Modified Langer-Zittartz method for the electrostatic excluded-volume problem

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A modified manifestly self-consistent Langer-Zittartz method is applied to the nonperturbative treatment of the electrostatic excluded-volume effects in the polyelectrolyte chain. The method is tested for the case of the ordinary excluded-volume problem for which it produces the standard Flory result, $(\langle R^2\rangle)^{1/2}\propto N^{3/5}$. When it is applied to the polyelectrolyte chain, for the totally unscreened case, it also gives the Flory result $(\langle R^2\rangle)^{1/2}\propto N$, which is confirmed by recent Monte Carlo simulations performed by Baumgärtner. Complications associated with effects of partial screening are considered as well. Explanations for the failure of the conventional renormalization-group methods for the polyelectrolyte chain are presented on the basis of comparisons between the polyelectrolyte problem and mathematically similar problems in solid-state physics.

I. INTRODUCTION

The excluded-volume problem for the single homopolymer chain has been studied extensively by both analytical and by computer simulation methods.[1] Various analytical methods, which include Flory-type mean-field and self-consistent-field approaches as well as position-space, real-space, and field-theoretic renormalization methods,[2] yield very similar results that are in agreement with Monte Carlo simulations. In contrast to this success, which for practical purposes solves the homopolymer excluded-volume problem, application of the same methods to the polyelectrolyte chain produces very conflicting results. A similar situation exists for other closely related models with Coulombic type of correlations, namely the "true" self-avoiding walk and the random walk in random-environment models,[3,4] where recent field-theoretic renormalization calculations differ from Flory-type predictions.[3] Recent Monte Carlo simulations by Baumgärtner[5] for the unscreened polyelectrolyte are in good agreement with Flory-type theories which give for the end-to-end distance ($\langle R^2\rangle \sim N^{\nu}$) exponent ν, the result $\nu=3/d$. In dimension $d=3$ the rigid-rod result ($\nu=1$) is obtained, which agrees with what is intuitively expected. The real-space renormalization[2] as well as the field-theoretic renormalization[6] give $\nu=2/(d-2)$, which is valid for $(4\le d\le 6)$ within the accuracy of the above methods. For $d<4$ and the totally unscreened polyelectrolyte chain, existing renormalization-group methods fail to produce meaningful physical results. This already poses a serious theoretical problem, consequences of which go beyond the polyelectrolyte problem as will be demonstrated below. In addition, as it was already indicated by Baumgärtner,[5] application of Monte Carlo methods to systems with long-range interactions is considerably more difficult than their application to standard short-range excluded-volume-type interactions. This is even more true when the concentration-dependent effects are considered.

Recently we made an attempt to describe the polyelectrolyte chain for the case when charges are partially screened due to counterions in the solvent.[7] Our analysis was based on the principle of correspondence which requires that in the limit of total screening the polyelectrolyte chain must behave as an ordinary homopolymer chain with the standard excluded-volume exponent $\nu=\frac{3}{5}$.[2] We found that the presence of electrostatic interactions under certain conditions, specified in our work, destabilizes the standard excluded-volume fixed point so that the chain tends to cross over from one scaling regime to, presumably, another which is not accessible within the conventional renormalization-group (RG) framework. The situation is similar to that found in the standard quantum electrodynamics,[8] where at short distances results of perturbation theory cannot be trusted because the coupling constant becomes too large. For the case of the polyelectrolyte chain, it is natural to assume that the crossover must take place between the good-solvent excluded-volume regime and the regime of the rigid rod which is described by a Flory-type exponent $\nu=3/d$. Because, upon approaching the unscreened limit, the renormalized parameters describing the polymer chain tend to be in the strong-coupling domain, we conclude that the fully unscreened chain cannot be described in a usual perturbative way so that some sort of nonperturbative treatment is required.

The nonperturbative solution, if it exists, has some additional advantages over the usual perturbative solutions. For instance, in the polyelectrolyte case the electrostatic persistence length is introduced,[7] which must be considered along with the usual excluded-volume persistence length.[9] In practice it is experimentally impossible to separate these two for the case of incomplete screening. Use of the nonperturbative methods removes the need to use the electrostatic stiffness, which is the averaged macroscopic product of rather complicated microscopic interactions. A microscopic model for the polyelectrolyte may be chosen analogous to that used by Baumgärtner,[5] which may be modified by introducing screening into the potential. The model used by Baumgärtner is a freely jointed chain of beads, all having the same charges, and rigid links between them. Electrostatic stiffness comes into this model as a result of some kind of averaging procedure and is not included at the outset.

In this work we use a continuum version of Baumgärtner's model.[5] Section II is devoted to the description of the microscopic model. Here the connection with our previous work on the polyelectrolyte chain[7] is established. In addition, the main quantities of interest and characteristic scales are defined. Section III presents the general features of the manifestly self-consistent modified Langer-Zittartz method.[10] It also establishes the connection with perturbation theory as well as shows what kind of approximations must be made in the "renormalized" Dyson's equation in order to obtain the above self-consistent-field equations for the case of homopolymer and polyelectrolyte chains. In Sec. IV we obtain some solutions of the above equations. Here we analytically obtain the well-known Flory results for the homopolymer $\nu=\frac{3}{5}$ $(d=3)$ and polyelectrolyte $\nu=1$ $(d=3)$. Section V is devoted to a discussion. We discuss here the connection of the polyelectrolyte problem with similar problems in solid-state physics.

II. MICROSCOPIC MODEL

We utilize here the same microscopic model as we previously used for the case of the weak-electrostatic-coupling limit.[7] In general, the polyelectrolyte chain has two types of interactions, short-range repulsive excluded-volume interaction, as in the case of uncharged polymers, as well as the screened Coulomb interaction between the charges on the chain. In the Monte Carlo simulations[5] only the electrostatic unscreened interactions were considered. To treat the problem analytically, we must adopt a simplified model in which the charges are uniformly distributed along the chain. For this model in d-dimensional space the dimensionless "Hamiltonian" is given as

$$H(\mathbf{c})=\frac{1}{2}\int_0^N d\tau\left[\frac{d\mathbf{c}}{d\tau}\right]^2 +\frac{1}{2}\int_0^N d\tau\int_0^N d\tau'\, W[\mathbf{c}(\tau)-\mathbf{c}(\tau')] +\frac{1}{2}b_{\mathrm{ev}}\int_0^N d\tau\int_0^N d\tau'[\mathbf{c}(\tau)-\mathbf{c}(\tau')]\;, \qquad |\tau-\tau'|\geq\Lambda \tag{2.1}$$

where Λ denotes some kind of cutoff for excluding the self-interactions, b_{ev} denotes the bare excluded-volume coupling constant, $\mathbf{c}(\tau)$ represents the continuous chain conformation in d-dimensional space with the contour variable τ in the range of 0 to N, where N is the length of the chain. The quantity W is the screened Coulombic interaction which in d-dimensional space is

$$W(r)=b_e\,|\mathbf{r}|^{-d+2}\exp(-\kappa|\mathbf{r}|)\;, \tag{2.2}$$

where b_e is some electrostatic coupling constant, and $\kappa=\lambda_{\mathrm{DH}}^{-1}$ the inverse Debye-Hückel screening length defined as

$$\kappa=\left[4\pi e^2\sum_i n_{0i}Z_i^2/\epsilon kT\right]^{1/2} \tag{2.3a}$$

$$=\left[4\pi\lambda_B\sum_i n_{0i}Z_i^2\right]^{1/2}\propto\left[\sum_i n_{0i}\right]^{1/2}, \tag{2.3b}$$

Z_i is the valence of the ith ion, n_{0i} is the number density of the ith component in the solution, and the sum ranges over all ions in a unit volume surrounding the charge on the polyelectrolyte chain being screened and including that charge. The Bjerrum length λ_B is defined by

$$\lambda_B=e^2/\epsilon kT\;, \tag{2.4}$$

where e has the dimensionality of charge, ϵ is the dielectric constant of the medium, k is Boltzmann's constant, and T is the absolute temperature.

If $\mathbf{r}(\tau)$ designates the spatial position of the polymer segment at the contour position τ then

$$\mathbf{c}(\tau)=\left[\frac{d}{L_t}\right]^{1/2}\mathbf{r}(\tau)\;, \tag{2.5}$$

where L_t is some persistence length. In our previous paper[7] we used the total persistence length, which is defined as $\max\{L_{\mathrm{ev}},L_{\mathrm{pe}}\}$ where L_{ev} is the persistence length of the uncharged homopolymer, by definition $L_{\mathrm{pe}}=\lambda_B\kappa^{-2}l^{-2}$, which is the electrostatic persistence length, and l is the distance between ions along the chain. When $\kappa\to 0$ (no screening), L_{pe} diverges and in the opposite limit we are left with just L_{ev}, as expected. Evidently the notion of L_{pe} is of some use only for the partially screened case so that *we shall avoid it completely in our nonperturbative treatment,* as was explained in the Introduction. We, in fact, adopt here Baumgärtner's model[5] of freely jointed links and beads having charges with modifications needed for a continuum version. Given our Hamiltonian (2.1) we can define the fixed-end vector distribution function as

$$G(\mathbf{R},N;b_{\mathrm{ev}},W)=\int_{\mathbf{c}(0)=0}^{\mathbf{c}(N)=\mathbf{R}}D[\mathbf{c}]\exp[-H(\mathbf{c})]\;, \tag{2.6}$$

where $D[\mathbf{c}]$ is a functional measure in the chain conformational space. This distribution function, in principle, enables us to calculate the moments like $\langle R^{2n}\rangle$ in a standard way. Having defined the quantities of interest, in the following section we proceed with the actual computations of these quantities.

III. THE MODIFIED LANGER-ZITTARTZ SELF-CONSISTENT-FIELD METHOD: GENERAL FORMALISM

Some time ago Langer and Zittartz[10] proposed a method for the computation of density of states for the Schrödinger equation with a random Gaussian potential. Since that time many authors[11-13] tried to solve the same problem using field-theoretic nonperturbative methods. The final results of their analyses were always in agreement with those obtained initially by Langer and Zittartz. We shall demonstrate shortly that the problem of the electrolyte chain given by Eqs. (2.1) and (2.6) can be presented in a form identical to that considered by Langer and Zittartz (L-Z).[10] Although more sophisticated nonperturbative field-theoretic methods[11–13] are applicable as well to the electrolyte problem, we choose here the original version of the L-Z method with minor modifications. The reasons for doing so are twofold. First, we already mentioned that other methods[11–13] give in the end the same results. Second, use of the L-Z method, as it will be demonstrated, permits us to obtain the results in the most economical way.

Using the definition of the distribution function [Eq. (2.6)] and $H(\mathbf{c})$, given in Eq. (2.1), we now want to consider the most general form of the binary interaction term in Eq. (2.1). Use of the Hubbard-Stratonovich (H-S) identity[9] produces for this term

$$\exp\left[-\tfrac{1}{2}\int_0^N d\tau\int_0^N d\tau'\, W[\mathbf{c}(\tau)-\mathbf{c}(\tau')]\right]$$
$$=\mathcal{N}\int D[\phi]\exp\left[-\tfrac{1}{2}\int\int d\mathbf{x}\,d\mathbf{x}'\,\phi(\mathbf{x}')W^{-1}(\mathbf{x}-\mathbf{x}')\phi(\mathbf{x})\right]\exp\left[-i\int_0^N d\tau\,\phi[\mathbf{c}(\tau)]\right], \quad (3.1\text{a})$$

where $W^{-1}(\mathbf{x}-\mathbf{x}')$ is defined from the following equation,

$$\int d\mathbf{x}'W(\mathbf{x}-\mathbf{x}')W^{-1}(\mathbf{x}'-\mathbf{x}'')=\delta(\mathbf{x}-\mathbf{x}''), \quad (3.1\text{b})$$

and

$$\mathcal{N}^{-1}=\int D[\phi]\exp\left[-\tfrac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\,W^{-1}(\mathbf{x}-\mathbf{x}')\times\phi(\mathbf{x})\phi(\mathbf{x}')\right]. \quad (3.1\text{c})$$

Combining Eq. (3.1a) with Eqs. (2.1) and (2.6) gives

$$G(\mathbf{R},N;W)=\int D[\phi]P[\phi]G(\mathbf{R},N\mid\phi), \quad (3.2)$$

where $G(\mathbf{R},N\mid\phi)$ is defined as

$$G(\mathbf{R},N\mid\phi)=\int_{\mathbf{c}(0)=0}^{\mathbf{c}(N)=\mathbf{R}}D[\mathbf{c}]\exp\left\{-\int_0^N\left[\tfrac{1}{2}\left[\frac{d\mathbf{c}}{d\tau}\right]^2+i\phi[\mathbf{c}(\tau)]\right]d\tau\right\}. \quad (3.3)$$

Equations (2.1), (2.6), and (3.1a) completely define function $P[\phi]$ in Eq. (3.2). The distribution function (3.3) satisfies the "equation of motion,"[9] which in the chosen system of units can be written as

$$\left[\frac{\partial}{\partial N}-\frac{1}{2}\nabla^2+i\phi(\mathbf{x})\right]G(\mathbf{x},\mathbf{y},N\mid\phi)=\delta(\mathbf{x}-\mathbf{y})\delta(N). \quad (3.4)$$

The above equation assumes that the contour distance L_t is equal to 1. For the Laplace-transformed distribution function we obtain the following equation:

$$[s-\tfrac{1}{2}\nabla^2+i\phi(\mathbf{R})]G(\mathbf{R},s\mid\phi)=\delta(\mathbf{R}), \quad (3.5)$$

where we choose the origin of coordinate system $\mathbf{y}=0$ and denoted s as the Laplace variable conjugate to N. Going back to Eq. (3.2) we can now write

$$G(\mathbf{R},N;W)=\frac{1}{2\pi i}\int_C ds\exp(sN)\int D[\phi]P[\phi]G(\mathbf{R},s\mid\phi). \quad (3.6)$$

Using Eq. (3.1) we can rewrite Eq. (3.6) as

$$G(\mathbf{R},N;W)=\frac{\mathcal{N}}{2\pi i}\int_C ds\exp(sN)\int D[\phi]\exp[-H(\mathbf{R}\mid\phi)], \quad (3.7)$$

where C denotes the inverse Laplace contour,

$$H(\mathbf{R}\mid\phi)=+\tfrac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\,\phi(\mathbf{x}')W^{-1}(\mathbf{x}-\mathbf{x}')\phi(\mathbf{x})-\ln[G(\mathbf{R},s\mid\phi)]. \quad (3.8)$$

The potential ϕ now is determined from the stationarity condition[10]

$$\frac{\delta H(\mathbf{R}\mid\phi)}{\delta\phi}=0, \quad (3.9)$$

which can be rewritten in the following manner:

$$\int d\mathbf{x}'\,W^{-1}(\mathbf{x}-\mathbf{x}')\phi(\mathbf{x}')=\frac{1}{G(\mathbf{R},s\mid\phi)}\frac{\delta G(\mathbf{R},s\mid\phi)}{\delta\phi(\mathbf{x})}. \quad (3.10)$$

The explicit form of the functional derivative in Eq. (3.10) can be obtained by applying to both sides of Eq. (3.5) the operator $\delta/\delta\phi(\mathbf{x})$. After elementary algebra we obtain

$$i\phi(\mathbf{x})=\int d\mathbf{y}\,W(\mathbf{x}-\mathbf{y})\frac{G(\mathbf{R},\mathbf{y},s\mid\phi)G(\mathbf{y},s\mid\phi)}{G(\mathbf{R},s\mid\phi)}. \quad (3.11)$$

Here $G(\mathbf{R},s\mid\phi)\equiv G(\mathbf{R},0,s\mid\phi)$, etc. Substitution of Eq. (3.11) back into (3.5) produces the desired self-consistent-field (SCF) equation. This equation, however, is hardly treatable because of the explicit dependence of the potential ϕ [Eq. (3.11)] on the end points $\mathbf{R}$ and $\mathbf{0}$. In order to eliminate such a dependence, Langer and Zittartz proposed using the spectral representation of the Green's function G in the standard form

$$G(\mathbf{x},\mathbf{x}',s\mid\phi)=\sum_n\frac{\psi_n(\mathbf{x}\mid\phi)\psi_n^*(\mathbf{x}'\mid\phi)}{E_n(\phi)-s}, \quad (3.12)$$

with the subsequent assumption about the ground-state dominance. Here we prefer to use an alternative representation of the Green's function,

$$G(\mathbf{x},\mathbf{x}',s\mid\phi)=\psi_s^{>}(\mathbf{x}_{>})\psi_s^{<}(\mathbf{x}_{<}), \quad (3.13)$$

where $|\mathbf{x}_{>}|$ is the larger of $|\mathbf{x}|$ and $|\mathbf{x}'|$ and $\psi^{>},\psi^{<}$

satisfy the appropriate boundary conditions for large and small $|\mathbf{x}|$, respectively. The difference between using Eqs. (3.12) and (3.13) was discussed by one of us recently in some detail in connection with the problem of the coil-globule transition.[14] Use of Eq. (3.13) instead of Eq. (3.12) and the assumption about the ground-state dominance in Eq. (3.11) shall be referred to as the modified L-Z method. Substitution of Eq. (3.13) into Eq. (3.11) produces

$$i\phi(\mathbf{x})=\int d\mathbf{y}\, W(\mathbf{x}-\mathbf{y})G(\mathbf{y},\mathbf{y},s\mid\phi) \tag{3.14}$$

for $0<|\mathbf{x}|<|\mathbf{R}|$.

Substitution of Eq. (3.14) back into Eq. (3.5) yields the result which (after the inverse Laplace transformation is performed) coincides with the first-order renormalized perturbation-theory result obtain by approximating the mass operator M in Dyson's equation

$$\left[\frac{\partial}{\partial N}-\frac{1}{2}\nabla^2\right]G(\mathbf{R},N)$$
$$=\delta(\mathbf{R})\delta(N)+\int_0^N d\tau\int d\mathbf{r}\, M(\mathbf{R},\mathbf{r};N-\tau)G(\mathbf{r},\tau)\ , \tag{3.15}$$

by its first-order "renormalized" perturbation correction.[14] By solving Eq. (3.15) iteratively we recover the usual perturbation expansion discussed in great detail in Kholodenko and Freed.[15] Because our goal is to find some kind of nonperturbative solution to Eq. (3.15), we cannot use an iterative method and have to rely upon other available methods.

IV. SOLUTIONS OF THE SELF-CONSISTENT-FIELD EQUATIONS

A. The WKB solutions

The distribution function satisfying the Laplace-transformed version of Eq. (3.15) contains more information than we might actually need. Indeed, if we are interested in computation of the free energy[14] or the moments of the distribution function,[7] then additional simplifications are possible. In fact, consider the following quantity,

$$\int d\mathbf{x}\int d\mathbf{x}'\, G(\mathbf{x},\mathbf{x}',s\mid\phi)\ , \tag{4.1}$$

which is related to the computation of the free energy.[14] In three dimensions, for example, we can expand the distribution function in terms of spherical harmonics $Y_{lm}(\boldsymbol{\Omega})$. This then produces

$$\begin{aligned}\int d\mathbf{x}\int d\mathbf{x}'\, G(\mathbf{x},\mathbf{x}',s\mid\phi)\\ &=\int dx\, x^2\int d\boldsymbol{\Omega}\int dx'\, x'^2\int d\boldsymbol{\Omega}'\sum_{(l,m);(l',m')}G_{lml'm'}(x,x's\mid\phi)Y_{lm}(\boldsymbol{\Omega})Y_{l'm'}(\boldsymbol{\Omega}')\\ &=4\pi\int dx\, x^2\int dx'x'^2G_{0000}(x,x',s\mid\phi)\ .\end{aligned} \tag{4.2}$$

Evidently the same kind of arguments can be repeated for the computation of moments of the distribution function, etc.

By assuming spherical symmetry, Eqs. (3.4) and (3.14) can be rewritten as

$$\left[\frac{1}{2x}\frac{d^2}{dx^2}x-\left[\int d\mathbf{y}\, W(|\mathbf{x}-\mathbf{y}|)G(\mathbf{y},\mathbf{y},s)\right]_\sigma-s\right]G(x,x',s)=-\delta(x-x')\ , \tag{4.3}$$

where the explicit ϕ dependence was omitted. The subscript σ indicates that only the contributions from the spherically symmetric part of the integrand are retained. The Green's-function representation [see Eq. (3.13)] now produces

$$G(x,x',s)=\begin{cases}\phi_s^{(1)}(x)\phi_s^{(2)}(x'), & x\geqq x'\\ \phi_s^{(1)}(x')\phi_s^{(2)}(x), & x\leqq x'\end{cases} \tag{4.4}$$

where $\phi_s^{(1)}(x)$ and $\phi_s^{(2)}(x)$ are two independent solutions of Eq. (4.3). By introducing $\chi_s^{(1)}(x)$ and $\chi_s^{(2)}(x)$ via $\phi_s^{(1),(2)}=\chi_s^{(1),(2)}/x$, Eq. (4.3) can be rewritten in the following manner:

$$\left[\frac{1}{2}\frac{d^2}{dx^2}-\left[\int d\mathbf{y}\, W(|\mathbf{x}-\mathbf{y}|)\times G(\mathbf{y},\mathbf{y},s)\right]_\sigma-s\right]\chi_s^{(1),(2)}(x)=0\ . \tag{4.5}$$

If we let $\widetilde{G}(x,x',s)=\chi_s^{(1)}(x)\chi_s^{(2)}(x')$, then it follows that $\widetilde{G}$ obeys the following relation for $\epsilon\rightarrow 0^+$:

$$\frac{d}{dx}\widetilde{G}(x,x',s)\big|_{x=x'+\epsilon}-\frac{d}{dx}\widetilde{G}(x,x',s)\big|_{x=x'-\epsilon}=-2\ . \tag{4.6}$$

In order for the free energy to exist, the integral (4.1) must be convergent. This means that the functions, $\chi_s^{(1)}$ or $\chi_s^{(2)}$, should obey such boundary conditions for $x\rightarrow\infty$ and $x\rightarrow 0$, respectively, that integral (4.1) is convergent. Given this requirement, we want to find a solution for Eq. (4.5) in a region not too close to the origin and which has the proper asymptotic behavior as $x\rightarrow\infty$. For this purpose we can use a WKB method in which we define $f(x,s)$ as

$$f^2(x,s)=2s+2\left[\int d\mathbf{y}\, W(|\mathbf{x}-\mathbf{y}|)G(\mathbf{y},\mathbf{y},s)\right]_\sigma\ . \tag{4.7}$$

Equation (4.5) now assumes the form

$$\left[\frac{d^2}{dx^2}-f^2(x,s)\right]\chi_s^{(1),(2)}(x)=0\ , \tag{4.5'}$$

which admits the well-known WKB solutions

$$\chi_s^{(1),(2)}(x) =[f(x,s)]^{-1/2}C_{1,2}\exp\left[\mp\int^x dy\, f(y,s)\right]\ , \tag{4.8}$$

where C_i, $i=1,2$, are determined from the condition (4.6). This gives the following representation for $\widetilde{G}$:

$$\widetilde{G}(x,x',s)=\begin{cases}2[f(x,s)f(x',s)]^{-1/2}\exp\left[-\int^x dy\, f(y,s)\right]\sinh\left[\int^{x'} dy\, f(y,s)\right], & x\geqq x'\\ 2[f(x,s)f(x',s)]^{-1/2}\sinh\left[\int^x dy\, f(y,s)\right]\exp\left[-\int^{x'} dy\, f(y,s)\right], & x\leqq x'\ .\end{cases} \tag{4.9a}$$

For large x and x' expression (4.9a) can be simplified to

$$\widetilde{G}(x,x',s)\cong\begin{cases}[f(x,s)f(x',s)]^{-1/2}\exp\left[\int_x^{x'} dy\, f(y,s)\right], & x\geqq x'\\ [f(x,s)f(x',s)]^{-1/2}\exp\left[-\int_x^{x'} dy\, f(y,s)\right], & x'\geqq x\ .\end{cases} \tag{4.9b}$$

In the region where Eq. (4.9b) is valid we can write the self-consistency condition as

$$\widetilde{G}(x,x,s)=f^{-1}=2^{-1/2}\left[s+\left[\int dx\; W(\,|\mathbf{x}-\mathbf{y}|\,)G(\mathbf{x},\mathbf{x},s)\right]_\sigma\right]^{-1/2}\ . \tag{4.10a}$$

Equation (4.10a) can be solved iteratively for the case of small s (i.e., large N), yielding for the first iterate the result

$$\widetilde{G}(x,x,s)\cong\{2s+[\widetilde{G}(x,x)]^{-2}\}^{-1/2}\ , \tag{4.10b}$$

where $\widetilde{G}(x,x)=\widetilde{G}(x,x,0)$ is the solution to Eq. (4.10a) for $s=0$. This solution may be used to construct the Green's function of Eq. (4.9b). In order to illustrate these ideas, it is instructive to consider several examples.

B. The standard excluded-volume problem

For the excluded-volume problem $W(\mathbf{x}-\mathbf{y})$ is given by[9,14]

$$W(\mathbf{x}-\mathbf{y})=b\delta(\mathbf{x}-\mathbf{y})\ . \tag{4.11}$$

By substitution of Eq. (4.11) into (4.10), the following self-consistency equation is obtained:

$$\frac{1}{[\widetilde{G}(x,x,s)]^2}=2s+\frac{2b}{x^2}\widetilde{G}(x,x,s)\ . \tag{4.12}$$

Equation (4.12) is easily solved for $s=0$, yielding

$$\widetilde{G}(x,x)=\widetilde{G}(x,x,0)=\left[\frac{1}{2b}\right]^{1/3}x^{2/3}\ , \tag{4.13}$$

which may be combined with Eqs. (4.9b) and (4.10b) to obtain an expression for $\widetilde{G}(x,x',s)$. Once this expression is known, the inverse Laplace transform of $\widetilde{G}(x,x',s)$ can, in principle, be performed. The procedure for the inverse Laplace transformation is presented in the Appendix. The computed $\widetilde{G}(x,x',N)$ contains more information than is actually needed. We recall the potential $\phi(\mathbf{x})$ used to calculate $\widetilde{G}$ is selected by a stationarity condition (3.9) which involves $G(\mathbf{R},N\,|\,\phi)$ of Eq. (3.3), whose path integral contains the boundary condition that one of the terminal ends of the chain is at the origin of the coordinate system. Thus to calculate the mean-square end-to-end distance $\langle R^2\rangle$, we may put x' in $\widetilde{G}(x,x',N)$ at the origin, thus producing a result for $\widetilde{G}$ which coincides with that of the field-theoretic mean-field treatment. We can then write the expression for $\langle R^2\rangle$ as

$$\langle R^2\rangle=\lim_{\epsilon\to 0}\frac{\int_0^\infty dx\, x^3[\gamma(x)]^{-1/2}\exp[-F(x)]}{\int_0^\infty dx\, x[\gamma(x)]^{-1/2}\exp[-F(x)]}\ , \tag{4.14}$$

where $\gamma(x)=\gamma(x,x'=\epsilon)$ with $\gamma(x,x')$ being given by Eq. (A13) of the Appendix, and $F(x)=F(x,0)$ with $F(x,x')$ being given by (A14). The above limit is taken after the indicated integrations are carried out, because $\gamma(x)$ contains self-interaction divergences at the origin (see the Appendix), which, as we will see, cancel for the ratio of integrals on the right-hand side of the Eq. (4.14) with small but finite ϵ. Self-interaction does not result in divergences at $x'=0$ for $F(x,x')$ (see the Appendix). It is convenient to introduce the dimensionless variables χ and τ instead of x and t in Eqs. (4.14) and (A12) to (A14).[16] Taking into account Eq. (4.13), we choose these variables in such a way that the combination $h(t)N^2/(\Delta x)^2$ in Eq. (A14) remains dimensionless. If one writes $x=c\chi$ and $t=c\tau$, then according to Eqs. (A13), (A6), and (A14), we obtain

$$\frac{h(t)N^2}{(\Delta x)^2}=\frac{N^2b^{2/3}}{c^{10/3}(\Delta\chi)^2}\left[\left[\frac{\sqrt{2}}{\tau}\right]^{4/3}-\left[\frac{\sqrt{2}}{\chi}\right]^{4/3}\right]\ .$$

It is natural to choose $c^{10/3}=N^2b^{2/3}$. Making this choice in Eq. (4.14), we obtain the final result

$$\langle R^2\rangle = b^{2/5}N^{6/5}\lim_{\epsilon\to 0}\frac{\int_0^\infty d\chi\,\chi^3[\bar\gamma(\chi)]^{-1/2}\exp[-N^{1/5}b^{2/5}\bar F(\chi)]}{\int_0^\infty d\chi\,\chi[\bar\gamma(\chi)]^{-1/2}\exp[-N^{1/5}b^{2/5}\bar F(\chi)]}\ . \tag{4.15}$$

The dimensionless functions $\bar\gamma(\chi)$ and $\bar F(\chi)$ are obtained from Eqs. (A13) and (A14) for $\gamma(x)$ and $F(x)$, respectively, by replacing (x,t) with (χ,τ) and the parameters b and N with unity. With appropriate changes in potentials, Eq. (4.15) is also applicable to electrolytes as is explained in the next subsection.

In the Appendix we note that the properties of $\bar F(\chi)$ imply it has a minimum in the domain of integration indicated in Eq. (4.15). We have found the minimum to be at $\chi=0.9819$ by a combination of numerical integration and interval halving to locate the real root of $d\bar F(\chi)/d\chi=0$. Thus in the limit $N\to\infty$, we can use a saddle-point method to calculate the above integrals. This then leaves the leading term proportional to $N^{6/5}$, which is the Flory result.[2,17]

C. Excluded volume (electrostatic)

We now wish to apply the manifestly self-consistent method to electrostatic interactions. Successful application to the general case, which includes both electrostatic and conventional excluded-volume interactions, could then be treated perturbatively by assuming that the conventional excluded volume is small compared to its electrostatic counterpart. The self-consistent equation in the form of Eq. (3.15) corresponds to a Hartree approximation of many-body theory.[18] In the theory of the large polaron it is known as Luttinger-Pekar equation and one of us provided its derivation directly using the Feynman path-integral methods.[19] Using the explicit form of the potential W given in Eq. (2.2), Eq. (4.5) can be written as

$$\left[\frac{1}{2}\frac{d^2}{dx^2}-Z^2\lambda_B\left[\int d\mathbf{y}\,G(\mathbf{y},\mathbf{y},s)\frac{\exp(-\kappa|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|}\right]_\sigma - s\right]\chi_s^{(1),(2)}=0\ . \tag{4.16}$$

In order to evaluate the integral of the above equation, we use the well-known multipole expansion[20]

$$\frac{\exp(ik|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|}=4\pi ik\sum_{l=0}^{\infty}\sum_{m=-l}^{l}Y^*_{lm}(\Omega_x)Y_{lm}(\Omega_y)\times\begin{cases}j_l(kx)h_l(ky), & y>x\\ j_l(ky)h_l(kx), & x>y\ .\end{cases} \tag{4.17a}$$

Only the spherically symmetric term needs to be retained which for $\kappa=-ik$ is given by the following equation:

$$\frac{\exp(-\kappa|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|}=\kappa\begin{cases}\dfrac{\sinh(\kappa x)}{\kappa x}\dfrac{\exp(-\kappa y)}{\kappa y}, & y>x\\[2ex] \dfrac{\sinh(\kappa y)}{\kappa y}\dfrac{\exp(-\kappa x)}{\kappa x}, & x>y\ .\end{cases} \tag{4.17b}$$

Substitution of this result into Eq. (4.27) yields

$$\left[s-\frac{1}{2}\frac{d^2}{dx^2}+\frac{4\pi Z^2\lambda_B}{\kappa}\left[\int_0^x dy\,\widetilde G(y,y,s)\frac{\sinh(\kappa y)}{y}\frac{\exp(-\kappa x)}{x}+\int_x^\infty dy\widetilde G(y,y,s)\frac{\exp(-\kappa y)}{y}\frac{\sinh(\kappa x)}{x}\right]\right]\chi_s^{(1),(2)}=0\ . \tag{4.18}$$

The general WKB method can now be used and the self-consistency equation (4.10a) produces the following result,

$$U=2sx+\frac{a^3}{\kappa}[S(x)\exp(-\kappa x)+E(x)\sinh(\kappa x)]\ , \tag{4.19}$$

where $a^3=8\pi Z^2\lambda_B$,[21]

$$U=\frac{x}{[\widetilde G(x,x,s)]^2}\ , \tag{4.20}$$

and $S(x)$ and $E(x)$ are the integral expressions

$$S(x)=\int_0^x dy\,\widetilde G(y,y,s)\frac{\sinh(\kappa y)}{y}\ , \tag{4.21}$$

$$E(x)=\int_x^\infty dy\,\widetilde G(y,y,s)\frac{\exp(-\kappa y)}{y}\ . \tag{4.22}$$

Differentiation of Eq. (4.19) along with the definitions given by Eqs. (4.20), (4.21), and (4.22) yields the following differential equation:

$$\frac{d^2U}{dx^2}-\kappa^2(U-2sx)=-\frac{a^3}{\sqrt{xU}}\ . \tag{4.23}$$

Consider first the limit $\kappa\to\infty$ (complete screening), in which case Eq. (4.23) gives the following simple result:

$$U=2sx\ . \tag{4.24}$$

Using the definition of U given in Eq. (4.20), we obtain $\widetilde G(x,x,s)=\sqrt{2s}$. Using Eq. (4.9a) we obtain the following result for the free propagator:

$$\widetilde G(x,x',s)=\begin{cases}\dfrac{2}{\sqrt{2s}}\exp(-x\sqrt{2s}\,)\sinh(x'\sqrt{2s}\,), & x\geq x'\\[2ex] \dfrac{2}{\sqrt{2s}}\sinh(x\sqrt{2s}\,)\exp(-x'\sqrt{2s}\,), & x\leq x'\ .\end{cases} \tag{4.25}$$

The above describes a Gaussian chain for which $\langle R^2\rangle\propto N$, as is expected for complete screening.

For $\kappa<\infty$ the preferred approach is to look for solutions to Eq. (4.23) and thereby take advantage of the many techniques for solving differential equations and obtaining systematic approximations to their solution. The $s=0$ solutions should conform to the boundary conditions

$$\lim_{x\to\infty}\left[\frac{dU}{dx}+\kappa U\right]=0\ , \tag{4.26}$$

$$\lim_{x\to 0}\left[\left[\frac{dU}{dx}+\kappa U\right]\Big/ a^3\int_x^\infty dy\frac{\exp(-\kappa y)}{\sqrt{yU}}\right]=1\ , \tag{4.27}$$

which are derived from the $s=0$ self-consistency condition [Eq. (4.19)] taking into account the limits of integration, 0 and ∞, in the integral expressions [Eqs. (4.21) and (4.22)] for $S(x)$ and $E(x)$, respectively.

In this work it is our purpose to apply this procedure to the unscreened case ($\kappa=0$), which will also serve to illustrate the technique for intermediate κ ($0<\kappa<\infty$). In order to obtain $\widetilde{G}(x,x',N)$ for $\kappa=0$, we need to solve Eq. (4.23) for $s=0$ in which case it reduces to

$$\frac{d^2U}{dx^2}=-\frac{a^3}{\sqrt{xU}}\ . \tag{4.28}$$

According to Kamke[22] the solutions to this equation are best studied after making the transformations $\rho=-\ln(\beta x)$ and $U=x\Phi(\rho)$ to yield

$$\frac{d^2\Phi}{d\rho^2}-\frac{d\Phi}{d\rho}=-\frac{a^3}{\sqrt{\Phi}}\ . \tag{4.29}$$

The constant β is introduced as an arbitrary scaling factor to render the logarithmic argument dimensionless and it will be determined by the boundary conditions on the solution to Eq. (4.29).

We use a perturbation procedure to obtain the systematic approximations to Φ by treating the $\sqrt{\Phi}(d^2\Phi/d\rho^2)$ term as a perturbation in the following form of Eq. (4.29):

$$\lambda\sqrt{\Phi}\frac{d^2\Phi}{d\rho^2}-\frac{2}{3}\frac{d\Phi^{3/2}}{d\rho}=-a^3\ , \tag{4.30}$$

where λ ($=1$) is the parameter used for convenience in keeping track of the various orders of the perturbation. The zeroth-order solution is clearly $(\frac{3}{2}a^3\rho)^{2/3}$ with higher-order terms being obtained by iterating the recursion formula

$$\frac{d\theta_{n+1}}{d\rho}=\tfrac{3}{2}S_n[\theta_n]\ , \tag{4.31}$$

where θ_n are defined by

$$\Phi^{3/2}=\tfrac{3}{2}a^3\rho+\sum_{n=1}^{\infty}\theta_n\lambda^n\ , \tag{4.32}$$

and $S_n[\theta_n]$ are the coefficients of a power-series expansion in λ of $\sqrt{\Phi}(d^2\Phi/d\rho^2)$ as is indicated by the equation

$$\sqrt{\Phi}\frac{d^2\Phi}{d\rho^2}=\frac{2}{3}\sum_{k=1}^{\infty}\lambda^k\frac{d^2\theta_k}{d\rho^2}-\frac{\frac{2}{9}\left[\sum_{k=1}^{\infty}\frac{d\theta_k}{d\rho}\lambda^k+\frac{3}{2}a^3\right]^2}{\frac{3}{2}a^3\rho+\sum_{k=1}^{\infty}\theta_k\lambda^k}$$

$$=\sum_{n=0}^{\infty}S_n[\theta_n]\lambda^n\ . \tag{4.33}$$

It is clear from the above equation that $S_n[\theta_n]$ is calculable from a knowledge of θ_k for $k\leq n$ and that $S_0=-\frac{1}{3}(a^3/\rho)$. It is also relatively easy to obtain θ_1 and θ_2 by iterating Eq. (4.31),

$$\theta_1=-\tfrac{1}{2}a^3\ln\rho\ , \tag{4.34}$$

$$\theta_2=\frac{a^3}{6\rho}(\ln\rho-4)\ . \tag{4.35}$$

The above suggests that θ_n is of $(n-1)$th order in $1/\rho$. One can see by examination of Eq. (4.33) that this implies that $S_n[\theta_n]$ is $(n+1)$th order in $1/\rho$. Thus iteration of Eq. (4.31) proves inductively that θ_{n+1} is nth order in $1/\rho$. The parameter a^3 appears as a multiplicative factor in each term of the perturbation expansion. For large n the dominant contribution to $S_n[\theta_n]$ is $d^2\theta_n/d\rho^2$. This implies that the general term in the perturbation series, Eq. (4.32), progresses as $(n-1)/\rho^{(n-1)}$ for large n and the series converges for $1/\rho<1$.

One finds that the application of boundary condition (4.26) for $\kappa\to 0$ yields a scaling constant β that approaches zero. This difficulty occurs because the integral for $E(x)$ in the original self-consistency condition has an upper-limit divergence. This divergence is an intrinsic difficulty of the unscreened electrolyte problem, which one could have predicted by examining results of the homopolymer case. The analysis of the latter case shows that $\widetilde{G}(x,x)\propto x^{\alpha}$ implies that $\nu=1/(1+\alpha)$. Since Monte Carlo calculations[5] have demonstrated that $\nu=1$ for unscreened electrolytes, one sees that extrapolation of the above result to the unscreened electrolyte limit yields $\alpha=0$ or $\widetilde{G}(x,x)=\text{const}$, which implies divergence of the integral $E(x)$. The reason for the difficulty is that the restriction of a finite contour length for nonzero s (finite N) is not contained in the equations. Such a restriction is not required for $\nu<1$, because the monomer density rapidly falls off to zero as distances x approach the size of the contour length. The finite-contour-length restriction disappears for the unscreened electrolyte when $s=0$ or $N\to\infty$, indicating that our equations produce only an asymptotic result in the limit of large N. In order to obtain this asymptotic result, we introduce an upper cutoff L, which we take to infinity with N at the end of our calculations. This procedure is meaningful if our final quantities of interest, namely $\langle R^2\rangle$, are independent of L.

We will rewrite the boundary conditions [Eqs. (4.26) and (4.27)] in terms of Φ and ρ for the unscreened case,

$$\lim_{x\to 0}\left[\left[\Phi-\frac{d\Phi}{d\rho}\right]\Big/\int_x^L\frac{dy}{y\sqrt{\Phi}}\right]=1\ , \tag{4.36}$$

$$\lim_{x\to L}\left[\Phi-\frac{d\Phi}{d\rho}\right]=0\ , \tag{4.37}$$

where the cutoff L has been introduced. Since the zeroth-order contribution to $\Phi=(\frac{3}{2}a^3\rho)^{2/3}$ dominates higher-order contributions as $x\to 0$, the boundary condition (4.36) reduces to

$$\lim_{\rho\to\infty}\frac{\rho^{2/3}-(\frac{2}{3})\rho^{-1/3}}{\rho^{2/3}-(\rho\,|_{x=L})^{2/3}}\to 1\ , \tag{4.38}$$

thus demonstrating that condition (4.36) is always satisfied. In applying the second boundary condition (4.37), we notice from Eqs. (4.32), (4.34), and (4.35) that the parameter a^2 appears in Φ only as a multiplicative factor. Thus when solving this boundary condition for ρ at $x=L$, the effect of a^2 cancels and one obtains for ρ a pure number which we express as $-\ln\xi$.[23] Using the definition of ρ, following Eq. (4.28), this demonstrates that β is inversely proportional to the cutoff L according to the relation

$$\beta=\frac{\xi}{L}\ . \tag{4.39}$$

We now write the result for Φ to within two orders of the perturbation expansion,

$$\Phi=(\tfrac{3}{2}a^3\rho)^{2/3}\left[1-\frac{2\ln\rho}{\rho}+\frac{2}{27\rho^2}\left[\ln\rho-\frac{(\ln\rho)^2}{6}-4\right]+\cdots\right]. \tag{4.40}$$

By noting that nth-order perturbative contributions to Φ are also of nth order in $1/\rho$, we see that the rapid convergence of the perturbation series is obtained for large ρ (or x small relative to the cutoff L): At the end of these calculations we will see that only small values of x relative to L contribute to $\langle R^2\rangle$ at high temperatures where a^3 [proportional to Bjerrum length of Eq. (2.4)] is sufficiently small. In this connection it is worthwhile to note that Baumgärtner's Monte Carlo calculations were performed for relatively high temperatures where the Bjerrum length was $\frac{1}{10}$ the segment length.[5]

In this work we will consider the high-temperature limiting case where we need only to consider the zeroth-order term of Eq. (4.40). By combining Eqs. (4.20) with the definition of Φ following Eqs. (4.28) and (4.29), we obtain

$$\frac{1}{[\widetilde{G}(x,x)]^2}=(\tfrac{3}{2}a^3\rho)^{2/3}=[-\tfrac{3}{2}a^3\ln(\beta x)]^{2/3}\ . \tag{4.41}$$

Using Eq. (A7) for $h(t)$ we can write the dimensionless ratio in Eqs. (A13) and (A14), $h(t)N^2/(\Delta x)^2$, in terms of dimensionless variables,

$$\frac{h(t)N^2}{(\Delta x)^2}=\frac{N^2a^2}{c^2(\Delta\chi)^2}\{[-\tfrac{3}{2}\ln(c\beta\tau)]^{2/3}-[-\tfrac{3}{2}\ln(c\beta\chi)]^{2/3}\}\ . \tag{4.42}$$

In order to evaluate c, we use an iterative procedure in which, at the beginning, we neglect the c dependence of the logarithmic factors which produces $c=c'Na$, where it is assumed that c' is a weak function of the parameter a. Using this expression for c and noting that $-\ln a\rightarrow\infty$ as $T\rightarrow\infty$, we expand the logarithmic portion of Eq. (4.42) in powers of $(-\ln a)^{-1}$,

$$\frac{N^2a^2}{c^2(\Delta\chi)^2}\left\{\left[-\tfrac{3}{2}\ln\left[\frac{Nac'\xi\tau}{L}\right]\right]^{2/3}-\left[-\tfrac{3}{2}\ln\left[\frac{Nac'\xi\chi}{L}\right]\right]^{2/3}\right\}=\frac{N^2a^2}{c^2(\Delta\chi)^2}\frac{\left[-\ln\left[\dfrac{\tau}{x}\right]\right]}{(-\tfrac{3}{2}\ln a)^{1/3}}[1+O((-\ln a)^{-1})]\ , \tag{4.43}$$

where Eq. (4.39) for β has been used and c' is a sufficiently weak function of the parameter a. We note that the cutoff (L) dependence has completely disappeared in the leading term in Eq. (4.43). According to Eq. (4.43) we obtain in this approximation the following expression for c:

$$c=\frac{Na}{(-\tfrac{3}{2}\ln a)^{1/6}}\ . \tag{4.44}$$

Since we put $L_t=1$ at the beginning, we recall that $\ln a$ should be understood to be $\ln(a/L_t^{1/3})$. Equation (4.44) shows that $c'=(-\tfrac{3}{2}\ln a)^{-1/6}$, verifying the weak dependence on the parameter a that is assumed for c' in the above iterative process.

We would now like to eliminate the remaining cutoff dependence in the expression for $\widetilde{G}(x,x',N)$ contributed by the term $\tfrac{1}{2}N[\widetilde{G}(x,x)]^{-2}$ [see Eqs. (A12) and (A14)]. To accomplish this, $\tfrac{1}{2}N[\widetilde{G}(x,x)]^{-2}$ is expanded in a fashion similar to Eq. (4.43),

$$\begin{aligned}\frac{N}{2}[\widetilde{G}(x,x)]^{-2}&=\frac{N}{2}[-\tfrac{3}{2}a^3\ln(\beta x)]^{2/3}\\&=-\frac{Na^2}{2(-\tfrac{3}{2}\ln a)^{1/3}}\left[\ln\chi+\ln\left[\frac{c'N\xi a^{3/2}}{L}\right]\right]\\&\quad\times[1+O((-\ln a)^{-1})]\ .\end{aligned} \tag{4.45}$$

The cutoff-dependent term

$$\tfrac{1}{2}Na^2\ln(c'N\xi a^{3/2}/L)/(-\tfrac{3}{2}\ln a)^{1/3}$$

in the above equation only contributes an x-independent prefactor to $\widetilde{G}(x,x',N)$ [see Eqs. (A12) and (A14)], which cancels in the calculation of $\langle R^2\rangle$ according to Eq. (4.14). Consequently, the arbitrariness of the cutoff completely disappears from our predicted $\langle R^2\rangle$ in the high-temperature limit where terms of order $(-\ln a)^{-1}$ are neglected.[24] Thus in the high-temperature large-N limit we have by saddle-point evaluation of the integrals in Eq. (4.15),

$$\langle R^2\rangle^{1/2}\propto aN\ . \tag{4.46}$$

The saddle point was found to be at $\chi=0.5835$ by the same numerical methods as were used for the standard excluded-volume case. The factor a is included in the above proportionality because it provides the dominant portion of the predicted temperature dependence. The prediction that $\langle R^2\rangle$ is proportional to N agrees with results of Flory-type theories and Baumgärtner's Monte Carlo results;[5] the latter, as we have already noted, also being obtained at relatively high temperatures.

V. DISCUSSION

In the preceding sections we have developed a nonperturbative method for obtaining the $\langle R^2 \rangle$, which is applicable to polyelectrolytes. In order to illustrate the method it was applied to the homopolymer and the unscreened polyelectrolyte chain yielding results in agreement with Flory's predictions[17] for the homopolymer case and results of Monte Carlo calculations[5] for unscreened polyelectrolytes.

Our treatment of the unscreened polyelectrolytes required the introduction of a cutoff which we eliminated from our results for $\langle R^2 \rangle$ in the high-temperature large-N limit. Corrections for lower temperatures and finite N could not be made without developing a procedure for systematic elimination of the cutoff dependence from the higher-order terms. We do not develop this question in the present paper. The cutoff problem does not occur for an intermediate screening ($0<\kappa<\infty$) where it is expected that $\nu<1$ and the methods described herein can be applied, as was demonstrated, without the introduction of cutoffs. Consequently, the detailed calculations describing the crossover between the excluded-volume ($\nu=\frac{3}{5}$) and rigid-rod ($\nu=1$) regimes are, in principle, possible and we hope to follow up this work with such calculations in the future.

We want to note that the problem of the large polaron[19] is, from a mathematical standpoint, surprisingly similar to the polyelectrolyte problem. Because the former problem for a reasonably large coupling constant does not permit the perturbative treatment, the same must be true for the polyelectrolyte chain. At the same time the variational approach used for the polaron would be hardly applicable to our case, especially when the finite concentration effects and other effects are considered. Moreover, unlike the polyelectrolytes in the regime of small screening, the predictions of the large-polaron theory were tested experimentally. These tests give additional support in favor of the nonperturbative treatments for the polyelectrolyte chain.

APPENDIX: THE LAPLACE INVERSION OF $\tilde{G}(x,x',s)$

In this portion of the Appendix we derive an expression for $\tilde{G}(x,x',N)$ based on the following iterative expression for $\tilde{G}(x,x',s)$ [see Eqs. (4.9b) and (4.10b)]:

$$\tilde{G}(x,x',s)=\frac{1}{(\{2s+[\tilde{G}(x,x)]^{-2}\}\{2s+[\tilde{G}(x',x')]^{-2}\})^{1/4}}\exp\left[-\int_{x'}^{x}dt\{2s+[\tilde{G}(t,t)]^{-2}\}^{1/2}\right]. \tag{A1}$$

for the case where $0<x'<x$. We begin by rewriting $\tilde{G}(x,x',s)$ in the following form:

$$\tilde{G}(x,x',s)=\tilde{G}^{0}(x,x',s)\Gamma(x,x',s)\ , \tag{A2}$$

$$\tilde{G}^{0}(x,x',s)=\frac{1}{\{2s+[\tilde{G}(x,x)]^{-2}\}^{1/2}}\exp(-\Delta x\{2s+[\tilde{G}(x,x)]^{-2}\}^{1/2})\ , \tag{A3}$$

$$\Gamma(x,x',s)=\frac{1}{\left[1+\dfrac{h(x')}{2s+[\tilde{G}(x,x)]^{-2}}\right]^{1/4}}\exp\left\{-\{2s+[\tilde{G}(x,x)]^{-2}\}^{1/2}\int_{x'}^{x}\left[\left[1+\frac{h(t)}{2s+[\tilde{G}(x,x)]^{-2}}\right]^{1/2}-1\right]dt\right\}, \tag{A4}$$

$$\Delta x=x-x'\ , \tag{A5}$$

$$h(t)=[\tilde{G}(t,t)]^{-2}-[\tilde{G}(x,x)]^{-2}\ . \tag{A6}$$

The above decomposition of $\tilde{G}(x,x',s)$ is done so that $h(t)$ and $h(x')$ are positive within the range of argument changes.

The function $\Gamma(x,x',s)$ can be expanded in the power series

$$\Gamma(x,x',s)=\sum_{n=1}^{\infty}\frac{A_n(x,x')}{\{2s+[\tilde{G}(x,x)]^{-2}\}^{n/2}}\ , \tag{A7}$$

which converges for sufficiently small $h(x')$ and $h(t)$. The product of $\tilde{G}^{0}(x,x',s)$ and the series expansion for $\Gamma(x,x',s)$ yields a general term whose Laplace inversion can be brought into convenient form[25] by the substitution $2s'=2s+\tilde{G}(x,x)^{-2}$,

$$\begin{aligned}\frac{A_n}{2\pi i}&\oint\{2s+[\tilde{G}(x,x)]^{-2}\}^{-(n+1)/2}\exp(-\Delta x\{2s+[\tilde{G}(x,x)]^{-2}\}^{1/2})\exp(sN)ds\\&=A_n(2)^{-(n+1)/2}\exp\left[-\frac{N}{2[\tilde{G}(x,x)]^2}\right]\frac{1}{2\pi i}\oint(s')^{-(n+1)/2}\exp[-\sqrt{s}\,(\sqrt{2}\,\Delta x)]\exp(s'N)ds'\\&=\tfrac{1}{2}A_n(2N)^{(n-1)/2}\exp\left[-\frac{N}{2[\tilde{G}(x,x)]^2}\right]I^{n-1}\mathrm{erfc}\left[\frac{\Delta x}{\sqrt{2N}}\right]\end{aligned} \tag{A8}$$

where $\mathrm{erfc}(z)$ is the integral $(2/\sqrt{\pi})\int_z^{\infty}\exp(-t^2)dt$ and I^n represents the integral operator which is defined by the recursion relation[25]

$$I^n\text{erfc}(z)=\int_z^{\infty} I^{n-1}\text{erfc}(t)dt \;. \tag{A9}$$

Since the methods herein described will be applied to cases where x and Δx are of the order N^{ν} with $\nu>\frac{1}{2}$, the argument of erfc, i.e., $\Delta x/\sqrt{2N}$, is very large, being of the order $N^{\nu-1/2}$ as $N\rightarrow\infty$. Therefore we only need to keep the dominant term of an asymptotic expansion of $I^n\text{erfc}(\Delta x/\sqrt{2N}\,)$, as indicated by the following relation:

$$I^{n-1}\text{erfc}\left[\frac{\Delta x}{\sqrt{2N}}\right]\cong\frac{2}{\sqrt{\pi}}\left[\frac{\sqrt{2N}}{2\Delta x}\right]^n\exp\left[-\frac{(\Delta x)^2}{2N}\right] . \tag{A10}$$

By substituting this asymptotic relation into Eq. (A8), we obtain

$$\mathcal{L}^{-1}\left[\frac{A_n}{\{2s+[\tilde{G}(x,x')]^{-2}\}^{n/2}}\tilde{G}^{\,0}(x,x',s)\right]=A_n\left[\frac{N}{\Delta x}\right]^n\frac{1}{(2\pi N)^{1/2}}\exp\left[-\frac{(\Delta x)^2}{2N}\right]\exp\left[-\frac{N}{2[\tilde{G}(x,x)]^2}\right] . \tag{A11}$$

Thus we see that within the framework of Eq. (A11), Laplace inversion ($\mathcal{L}^{-1}$) is accomplished by replacement of $\tilde{G}^{\,0}(x,x',s)$ with

$$\exp\left[-\frac{(\Delta x)^2}{2N}\right]\exp\left[-\frac{N}{2[\tilde{G}(x,x)]^2}\right]\Big/\sqrt{2\pi N}$$

and $\{2s+[\tilde{G}(x,x)]^{-2}\}^{-n/2}$ with $(N/\Delta x)^n$. Making the latter substitution in the series expansion for $\Gamma(x,x',s)$ [see Eq. (A7)] permits us to find a sum of the infinite series in a closed form so that we obtain for $\tilde{G}(x,x',N)$,

$$\tilde{G}(x,x',N)\cong\frac{1}{[2\pi N\gamma(x,x')]^{1/2}}\exp[-F(x,x')] \;, \tag{A12}$$

where

$$\gamma(x,x')=\left[1+\frac{h(x')N^2}{(\Delta x)^2}\right]^{1/2} , \tag{A13}$$

and

$$F(x,x')=\frac{(\Delta x)^2}{2N}+\frac{N}{2[\tilde{G}(x,x)]^2}+\frac{\Delta x}{N}\int_{x'}^{x}\left[\left[1+\frac{h(t)N^2}{(\Delta x)^2}\right]^{1/2}-1\right]dt \;. \tag{A14}$$

Since we are able to collapse the series expansion of $\Gamma(x,x',s)$ back to the analytic form after Laplace inversion, we assume analytic continuation of our final Eq. (A12) to regions of x and x' beyond the sphere of convergence of the series in Eq. (A7). Since the decomposition of $\tilde{G}(x,x',s)$ was done so that $h(t)$ is positive, and quantities taken to fractional powers in Eqs. (A12) to (A14) are real for the region $0<x'<x$, the analytic continuation of Eq. (A12) may span the same region.

We note from Eqs. (4.13) and (4.41) that $[\tilde{G}(t,t)]^{-2}$ is proportional to $t^{-4/3}$ and $[-\frac{3}{2}a^3\ln(\beta t)]^{2/3}$ for the homopolymer and polyelectrolyte problems, respectively. These singularities are contained in $h(t)$ and $\gamma(x,x')$. As a consequence, the moments of the distribution function must be evaluated using $\tilde{G}(x,\epsilon,N)$ and the limit $\epsilon\rightarrow 0$ be taken at the end of the calculations as indicated by Eq. (4.14). This limiting procedure is simplified by noting that $F(x,x')$ contains no singularity at $x'=0$. In order to see this, we note that singularities in the integrand of the integral expression of Eq. (A14) take on the form $[h(t)]^{1/2}$ for small t and finite Δx. These reduce to $t^{-2/3}$ and $[-\frac{2}{3}a^3\ln(\beta t)]^{1/3}$ for the homopolymer and polyelectrolyte, respectively, according to Eq. (A6). Since both are integrable singularities we can for these cases extend the lower limit of integration x' to 0. The remaining terms in the expression for $F(x,x')$ are nonsingular at $x'=0$.

We also observe that the integral expression contained in Eq. (A14) for $F(x,x')$ is positive because $h(t)>0$. Since the other terms are also positive and one of them, $x^2/2N$, increases without bound for large x while the other, $\frac{1}{2}N[\tilde{G}(x,x)]^{-2}$, increases without bound for small x, $F(x,0)$ clearly should have a minimum. This property of $F(x,0)$ permits the possibility of saddle-point evaluations of integrals involving $\tilde{G}(x,0,N)$.

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[21] Because of the convention we choose in Eq. (2.5), the dimensionality of a^3 is $[a^3]=L$ with L being some arbitrary length scale. But, in the normal system of units (i.e., if we keep track of factors L_t and/or L_{pe} and L_{ev} introduced in Sec. II) to make the Hamiltonian (2.1) dimensionless, we should require $[a^3]=L^{3/2}$.

[22] E. Kamke, *Differentialgleichungen Lösungsmethoden und Lösungen* (Chelsea, New York, 1948).

[23] It is possible that boundary condition (4.37) is satisfied in a domain ($\rho<1$) where the perturbation series for Φ does not converge. This would not affect our method because the only role of the perturbation series in the application of this boundary condition is to demonstrate that Φ contains a^2 only as a multiplicative factor.

[24] The cutoff L is arbitrary within the framework that it is taken to infinity as N (or L/N remains finite) when $N\rightarrow\infty$. This assures us that temperatures can be selected sufficiently high so terms of order $(-\ln a)^{-1}$ in Eq. (4.43) remain negligible as $N\rightarrow\infty$.

[25] *Handbook of Mathematical Functions,* edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1970).