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Polymer systems with attractive interactions: Polyelectrolyte complex formation

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The theoretical treatment of polymers with attractive interactions is introduced. It is suggested that this unsolved problem is treated by new collective coordinates, such as pair fields, which are sensitive to pairs of different components of the system. Such pair fields are known from the BCS theory of superconductivity. Their correlation functions and integral equations show instabilities which correspond to the formation of complexes and/or aggregations. Physical examples for such considerations are semidilute polyelectrolyte solutions containing oppositely charged polyions.

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I. INTRODUCTION AND MOTIVATION

To treat the effect of attractive interactions in physics is a hard problem. A system of attractive particles will immediately collapse to a dense ball of a given size according to its density. In more dilute systems clusters will be formed and these clusters will be eventually aggregated as time passes. If the particles have internal structure, as in the case of polymers, the situation becomes more complicated, because the polymers will form an assembly of complicated complexes. The structure of such complexes will be difficult to describe formally but the essential physics can be described as will be shown below. A physical example for such a polymer problem is given in the case of oppositely charged polyelectrolyte molecules immersed in a "complex" solvent which contains solvent molecules and counterions of carrying charges of opposite sign to maintain overall electroneutrality [1]. A dilute system of, say, two oppositely charged polyelectrolytes dissolved in such a charged fluid is very difficult to describe physically, since, first, the complete renormalization group physics for dilute polymer systems has to be applied [2] and second, due to the presence of long-range electrostatic forces, additional problems come into play which dispute the subject still [3]. Moreover, only little is known for partially attractive chains and one of the most reliable theoretical methods to treat such problems has been introduced by Lifshitz, Gredeskut, and Pastur for the electron localization problem [4]. Lifshitz, Grosberg, and Khoklov [5] demonstrated the applicability of this method to the problem of the polymer collapse, i.e., a polymer chain immersed in a poor solvent where the effective monomer-monomer interaction becomes attractive.

The problem which will be studied in this paper avoids such difficulties by introducing a large number of polyelectrolyte chains into the solvent. It is crucial for what will be presented below that the chains form a "strong solution" (in the terminology introduced by Doi and Edwards [6]), i.e., the overall concentration satisfies $c > c^*$, where c^* is the overlap concentration of the corresponding neutral polymer solution. In most such cases mean field methods can be applied and the random phase approximation (RPA) has been proven to be a very powerful basis for further extensions [2,7]. Nevertheless, the problem is far from being trivial because the formulation of the RPA on the classical level is not sensitive to the presence of attractive interactions. This can be seen from the following example.

The dimensionless Edwards-Wiener Hamiltonian for an interacting polymer system can be generally written as

$$H=\frac{1}{2}\sum_{\mu=1}^{2}\sum_{i=1}^{n}\int_0^N ds\,\dot{\mathbf{r}}_{\mu i}^2 +\frac{1}{2}\sum_{\mu,\nu=1}^{2}(2\pi)^{-3}\int d^3\mathbf{k}\,\rho_\mu(\mathbf{k})V_{\mu\nu}(\mathbf{k})\rho_\nu(-\mathbf{k})\ , \tag{1.1}$$

where the first term is the usual Wiener measure for all the chains involved in the system. The second term denotes the interaction for a two-component interacting polymer system. $\mathbf{r}_{\mu i}(s)$ is the chain variable of the ith chain of component μ and $\rho_\mu(\mathbf{k})$ is the collective density field component. $V_{\mu\nu}$ denotes the interaction matrix between all monomers.

It is now assumed that both monomer types ν and μ have repulsive interactions, whereas when V_{12} is attractive a fundamental problem becomes obvious. The effective Hamiltonian for component 1 can be obtained by integrating out component 2. This yields the Hamiltonian in a standard way [7],

$$H_1=\frac{1}{2}\sum_{i=1}^{n}\int_0^N ds\,\dot{\mathbf{r}}_{1i}^2+\frac{1}{2}\sum_{i,j=1}^{n}\int_0^N ds\int_0^N ds'(2\pi)^{-3}\int d^3\mathbf{k}\,V_{\text{eff}}(\mathbf{k})\exp\{i\mathbf{k}\cdot[\mathbf{r}_{1i}(s)-\mathbf{r}_{1j}(s')]\}\ , \tag{1.2}$$

where $V_{\mathrm{eff}}(\mathbf{k})$ is the effective interaction given by

$$V_{\mathrm{eff}}(\mathbf{k})=\left\{V_{11}(\mathbf{k})-\frac{V_{12}^2(\mathbf{k})}{1/S_2(\mathbf{k})+V_{22}(\mathbf{k})}\right\} \tag{1.3}$$

and $S_2(\mathbf{k})$ denotes the bare densities correlation function for component 2. Obviously the effective interaction does *not* depend on the sign of V_{12}. It does not matter if V_{12} is attractive or repulsive; the standard RPA yields identical results. This is unphysical, and a new formulation of the RPA has to be established since complex formation cannot be described by Eq. (1.2).

It will be shown later in the paper that for such attractive pair interactions a pair field $\Delta(\mathbf{r}_1,\mathbf{r}_2)$ has to be introduced, instead of a single component density field $\rho_\mu(\mathbf{r})$. In contrast to the single component field $\rho_\mu(\mathbf{r})$, the pair field is sensitive to both types of chains. Their correlation function $\langle\Delta(\mathbf{r}_1,\mathbf{r}_2)\Delta(\mathbf{r}_3,\mathbf{r}_4)\rangle$ determines instabilities which correspond to the onset of complex formation. The situation is very similar to the phenomenon of superconductivity where the pair field is equivalent to the gap parameter which describes the Cooper pair formation [8].

The paper is organized as follows. In Sec. II we recall the physical quantities of interest in the framework of the continuous model proposed by Edwards. In Sec. III the pair-field Hamiltonian is introduced. In Sec. IV, the correlation function of two oppositely charged polyions is calculated and its connection to complex formation is derived. The last section is devoted to the discussion.

II. BASIC EQUATIONS AND FORMULATION OF THE PROBLEM

We consider for simplicity a fully symmetric polyelectrolyte system consisting of n polyanions and n polycations both with N monomers in each macromolecule. Assuming that the Debye screening length is much smaller than the radius of gyration the Edwards model [6] may be used, whereby the charges are uniformly smeared along the chains. The dimensionless Hamiltonian for this system is given by

$$H=\frac{1}{2}\sum_{\mu=1}^{2}\sum_{i=1}^{n}\int_0^N ds\,\dot{\mathbf{r}}_{\mu i}^2+\frac{1}{2}\sum_{\mu,\nu=1}^{2}\sum_{i,j=1}^{n}\int_0^N ds\int_0^N ds'\,V_{\mu\nu}[\mathbf{r}_{\mu i}(s)-\mathbf{r}_{\nu j}(s')]\ , \tag{2.1}$$

where we have absorbed the factor of $(k_BT)^{-1}$ into H. Furthermore, units are used in Eq. (2.1) such that $\mathbf{r}=\sqrt{3}\mathbf{x}/l$, where l is the Kuhn length and $\mathbf{x}$ denotes the spatial position of a polymer segment. The potential $V_{\mu\nu}$ is a superposition of excluded-volume effect and screened Coulomb interaction. We have

$$V_{\mu\nu}(\mathbf{r})=u\delta(\mathbf{r})+(-1)^{\mu+\nu}\lambda_B f^2\frac{\exp[-|\mathbf{r}|/\lambda_D]}{|\mathbf{r}|}\ , \tag{2.2}$$

where λ_B is the Bjerrum length

$$\lambda_B=\frac{e^2/k_BT}{4\pi\varepsilon_0 D}\frac{\sqrt{3}}{l}\ , \tag{2.3}$$

λ_D denotes the Debye screening length

$$\lambda_D^{-2}=\lambda_B c_i\frac{l^2}{3}\ , \tag{2.4}$$

c_i is the concentration of the counterions and the added low molecular salt, e, is the unit electrical charge, ε_0 is the permittivity of vacuum, D is the dielectrical constant of the solvent, and f denotes the fraction of charged monomers in a polyion. The partition function can be written in terms of a path integral [9] as

$$Z=\int\prod_{i=1}^{n}D\mathbf{r}_{1i}D\mathbf{r}_{2i}\exp[-H]\ , \tag{2.5}$$

where $\int D\mathbf{r}$ represents the summation over all possible configurations of the chains.

Our aim is to find an effective partition function Z_{12} for two oppositely charged polyions. We have therefore to integrate out all chains except two. Due to the coupling of polymers this calculation would be very complicated. For this reason we use the well-known RPA decoupling scheme [7] to get

$$Z_{12}=\int D\mathbf{r}_1 D\mathbf{r}_2\exp(-H_{12}[\mathbf{r}_1,\mathbf{r}_2])\ . \tag{2.6}$$

The Hamiltonian H_{12} for this effective two-polymer system reads

$$H_{12}=\frac{1}{2}\sum_{i=1}^{2}\int_0^N ds\,\dot{\mathbf{r}}_i^2+\frac{1}{2}\sum_{i,j=1}^{2}\int_0^N ds\int_0^N ds'\,w_{ij}[\mathbf{r}_i(s)-\mathbf{r}_j(s')]\ . \tag{2.7}$$

After introducing the Fourier transform of the w_{ij}'s one obtains after standard manipulations

$$w_{12}(\mathbf{k})=\frac{u-v(\mathbf{k})}{[1+2\rho v(\mathbf{k})S(\mathbf{k})][1+2\rho u S(\mathbf{k})]}\ , \tag{2.8}$$

where $v(\mathbf{k})$ is the Debye potential given by

$$v(\mathbf{k})=\int d^3\mathbf{r}\exp[-i\mathbf{k}\mathbf{r}]\lambda_B f^2\frac{\exp[-|\mathbf{r}|/\lambda_D]}{|\mathbf{r}|}=\frac{4\pi\lambda_B f^2}{\mathbf{k}^2+\lambda_D^{-2}}\ , \tag{2.9}$$

ρ is the concentration of all polymers, and S is the unperturbed scattering function defined by [6]

$$S(\mathbf{k})=N^2\left\{\frac{2}{\mathbf{k}^2N}-\left[\frac{2}{\mathbf{k}^2N}\right]^2[1-\exp(-\mathbf{k}^2N/2)]\right\}\ . \tag{2.10}$$

The intramolecular potential w_{ii} becomes

$$w_{ii}(\mathbf{k})=w_{12}(\mathbf{k})+\frac{2v(\mathbf{k})}{1+2\rho v(\mathbf{k})S(\mathbf{k})}\ . \tag{2.11}$$

The probability distribution function $G_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2';N_1,N_2)$ is obtained from averaging over all possible chain conformations with fixed end-point vectors $\mathbf{r}_1,\mathbf{r}_1'$ and $\mathbf{r}_2,\mathbf{r}_2'$. This average can be written in terms of a path integral as

$$G_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2';N_1,N_2)=\int D\mathbf{R}_1 D\mathbf{R}_2 \exp(-H_{12}[\mathbf{R}_1,\mathbf{R}_2])\delta(\mathbf{R}_1(0)-\mathbf{r}_1)$$
$$\times\delta(\mathbf{R}_1(N_1)-\mathbf{r}_1')\delta(\mathbf{R}_2(0)-\mathbf{r}_2)\delta(\mathbf{R}_2(N_2)-\mathbf{r}_2') \; . \qquad (2.12)$$

There is another approach for calculating statistical properties of polymer chains which makes use of the polymer-magnet analogy introduced by de Gennes [2]. The correlation function is after the Laplace transform

$$G_{12}(E_1,E_2)=\int_0^\infty dN_1 \int_0^\infty dN_2 \exp[-E_1N_1-E_2N_2] \times G_{12}(N_1,N_2) \qquad (2.13)$$

that of an $O(n)$ field theory in the limit $n \to 0$. The starting point is the Hamiltonian

$$L_{12}[\phi_1,\phi_2]=\tfrac{1}{2}\sum_{i=1}^{2}\int d^3\mathbf{r}\,d^3\mathbf{r}'\phi_i(\mathbf{r})G_i^{-1}(\mathbf{r},\mathbf{r}';E_i)\phi_i(\mathbf{r}')$$
$$+\tfrac{1}{2}\sum_{i,j=1}^{2}\int d^3\mathbf{r}\,d^3\mathbf{r}'\phi_i^2(\mathbf{r})w_{ij}(\mathbf{r}-\mathbf{r}')\phi_j^2(\mathbf{r}') \; , \qquad (2.14)$$

where

$$G_i^{-1}(\mathbf{r},\mathbf{r}';E_i)=\delta(\mathbf{r}-\mathbf{r}')(E_i-\tfrac{1}{2}\nabla_r^2) \qquad (2.15)$$

is the inversion of the bare propagator. The correlation function G_{12} can be calculated using a generating functional defined by

$$Y[h_1,h_2]=\int D\phi_1 D\phi_2 \exp\left[-L_{12}[\phi_1,\phi_2] - \sum_{i=1}^{2}\int d^3\mathbf{r}\,h_i(\mathbf{r})\phi_i(\mathbf{r})\right] . \qquad (2.16)$$

Then we get

$$G_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2';E_1,E_2) = \left.\frac{\delta^4 Y[h_1,h_2]}{\delta h_1(\mathbf{r}_1)\delta h_1(\mathbf{r}_1')\delta h_2(\mathbf{r}_2)\delta h_2(\mathbf{r}_2')}\right|_{h_1,h_2\to 0} , \qquad (2.17)$$

where the symbol δ denotes the functional derivative with respect to vanishing external fields h_1 and h_2.

The sign of the potential w_{12} is crucial. This circumstance can be proved within the framework of the renormalization group (RG) technique. From RG it is known that the Hamiltonian (2.14) corresponds formally to a system with cubic anisotropy [10]. Provided that the w_{ii}'s are positive and short ranged a second-order transition and a fixed-point behavior of all coupling parameters are found when w_{12} is positive and short ranged too. In contrast to that no fixed-point behavior is obtained for $w_{12}<0$. In the latter case the macroscopic properties of the system depend sensitively on the interaction. This requires a theoretical approach different from that of RG which will be given in the next section.

III. EFFECTIVE HAMILTONIAN FOR THE PAIR FIELD.
RPA FOR ATTRACTIVE SPECIES

A characteristic feature of the system under consideration is the pairing between oppositely charged polyions. If pair effects are dominant a conventional perturbation expansion is unable to predict this kind of phenomenon. To overcome this difficulty we shall introduce a pair field which has the advantage of taking into account pairing explicitly [8]. After rewriting the generating functional (2.16) in terms of the pair field a suitable starting point for a perturbation expansion is obtained.

In order to remove all quartic interaction terms in Eq. (2.14) we introduce further auxiliary fields $\gamma_i(\mathbf{r})$. Starting from the identities (see Appendixes A and B)

$$\exp\left[-\tfrac{1}{2}\int d^3\mathbf{r}\,d^3\mathbf{r}'\phi_i^2(\mathbf{r})w_{ii}(\mathbf{r}-\mathbf{r}')\phi_i^2(\mathbf{r}')\right]$$
$$=\text{const}\times\int d\gamma_i \exp\left[-\tfrac{1}{2}\int d^3\mathbf{r}\,d^3\mathbf{r}'\gamma_i(\mathbf{r})w_{ii}^{-1}(\mathbf{r}-\mathbf{r}')\gamma_i(\mathbf{r}')-i\int d^3\mathbf{r}\,\gamma_i(\mathbf{r})\phi_i^2(\mathbf{r})\right] \qquad (3.1)$$

and

$$\exp\left[-\int d^3\mathbf{r}\,d^3\mathbf{r}\phi_1^2(\mathbf{r})w_{12}(\mathbf{r}-\mathbf{r}')\phi_2^2(\mathbf{r}')\right]$$
$$=\text{const}\int D\Delta_s D\Delta_a \exp\left[\int d^3\mathbf{r}\,d^3\mathbf{r}'\frac{[\Delta_s(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')}+\int d^3\mathbf{r}\,d^3\mathbf{r}'\frac{[\Delta_a(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')}\right.$$
$$\left.+\int d^3\mathbf{r}\,d^3\mathbf{r}'\begin{bmatrix}\phi_1(\mathbf{r})\\ \phi_2(\mathbf{r})\end{bmatrix}\begin{bmatrix}0 & \Delta_s+\Delta_a\\ \Delta_s-\Delta_a & 0\end{bmatrix}(\mathbf{r},\mathbf{r}')\begin{bmatrix}\phi_1(\mathbf{r}')\\ \phi_2(\mathbf{r}')\end{bmatrix}^T\right] , \qquad (3.2)$$

one gets after inserting these into Eq. (2.16)

$$
\begin{aligned}
Y[h_1,h_2]=\int \prod_{i=1}^{2} D\phi_i D\gamma_i D\Delta_s D\Delta_a \exp \Bigg[& -\sum_{i=1}^{2} \int d^3\mathbf{r}\, h_i(\mathbf{r})\phi_i(\mathbf{r}) + \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\Delta_s(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} + \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\Delta_a(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} \\
& -\tfrac{1}{2} \sum_{i=1}^{2} \int d^3\mathbf{r} d^3\mathbf{r}' \gamma_i(\mathbf{r}) w_{ii}^{-1}(\mathbf{r}-\mathbf{r}')\gamma_i(\mathbf{r}') \\
& -\tfrac{1}{2} \int d^3\mathbf{r}\, d^3\mathbf{r}' \begin{bmatrix} \phi_1(\mathbf{r}) \\ \phi_2(\mathbf{r}) \end{bmatrix} \begin{bmatrix} K_1^{-1} & -2\Delta_s-2\Delta_a \\ -2\Delta_s+2\Delta_a & K_2^{-1} \end{bmatrix} (\mathbf{r},\mathbf{r}') \begin{bmatrix} \phi_1(\mathbf{r}') \\ \phi_2(\mathbf{r}') \end{bmatrix}^T \Bigg] , \qquad (3.3)
\end{aligned}
$$

where

$$
K_i^{-1}(\mathbf{r},\mathbf{r}';E_i) = G_i^{-1}(\mathbf{r},\mathbf{r}';E_i) + i2\gamma_i(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') . \qquad (3.4)
$$

Δ_s denotes the symmetric part of the pair field and Δ_a is the corresponding antisymmetric one. Note that $1/w_{12}$ has to be understood as numeric division in contrast to the inversion of w_{ii}^{-1}. Furthermore we have omitted the irrelevant prefactor for convenience. The integration over the ϕ's is Gaussian, yielding

$$
\begin{aligned}
Y[h_1,h_2]=\int \prod_{i=1}^{2} D\gamma_i D\Delta_s D\Delta_a \exp \Bigg[& -\tfrac{1}{2} \sum_{i=1}^{2} \int d^3\mathbf{r} d^3\mathbf{r}' \gamma_i(\mathbf{r}) w_{ii}^{-1}(\mathbf{r}-\mathbf{r}')\gamma_i(\mathbf{r}') + \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\Delta_s(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} \\
& + \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\Delta_a(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} - \tfrac{1}{2} \mathrm{Tr} \ln \begin{bmatrix} K_1^{-1} & -2\Delta_s-2\Delta_a \\ -2\Delta_s+2\Delta_a & K_2^{-1} \end{bmatrix} \\
& + \tfrac{1}{2} \int d^3\mathbf{r}\, d^3\mathbf{r}' \begin{bmatrix} h_1(\mathbf{r}) \\ h_2(\mathbf{r}) \end{bmatrix} \begin{bmatrix} K_1^{-1} & -2\Delta_s-2\Delta_a \\ -2\Delta_s+2\Delta_a & K_2^{-1} \end{bmatrix}^{-1} \\
& \times (\mathbf{r},\mathbf{r}') \begin{bmatrix} h_1(\mathbf{r}') \\ h_2(\mathbf{r}') \end{bmatrix}^T \Bigg] , \qquad (3.5)
\end{aligned}
$$

where the trace Tr stands for

$$
\mathrm{Tr}B = \sum_{i=1}^{2} \int d^3\mathbf{r}\, B_{ii}(\mathbf{r},\mathbf{r}) . \qquad (3.6)
$$

The logarithm $\ln B$ may be expanded in the standard fashion as

$$
\ln B = -\sum_{\nu=1}^{\infty} \frac{1}{\nu} [-(B-I)]^{\nu} . \qquad (3.7)
$$

The generating functional (3.5) establishes a Hamiltonian which depends only on the auxiliary fields γ_i and the pair field Δ. The matrix

$$
\begin{bmatrix} K_1^{-1} & -2\Delta_s-2\Delta_a \\ -2\Delta_s+2\Delta_a & K_2^{-1} \end{bmatrix} \qquad (3.8)
$$

shows a structural equality with the Gorkov equation in the theory of type II superconductors [8]. In some respects the pair field corresponds therefore to the gap parameter. To see that Δ describes pairing explicitly let us examine its meaning at the classical level. The application of the Euler-Lagrange equation to the exponent of Eq. (3.3) produces in the limit $h_i \rightarrow 0$

$$
\Delta_s(\mathbf{r},\mathbf{r}') = w_{12}(\mathbf{r}-\mathbf{r}')\tfrac{1}{2}[\phi_1(\mathbf{r})\phi_2(\mathbf{r}') + \phi_1(\mathbf{r}')\phi_2(\mathbf{r})] \qquad (3.9)
$$

and

$$
\Delta_a(\mathbf{r},\mathbf{r}') = w_{12}(\mathbf{r}-\mathbf{r}')\tfrac{1}{2}[\phi_1(\mathbf{r})\phi_2(\mathbf{r}') - \phi_1(\mathbf{r}')\phi_2(\mathbf{r})] . \qquad (3.10)
$$

From Eqs. (3.9) and (3.10) it follows that Δ is connected with the product $\phi_1\phi_2$ which corresponds to the correlation of monomers with different sign.

To construct a Hamiltonian from the generating functional (3.5) in terms of the order parameter Δ we have to perform the trace. This yields a Hamiltonian with an infinite number of terms. Therefore we make use of the fact that the path integral is dominated by the minimum of Δ when $w_{12} \rightarrow -0$. Then the saddle point expansion implies that the Gaussian approximation is sufficient to calculate the path integral [11]. We shall see that the quadratic term of Δ_a does not contribute to the correlation function G_{12} when the system is highly symmetric.

The generating functional (3.5) is evaluated up to second order of Δ_s and Δ_a as

$$
\begin{aligned}
Y[h_1,h_2]=\int \prod_{i=1}^{2} D\gamma_i D\Delta_s D\Delta_a \exp\Bigg[& -\tfrac{1}{2}\sum_{i=1}^{2}\int d^3\mathbf{r}\, d^3\mathbf{r}'\gamma_i(\mathbf{r})w_{ii}^{-1}(\mathbf{r}-\mathbf{r}')\gamma_i(\mathbf{r}')+2\,\mathrm{tr}(K_1\Delta_s K_2\Delta_s)-2\,\mathrm{tr}(K_1\Delta_a K_2\Delta_a) \\
& +\tfrac{1}{2}\sum_{i=1}^{2}\int d^3\mathbf{r}\, d^3\mathbf{r}' h_i(\mathbf{r})K_i(\mathbf{r},\mathbf{r}';E_i)h_i(\mathbf{r}') \\
& +\int d^3\mathbf{r}\, d^3\mathbf{r}' h_1\circ[K_1\circ\Delta_s\circ K_2+K_2\circ\Delta_s\circ K_1]\circ h_2 \\
& +\int d^3\mathbf{r}\, d^3\mathbf{r}' h_1\circ[K_1\circ\Delta_a\circ K_2-K_2\circ\Delta_a\circ K_1]\circ h_2+\int d^3\mathbf{r}\, d^3\mathbf{r}'\frac{[\Delta_s(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} \\
& +\int d^3\mathbf{r}\, d^3\mathbf{r}'\frac{[\Delta_a(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')}-\tfrac{1}{2}\mathrm{Tr}\ln\begin{bmatrix}K_1^{-1} & 0\\ 0 & K_2^{-1}\end{bmatrix}\Bigg], \qquad (3.11)
\end{aligned}
$$

where tr in contrast to Tr means

$$\mathrm{tr}B=\int d^3\mathbf{r}\, B(\mathbf{r},\mathbf{r}), \qquad (3.12)$$

and the symbol ∘ stands for the convolution

$$B\circ C=\int d^3\mathbf{R}\, B(\mathbf{r}-\mathbf{R})C(\mathbf{R}-\mathbf{r}'). \qquad (3.13)$$

Note that the inversion of matrix (3.8) is calculated to first order of Δ_s and Δ_a because the second-order term produces corrections to Y which are irrelevant for calculating G_{12} due to Eq. (2.17). For highly symmetric systems the expression

$$\int d^3\mathbf{r}\, d^3\mathbf{r}' h_1\circ[K_1\circ\Delta_a\circ K_2-K_2\circ\Delta_a\circ K_1]\circ h_2 \qquad (3.14)$$

can be neglected. Integrating out the Δ_a field an irrelevant prefactor is obtained. After tedious but straightforward algebra one verifies that the integration over the Δ_s field yields

$$
\begin{aligned}
Y[h_1,h_2]=\int D\gamma_1 D\gamma_2 \exp\Bigg[& \tfrac{1}{2}\sum_{i=1}^{2}\int d^3\mathbf{r} d^3\mathbf{r}' h_i(\mathbf{r})K_i(\mathbf{r},\mathbf{r}';E_i)h_i(\mathbf{r}')-\tfrac{1}{2}\sum_{i=1}^{2}\int d^3\mathbf{r}\, d^3\mathbf{r}'\gamma_i(\mathbf{r})w_{ii}^{-1}(\mathbf{r}-\mathbf{r}')\gamma_i(\mathbf{r}') \\
& -\tfrac{1}{2}\mathrm{Tr}\ln\begin{bmatrix}K_1^{-1} & 0\\ 0 & K_2^{-1}\end{bmatrix}-\int d^3\mathbf{r}_1 d^3\mathbf{r}_1' d^3\mathbf{r}_2 d^3\mathbf{r}_2' h_1(\mathbf{r}_1)h_1(\mathbf{r}_1')\Omega_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')h_2(\mathbf{r}_2)h_2(\mathbf{r}_2')\Bigg],
\end{aligned}
\qquad (3.15)
$$

where Ω_{12} is the abbreviation of

$$
\begin{aligned}
\Omega_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')=\int & d^3\mathbf{R}\, d^3\mathbf{R}' K_1(\mathbf{r}_1,\mathbf{R})K_2(\mathbf{r}_2,\mathbf{R}') \\
& \times w_{12}(\mathbf{R}-\mathbf{R}')\Gamma_{12}(\mathbf{R},\mathbf{r}_1',\mathbf{R}',\mathbf{r}_2'),
\end{aligned}
\qquad (3.16)
$$

and Γ_{12} is the solution of the linear integral equation

$$
\begin{aligned}
\Gamma_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')= & K_1(\mathbf{r}_1,\mathbf{r}_1')K_2(\mathbf{r}_2,\mathbf{r}_2') \\
& -2\int d^3\mathbf{R}\, d^3\mathbf{R}' K_1(\mathbf{r}_1,\mathbf{R})K_2(\mathbf{r}_2,\mathbf{R}') \\
& \times w_{12}(\mathbf{R}-\mathbf{R}')\Gamma_{12}(\mathbf{R},\mathbf{r}_1',\mathbf{R}',\mathbf{r}_2').
\end{aligned}
\qquad (3.17)
$$

In order to integrate out the γ_i fields let us decompose them into two parts,

$$\gamma_i^{(0)}=\frac{\int d^3\mathbf{r}\gamma_i(\mathbf{r})}{\int d^3\mathbf{r}} \qquad (3.18)$$

and

$$\gamma_i^{(1)}(\mathbf{r})=\gamma_i(\mathbf{r})-\gamma_i^{(0)}. \qquad (3.19)$$

Note that $\gamma_i^{(0)}$ does not depend on $\mathbf{r}$. From Eqs. (3.18) and (3.19) one gets

$$\int d^3\mathbf{r}\gamma_i^{(1)}(\mathbf{r})=0. \qquad (3.20)$$

Furthermore both fields are independent from each other, i.e.,

$$
\begin{aligned}
& \int d^3\mathbf{r}[\gamma_i^{(0)}+\gamma_i^{(1)}(\mathbf{r})]^2 \\
& \quad =(\gamma_i^{(0)})^2\int d^3\mathbf{r}+\int d^3\mathbf{r}[\gamma_i^{(1)}(\mathbf{r})]^2.
\end{aligned}
\qquad (3.21)
$$

If we restrict ourselves to $O(\gamma_i^2)$ then the integration in Eq. (3.15) with respect to γ_i can be performed exactly. Using Eqs. (3.18)–(3.21) it can be easily verified that the linear contribution of the trace comes only from $\gamma_i^{(0)}$. The quadratic term of $\gamma_i^{(1)}(\mathbf{r})$ is irrelevant for calculating the correlation function G_{12}. Hence the only effect of the γ_i integrations in Gaussian approximation is the replacement

$$E_i\rightarrow E_i+i2\gamma_i^{(0)}. \qquad (3.22)$$

It is shown in Ref. [12] that the usage of E_i or of Eq. (3.22) does not play an important role as soon as mean values such as end-to-end distances are calculated. Therefore we shall replace K_i by G_i in the following.

Ignoring a prefactor the generating functional becomes

$$Y[h_1,h_2]=\exp\Bigg[\tfrac{1}{2}\sum_{i=1}^{2}\int d^3\mathbf{r}\,d^3\mathbf{r}'h_i(\mathbf{r})G_i(\mathbf{r},\mathbf{r}';E_i)h_i(\mathbf{r}')$$
$$-\int d^3\mathbf{r}_1d^3\mathbf{r}_1'd^3\mathbf{r}_2d^3\mathbf{r}_2'h_1(\mathbf{r}_1)h_1(\mathbf{r}_1')$$
$$\times\Omega_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')$$
$$\times h_2(\mathbf{r}_2)h_2(\mathbf{r}_2')\Bigg]\ . \tag{3.23}$$

After applying relationship (2.17) to Eq. (3.23) the correlation function reads

$$G_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')=\Gamma_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')$$
$$-2\int d^3\mathbf{R}\,d^3\mathbf{R}'G_1(\mathbf{r}_1,\mathbf{R})G_2(\mathbf{r}_2,\mathbf{R}')$$
$$\times w_{12}(\mathbf{R}-\mathbf{R}')\Gamma_{12}(\mathbf{R},\mathbf{r}_1',\mathbf{R}',\mathbf{r}_2')\ . \tag{3.24}$$

The expression obtained for the correlation function is connected with an integral equation which is clearly beyond a simple perturbation expansion. The evaluation of Eq. (3.24) is the topic of the next section.

IV. THE CORRELATION FUNCTIONS. COMPLEX FORMATION

To calculate the mean distance between the ends of two oppositely charged polyions a new set of coordinates is needed. We remark that due to translational invariance, i.e.,

$$G_i(\mathbf{r},\mathbf{r}')=G_i(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R})\ , \tag{4.1}$$

the auxiliary function Γ_{12} as well as the correlation function G_{12} also obey translational invariance, i.e.,

$$\Gamma_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')=\Gamma_{12}(\mathbf{r}_1+\mathbf{R},\mathbf{r}_1'+\mathbf{R},\mathbf{r}_2+\mathbf{R},\mathbf{r}_2'+\mathbf{R}) \tag{4.2}$$

and

$$G_{12}(\mathbf{r}_1,\mathbf{r}_1',\mathbf{r}_2,\mathbf{r}_2')=G_{12}(\mathbf{r}_1+\mathbf{R},\mathbf{r}_1'+\mathbf{R},\mathbf{r}_2+\mathbf{R},\mathbf{r}_2'+\mathbf{R})\ . \tag{4.3}$$

Without loss of generality we may identify $\mathbf{r}_2'$ with the origin. Then Γ_{12} and G_{12} depend only on three vectors. The new set of coordinates is defined as

$$\mathbf{r}=\mathbf{r}_2\ , \tag{4.4a}$$

$$\mathbf{r}_{12}'=\mathbf{r}_1'\ , \tag{4.4b}$$

and

$$\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2\ , \tag{4.4c}$$

whereby the Jacobian is unchanged. Then the integral equation (3.17) takes the form

$$\Gamma_{12}(\mathbf{r}_{12}+\mathbf{r},\mathbf{r}_{12}',\mathbf{r},\mathbf{0})=G_1(\mathbf{r}_{12}+\mathbf{r},\mathbf{r}_{12}')G_2(\mathbf{r},\mathbf{0})$$
$$-2\int d^3\mathbf{R}_{12}d^3\mathbf{R}\,G_1(\mathbf{r}_{12}+\mathbf{r},\mathbf{R}_{12}+\mathbf{R})G_2(\mathbf{r},\mathbf{R})w_{12}(\mathbf{R}_{12})\Gamma_{12}(\mathbf{R}_{12}+\mathbf{R},\mathbf{r}_{12}',\mathbf{R},\mathbf{0})\ . \tag{4.5}$$

The integration with respect to $\mathbf{r}$ defines a new auxiliary function. We have

$$\Gamma_{12}(\mathbf{r}_{12},\mathbf{r}_{12}')=\int d^3\mathbf{r}\,\Gamma_{12}(\mathbf{r}_{12}+\mathbf{r},\mathbf{r}_{12}',\mathbf{r},\mathbf{0}) \tag{4.6}$$

and

$$\Gamma_{12}(\mathbf{r}_{12},\mathbf{r}_{12}')=\int d^3\mathbf{r}\,G_1(\mathbf{r}_{12}+\mathbf{r},\mathbf{r}_{12}')G_2(\mathbf{r},\mathbf{0})$$
$$-2\int d^3\mathbf{R}_{12}d^3\mathbf{r}\,G_1(\mathbf{r}_{12}+\mathbf{r},\mathbf{R}_{12})G_2(\mathbf{r},\mathbf{0})$$
$$\times w_{12}(\mathbf{R}_{12})\Gamma_{12}(\mathbf{R}_{12},\mathbf{r}_{12}')\ . \tag{4.7}$$

Using

$$G_{12}(\mathbf{r}_{12},\mathbf{r}_{12}')=\int d^3\mathbf{r}\,G_{12}(\mathbf{r}_{12}+\mathbf{r},\mathbf{r}_{12}',\mathbf{r},\mathbf{0})\ , \tag{4.8}$$

one finds

$$G_{12}(\mathbf{r}_{12},\mathbf{r}_{12}')=\Gamma_{12}(\mathbf{r}_{12},\mathbf{r}_{12}')$$
$$-2\int d^3\mathbf{R}_{12}d^3\mathbf{r}\,G_1(\mathbf{r}_{12}+\mathbf{r},\mathbf{R}_{12})G_2(\mathbf{r},\mathbf{0})$$
$$\times w_{12}(\mathbf{R}_{12})\Gamma_{12}(\mathbf{R}_{12},\mathbf{r}_{12}')\ . \tag{4.9}$$

Equation (4.9) defines a correlation function which depends only on both distances between the ends of oppositely charged chains. The knowledge of such a function is sufficient to calculate the mean distance between the polyions.

Up to now we have confined ourselves to the real-space representation. It is more convenient for our purpose to introduce Fourier transformed quantities, which are

$$\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_2)=G_1(\mathbf{k}_1)G_2(\mathbf{k}_1)(2\pi)^3\delta(\mathbf{k}_1+\mathbf{k}_2)$$
$$-2G_1(\mathbf{k}_1)G_2(\mathbf{k}_1)(2\pi)^{-3}$$
$$\times\int d^3\mathbf{q}\,w_{12}(\mathbf{k}_1-\mathbf{q})\Gamma_{12}(\mathbf{q},\mathbf{k}_2)\ , \tag{4.10}$$

where

$$f(\mathbf{k})=\int d^3\mathbf{r}\exp[-i\mathbf{k}\cdot\mathbf{r}]f(\mathbf{r}) \tag{4.11}$$

and

$$f(\mathbf{r})=(2\pi)^{-3}\int d^3\mathbf{k}\exp[i\mathbf{k}\cdot\mathbf{r}]f(\mathbf{k}) \tag{4.12}$$

are the standard Fourier transformations. According to Eq. (4.9) the correlation function G_{12} reads

$$G_{12}(\mathbf{k}_1,\mathbf{k}_2)=\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_2)-2G_1(\mathbf{k}_1)G_2(\mathbf{k}_1)(2\pi)^{-3}\times\int d^3\mathbf{q}\,w_{12}(\mathbf{k}_1-\mathbf{q})\times\Gamma_{12}(\mathbf{q},\mathbf{k}_2)\ . \tag{4.13}$$

After the inverse Laplace transform [13]

$$\frac{-1}{4\pi^2}\int_{c-i\infty}^{c+i\infty}dE_1\int_{d-i\infty}^{d+i\infty}dE_2\exp[E_1N_1+E_2N_2]G(E_1,E_2)=G(N_1,N_2)\ , \tag{4.14}$$

Eq. (4.13) becomes

$$G_{12}(\mathbf{k}_1,\mathbf{k}_2;N_1,N_2)=\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_2;N_1,N_2)-2(2\pi)^{-3}\times\int d^3\mathbf{q}\int_0^{N_1}d\tau_1\int_0^{N_2}d\tau_2G_1(\mathbf{k}_1;N_1-\tau_1)G_2(\mathbf{k}_1;N_2-\tau_2)w_{12}(\mathbf{k}_1-\mathbf{q})\Gamma_{12}(\mathbf{q},\mathbf{k}_2;\tau_1,\tau_2)\ . \tag{4.15}$$

The mean-square distance between the ends of different chains can be related to G_{12} in the following way [14]:

$$\langle\mathbf{r}_{12}^2\rangle=\left.\frac{-\dfrac{\partial^2}{\partial\mathbf{k}^2}G_{12}(0,\mathbf{k};N_1,N_2)}{G_{12}(0,\mathbf{k};N_1,N_2)}\right|_{\mathbf{k}\to0}\ , \tag{4.16}$$

and the corresponding integral equation reads

$$G_{12}(0,\mathbf{k};N_1,N_2)=\Gamma_{12}(0,\mathbf{k};N_1,N_2)-2(2\pi)^{-3}\int d^3\mathbf{q}\,w_{12}(\mathbf{q})\int_0^{N_1}d\tau_1\int_0^{N_2}d\tau_2\Gamma_{12}(\mathbf{q},\mathbf{k};\tau_1,\tau_2)\ . \tag{4.17}$$

Using the bare propagator

$$G_i^{-1}(\mathbf{k};E_i)=\tfrac{1}{2}\mathbf{k}^2+E_i\ , \tag{4.18}$$

the bilinear expansion of Eq. (4.10) becomes [11]

$$\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_2;E_1,E_2)=\sum_n\frac{1}{\lambda_n+E_1E_2}\psi_n(\mathbf{k}_1;E_1E_2)\psi_n(-\mathbf{k}_2;E_1,E_2)\ , \tag{4.19}$$

where ψ_n is the eigenfunction of the integral equation

$$[\tfrac{1}{4}(\mathbf{k}^2)^2+\tfrac{1}{2}(E_1+E_2)\mathbf{k}^2]\psi_n(\mathbf{k};E_1,E_2)+2(2\pi)^{-3}\int d^3\mathbf{q}w_{12}(\mathbf{k}-\mathbf{q})\psi_n(\mathbf{q};E_1,E_2)=\lambda_n\psi_n(\mathbf{k};E_1,E_2)\ . \tag{4.20}$$

We are mainly interested in the limit of long chains, i.e., $N_i\to\infty$. The application of the inversion formula (4.14) to $\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_2;N_1,N_2)$ yields

$$\frac{-1}{4\pi^2}\int_{c-i\infty}^{c+i\infty}dE_1\int_{d-i\infty}^{d+i\infty}dE_2\exp[E_1N_1+E_2N_2+\ln\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_2;E_1,E_2)]=\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_{2;}N_1,N_2)\ . \tag{4.21}$$

The saddle point approximation states for $N_1=N_2=N$

$$N+\left.\frac{\partial}{\partial E_*}\ln\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_2;E_*,E)\right|_{E=E_*}=0\ . \tag{4.22}$$

Provided that ψ_n is analytic with respect to E the solution of Eq. (4.22) is given by that pole of Eq. (4.19) which corresponds to the lowest eigenvalue of Eq. (4.20). Then E_* is independent of the $\mathbf{k}$'s and reads

$$E_*=\sqrt{-\lambda_0}\ . \tag{4.23}$$

Note that λ_0 itself depends on E_* through Eq. (4.20). From Eq. (4.21) it follows that

$$\Gamma_{12}(\mathbf{k}_1,\mathbf{k}_2;N\to\infty,N\to\infty)\propto\exp[2E_*N]\psi_0(\mathbf{k}_1;E_*,E_*)\times\psi_0(-\mathbf{k}_2;E_*,E_*)\ . \tag{4.24}$$

It can be seen that in the limit $N\to\infty$, Γ_{12} is determined by the lowest (negative) eigenvalue and its corresponding eigenvalue function. This proves the ground state dominance. From Eq. (4.17) one deduces that

$$G_{12}(0,\mathbf{k};N\to\infty,N\to\infty)\propto\exp[2E_*N]\psi_0(-\mathbf{k};E_*,E_*)\ . \tag{4.25}$$

For further considerations it is of interest to get an exact expression of Eq. (4.25). Therefore we shall restrict ourselves for a moment to a δ-like potential, i.e., $w_{12}(\mathbf{r})=w_{12}\delta(\mathbf{r})$ before we come back to the more realistic case. Then it follows from Eq. (4.20)

$$\psi_0(\mathbf{k};E_*,E_*)=\frac{\text{const}}{\frac{1}{4}(\mathbf{k}^2)^2+E_*\mathbf{k}^2-\lambda_0}\ , \tag{4.26}$$

where const depends only on w_{12} and E_*. The lowest eigenvalue λ_0 is obtained by minimizing Eq. (4.20) with respect to the eigenfunction (4.26). One gets

$$\lambda_0=-\frac{w_{12}^4}{\pi^4}+\frac{2w_{12}^2}{\pi^2}E_*-E_*^2\ . \tag{4.27}$$

The condition (4.23) gives

$$E_*=\frac{w_{12}^2}{2\pi^2}\ , \tag{4.28}$$

so that the (un-normalized) eigenfunction reads

$$\psi_0\left[\mathbf{k};E_*=\frac{w_{12}^2}{2\pi^2},E_*=\frac{w_{12}^2}{2\pi^2}\right]=\frac{1}{\frac{1}{4}(\mathbf{k}^2)^2+(w_{12}^2/2\pi^2)\mathbf{k}^2+w_{12}^4/4\pi^4}\ . \tag{4.29}$$

According to Eqs. (4.16) and (4.25) the mean-square distance between chain ends becomes

$$\langle \mathbf{r}_{12}^2\rangle=\frac{4\pi^2}{w_{12}^2}\ . \tag{4.30}$$

Equation (4.30) tells us that $\langle \mathbf{r}_{12}^2\rangle$ is fully determined by the interaction strength w_{12}. Dissolution occurs when w_{12} or the eigenvalue λ_0 vanishes.

Let us come back to the more realistic potential (2.8). To enable further calculation we use a Padé fit for the scattering function (2.10) given by

$$S(\mathbf{k})=\frac{N^2}{2+\mathbf{k}^2N/2}\ . \tag{4.31}$$

By assuming that the Debye screening length (2.4) is much smaller than the radius of gyration, i.e., $R_g^2=N/2$, the approximation

$$w_{12}(\mathbf{k})=\left[u-\frac{4\pi\lambda_B f^2}{\mathbf{k}^2+\lambda_D^{-2}}\right]\frac{(\mathbf{k}^2)^2}{(\mathbf{k}^2+\xi_E^{-2})(\mathbf{k}^2+\xi_C^{-2})} \tag{4.32}$$

holds, where ξ_E is the Edwards screening length defined as

$$\xi_E^{-2}=4\rho N u\ , \tag{4.33}$$

and ξ_C is an effective Edwards screening length corresponding to an excluded-volume effect which is induced by the screened Coulombic interaction. Therefore

$$\xi_C^{-2}=8\pi\rho N\lambda_B f^2\lambda_D^2\ . \tag{4.34}$$

Unfortunately the eigenvalue problem (4.20) with respect to Eq. (4.32) is not solvable exactly. If ξ_E and ξ_C are much larger than λ_D the potential (4.32) may be considered approximately as δ-like. Then Eq. (4.26) may be used as a trial function. For computational reasons this would not be a good choice. Therefore we use the 1*s* wave function of a hydrogen atom,

$$\psi(\mathbf{k})=8\pi\left[\frac{a^3}{\pi}\right]^{1/2}\frac{a}{(a^2+\mathbf{k}^2)^2}\ , \tag{4.35}$$

where a is the variational parameter. Note that Eq. (4.35) produces the results of Eqs. (4.28) and (4.30) with a failure smaller than 1%.

The solution of Eq. (4.23) requires self-consistency which is, even in the case of the approximations used, (4.32) and (4.35), very difficult to obtain. We shall therefore restrict ourselves to the condition for which the lowest eigenvalue vanishes. After minimizing Eq. (4.20) for vanishing E_* one obtains, neglecting terms of $O((\xi_E^{-1}+\xi_C^{-1})^2\lambda_D^2)$, the following result:

$$u-4\pi\lambda_B f^2\lambda_D^2+(\xi_E^{-1}+\xi_C^{-1})\left[\frac{5\pi}{32}+4\pi\lambda_B f^2\lambda_D^3\right]=0\ . \tag{4.36}$$

Equation (4.36) yields a critical polymer concentration ρ_* above which complex formation is no longer possible. The functional dependence of ρ_* on temperature, solvent quality (dielectric constant), and polymer properties such as Kuhn length l, excluded volume u, or charge fraction f, and low molecular salt concentration is very complicated and a quantitative discussion seems to be difficult. Moreover, the Hamiltonian (2.1) together with the interaction (2.2) are, however, a phenomenological model which does not allow a quantitative comparison to a real experimental situation. Nevertheless, the effective potential shows a change of sign at $k=k_c$ and its physical consequences will be discussed below.

V. DISCUSSION

The condition for the lowest eigenvalue to be zero immediately yields a nontrivial zero for the effective potential $w_{12}(\mathbf{k})$ calculated in Eq. (4.32). The potential $w_{12}(\mathbf{k})$ vanishes for the wave vector

$$k_c^2=\frac{\lambda_D^{-2}}{1-(\xi_E^{-1}+\xi_C^{-1})(\lambda_D+5/128\lambda_B f^2\lambda_D^2)}-\lambda_D^{-2}\ . \tag{5.1}$$

It is interesting to note that w_{12} $(k>k_c)$ is repulsive, whereas for $0<k<k_c$ the potential becomes attractive:

$$w_{12}(k)\begin{cases}>0\ , & k_c<k<\infty\\ <0\ , & 0<k<k_c\ .\end{cases} \tag{5.2}$$

This observation tempts one to postulate a "blob model" where the size of the blobs ξ_b is roughly given by $\xi_b\propto k_c^{-1}$. At large distances the tagged chain embedded in the medium experiences an attraction whereas at small distances the chain is still self-avoiding. This conclusion needs, however, a more detailed consideration.

First, it is important to notice that the existence of a finite k_c is the direct result of the Edwards screening of the excluded-volume potential, i.e., for

$$\xi_E^{-1}\rightarrow 0 \tag{5.3a}$$

or

$$c\rightarrow 0 \tag{5.3b}$$

(c being the monomer concentration) a dissolution of the complex can take place when low molecular salt is added. Equation (4.36) predicts then a compensation of excluded volume and the Debye potential. If this happens the effective interaction $w_{12}(\mathbf{k})$ vanishes at zero wave vector. For finite monomer concentration $c=c_*$ no such compensation at zero wave vector takes place, but at finite wave vector $k=k_c$. This is a direct consequence of the Edwards screening. Therefore the chains are partially attractive. A physical picture is given in Fig. 1.

This picture, however, is not as strong as the de Gennes blob picture for neutral solutions [2]. To see this

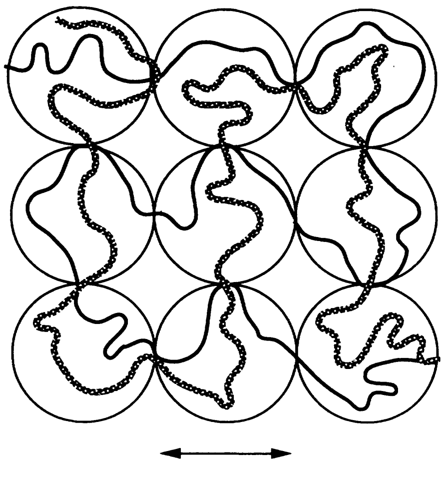

FIG. 1. The physical picture of the complex formation. The potential $w_{12}(k)$ [Eq. (4.32)] changes sign at a certain wave vector k_c [Eq. (5.1)]. This suggests that on scales larger than $\xi_b \propto 1/k_c$ the chains attract each other, whereas at smaller scales the chains are repulsive. The two differently charged chains are drawn black and gray.

consider the conformational free energy

$$\exp[-F]=\int d^3\mathbf{r}_{12}\, d^3\mathbf{r}'_{12} G_{12}(\mathbf{r}_{12},\mathbf{r}'_{12};N_1,N_2) \tag{5.4}$$

for the symmetric case $N=N_1=N_2$. For $N\rightarrow\infty$ the ground state dominance is satisfied [see Eq. (4.25)] and we find

$$\frac{F(w_{12}\neq 0)-F(w_{12}=0)}{2N}=-\sqrt{-\lambda_0}=-E_* \ . \tag{5.5}$$

Therefore for $w_{12}\neq 0$ and $E_*=0$ the free energy is identical with that of the case $w_{12}=0$. This yields the conclusion that a small attractive part of w_{12} does not automatically yield a bound state, i.e., a complex.

Finally we would like to add a few remarks for the outlook of this approach. In this paper the calculation has been illustrated for the case of complex formation in oppositely charged polyelectrolytes. There are many important physical problems that can also be solved with this approach. One possible extension of this work is to study dense systems (close c_*) and work out the stability condition. In this case we expect a microphase separation transition at a wave vector k_* which is very much related to the critical wave vector k_c given in this paper. This leads to compatibility enhancement of the species similarly to the case treated previously the first time [15].

Other interesting systems are ionomers, polyampholytes, etc. In such systems the strongly attractive *and* repulsive units are replaced along the chains (see also [15] and references therein). The application of the pair-field formalism introduced here has been successfully treated in [16].

It is also of interest to study single polymer chains in critical fluids such as mixed solvents near their consolute point [17,18]. In these systems effective attractive interactions for the chain itself are induced by the critical fluctuations of the fluid and the chain eventually collapses. The path-integral treatment has been given recently [19] and the wave vector dependent (negative) second virial coefficient was calculated. The combination of these problems is certainly interesting, i.e., the effect of underlying criticality on the pair-field correlation function.

APPENDIX A

In this appendix we derive identity (3.1). Introducing an auxiliary field λ_i according to

$$\lambda_i(\mathbf{r})=\gamma_i(\mathbf{r})+i\int d^3\mathbf{R}\, w_{ii}(\mathbf{r}-\mathbf{R})\phi_i^2(\mathbf{R}) \tag{A1}$$

then the differential D is unchanged, i.e.,

$$D\lambda_i=D\gamma_i \ . \tag{A2}$$

After applying the relationship

$$\int d^3\mathbf{R}\, w_{ii}^{-1}(\mathbf{r}-\mathbf{R})w_{ii}(\mathbf{R}-\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}') \tag{A3}$$

to the product

$$\begin{aligned}-\lambda_i(\mathbf{r})\lambda_i(\mathbf{r}')=&-\gamma_i(\mathbf{r})\gamma_i(\mathbf{r}')-i\gamma_i(\mathbf{r})\int d^3\mathbf{R}\, w_{ii}(\mathbf{r}'-\mathbf{R})\phi_i^2(\mathbf{R})-i\gamma_i(\mathbf{r}')\int d^3\mathbf{R}\, w_{ii}(\mathbf{r}-\mathbf{R})\phi_i^2(\mathbf{R})\\&+\int d^3\mathbf{R}\, d^3\mathbf{R}' w_{ii}(\mathbf{r}-\mathbf{R})w_{ii}(\mathbf{r}'-\mathbf{R}')\phi_i^2(\mathbf{R})\phi_i^2(\mathbf{R}')\end{aligned} \tag{A4}$$

Eq. (3.1) follows when using Eq. (A2), where const denotes

$$1/\text{const}=\int D\lambda_i \exp\left[-\tfrac{1}{2}\int d^3\mathbf{r}\, d^3\mathbf{r}',\lambda_i(\mathbf{r})w_{ii}^{-1}(\mathbf{r}-\mathbf{r}')\lambda_i(\mathbf{r}')\right] . \tag{A5}$$

APPENDIX B

Here we derive identity (3.2). Because $\Delta(\mathbf{r},\mathbf{r}')$ is a function of two parameters it is necessary to divide it into symmetric and antisymmetric parts. Starting from

$$\omega_s(\mathbf{r},\mathbf{r}')=\Delta_s(\mathbf{r},\mathbf{r}')-w_{12}(\mathbf{r}-\mathbf{r}')\tfrac{1}{2}[\phi_1(\mathbf{r})\phi_2(\mathbf{r}')+\phi_1(\mathbf{r}')\phi_2(\mathbf{r})] \tag{B1}$$

and

$$\omega_a(\mathbf{r},\mathbf{r}')=\Delta_a(\mathbf{r},\mathbf{r}')-w_{12}(\mathbf{r}-\mathbf{r}')\tfrac{1}{2}[\phi_1(\mathbf{r})\phi_2(\mathbf{r}')-\phi_1(\mathbf{r}')\phi_2(\mathbf{r})] \ , \tag{B2}$$

then the identities

$$D\omega_s = D\Delta_s \tag{B3}$$

and

$$D\omega_a = D\Delta_a \tag{B4}$$

hold. It follows immediately from Eqs. (B1) and (B2) that

$$\begin{aligned}
&\int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\omega_s(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} + \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\omega_a(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} \\
&\quad = \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\Delta_s(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} + \int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\Delta_a(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} + \int d^3\mathbf{r}\, d^3\mathbf{r}' \phi_1^2(\mathbf{r}) w_{12}(\mathbf{r}-\mathbf{r}') \phi_2^2(\mathbf{r}') \\
&\qquad - \int d^3\mathbf{r}\, d^3\mathbf{r}' [\Delta_s(\mathbf{r},\mathbf{r}') - \Delta_a(\mathbf{r},\mathbf{r}')] \phi_1(\mathbf{r}) \phi_2(\mathbf{r}') - \int d^3\mathbf{r}\, d^3\mathbf{r}' [\Delta_s(\mathbf{r},\mathbf{r}') + \Delta_a(\mathbf{r},\mathbf{r}')] \phi_1(\mathbf{r}') \phi_2(\mathbf{r}) \, .
\end{aligned} \tag{B5}$$

Equation (B5) plays the role of the exponent in Eq. (3.2) which may be obtained using Eqs. (B3) and (B4). Note that const means

$$1/\text{const} = \int D\omega_s D\omega_a \exp\left[\int d^3\mathbf{r}\, d^3\mathbf{r}' \frac{[\omega_s(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} + \int d^3\mathbf{r} d^3\mathbf{r}' \frac{[\omega_a(\mathbf{r},\mathbf{r}')]^2}{w_{12}(\mathbf{r}-\mathbf{r}')} \right] . \tag{B6}$$

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