A variational approach to charged polymer chains: Polymer mediated interactions

R. Podgornik
Physical Chemistry 2, Chemical Center, P.O. Box 124, S-22100 Lund, Sweden
(Received 10 December 1992; accepted 8 July 1993)

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 recently1,2 after it was realized3 that the connectivity of polymer chains can confer a strong attraction to nominally 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 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 approaches1-3 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 Muthukumar5 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 physics6 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
treated exactly. When one tries to implement this idea formally, one is basically applying a modified Feynman-Kleinert variational principle to the statistics of a self-interacting polymer chain.

Variational principles of a similar type have been applied to other problems as well as to polymers before. As already stated, the "effective medium" theory, implemented for the polymer case by Edwards and Singh, has found a wide variety of applications. 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. The variational procedure employed in this case was in fact the original Feynman approach. 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. The variational equations have been solved numerically for a Coulombic polymer and found to comply almost exactly with Monte Carlo simulations. 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 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

$$\Xi(N) = \int \mathcal{D} \mathbf{r}(r) e^{-\beta \mathcal{H}(N)},$$

(2.1)

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

$$\beta \mathcal{H}(N) = \frac{3}{2L} \int_0^N \frac{d^2r(n)^2}{d\mathbf{r}(n)} dn + \frac{1}{2} \beta \int_0^N \int u[r(n),r(n')] dn dn'$$

$$+ \beta \int_0^N \phi_{\text{ext}}[\mathbf{r}(n)] dn,$$

(2.2)

where $u[r(n),r(n')]$ is the intersegment interaction energy, $\phi_{\text{ext}}[\mathbf{r}(n)]$ 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 for the instantaneous configuration of the chain

$$\mathbf{r}(n) = r_0 + \sum_{p=1}^{\infty} r_C(p) \cos \omega_p n + \sum_{p=1}^{\infty} r_S(p) \sin \omega_p n,$$

with $\omega_p = 2\pi p / N$ (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 $r_0$ 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

$$\frac{3}{2L} \int_0^N \left[ \frac{d^2r(n)}{dn} \right]^2 dn = \frac{3N}{8L^3} \sum_{p=1}^{\infty} \omega_p^2 \left[ r_C^2(p) + r_S^2(p) \right]$$

(2.4)

effectively damps all the higher order ($p \geq 1$) contributions to the polymer total energy that correspond to more convoluted polymer configurations. One could thus hope that the contribution of the $p \geq 1$ terms to the partition function would be adequately represented by an effective harmonic configurational Hamiltonian of the form
so that the partition function could be obtained from an effective one particle configurational sum as

\[
\Xi_0(N) = \int \mathcal{D} \mathbf{r}(n) e^{-\beta \mathcal{H}_0(n)} = \int d^3 r_0 e^{-\beta \mathcal{H}_0(0)}.
\]

The whole polymer chain would be thus represented as an effective single particle with the as yet unspecified parameters \( \xi_0(0_0) \) and \( \mathcal{L}_0(0_0) \) 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 \((\xi_0 \text{ and } \mathcal{L}_0)\), while in his case, they are the variance of the Gaussian and the effective step length \((\xi_0 \text{ and } \mathcal{L}_0)\).

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-Stratonovich) 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

\[
\Xi(N) = \int \mathcal{D} \mathbf{r}(n) e^{-\beta \mathcal{H}_d(n)}
\]

\[
= \Xi_d(N) \int \mathcal{D} \mathbf{r}(n) \mathcal{D} \phi(n) e^{-\beta \mathcal{H}_d(n)}
\]

\[
= \langle \langle e^{-\beta \mathcal{H}_d(n)} \rangle \rangle_{\phi(n)}
\]

\[
= \langle e^{-\beta \mathcal{H}_d(n)} \rangle.
\]

The triangular bracket notation, as in \(\langle \cdots \rangle_{\phi(n)}\), 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 \(\lim_{\mathcal{L}_d \to 0} d \phi (1) d \phi (2) \cdots d \phi (N) \to \mathcal{D} \phi (n)\). Apart from that, the following notation was introduced in the above equation:

\[
\Xi_d(N) = \left\{ \text{det} [\mathcal{L}_d(r,r')] \right\}^{1/2}
\]

\[
\times \exp \left\{ -\frac{1}{2} \beta \int_0^N u [\mathbf{r}(n), \mathbf{r}(n)] dn \right\},
\]

\[
\beta \mathcal{H}_d(n) = \frac{3}{2 \beta} \int_0^N \frac{[d \mathbf{r}(n)]^2}{dn} dn + \beta N \mathcal{L}_0(0_0)
\]

\[
= \langle \langle e^{-\beta \mathcal{H}_d(n)} \rangle \rangle_{\phi(n)}
\]

\[
= \langle e^{-\beta \mathcal{H}_d(n)} \rangle.
\]

With \(\Delta \mathcal{H}_d(n) = \mathcal{H}_d(n) - \mathcal{H}_0(n)\). By writing \(\langle \cdots \rangle_{\mathcal{H}_d(n)}\), we emphasize the fact that \(\mathcal{H}_d(n)\) 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 \(\langle \cdots \rangle\). Since the free energy is \(\mathcal{F} = -kT \ln \Xi(N)\), we can derive the following (Gibbs-Bogolyubov) inequality valid between \(\mathcal{F}\) and \(\mathcal{F}_0\)

\[
= -kT \ln \Xi_0(N),
\]

\[
\mathcal{F} < \mathcal{F}_0 + \Delta \mathcal{H}_d(n)
\]

\[
= \mathcal{F}_0 - kT \ln \langle \exp \{ -\beta \mathcal{H}_d(n) \} \rangle_{\phi(n)}.
\]

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 \( \langle \Delta \mathcal{H}_f(N) \rangle \)

We start by evaluating

\[
\beta \langle \mathcal{H}_f(N) - \mathcal{H}_0(N) \rangle_{\mathcal{H}_f[r(n)]} = -\beta \int_0^N \langle \phi[r(n)] \rangle_{\mathcal{H}_f[r(n)]} dn + \beta \int_0^N \langle \phi_\alpha[r(n)] \rangle_{\mathcal{H}_f[r(n)]} \frac{3}{2} \int_0^N \langle \xi_0^2(r_0) [r(n) - r_0]^2 \rangle_{\mathcal{H}_f[r(n)]} dn 
- \beta N \langle \mathcal{L}_0(r_0) \rangle_{\mathcal{H}_f[r(n)]} + \frac{1}{2} \beta \int \phi(r) u^{-1}(r,r') \phi(r') d^3r d^3r'.
\] (4.1)

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

\[
\langle f[r(n)] \rangle_{\mathcal{H}_f[r(n)]} = \int \frac{d^3k}{(2\pi)^3} f(k) \langle \xi_0^2(r_0) \rangle_{\mathcal{H}_f[r(n)]} = \int \frac{d^3k}{(2\pi)^3} f(k) \left( e^{kr_0} \exp \left[ -\frac{1}{2} k^2 \frac{1}{2} \langle [r(n) - r_0]^2 \rangle \right] \right) \bigg|_{r_0}.
\] (4.2)

The final averaging over \( r_0 \) is in general non-Gaussian and cannot be evaluated explicitly. We indicate this by \( \langle \cdot \cdot \cdot \rangle_{r_0} \) in the expressions where the Gaussian integrals have been evaluated. It is in this form of the general average \( \langle f[r(n)] \rangle_{\mathcal{H}_f[r(n)]} \) 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:

\[
a^2(r_0) = \frac{1}{3} \langle [r(n) - r_0]^2 \rangle = \frac{4\rho}{3N} \sum_{p=1}^\infty \frac{1}{\sigma_p^2 + \xi_0^2(r_0)} = \frac{\rho}{3\xi_0^2} \mathcal{L}(\xi_0 N) / 2.
\] (4.3)

with \( \mathcal{L}(x) \) the standard Langevin function \( \mathcal{L}(x) = \tanh x - (1/x) \). The averaging in the above equation refers only to \( p > 1 \) (Gaussian) Rouse components, therefore \( a^2 = a^2(r_0) \). Thus we obtain the average of a general function depending on polymer coordinates in the form of a convolution

\[
\int_0^N \langle f[r(n)] \rangle_{\mathcal{H}_f[r(n)]} dn = \left\langle \int d^3r f(r) \rho_\alpha(r, r_0) \right\rangle_{r_0}, \quad \text{with} \quad \rho_\alpha(r, r') = N(2\pi a^2)^{-3/2} \exp \left( -\frac{|r - r'|^2}{2a^2} \right),
\] (4.4)

where \( \rho_\alpha \) is the Green’s function of diffusion equation. With this, we can go back to the expression for \( \langle \mathcal{H}_f(N) - \mathcal{H}_0(N) \rangle_{\mathcal{H}_f[r(n)]} \) [Eq. (4.1)] obtaining

\[
\beta \langle \mathcal{H}_f(N) - \mathcal{H}_0(N) \rangle_{\mathcal{H}_f[r(n)]} = \beta \left\langle \int d^3r f(r) \rho_\alpha(r, r_0) \right\rangle_{r_0} + \beta \left\langle \int d^3r \phi_\alpha(r) \rho_\alpha(r, r_0) \right\rangle_{r_0} - \frac{3}{2} \frac{\xi_0^2(r_0)}{\xi_0 N a^2(r_0)}
- \beta N \langle \mathcal{L}_0(r_0) \rangle_{r_0} + \frac{1}{2} \beta \int \phi(r) u^{-1}(r,r') \phi(r') d^3r d^3r'.
\] (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 \( \phi(r) \) integration, which is again Gaussian and can be evaluated exactly leading to

\[
\langle \exp[-\beta \mathcal{H}_f(N) - \mathcal{H}_0(N)] \rangle_{\mathcal{H}_f[r(n)]} = \int \mathcal{D} \phi(r) \exp[-\beta \mathcal{H}_f(N) - \mathcal{H}_0(N)]
= \det[\beta u^{-1}(r,r')]^{-1/2} \exp[-\beta \mathcal{H}_f(N) > 1]. \tag{4.6}
\]

We have thus derived the expression for \( \langle \Delta \mathcal{H}_f(N) \rangle \) that has a succinctly simple form resembling that of a potential energy of a smeared “particle” with a Gaussian density distribution, i.e.,
β(ΔH_{\phi}(N)) = -\frac{3}{2}\langle\xi_0(r_0)Na^2(r_0)\rangle_{r_0} - \beta N\langle\mathcal{L}_0(r_0)\rangle_{r_0} + \beta \int_0^1 d^3r \phi_{ex}(r) \rho_{\phi}(r,r_0) + \frac{1}{2} \beta \int_0^1 d^3r d^3r' \rho_{\phi}(r,r_0)u(r,r')\rho_{\phi}(r',r_0).

(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 $\mathcal{F}_0$, which apart from the final $r_0$ integration, again reduces to Gaussian integrals yielding

$$\mathcal{F}_0 = -kT \ln \langle e^{-\beta \mathcal{H}_0(N)}\rangle_{r_0} = -kT \int d^3r_0 \exp(-\beta N\mathcal{L}_0(r_0) - 3 \ln \sinh([\xi(r_0)N]/2)/[\xi(r_0)N]/2).$$

(4.8)

V. VARIATIONAL DETERMINATION OF $\xi_0(r_0)$ AND $\mathcal{L}_0(r_0)$

We showed before that $\mathcal{F}_{\text{trial}} = \mathcal{F}_0 + \langle \Delta \mathcal{H}_{\phi}(N) \rangle$ is always an upper bound for the exact free energy of the system. By minimizing it with respect to $\xi_0(r_0)$ as well as $\mathcal{L}_0(r_0)$, we obtain, following Kleinert, from the first variation $\delta \mathcal{L}_0(r_0)\mathcal{F}_{\text{trial}}[\xi_0(r_0),\mathcal{L}_0(r_0)] = 0$, \[ \beta N\mathcal{L}_0(r_0) = -\frac{3}{2}\xi_0^2(r_0)Na^2 + \beta W(r_0), \]

(5.1)

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

$$W(r_0) = \int d^3r \phi_{ex}(r) \rho_{\phi}(r,r_0) + \frac{1}{2} \beta \int_0^1 d^3r d^3r' \rho_{\phi}(r,r_0)u(r,r')\rho_{\phi}(r',r_0).$$

(5.2)

Also from $\delta \xi_0(r_0)\mathcal{F}_{\text{trial}}[\xi_0(r_0),\mathcal{L}_0(r_0)] = 0$, it follows, after taking into account the definition of $a^2$, i.e., Eq. (4.3), that

$$\frac{3}{2}\xi_0^2(r_0)N = \beta \frac{\partial}{\partial a^2} W(r_0).$$

(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

$$\mathcal{F} = -kT \int d^3r_0 e^{-\beta F_0(r_0)},$$

(5.4)

where $F_0(r_0)$ is now the effective one particle Hamiltonian that has the form

$$\beta F_0(r_0) = 3 \ln \sinh([\xi(r_0)N]/2)/[\xi(r_0)N]/2) \left[\frac{3}{2}\xi_0^2(r_0)Na^2 + \beta W(r_0).\right.$$}

(5.5)

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

$$\mathcal{G}_0(n,m) = \langle r(n) r(m) \rangle_{\mathcal{G}_{\xi_0}(N)}$$

$$= \left\{ \rho_0^2 + \sum_{p=1}^\infty \rho_2^2(p) \cos \omega_p \cos \omega_m + \sum_{p=1}^\infty \rho_3^2(p) \sin \omega_p \sin \omega_m \right\}_{\mathcal{G}_{\xi_0}(N)}.$$

(6.1)

As before, the $\langle \cdots \rangle_{\mathcal{G}_{\xi_0}(N)}$ average in the above equation consists of averaging over the Gaussian variables $r_0(p)$ and $r_2(p)$, as well as in the final averaging over $r_0$. Thus we can derive from the above definition

$$\mathcal{G}_0(n,m) = \left\{ \rho_0^2 + \sum_{p=1}^\infty \rho_2^2(p) \cos \omega_p (n-m) \right\}_{\mathcal{G}_{\xi_0}(N)}$$

$$= \left\{ \rho_0^2 + \frac{\mu}{\xi_0} \left[ \cosh \xi_0 [(N/2) - |n-m|] \right. \right.$$

$$\left. - \frac{2}{\xi_0^2 N} \right|_{r_0}. \right\}$$

(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

$$\mathcal{R} = \left\{ \left[ \frac{N}{2} - r(0) \right]^2 \right\}_{\mathcal{G}_{\xi_0}(N)}$$

$$= 2 \mathcal{G}_0(N/2, N/2) - \mathcal{G}_0(N/2, 0)$$

$$- \frac{2\mu}{\xi_0^2} \tan \xi_0 \frac{N}{4} \left|_{r_0}. \right\}$$

(6.3)

as well as the mean radius of gyration.
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

$$R^2(n,m) = \langle [r(n) - r(m)]^2 \rangle_{P_0(N)} = 2 \left[ \mathcal{G}_0(n,n) - \mathcal{G}_0(n,m) \right] = \left\{ \begin{array}{l}
\frac{2^D}{\zeta_0} \left[ \coth \frac{\zeta_0 N}{2} - \frac{4}{(\zeta_0 N)^2} \tanh \left( \frac{\zeta_0 N}{4} \right) \right]
\end{array} \right\}_{r_0}.
$$

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

$$\langle n(n)n(m) \rangle - \left\{ \frac{d[r(n)]}{dn} \right\} \left\{ \frac{d[r(m)]}{dm} \right\} = \frac{1}{2} \int d^2d^2d^2 \mathcal{G}_0(n,m) = \left\{ \begin{array}{l}
\frac{2^D}{\zeta_0} \left[ \coth \frac{\zeta_0 N}{2} - \frac{4}{(\zeta_0 N)^2} \tanh \left( \frac{\zeta_0 N}{4} \right) \right]
\end{array} \right\}_{r_0}.
$$

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 $\rho = 0$ 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:

$$W = \frac{1}{2} \int d^D r \int d^D r' \rho_2(r,r_0)u(r,r') \rho_2(r',r_0)
$$

$$= \int \frac{d^D k}{(2\pi)^D} \rho_2(k) |u(k)|^2
$$

that does not depend on $r_0$. In the above equation, we assumed that $u(r,r')$ and $\rho_2(r,r')$ 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 $u(k) = \left( e^2 / e_0 \right) k^{-2}$, where $e_0$ is the charge residing on each monomer, while other symbols are standard. In this case, we get

$$W = \frac{1}{2} \int \frac{d^D k}{(2\pi)^D} \rho_2(k) \left( e^2 / e_0 \right) k^{-2}
$$

$$= \frac{1}{2} \int \frac{d^D k}{(2\pi)^D} \rho_2(k) \left( e^2 / e_0 \right) k^{-2}
$$

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

$$\frac{D}{2} \zeta_0 N^2 = -\frac{2 \beta e_0^2}{3 \pi^2 \alpha^4} \frac{N^3 - (D/2)}{(\alpha^2/N)^{D/2}}
$$

and

$$\frac{D}{2} \zeta_0 N^2 = -\frac{2 \beta e_0^2}{3 \pi^2 \alpha^4} \frac{N^3 - (D/2)}{(\alpha^2/N)^{D/2}}
$$

The dependence of $R^2$ 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 \( R^2(D=3) \sim N^3 \) (the stiff rod limit). By Eq. (6.4), we also have

\[
R^2_0 = \frac{1}{N} \left( \int_0^N \left[ \frac{\langle r(n) - r(m) \rangle^2}{N} \right] \right)_{m=0}^{N} - 3a^2. \tag{7.7}
\]

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)

\[
\rho^2(n,m) = \langle [r(n) - r(m)]^2 \rangle_{\rho_0(N)}
\]

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

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

\[
\langle n(n) n(m) \rangle = \left( \frac{\langle dr(n) \rangle \langle dr(m) \rangle}{2\pi} \right)_{\rho_0(N)}
\]

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

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 \( D \leq 3 \). 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 rod-like.

Let us now examine the excluded volume intrachain potential \( u(r,r') = bG(r-r') \) 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, \( b = e^2/e_0 \varepsilon_0 k^2 \). We can derive quite straightforwardly that Eq. (7.3) assumes in this case the form

\[
\left( \xi_0 N \right)^2 = \frac{b^2}{6(4\pi)^{D/2}} \frac{N^D}{(a^2/N)^{(D/2)+1}}
\]

and

\[
\frac{L}{\xi_0 N} = \frac{a^2}{N}. \tag{7.10}
\]

We see from these identities that the upper critical dimensionality in this case is \( D=4 \). 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

\[
a^2 = C'(D)N^{(D+2)}, \tag{7.11}
\]

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 \( r_0 \). The analysis outlined in previous sections could thus proceed only numerically as the final \( r_0 \) 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 and consists of the additional (saddle point) minimization of the effective free energy \( \mathcal{F}_0 \) with respect to \( r_0 \). This procedure is strictly correct only in the limit when \( \mathcal{F}_0 \) 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 \( r_1 \). This problem is a distant relative of the problem of polymer adsorption to a planar surface. By the general formula (5.2), we have in this case

\[
W(r_0) = -\varepsilon_0 N \frac{e_0^2}{e_0} \mathcal{F}_0(r_0, r_1)
\]

\[
\rho_0^2 \left( \frac{2}{e_0^2} \varepsilon_0 \right) \int \frac{d^Dk}{(2\pi)^D} \rho_0^2(k) |u(k)|^2 u(k), \tag{8.1}
\]

where we introduced

\[
\mathcal{F}_0^2(r,r') = \int \frac{d^Dk}{(2\pi)^D} \rho_0^2(k) u(k) \rho_0^2(k), \tag{8.2}
\]

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

\[
\mathcal{F}_0^2(r,r') = \frac{2^D}{(2\pi)^D} \left[ \frac{1}{(D/2)^2} \right] \left| r-r' \right|^2 \left( \frac{D}{2} - 1 - \frac{1}{2a^2} \left| r-r' \right|^2 \right)
\]

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

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

J. Chem. Phys., Vol. 99, No. 9, 1 November 1993

Downloaded 14 Jan 2001 to 193.2.6.183. Redistribution subject to AIP copyright, see http://ojps.aip.org/jcpo/jcpcpyrts.html.
\[
\frac{D}{2} (\xi_0 N)^2 = \frac{\beta \ell^2}{6 \varepsilon \varepsilon_0 (4 \pi)^D/2} \left( \frac{N}{\ell} \right)^{D/2} \times (\varepsilon \varepsilon_0 \ell^{D/2} e^{-(|r_0 - r_1|^2)/(2 \ell^2)} - \varepsilon_0^2 N)
\]

and

\[
\frac{\ell^2}{3 (\xi_0 N)} = \frac{a^2}{N}.
\]

The above relation embodies in the clearest way the distinction between the approach devised by Muthukumar, 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 \( r \). This gives us \( r = r_0 \). 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 \( r \) obtained from the minimization of the free energy, i.e. \( r_0 \). The solution of Eqs. (8.4) now depends solely on the sign and magnitude of \( \varepsilon = (\varepsilon \varepsilon_0 \ell^{D/2} - \varepsilon_0^2 N) \). If \( \varepsilon < 0 \), we are back to the solution (7.5). In the opposite case, we obtain a new type of behavior

\[
D/2 (\xi_0 N)^2 = \frac{D}{2} \frac{b^2}{6 (4 \pi)^D/2} \left( \frac{a^2}{N} \right)^{D/2+1} \times \{b^2 \ell^{D/2} \exp[-(|r_0 - r_1|^2)/(2 a^2)] - b N\}.
\]

Clearly in this case the upper critical dimensionality for the localization to set in is \( D = 2 \) [i.e., for \( - \frac{D}{2} < 0 \)] 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 \( \xi_0 \), 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

\[
R^2 \rightarrow 6 a^2, \quad R_G^2 \rightarrow 3 a^2.
\]

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,

\[
\langle n(n) \rangle \rightarrow \frac{a^2}{3 a^2} \exp[-(R^2/3 a^2)|n - m|].
\]

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. 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 \( e_0 > 0 \) situated at \( r = r_1 \) and \( r = r_2 \), then the variational equations can be derived in the form

\[
J. Chem. Phys., Vol. 99, No. 9, 1 November 1993
\]

Downloaded 14 Jan 2001 to 193.2.6.183. Redistribution subject to AIP copyright, see http://ojps.aip.org/jcp/jcpcpyrts.html.
The effective free energy (5.5) for this system can be cast into the form

\[ \beta F_{\text{tot}} = \frac{\beta \varepsilon_0 e_2}{4 \pi \varepsilon_0 |r_1 - r_2|} + \beta F_{\text{d}0} \]

(9.3)

where the definition of \( F_{\text{d}0}(r_0, r_1) \) is the same as before. Clearly, the dependence of \( F_{\text{tot}} \) 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 \( r_0 \) is not trivial either. Approximate analytical solutions can only be derived for the limit of small and/or large \(|r_1 - r_2|\).

The limit of \( |r_1 - r_2| \gg 2a^2 \) can only be strictly attained in the case that \( a^2 \rightarrow \text{const} \), 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 \(|r_1 - r_2|\), \( a \) can be larger if only we choose a large enough \( N \). In the asymptotic limit of large \(|r_1 - r_2|\), it is thus enough to analyze only the case of a localized chain.

The minimizing of the free energy (9.3) in the limit of large \(|r_1 - r_2|\) gives two solutions, either \( r_0 = r_1 \) or \( r_0 = r_2 \). 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 \( (e_1^2 N^2 - 2D^2 e_1 e_0 N) \approx 0 \), 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 \( F_{\text{d}0}(r, r') \) function, we can derive the total free energy of the system as

\[ \beta F_{\text{tot}} \approx \frac{D^2}{6} \left( \frac{N}{a^2} \right) \left[ \frac{4 - D}{D - 2} + \frac{2 D^2 (e_1 + e_2) e_0 N}{2 D^2 (e_1 + e_2) e_0 N - e_0^2 N^2} \right] \left| r_1 - r_2 \right|^2 + \cdots. \]

(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 \( |r_1 - r_2| \). If, however, we have \( 2D^2 (e_1 + e_2) e_0 N - e_0^2 N^2 \ll 0 \), 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

\[ \beta F_{\text{tot}} \approx \frac{\beta \varepsilon_0 e_2}{4 \pi \varepsilon_0 |r_1 - r_2|} - \frac{3 D a^2}{2} \left( \frac{a^2}{a^2} \right) - D \ln \left( \frac{3 D}{a^2} \right) \left( \frac{a^2}{a^2} \right) + \frac{3 \pi^2}{2} \frac{D^2 (e_1 + e_2) e_0 N}{2 D^2 (e_1 + e_2) e_0 N - e_0^2 N^2} \left| r_1 - r_2 \right|^2 + \cdots. \]

(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 \( r_0 \) in both limits is either \( \frac{1}{2}(r_1 + r_2) \) or \( r_1 \), where \( i = 1 \) or \( 2 \), there should be a symmetry breaking transition at an intermediate separation \( |r_1 - r_2| = D_c \) that we can derive from Eq. (9.1) as

\[
D_c^2 = 2N^2 \ln \frac{e_0 e_0 e_0^2}{(\Delta e_0 - e_0 e_0^2) \Delta^2}. \tag{9.7}
\]

For \( |r_1 - r_2| < D_c \), 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 configuration of point charges \(-e_i\) (with \( i = 1, M \)), then the effective free energy would contain terms of the form \( \sum_{i=1}^{M} F_i(r_0, r_i) \). The variational condition (9.1) would thus contain a sum of Gaussians centered at \( r_i \). Should we now apply the minimization with respect to \( r_0 \) to the effective free energy, we would obtain \( M \) approximate solutions \( r_0 \approx r_i \) for the case where \( \langle |r_i - r_0|/a \rangle \gg 1 \). That would mean that the polymer mediated interaction in this limit is pairwise additive. In the opposite limit of \( \langle |r_i - r_0|/a \rangle \ll 1 \), an approximate solution would be \( r_0 \approx (1/M) \sum_{i=1}^{M} r_i \). 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\(^3\) 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 appro-
priate 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.

ACKNOWLEDGMENTS

I would like to thank Dr. Bo Jönsson, Dr. Torbjörn Åkesson, and Dr. Robert Penfold for many enlightening discussion on Coulomb fluids, DLVO forces, and polyelectrolyte-mediated interactions, in particular, as well as for their reading and comments on the manuscript. I also gratefully acknowledge a travel grant from the Ministry of Science and Technology of Slovenia and a research fellowship from the Swedish Research Council.