A variational approach to charged polymer chains: Polymer mediated interactions

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A variational approach, based on a quadratic trial Hamiltonian is used to determine the configurational as well as the mechanical properties of a system composed of two point charges plus a neutralizing charged polymer, considered as a model of polyelectrolyte–macroion interactions. The quadratic variational *ansatz* used in the context of charged polymers presents a variant of the Feynman–Kleinert approach properly generalized to include polymer self-interactions. Conditions for chain localization in the field of a point charge are derived and its consequences for polymer-mediated forces between two point charges are analyzed. It is established that in three dimensions the polymer can confer long range attraction to nominally equally charged point ions. At small separations, the polymer mediated force is elastic in origin, stemming from the soft electrostatic anchoring of the chain to both point charges, but with a force constant much stronger than expected from entropic elasticity alone. At large separations, the polymer mediated interactions are of long range and are due to polymer-induced charge reversal on one of the external point charges.

I. INTRODUCTION

The interest in forces between macroscopic charged bodies mediated by oppositely charged long polymer chains grew recently[1,2] after it was realized[3] that the connectivity of polymer chains can confer a strong attraction to nominaly equally charged bodies—a result quite perplexing from a naive perspective on Coulomb interactions, where the force between equally charged bodies is deemed to be repulsive. But even with a deeper insight and with a knowledge of the correlation attraction in higher valency salts,[4] one still remains surprised after realizing that the polymer-mediated attraction is a *mean field* effect and is not connected with any breakdown of the Poisson–Boltzmann theory. Rather, it is a consequence of *bridging* of the same polymer chain between two apposed surfaces with the electrostatic interactions playing the role of anchoring the chain to the surfaces, while the chain's connectivity provides the entropic elastic force that draws the surfaces towards each other. Aside from the Monte Carlo simulations,[3] three different analytical approaches[1–3] to the polyelectrolyte-mediated electrostatic interactions have been proposed, all of them based on mean-field type approximations, trying to upgrade in one way or another the Poisson–Boltzmann (PB) equation for inhomogeneous electrolytes. In the PB type mean-field theories, the electrostatic self-interaction of the polyelectrolyte chain does not at any point enter the discussion. This is not a problem with Coulomb fluids composed of simple entities, e.g., ions, but in the case of polyelectrolyte chains, the self-interaction severely affects the dimensions and the stiffness of the polymer chain that both enter the mean-field equations for the polyelectrolyte local charge density (see Ref. 3 for details). This effect of the self-interaction should thus in one way or another be incorporated into the mean-field description of a polymer chain in external fields.

One approach was exploited by Muthukumar[5] in a similar context of adsorption of a charged polymer chain to an oppositely charged surface. He tried to upgrade the work of Wiegel,[5] where the chain was considered to be Gaussian in an external field describing the interaction with the surface, by deriving an independent estimate of the effect of the intrachain Coulombic (as well as steric) repulsions on the dimensions of the polymer chain. This effect was expressed in terms of an effective step length of the polymer chain that was then used in the standard mean-field equations. These type of "effective medium" theories are quite common in polymer physics[6] and work well for bulk problems. They are, however, inappropriate for strongly inhomogeneous systems since they treat the (internal) segment–segment interactions and the interactions with an external field additively. One would thus like to see the intrachain interactions included into the theory on the same level as the external fields, without invoking additivity beforehand. This is what we shall set ourselves to do.

The basic idea is very simple. We try to progressively integrate out the polymer configurations in the partition function by applying the following basic distinction between different configurations: The configurations of a highly convoluted chain are not very probable since they entail large configurational energy, thus we can treat them approximately on an effective (see below) Gaussian level. On the other hand, configurations corresponding to displacements of the whole chain in an external field cost no configurational energy, but depend only on the coupling of the chain to the external field and they can in principle be

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treated exactly. When one tries to implement this idea formally, one is basically applying a modified Feynman–Kleinert[7] variational principle to the statistics of a self-interacting polymer chain.

Variational principles of a similar type have been applied to other problems[8] as well as to polymers before.[9] As already stated, the "effective medium" theory, implemented for the polymer case by Edwards and Singh, has found a wide variety of applications.[10] It could be thought of as a zero-order variational approach since the polymer interactions are lumped into an effective free polymer Hamiltonian. The next order variational approach corresponds to a quadratic trial Hamiltonian that has been used in the problem of localization of a polymer chain in random media.[9,11] The variational procedure employed in this case was in fact the original Feynman approach.[12] There have also been several recent efforts to implement a general quadratic ansatz to the configurational statistics of a polymer chain with long range interactions.[13,14] The variational equations have been solved numerically for a Coulombic chain and found to comply almost exactly with Monte Carlo simulations.[15] Our own efforts, as detailed below, could be viewed as an application of a "diagonal" effective Gaussian *ansatz* to the problem of polymer configurational statistics and polymer-mediated forces. In the "diagonal" representation of the variational *ansatz*, the Euler–Lagrange equations emerge in a particularly simple form, making various analytical estimates quite straightforward. This we consider to be the major advantage of the approach advocated here. In our implementation of the diagonal Gaussian variational *ansatz*, there is one major drawback, since we set the formalism up only for a ring polymer chain, where the beginning and the end of the chain coincide. This proved to be instrumental in terms of the complexity of the Euler–Lagrange equations. It is, however, not a fatal limitation since it can easily be amended, leading to more complex Euler–Lagrange equations that do not lend themselves to easy limiting laws. Since we will mostly be interested in the scaling limit of polymer configurational properties, it does not particularly matter whether the polymer chain is open or closed.

The outline of the paper is as follows: We shall apply the general variational equations derived in the first four sections of the paper to the problem of an electrostatically self-interacting chain. First of all, without any external fields, to check the results derived by our method with previous work, and then in external fields—most notably to the problem of polyelectrolyte chain mediated electrostatic interactions between point charges. We will show that long range electrostatic interactions (contrary to the short range excluded volume interactions) can localize the chain in the vicinity of an external point charge, leading to pronounced consequences in terms of the effective interaction between external charges. We shall derive approximate analytical forms of the polyelectrolyte-mediated electrostatic forces valid at small and asymptotically large separations between external charges. We shall also argue to the effect that with many external charges, the polymer-mediated forces are not pairwise additive if the separations between the external charges are small.

II. MOTIVATION

We start our discussion by considering a self-interacting polymer chain in an external field. The partition function of a polymer in a continuous chain representation is standardly written in the form[16]

$$\Xi(N)=\int \mathscr{D}\mathbf{r}(n)e^{-\beta\mathscr{H}(N)}, \tag{2.1}$$

where the functional integral measure is represented by the usual shorthand $d^3\mathbf{r}(0)d^3\mathbf{r}(1)\cdots d^3\mathbf{r}(N)\rightarrow\mathscr{D}\mathbf{r}(n)$. The configurational part of the chain Hamiltonian has the form

$$\begin{aligned}\beta\mathscr{H}(N)=&\frac{3}{2l^2}\int_0^N\left[\frac{d\mathbf{r}(n)}{dn}\right]^2dn\\&+\frac{1}{2}\beta\int_0^N\int u[\mathbf{r}(n),\mathbf{r}(n')]dn\,dn'\\&+\beta\int_0^N\phi_{\mathrm{ex}}[\mathbf{r}(n)]dn,\end{aligned} \tag{2.2}$$

where $u[\mathbf{r}(n),\mathbf{r}(n')]$ is the intersegment interaction energy, $\phi_{\mathrm{ex}}[\mathbf{r}(n)]$ is the external potential acting on the segments of the polymer chain, and N is the number of the segments of the chain. Let us choose now the following Rouse (Fourier) representation[16] for the instantaneous configuration of the chain

$$\mathbf{r}(n)=\mathbf{r}_0+\sum_{p=1}^{\infty}\mathbf{r}_C(p)\cos\omega_pn+\sum_{p=1}^{\infty}\mathbf{r}_S(p)\sin\omega_pn,$$

$$\text{with }\omega_p=2\pi\frac{p}{N} \tag{2.3}$$

that describes a ring chain where the beginning and the end of the chain coincide. We shall nevertheless indicate in the following at what points in the discussion the ring polymer variational equations would differ from the case of an open polymer. The zero order $\mathbf{r}_0$ term in the sum (2.3) describes the center of mass of the polymer chain, while higher order p terms in the Rouse representation describe chain configurational fluctuations on increasingly smaller scales. Clearly, for small N, the "kinetic energy" part of the Hamiltonian

$$\frac{3}{2l^2}\int_0^N\left[\frac{d\mathbf{r}(n)}{dn}\right]^2dn=\frac{3N}{8l^2}\sum_{p=1}^{\infty}\omega_p^2[\mathbf{r}_C^2(p)+\mathbf{r}_S^2(p)] \tag{2.4}$$

effectively damps all the higher order ($p\geqslant1$) contributions to the polymer total energy that correspond to more convoluted polymer configurations. One could thus hope that the contribution of the $p\geqslant1$ terms to the partition function would be adequately represented by an effective harmonic configurational Hamiltonian of the form

$$\beta\mathcal{H}_0(N)=\frac{3}{2l^2}\int_0^N\left[\frac{d\mathbf{r}(n)}{dn}\right]^2dn+\frac{3}{2}\zeta_0^2(\mathbf{r}_0)\times\int_0^N[\mathbf{r}(n)-\mathbf{r}_0]^2dn+\beta N\mathcal{L}_0(\mathbf{r}_0), \tag{2.5}$$

so that the partition function could be obtained from an effective one particle configurational sum as

$$\Xi_0(N)=\int\mathcal{D}\mathbf{r}(n)e^{-\beta\mathcal{H}_0(N)}=\int d^3\mathbf{r}_0e^{-\beta\mathcal{F}_0(\mathbf{r}_0)}. \tag{2.6}$$

The whole polymer chain would be thus represented as an effective single particle with the as yet unspecified parameters $\zeta_0(\mathbf{r}_0)$ and $\mathcal{L}_0(\mathbf{r}_0)$ determined in such a way that $\Xi_0(N)$ would be an "optimal" approximation to the original partition function. The main difference between this approach and the formalism of Muthukumar[9] lies in the identification of the variational parameters as well as in the form of the variational *ansatz* [cf. Eq. (2.5) of the present work with Eq. (3.21) in Ref. 9]. In our case, the variational parameters are the variance of the Gaussian describing the monomer density distribution, as well as the effective "single particle" free energy (ζ_0 and $\mathcal{L}_0$), while in his case, they are the variance of the Gaussian and the effective step length (ζ_0 and l_{eff}).

The term diagonal that we used in the Introduction refers to the form $\zeta_0^2\int\mathbf{r}(n)^2dn$, which is a diagonalized version of a more general *ansatz*[14] $\int\int\zeta_{n,m}^2\mathbf{r}(n)\mathbf{r}(m)dn\,dm$. The main difference between the two is in the range of correlations that they describe. In this sense, the diagonal variational *ansatz* is local, while the general quadratic one also includes long range correlations between distant monomers along the chain. It is probably due to these long range correlations that it is not applicable to the short range (excluded volume) interaction potential (see the discussion in Ref. 17).

Thus, in the specified approximation scheme, one can recognize a straightforward application and generalization, due to the presence of the intersegment polymer interaction potential, of the Feynman–Kleinert variational principle[7] that has already proved to be a valuable tool in other areas of statistical mechanics.[18]

III. LOWER BOUND FOR $\Xi(N)$

Let us first write $\Xi(N)$ in a different way, introducing the s.c. auxiliary field (the Hubbard–Stratonowich) representation of the partition function. It relies on a representation[2] of the Boltzmann factor for the intrachain potential by a functional Gaussian integral over auxiliary fields such that

$$\begin{aligned}\Xi(N)&=\int\mathcal{D}\mathbf{r}(n)e^{-\beta\mathcal{H}(N)}\\&=\Xi_S(N)\int\mathcal{D}\mathbf{r}(n)\mathcal{D}\phi(\mathbf{r})e^{-\beta\mathcal{H}_\phi(N)}\\&=\langle\langle\langle e^{-\beta\mathcal{H}_\phi(N)}\rangle_{\mathbf{r}(n)}\rangle\rangle_{\phi(\mathbf{r})}\\&=\langle e^{-\beta\mathcal{H}_\phi(N)}\rangle.\end{aligned} \tag{3.1}$$

The triangular bracket notation, as in $\langle\cdots\rangle_{\mathbf{r}(n)}$, is really self-explanatory and we leave it at that, while the auxiliary field functional integration measure is defined again in the standard way as $\lim_{\mathcal{N}\to\infty}d\phi\,\mathbf{r}(1)d\phi\,\mathbf{r}(2)\cdots d\phi\,\mathbf{r}(\mathcal{N})\to\mathcal{D}\phi(\mathbf{r})$. Apart from that, the following notation was introduced in the above equation:

$$\begin{aligned}\Xi_S(N)&=\{\det[\beta u^{-1}(\mathbf{r},\mathbf{r}')]\}^{1/2}\\&\quad\times\exp\left\{-\frac{1}{2}\beta\int_0^N u[\mathbf{r}(n),\mathbf{r}(n)]dn\right\},\end{aligned} \tag{3.2}$$

$$\begin{aligned}\beta\mathcal{H}_\phi(N)&=\frac{3}{2l^2}\int_0^N\left[\frac{d\mathbf{r}(n)}{dn}\right]^2dn+\beta\int_0^N\phi_{\text{ex}}[\mathbf{r}(n)]dn\\&\quad+i\beta\int_0^N\phi[\mathbf{r}(n)]dn+\frac{1}{2}\beta\int\int\phi(\mathbf{r})\\&\quad\times u^{-1}(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}')d^3\mathbf{r}\,d^3\mathbf{r}',\end{aligned}$$

where i is the imaginary unit. We now introduce the zero order Hamiltonian $\beta\mathcal{H}_0$ [Eq. (2.5)] into the definition of the partition function $\Xi(N)$, thus obtaining an estimate

$$\begin{aligned}&\langle e^{-\beta\mathcal{H}_\phi(N)}\rangle\\&\geqslant\langle e^{-\beta\mathcal{H}_0(N)}\rangle_{\mathbf{r}(n)}\\&\quad\times\langle\langle\exp[-\beta\langle\mathcal{H}_\phi(N)-\mathcal{H}_0(N)\rangle_{\mathcal{H}_0[\mathbf{r}(n)]}]\rangle\rangle_{\phi(\mathbf{r})}\\&=\langle e^{-\beta\mathcal{H}_0(N)}\rangle_{\mathbf{r}(n)}\exp[-\beta<\Delta\mathcal{H}_\phi(N)>],\end{aligned} \tag{3.3}$$

with $\Delta\mathcal{H}_\phi(N)=\mathcal{H}_\phi(N)-\mathcal{H}_0(N)$. By writing $\langle\cdots\rangle_{\mathcal{H}_0[\mathbf{r}(n)]}$, we emphasize the fact that $\mathcal{H}_0(N)$ depends only on the chain (and not the auxiliary field) degrees of freedom. The Jensen–Peierls inequality, valid for convex functionals with any measure,[7] was used while deriving the above estimate. Equation (3.3) should also serve as a definition of the average $<\cdots>$. Since the free energy is $\mathcal{F}=-kT\ln\Xi(N)$, we can derive the following (Gibbs–Bogolyubov) inequality valid between $\mathcal{F}$ and $\mathcal{F}_0=-kT\ln\Xi_0(N)$,

$$\begin{aligned}\mathcal{F}&\leqslant\mathcal{F}_0+<\Delta\mathcal{H}_\phi(N)>\\&=\mathcal{F}_0-kT\ln\langle\langle\exp[-\beta\langle\mathcal{H}_\phi(N)\\&\quad-\mathcal{H}_0(N)\rangle_{\mathcal{H}_0[\mathbf{r}(n)]}]\rangle\rangle_{\phi(\mathbf{r})}.\end{aligned} \tag{3.4}$$

Through variational optimization of the second term in the above equation, we will get a good estimate for the free energy of the system.

IV. CALCULATION OF $\langle\Delta\mathscr{H}_\phi(N)\rangle$

We start by evaluating

$$\beta\langle\mathscr{H}_\phi(N)-\mathscr{H}_0(N)\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}$$

$$=i\beta\int_0^N\langle\phi[\mathbf{r}(n)]\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}dn+\beta\int_0^N\langle\phi_{\mathrm{ex}}[\mathbf{r}(n)]\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}dn-\frac{3}{2}\int_0^N\langle\zeta_0^2(\mathbf{r}_0)[\mathbf{r}(n)-\mathbf{r}_0]^2\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}dn$$

$$-\beta N\langle\mathscr{L}_0(\mathbf{r}_0)\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}+\frac{1}{2}\beta\int\int\phi(\mathbf{r})u^{-1}(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}')d^3\mathbf{r}\,d^3\mathbf{r}'. \tag{4.1}$$

The average $\langle\cdots\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}$ in the above equation affects only those quantities that depend on the chain degrees of freedom. Since $\mathscr{H}_0[\mathbf{r}(n)]$ has a general Gaussian form, these averages can be calculated explicitly. First of all, we have

$$\langle f[\mathbf{r}(n)]\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}=\int\frac{d^3\mathbf{k}}{(2\pi)^3}f(\mathbf{k})\langle e^{i\mathbf{k}\mathbf{r}(n)}\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}=\int\frac{d^3\mathbf{k}}{(2\pi)^3}f(\mathbf{k})\left\langle e^{i\mathbf{k}\mathbf{r}_0}\exp\left\{-\frac{1}{2}k^2\frac{1}{3}\langle[\mathbf{r}(n)-\mathbf{r}_0]^2\rangle\right\}\right\rangle_{\mathbf{r}_0}. \tag{4.2}$$

The final averaging over $\mathbf{r}_0$ is in general non-Gaussian and cannot be evaluated explicitly. We indicate this by $\langle\cdots\rangle_{\mathbf{r}_0}$ in the expressions where the Gaussian integrals have been evaluated. It is in this form of the general average $\langle f[\mathbf{r}(n)]\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}$ that the ring nature of the polymer chain comes into play. For a ring polymer namely this average does not depend on n, since all the positions along the chain are equivalent.

From Eq. (4.2), we obtain the following simple expression:

$$a^2(\mathbf{r}_0)=\frac{1}{3}\langle[\mathbf{r}(n)-\mathbf{r}_0]^2\rangle=\frac{4l^2}{3N}\sum_{p=1}^{\infty}\frac{1}{\omega_p^2+\zeta_0(\mathbf{r}_0)}=\frac{l^2}{3\zeta_0}\mathscr{L}\left(\frac{\zeta_0 N}{2}\right), \tag{4.3}$$

with $\mathscr{L}(x)$ the standard Langevin function $\mathscr{L}(x)=\mathrm{cth}\,x-(1/x)$. The averaging in the above equation refers only to $p\geqslant 1$ (Gaussian) Rouse components, therefore $a^2=a^2(\mathbf{r}_0)$. Thus we obtain the average of a general function depending on polymer coordinates in the form of a convolution

$$\int_0^N\langle f[\mathbf{r}(n)]\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}dn=\left\langle\int d^3\mathbf{r}f(\mathbf{r})\rho_{a^2}(\mathbf{r},\mathbf{r}_0)\right\rangle_{\mathbf{r}_0},\quad\text{with}\quad\rho_{a^2}(\mathbf{r},\mathbf{r}')=N(2\pi a^2)^{-3/2}\exp\left(-\frac{|\mathbf{r}-\mathbf{r}'|^2}{2a^2}\right), \tag{4.4}$$

where $\rho_{a^2}(\mathbf{r},\mathbf{r}')$ is the Green's function of diffusion equation. With this, we can go back to the expression for $\langle\mathscr{H}_\phi(N)-\mathscr{H}_0(N)\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}$ [Eq. (4.1)] obtaining

$$\beta\langle\mathscr{H}_\phi(N)-\mathscr{H}_0(N)\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}=i\beta\left\langle\int d^3\mathbf{r}\phi(\mathbf{r})\rho_{a^2}(\mathbf{r},\mathbf{r}_0)\right\rangle_{\mathbf{r}_0}+\beta\left\langle\int d^3\mathbf{r}\phi_{\mathrm{ex}}(\mathbf{r})\rho_{a^2}(\mathbf{r},\mathbf{r}_0)\right\rangle_{\mathbf{r}_0}-\left\langle\frac{3}{2}\zeta_0^2(\mathbf{r}_0)Na^2(\mathbf{r}_0)\right\rangle_{\mathbf{r}_0}$$

$$-\beta N\langle\mathscr{L}_0(\mathbf{r}_0)\rangle_{\mathbf{r}_0}+\frac{1}{2}\beta\int\int\phi(\mathbf{r})u^{-1}(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}')d^3\mathbf{r}\,d^3\mathbf{r}'. \tag{4.5}$$

We note at this point that the "3" in the third term of the right-hand side of the above equation refers simply to the number of components of a vector. In a D-dimensional space, we would thus have 3 → D (see below). What remains now is the final $\phi(\mathbf{r})$ integration, which is again Gaussian and can be evaluated exactly leading to

$$\langle\langle\exp[-\beta\langle\mathscr{H}_\phi(N)-\mathscr{H}_0(N)\rangle_{\mathscr{H}_0[\mathbf{r}(n)]}]\rangle\rangle_{\phi(\mathbf{r})}=\int\mathscr{D}\phi(\mathbf{r})\exp[-\beta\langle\mathscr{H}_\phi(N)-\mathscr{H}_0(N)\rangle_{\mathscr{H}_0(\mathbf{r}(n))}]$$

$$=\det[\beta u^{-1}(\mathbf{r},\mathbf{r}')]^{-1/2}\exp[-\beta<\Delta\mathscr{H}_\phi(N)>]. \tag{4.6}$$

We have thus derived the expression for $\langle\Delta\mathscr{H}_\phi(N)\rangle$ that has a succinctly simple form resembling that of a potential energy of a smeared "particle" with a Gaussian density distribution, i.e.,

$$\beta\langle\Delta\mathscr{H}_\phi(N)\rangle=-\frac{3}{2}\langle\zeta_0^2(\mathbf{r}_0)Na^2(\mathbf{r}_0)\rangle_{\mathbf{r}_0}-\beta N\langle\mathscr{L}_0(\mathbf{r}_0)\rangle_{\mathbf{r}_0}+\beta\int d^3\mathbf{r}\langle\phi_{\mathrm{ex}}(\mathbf{r})\rho_{a^2}(\mathbf{r},\mathbf{r}_0)\rangle_{\mathbf{r}_0}$$
$$+\frac{1}{2}\beta\int\int d^3\mathbf{r}\,d^3\mathbf{r}'\langle\rho_{a^2}(\mathbf{r},\mathbf{r}_0)u(\mathbf{r},\mathbf{r}')\rho_{a^2}(\mathbf{r}',\mathbf{r}_0)\rangle_{\mathbf{r}_0}. \tag{4.7}$$

It is the last term in the above expression that sets it apart from the original Feynman–Kleinert variational equations. At this point, it is also easy to calculate $\mathscr{F}_0$, which apart from the final $\mathbf{r}_0$ integration, again reduces to Gaussian integrals yielding

$$\mathscr{F}_0=-kT\ln\langle e^{-\beta\mathscr{H}_0(N)}\rangle_{\mathbf{r}(n)}=-kT\ln\int d^3\mathbf{r}_0\exp(-\beta N\mathscr{L}_0(\mathbf{r}_0)-3\ln\sinh\{[\zeta(\mathbf{r}_0)N]/2\}/[\zeta(\mathbf{r}_0)N]/2). \tag{4.8}$$

V. VARIATIONAL DETERMINATION OF $\zeta_0(\mathbf{r}_0)$ AND $\mathscr{L}_0(\mathbf{r}_0)$

We showed before that $\mathscr{F}_{\mathrm{trial}}=\mathscr{F}_0+<\Delta\mathscr{H}_\phi(N)>$ is always an upper bound for the exact free energy of the system. By minimizing it with respect to $\zeta_0(\mathbf{r}_0)$ as well as $\mathscr{L}_0(\mathbf{r}_0)$, we obtain, following Kleinert,[7] from the first variation $\delta_{\mathscr{L}_0(\mathbf{r}_0)}\mathscr{F}_{\mathrm{trial}}[\zeta_0(\mathbf{r}_0),\mathscr{L}_0(\mathbf{r}_0)]=0$,

$$\beta N\mathscr{L}_0(\mathbf{r}_0)=-\tfrac{3}{2}\zeta_0^2(\mathbf{r}_0)Na^2+\beta W(\mathbf{r}_0), \tag{5.1}$$

where we introduced the "chain smeared" potential energy of the form

$$W(\mathbf{r}_0)=\int d^3\mathbf{r}\,\phi_{\mathrm{ex}}(\mathbf{r})\rho_{a^2}(\mathbf{r},\mathbf{r}_0)$$
$$+\frac{1}{2}\int\int d^3\mathbf{r}\,d^3\mathbf{r}'\rho_{a^2}(\mathbf{r},\mathbf{r}_0)u(\mathbf{r},\mathbf{r}')\rho_{a^2}(\mathbf{r}',\mathbf{r}_0). \tag{5.2}$$

Also from $\delta_{\zeta_0(\mathbf{r}_0)}\mathscr{F}_{\mathrm{trial}}[\zeta_0(\mathbf{r}_0),\mathscr{L}_0(\mathbf{r}_0)]=0$, it follows, after taking into account the definition of a^2, i.e., Eq. (4.3), that

$$\frac{3}{2}\zeta_0^2(\mathbf{r}_0)N=\beta\frac{\partial}{\partial a^2}W(\mathbf{r}_0). \tag{5.3}$$

Equations (5.1) and (5.3) are the Euler–Lagrange equations pertaining to the variational problem. Evaluating the minimized free energy, we obtain

$$\mathscr{F}=-kT\ln\int d^3\mathbf{r}_0e^{-\beta F_0(\mathbf{r}_0)}, \tag{5.4}$$

where $F_0(\mathbf{r}_0)$ is now the effective one particle Hamiltonian that has the form

$$\beta F_0(\mathbf{r}_0)=3\ln\sinh\{[\zeta(\mathbf{r}_0)N]/2\}/\{[\zeta(\mathbf{r}_0)N]/2\}$$
$$-\frac{3}{2}\zeta_0^2(\mathbf{r}_0)Na^2(\mathbf{r}_0)+\beta W(\mathbf{r}_0). \tag{5.5}$$

One should note here that dependence on $\mathbf{r}_0$ of the effective one particle Hamiltonian is in no way simple in general. Only if the external field is zero and the intrachain potential is independent of the absolute coordinates, thus restoring the homogeneity of the space, does $F_0(\mathbf{r}_0)$ not depend on $\mathbf{r}_0$ and becomes equal to the minimized free energy.

VI. CONFIGURATIONAL PROPERTIES OF THE POLYMER CHAIN

Configurational properties of the polymer chain are represented by different averages that can be traced back to a single segment–segment correlation function of the form

$$\mathscr{G}_0(n,m)=\langle\mathbf{r}(n)\mathbf{r}(m)\rangle_{\mathscr{H}_0(N)}$$
$$=\left\langle r_0^2+\sum_{p=1}^{\infty}r_C^2(p)\cos\omega_pn\cos\omega_pm\right.$$
$$\left.+\sum_{p=1}^{\infty}r_S^2(p)\sin\omega_pn\sin\omega_pm\right\rangle_{\mathscr{H}_0(N)}. \tag{6.1}$$

As before, the $\langle\cdots\rangle_{\mathscr{H}_0(N)}$ average in the above equation consists of averaging over the Gaussian variables $\mathbf{r}_C(p)$ and $\mathbf{r}_S(p)$, as well as in the final averaging over $\mathbf{r}_0$. Thus we can derive from the above definition

$$\mathscr{G}_0(n,m)=\left\langle r_0^2+\sum_{p=1}^{\infty}r_C^2(p)\cos\omega_p(n-m)\right\rangle_{\mathscr{H}_0(N)}$$
$$=\left\langle r_0^2+\frac{l^2}{\zeta_0}\left\{\frac{\cosh\zeta_0[(N/2)-|n-m|]}{\sinh[(\zeta_0N)/2]}\right.\right.$$
$$\left.\left.-\frac{2}{\zeta_0N}\right\}\right\rangle_{\mathbf{r}_0}. \tag{6.2}$$

Other quantities that are of importance in the chain statistics follow simply from this expression. First of all, there are the two quantities describing the global statistical properties of the chain as a whole. These are the mean dimension of the chain (the mean end to end separation of the chain for an open chain) defined in the case of a ring chain as

$$\mathscr{R}^2=\left\langle\left[\mathbf{r}\left(\frac{N}{2}\right)-\mathbf{r}(0)\right]^2\right\rangle_{\mathscr{H}_0(N)}$$
$$=2\left[\mathscr{G}_0\left(\frac{N}{2},\frac{N}{2}\right)-\mathscr{G}_0\left(\frac{N}{2},0\right)\right]$$
$$=\left\langle\frac{2l^2}{\zeta_0}\tanh\frac{\zeta_0N}{4}\right\rangle_{\mathbf{r}_0}, \tag{6.3}$$

as well as the mean radius of gyration

$$\mathscr{R}_G^2=\frac{1}{N}\left\langle \int_0^N \left[\mathbf{r}(n)-\frac{1}{N}\int_0^N \mathbf{r}(m)dm\right]^2 dn\right\rangle_{\mathscr{H}_0(N)}$$

$$=\mathscr{G}_0(N,N)-\frac{1}{N^2}\int_0^N\int \mathscr{G}_0(n,m)dn\,dm=\left\langle \frac{l^2}{\zeta_0}\left[\coth\frac{\zeta_0 N}{2}-\frac{4}{(\zeta_0 N)}+\frac{4}{(\zeta_0 N)^2}\tanh\frac{\zeta_0 N}{4}\right]\right\rangle_{\mathbf{r}_0}. \tag{6.4}$$

One can define also quantities that describe the properties of the chain locally. One of them is the mean square distance between two segments along the chain that can be derived as

$$\mathscr{R}^2(n,m)=\langle[\mathbf{r}(n)-\mathbf{r}(m)]^2\rangle_{\mathscr{H}_0(N)}=2[\mathscr{G}_0(n,n)-\mathscr{G}_0(n,m)]=\left\langle \frac{2l^2}{\zeta_0}\left\{\coth\frac{\zeta_0 N}{2}-\frac{\cosh\zeta_0[(N/2)-|n-m|]}{\sinh[(\zeta_0 N)/2]}\right\}\right\rangle_{\mathbf{r}_0}. \tag{6.5}$$

Another quantity describing a local property of the chain is the orientational correlation function, whose regular part [thus the part aside from $l^2\delta(n-m)$] can be obtained in the form

$$\langle\mathbf{n}(n)\mathbf{n}(m)\rangle=\left\langle\left[\frac{d\mathbf{r}(n)}{dn}\right]\left[\frac{d\mathbf{r}(m)}{dm}\right]\right\rangle_{\mathscr{H}_0(N)}=-\frac{1}{2}\frac{d^2}{dn\,dm}\mathscr{R}^2(n,m)=\left\langle l^2\zeta_0\frac{\cosh\zeta_0[(N/2)-|n-m|]}{\sinh[(\zeta_0 N)/2]}\right\rangle_{\mathbf{r}_0}. \tag{6.6}$$

Some caution has to be exercised while deriving the $\zeta_0\to 0$ limit in the above equations. The appropriate procedure is to include the $p=0$ term into the different summations, and only then make the $\zeta_0\to 0$ limit. This does not effect the results for $\zeta_0\neq 0$, but gives the correct form of the Gaussian limit.

VII. PROPERTIES OF A CHAIN WITH INTRACHAIN INTERACTIONS

If there is no external potential, then we remain with the following expression for the "chain smeared" potential energy in D-dimensional space:

$$W=\frac{1}{2}\int\int d^D\mathbf{r}\,d^D\mathbf{r}'\rho_{a^2}(\mathbf{r},\mathbf{r}_0)u(\mathbf{r},\mathbf{r}')\rho_{a^2}(\mathbf{r}',\mathbf{r}_0)$$

$$=\frac{1}{2}\int\frac{d^D\mathbf{k}}{(2\pi)^D}|\rho_{a^2}(\mathbf{k})|^2u(\mathbf{k}) \tag{7.1}$$

that does not depend on $\mathbf{r}_0$. In the above equation, we assumed that $u(\mathbf{r},\mathbf{r}')$ and $\rho_{a^2}(\mathbf{r},\mathbf{r}')$ have Fourier transforms.

The first case we treat explicitly is the electrostatic intersegment potential, which is a solution of the Laplace equation in D dimensions and whose Fourier transform should thus have the form $u(\mathbf{k})=(e_0^2/\epsilon\epsilon_0)k^{-2}$, where e_0 is the charge residing on each monomer, while other symbols are standard. In this case, we get

$$W=\frac{e_0^2N^2}{2\epsilon\epsilon_0(4\pi)^{D/2}[(D/2)-1](a^2)^{(D/2)-1}}. \tag{7.2}$$

The variational condition (5.3) together with the definition (4.3), thus read

$$\frac{D}{2}(\zeta_0 N)^2=-\frac{\beta e_0^2l^2}{6\epsilon\epsilon_0(4\pi)^{D/2}}\frac{N^{3-(D/2)}}{(a^2/N)^{D/2}}$$

and

$$\frac{l^2}{3(\zeta_0 N)}\mathscr{L}\left(\frac{\zeta_0 N}{2}\right)=\frac{a^2}{N} \tag{7.3}$$

and have to be solved simultaneously. It follows from the above two equations that ζ_0 has to be imaginary (its square has to be negative). This is no surprise since the presence of an intrachain repulsive potential in general swells the chain. Also we note that for $D\geqslant 6$ [i.e., for $3-(D/2)<0$], the solution of the above equations will always be $a^2/N=\text{const.}$, which corresponds to a random flight chain. The borderline dimensionality $D=6$ is thus the upper critical dimension for the electrostatically self-interacting chain, in complete accord with the Lagrangian renormalization group calculations.[19] Below $D=6$ (and thus also in three dimensions), we derive the following approximate (Flory type) equation, satisfied by a^2/N in the scaling limit $N\gg 1$,

$$(\zeta_0 N)^2\cong(2\pi)^2\left[1-\frac{2l^2}{3\pi^2}\frac{N}{a^2}+O(a^{-4})\right]=b(D)\frac{N^{3-(D/2)}}{(a^2/N)^{D/2}}, \tag{7.4}$$

where $b(D)$ depends only on the strength of the electrostatic potential and dimensionality, but does not depend on the length of the chain. The lowest order solution of Eq. (7.4) is

$$a^2\cong C(D)N^{6/D} \tag{7.5}$$

with an appropriate definition of $C(D)$.

The average dimensions of the chain, defined in Eq. (6.3) for the limiting case of Eq. (7.5), can be obtained in the form

$$\mathscr{R}^2=\left\langle\left[\mathbf{r}\left(\frac{N}{2}\right)-\mathbf{r}(0)\right]^2\right\rangle_{\mathscr{H}_0(N)}\to 12a^2. \tag{7.6}$$

The dependence of $\mathscr{R}^2$ on the length of the chain indicates that electrostatic intrachain repulsions substantially stiffen up the chain, as can be easily discerned in three dimensions where $\mathscr{R}^2(D=3)\sim N^2$ (the stiff rod limit). By Eq. (6.4), we also have

$$\mathscr{R}^2_G=\frac{1}{N}\left\langle \int_0^N \left[\mathbf{r}(n)-\frac{1}{N}\int_0^N \mathbf{r}(m)dm\right]^2 dn\right\rangle_{\mathscr{H}_0(N)} \rightarrow 3a^2. \tag{7.7}$$

The quantities describing local statistical properties of the chain are the mean square distance between two segments along the chain obtained from Eq. (6.5)

$$\mathscr{R}^2(n,m)=\langle[\mathbf{r}(n)-\mathbf{r}(m)]^2\rangle_{\mathscr{H}_0(N)}$$

$$\rightarrow 6a^2\left(1-\cos 2\pi\frac{|n-m|}{N}\right), \tag{7.8}$$

while the orientational correlation function can be derived in the form (6.6)

$$\langle\mathbf{n}(n)\mathbf{n}(m)\rangle=\left\langle\left[\frac{d\mathbf{r}(n)}{dn}\right]\left[\frac{d\mathbf{r}(m)}{dm}\right]\right\rangle_{\mathscr{H}_0(N)}$$

$$\rightarrow 12\pi^2\frac{a^2}{N^2}\cos 2\pi\frac{|n-m|}{N}. \tag{7.9}$$

It follows from this form of the orientational correlation function that long range orientational correlations along the charged chain are possible only if a^2/N^2 remains finite in the scaling limit, a case attainable for a^2 given by Eq. (7.5) only if $D\leqslant 3$. This is an interesting result. A charged chain in three dimensions should thus not only be fully extended, but should also exhibit long range orientational correlations along the chain.

Equations (7.6)–(7.9) describe a chain of a toroidal statistical shape, a fact consistent with the original presumption of a ring polymer. For an open chain, the situation would be more complicated since long range monomer–monomer interactions would break the symmetry of the space making the polymer chain essentially rodlike.

Let us now examine the excluded volume intrachain potential $u(\mathbf{r},\mathbf{r}')=b\delta^D(\mathbf{r}-\mathbf{r}')$ that can describe not only "ordinary" excluded volume effects, but also the "electrostatic excluded volume" obtained in the case of a strongly screened Coulomb potential. In this case, $b=e_0^2/\epsilon\epsilon_0\kappa^2$. We can derive quite straightforwardly that Eq. (7.3) assumes in this case the form

$$(\zeta_0 N)^2=-\frac{bl^2}{6(4\pi)^{D/2}}\frac{N^{2-(D/2)}}{(a^2/N)^{(D/2)+1}}$$

$$\text{and}\quad \frac{l^2}{3(\zeta_0 N)}\mathscr{L}\left(\frac{\zeta_0 N}{2}\right)=\frac{a^2}{N}. \tag{7.10}$$

We see from these identities that the upper critical dimensionality in this case is $D=4$.[16] The rest of the analysis is the same as in the electrostatic case and we shall not repeat it. The final result that we get is

$$a^2\cong C'(D)N^{6/(D+2)}, \tag{7.11}$$

with the appropriate definition of $C'(D)$. The rest of the general formulas (7.6)–(7.9) remain unchanged if we insert the appropriate definition of a^2, i.e., Eq. (7.11), leading thus to Flory's result for the chain's dimensions in the scaling limit. What needs to be additionally emphasized here is that a chain swollen by excluded volume intrachain interactions does not, in distinction with the electrostatically self-interacting chain, exhibit long range orientational correlations. This simply follows from Eq. (7.9), since with a^2 given by Eq. (7.11), the ratio a^2/N^2 does not remain finite for $N\gg 1$.

VIII. PROPERTIES OF A CHAIN IN EXTERNAL FIELDS

External fields break the symmetry of space, and W in this case depends explicitly on $\mathbf{r}_0$. The analysis outlined in previous sections could thus proceed only numerically as the final $\mathbf{r}_0$ integration is in no way trivial. There is nevertheless a way towards at least a qualitative analytical estimate of the numerical results. It is similar to the procedure used by Büttner and Flytzanis[18] and consists of the additional (saddle point) minimization of the effective free energy $\mathscr{F}_0$ with respect to $\mathbf{r}_0$. This procedure is strictly correct only in the limit when $\mathscr{F}_0$ scales with a positive power of N and $N\gg 1$.

Let us first of all derive the variational equations for the case of electrostatically self-interacting chain in an attractive external field produced by a single point charge e located at $\mathbf{r}_1$. This problem is a distant relative of the problem of polymer adsorption to a planar surface.[5] By the general formula (5.2), we have in this case

$$W(\mathbf{r}_0)=-\frac{ee_0N}{\epsilon\epsilon_0}\mathbf{F}_{a^2}(\mathbf{r}_0,\mathbf{r}_1)$$

$$+\frac{e_0^2N^2}{2\epsilon\epsilon_0}\int\frac{d^D\mathbf{k}}{(2\pi)^D}|\rho_{a^2}(\mathbf{k})|^2u(\mathbf{k}), \tag{8.1}$$

where we introduced

$$\mathbf{F}_{a^2}(\mathbf{r},\mathbf{r}')=\int\frac{d^D\mathbf{k}}{(2\pi)^D}e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}u(\mathbf{k})\rho_{a^2}(\mathbf{k}) \tag{8.2}$$

with $u(\mathbf{k})$ again being the Fourier transform of the Coulomb potential, i.e., $u(\mathbf{k})=k^{-2}$. Evaluating the last integral explicitly in D dimensions, we remain with

$$\mathbf{F}_{a^2}(\mathbf{r},\mathbf{r}')=\frac{2^{(D/2)-2}}{(2\pi)^{D/2}}|\mathbf{r}-\mathbf{r}'|^{2-D}\gamma\left(\frac{D}{2}-1;\frac{|\mathbf{r}-\mathbf{r}'|^2}{2a^2}\right)$$

$$=\frac{1}{2(2\pi)^{D/2}[(D/2)-1](a^2)^{(D/2)-1}}$$

$$\times\left[1-\left(1-\frac{2}{D}\right)\frac{|\mathbf{r}-\mathbf{r}'|^2}{2a^2}+O\left(\frac{|\mathbf{r}-\mathbf{r}'|^4}{4a^4}\right)\right]. \tag{8.3}$$

The function $\gamma(\alpha;x)$ is the incomplete gamma function.[20] We are now ready to write down the variational conditions Eqs. (5.3) and (4.3) that assume the form

$$\frac{D}{2}(\zeta_0 N)^2 = \frac{\beta l^2}{6\epsilon\epsilon_0(4\pi)^{D/2}} \frac{N^{2-(D/2)}}{\left(\frac{a^2}{N}\right)^{D/2}} \times (ee_0 2^{D/2} e^{-[(|\mathbf{r}_0-\mathbf{r}_1|^2)/(2\alpha^2)]} - e_0^2 N)$$

and

$$\frac{l^2}{3(\zeta_0 N)} \mathscr{L}\left(\frac{\zeta_0 N}{2}\right) = \frac{a^2}{N}. \tag{8.4}$$

The above relation embodies in the clearest way the distinction between the approach devised by Muthukumar,[5] where an effective step length is determined irrespective of the strength of the external potential, and the approach advocated here where both the external and the intersegment potentials compete in the determination of the "effective step length."

As already announced, we shall proceed towards obtaining simplified analytic solutions through an additional minimization of the effective free energy with respect to $\mathbf{r}_0$. This gives us $\mathbf{r}_0 \cong \mathbf{r}_1$. A further consequence of this additional minimization of the free energy is that the monomer density is now simply a Gaussian centered at the value of $\mathbf{r}$ obtained from the minimization of the free energy, i.e. $\mathbf{r} \cong \mathbf{r}_1$. The solution of Eqs. (8.4) now depends solely on the sign and magnitude of $\varepsilon = (ee_0 2^{D/2} - e_0^2 N)$. If $\varepsilon \ll 0$, we are back to the solution (7.5). In the opposite case, we obtain a new type of behavior

$$a^2 = C''(D)\left(\frac{e}{e_0}\right)^{2/(D-4)} \tag{8.5}$$

with an appropriate definition of $C''(D)$ that is independent of N. As is clear from Eq. (8.4), this type of behavior can set in only if $D<4$ [i.e., for $2-(D/2)>0$]. We note that a^2 in this case does not depend on N at all. It only depends on the strength of the external potential $|u| \sim e/e_0$, as $a^2(D=3) \sim |u|^{-2}$, and $a^2(D=2) \sim |u|^{-1}$. This observation remains valid only for not too long chains, while for long chains, we should have $a^2(D=3) \sim N^{2/3}$, if the three-body potential would be taken into account.[9]

Result (8.5) is typical for a spatially localized chain,[11] where the overwhelming strength of the external field is counteracted only by the chain entropy and not by intrachain repulsions. The upper critical dimension for localization of the chain is $D=4$. For $6 > D \geqslant 4$, the chain is always swollen, while for $D \geqslant 6$, we are back to the free flight results. A sequence localized-swollen Gaussian is therefore typical for this problem as one goes from low to high dimensionalities.

Interestingly enough, these results do not hold any more for an excluded volume chain in a delta-like (contact) external potential, thus for $\phi_{\mathrm{ex}}(\mathbf{r}) = -b'\delta(\mathbf{r}-\mathbf{r}_1)$. In this case, it follows straightforwardly from Eq. (5.3)

$$\frac{D}{2}(\zeta_0 N)^2 = \frac{D}{2} \frac{bl^2}{6(4\pi)^{D/2}} \frac{N^{1-(D/2)}}{(a^2/N)^{(D/2)+1}} \times \{b' 2^{D/2} \exp - [(|\mathbf{r}_0-\mathbf{r}_1|^2)/(2a^2)] - bN\}. \tag{8.6}$$

Clearly in this case the upper critical dimensionality for the localization to set in is $D=2$ [i.e., for $1-(D/2)<0$] and the physically interesting case is within the domain of a swollen chain. This conclusion is quite important for the effective polymer chain mediated forces between two point attractive potentials.

Returning now to the statistical properties of a spatially localized polymer chain, we first of all note that the solution (8.5) implies a real value for ζ_0, as opposed to its imaginary value in the case of a swollen chain [Eq. (7.5)]. The mean end–end separation squared and the radius of gyration squared in this case behave as

$$\mathscr{R}^2 \to 6a^2, \quad \mathscr{R}_G^2 \to 3a^2. \tag{8.7}$$

The local statistical properties of the chain suggest a picture of a locally stiff chain, with an effective stiffness depending on the magnitude of the external potential,

$$\mathscr{R}^2(n,m) \to 6a^2\{1-\exp[-(l^2/3a^2)|n-m|]\},$$
$$\langle \mathbf{n}(n)\mathbf{n}(m) \rangle_{\mathscr{H}_0(N)} \to \frac{l^4}{3a^2} \exp[-(l^2/3a^2)|n-m|]. \tag{8.8}$$

The polymer chain could thus be envisioned in this limit as being stiff on a very small scales [Eq. (8.8)] becoming progressively floppier as we go to larger scales, behaving finally globally as Eq. (8.7), a result which is certainly not close to a persistent chain limit.[21] The statistical properties of a localized chain thus belong to a special class, being quite different from the properties of a swollen or of a random flight chain.

IX. POLYMER CHAIN MEDIATED ELECTROSTATIC INTERACTIONS

We now address the situation where a polymer chain is in an attractive external (electrostatic) potential of several (two in this case) point charge carriers. After integrating the partition function over the polymer degrees of freedom, we remain with a free energy that depends only on the coordinates of the external point charge carriers. It thus makes sense to talk of a polymer-mediated force between point charges, stemming from the dependence of the effective free energy on their coordinates.

If we have two point charges of magnitudes e_1 and e_2, and of sign opposite to the resident monomer charges (e_0) situated at $\mathbf{r}=\mathbf{r}_1$ and $\mathbf{r}=\mathbf{r}_2$, then the variational equations can be derived in the form

$$\frac{D}{2}(\zeta_0N)^2=\frac{\beta l^2}{6\epsilon\epsilon_0(4\pi)^{D/2}}\frac{N^{2-(D/2)}}{(a^2/N)^{D/2}}$$
$$\times\{e_1e_02^{D/2}\exp-[(|\mathbf{r}_0-\mathbf{r}_1|^2)/(2a^2)]$$
$$+e_2e_02^{D/2}\exp-[(|\mathbf{r}_0-\mathbf{r}_2|^2)/(2a^2)]-e_0^2N\} \tag{9.1}$$

together with

$$\frac{l^2}{3(\zeta_0N)}\mathscr{L}\left(\frac{\zeta_0N}{2}\right)=\frac{a^2}{N}. \tag{9.2}$$

The effective free energy (5.5) for this system can be cast into the form

$$\beta\mathscr{F}_{\mathrm{tot}}=\frac{\beta e_1e_2}{4\pi2\epsilon\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|}+\beta\mathscr{F}_0$$
$$=\frac{\beta e_1e_2}{4\pi\epsilon\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|}+D\ln\frac{\sinh\zeta_0N}{\zeta_0N}-\frac{3D}{2l^2}(\zeta_0N)^2\left(\frac{a^2}{N}\right)$$
$$+\frac{\beta[e_0^2N^2-2^{(D/2)-1}(e_1e_0+e_2e_0)N]}{2\epsilon\epsilon_0(4\pi)^{D/2}[(D/2)-1](a^2)^{(D/2)-1}}$$
$$-\frac{\beta e_1e_0N}{\epsilon\epsilon_0}\mathbf{F}_{a^2}(\mathbf{r}_0,\mathbf{r}_1)-\frac{\beta e_2e_0N}{\epsilon\epsilon_0}\mathbf{F}_{a^2}(\mathbf{r}_0,\mathbf{r}_2), \tag{9.3}$$

where the definition of $\mathbf{F}_{a^2}(\mathbf{r},\mathbf{r}')$ is the same as before. Clearly, the dependence of $\mathscr{F}_{\mathrm{tot}}$ on the separation between the external charges is composed of two terms, the first one being the direct electrostatic interaction between the two point charges and the second one denoting the polymer chain-mediated interaction. The solution of the variational equations (9.1) and (9.2) is obviously not straightforward and we introduce here the same device as in the previous section to make it tractable. However, one immediately notes that the minimization of Eq. (9.3) with respect to $\mathbf{r}_0$ is not trivial either. Approximate analytical solutions can only be derived for the limit of small and/or large $(|\mathbf{r}_1-\mathbf{r}_2|^2)/(2a^2)$.

The limit of $(|\mathbf{r}_1-\mathbf{r}_2|^2)/(2a^2)\gg 1$ can only be strictly attained in the case that $a^2\rightarrow$const, i.e., in the case of a localized chain [Eq. (8.5)]. If the chain is not localized, then it is generally swollen and a^2 scales with a positive power of N. Thus for any value of $|\mathbf{r}_1-\mathbf{r}_2|$, a can be larger if only we choose a large enough N. In the asymptotic limit of large $|\mathbf{r}_1-\mathbf{r}_2|$, it is thus enough to analyze only the case of a localized chain.

The minimization of the free energy (9.3) in the limit of large $|\mathbf{r}_1-\mathbf{r}_2|$ gives two solutions, either $\mathbf{r}_0\cong\mathbf{r}_1$ or $\mathbf{r}_0\cong\mathbf{r}_2$. They are equivalent only if $e_1=e_2$. If this is not the case, then the localized solution is the one, for which one has $(e_0^2N^2-2^{D/2}e_ie_0N)\leqslant 0$, with index i being either one or two [compare the discussion following Eq. (8.4)]. If the chain is localized in the vicinity of the charge e_1 and taking note of the small argument expansion of the $\mathbf{F}_{a^2}(\mathbf{r},\mathbf{r}')$ function, we can derive the total free energy of the system as

$$\beta\mathscr{F}_{\mathrm{tot}}\cong\frac{Dl^2}{6}\left(\frac{N}{a^2}\right)+\frac{\beta(e_0^2N^2-2^{D/2}e_1e_0N)}{2\epsilon\epsilon_0(4\pi)^{D/2}[(D/2)-1](a^2)^{(D/2)-1}}$$
$$+\frac{\beta(e_1e_2-e_1e_0N)}{4\pi\epsilon\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|}, \tag{9.4}$$

where a^2 is given by Eq. (8.5) and depends solely on the value of the charges of the two point sources. A similar expression can be derived for the chain localization at the point $\mathbf{r}_0\cong\mathbf{r}_2$. The total free energy thus contains a long range interaction term whose magnitude depends on the magnitudes of the charges involved. The long range polymer-mediated forces have an interesting twist to them in the case that $e_1=e_2=\frac{1}{2}e_0N$, corresponding to an overall electrically neutral system. Then it follows from Eq. (9.1) that only if $2<D<4$ can there be chain localization and a long range attraction at large separations between the two charges. This condition is fulfilled **only** for the physically interesting case of $D=3$. Also, in this case, the interaction between the two charges is the same as if the polymer was absent, but with a sign reversed (attraction instead of repulsion). This result is expected but it is quite surprising that it is valid only in $D=3$.

Now we analyze the small separation expansion, i.e., the case $(|\mathbf{r}-\mathbf{r}'|^2)/(2a^2)\ll 1$. For a swollen chain, this is the limit valid for practically all separations if only the chain is long enough. The minimization of the free energy with respect to $\mathbf{r}_0$ gives in this case $\mathbf{r}_0\cong\frac{1}{2}(\mathbf{r}_1+\mathbf{r}_2)$. By expanding the free energy (9.3) as well as the variational equation (9.1) to the second order in $(|\mathbf{r}-\mathbf{r}'|)/(\sqrt{2}a)$, we obtain the following limiting behavior: If $[2^{D/2}(e_1+e_2)e_0N-e_0^2N^2]\gg 0$, then the solution of the variational equation (9.1) is given in the lowest order by Eq. (8.5), while the free energy expansion is

$$\beta\mathscr{F}_{\mathrm{tot}}\cong\frac{\beta e_1e_2}{4\pi\epsilon\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|}+\frac{Dl^2}{6}\left(\frac{N}{a^2}\right)\left[-\frac{4-D}{D-2}+\frac{2^{D/2}(e_1+e_2)e_0N}{2^{D/2}(e_1+e_2)e_0N-e_0^2N^2}\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{Da^2}+\cdots\right]. \tag{9.5}$$

The polymer-mediated part of this free energy scales as N and is bound to be very large in the scaling limit overwhelming the direct Coulomb repulsion for not too small values of $|\mathbf{r}_1-\mathbf{r}_2|$. If, however, we have $[2^{D/2}(e_1+e_2)e_0N-e_0^2N^2]\leqslant 0$, then the variational equation has the lowest order solution (7.5) and the free energy has the expansion

$$\beta\mathscr{F}_{\mathrm{tot}}\cong\frac{\beta e_1e_2}{4\pi\epsilon\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|}-D+\frac{3D\pi^2}{2}\frac{D}{D-2}\left(\frac{a^2}{l^2N}\right)-D\ln\frac{a^2}{l^2N}+\frac{3\pi^2}{2}\frac{2^{D/2}(e_1+e_2)e_0N}{e_0^2N^2-2^{D/2}(e_1+e_2)e_0N}\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{Nl^2}\left(1-\frac{Nl^2}{a^2}\right)+\cdots. \tag{9.6}$$

The polymer part of the last result is basically the Gaussian limit for a free flight chain under elastic traction. Since the polymer-mediated interactions scale inversely to the length of the chain in this limit, they are bound to be small. We note that for very small separation between external charges, the direct Coulomb repulsion always dominates the interactions.

There is another interesting conclusion that follows from the approximate expressions above, in the case of a chain that is localized at small as well as at large interionic separations. Since the minimized $\mathbf{r}_0$ in both limits is either $\frac{1}{2}(\mathbf{r}_1+\mathbf{r}_2)$ or $\mathbf{r}_i$, where $i=1$ or 2, there should be a symmetry breaking transition at an intermediate separation $|\mathbf{r}_1-\mathbf{r}_2|=D_c$ that we can derive from Eq. (9.1) as

$$D_c^2 \cong 2Nl^2 \ln \frac{e_2 e_0 2^{D/2}}{e_0^2 - e_1 e_0 2^{D/2}}. \tag{9.7}$$

For $|\mathbf{r}_1-\mathbf{r}_2| \leqslant D_c$, the chain should be symmetrically distributed with respect to both point charges, whereas in the opposite case, it should be preferentially localized around one of the point charges. This transition is closely related to the monomodal–bimodal symmetry breaking transition observed with a polyelectrolyte chain confined inside a planar slab.[2]

X. DISCUSSION

The variational principle as applied to an effective Gaussian *ansatz* (2.6) proved to be quite instrumental for derivation of simple limiting or asymptotic relations valid for a charge polymer chain in external fields in the scaling limit. In this limit, our original supposition of a closed chain is not particularly important, but does help substantially to keep the algebra as transparent as possible. The results obtained in Sec. VII for a bulk electrostatically self-interacting chain conform favorably to previous nonperturbative derivations of the charged polymer properties. Result (7.5) together with Eq. (7.6) conforms to the Flory-type derivation, but in general differs from the Lagrangian renormalization group and scaling results.[19] It also conforms closely to the results of other nonperturbative methods such as those based on the "effective medium" theories[22] or the Langer–Zittartz method.[23] The result for the sterically self-interacting chain (7.11) is again the same as the one given by the Flory-type derivation. Also, it is interesting to note that the diagonal variational *ansatz* leads to good approximations even in the case of excluded volume interactions (short range delta potential), where the more general quadratic *ansatz* fails.[17]

The configurational properties of an electrostatically stiffened chain [cf. Eqs. (7.8) and (7.9)] were found to display long range orientational correlations even in the limit of large N. A Coulombic chain should thus belong to a wholly different "universality class" that is not reducible to a Gaussian chain in any limit, in contradiction to the persistent chain that always attains a Gaussian like behavior if only it is long enough.

The picture of a localized chain provided by Eqs. (8.7) and (8.8) is intuitively clear. The chain is packed into a very small volume and is stiff on the scales of the order of $|u|^{-2}$, where $|u|$ is the strength of the external potential. This scale of the stiffening of the chain can become quite large in the case that $(ee_0 2^{D/2} - e_0^2 N) \gtrsim 0$. The quantity a would in this case essentially play the role of a correlation length close to a second order phase transition, corresponding in the scaling limit $N \to \infty$ to a localized→free chain transformation.

Localization of the charged chain in three dimensions in the case of an electrostatically neutral system (the charge residing on the polymer is equal but of opposite sign to the magnitude of the two point charges) has profound influences on their interaction. In this case, the total force between the two charges is quasielastic at small separations, i.e., it goes approximately as the separation between the two [see Eq. (9.5)]. The magnitude of this force is quite large and scales linearly with the length of the chain. This is quite unexpected since the ordinary elastic energy of the chain should look more like Eq. (9.6), being inversely proportional to N. Even more so is the force at large separations, i.e., Coulombic in its form, but of opposite sign [see Eq. (9.4)]. The localization of the chain together with its symmetry breaking leap to one of the external charges leads to a charge reversal of that particular point charge. These conclusions are quite intuitive, but it does come as a surprise that they are valid only in $D=3$ (see Sec. IX). They are thus not valid for, e.g., polymers adsorbed to a surface that lie mostly in the plane of adsorption.

There is another interesting general conclusion that one can draw regarding the polymer mediated interactions. If the polymer chain is in a field created by a frozen configuration of point charges e_i (with $i=1, M$), then the effective free energy would contain terms of the form $\Sigma_{i=1}^{M} \mathbf{F}_{a^2}(\mathbf{r}_0,\mathbf{r}_i)$. The variational condition (9.1) would thus contain a sum of Gaussians centered at $\mathbf{r}_i$. Should we now apply the minimization with respect to $\mathbf{r}_0$ to the effective free energy, we would obtain M approximate solutions $\mathbf{r}_0 \cong \mathbf{r}_i$ for the case where $(|\mathbf{r}_i-\mathbf{r}_k|)/a \gg 1$. That would mean that the polymer mediated interaction in this limit is pairwise additive. In the opposite limit of $(|\mathbf{r}_i-\mathbf{r}_k|)/a \ll 1$, an approximate solution would be $\mathbf{r}_0 \cong (1/M)\Sigma_{i=1}^{M}\mathbf{r}_i$. This solution leads to nonpairwise additive forces. Introduction of an effective interparticle potential to describe the interactions between the M charged particles would thus only make sense at extreme dilution.

There are several obvious ways of generalizing the variational approach to self-interacting polymer chains as was detailed above. Aside from relaxing the ring chain constraint, one direction would be to generalize the *ansatz* (2.5) itself, let us say by treating the first P and not just $p=0$, treating Rouse components explicitly, and the rest quadratically. Also the quadratic coupling in Eq. (2.5) could be generalized in the sense to include nondiagonal Rouse components as well. The generalizations of this type have been considered in detail by Kleinert[7] and shown to lead to no spectacular improvements of the original variational *ansatz*. On the other hand, the introduction of the full non"diagonalized" quadratic *ansatz*, as in the work of Jönsson, Peterson, and Söderberg,[15] is apparently appropriate only for long range potentials, where it is extremely accurate, and does not lend itself to easily analytical estimates. Our work might thus be seen as complementary to variational approaches of this type.

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