Partitioning of a polymer chain between two confining cavities: The role of electrostatic interactions

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A recently developed lattice field theory approach to the statistical mechanics of charged polymers in electrolyte solutions [S. Tsonchev, R. D. Coalson, and A. Duncan, Phys. Rev. E **60**, 4257, (1999)] is generalized to the case where ground-state dominance in the polymer's Green's function does not apply. The full mean-field equations for the system are derived and are shown to possess a unique solution. The approach is applied to the problem of a charged Gaussian polymer chain confined to move within the region defined by two fused spheres. The failure of the notion of ground-state dominance under certain conditions even in the limit of large monomer number is demonstrated.

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I. INTRODUCTION

The problem of partitioning of a polymer chain between cavities of different size has been of interest for some time [1–3]. Investigations of this phenomenon are motivated by the practical importance of techniques for separation of macromolecules according to their size, such as gel electrophoresis, size exclusion chromatography, membrane separation, filtration, etc. [4]. All these methods rely on the size dependence of macromolecular mobility to migrate through a porous network of random obstacles. Such networks can be modeled as a complex system of interconnected cavities and channels available to the polymer chain. Hence, understanding how a polymer partitions itself between such cavities can lead to more efficient separation methods. Ultimately, one hopes to utilize the dependence of polymer partitioning on molecular properties, such as polymer length, electrical charge and electrolyte composition, to selectively separate chains according to their molecular weight.

Recently, experimental and theoretical investigations [5,6] have explored the ''entropic trapping'' of polymer chains in large spherical voids etched into a hydrogel, and have opened the door to potential new methods of macromolecular separation. Entropic trapping describes the process of preferential localization of a polymer chain inside a void of larger size than the typical volume pockets in a gel, due to the larger conformational entropy experienced by the polymer in the large void as compared to that in the smaller pockets of space within the gel. The trapping of the polymer in the large spherical cavity is characterized by the partition coefficient K, which in the case of a gel is defined as the ratio of the polymer concentrations inside and outside the cavity.

In a recent paper [7] we investigated the role of excluded volume interactions between monomers on the partitioning of a polymer chain between two connected spheres. In particular, we determined the dependence of the partition coefficient K (in this case, the ratio of the average number of monomers in each of the two spheres) on the total number of monomers in the chain. The results, which are in qualitative accord with recent experiments [5] and computer simulations [6], showed that previous explanations of polymer partitioning based on scaling arguments [1–3] do not provide adequate means for calculating K at all polymer chain lengths when excluded volume effects are significant. It was also shown that for some systems the notion of ground-state dominance of the polymer's Green's function fails even in the limit of large number of monomers.

In this paper we investigate the role of electrostatic interactions on the partitioning of a charged polymer chain between two confining spherical cavities of different size. We have carried out calculations using the lattice field theory (LFT) approach [8], based on a formalism which has a number of antecedents in the literature [9–14].

In Sec. II we generalize the LFT approach to the situation where ground-state dominance of the polymer's Green's function is not assumed. Then, in Sec. III, we discuss the general shape of the total free-energy functional of the system at the mean-field level, and prove that it has a unique minimum, thus guaranteeing the existence of a unique solution of the mean-field equations. Numerical results from calculations using three-dimensional (3D) LFT are presented in Sec. IV, and in Sec. V we summarize our conclusions.

II. LATTICE FIELD THEORY OF CHARGED POLYMER CHAINS IN ELECTROLYTE SOLUTION

We first extend the formalism presented in [8] to the general case where ground-state dominance of the polymer's Green's function does not apply. In Ref. [8] we showed that the full partition function of a charged polymer in an electrolyte solution with short-range monomer repulsion interactions can be written as a functional integral:

$$Z = \int D\chi(\vec{r}) D\omega(\vec{r}) \exp\left\{ (\beta\epsilon/8\pi) \int \chi\Delta\chi d\vec{r} - \lambda/2 \int \omega(\vec{r})^2 d\vec{r} \right.$$

$$\left. + c_+ \int e^{ie\beta\chi} d\vec{r} + c_- \int e^{-ie\beta\chi} d\vec{r} \right\} Z_{\text{Schr}}(\chi,\omega), \quad (1)$$

where $\beta = 1/kT$ is the inverse temperature, ϵ is the dielectric constant of the solution, e is the electron charge, λ is a measure of the strength of the excluded volume interaction, χ and ω are auxiliary fields, $c_{\pm} = e^{\beta \mu_{\pm}}/\lambda_{\pm}^3$ with $\mu_{\pm}$ and $\lambda_{\pm}$ being the chemical potentials and the thermal deBroglie wavelengths for the ions, respectively, and

$$Z_{\text{Schr}}(\chi,\omega) \equiv \int D\vec{x}(s)\exp\left\{-(3/2a_p^2)\int_0^M ds\dot{\vec{x}}^2(s) - ipe\beta\right.$$
$$\left. \times \int ds\chi(\vec{x}(s)) - i\lambda \int ds\omega(\vec{x}(s))\right\}, \quad (2)$$

with M being the total number of monomers in the chain, p the charge per monomer, and a_p the Kuhn length.

As before [8], the functional integral (1) can be rerouted through a complex saddle point at $\chi = -i\chi_c$ and $\omega = -i\omega_c$, where χ_c and ω_c are purely real, reducing the computation of $Z_{\text{Schr}}(\chi,\omega)$ at the saddle point to a conventional 3D Schrödinger Hamiltonian problem, that is, the computation of matrix elements of e^{-HT}, with Euclidean time extent of the evolution $T = M$ and

$$H \equiv -\frac{a_p^2}{6}\vec{\nabla}^2 + \lambda\omega_c(\vec{r}) + \beta pe\chi_c(\vec{r}). \quad (3)$$

As usual, the equations determining the saddle-point configuration fields χ_c, ω_c are obtained by setting the variational derivative of the exponent in the full functional integral (1) to zero. In the general case of a polymer chain with free ends the polymer part of the partition function can be written

$$Z_{\text{Schr}} = \int dx_i dx_f \sum_n \Psi_n(x_i)\Psi_n(x_f)e^{-ME_n}$$

$$= \sum_n A_n^2 e^{-ME_n} \equiv e^{F_{pol}}, \quad (4)$$

where E_n is the nth energy eigenvalue,

$$A_n \equiv \int d\vec{r}\Psi_n(\vec{r}), \quad (5)$$

and

$$F_{pol} = \ln\left(\sum_n A_n^2 e^{-ME_n}\right) \quad (6)$$

is the negative of the polymer contribution to the free energy. Thus the negative of the total free energy at the saddle point becomes

$$F = \int d\vec{r}\left\{\frac{\beta\epsilon}{8\pi}|\vec{\nabla}\chi_c|^2 + \frac{\lambda}{2}\omega_c^2 + c_+ e^{\beta e\chi_c} + c_- e^{-\beta e\chi_c}\right\}$$
$$+ F_{pol}(\chi_c,\omega_c). \quad (7)$$

As before [8], we have

$$\frac{\delta E_n}{\delta\chi_c(\vec{r})} = \beta pe|\Psi_n(\vec{r})|^2, \quad (8)$$

$$\frac{\delta E_n}{\delta\omega_c(\vec{r})} = \lambda|\Psi_n(\vec{r})|^2. \quad (9)$$

Considering the variation of the potential energy V, $\delta V = \beta pe\,\delta\chi_c$, we have

$$\delta\Psi_n(\vec{r}) = \sum_{m,m\neq n}\frac{\langle m|\delta V|n\rangle}{E_n - E_m}\Psi_m(\vec{r})$$

$$= \beta pe\sum_{m,m\neq n}\frac{\Psi_m(\vec{r})}{E_n - E_m}\int d\vec{r}''\Psi_m(\vec{r}'')\Psi_n(\vec{r}'')\delta\chi_c(\vec{r}''),$$
$$(10)$$

so that

$$\frac{\delta\Psi_n(\vec{r}')}{\delta\chi_c(\vec{r})} = \beta pe\sum_{m,m\neq n}\frac{\Psi_m(\vec{r}')\Psi_m(\vec{r})\Psi_n(\vec{r})}{E_n - E_m}. \quad (11)$$

Hence,

$$\frac{\delta}{\delta\chi_c(\vec{r})}(A_n^2 e^{-ME_n}) = 2\beta peA_n\Psi_n(\vec{r})\sum_{m,m\neq n}\frac{A_m\Psi_m(\vec{r})}{E_n - E_m}e^{-ME_n}$$
$$- \beta peMA_n^2\Psi_n^2(\vec{r})e^{-ME_n}, \quad (12)$$

and

$$\frac{\delta F_{pol}}{\delta\chi_c(\vec{r})} = \frac{\sum_n \frac{\delta}{\delta\chi_c(\vec{r})}(A_n^2 e^{-ME_n})}{\sum_n A_n^2 e^{-ME_n}} = \beta pe\frac{\sum_{n,m,m\neq n}\frac{2A_n\Psi_n(\vec{r})A_m\Psi_m(\vec{r})}{E_n - E_m}e^{-ME_n} - M\sum_n (A_n\Psi_n(\vec{r}))^2 e^{-ME_n}}{\sum_n A_n^2 e^{-ME_n}}. \quad (13)$$

Considering the fact that

$$\sum_{n,m,m\neq n}\frac{A_n\Psi_n A_m\Psi_m}{E_n - E_m}e^{-ME_n} = \sum_{m,n,n\neq m}\frac{A_n\Psi_n A_m\Psi_m}{E_m - E_n}e^{-ME_m}$$

$$= \frac{1}{2}\sum_{n,m,m\neq n}\frac{A_n\Psi_n A_m\Psi_m}{E_n - E_m}(e^{-ME_n} - e^{-ME_m}), \quad (14)$$

and

$$\frac{A_n\Psi_n A_m\Psi_m}{E_n-E_m}(e^{-ME_n}-e^{-ME_m})_{E_n\to E_m}-M(A_n\Psi_n)^2 e^{-ME_n},$$

$$(15)$$

we can write Eq. (13) as an unconstrained double sum over states:

$$\frac{\delta F_{pol}}{\delta\chi_c(\vec{r})}=\beta pe\,\frac{\displaystyle\sum_{n,m}\frac{A_n\Psi_n A_m\Psi_m}{E_n-E_m}(e^{-ME_n}-e^{-ME_m})}{\displaystyle\sum_n A_n^2 e^{-ME_n}}.$$

$$(16)$$

In a similar fashion we obtain

$$\frac{\delta F_{pol}}{\delta\omega_c(\vec{r})}=\lambda\,\frac{\displaystyle\sum_{n,m}\frac{A_n\Psi_n A_m\Psi_m}{E_n-E_m}(e^{-ME_n}-e^{-ME_m})}{\displaystyle\sum_n A_n^2 e^{-ME_n}}.\quad(17)$$

As shown below, the quantity

$$\rho(\vec{r})\equiv-\,\frac{\displaystyle\sum_{n,m}\frac{A_n\Psi_n A_m\Psi_m}{E_n-E_m}(e^{-ME_n}-e^{-ME_m})}{\displaystyle\sum_n A_n^2 e^{-ME_n}}\quad(18)$$

is the total monomer density. Thus, we can finally write down the equations determining the saddle-point configuration fields χ_c, ω_c:

$$\frac{1}{\beta e}\frac{\delta F}{\delta\chi_c(\vec{r})}=-\frac{\epsilon}{4\pi e}\vec{\nabla}^2\chi_c(\vec{r})+c_+e^{\beta e\chi_c(\vec{r})}$$

$$-c_-e^{-\beta e\chi_c(\vec{r})}-p\rho(\vec{r})$$

$$=0,\quad(19)$$

$$\frac{1}{\lambda}\frac{\delta F}{\delta\omega_c(\vec{r})}=\omega_c(\vec{r})-\rho(\vec{r})=0.\quad(20)$$

Using Eq. (20) the auxiliary field $\omega_c(\vec{r})$ can be eliminated, leaving the following pair of coupled nonlinear equations to describe, at mean-field level, the equilibrium properties of a charged polymer interacting with ions in an electrolyte solution:

$$\frac{\epsilon}{4\pi e}\vec{\nabla}^2\chi_c(\vec{r})=c_+e^{\beta e\chi_c(\vec{r})}-c_-e^{-\beta e\chi_c(\vec{r})}-p\rho(\vec{r}),\quad(21)$$

$$\frac{a_p^2}{6}\vec{\nabla}^2\Psi_n(\vec{r})=\lambda\rho(\vec{r})\Psi_n(\vec{r})+\beta pe\chi_c(\vec{r})\Psi_n(\vec{r})-E_n\Psi_n(\vec{r}).$$

$$(22)$$

Equations (21) and (22) are generalizations of Eqs. (20) and (21) in [8], as they involve the total monomer density, $\rho(\vec{r})$, given by Eq. (18), instead of $M\Psi_0^2(\vec{r})$, which would be appropriate only in the limit of ground-state dominance. The equations presented here apply for polymer chains of arbitrary length. Inclusion of single-particle potentials, which

can be used to enforce exclusion regions for either the ions or monomers, is straightforward [8]. Note that the parameters $c_\pm$ are exponentials of the chemical potentials $\mu_\pm$ for positively and negatively charged ions. The numbers of these ions must be fixed by suitably adjusting $c_\pm$ to satisfy the relations

$$n_\pm=c_\pm\frac{\partial\log(Z)}{\partial c_\pm}=c_\pm\int e^{\pm\beta e\chi_c}d\vec{r}.\quad(23)$$

Next we show that $\rho(\vec{r})$ is in fact the monomer density. Starting from the average of the local monomer density, $\rho_n(\vec{r})$ [15], we have

$$\rho_n(\vec{r})=\langle\delta(\vec{r}-\vec{R}_n)\rangle$$

$$=\frac{\displaystyle\int d\vec{R}_0 d\vec{R}_M\langle\vec{R}_M|e^{-(M-n)\hat{H}}|\vec{r}\rangle\langle\vec{r}|e^{-n\hat{H}}|\vec{R}_0\rangle}{\displaystyle\int d\vec{R}_0 d\vec{R}_M\langle\vec{R}_M|e^{-M\hat{H}}|\vec{R}_0\rangle}.$$

$$(24)$$

Then the total density is

$$\rho(\vec{r})=\sum_{n=0}^{M}\rho_n(\vec{r})$$

$$\approx\int_0^M dn\,\rho_n(\vec{r})$$

$$=\frac{\displaystyle\int_0^M dn\int d\vec{R}_0 d\vec{R}_M\langle\vec{R}_M|e^{-(M-n)\hat{H}}|\vec{r}\rangle\langle\vec{r}|e^{-n\hat{H}}|\vec{R}_0\rangle}{\displaystyle\int d\vec{R}_0 d\vec{R}_M\langle\vec{R}_M|e^{-M\hat{H}}|\vec{R}_0\rangle}.$$

$$(25)$$

Invoking spectral decomposition

$$\langle\vec{r}_2|e^{-m\hat{H}}|\vec{r}_1\rangle=\sum_{j=0}^{\infty}\langle\vec{r}_2|\Psi_j\rangle\langle\Psi_j|\vec{r}_1\rangle e^{-mE_j}$$

$$=\sum_{j=0}^{\infty}\Psi_j(\vec{r}_2)\Psi_j(\vec{r}_1)e^{-mE_j},\quad(26)$$

we obtain

$$\int d\vec{R}_0 d\vec{R}_M\langle\vec{R}_M|e^{-M\hat{H}}|\vec{R}_0\rangle$$

$$=\sum_{j=0}^{\infty}\int d\vec{R}_0 d\vec{R}_M\Psi_j(\vec{R}_0)\Psi_j(\vec{R}_M)e^{-ME_j}$$

$$=\sum_{j=0}^{\infty}A_j^2 e^{-ME_j}.\quad(27)$$

Letting

$$I(n) = \int d\vec{R}_0 d\vec{R}_M \langle \vec{R}_M | e^{-(M-n)\hat{H}} | \vec{r} \rangle \langle \vec{r} | e^{-n\hat{H}} | \vec{R}_0 \rangle$$

$$= \int d\vec{R}_0 d\vec{R}_M \left[\sum_{j=0}^{\infty} \Psi_j(\vec{R}_M) \Psi_j(\vec{r}) e^{-(M-n)E_j} \right]$$

$$\times \left[\sum_{k=0}^{\infty} \Psi_k(\vec{R}_0) \Psi_k(\vec{r}) e^{-nE_k} \right]$$

$$= \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} A_j A_k \Psi_j \Psi_k e^{-ME_j} e^{-n(E_k - E_j)}, \qquad (28)$$

then

$$\int_0^M dn I(n) = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} A_j A_k \Psi_j \Psi_k e^{-ME_j} \int_0^M dn e^{-n(E_k - E_j)}$$

$$= \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} A_j A_k \Psi_j \Psi_k f(M; E_j, E_k), \qquad (29)$$

where

$$f(M; E_j, E_k) = \begin{cases} \dfrac{e^{-ME_j} - e^{-ME_k}}{E_k - E_j}; & \text{for } E_j \neq E_k, \\ M e^{-ME_j}; & \text{for } E_j = E_k. \end{cases}$$

Thus, all in all

$$\rho(\vec{r}) = \frac{\displaystyle\sum_{j=0}^{\infty} \sum_{k=0}^{\infty} A_j A_k \Psi_j \Psi_k f(M; E_j, E_k)}{\displaystyle\sum_{j=0}^{\infty} A_j^2 e^{-ME_j}}, \qquad (30)$$

thereby recovering Eq. (18). It is easy to see that in the case of ground-state dominance, that is, if

$$M(E_1 - E_0) \gg 1, \qquad (31)$$

we recover the familiar relationship

$$\rho(\vec{r}) = M \Psi_0^2(\vec{r}), \qquad (32)$$

and Eqs. (21) and (22) become identical with Eqs. (20) and (21) in [8].

In concluding this section, we should mention that the functional $F(\chi_c, \omega_c)$ in Eq. (7) represents a ''mixed'' free energy, since the partition function Z in Eq. (1) is canonical with respect to the polymer chain and grand canonical with respect to the mobile ions. The advantage of working with F is that, as will be shown in the next section, it has a unique minimum [corresponding to the solution of the mean field Eqs. (21) and (22)], and thus can be used to guide a numerical search for the mean electrostatic and monomer density fields. Once the mean fields have been computed, the defining relation $\ln Z \cong F(\chi_c, \omega_c)$ can be used to obtain free energies of various types. For example, the Helmholtz free energy A (corresponding to fixed numbers of monomers and impurity ions) is given by

$$\beta A = n_+ \ln c_+ + n_- \ln c_- - F(\chi_c, \omega_c). \qquad (33)$$

III. GENERAL FORM OF THE FREE-ENERGY FUNCTIONAL

In our previous work [8] we showed that in the case of ground-state dominance the negative of the free energy, F, is in fact convex, thus guaranteeing a unique solution to the field equations. Of course, convexity, although a sufficient condition, is not necessary for the existence of a unique local minimum of F. We shall see shortly that a weaker, but nevertheless sufficient condition for the existence of a unique minimum of F is the convexity of the functional e^F. This latter convexity will be established below for arbitrary boundary conditions (open or closed) for the polymer chain, implying a unique minimum of F—a property essential for the stability and reliability of the numerical algorithms we employ to solve the mean-field equations of the theory.

The convexity of e^F implies the existence of a unique local minimum of F. This connection is due to the fact that local minima of F are inherited by e^F, so that the presence of *more than one* local minimum of F would necessarily violate the convexity of e^F. The exponential of the negative of the mean-field free energy given in Eq. (7) can be expressed as

$$e^{F(\omega_c, \chi_c)} = \int D\vec{x}(s) \exp\left\{ -(3/2a_p^2) \int ds \dot{\vec{x}}^2(s) \right\}$$

$$\times \mathcal{G}(\omega_c, \vec{x}(s)) \mathcal{H}(\chi_c, \vec{x}(s)), \qquad (34)$$

where

$$\mathcal{G}(\omega_c, \vec{x}(s)) \equiv \exp\left\{ (\lambda/2) \int \omega_c^2 d\vec{r} - \lambda \int ds \, \omega_c(\vec{x}(s)) \right\}, \qquad (35)$$

$$\mathcal{H}(\chi_c, \vec{x}(s)) \equiv \exp\left\{ -(\beta\epsilon/8\pi) \int \chi_c \Delta \chi_c d\vec{r} + c_+ \int e^{e\beta\chi_c} d\vec{r} \right.$$

$$\left. + c_- \int e^{-e\beta\chi_c} d\vec{r} - pe\beta \int ds \chi_c(\vec{x}(s)) \right\}. \qquad (36)$$

[This can also be seen by inspection of Eqs. (1) and (2) with χ, ω fixed at the saddle point to $-i\chi_c, -i\omega_c$, respectively.] Introducing the line distribution $j(\vec{r}) \equiv \int ds \, \delta(\vec{r} - \vec{x}(s))$, Eqs. (35), (36) become

$$\mathcal{G}(\omega_c, \vec{x}(s)) \equiv \exp\left\{ (\lambda/2) \int \omega_c^2 d\vec{r} - \lambda \int \omega_c(\vec{r}) j(\vec{r}) d\vec{r} \right\}, \qquad (37)$$

$$\mathcal{H}(\chi_c, \vec{x}(s)) \equiv \exp\left\{ -(\beta\epsilon/8\pi) \int \chi_c \Delta \chi_c d\vec{r} + c_+ \int e^{e\beta\chi_c} d\vec{r} \right.$$

$$\left. + c_- \int e^{-e\beta\chi_c} d\vec{r} - pe\beta \int \chi_c(\vec{r}) j(\vec{r}) d\vec{r} \right\}. \qquad (38)$$

From Eq. (34), it is apparent that the exponential of F is a sum (over polymer configurations) of positively weighted products of functionals of the fields ω_c and χ_c *separately*. Accordingly, the convexity of e^F will be guaranteed once we can demonstrate the convexity of the functionals $\mathcal{G}$ (as a

function of ω_c) and $\mathcal{H}$ (as a function of χ_c) for any arbitrary fixed polymer configuration $\vec{x}(s)$.

The second functional derivative of $\mathcal{G}$ is found after a short calculation to be

$$K_G(\vec{r},\vec{r}') \equiv \frac{\delta^2 \mathcal{G}}{\delta\omega_c(\vec{r})\,\delta\omega_c(\vec{r}')}$$

$$= \{\lambda\,\delta(\vec{r}-\vec{r}') + \lambda^2[\omega_c(\vec{r})-j(\vec{r})]$$

$$\times[\omega_c(\vec{r}')-j(\vec{r}')]\}\mathcal{G}. \tag{39}$$

A necessary and sufficient condition for a function $W(\vec{r},\vec{r}')$ to be positive semidefinite is that

$$\int d\vec{r}\int d\vec{r}'\,f(\vec{r})W(\vec{r},\vec{r}')f(\vec{r}')\geq 0 \tag{40}$$

for any function $f(\vec{r})$. The positivity of the kernel K_G in Eq. (39) is apparent and can be demonstrated by verifying Eq. (40):

$$\int d\vec{r}\int d\vec{r}'\,f(\vec{r})K_G(\vec{r},\vec{r}')f(\vec{r}')$$

$$= \lambda\mathcal{G}\int d\vec{r}f^2(\vec{r}) + \lambda^2\mathcal{G}\left\{\int d\vec{r}f(\vec{r})[\omega_c(\vec{r})-j(\vec{r})]\right\}^2$$

$$\geq 0. \tag{41}$$

The exponent of $\mathcal{H}$ can be written

$$-\frac{\beta\epsilon}{8\pi}\int \chi_c\Delta\chi_c d\vec{r} + c_+\int e^{e\beta\chi_c}d\vec{r} + c_-\int e^{-e\beta\chi_c}d\vec{r} - pe\beta\int \chi_c(\vec{r})j(\vec{r})d\vec{r}$$

$$= -\frac{\beta\epsilon}{8\pi}\int \left(\chi_c\Delta\chi_c + \frac{8\pi pe}{\epsilon}\chi_c(\vec{r})j(\vec{r})\right)d\vec{r} + c_+\int e^{e\beta\chi_c}d\vec{r} + c_-\int e^{-e\beta\chi_c}d\vec{r}$$

$$= -\frac{\beta\epsilon}{8\pi}\left[\int \left(\chi_c + \frac{1}{\Delta}\frac{4\pi pe}{\epsilon}j\right)\Delta\left(\chi_c + \frac{1}{\Delta}\frac{4\pi pe}{\epsilon}j\right)d\vec{r} - \left(\frac{4\pi pe}{\epsilon}\right)^2\int j\Delta^{-1}jd\vec{r}\right] + c_+\int e^{e\beta\chi_c}d\vec{r} + c_-\int e^{-e\beta\chi_c}d\vec{r}$$

$$= -\frac{\beta\epsilon}{8\pi}\int (\chi_c+\hat{\jmath})\Delta(\chi_c+\hat{\jmath})d\vec{r} - \left(\frac{4\pi pe}{\epsilon}\right)^2\int j\Delta^{-1}jd\vec{r} + c_+\int e^{e\beta\chi_c}d\vec{r} + c_-\int e^{-e\beta\chi_c}d\vec{r}, \tag{42}$$

where

$$\hat{\jmath} \equiv \frac{1}{\Delta}\frac{4\pi pe}{\epsilon}j. \tag{43}$$

Hence,

$$\frac{\delta\mathcal{H}}{\delta\chi_c(\vec{r})} = \left[-\frac{\beta\epsilon}{4\pi}\Delta(\chi_c+\hat{\jmath})(\vec{r}) + c_+e\beta e^{e\beta\chi_c(\vec{r})} - c_-e\beta e^{-e\beta\chi_c(\vec{r})}\right]\mathcal{H}, \tag{44}$$

and, therefore,

$$K_H(\vec{r},\vec{r}') \equiv \frac{\delta^2\mathcal{H}}{\delta\chi_c(\vec{r})\,\delta\chi_c(\vec{r}')}$$

$$= \left[-\frac{\beta\epsilon}{4\pi}\Delta(\chi_c+\hat{\jmath})(\vec{r}) + c_+e\beta e^{e\beta\chi_c(\vec{r})} - c_-e\beta e^{-e\beta\chi_c(\vec{r})}\right]\left[-\frac{\beta\epsilon}{4\pi}\Delta(\chi_c+\hat{\jmath})(\vec{r}') + c_+e\beta e^{e\beta\chi_c(\vec{r}')} - c_-e\beta e^{-e\beta\chi_c(\vec{r}')}\right]\mathcal{H}$$

$$- \frac{\beta\epsilon}{4\pi}\Delta_{\vec{r}}\delta(\vec{r}-\vec{r}')\mathcal{H} + e^2\beta^2\delta(\vec{r}-\vec{r}')(c_+e^{e\beta\chi_c(\vec{r})} + c_-e^{-e\beta\chi_c(\vec{r})})\mathcal{H}. \tag{45}$$

Property (40) can be easily verified for the first and third terms of Eq. (45). For the second term one finds

$$\int d\vec{r}\int d\vec{r}'\,f(\vec{r})[-\Delta_{\vec{r}}\delta(\vec{r}-\vec{r}')]f(\vec{r}')\mathcal{H} = \int d\vec{r}f(\vec{r})[-\Delta f(\vec{r})]\mathcal{H}$$

$$= \int d\vec{r}|\vec{\nabla}f|^2\mathcal{H} \geq 0. \tag{46}$$

This establishes the positivity of the kernel K_H, which together with the positivity of K_G proves the convexity of e^F, and consequently the existence of unique minimum of F, which itself guarantees uniqueness of the solution of the mean-field equations.

IV. THREE-DIMENSIONAL LATTICE FIELD THEORY RESULTS FOR A CHARGED POLYMER CHAIN CONFINED TO TWO CONNECTED SPHERES OF DIFFERENT RADII

We have used a recently developed LFT approach [8] in order to obtain results of the solution of the mean-field equations (21) and (22), for polymer chains confined to 3D cavities. In this section we present results of the calculation of the equilibrium monomer distribution of a charged polymer chain constrained to move inside the volume of two connected spheres [16].

After rescaling according to $f(\vec{r}) \to \beta e \chi_c(\vec{r})$, $\Psi_N(\vec{r}) \to a_l^{3/2} \Psi_N(\vec{r})$, and multiplying Eq. (21) by a_l^3 (a_l being the lattice spacing), we solve the discretized version of Eqs. (21) and (22) on a 3D lattice:

$$\alpha \sum_{\vec{m}} \Delta_{\vec{n}\vec{m}} f_{\vec{m}} = \gamma_+ e^{f_{\vec{n}}} - \gamma_- e^{-f_{\vec{n}}} - p \rho_{\vec{n}}, \qquad (47)$$

$$\frac{a_p^2}{6a_l^2} \sum_{\vec{m}} \Delta_{\vec{n}\vec{m}} \Psi_{N,\vec{m}} = \frac{\lambda}{a_l^3} \rho_{\vec{n}} \Psi_{N,\vec{n}} + p f_{\vec{n}} \Psi_{N,\vec{n}} - E_N \Psi_{N,\vec{n}}, \qquad (48)$$

where

$$\alpha = \frac{\varepsilon a_l}{4\pi\beta e^2}, \qquad (49)$$

$$\gamma_{\pm} = \frac{n_{\pm}}{\sum_{\vec{n}} e^{\pm f_{\vec{n}}}}, \qquad (50)$$

and the wave functions are dimensionless and normalized according to

$$\sum_{\vec{n}} \Psi_{N,\vec{n}}^2 = 1; \qquad (51)$$

thus, the density $\rho_{\vec{n}}$ sums to the total number of monomers, M.

Equations (47) and (48) are solved simultaneously via the following relaxation procedure [8]. First, the Schrödinger Eq. (48) is solved using the Lanczos method [18], setting $f_{\vec{n}}=0$ and ignoring the nonlinear (monomer repulsion) potential term. The resulting $\Psi_{N,\vec{n}}$'s and corresponding energy levels E_N (wave functions and energy eigenvalues of a particle confined to a "box" consisting of two fused spheres) are used to calculate $\rho_{\vec{n}}$, then the Poisson-Boltzmann Eq. (47) is solved at each lattice point using a simple line minimization procedure [17]. The process is repeated and the coefficients $\gamma_{\pm}$ are updated after a few iterations until a predetermined accuracy is achieved. Then the resulting $f_{\vec{n}}$ is used in Eq. (48), which is solved for a new set of $\Psi_{N,\vec{n}}$'s to
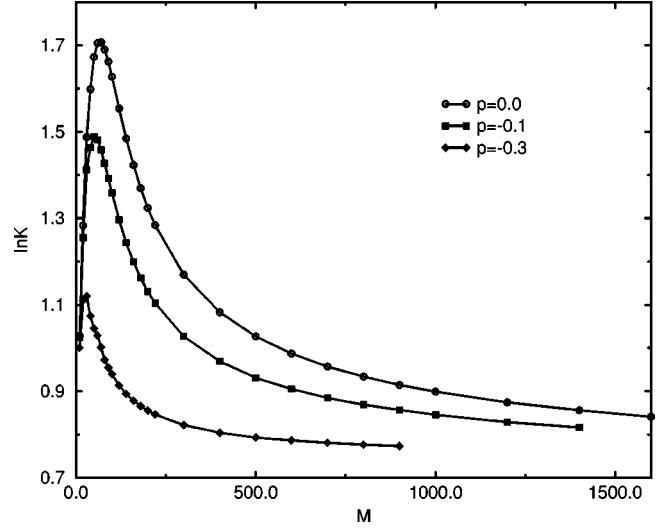

FIG. 1. The ratio $\ln K$ vs M for system (1) for varying monomer charge p and fixed number of negative impurity ions $n=600$, which corresponds to molar concentration $C \approx 0.75M$.

be used in calculating an updated version of the monomer density $\rho_{\vec{n}}$. This density is then inputted into Eq. (47) and a new version of $f_{\vec{n}}$ is computed. For numerical stability, the updated $f_{\vec{n}}$ inputted into Eq. (48) is obtained by adding a small fraction of the new $f_{\vec{n}}$ [just obtained from Eq. (47)] to the old one (obtained from the previous iteration). The same "slow charging" procedure is used for updating $\rho_{\vec{n}}$ in the nonlinear potential term of the Schrödinger equation (48).

This procedure has been applied to two systems:

(1) A polymer in a cavity consisting of two spheres of radii R_1 and R_2, carved out and sharing one common point on a lattice, the distance between the centers of the two spheres being $R_1 + R_2$.

(2) Same as (1), except that the spheres are now embedded in each other by one more lattice spacing, that is, the distance between their centers is now $R_1 + R_2 - a_l$.

We have used the following parameters in relative units: $R_1 = 1.0$, $R_2 = 0.8$, $a_p = 0.2$, $\lambda = 0.001$, and the two spheres are carved inside a cube of 44 lattice points on each side with $a_l = 0.1$. In absolute units $a_p = 5$ Å.

We have computed the partition coefficient $K \equiv \langle M_1 \rangle / \langle M_2 \rangle$ as a function of the total number of monomers in the system, $M = \langle M_1 \rangle + \langle M_2 \rangle$, for varying monomer charge p and varying number of ions in the system. The results for system (1) are plotted in Figs. 1 and 2, with n being the number of negative impurity ions in the system, while the number of positive ions is adjusted so that electroneutrality is preserved. Similar to what was found in the case of neutral polymers [7], we see here that for small M, $\ln K$ increases essentially linearly with M. This is followed by a turnover region, after which $\ln K$ decreases with M, and for very large M approaches a limit bounded from below by the log of the ratio of the volumes of the two spheres.

In Fig. 1 we show results for varying monomer charge p, keeping the number of impurity ions fixed. It is apparent that smaller monomer charge favors larger $\ln K$, thus making polymer separation easier. In Fig. 2 we vary the number of impurity ions, showing that a large number of impurity ions
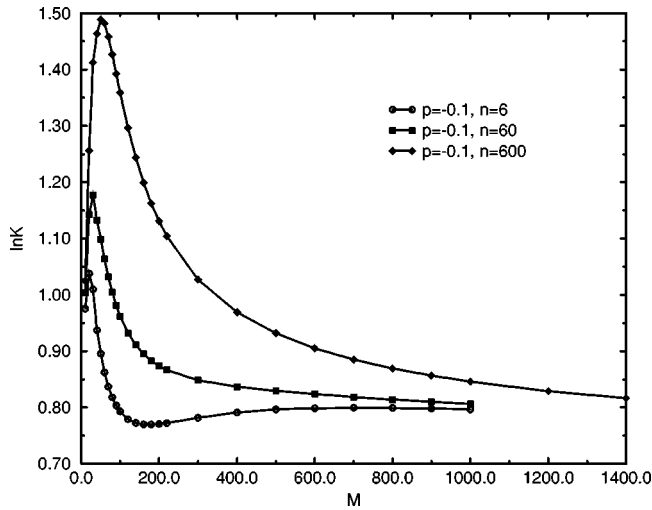
FIG. 2. The ratio ln$K$ vs M for system (1) for varying number of negative impurity ions n and fixed monomer charge p. The corresponding molar concentrations are $C(n=6)\approx0.75\times10^{-2}M$, $C(n=60)\approx0.75\times10^{-1}M$, and $C(n=600)\approx0.75M$, respectively.

FIG. 4. The ratio ln$K$ vs M for system (2) for varying number of negative impurity ions n and fixed monomer charge p. The corresponding molar concentrations are $C(n=6)\approx0.75\times10^{-2}M$, $C(n=60)\approx0.75\times10^{-1}M$, and $C(n=600)\approx0.75M$, respectively.

leads to screening of the monomer charges from each other and thus to a behavior resembling that of a neutral chain. We observe an interesting feature in the case of a small number of ions: the ln$K$ curve goes through a turnover, then through a minimum and a maximum, before approaching its asymptotic value at large M.

In Figs. 3 and 4 we show the analogous results to those of Figs. 1 and 2, respectively, for system (2). The same basic behavior is observed, with the partition coefficient being smaller for system (2) than for system (1) under identical conditions of polymer length, monomer charge, and impurity ion concentration. This is because of the wider conduit in system (2), which diminishes the isolation of one sphere from the other, thus enabling the polymer to move more freely between the two.
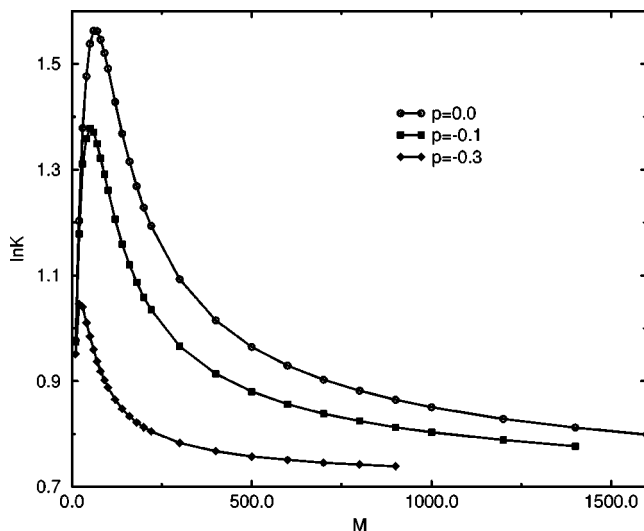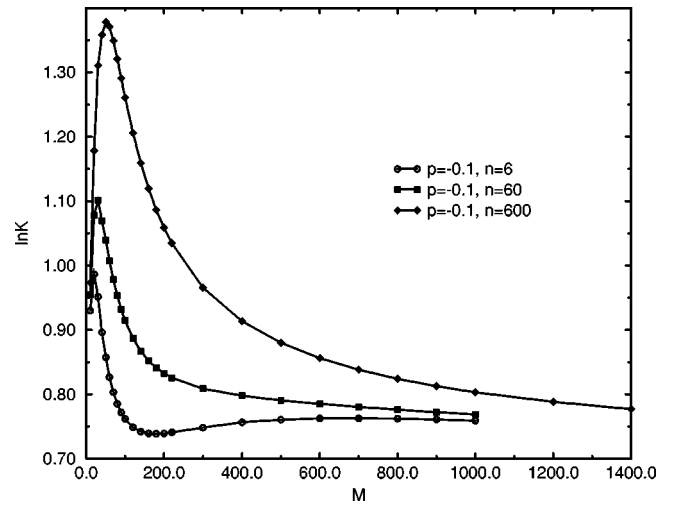
These results are consistent with the ideas presented in our previous work [8], namely, that higher impurity ion (electrolyte) concentrations would favor better polymer separation between cavities of different size.

Note that, as we found previously for an uncharged polymer chain [7], in the case of system (1) ground-state dominance of the polymer's Green's function does not set in for any M. As we increase the total number of monomers, the first two energy levels come closer together and couple. Thus, even in the large-M limit we must retain both these states in order to calculate an accurate monomer density $\rho(\vec{r})$. In Fig. 5 we plot $\Delta\equiv\exp[-M(E_1-E_0)]$ vs M as an indicator of ground-state dominance ($\Delta\to0$ as $M\to\infty$) for $p=-0.3$ and $n=600$ for both systems (1) and (2). It is clear that in the case of system (1) ground-state dominance does

FIG. 3. The ratio ln$K$ vs M for system (2) for varying monomer charge p and fixed number of negative impurity ions $n=600$, which corresponds to molar concentration $C\approx0.75M$.
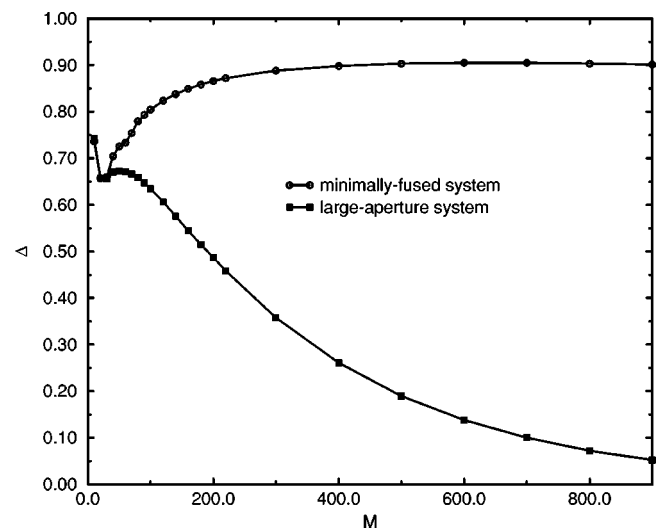

FIG. 5. The number $\Delta\equiv\exp[-M(E_1-E_0)]$ as a function of M for system (1) (minimally-fused system) and system (2) (large-aperture system) for monomer charge $p=-0.3$ and number of negative impurity ions $n=600$.

not occur, while for system (2) it occurs, as would be expected for a polymer moving in a single cavity.

V. CONCLUSIONS

We have extended the lattice field theory approach for the statistical mechanics of charged polymers in electrolyte solutions [8] to the case where ground-state dominance fails in the polymer's Green's function. At the mean-field level all thermodynamic properties of the system are obtained from the solution of two coupled nonlinear equations. These equations involve the full monomer density, which in general contains contributions from excited states in the spectral decomposition of the polymer's Green's function. We have also discussed the general shape of the functional F in Eq. (7), whose extremization solves the mean-field equations of interest. In particular we have shown that F possesses a single minimum, thus guaranteeing that a unique solution of these equations exists.

We have used this approach to calculate the equilibrium partition coefficient K of a charged Gaussian polymer chain in a system of two spheres connected by a narrow aperture, and have observed the same generic behavior seen in the case of excluded volume interactions only [7]: the log of the partition coefficient increases essentially linearly with the number of monomers in the chain, M, for small M, then it goes through a turnover region with a maximum, after which at large M it decreases to an asymptotic value bounded from below by the log of the ratio of the volumes of the two spheres. Increasing the monomer charge makes this behavior less pronounced and reduces the maximum in the $\ln K$ vs M curve, while increasing the impurity ion concentration leads to screening of the monomer charges, and makes the $\ln K$ vs M curve similar to the one in the case of a neutral polymer with excluded volume interactions. This supports our previous contention [8] that higher impurity ion concentrations should lead to better polymer separation between cavities of different size, such as the cavities in a gel used to observe the entropic trapping phenomenon [5].

The present work demonstrates the failure of the notion of ground-state dominance in the case of a very narrow conduit between the two spheres. For such a system, even in the large-M limit the first excited state of the polymer's Green's function must be retained in order to obtain an accurate mean-field solution to the problem.

Of course, the accuracy of the mean-field approximation [15,19] for the systems considered here remains an outstanding issue. In the case of electrically neutral polymers, Monte Carlo simulations may provide valuable benchmarks against which mean-field predictions can be compared. Such computations are currently under way.

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