model is then dependent on

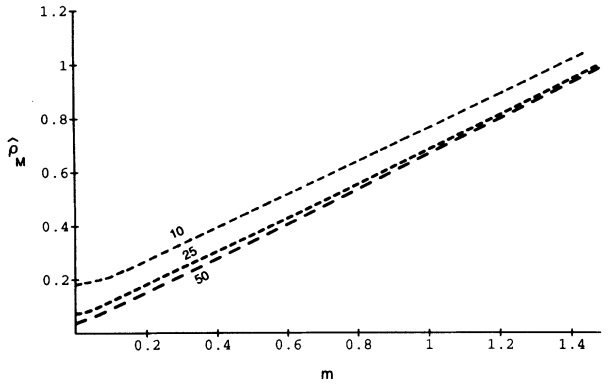

FIG. 1. Fraction of adsorbed monomers $\hat{\rho}_M$ as a function of an inverse rigidity m [Eq. (7.46)] for polymer chains of different lengths N ($N=10, 25, 50$).

the questions under discussion.

Unlike the continuum results of Dolan and Edwards [18], our calculations are *not* limited to the infinitely strong surface repulsion. The present calculations are simplified by a demonstration that the half-space and the parallel-plate problems are mathematically interrelated. This observation allows for an extension of the Dolan and Edwards theory to the case of arbitrary strengths (attraction or repulsion) of the polymer-surface interaction and for an extension of the half-space results of Ref. [17], to chains of arbitrary flexibility.

This paper is organized as follows. In Sec. II we provide some auxiliary background material related to Dirac-type descriptions of semiflexible polymers [2–8]. In Sec. III we reconsider the problems of description of conformational properties of fully flexible polymers confined to half space and between the parallel plates and demonstrate how they are interrelated. In Sec. IV we extend these results to semiflexible polymers. Section V is devoted to general discussion related to calculations of basic single chain properties, while in Sec. VI we provide explicit calculation of these properties for the case of fully flexible chains. In Sec. VII we provide detailed calculations of the same properties for chains having arbitrary flexibility, while in Sec. VIII we discuss our results in connection with related problems to be considered in the future.

II. GENERAL BACKGROUND

The conformational properties of fully flexible polymers in the absence of excluded volume are described with the help of the moment generating function $G_0(\mathbf{k},N)=\exp(-\mathbf{k}^2lN/2d)$ where N is the length of polymer chain, l is Kuhn's step length ($l \ll N$), and d is the dimensionality of space. This generating function is just Fourier transform of the Gaussian chain end-to-end distribution function appropriate for random walks [1]. With the help of $G_0(k,N)$ the moments such as $\langle \mathbf{R}^2 \rangle$, etc. of the distribution function are obtained, e.g., $\langle \mathbf{R}^2 \rangle = Nl$. In the case when Kuhn's length l becomes comparable with N, the Gaussian distribution function can no longer be used, and we have to replace $G_0(\mathbf{k},N)$ by a generating function appropriate for semiflexible chains. Such a function was determined recently [2–8] and is given by

$$\hat{G}_0(\mathbf{k},N)=2\cosh(mEN)+\frac{2}{E}\sinh(mEN) , \tag{2.1}$$

where $E^2=1-\mathbf{k}^2/2dm^2$ and the "mass" parameter m is directly related to the rigidity of polymer chain (more exactly, $m \propto a^{-1}$ where a is the persistence length). Application of a Laplace transform to Eq. (2.1) converts it into

$$\frac{1}{2\sqrt{d}}\hat{G}_0(\mathbf{k},s)=\frac{\sqrt{d}\,(s+m)}{\mathbf{k}^2/2+M^2} , \tag{2.2}$$

where $M^2=d(s^2-m^2)$. For further use it is convenient to rescale the momentum $\mathbf{k}$ so that Eq. (2.2) acquires the form

$$\frac{1}{2d}\hat{G}_0(\mathbf{k},s)=\frac{s+m}{\mathbf{k}^2+s^2-m^2} . \tag{2.3}$$

We would like now to demonstrate directly how Eq. (2.3) can be obtained with the help of the Euclidean version of the $4d$ Dirac propagator G_E. Using Ref. [8] we write

$$G_E(\mathbf{k},s)=\frac{-i}{\not{k}+m}=i\frac{\not{k}-m}{k^2+m^2}\equiv\hat{G}_0(k,s) , \tag{2.4}$$

where $k^2=\mathbf{k}^2+s^2$, $\not{k}=\gamma^\mu k_\mu$ being Euclidean-type Dirac matrices so that $\{\gamma^\mu,\gamma^\nu\}=2\delta^{\mu\nu}$. Now let $m\rightarrow im$ in Eq. (2.4), so that we then obtain

$$\mathrm{Tr}\hat{G}_0(\mathbf{k},s)=\frac{m}{\mathbf{k}^2+s^2-m^2} , \tag{2.5}$$

where we have taken into account that $\mathrm{Tr}\gamma^\mu=0$ and $\mathrm{Tr}(\gamma^\mu)^2=-1$. Although the right-hand side of Eq. (2.5) is not exactly the same as that of Eq. (2.3), we shall demonstrate shortly that both Eq. (2.3) and Eq. (2.5) could be used for description of semiflexible polymers. Moreover, they are naturally connected with each other. Indeed, as discussed in Refs. [3,4], the lattice version of the Dirac propagator is obtained only if the proper averaging over the initial states and summation over the final states of the lattice walks is made (as it is also done in continuous limit for the Dirac particle [3]). In the continuous limit the polarization density matrix ρ is used [e.g., we can choose $\rho=\frac{1}{4}(\mathbf{I}+a_\mu\gamma^\mu)$ so that $\mathrm{Tr}\rho=1$ and a_μ could be assigned to properly account for the orientation of the initial and final states.] If we choose ρ in the form $\rho=\frac{1}{4}(\mathbf{I}+i\gamma^4)$, then multiplying both sides of Eq. (2.4) by ρ and taking the trace brings us back to Eq. (2.3) as required (of course, after replacement $m\rightarrow im$, as before). We would like to note also that in the case of Kratky-Porod (KP) type chains the above averaging over initial and final states is also crucially required [3]. Let $G(\mathbf{k},N)$ be generating function for random walk [i.e., $G(\mathbf{k},N)=G_0$ or $\hat{G}_0$], then the mean square end-to-end distance $\langle \mathbf{R}^2 \rangle$ can be calculated according to the equation

$$\langle \mathbf{R}^2 \rangle=-2d\frac{\partial}{\partial \mathbf{k}^2}\ln G(\mathbf{k},N)|_{\mathbf{k}=0} . \tag{2.6}$$

It is easy to check that this prescription produces the

correct results for Gaussian walks and, hence, by complementarity and continuity, it is expected to produce correct results in more general cases. Equation (2.6) can be equivalently rewritten as

$$\langle \mathbf{R}^2 \rangle = -2d \left. \frac{L^{-1}\left[\frac{\partial}{\partial k^2} G(\mathbf{k},s)\right]}{L^{-1}[G(\mathbf{k},s)]} \right|_{k=0}, \tag{2.7}$$

where L^{-1} is the operation of taking the inverse Laplace transform. Using Eq. (2.2), we obtain

$$\langle \mathbf{R}^2 \rangle = \frac{N}{2m} - \frac{1}{4m}(1-e^{-2mN}), \tag{2.8}$$

which, upon rescaling $N \to \sqrt{2}N, m = (2\sqrt{2a})^{-1}$, produces the well-known KP result

$$\langle \mathbf{R}^2 \rangle = a^2 \rho^2(x), \tag{2.9}$$

where a was already defined, e.g., see Eq. (2.1), and $\rho^2(x) = 2[x - 1 + \exp(-x)]$ with $x = N/a$. For $a \ll N$ we again obtain the Gaussian result $\langle \mathbf{R}^2 \rangle = 2aN$ so that in *this* limit we can make an identification: $l = 2a$. In the opposite case $a \geq N$ (i.e., $m \to 0$) we obtain the rigid rod result: $\langle \mathbf{R}^2 \rangle = N^2$. Let us now use Eq. (2.5) in order to calculate $\langle \mathbf{R}^2 \rangle$. By combining Eqs. (2.5) and (2.7) we obtain

$$\langle \mathbf{R}^2 \rangle = \frac{dN}{m} \mathcal{L}(mN), \tag{2.10}$$

where $\mathcal{L}(x)$ is the Langevin function: $\mathcal{L}(x) = \coth x - 1/x$. Now let $d = 3$ and $m = 3/2a$, then the last result can be rewritten as

$$\langle \mathbf{R}^2 \rangle = \frac{4a^2}{3} x \mathcal{L}(x), \tag{2.11}$$

where $x = 3N/2a$. For the Langevin function it is known that $\mathcal{L}(x \to 0) = x/3$ which produces $\langle \mathbf{R}^2 \rangle = N^2$ as before while $\mathcal{L}(x \to \infty) = 1$, which produces $\langle \mathbf{R}^2 \rangle = 2Na$ also as before. Graphical comparison [8] between the right-hand sides of Eqs. (2.9) and (2.11) shows that they practically coincide for all values of x (except for $x \approx 1$ where they slightly differ). In Ref. [8] we have demonstrated that it is more advantageous to use Eq. (2.5) than (2.2) in the case where the higher moments, e.g., $\langle \mathbf{R}^6 \rangle$ etc. are of interest. It is because the Dirac propagator, Eq. (2.5), permits us to obtain a closed form expression for the scattering function $S(\mathbf{k})$ valid for arbitrary k's and chain stiffness a while the use of Eq. (2.2) produces correct results for $S(\mathbf{k})$ only in the limit $\mathbf{k} \to 0$ (i.e., at the level of $\langle \mathbf{R}^2 \rangle$ calculations). In view of this, we shall use in the rest of this paper the Dirac propagator, Eq. (2.5), keeping in mind that the alternative form, Eq. (2.2), could be used in principle if it is physically necessary.

Because the differences between Eqs. (2.2) and (2.6) are caused by the difference in performing the orientational averaging over the chain ends, it is appropriate to mention here that the above two forms do not exhaust the existing possibilities. For example, if we would like to study the conformational properties of a polymer which has one of its ends anchored at some surface, then there could be some obvious asymmetry with respect to averaging of its ends. The last situation is very common in the case of nematic liquid crystals confined by surfaces [24]. The formalism which we had already developed [2–8] can be extended without difficulty to the case of anchoring. To this purpose it is sufficient only to perform the averaging *separately* for the beginning and for the end of the polymer chain (this is achieved most effectively when the averaging of the discrete analog of the Dirac equation is considered [3,4] and *then* the continuous limit is taken). In the case of a polymer chain confined between two parallel plates there are several possibilities, e.g., one end may be fixed while another is free, both ends are fixed on the same (separate) plate(s), etc. In each case we could, in principle, treat the beginning and the end of the chain differently, if necessary.

In the present study we do not want to obscure our results with the above complications for reasons which will become obvious upon reading. In the case where geometrical constraints are imposed, e.g., half plane, parallel plates, etc., it is convenient to use an alternative representation of the propagator $G(\mathbf{k},N)$. We first consider the simpler case of flexible polymers where the Laplace-transformed propagator $G_0(\mathbf{k},s)$ can be written as

$$G_0(\mathbf{k},s) = \frac{1}{\mathbf{k}^2 + s}, \tag{2.12}$$

where we had adsorbed all unimportant constants by appropriately rescaling $\mathbf{k}$ and s. Next, we introduce "mixed" representation of the same propagator via

$$G_0(\mathbf{x};s) = \int_{-\infty}^{\infty} \frac{d\mathbf{k}}{(2\pi)^d} \frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{\mathbf{k}^2 + s}. \tag{2.13}$$

Without loss of generality, consider the one-dimensional case of Eq. (2.13):

$$G_0(\mathbf{x};s) = \int_{-\infty}^{\infty} \frac{dk}{(2\pi)} \frac{e^{ik\cdot x}}{(k - i\sqrt{s})(k + i\sqrt{s})}. \tag{2.14}$$

Using Jordan's lemma the above integral could be easily calculated with the result

$$G_0(\mathbf{x};s) = \frac{1}{2\sqrt{s}} e^{-\sqrt{s}|x|}. \tag{2.15}$$

In the case of d dimensions we treat x as the dimension normal to surface of dimension $d-1$. This generalization involves no additional calculations. Simply we have to replace s by $s + \mathbf{k}_\parallel^2$ in Eq. (2.15) where $\mathbf{k}_\parallel^2 = k_1^2 + k_2^2 + \cdots + k_{d-1}^2$ to obtain $G_0(x,\mathbf{k}_\parallel;s)$ instead of $G_0(x;s)$. Consider now the case of the Dirac propagator. As before, we have

$$\hat{G}_0(x;s) = i \int \frac{dp}{2\pi} \frac{p\gamma_3 + s\gamma_0 - m}{p^2 + s^2 + m^2} e^{ipx} = I_1 + I_2, \tag{2.16}$$

where

$$I_1 = i\gamma_3 \int_{-\infty}^{\infty} \frac{dp}{2\pi} \frac{p e^{ipx}}{p^2 + s^2 + m^2} \tag{2.17a}$$

and

$$I_2 = i\int_{-\infty}^{\infty}\frac{dp}{2\pi}\frac{(s\gamma_0 - m)e^{ipx}}{p^2+s^2+m^2}\ . \tag{2.17b}$$

The matrix γ_3 is taken to represent the x direction.

Consider now I_1 in some detail. If $x>0$, then we obtain

$$I_1 = \gamma_3\frac{\partial}{\partial x}\int_{-\infty}^{\infty}\frac{dp}{2\pi}\frac{e^{ipx}}{p^2+s^2+m^2}\ , \tag{2.18a}$$

while if $x<0$, we get

$$I_1 = -\gamma_3\frac{\partial}{\partial x}\int_{-\infty}^{\infty}\frac{dp}{2\pi}\frac{e^{ipx}}{p^2+s^2+m^2}\ . \tag{2.18b}$$

In compete analogy with the scalar case [e.g., see Eqs. (2.13)–(2.15)], we obtain

$$\int_{-\infty}^{\infty}\frac{dp}{2\pi}\frac{e^{ipx}}{p^2+s^2+m^2} = \frac{1}{2\tilde{\omega}}e^{-\tilde{\omega}|x|}\ , \tag{2.19}$$

where $\tilde{\omega}=\sqrt{s^2+m^2}$. Therefore, using Eqs. (2.18a) and (2.18b), we find

$$I_1 = -\frac{\gamma_3}{2}\mathrm{sgn}(x)e^{-\tilde{\omega}|x|}\ . \tag{2.20}$$

The case of I_2 does not require any additional effort so that we can write the final result without delay:

$$\hat{G}_0(x,s) = \frac{1}{2\omega}[s\tilde{\gamma}+m-\gamma_3\omega\,\mathrm{sgn}(x)]e^{-\omega|x|}\ , \tag{2.21}$$

where we have made replacement: $m\to im$; $\omega=\sqrt{s^2-m^2}$ and $\tilde{\gamma}=i\gamma_0$. Extension of the above result to d dimensions requires, as before, replacement of s^2 by $s^2+\mathbf{k}_\parallel^2$. The results presented above admit an easy extension to the cases when geometrical or topological constraints are present. Some of these cases will be considered below.

III. PROPAGATORS FOR FULLY FLEXIBLE CHAINS IN THE PRESENCE OF GEOMETRICAL CONSTRAINTS

In the presence of some external potential $V(\mathbf{r})$ the equation of "motion" for the distribution function of fully flexible chains is given by [1]

$$\left[\frac{\partial}{\partial N}-\frac{l}{2d}\nabla_{\mathbf{r}}^2+V(\mathbf{r})\right]G(\mathbf{r},\mathbf{r}';N|V)=\delta(N)\delta(\mathbf{r}-\mathbf{r}') \tag{3.1}$$

so that $G_0(\mathbf{k},N)$ considered in Sec. II is just a Fourier-transformed version of $G(\mathbf{r},\mathbf{r}';N|V=0)$. It is convenient to rewrite Eq. (3.1) in the form of integral equation [25]

$$G(\mathbf{r},\mathbf{r}';N|V)=G_0(\mathbf{r}-\mathbf{r}';N) - \int_0^N d\tau\int d\mathbf{r}''G_0(\mathbf{r}-\mathbf{r}'';N-\tau)V(\mathbf{r}'') \times G(\mathbf{r}'',\mathbf{r}';\tau|V)\ . \tag{3.2}$$

The above equation can be further rewritten by taking a Laplace transform of both sides:

$$G(\mathbf{r},\mathbf{r}';s|V)=G_0(\mathbf{r}-\mathbf{r}';s)-\int d\mathbf{r}''G_0(\mathbf{r}-\mathbf{r}'';s)V(\mathbf{r}'') \times G(\mathbf{r}'',\mathbf{r}';s|V)\ . \tag{3.3}$$

This form is especially useful, as we are going to demonstrate now. Consider Eq. (3.3) for the case of one dimension and choose the potential $V(\mathbf{r})=\delta_0\delta(x)$, so that we obtain

$$G(x,x';s)=G_0(x-x';s)-\delta_0G_0(x;s)G(0,x';s)\ , \tag{3.4}$$

where $G_0(x-x';s)$ is given by Eq. (2.15). We have introduced the abbreviation $G(x,x';s)=G(x,x';s|V)$. Now let $x=0$ in Eq. (3.4), then, by combining Eqs. (2.15) and (3.4), we obtain a closed form representation for $G(0,x';s)$ given by

$$G(0,x';s)=\frac{G_0(x';s)}{1+\delta_0G_0(0;s)}\ . \tag{3.5}$$

By combining this result with Eq. (3.4) we obtain

$$G(x,x';s)=G_0(x-x';s)-\frac{\delta_0}{1+\delta_0/2\sqrt{s}}G_0(x,s)G_0(x';s) \tag{3.6}$$

or

$$G(x,x';s) = \frac{1}{2\sqrt{s}}\left[\exp(-\sqrt{s}\,|x-x'|) - \frac{\delta_0}{\delta_0+2\sqrt{s}}\exp(-\sqrt{s}\,|x|-\sqrt{s}\,|x'|)\right]\ . \tag{3.7}$$

In arriving at Eq. (3.7) we choose a system of units (e.g., $l=2d$) in such a way that Eq. (2.15) can be used directly. This can be seen by taking limit $\delta_0\to 0$ in Eq. (3.7). The choice of potential made in Eq. (3.4) corresponds to a *penetrable surface*. In contrast, an impenetrable surface restricts the chain to the half-space regardless of the strength of polymer-surface interaction. The distinction between the modeling of these *very different* types of surfaces is discussed in Ref. [26]. The penetrable model should be applicable to liquid-liquid interface since in this instance a chain can legitimately "tunnel" through the interface [27]. The impenetrable surface model is more appropriate for a liquid-solid interface.

The penetrable surface model can also be formulated directly in terms of the path integral of the following type [17]:

$$G(x,x';N|V)=\int_{x(0)=0}^{x(N)=x}D[x(\tau)] \times\exp\left\{-\int_0^N d\tau H[x(\tau)]\right\}\ , \tag{3.8}$$

where

$$H[x(\tau)]=\frac{1}{4}\left[\frac{dx}{d\tau}\right]^2+\delta_0\delta(x(\tau)) . \tag{3.9}$$

Laplace transforming Eq. (3.1) (and choosing again $l=2d$) we can obtain an alternative path-integral representation of $G(x,x';s)$ given by [17]

$$G(x,x';s)=\frac{\int D[\phi]\phi_s(x)\phi_s(x')\exp\{-S[\phi]\}}{\int D[\phi]\exp\{-S[\phi]\}} , \tag{3.10}$$

where

$$S[\phi]=\frac{1}{2}\int dx\,\phi(x)\left[-\frac{d^2}{dx^2}+s+\delta_0\delta(x)\right]\phi(x) . \tag{3.11}$$

Both path integrals, Eqs. (3.8) and (3.10), are equivalent when solved [28,29] to representation of $G(x,x';s)$ given by Eq. (3.7). The solution given by Eq. (3.7), however, is *not* the same as usually discussed in connection with the impenetrable surface model. In the last case, to solution given by the right-hand side of Eq. (3.7) another function is added [30] which represents the nonsingular solution $\tilde{G}$ of the equation

$$\left[\frac{\partial}{\partial N}-\nabla_x^2+V(\mathbf{r})\right]\tilde{G}(x,x';N)=0 . \tag{3.12}$$

Following Ref. [30] the solution for G for the impenetrable surface can be obtained with the help of the already existing Eq. (3.7), if we replace x' by $-x'$ in the right-hand side of Eq. (3.7). Adding this obtained result for $\tilde{G}$ with G and, *in addition, assuming that both* x *and* $x'>0$, we obtain finally

$$G(x,x';s)=\frac{1}{2\sqrt{s}}\left[e^{-\sqrt{s}|x-x'|}+\frac{\sqrt{s}-\delta}{\sqrt{s}+\delta}e^{-\sqrt{s}(x+x')}\right] , \tag{3.13}$$

where $\delta=\delta_0/2$ and we have used the same symbol for G in Eq. (3.1) and here. The last condition $(x,x'>0)$ was not stated explicitly in Ref. [30], but it is essential in arriving at the result Eq. (3.13). From the above detailed derivation of the result, Eq. (3.13), it follows that, in contradistinction with the results of Ref. [17], Eq. (3.13) *cannot* be directly obtained from the path integral, Eq. (3.10). This circumstance may or may not be important, however, because if in perturbational calculations the diagrammatic methods are used, then it is always possible to formally replace the propagator given by the right-hand side of Eq. (3.7) with that given by the right-hand side of Eq. (3.13) [30]. Under such conditions, the path-integral method could be considered only as a convenient tool for development of the diagrammatic perturbational expansions. The nonperturbative treatments, however, could be affected by the above discrepancy and this fact was recently noticed in Ref. [31].

Equation (3.13) could be considered from a somewhat different angle. In the limiting cases $\delta_0=0$ and $\delta_0\to\pm\infty$ we obtain, respectively,

$$G(x,x';s)=\frac{1}{2\sqrt{s}}\{\exp(-\sqrt{s}\,|x-x'|)+\exp[-\sqrt{s}\,(x+x')]\} , \tag{3.14}$$

$$G(x,x';s)=\frac{1}{2\sqrt{s}}\{\exp(-\sqrt{s}\,|x-x'|)-\exp[-\sqrt{s}\,(x+x')]\} . \tag{3.15}$$

Comparison with the similar problems in quantum mechanics [32] indicates that Eq. (3.14) could be interpreted as a Euclidean-type version of two-particle relative amplitude for two bosons, while Eq. (3.15) represents the two-particle relative amplitude for fermions (e.g., see p. 225 of Ref. [32] for the corresponding quantum-mechanical analogs). Hence the strengths δ_0 of the potential $V(x)$ effectively change the statistics of the problem from bosonic ($\delta_0=0$) to fermionic ($\delta_0\to\pm\infty$). Notice that Eq. (3.7) cannot provide the above fermion-boson transmutation and hence the path integrals, Eqs. (3.8) and (3.10), do not possess this property as well. At the same time, the limiting cases, Eqs. (3.14) and (3.15), could be obtained with the help of path-integral methods (e.g., see Ref. [32], Chaps. 6 and 7) and the problem of extending these results to arbitrary δ_0 naturally arises.

In the present paper we do not need a complete path-integral solution to the above problem. Instead, we would like now to demonstrate that the description of configurational flexible polymers confined between the parallel plates is closely related to the problem of a polymer in a half-space which was just discussed.

Let $\tilde{d}$ be the distance between two parallel plates. The end-to-end distribution function for the polymer chain confined between *totally repulsive* walls separated by the distance $\tilde{d}$ was obtained by Dolan and Edwards [18] who, in turn, used earlier results of Carslaw and Jaeger [33] for distribution of heat between two parallel plates.

By noticing that the propagator, Eq. (2.15), when written in (x,N) space, produces

$$G_0(x,N)=\frac{1}{\sqrt{\pi N}}\exp\left[-\frac{x^2}{N}\right] \tag{3.16}$$

we rewrite Dolan and Edward's previous result [Eq. (2) of Ref. [18]] using our normalization and notations as

$$G_{\parallel}(x,x';N)=\frac{1}{\sqrt{\pi N}}\sum_{M=-\infty}^{\infty}\left\{\exp\left[-\frac{1}{N}(x-x'-2M\tilde{d})^2\right]-\exp\left[-\frac{1}{N}(x+x'-2M\tilde{d})\right]\right\} . \tag{3.17}$$

Consider now the following chain of transformations:

$$\sqrt{\pi}G_1(x,x',N)=\frac{1}{N^{1/2}}\sum_{M=-\infty}^{\infty}\exp\left[-\frac{1}{N}(x-x'-2M\tilde{d})^2\right]$$
$$=\frac{1}{N^{1/2}}\sum_{M=-\infty}^{\infty}\exp\left[-\frac{4\tilde{d}^2(\tilde{x}-\tilde{x}'-M)^2}{N}\right]$$
$$=\frac{1}{2\tilde{d}}\frac{1}{\tau^2}\sum_{M=-\infty}^{\infty}\exp\left[-\frac{(\tilde{x}-\tilde{x}'-M)^2}{\tau}\right]$$
$$=\frac{\sqrt{\pi}}{2\tilde{d}}\Theta\left[\frac{x-x'}{2\tilde{d}};\frac{iN\pi}{4\tilde{d}^2}\right]\equiv\frac{\sqrt{\pi}}{2\tilde{d}}\Theta(\tilde{x}-\tilde{x}';i\tau)\ . \tag{3.18}$$

Here we have introduced the elliptic theta function Θ using notations of Ref. [34] (e.g., see Chap. 1, Sec. 8). With the help of Eq. (3.18) we can rewrite Eq. (3.17) as follows:

$$2\tilde{d}G_{\parallel}(x,x';N)=\Theta(\tilde{x}-\tilde{x}';i\tau)-\Theta(\tilde{x}+\tilde{x}';i\tau)\ . \tag{3.19}$$

The last equation is strikingly similar to Eq. (3.15) (when it is being inverse Laplace transformed) and we observe that *at least for the case of infinitely repulsive walls Eq. (3.19) for plates can be obtained from that for the half-space, Eq. (3.15), upon the formal replacement*

$$\frac{1}{\sqrt{\pi N}}\exp\left[-\frac{x^2}{N}\right]\rightarrow\frac{1}{2\tilde{d}}\Theta(\tilde{x},i\tau)\ . \tag{3.20}$$

The question now arises: Can the above replacement be made for the arbitrary value of the parameter δ_0 or, more specifically, is it possible to obtain an analogous equation for the parallel-plate case?

We would like now to provide an affirmative answer to the above question. Begin with the observation that theta function $\Theta(x,\tau)$ is the Green's function for the quantum-mechanical problem of quantization of a particle whose motion is constrained to a circle [32,35] and plays for this problem the same role as $G_0(x,N)$ given by Eq. (3.16). In complete analogy with Eq. (3.1), it is possible to consider an analogous Schrödinger-like problem of the "motion" of such a particle in the presence of a δ-like potential located somewhere on the circle. Fortunately, this problem was already considered [28] so that we provide only some comments which are required to make our presentation self-contained. For this purpose we consider Eq. (3.6) once again. Noticing from Eq. (2.15) that $G_0(x;s)G_0(x',s)=(1/2\sqrt{s})G_0(|x|+|x'|;s)$ and taking into account the integral representation,

$$\frac{1}{\sqrt{s}+\delta_0/2}=\int_0^{\infty}dt\,e^{-t(\sqrt{s}+\delta_0/2)}\ , \tag{3.21}$$

we can rewrite Eq. (3.6) as follows:

$$G(x,x';s)=G_0(x-x';s)$$
$$-\frac{\delta_0}{2}\int_0^{\infty}dt\,e^{-t\delta_0/2}G_0(|x|+|x'|+t;s)\ . \tag{3.22}$$

The above presentation of Eq. (3.6) coincides with that given in Ref. [28]. To see this, we need first to Laplace transform Eq. (3.19) of Ref. [28] and then to make an identification: $\delta_0/2\rightarrow -a$ (where a is the parameter used in Ref. [28]). After this observation, the transition to the circular problem is straightforward and solution could be read off directly from Eq. (3.17) of Ref. [28].

Now, in view of this fact, and taking into account Eqs. (3.6), (3.7), (3.13), (3.15), (3.17), and (3.19), we can write, in complete accord with Eq. (3.13), the following result for the parallel-plate Green's function:

$$G_{\parallel}(x,x';s)=\frac{1}{2\sqrt{s}}\sum_{M=-\infty}^{\infty}\left\{\exp\{-\sqrt{s}\,|x-x'-2M\tilde{d}|\}+\frac{\sqrt{s}-\delta}{\sqrt{s}+\delta}\exp\{-\sqrt{s}\,|x+x'+2M\tilde{d}\}\right\}\ . \tag{3.23}$$

Finally, unlike the usual free particle propagator, Eq. (3.16), which is Green's function of the "diffusion" equation (3.1) [with $V(x)=0$], the propagator $\Theta(x,\tau)$ is not only the solution for the problem of a free particle moving on the circle but is also directly related to stationary solution of the nonlinear Korteveg–de Vries (KdV) equation [34]. Development of path-integral methods which take into account this fact is outlined briefly in Ref. [36]. We are not going to use the above connection with KdV in this work but we only would like to mention that the above connection could be used to study fermi-bose crossover [e.g., see discussion after Eq. (3.15)] for the case of statistical mechanics problems which involve finite-temperature one-dimensional quantum gases [36].

The results obtained so far admit a generalization to the case of semiflexible polymers to be considered in the next section.

IV. PROPAGATORS FOR CHAINS OF ARBITRARY FLEXIBILITY IN THE PRESENCE OF GEOMETRICAL CONSTRAINTS

As in the fully flexible case, we begin our discussion with an equation of "motion." Because we have this time a Dirac propagator we obtain (in the absence of external fields) the following result [e.g., see Eq. (2.110) of Ref. [37]]:

$$(i\not{\partial}_x - m)\hat{G}_0(x-x') = i\delta^{(4)}(x-x') \ . \tag{4.1}$$

Here, as usual, $\not{\partial}_x = \gamma^\mu \partial_\mu$, $x=\{x_1,x_2,x_3,N\}$, and $\hat{G}_0$ is the *retarded* Dirac Green's function [because $\hat{G}_0$ in Eqs. (3.1) and (3.2) is also retarded]. Equation (4.1) is written in accord with Eq. (2.4) so that γ^μ are Euclidean Dirac matrices. The "relativistic" analog of Eq. (3.1) can be written now with the help of Eq. (4.1) as follows:

$$[i\not{\partial}_x - \not{A}(x) - m]\hat{G}(x,x'|A) = i\delta^{(4)}(x-x') \ . \tag{4.2}$$

We shall be concerned here only with potential scattering so that $\not{A}(x)=\gamma^0 A_0(x)$. As in the fully flexible case, it is convenient to rewrite Eq. (4.2) in the form of integral equation. This can be accomplished as follows [37]. First, we multiply both sides of Eq. (4.2) by $\hat{G}_0(x''-x)$ and then integrate both sides over d^4x, so that we get

$$\begin{aligned} i\hat{G}_0(x''-x') &= \int d^4x\, \hat{G}_0(x''-x')[i\overrightarrow{\not{\partial}}_x - \not{A}(x) - m] \\ &\quad \times \hat{G}(x,x'|A) \\ &= \int d^4x\, \hat{G}_0(x''-x)[-i\overleftarrow{\not{\partial}}_x - \not{A}(x) - m] \\ &\quad \times \hat{G}(x,x'|A) \ , \end{aligned} \tag{4.3}$$

where the arrow indicates direction of the action of the differential operator. If we notice that [37]

$$\hat{G}_0(x-x')(-i\overleftarrow{\not{\partial}}_x - m) = i\delta^{(4)}(x-x') \ , \tag{4.4}$$

then we obtain

$$\begin{aligned} &\hat{G}(x,x'|A) \\ &\quad = \hat{G}_0(x-x') - i\int_0^N d\tau \int d^3x''\hat{G}_0(\mathbf{x}-\mathbf{x}'';N-\tau) \\ &\qquad \times \not{A}(x'')\hat{G}(\mathbf{x}'',\mathbf{x}';\tau|A) \ . \end{aligned} \tag{4.5}$$

Noticing that in the case of potential scattering the Euclidean γ^0 is [38]

$$\gamma^0 = i\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = i\hat{\gamma} \ , \tag{4.6}$$

so that we obtain finally

$$\begin{aligned} \hat{G}(\mathbf{x},\mathbf{x}';N|V) &= \hat{G}_0(\mathbf{x}-\mathbf{x}',N) \\ &\quad - \int_0^N d\tau \int d^3x''\hat{G}_0(\mathbf{x}-\mathbf{x}'';N-\tau)V(\mathbf{x}'') \\ &\quad \times G(\mathbf{x}'',\mathbf{x}';\tau|V) \ , \end{aligned} \tag{4.7}$$

where $V(x'')=-\hat{\gamma}A_0(\mathbf{x})$ and, in view of Eq. (2.5), we are interested only in $\mathrm{Tr}\hat{G}(\mathbf{x},\mathbf{x}';N|V)$. The above equation formally looks like Eq. (3.2) but, unlike Eq. (3.2), it is a matrix equation. This circumstance does not introduce many additional complications, as we now demonstrate.

As in the "nonrelativistic" case, we begin with conversion of Eq. (4.7) into its Laplace-transformed form,

$$\begin{aligned} \hat{G}(\mathbf{x},\mathbf{x}';s|V) &= \hat{G}_0(\mathbf{x}-\mathbf{x}';s) \\ &\quad - \int d^3x''\hat{G}_0(\mathbf{x}-\mathbf{x}'';s) \\ &\quad \times V(\mathbf{x}'')\hat{G}_0(\mathbf{x}'',\mathbf{x}';s|V) \ , \end{aligned} \tag{4.8}$$

where $\hat{G}_0(\mathbf{x},s)$ is defined in Eq. (2.21). Now, as before, consider only the one-dimensional case and let $V(x)=\hat{\gamma}\delta\delta(x)$, then Eq. (4.8) is converted into

$$\hat{G}(x,x';s) = \hat{G}_0(x-x';s) - \delta\hat{G}_0(x;s)\hat{\gamma}\hat{G}(0,x';s) \ , \tag{4.9}$$

where we have used the same abbreviation $\hat{G}(x,x';s|V)\equiv G(x,x';s)$ as in the "nonrelativistic" case. Unlike the "nonrelativistic" case, we have to establish first the matrix nature of $\hat{G}(x,x';s)$. To this purpose two observations are helpful. First, in view of Eqs. (2.5) and (2.21) we have for $\delta=0$ the result

$$\mathrm{tr}\hat{G}(x,x';s) = \frac{m}{2\omega}e^{-\omega|x|} \ , \tag{4.10}$$

to be compared with Eq. (2.15). Second, the matrix nature of $\hat{G}(x,x';s)$ cannot be changed if in Eq. (4.9) we set $x=x'=0$. Then, in view of Eq. (2.21) and taking into account the results of Ref. [27], we have to look for solution for $\hat{G}(0,0;s)$ in the form

$$\hat{G} = aI + \hat{\gamma}b + \gamma_3 c + \gamma_3\hat{\gamma}d \ , \tag{4.11}$$

where I is unit matrix and a,b,c,d are some yet unknown functions of s. Substituting the right-hand side of Eq. (4.11) into Eq. (4.9) and collecting the corresponding terms near $I,\hat{\gamma},\gamma_3$ and $\gamma_3\hat{\gamma}$, we obtain four algebraic equations (to determine a, b, c, and d) by equating the above terms to zero. Actual computations indicate, however, that the expressions obtained are cumbersome (especially in view of the expected subsequent inverse Laplace transform performed on $\hat{G}$). To simplify the situation, we impose additional constraints on $\hat{G}$. First, in the "nonrelativistic" limit we expect that our $\hat{G}$ will smoothly go into $G(x,x';s)$ [e.g., see Eq. (3.4)]. Second, in the rigid rod limit the potential should not affect the rigid rod conformational properties. With these restrictions we can try a much simpler ansatz:

$$\hat{G} = aI + \hat{\gamma}b \ . \tag{4.12}$$

Substituting this ansatz into Eq. (4.9) and using Eq. (2.21) produces

$$aI + \hat{\gamma}b = \frac{1}{2\omega}[mI - s\hat{\gamma} - \delta(mI - \hat{\gamma}s)\hat{\gamma}(aI + \hat{\gamma}b)] \ . \tag{4.13}$$

Using the identity $\hat{\gamma}^2 = I$ we obtain

$$a = n\frac{m}{2\omega}(1+\delta b) \ , \tag{4.14a}$$

$$b=-\frac{n}{2\omega}(s+\delta ma)\ , \tag{4.14b}$$

where $n=(1-\delta s/2\omega)^{-1}$. From here we get

$$a=\frac{m}{2\omega}\frac{1}{1-\delta s/2\omega}\ . \tag{4.15}$$

This result could be substituted back into Eq. (4.14b) in order to obtain b. The resulting expression for b, although not too analytically cumbersome, is still too complicated for use in analytical calculations which are presented below.

The above calculations were presented only with the purpose of demonstrating generality of the methods of solving the matrix structure of $\hat{G}$ [e.g., see Eqs. (4.9), (4.11)]. To obtain explicit analytical results, we need to make some additional approximations, e.g., $\hat{G}(0,0;s)=aI$. Then, using Eq. (4.9) and again taking into account that $\hat{\gamma}^2=1$ and that we are ultimately interested only in traces [e.g., see Eq. (2.5)] of $\hat{G}$, we obtain

$$a=\frac{1}{2\omega}(m+\delta as)\ , \tag{4.16}$$

which reproduces the result (4.15). Following the same steps which lead us to Eq. (3.7) produces now

$$\hat{G}(x,x';s)=\frac{m}{2\omega}\left[e^{-\omega|x-x'|}-\frac{\delta_0 s}{2\omega+\delta_0 s}e^{-\omega|x|-\omega|x'|}\right]\ , \tag{4.17}$$

where we have set $\delta\rightarrow-\delta_0$. Repeating arguments which lead to Eq. (3.13) we obtain our "relativistic" analog of Eq. (3.13):

$$\hat{G}(x,x';s)=\frac{m}{2\omega}\left[e^{-\omega|x-x'|}+\frac{\omega-\delta s}{\omega+\delta s}e^{-\omega(x+x')}\right]\ , \tag{4.18}$$

where, as before, $\delta=\delta_0/2$

Explicit calculations below show that the above truncated result for $\hat{G}$ produces meaningful physical results for the whole range of permissible values of the inverse rigidity parameter m. Extension of the above results to the parallel-plate case is now straightforward and follows exactly the same steps as in the "nonrelativistic" problem. This is permissible because in the "nonrelativistic" limit ($m\rightarrow\infty$) Eq. (4.18) produces the same results as Eq. (3.13) and, therefore, by the requirements of complementarity and continuity, we arrive at the final result for parallel plates:

$$\hat{G}_{\parallel}(x,x';s)=\frac{m}{2\omega}\sum_{M=-\infty}^{\infty}\left\{\exp\{-\omega|x-x'-2M\tilde{d}|\}+\frac{\omega-\delta s}{\omega+\delta s}\times\exp\{-\omega|x+x'-2M\tilde{d}|\}\right\}\ . \tag{4.19}$$

This concludes our discussion of semiflexible chain propagators in the presence of geometrical constraints.

V. CALCULATION OF BASIC SINGLE-CHAIN PROPERTIES. GENERAL CONSIDERATION

We begin with some simple illustrative calculations which we shall need as a reference in more complicated situations. Let us start with fully flexible chains. Using Eq. (2.15), we would like to recalculate first $\langle\mathbf{R}^2\rangle$. We have

$$\langle\mathbf{R}^2\rangle_{\text{bulk}}=\frac{L^{-1}\left[\frac{1}{\sqrt{s}}\int_0^\infty dx\,x^2e^{-\sqrt{s}x}\right]}{L^{-1}\left[\frac{1}{\sqrt{s}}\int_0^\infty dx e^{-\sqrt{s}x}\right]}=2N \tag{5.1}$$

and the d-dimensional result merely involves multiplication by the dimension d. Similarly, if we use Eq. (4.10) for semiflexible polymers, we obtain

$$\langle\mathbf{R}^2\rangle_{\text{bulk}}=\frac{L^{-1}\left[\frac{1}{\omega}\int_0^\infty dx\,x^2e^{-\omega x}\right]}{L^{-1}\left[\frac{1}{\omega}\int_0^\infty dx\,e^{-\omega x}\right]}=\frac{2L^{-1}\left\{\frac{1}{\omega^4}\right\}}{L^{-1}\left\{\frac{1}{\omega^2}\right\}}\ . \tag{5.2}$$

The last result was discussed earlier, e.g., see Eq. (2.10). From this discussion it follows that if $mN\rightarrow\infty$ we obtain $\langle\mathbf{R}^2\rangle=N/m$ while in the opposite limit, $mN\rightarrow0$, we get $\langle\mathbf{R}^2\rangle=N^2/3$. This result is obtained if we set $d=1$ in Eq. (2.10). This, however, is not permissible in general because Eq. (2.5), which was used to obtain Eq. (2.10), involves a three-dimensional angular averaging which produces the correct three-dimensional scattering function $S(\mathbf{k})$ as we have explained in Sec. II. At the same time, the propagator given in Eq. (2.2) produces well-defined one-dimensional results for arbitrary values of m. Because of negligible numerical discrepancy between Eqs. (2.9) and (2.11), it is technically more advantageous to use the propagator given by Eq. (2.5). Moreover, if we recall that the result $2N$, given in Eq. (5.1), is written in terms of the reduced variables [e.g., see the discussion after Eq. (2.12)], then, by restoring them, we should have $\langle\mathbf{R}^2\rangle=lN=2aN=(3/m)N$ [the last result is written with account of Eq. (2.11)]. To reconcile Eqs. (5.1) and (5.2) we allow m to vary between 0 and $\frac{3}{2}$ while multiplying both sides of Eq. (5.2) by a factor of 3 [i.e., by d, according to Eq. (2.10)].

Consider now the case of the rigid rod limit of Eq. (4.18). In this limit $\omega=s$ and, if we keep x' on the surface (i.e., the requirement $x'=0$ means that our chain is anchored at one of its ends), then calculation of $\langle\mathbf{R}^2\rangle$ produces

$$\langle\mathbf{R}^2\rangle_{\perp}=3\frac{2L^{-1}\{1/s^4\}}{L^{-1}\{1/s^2\}}=N^2\ . \tag{5.3}$$

The $\perp$ subscript denotes chain dimensions normal to the surface [17]. Note that the chain dimensions exhibit no dependence on δ_0. This result is in perfect agreement with the requirements on $\hat{G}$ discussed in Sec. IV. The

above agreement is *not* sufficient, however, in order to prove that Eq. (4.18) is the correct "relativistic" extension of Eq. (3.13). We shall provide additional justification of its correctness in this and subsequent sections.

We would like to note also that unlike the "nonrelativistic" case for which $\langle \mathbf{R}^2 \rangle_\perp / \langle \mathbf{R}^2 \rangle_{\text{bulk}}$ showed dependence upon the strength of the coupling constant δ (see below), in the "relativistic" limit such dependence disappears entirely. This is in accord with our intuitive expectation that a rigid rod anchored by one of its ends to the wall will remain a rigid rod irrespective of the strength and the sign of δ.

Let us define now the quantities of interest and calculate them. For the half-space case we calculate the ratio $\langle \mathbf{R}^2 \rangle_\perp / \langle \mathbf{R}^2 \rangle_{\text{bulk}}$ for arbitrary values of m and δ. $\langle \mathbf{R}^2 \rangle_\perp$ is defined as

$$\langle \mathbf{R}^2 \rangle_\perp = \frac{3L^{-1}\left[\int_0^\infty dx\, x^2 \hat{G}(x,x'=0;s)\right]}{L^{-1}\left[\int_0^\infty dx\, \hat{G}(x,x'=0;s)\right]} , \tag{5.4}$$

while $\langle \mathbf{R}^2 \rangle_{\text{bulk}}$ is given by Eq. (2.10) (for $d=3$, and for $d=1$ this result stays practically the same as we had already discussed). The more general case, $x' \neq 0$, is also readily considered [17], but it is not very illuminating (because of its analytical complexity) even in the "nonrelativistic" case and, therefore, it will not be considered here. The case $x' \neq 0$ is of physical interest, however, because it provides information about the surface profile. We shall present these results in a separate publication.

The partition function is given by

$$Z(\delta,N) = L^{-1}\left[\int_0^\infty dx\, \hat{G}(x,x'=0;s)\right] , \tag{5.5}$$

so that the average density of monomers $\langle \rho_M(0) \rangle$ absorbed at the wall could be defined according to Refs. [17,39] as

$$\langle \rho_M(0) \rangle = -\frac{\partial}{\partial \delta} \ln Z(\delta,N) . \tag{5.6}$$

This quantity, however, is not too informative. Indeed, let us recall that the microscopic monomer density at the point $\mathbf{r}$ is given by [25]

$$\rho_M(\mathbf{r}) = \int_0^N d\tau\, \delta(\mathbf{r} - \mathbf{r}(\tau)) \tag{5.7}$$

so that, if the average monomer density is given by

$$\langle \rho_M(\mathbf{r}) \rangle = \int_0^N d\tau \langle \delta(\mathbf{r} - \mathbf{r}(\tau)) \rangle , \tag{5.8}$$

then for a single chain we can write [25]

$$\langle \rho_M(\mathbf{r}) \rangle = \frac{\int_0^N d\tau \int d\mathbf{r}' \int d\mathbf{r}'' G(\mathbf{r}',\mathbf{r};\tau) G(\mathbf{r},\mathbf{r}'',N-\tau)}{\int d\mathbf{r}' \int d\mathbf{r}'' G(\mathbf{r}',\mathbf{r};N)} , \tag{5.9}$$

where G stands for the full one-chain Green's function (relativistic or not). By construction, we obtain, using Eq. (5.9),

$$\int d\mathbf{r} \langle \rho_M(\mathbf{r}) \rangle = N , \tag{5.10}$$

or, equivalently,

$$\frac{1}{N} \int d\mathbf{r} \langle \rho_M(\mathbf{r}) \rangle = 1 . \tag{5.11}$$

Now let $\rho_{\max}$ be the maximum value of $\langle \rho_M(\mathbf{r}) \rangle$ for all permissible $\mathbf{r}$'s, then, evidently (because ρ_M is nonnegative for all r's) we obtain the inequality

$$\frac{\rho_{\max}}{N} \int d\mathbf{r} \geq \frac{1}{N} \int d\mathbf{r} \langle \rho_M(\mathbf{r}) \rangle = 1 . \tag{5.12}$$

In the case of very strong absorption, $|\delta| \to \infty$, we expect that eventually all monomers belonging to a polymer chain are going to be absorbed and, under these conditions, we have an equality sign in Eq. (5.12). In the one-dimensional approximation we have $\int d\mathbf{r} \to \int dx$, and for $|\delta| \to \infty$, we anticipate $\langle \rho_M(x) \rangle = \rho_{\max} \Theta(\epsilon - x)$ where $\epsilon \to 0^+$ and $\Theta(x)$ is a step function. Then, we obtain $\rho_{\max}/N = 1$. This result should be compared with the result of Ref. [17] [Eqs. (II.49)], which produces $\rho_{\max}/N = 2|\delta|$ (in our notations) and, whence, $2|\delta| \leq 1$. This restriction will be essential in our calculations below. To this purpose, following Ref. [23], we define the fraction of absorbed monomers $\hat{\rho}_M$ according to the equation

$$\hat{\rho}_M = \frac{1}{N} \langle \rho_M(0) \rangle \quad (2|\delta| \leq 1) . \tag{5.13}$$

It should be noted, however, *that Eq. (5.6) which produces* $\langle \hat{\rho}_M(0) \rangle$ *originates from the path integral, Eq. (3.8), which is not the same thing as propagator Eq. (3.13).* Because of this observation, the validity of Eq. (5.6) is rather limited in general and the results for the fraction $\hat{\rho}_M$ should be considered only from the qualitative point of view. This is supported by direct calculations presented in Sec. VII, Eq. (7.47), and Fig. 1. On the other hand, because the δ potential is itself an oversimplification of the real short-range interaction potential, we expect that the above difficulty is rather artificial in the sense that it only could affect the actual magnitude of δ which is considered as a parameter in our theory anyway.

A related quantity of interest is the fraction of absorbed monomers when both ends of our chain are anchored at the surface. In this case we can define $\hat{\rho}_M^{00}$

$$\hat{\rho}_M^{00} = -\frac{1}{N} \frac{\partial}{\partial \delta} \ln L^{-1}[\hat{G}(x=x'=0;s)] , \tag{5.14}$$

with the same restrictions on the strength of δ. Analogously, we can define similar quantities for the case of parallel plates. In this case, in addition to the possibilities just discussed, we could also consider the situation when one chain end is anchored at one plane surface while the other end is at another surface. For this case we get

$$\hat{\rho}_M^{\parallel} = -\frac{1}{N} \frac{\partial}{\partial \delta} \ln L^{-1}[\hat{G}_\parallel(x=0,x'=\tilde{d};s)] , \tag{5.15}$$

where the $\parallel$ subscript denotes the surface confined chain.

In addition to the above quantities, it is of interest to calculate the mean force (pressure) between the plates [18]. This is perhaps the most interesting property from a physical standpoint. To this purpose, following the

usual thermodynamic prescription, we define the free energy F. For example, for the case when only one end of the chain is anchored at one of the plates we obtain

$$F_1^0=-kT\ln L^{-1}\left[\int_0^{\tilde{d}}dx\,\hat{G}_{\parallel}(x,x'=0;s)\right]. \tag{5.16}$$

The pressure (force $\mathcal{f}$) is obtained from the relation

$$\mathcal{f}_1^0=-\frac{\partial F_1^0}{\partial\tilde{d}}. \tag{5.17}$$

Other situations are treated analogously, e.g., Eq. (5.15) implies [$\beta=(kT)^{-1}$]

$$\beta\mathcal{f}^{\parallel}=\frac{\partial}{\partial\tilde{d}}\ln L^{-1}[\tilde{d}\hat{G}_{\parallel}(x=0,x'=\tilde{d};s)], \tag{5.18}$$

etc. This concludes our general discussion of quantities to be calculated.

VI. CALCULATION OF PROPERTIES OF FULLY FLEXIBLE POLYMERS

Although the case of fully flexible polymers has already been discussed in the literature [17,18,26,39], we nevertheless would like to reproduce some of the known results in order to compare these results with the more general case of polymers of arbitrary flexibility to be considered in the next section. It is convenient to subdivide this section into subsections for the sake of clarity of our presentation.

A. Calculations of the partition functions

The partition function was defined earlier by Eq. (5.5) [where we have to use the "nonrelativistic" analog of $\hat{G}$ given by Eq. (3.13)]. Setting $x'=0$ in Eq. (3.13) and integrating over x we obtain (after inverse Laplace transforming)

$$Z(\delta,N)=e^{\delta^2 N}\operatorname{erfc}(\delta\sqrt{N}). \tag{6.1}$$

The last result coincides with Eq. (II.19) of Ref. [17] (if we set $z'=0$) as expected. This result admits an easy generalization [40] to variable dimension (Euclidean) surfaces and to fractal surfaces. In the integral equation formalism [e.g., see Eq. (3.6)] of the surface interacting polymer problem it is sufficient to replace the $\sqrt{s}$ term by fractional power of the s term which is related to the fractal dimension d_s of surface and the embedding space dimension d.

For further reference, we would like to present the asymptotic expressions for $Z(\delta,N)$. If $\delta>0$, the asymptotic formula

$$\operatorname{erf}x\simeq 1-\frac{e^{-x^2}}{x\sqrt{\pi}},\quad x\to\infty \tag{6.2}$$

could be used in Eq. (6.1), producing [with help of the relation $\operatorname{erfc}(x)=1-\operatorname{erf}(x)$] the final result

$$Z(\delta,N)\simeq\frac{1}{8\sqrt{\pi N}},\quad |\delta N^{1/2}|\to\infty, \tag{6.3}$$

while if $\delta<0$ we can use the relation $\operatorname{erf}(-x)=-\operatorname{erf}(x)$.

By combining Eqs. (6.1) and (6.2) we now obtain

$$Z(\delta,N)=2e^{\delta^2 N},\quad |\delta N^{1/2}|\to\infty. \tag{6.4}$$

Equations (6.3) and (6.4) coincide with the corresponding expressions in Ref. [17], as expected.

Although Dolan and Edwards [18] had considered the parallel-plate case, in view of the discussion presented in Secs. III and IV, we found it desirable to recalculate their results. Consider first the same conditions as in Ref. [18], i.e., we keep one end of the chain at $x'=0$. Then, using Eqs. (3.23) and (5.5) we obtain

$$Z_{\parallel}(\delta,N)=L^{-1}\left[\int_0^{\tilde{d}}dx\frac{1}{2\sqrt{s}}\sum_{M=-\infty}^{\infty}\left\{\exp\{-\sqrt{s}\,|x-2M\tilde{d}|\}+\frac{\sqrt{s}-\delta}{\sqrt{s}+\delta}\exp\{-\sqrt{s}\,|x+M\tilde{d}|\}\right\}\right]. \tag{6.5}$$

Although it is possible in principle to obtain a closed form result for $Z_{\parallel}(\delta,N)$, the actual computation shows [just like in the case of Eq. (6.1)] that only the asymptotic results are physically comprehensible. In view of the potential importance of the above calculations for the problem of stabilization of colloids by polymers [13], it is instructive to consider in detail only the case $\tilde{d}\to 0$.

Noticing that both sums in Eq. (6.5) are actually the same, we can perform the inverse Laplace transform first. This produces

$$Z_{\parallel}(\delta,N)=\sum_{M=-\infty}^{\infty}\int_0^{\tilde{d}}dx\left[\frac{e^{-(x+2M\tilde{d})^2/4N}}{\sqrt{\pi N}}-\delta e^{\delta|x+2M\tilde{d}|}e^{\delta^2 N}\operatorname{erfc}\left[\delta\sqrt{N}+\frac{|x+2M\tilde{d}|}{2\sqrt{N}}\right]\right]. \tag{6.6}$$

For $N\to\infty,\tilde{d}\to 0,\delta>0$ we can use Eq. (6.2) to obtain the following estimate:

$$\delta e^{\delta|x+2M\tilde{d}|}e^{\delta^2 N}\operatorname{erfc}\left[\delta\sqrt{N}+\frac{|x+2M\tilde{d}|}{2\sqrt{N}}\right]\approx\frac{e^{-(x+2M\tilde{d})^2/4N}}{\sqrt{\pi N}}\left[1-\frac{|x+2M\tilde{d}|}{2\delta N}+\cdots\right],\quad \delta N^{1/2}\to\infty. \tag{6.7}$$

By substituting this result back into Eq. (6.6) we obtain

$$Z_{\parallel}(\delta,N)\simeq\frac{1}{2\delta N}\sum_{M=-\infty}^{\infty}\int_0^{\tilde{d}}dx\,|x+2M\tilde{d}|\frac{e^{-(x+2M\tilde{d})^2/4N}}{\sqrt{\pi N}} \tag{6.8}$$

This result coincides with that given by Dolan and Edwards [18] [e.g., see their Eq. (4)] if their λ is being replaced by our $1/\delta$. To perform summation over M, consider the following steps. First, notice that the combination

$$|x+2M\tilde{d}|e^{-(x+2M\tilde{d})^2/4N} \tag{6.9}$$

could be obtained as follows:

$$|x+2M\tilde{d}|e^{-(x+2M\tilde{d})^2/4N}=-2N\frac{\partial}{\partial x'}e^{-(x+x'+2M\tilde{d})^2/4N}\Big|_{x'=0}. \tag{6.10}$$

Second, in view of Eqs. (6.7) and (6.10) it is useful to recall the identity [33] [e.g., see Eq. (5) on p. 275]

$$\sum_{M=-\infty}^{\infty}e^{-(x+x'+2M\tilde{d})^2/4N}=\frac{\sqrt{\pi N}}{\tilde{d}}\left[1+2\sum_{n=1}^{\infty}\cos\left[\frac{\pi(x+x')n}{\tilde{d}}\right]e^{-n^2\pi^2N/\tilde{d}^2}\right]. \tag{6.11}$$

For $\tilde{d}\to 0$ we can keep only the one term in summation over M. By combining Eqs. (6.8), (6.10), and (6.11) we then obtain

$$\frac{1}{2\delta N\sqrt{\pi N}}\sum_{M=-\infty}^{\infty}|x+2M\tilde{d}|e^{-(x+2M\tilde{d})^2/4N}=\frac{2\pi}{\delta d^2}\sin\left[\frac{\pi x}{\tilde{d}}\right]e^{-\pi^2N/\tilde{d}^2}. \tag{6.12}$$

Finally, performing x integration in Eq. (6.9) with the help of Eq. (6.13) we obtain

$$Z_{\parallel}(\delta,N)=\frac{4}{\delta\tilde{d}}e^{-\pi^2N/\tilde{d}^2}. \tag{6.13}$$

The last result is in agreement with Eq. (10) of Ref. [18] (if only one term in the summation is being kept).

Consider now the case when $\delta<0$. Then, using Eqs. (6.5) and (6.6) we find

$$Z_{\parallel}(\delta,N)=\sum_{M=-\infty}^{\infty}\int_0^{\tilde{d}}dx\left[\frac{e^{-(x+2M\tilde{d})^2/4N}}{\sqrt{\pi N}}+2|\delta|e^{-|\delta||x+2M\tilde{d}|}e^{\delta^2N}\right]. \tag{6.14}$$

With the help of Eq. (6.11) the first term in Eq. (6.14) can be transformed at once, thus working with the second term we obtain finally

$$Z_{\parallel}(\delta,N)=1+2|\delta|e^{\delta^2N}\int_0^{\tilde{d}}dx\left[e^{-|\delta|x}+2\cosh(|\delta|x)\sum_{M=1}^{\infty}e^{-|\delta|2M\tilde{d}}\right]$$
$$=1+2e^{\delta^2N}\left\{1-e^{|\delta|d}+2\sinh(|\delta|\tilde{d})\frac{e^{-|\delta|2\tilde{d}}}{1-e^{-2|\delta|\tilde{d}}}\right\}. \tag{6.15}$$

In the limit $\tilde{d}\to 0$ Eq. (6.17) reduces to

$$Z_{\parallel}(\delta,N)\simeq 2e^{\delta^2N}(1+|\delta|\tilde{d}). \tag{6.16}$$

The last result is written for the case when the combination δ^2N is much bigger than one (which is always the case for $N\to\infty$).

Let us now consider a somewhat different situation when the ends of the polymer chain belong to different plates. In this case, by using Eqs. (3.23) we obtain

$$Z_{\parallel}(\delta,N)=\sum_{M=-\infty}^{\infty}L^{-1}\left[\frac{\tilde{d}}{\sqrt{s}}\exp\{-\sqrt{s}\,|\tilde{d}-2M\tilde{d}|\}\left[1-\frac{\delta}{\sqrt{s}+\delta}\right]\right]$$
$$=\tilde{d}\sum_{M=-\infty}^{\infty}\left[\frac{e^{-[(\tilde{d}-2M\tilde{d})^2/4N]}}{\sqrt{\pi N}}-\delta e^{\delta|\tilde{d}-2M\tilde{d}|}e^{\delta^2N}\operatorname{erfc}\left[\delta\sqrt{N}+\frac{|\tilde{d}-2M\tilde{d}|}{2\sqrt{N}}\right]\right]. \tag{6.17}$$

For $\delta>0$ repeating all arguments of the previously considered case we arrive at the result which is similar to Eq. (6.12), i.e.,

$$Z_{\parallel}(\delta,N)\approx\frac{4\pi}{\delta\tilde{d}}\sin\left[\frac{\pi\epsilon}{\tilde{d}}\right]e^{-\pi^2N/\tilde{d}^2}, \tag{6.18}$$

where we have introduced the small parameter $\epsilon\to 0^+$ which we shall take as zero at the end of the calculation. Equation (6.18) looks very much like Eq. (6.13) and therefore will produce the same result for the force (pressure) to be discussed shortly. Consider now the case $\delta<0$. Then, by analogy with Eqs. (6.14) and (6.15) we obtain

$$Z_{\parallel}(\delta,N)=\tilde{d}\left[1+2|\delta|e^{\delta^2 N}\left[e^{-|\delta|\tilde{d}}+2\cosh(|\delta|\tilde{d})\times\frac{e^{-|\delta|2\tilde{d}}}{1-e^{-2|\delta|\tilde{d}}}\right]\right] . \quad (6.19)$$

For $\tilde{d}\to 0$ we obtain

$$Z_{\parallel}(\delta,N)\approx 2e^{\delta^2 N}(1-|\delta|\tilde{d}) . \quad (6.20)$$

B. Casimir forces (pressures) and the adsorbed monomer fractions

Using the definitions given in Sec. V we now calculate the forces. Using Eqs. (5.16), (5.17), (6.13), and (6.16) we obtain for $\delta>0$ the following result:

$$\beta\mathcal{F}_1^0=-\frac{\partial}{\partial\tilde{d}}\left[\ln\tilde{d}+\frac{\pi^2 N}{\tilde{d}^2}\right]=\frac{-1}{\tilde{d}}+\frac{2\pi^2 N}{\tilde{d}^3} , \quad (6.21)$$

while for $\delta<0$ we obtain as well

$$\beta\mathcal{F}_1^0=\frac{\partial}{\partial\tilde{d}}[\ln\tilde{d}(1+|\delta|\tilde{d})]=\frac{|\delta|}{1+|\delta|\tilde{d}} . \quad (6.22)$$

As can be seen from both Eqs. (6.23) and (6.26) in *both* cases ($\delta>0$ and $\delta<0$) we obtain the repulsive force at short distances. This repulsive force is being counterbalanced by the attractive van der Waals–type force potential given by [18] $V=-A/\tilde{d}^2$ with A being some known (Hamaker) constant. The counterbalance between the repulsion, Eq. (6.21), and van der Waals attraction plays a major role in the polymer stabilization of colloids.

Consider now the cases described by Eqs. (6.18) and (6.20). In the case of Eq. (6.18) we obtain the same result, Eq. (6.21), when $\delta>0$, while for $\delta<0$ we obtain

$$\beta\mathcal{F}^{\parallel}=\frac{\partial}{\partial\tilde{d}}\ln(1-|\delta|\tilde{d})=-\frac{|\delta|}{1-|\delta|\tilde{d}} . \quad (6.23)$$

Evidently, this result is valid only if $\tilde{d}|\delta|<1$. In view of our estimate, Eq. (5.13), we expect $|\delta|\le\frac{1}{2}$. Let, for instance, $|\delta|=\frac{1}{2}$, then for $\tilde{d}\ll 2$ we obtain attraction while for $\tilde{d}\gg 2$ use of Eqs. (6.18) and (6.19) produces

$$\beta\mathcal{F}^{\parallel}\cong\frac{1}{\tilde{d}}-|\delta| , \quad (6.24)$$

i.e., attraction again. A change in the force sign has been observed experimentally [41,42], in the form of oscillations. Such a sign reversal is apparently possible even at infinite dilution, e.g., see Eq. (7.25) below.

Consider now calculations of monomer fractions. Using Eqs. (5.6), (5.13), (6.3), and (6.4) we obtain

$$\hat{\rho}_M=\begin{cases}(\delta N)^{-1}, & \delta>0\\ 2|\delta|, & \delta<0 .\end{cases} \quad (6.25)$$

Analogously, for the Dolan-Edwards case we have

$$\hat{\rho}_M^{01}=\begin{cases}(\delta N)^{-1}, & \delta>0\\ 2|\delta|-\dfrac{\tilde{d}}{1+|\delta|\tilde{d}}\dfrac{1}{N}, & \delta<0\end{cases} \quad (6.26)$$

which practically coincides with the half-space results, Eq. (6.28), as expected. In the other case which we had considered we obtain

$$\hat{\rho}_{M1}^1=\begin{cases}(\delta N)^{-1}, & \delta>0\\ 2|\delta|-\dfrac{1}{|\delta|}\dfrac{1}{N}+\dfrac{\tilde{d}}{1-|\delta|\tilde{d}}\dfrac{1}{N}, & \delta<0\end{cases} \quad (6.27)$$

i.e., again the same results as in half-space.

C. Calculation of $\langle R^2\rangle_\perp/\langle \mathbf{R}^2\rangle_{\text{bulk}}$

Using results of Secs. III and V and, in particular, using Eqs. (3.13), (5.1), and (6.1), we obtain

$$\langle\mathbf{R}^2\rangle_\perp=\frac{2}{Z(\delta,N)}L^{-1}\left[\frac{1}{s^2}\left[1-\frac{\delta}{\sqrt{s}+\delta}\right]\right] . \quad (6.28)$$

In order to perform the inverse Laplace transform in Eq. (6.31) some technical elements need to be introduced. They are discussed in Appendix A. Here we provide only the final result:

$$Z(\delta,N)\langle\mathbf{R}^2\rangle_\perp=\frac{2}{\delta^2}e^{\delta^2 N}-\frac{2}{\delta^2}-4\delta e^{\delta^2 N}\left[-\frac{\partial}{\partial\delta^2}\right]\frac{1}{\delta}\operatorname{erf}(\delta\sqrt{N}) . \quad (6.29)$$

For $\delta>0$ and $N\to\infty$ we can use, as before, Eq. (6.2). After straightforward algebra this gives

$$\left[-\frac{\partial}{\partial\delta^2}\right]\frac{1}{\delta}\operatorname{erf}(\delta\sqrt{N})=\frac{1}{2}\frac{1}{\delta^3}\left[1-\frac{e^{-\delta^2 N}}{\delta\sqrt{\pi N}}\right]-\frac{Ne^{-\delta^2 N}}{\delta^2\sqrt{\pi N}}-\frac{e^{-\delta^2 N}}{2\delta^4\sqrt{\pi N}} . \quad (6.30)$$

Combining Eqs. (6.29) and (6.30) and using Eq. (6.3) we obtain

$$\langle\mathbf{R}^2\rangle_\perp=\frac{4N}{\delta\sqrt{\pi N}}\frac{1}{Z(\delta,N)}=4N, \quad |\delta N^{1/2}\to\infty| . \quad (6.31)$$

Combining now Eqs. (6.31) and (5.1) produces

$$R_>\equiv\frac{\langle\mathbf{R}^2\rangle_\perp}{\langle\mathbf{R}^2\rangle_{\text{bulk}}}=\frac{4N}{2N}=2, \quad \delta>0 . \quad (6.32)$$

$\langle\mathbf{R}^2\rangle_{\text{bulk}}$ denotes the component of the mean square end-to-end dimensions in a bulk solution along a particular direction (e.g., perpendicular to surface). The result, Eq. (6.32), coincides with that given in Ref. [17] [e.g., see Eq. (II.36)].

For the case $\delta<0$, by combining Eqs. (6.4) and (6.29) we obtain after some algebra

$$\langle\mathbf{R}^2\rangle_\perp=\frac{4}{\delta^2}e^{\delta^2 N}\frac{1}{Z(\delta,N)}=\frac{2}{\delta^2}, \quad |\delta N^{1/2}|\to\infty . \quad (6.33)$$

Combining Eq. (6.33) with Eq. (5.1) produces

$$R_<\equiv\frac{\langle\mathbf{R}^2\rangle_\perp}{\langle\mathbf{R}^2\rangle_{\text{bulk}}}=\frac{1}{\delta^2 N}, \quad \delta<0, \quad |\delta N^{1/2}|\to\infty . \quad (6.34)$$

The last result is also in accord with that presented in Ref. [17].

VII. CALCULATION OF PROPERTIES OF SEMIFLEXIBLE POLYMERS

Using the results of the preceding section, it is convenient also to subdivide this section into subsections in order to make connections with the fully flexible results.

A. Calculation of the partition function

By combining Eqs. (4.18) and (5.5) and, in view of Eq. (6.1), we write for the half-space case partition function

$$\begin{aligned} Z(\delta,N)&=L^{-1}\left[\int_0^\infty dx\,\hat{G}(x,x'=0;s)\right] \\ &=mL^{-1}\left[\frac{1}{\omega^2}\left[1-\frac{s\delta}{\omega+s\delta}\right]\right] \\ &=(\mathrm{a})+(\mathrm{b})\ . \end{aligned} \tag{7.1}$$

The calculations of Eq. (7.1) are rather involved and presented in Appendix B. Here we provide only the final result:

$$Z(\delta>0,N)=\frac{\delta}{\pi}\int_0^\pi d\theta\frac{e^{[\cos\theta]mN}\cos\theta}{\sin^2\theta+\delta^2\cos^2\theta}\ , \tag{7.2}$$

where in going from Eq. (B15) to (7.2) we have made a change of integration variable: $\theta=\pi-\alpha$ and then set again $\alpha=\theta$.

The integral in the right-hand side of Eq. (7.2) can be easily calculated numerically for arbitrary δ, m, and N. We would like, however, to make sure that the above result is in agreement with its "nonrelativistic" counterpart [Eqs. (6.3) and (6.4)]. To this purpose, use of asymptotic methods is helpful. Noticing that the exponent in Eq. (7.12) acquires its maximum value at $\theta=0$, we expand terms under the integral in a Taylor series around $\theta=0$. Let $\delta>0$, so that we obtain

$$Z(\delta>0,N)\simeq\frac{\delta}{\pi}e^{mN}\int_0^\pi d\alpha\frac{(1-\alpha^2/2+\cdots)e^{-(\alpha^2/2)mN}}{\alpha^2+\delta^2(1-\alpha^2/2+\cdots)}\ . \tag{7.3}$$

Let $\delta^2mN/2=y^2$, so that the right-hand side of (7.3) becomes

$$\begin{aligned} &\frac{\delta}{\pi}e^{mN}\left[\frac{2}{mN}\right]^{1/2}\int_0^{\pi\sqrt{mN/2}}dy\frac{e^{-y^2}(1-\cdots)}{\delta^2+\frac{2}{mN}y^2(1-\delta^2/2)+\cdots} \\ &\qquad\simeq\frac{e^{mN}}{\delta\sqrt{\pi mN}}\mathrm{erf}\left[\pi\left[\frac{mN}{2}\right]^{1/2}\right]\ . \end{aligned} \tag{7.4}$$

Using Eq. (6.2) and noticing that $Z(\delta,N)$ is always defined up to normalization constant, we can choose this constant $\frac{1}{2}e^{-mN}$, and set $mN=4N/a$, $a=2$ (e.g., see Sec. II) to reobtain Eq. (6.3). Consider now the opposite limit, $\delta<0$. To study this limit we have to go back to Eq. (B3) and change the sign in front of the first term. Then, going through the same steps as before we obtain

$$\begin{aligned} Z(\delta<0,N)&=2\alpha\sinh(\alpha mN)-\frac{|\delta|}{\pi}\int_0^\pi d\theta\frac{e^{[\cos\theta]mN}\cos\theta}{\sin^2\theta+\delta^2\cos^2\theta} \\ &\approx\frac{1}{\sqrt{1-\delta^2}}e^{mN/\sqrt{1-\delta^2}}\ , \end{aligned} \tag{7.5}$$

where in going from the first line to the second we had used Eq. (7.4), and α is defined after Eq. (B4). If we, as before, extract the factor $\frac{1}{2}e^{-mN}$ from the right-hand side of Eq. (7.21), then we would obtain

$$Z(\delta<0,N)\simeq\frac{2}{\sqrt{1-\delta^2}}e^{mN(1/\sqrt{1-\delta^2}-1)}\ . \tag{7.6}$$

Finally, expanding the square roots and choosing, as before, $m=a/4$, $a=2$, we reobtain the result Eq. (6.4) as required.

In order to finish our discussion of the partition function for the half-space, several comments are in order. First, in spite of the agreement for large m and N with the nonrelativistic case, the rigid rod limit ($m\to0$) is left without discussion. To correct this deficiency, the following steps must be taken.

First, by going back to Eq. (7.1) and letting there $m=0$, we obtain

$$\frac{Z(\delta,N)}{m}=N\left[\frac{1}{1+\delta}\right],\quad \delta>0 \tag{7.7}$$

with analogous expression for $\delta<0$ [e.g., see Eq. (7.23) below]. Second, in view of Eq. (7.5), let us consider again Eq. (7.2). In the limit $m\to0$ we obtain

$$\begin{aligned} \frac{Z(\delta,N)}{m}&=\frac{\delta N}{\pi}\int_0^\pi d\theta\frac{\cos^2\theta}{\sin^2\theta+\delta^2\cos^2\theta} \\ &=N\left[\frac{1}{1+\delta}\right],\quad \delta>0\ . \end{aligned} \tag{7.8}$$

The last result is easily obtainable because the integral in Eq. (7.8) can be calculated exactly. The case $\delta<0$ is treated analogously, whence, indeed, Eqs. (7.7) and (7.8) are in complete agreement with each other. This means that in order for Eqs. (7.2) and (7.5) to be utilized *for all m's, both sides of these equations should be divided by m.* This will be assumed in the rest of our calculations.

Second, in all our calculations performed so far we had assumed that δ is less than unity, in agreement with Eq. (B4). But this requirement also emerges naturally from our calculation of the partition function: if we set $|\delta|>1$ in Eq. (B4) we would *not* be able to obtain the correct "nonrelativistic" limit, Eq. (7.6), for the partition function.

Consider now the case of parallel plates. For the sake of illustration, we shall consider in detail only the Dolan-Edwards case [18]. The rest of the cases could be worked out analogously (as is explained in Sec. VI). Using Eq. (4.19) and results of Secs. V and VI we obtain

$$Z_{\parallel}(\delta,N)=\sum_{l=-\infty}^{\infty}L^{-1}\left[\int_0^{\bar{d}}dx\frac{1}{\omega}e^{-\omega|x-2l\bar{d}|}\left[1-\frac{s\delta}{\omega+s\delta}\right]\right]\ . \tag{7.9}$$

In order to analyze this expression further, the following observation is helpful. Let $\delta_0 = s\delta$ and let $\omega = \sqrt{S}$ where S is the new Laplace variable which, for the time being, is totally independent of s. We then introduce the transform,

$$\mathcal{L}(S) = \int_0^\infty d\mathcal{N}\, e^{-\mathcal{N}S} \mathcal{L}(\mathcal{N}) \tag{7.10}$$

and its inverse,

$$\mathcal{L}(\mathcal{N}) = \frac{1}{2\pi i} \int_c dS\, e^{S\mathcal{N}} \mathcal{L}(S) \ . \tag{7.11}$$

By introducing the new Laplace variable we can repeat, in principle, all the steps of our calculations presented in Sec. VI [i.e., we use Eqs. (6.5)–(6.13) for $\delta > 0$ and, then, Eqs. (6.14)–(6.16) for $\delta < 0$]. Using Eq. (6.13) (for $\delta > 0$) with $\delta \rightleftarrows \delta_0$ and $N \rightleftarrows \mathcal{N}$ and performing the direct Laplace transform according to Eq. (7.10) gives

$$Z_\parallel(\delta, N) \simeq L^{-1}\left[\frac{4}{\delta s \tilde{d}} \frac{1}{s^2 - m^2 + \pi^2/\tilde{d}^2} \right] . \tag{7.12}$$

After performing the "usual" inverse Laplace transform of Eq. (7.12) we find

$$Z_\parallel(\delta, N) = \frac{4}{\delta \tilde{d}} \frac{1}{m^2 - \pi^2/\tilde{d}^2} \times \left\{ \cosh\left[\left[m^2 - \frac{\pi^2}{\tilde{d}^2} \right]^{1/2} N \right] - 1 \right\} . \tag{7.13}$$

In the "nonrelativistic" limit ($m \to \infty$) we obtain

$$Z_\parallel(\delta, N) \simeq \frac{4}{\delta \tilde{d}} \frac{e^{mN}}{m^2} e^{-(\pi^2/2\tilde{d}^2)(N/m)} \ . \tag{7.14}$$

In view of the discussion following Eq. (7.4), we conclude that the result, Eq. (7.14), practically coincides with that given by Eq. (6.13) as required. At the same time, in the "relativistic" limit ($m \to 0$) we formally obtain

$$Z_\parallel(\delta, N) = \frac{4}{\delta} \frac{\tilde{d}}{\pi^2 - \tilde{d}^2 m^2} \left[1 - \cos\left(\sqrt{\pi^2 - \tilde{d}^2 m^2} \frac{N}{\tilde{d}} \right) \right] . \tag{7.15}$$

This result should be used with some caution. Indeed, in arriving at Eq. (7.12) we had repeated the asymptotic analysis [e.g., see Eqs. (6.6)–(6.13)] appropriate for the nonrelativistic case, i.e., we essentially used the fact that $N \to \infty$. Because in the present case instead of N we have used $\mathcal{N}$ it is not immediately clear that $\mathcal{N} \to \infty$. Because in the present case we cannot just require $\mathcal{N} \to \infty$, this implies that the results such as Eqs. (6.7) and (6.8) might be invalid in the present case. To understand this situation better, we would like to consider the limiting case, $m = 0$, in Eq. (7.9) directly. For $m = 0$ we have $\omega = s$ and, whence, we obtain

$$Z_\parallel(\delta, N) \frac{\tilde{d}}{1+\delta} \sum_{l=-\infty}^{\infty} L^{-1}\left[\int_0^t dx \frac{e^{-s\tilde{d}|x-2l|}}{s} \right] = \frac{\tilde{d}}{1+\delta} \sum_{l=-\infty}^{\infty} \int_0^1 dx\, \theta(N - \tilde{d}|x-2l|) \ . \tag{7.16}$$

Because of the nature of our problem, we require in the rigid rod limit $N \le \hat{d}$. Then, using Eq. (7.16) we arrive at

$$Z_\parallel(\delta, N) = \theta(\tilde{d} - N) \frac{N}{1+\delta} \ , \tag{7.17}$$

which obviously coincides with Eq. (7.7) for $\delta > 0$, $N < \tilde{d}$, as required. If, instead, we set $m = 0$ in Eq. (7.15) we obtain

$$Z_\parallel(\delta, N) = \frac{4\tilde{d}}{\delta \pi^2} \left[1 - \cos\left[\frac{\pi N}{\tilde{d}} \right] \right] . \tag{7.18}$$

This result is in obvious disagreement with the previous one. We attribute this disagreement to the above-mentioned failure of the asymptotic results. Equations (7.13) and (7.15) could be used, however, beyond their "nonrelativistic" limits with some caution. Indeed, the experimental data [41] and some independent theoretical calculations [42] indicate that the measured force between parallel plates tends to oscillate (see also discussion below). This is possible only if the underlying potential [e.g., Eq. (7.15)] has some oscillating component.

Consider now the case when $\delta < 0$. Repeating the same arguments as in the $\delta > 0$ case we arrive at the analog of Eq. (7.12) given by

$$Z_\parallel(\delta, N) \simeq L^{-1}\left[\frac{1 + \tilde{d}s|\delta|}{s^2 - m^2 - s^2\delta^2} \right] \tag{7.19}$$

or

$$Z_\parallel(\delta, N) = \left[\frac{\alpha}{m} \right] \sinh(m\alpha N) + \tilde{d}|\delta| \cosh(m\alpha N) \ , \tag{7.20}$$

where α was defined before Eq. (B5). In the "nonrelativistic" limit the above result reduces to

$$Z_\parallel(\delta, N) \simeq \frac{\alpha}{m} \sinh(m\alpha N) \left[1 + \frac{\tilde{d}|\delta| m}{\alpha} \right] , \tag{7.21}$$

which is in agreement with Eq. (6.16) in view of the discussion presented in Sec. V. In the "relativistic" limit we obtain instead

$$Z_\parallel(\delta, N) \simeq \alpha^2 N + \tilde{d}|\delta| = \frac{N}{(1+|\delta|)(1-|\delta|)} + \tilde{d}|\delta| \ . \tag{7.22}$$

Taking into account that in this limit $N \le \tilde{d}$ and using Eq. (7.1) (for $\delta < 0$) we obtain

$$Z_\parallel(\delta, N) \approx N \left[\frac{1 + |\delta| - |\delta|^3}{(1-|\delta|)(1+|\delta|)} \right] \approx \frac{N}{1-|\delta|} + O(\delta^3) \ , \tag{7.23}$$

whence, for $\delta < 0$, Eq. (7.20) represents fairly good approximation in the whole range of m's.

B. Calculation of forces and the monomer fractions

Calculation of forces proceeds now in the same way as it was done for the "nonrelativistic" case. In particular, for $\delta > 0$ using Eqs. (7.13) and (7.15) we obtain

$$\beta\mathcal{F}_1^0=\begin{cases}\dfrac{1}{\tilde{d}}-\dfrac{2\tilde{d}m^2}{\tilde{d}^2m^2-\pi^2}+\dfrac{\tilde{d}m^2}{\sqrt{m^2\tilde{d}^2-\pi^2}}\dfrac{\sinh[\sqrt{m^2\tilde{d}^2-\pi^2}(N/\tilde{d})]}{\cosh[\sqrt{m^2\tilde{d}^2-\pi^2}(N/\tilde{d})]-1} & (m\tilde{d}>\pi)\\ \dfrac{1}{\tilde{d}}+\dfrac{2\tilde{d}m^2}{\pi^2-\tilde{d}^2m^2}-\dfrac{\tilde{d}m^2}{\sqrt{\pi^2-\tilde{d}^2m^2}}\dfrac{\sin[\sqrt{\pi^2-\tilde{d}^2m^2}(N/\tilde{d})]}{1-\cos[\sqrt{\pi^2-\tilde{d}^2m^2}(N/\tilde{d})]} & (m\tilde{d}<\pi)\ .\end{cases} \tag{7.24}$$

Because, as we had discussed in Sec. VII A, the above expressions are *not* exact and only, strictly speaking, valid only in the nonrelativistic limit, we cannot study Eq. (7.24) in the limit $m=0$. But for $m\neq 0$ we expect them to be meaningful even away from the nonrelativistic limit. In which case for $\tilde{d}\to 0$ we can further approximate the above results by

$$\beta\mathcal{F}_1^0\approx\frac{1}{\tilde{d}}-\frac{\tilde{d}m^2}{\pi}\frac{\sin(\pi N/\tilde{d})}{1-\cos(\pi N/\tilde{d})}\ . \tag{7.25}$$

Expanding sine and cosine terms in Eq. (7.25) we find that the second term is nonsingular in the limit $\tilde{d}\to 0$ and hence can be ignored. But for *finite* $\tilde{d}$ its presence is important because it causes the force to oscillate.

Consider now the case $\delta<0$. Using Eq. (7.20) we obtain as well

$$\beta\mathcal{F}_1^0=\frac{(m/\alpha)|\delta|\coth(m\alpha N)}{1+\tilde{d}|\delta|(m/\alpha)\coth(m\alpha N)}\ . \tag{7.26}$$

For m finite and $N\to\infty$ this produces:

$$\beta\mathcal{F}_1^0\simeq\frac{|\delta|(m/\alpha)}{1+\tilde{d}|\delta|(m/\alpha)}\ , \tag{7.27}$$

while for $m\to 0$ we obtain

$$\beta\mathcal{F}_1^0\simeq\frac{|\delta|(1-\delta^2)N^{-1}}{1+\tilde{d}|\delta|(1-\delta^2)N^{-1}}\ . \tag{7.28}$$

But from our discussion in Sec. VII A we know that in this limit $N\leq\tilde{d}$ and, thus, the above result could be rewritten again as

$$\beta\mathcal{F}_1^0\simeq\frac{1}{\tilde{d}}\frac{|\delta|(1-\delta^2)}{1+|\delta|(1-\delta^2)}\ , \tag{7.29}$$

i.e., irrespective of the sign of δ, we obtain repulsive force $\sim 1/\tilde{d}$. It is important to realize that the actual $\tilde{d}$ dependence of the above repulsive force is *different* in the flexible ("nonrelativistic") case [e.g., see Eqs. (6.21) and (6.22)] as compared to the stiff ("relativistic") case. This difference will certainly affect colloidal stabilization conditions [13,18] and requires a detailed additional study to be presented elsewhere.

Consider now the fraction of absorbed monomers for the half-space problem. Evidently, in view of "nonrelativistic" results presented in Sec. VI we can restrict ourself by the case $\delta<0$ only [e.g., see Eq. (6.25)]. Using Eqs. (5.6), (5.13), and (7.5) we obtain

$$\hat{\rho}_M=-\frac{\partial}{\partial|\delta|}\ln\left[2\alpha\sinh(\alpha mN)-\frac{|\delta|}{\pi}\int_0^\pi d\theta\frac{e^{[\cos\theta]mN}\cos\theta}{\sin^2\theta+\delta^2\cos^2\theta}\right] \tag{7.30}$$

or

$$\hat{\rho}_M=\frac{1}{Nv}\left[2|\delta|\alpha^3\sinh(\alpha mN)+2\alpha^4|\delta|mN\cosh(\alpha mN)-\frac{1}{\pi}\int_0^\pi d\theta\frac{e^{[\cos\theta]mN}\cos\theta}{\sin^2\theta+\delta^2\cos^2\theta}+\frac{2\delta^2}{\pi}\int_0^\pi d\theta\frac{e^{[\cos\theta]mN}\cos^3\theta}{[\sin^2\theta+\delta^2\cos^2\theta]^2}\right]\ , \tag{7.31}$$

where $\alpha=1/\sqrt{1-\delta^2}$, as before, and v equals the argument of the ln term in Eq. (7.30). The results of our calculations of $\hat{\rho}_M$ are presented in Fig. 1. As we had discussed already, e.g., see discussion after Eq. (5.13), the results for $\hat{\rho}_M$ have only qualitative value.

C. Calculation of $\langle\mathbf{R}^2\rangle_\perp/\langle\mathbf{R}^2\rangle_{\text{bulk}}$

By analogy with Eq. (6.28) and taking into account Eqs. (4.18) and (5.3) we write

$$\langle\mathbf{R}^2\rangle_\perp=\frac{6}{Z(\delta,N)}L^{-1}\left[\frac{1}{\omega^4}\left[1-\frac{\delta s}{\omega+\delta s}\right]\right]\ . \tag{7.32}$$

Consider first the "ultrarelativistic" case: $m=0$. In this limit $\omega=s$ and we obtain ($\delta>0$)

$$\langle\mathbf{R}^2\rangle_\perp=\frac{6}{\Gamma(4)Z(\delta,N)}\frac{N^3}{1+\delta}=N^2\ , \tag{7.33}$$

where we used the fact that $Z(\delta,N)$ is given by Eq. (7.7). The result just obtained coincides with the one already obtained, Eq. (5.3), and is reproduced here for the reader's convenience. Using Eqs. (2.11) and (7.33) we obtain

$$R_>=\frac{\langle\mathbf{R}^2\rangle_\perp}{\langle\mathbf{R}^2\rangle_{\text{bulk}}}=1 \tag{7.34}$$

to be compared with the nonrelativistic limit, Eq. (6.32). We again emphasize that $\langle\mathbf{R}^2\rangle_{\text{bulk}}$ corresponds only to the projection of the mean square chain dimensions along a particular direction. Evidently, Eq. (7.34) will remain the same for $\delta<0$ in the limit $m=0$.

Consider now the more interesting case of arbitrary m. We shall treat now the $\delta>0$ and $\delta<0$ cases simultaneously by writing [e.g., see Eq. (7.32)]

$$\frac{1}{\omega^4}\left[1\mp\frac{\delta s}{\omega\pm\delta s}\right]=\frac{1}{\omega^4}\mp\frac{\delta s}{\omega^4}\frac{(\omega\mp\delta s)}{\omega^2-\delta^2 s^2}$$
$$=\mp\frac{\delta s}{\omega^3}\frac{1}{\omega^2-\delta^2 s^2}+\frac{1}{\omega^2(\omega^2-\delta^2 s^2)}$$
$$=(\mathrm{i})+(\mathrm{ii})\ . \tag{7.35}$$

By arriving at the last line of Eq. (7.35), we notice that the difference between the $\delta>0$ and $\delta<0$ cases is only reflected in the first term (i) where the upper sign corresponds to $\delta>0$. The inverse Laplace inversion of (ii) produces after some algebra

$$L^{-1}[(\mathrm{ii})]=\frac{1}{\delta^2 m^3}\left[\frac{1}{\alpha}\sinh(\alpha mN)-\sinh(mN)\right]\ . \tag{7.36}$$

As for (i), it is convenient to rewrite it first into the form

$$(\mathrm{i})=\pm\frac{1}{m^2|\delta|}\frac{s}{(s^2-m^2)^{1/2}}\left[\frac{1}{s^2-m^2}-\frac{1}{s^2-\alpha^2 m^2}\right]$$
$$=(\mathrm{a})+(\mathrm{b})\ . \tag{7.37}$$

Here the sign "+" corresponds to $\delta>0$. Noticing that

$$(\mathrm{a})=\pm\frac{s}{m^2\delta}\left\{\frac{1}{(s-m)^{3/2}}\frac{1}{(s+m)^{3/2}}\right\}, \tag{7.38}$$

we obtain

$$L^{-1}[(\mathrm{a})]=\pm\frac{N}{m^2\delta}I_0(mN)\ , \tag{7.39}$$

where $I_0(mN)$ is the modified Bessel function. As for (b), it is sufficient to compare it with (i) defined by Eq. (B2). Because of such comparison, we can write the final Laplace inverted result without delay,

$$L^{-1}[(\mathrm{b})]=\mp\frac{1}{m^3\delta\alpha}\sin(\alpha mN)$$
$$\pm\frac{1}{\alpha^2 m^3\delta}\frac{1}{\pi}\int_0^{\pi}d\theta\frac{e^{[\cos\theta]mN}\cos\theta}{\sin^2\theta+\delta^2\cos^2\theta}\ . \tag{7.40}$$

Collecting all terms together we obtain

$$\frac{1}{6}Z(\delta,N)\langle\mathbf{R}^2\rangle_{\perp}=\frac{1}{\delta^2 m^3}\left[\frac{1}{\alpha}\sinh(\alpha mN)-\sinh(mN)\right]$$
$$\pm\frac{N}{m^2\delta}I_0(mN)\mp\frac{1}{m^3\delta\alpha}\sinh(\alpha mN)$$
$$\pm\frac{1}{\alpha^2 m^3\delta}\frac{1}{\pi}\int_0^{\pi}d\theta\frac{e^{[\cos\theta]mN}\cos\theta}{\sin^2\theta+\delta^2\cos^2\theta}\ , \tag{7.41}$$

where $Z(\delta,N)$ is given by Eq. (7.2) for $\delta>0$ and by Eq. (7.5) for $\delta<0$. To check the correctness of the above results we need to study them in two limits $m\to 0$ and m finite but $N\to\infty$. The limit $m\to 0$ is nontrivial and requires rather lengthy calculations which we have done but we omit here in view of Figs. 2 and 3 presented in this paper. The "nonrelativistic" limit is easier to study and therefore we provide here some essential details. Analyzing the procedure which has led us to Eqs. (7.4) and (7.5) we obtain asymptotically

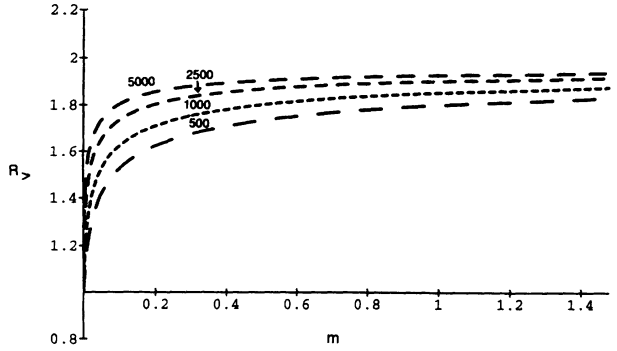

FIG. 2. Expansion factor $R_>$ as a function of an inverse rigidity m for polymer chains of various lengths N, $\delta>0$.

$$\frac{1}{6}Z(\delta,N)\langle\mathbf{R}^2\rangle_{\perp}=\frac{1}{\delta^2 m^3}\left[\frac{e^{\alpha mN}}{2\alpha}-\frac{e^{mN}}{2}\right]$$
$$\pm\frac{N}{m^2\delta}\frac{e^{mN}}{\sqrt{2\pi mN}}\mp\frac{e^{\alpha mN}}{2\alpha m^3\delta^2}$$
$$\pm\frac{e^{mN}}{\alpha^2 m^3\delta^3\sqrt{\pi mN}}\mathrm{erf}\left[\pi\left[\frac{mN}{2}\right]^{1/2}\right]\ . \tag{7.42}$$

Let now $\delta>0$, then Eq. (7.4) should be used (divided by a factor of m) for $Z(\delta,N)$ while in the right-hand side of Eq. (7.42) the dominant term is

$$+\frac{N}{m^2\delta}\frac{e^{mN}}{\sqrt{2\pi mN}}\ .$$

This produces for $\langle\mathbf{R}^2\rangle_{\perp}$ the following result:

$$\langle\mathbf{R}^2\rangle_{\perp}=\frac{N}{m}\frac{6}{\sqrt{2}}\ . \tag{7.43}$$

To get rid of the undesired factor of $(\sqrt{2})^{-1}$, we need to go back to Eq. (7.4) and to consider once again the combination

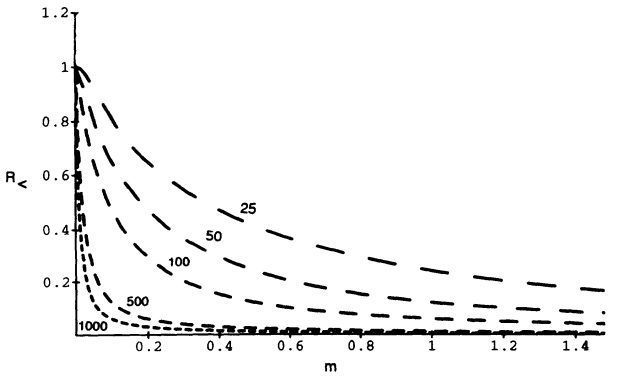

FIG. 3. Contraction factor $R_<$ as a function of an inverse rigidity m for polymer chains of various lengths N, $\delta<0$.

$$\frac{1}{\sqrt{\pi mN}}\operatorname{erf}\left[\pi\left[\frac{mN}{2}\right]^{1/2}\right]=\frac{1}{\pi}\left[\frac{2}{mN}\right]^{1/2}\int_0^{\pi\sqrt{mN/2}}dx\,e^{-x^2}=\frac{1}{\pi}\left[\frac{2}{mN}\right]^{1/2}\left[\int_0^{\infty}dx\,e^{-x^2}-\int_{\pi\sqrt{mN/2}}^{\infty}dx\,e^{-x^2}\right]$$

$$\xrightarrow[N\to\infty]{}\frac{1}{2\pi}\left[\frac{2}{mN}\right]^{1/2}\sqrt{\pi}=\frac{1}{\sqrt{2\pi mN}}\ . \tag{7.44}$$

The above result, when used in Eqs. (7.4) and (7.42), produces the desired answer:

$$\langle\mathbf{R}^2\rangle_{\perp}=\frac{N}{m}6\ . \tag{7.45}$$

Finally, using Eq. (2.10), we obtain

$$R_{>}=\frac{\langle\mathbf{R}^2\rangle_{\perp}}{\langle\mathbf{R}^2\rangle_{\text{bulk}}}=2\ ,$$

which is in agreement with Eq. (6.32).

Consider now the case $\delta<0$. Using Eq. (7.41), the dominant term in the right-hand side of Eq. (7.41) is going to be ($\alpha>1$)

$$\frac{1}{\delta^2m^3}\frac{e^{\alpha mN}}{\alpha}\ .$$

Using this result and Eq. (7.5) (divided by m, as before) we obtain

$$\langle\mathbf{R}^2\rangle_{\perp}=\frac{6}{\delta^2m^2}(1-\delta^2) \tag{7.46}$$

and, whence,

$$R_{<}=\frac{\langle\mathbf{R}^2\rangle_{\perp}}{\langle\mathbf{R}^2\rangle_{\text{bulk}}}=\frac{2}{\delta^2mN}(1-\delta^2)\ . \tag{7.47}$$

This result is in complete agreement with Eq. (6.34) if we choose $2(1-\delta^2)=m$. Taking into account that $|\delta|\le\frac{1}{2}$, we obtain $m=\frac{3}{2}$, which agrees with results for m [e.g., see the discussion before Eq. (5.3)].

VIII. DISCUSSION

The results obtained above do not exhaust the existing possibilities for surface interacting polymers. For example, Rubin [43] had considered adsorbtion of fully flexible polymers onto rods while Taniguchi, Kawakatsu, and Kawasaki [44] had considered an adsorbtion of the fully flexible polymers into spheres, etc. In addition, when the surfaces are flexible and fluctuating, study of polymer absorbtion and forces between surfaces becomes technically complicated [45,46]. Nevertheless, the methods developed in this work will enable the study of the above problems through a straightforward extension of results already obtained for fully flexible chain results.

The single-chain results discussed in our work are useful only in the limiting case of low polymer concentrations. The effects of higher polymer concentrations as well as the excluded volume in the case of fully flexible polymers can be accounted for by using the integral equation methods [13]. Thus these methods admit straightforward extension to the case of semiflexible polymers by using the methods presented in our paper.

It is important to realize that the excluded volume and the rigidity effects actually play very similar roles [8], i.e., it is always possible to mimic the chain extension caused by the excluded volume effects by considering semiflexible chain *(without* excluded volume) with carefully chosen inverse rigidity m and, because in concentrated solutions the excluded volume effects become screened [1], our single-chain results could actually be used with some caution in a wider range of polymer concentrations (if, of course, we know the effective rigidity of a single chain which could be determined, for example, variationally [47]).

The fact that the excluded volume plays a role similar to rigidity of the chain could also be seen *directly* by comparing the results depicted in our Fig. 2 with that depicted in Fig. 1 of Ref. [22]. At the same time, the results depicted in Fig. 3 can be interpreted also in terms of unbinding transition, e.g., see Fig. 1 of Ref. [48]. Such an interpretation might be especially useful for description of unbinding transitions in simplified interface models described in Refs. [49,50].

APPENDIX A: CALCULATIONS RELATED TO EQ. (6.28)

In order to Laplace invert the expression given in Eq. (6.28) we use the following chain of identities:

$$\frac{1}{s^2}\frac{1}{\sqrt{s}+\delta}=\frac{\sqrt{s}-\delta}{s^2(s-\delta)}$$

$$=\frac{1}{s^{1/2}}\frac{1}{s-\delta}-\frac{\delta}{s^2(s-\delta^2)}=(\text{a})-(\text{b})\ . \tag{A1}$$

In the case of (a) we notice that

$$\frac{1}{s^{3/2}}=\frac{1}{\Gamma(\frac{3}{2})}\int_0^{\infty}dx\,x^{1/2}e^{-xs}\ . \tag{A2}$$

This produces

$$L^{-1}\left\{\frac{e^{-xs}}{s-\delta^2}\right\}=e^{\delta^2(N-X)},\quad N>x\ . \tag{A3}$$

Combining Eqs. (A2) and (A3) we get

$$\frac{2e^{\delta^2 N}}{\sqrt{\pi}}\int_0^N dx\, x^{1/2}e^{-\delta^2 x}$$
$$=\frac{4e^{\delta^2 N}}{\sqrt{\pi}}\int_0^{\sqrt{N}} dy\, y^2 e^{-\delta^2 y^2}$$
$$=\frac{4}{\sqrt{\pi}}e^{\delta^2 N}\left[-\frac{\partial}{\partial\delta^2}\right]\int_0^{\sqrt{N}} dy\, e^{-\delta^2 y^2}$$
$$=2e^{\delta^2 N}\left[-\frac{\partial}{\partial\delta^2}\right]\frac{1}{\delta}\mathrm{erf}(\delta\sqrt{N})\ . \tag{A4}$$

As for (b), we obtain

$$(\mathrm{b})=-\left[\frac{1}{\delta^3}+\frac{N}{\delta}\right]+\frac{1}{\delta^3}e^{\delta^2 N}\ . \tag{A5}$$

APPENDIX B: CALCULATIONS RELATED TO EQ. (7.1)

We have

$$(\mathrm{a})=L^{-1}[m/\omega^2]=\sinh mN\ , \tag{B1}$$
$$(\mathrm{b})=-L^{-1}\left[\frac{m\delta s}{\omega^2}\left[\frac{1}{\omega+\delta s}\right]\right]$$
$$=-m\delta\left[\frac{s}{\omega^2-\delta^2 s^2}\frac{1}{\omega}\right]+m\delta^2\left[\frac{s^2}{\omega^2-\delta^2 s^2}\frac{1}{\omega^2}\right]$$
$$=(\mathrm{i})+(\mathrm{ii})\ . \tag{B2}$$

For (ii) we have in addition

$$(\mathrm{ii})=L^{-1}\left[\frac{m\delta^2 s^2}{\omega^2(\omega^2-\delta^2 s^2)}\right]$$
$$=-L^{-1}\left[\frac{m}{\omega^2}\right]+mL^{-1}\left[\frac{1}{\omega^2-\delta^2 s^2}\right]\ . \tag{B3}$$

The first term in Eq. (B4) cancels with (a) while for the second term we write

$$(\mathrm{iii})=mL^{-1}\left[\frac{1}{s^2(1-\delta^2)-m^2}\right]\ . \tag{B4}$$

Noticing that for $\delta=1$ we get (iii)=0, we shall consider only the case $\delta<1$ below. This is in accord with our earlier result, Eq. (5.13). Introduce $\alpha^2=1/(1-\delta^2)$, then we obtain

$$m\alpha^2 L^{-1}\left[\frac{1}{s^2-m^2\alpha^2}\right]=\alpha\sinh(m\alpha N)\ . \tag{B5}$$

Going now back to (i), Eq. (B2), we find

$$\frac{s}{\omega^2-\delta^2 s^2}=\frac{s\alpha^2}{s^2-\alpha^2 m^2}=\frac{\alpha^2}{2}\left[\frac{1}{s+\alpha m}+\frac{1}{s-\alpha m}\right]\ . \tag{B6}$$

Noticing also that

$$\frac{1}{\omega}=\frac{1}{\sqrt{s^2-m^2}}$$
$$=\frac{1}{\sqrt{(s-m)(s+m)}}$$
$$=\frac{\Gamma(1)}{[\Gamma(\frac{1}{2})]^{1/2}}\int_0^1 dx\frac{x^{-1/2}(1-x)^{-1/2}}{[(1-x)(s+m)+x(s-m)]} \tag{B7}$$

and introducing notations

$$(1-x)(s+m)+x(s-m)=s+m(1-2x)\equiv s+M^2\ ,$$

we are ready to consider the following inverse Laplace transforms:

$$L^{-1}\left\{\frac{1}{s+M^2}\frac{1}{s\pm\alpha m}\right\}=\frac{-1}{M^2\mp\alpha m}e^{-M^2 N}$$
$$+\frac{(-1)}{\pm\alpha m-M^2}e^{\mp\alpha MN}\ . \tag{B8}$$

This produces

$$L^{-1}\left\{\frac{1}{s+M^2}\frac{1}{s+\alpha m}\right\}+L^{-1}\left\{\frac{1}{s+M^2}\frac{1}{s-\alpha m}\right\}$$
$$=-e^{-M^2 N}\left[\frac{2M^2}{(M^2)^2-\alpha^2 m^2}\right]+\left[\frac{(M^2+\alpha m)e^{-\alpha mN}}{(M^2)^2-\alpha^2 m^2}+\frac{(M^2-\alpha m)e^{+\alpha mN}}{(M^2)^2-\alpha^2 m^2}\right]\ . \tag{B9}$$

By combining Eq. (B2) [for (i)] with Eqs. (B6)–(B9) we obtain

$$(\mathrm{i})=-\frac{m\alpha^2\delta}{\pi}\int_0^1 dx\, x^{-1/2}(1-x)^{-1/2}$$
$$\times[-e^{-M^2 N}M^2+M^2\cosh(\alpha mN)$$
$$-\alpha m\sinh(\alpha mN)]\frac{1}{(M^2)^2-\alpha^2 m^2}\ . \tag{B10}$$

Noticing that $M^2=m(1-2x)$, the above result can be rewritten further as

$$(\mathrm{i})=\frac{\delta}{\pi}\int_0^1 dx\frac{x^{-1/2}(1-x)^{-1/2}}{1-\alpha^{-2}(1-2x)^2}[-e^{-(1-2x)Nm}(1-2x)$$
$$+(1-2x)\cosh(\alpha mN)$$
$$-\alpha\sinh(\alpha mN)]\ . \tag{B11}$$

Now let $x=y^2$ and then let $y=\sin\theta$; after these substitutions we obtain

$$(\mathrm{i})=\frac{\delta}{\pi}\int_0^{\pi}d\theta\frac{1}{1-\alpha^{-2}\cos^2\theta}\left[-\frac{e^{-[\cos\theta]mN}\cos\theta}{(j)}+\frac{[\cos\theta]\cosh(\alpha mN)}{(jj)}-\frac{\alpha\sinh(\alpha mN)}{(jjj)}\right]. \tag{B12}$$

Noticing that [for (jjj)]

$$\int_0^{\pi}d\theta\frac{1}{1-\alpha^2\cos^2\theta}=\frac{\pi}{\delta} \tag{B13}$$

while [for (jj)]

$$\int_0^{\pi}d\theta\frac{\cos\theta}{1-\alpha^{-2}\cos^2\theta}=0 \tag{B14}$$

we obtain

$$(\mathrm{ii})=-\alpha\sinh(\alpha mN)-\frac{\delta}{\pi}\int_0^{\pi}d\theta\frac{e^{-[\cos\theta]mN}\cos\theta}{\sin^2\theta+\delta^2\cos^2\theta}. \tag{B15}$$

The first term in Eq. (B15) cancels against that given in Eq. (B5) so that we are left with the result given in the main text as Eq. (7.2).

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