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# Microscopic Theory of Polymer Chains Containing Attractive Units: Copolymers, Ionomers, and Complex Formation

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ABSTRACT: In this paper a simple microscopic theory for partially attractive polymer chains is developed. For attractive polymer chains no simple theories such as the random phase approximation (RPA) or renormalization group (RG) exist, in contrast to repulsive chains. The approach used in this paper has strong similarities with the theory of superconductors. Apart form normal microscopic density fields special pair fields are introduced, whose physical properties are sensitive to the behavior of two monomers of the attractive kind. A new version of the RPA is introduced, that is valid for attractive polymer systems. The collapse transition, globule formation, or ionomer binding can be mapped onto the formation of cooper pairs in the BCS theory. This theory can be applied to polymers in bad solvent, ionomers, polyampholytes, and the complex formation in multiple charged polyelectrolyte solutions.

## 1. Introduction

The study of chains which attract each other is generally a very complicated problem. There is not such a wide accepted theory as in the case where the chains repel each other.[1,2] The collapse of chains in bad solvent, i.e. in cases where the second virial coefficient is negative, is a typical example. One of the most successful theories is the Lifshitz theory.[1,3] In this theory a simple expression for the entropy of the chain in terms of the local density has been found. The use of this theory enables us to study to some extent the properties of isolated collapsed chains. Theories of the RPA type[1,2,4] are not useful since these theories do not contain the essential physics of pair formation. The situation is even more subtle in the case of dense melts of chains containing units which attract each other. In this case not only single chains attract themselves but also neighboring chains. The result will be a network of chains where the cross-links are formed by clusters of attractive points. Such polymer chains are used in practice to compatibilize polymer blends as described in the following example. Imagine two different polymers, A and B, e.g. Most of the different polymer species are not compatible and therefore not miscible in a wide range of temperatures.[4] Significant material modification by blending is one of the goals in industry, but the range of miscible materials is very limited. One possibility is to find partially compatible polymers which mix at high temperatures. When these polymers are cooled to the temperature where the blend is going to be used, these polymers usually demix. A macroscopic phase separation is not possible if these polymers are chemically modified in a way that they contain a certain fraction of attractive monomers or dipoles. A microscopic theory of such materials is not simple but has been started first in refs 5 and 6. A phenomenological estimate of the phase diagrams has been put forward by Khokhlov and co-workers,[7] but in these theories no systematic microscopic theory which starts from a chain Hamiltonian has been considered. On the other hand detailed models on attractive polymer types such as ionomers are studied. A seminal paper has been published by Cates and Witten[8] who treat the problem of ionomers perturbatively. Recent simulations by Baljon-Haakman and Witten[9] have to be mentioned that predict conformational properties on the ionomer chain. In these studies the problem is drawn back to the comparison of the return probability of two segments which attract each other and the gain in sticking energy of the two attractive monomers. These studies find chain properties relatively insensitive to temperature changes. This is intuitively clear, as large attraction energies are assumed. Moreover the attractive forces between the attractive monomers (=*stickers*) are very large. The results are irreversible aggregates of nonequilibrium configurations.

In the present study we do not aim for such specific and very complicated situations. However, we apply our recent developments in the theory of polyelectrolyte blends[10] to the case of attractive chains. In this first study on this subject we leave the detailed models and do not consider such models as in refs 8 and 9. On the other hand we do go beyond the phenomenological models that use only modified mean-field Flory-Huggins type approximation, ignoring any fluctuations as, for example, suggested in ref 7. Therefore the aim of our paper is 2-fold: We first would like to present a novel method for the physical description of attractive polymer chains; secondly, we put forward our method on simple attractive systems. Let us discuss briefly the first point before going to more details.

Recently, we introduced a new approach[10] where the RPA has been formulated in terms of collective density variables which contain not only information of only one type of monomers but also information of two physically different monomers as they attract each other and form bound states. Pair fields have been introduced to study the problem of complex formation in mixtures of two differently charged polymers. The formulation of the theory started from the Edwards model for flexible polymers and led to a generalization of the usual RPA. The behavior of the pair field correlation function is sensitive to complex formation, i.e. the attraction between several monomers or dipoles of the same type. In ref 10 the theory has been formulated for mixtures of attractive polymers, such as differently charged polyelectrolytes. In this paper the formulation for copolymers is introduced.

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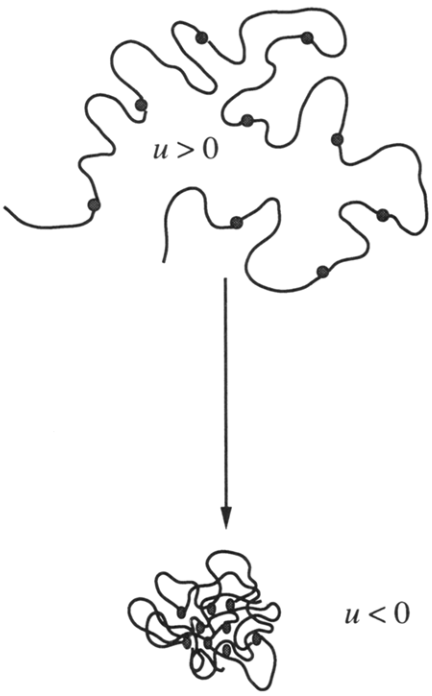

**Figure 1.** Schematic representation of a polymer with attractive monomers placed along its contour. When the net attraction becomes larger than a critical value the polymer collapses and forms a globule.

This will naturally lead to different phenomena.

There are many physical situations when polymer segments attract each other. All these specific systems require their own detailed consideration, but we present below one type of theory that could be a basis for further studies. Let us therefore describe several systems that are interesting in the context of our theory presented below.

One example is polymers which consist of several species of monomers in one chain, A and B, e.g. It is assumed that the B monomers attract each other strongly with a certain short range potential $U_{BB}$, whereas all other monomer potentials are repulsive. The polymer can be regarded as a copolymer where the B units are distributed along the chain. For simplicity it is assumed throughout this paper that the B unit are smeared out along the polymer chain. This assumption is useful and will simplify calculations but will not change the results significantly compared to the more realistic case where the B monomers are equally distributed, i.e. at a certain distance (see Figure 1) along the chain. In fact these types of approximations are frequently used in several theories of polyelectrolytes.[15,17] These assumptions will lead to a calculation which can be performed by using annealed averages compared to quenched averages. The latter case will become important if the B units are distributed randomly along the chain. Such molecules can be viewed as random copolymers and will be treated in a separate publication, where these pair fields will be combined with the replica formulation of disordered systems.[13] In this introductory paper we avoid these complications on purpose. Although these systems require a detailed mathematical analysis of their averages, we present the model in a much simplified version. Therefore, we smear out the attractive units along the chain. By doing this, we lose the essentials of the quenched average for random systems, but nevertheless keep the basic physics of attractive systems. It is demonstrated that the problems that occur in attractive systems can be analyzed nonperturbatively by the introduction of the above mentioned pair field.

The paper is organized as follows. In the following section the model and the definitions will be introduced. The mathematical model is formulated in terms of the continuous version of the Edwards model, and the interactions will be treated as short range effective interactions (pseudopotentials). In section 3 the Edwards model will be turned into a field theory and the pair field will be introduced to handle the onset of the collapse. Section 4 discusses the thermodynamics and the conformational statistics. In section 5 a Flory type argument for calculating the end-to-end distance is given. Section 6 is devoted to the conclusions.

## 2. Edwards Hamiltonian and Definitions

In this section the model used in the paper is introduced and defined. The Edwards Hamiltonian of an interacting polymer chain consists of two parts, i.e. the entropy and the energetic part. The conformational part of the Hamiltonian of the chain is represented in the simplest version by a bead spring model, i.e. a summation over harmonic springs. These entropic contributions can be written as

$$\frac{E_{\mathrm{el}}(\{\mathbf{r}_n\})}{k_{\mathrm{B}}T} = \frac{3}{2l^2}\sum_{n=1}^{N}(\mathbf{r}_n - \mathbf{r}_{n-1})^2 \tag{1}$$

where $l$ is the bond length, $\mathbf{r}_n$ is the spatial position of the position of the $n$th monomer, $k_{\mathrm{B}}$ is Boltzmann's constant, and $T$ is the absolute temperature. $N$ is the total number of monomers; i.e. it counts both of the species A and B. The introduction of density fields $\rho_i(\mathbf{r})$ which define the local monomer concentration of species $i$ at $\mathbf{r}$, yields the following representation of the energetic part of the Hamiltonian:

$$\frac{E_{\mathrm{int}}(\{\mathbf{r}\})}{k_{\mathrm{B}}T} = \frac{1}{2}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\,\{\rho_{\mathrm{A}}(\mathbf{r})U_{\mathrm{AA}}(\mathbf{r}-\mathbf{r}')\rho_{\mathrm{A}}(\mathbf{r}') + 2\rho_{\mathrm{A}}(\mathbf{r})U_{\mathrm{AB}}(\mathbf{r}-\mathbf{r}')\rho_{\mathrm{B}}(\mathbf{r}') + \rho_{\mathrm{B}}(\mathbf{r})U_{\mathrm{BB}}(\mathbf{r}-\mathbf{r}')\rho_{\mathrm{B}}(\mathbf{r}')\} \tag{2}$$

This expression can be simplified further when $\rho(\mathbf{r})$ is the average concentration of an arbitrary monomer at position $\mathbf{r}$. Then we can write for the local density of the A species

$$\rho_{\mathrm{A}}(\mathbf{r}) = (1-f)\rho(\mathbf{r}) \tag{3}$$

and similarly for the B species

$$\rho_{\mathrm{B}}(\mathbf{r}) = f\rho(\mathbf{r}) \tag{4}$$

Here $f$ is the fraction of B monomers. The total interaction energy of such AB copolymers can then be written as

$$\frac{E_{\mathrm{int}}(\{\mathbf{r}\})}{k_{\mathrm{B}}T} = \frac{1}{2}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\,\rho(\mathbf{r})\rho(\mathbf{r}')\{(1-f)^2U_{\mathrm{AA}}(\mathbf{r}-\mathbf{r}') + 2(1-f)fU_{\mathrm{AB}}(\mathbf{r}-\mathbf{r}') + f^2U_{\mathrm{BB}}(\mathbf{r}-\mathbf{r}')\} \tag{5}$$

The entire statistical weight of the polymer conformation $\{\mathbf{r}\}$ is thus given by the Boltzmann factor

$$\exp\left\{-\frac{E_{\mathrm{el}}(\{\mathbf{r}\})}{k_{\mathrm{B}}T} - \frac{E_{\mathrm{int}}(\{\mathbf{r}\})}{k_{\mathrm{B}}T}\right\} \tag{6}$$

The continuous limit is taken in the usual way, i.e. $l \to 0$, $N \to \infty$, and $lN = L$, where $L$ is the (finite) contour length.

The probability density for a chain with fixed ends $\mathbf{0}$ and $\mathbf{R}$ is given by the following propagator

$$G(\mathbf{R},N) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(N)=\mathbf{R}} \mathrm{d}\{\mathbf{r}(s)\} \exp\left\{-\frac{3}{2l^2}\int_0^N \mathrm{d}s \left(\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}s}\right)^2 - \frac{1}{2}\int_0^N \mathrm{d}s \int_0^N \mathrm{d}s' \, [(1-f)^2 U_{\mathrm{AA}}(\mathbf{r}(s)-\mathbf{r}(s')) + 2(1-f)fU_{\mathrm{AB}}(\mathbf{r}(s)-\mathbf{r}(s')) + f^2 U_{\mathrm{BB}}(\mathbf{r}(s)-\mathbf{r}(s'))]\right\} \quad (7)$$

The mean square end-to-end distance can be calculated simply by the average

$$\langle \mathbf{R}^2 \rangle = \frac{\int \mathrm{d}\mathbf{R}\, \mathbf{R}^2 G(\mathbf{R},N)}{\int \mathrm{d}\mathbf{R}\, G(\mathbf{R},N)} \quad (8)$$

The universal properties of such polymers can already be studied in a psuedopotential approximation; i.e. the potentials can be replaced by short ranged $\delta$-functions with a certain strength

$$U_{ij}(\mathbf{r}) = u_{ij}\delta(\mathbf{r}) \quad (9)$$

In this case the total interaction energy can be simplified to

$$U(\mathbf{r}) = u\delta(\mathbf{r}) = [(1-f)^2 u_{\mathrm{AA}} + 2(1-f)fu_{\mathrm{AB}} + f^2 u_{\mathrm{BB}}]\delta(\mathbf{r}) \quad (10)$$

Now let us assume that the AA and the AB interactions are repulsive, i.e. $u_{\mathrm{AA}} > 0$ and $u_{\mathrm{AB}} > 0$, whereas the B monomers attract each other, i.e. $u_{\mathrm{BB}} < 0$. A critical value for the fraction of B monomers is defined immediately by the model itself which is denoted by $f_*$. For $f > f_*$, the entire chain collapses and forms a dense globule, whereas for $f < f_*$ the repulsive interactions are dominant and the chain keeps the swollen configuration. The critical value for the B fraction $f_*$ is given by

$$f_* = \frac{u_{\mathrm{AA}} - u_{\mathrm{AB}} - (u_{\mathrm{AB}}^2 + u_{\mathrm{AA}}|u_{\mathrm{BB}}|)^{1/2}}{u_{\mathrm{AA}} - 2u_{\mathrm{AB}} - |u_{\mathrm{BB}}|} \quad (11)$$

This value for $f$ is the only point where attraction comes into play physically. The model presented now seems to be oversimplified in connection with realistic systems of ionomers or random copolymers, but it is, however, simple enough to demonstrate the essence of the method put forward here. It can be seen easily that, indeed, for this value of the fraction of B monomers the total interaction $u < 0$, and the interaction energy of the chain is negative. Near the critical value $f_*$, i.e. $f \approx f_*$, the total interaction energy can be approximated linearly in $f$ and we write

$$u \propto (f_* - f)/f_* \quad (12)$$

As a remark aside we note that this model can also be used to describe the coil–globule transition for chains in a bad solvent or more generally for polyampholyte chains in polar solvent. The generalization to these cases is not a major problem. For example let $c_*$ be the critical low molecular weight salt concentration. For salt concentrations above $c_*$ Coulomb forces are screened out and the polymer shows swollen coil conformations. Near the critical salt concentration $c_*$ the total interaction can also be written as

$$u \propto (c - c_*)/c_* \quad (13)$$

On the basis of the model the coil–globule transition will be analyzed. The use of Edwards type path integrals is very difficult and will not lead to simple solutions. Open questions for example are the structure of the globule and the onset of the globule transition. To get deeper inside this problem, the model described in this section will be turned into a field theory. It is already obvious from what has been said before in this section that the use of single collective density fields is not sufficient. What is needed are fields which are sensitive to pair interactions between the same or different species and which do, however, not separate into a product form as the corresponding standard RPA pair interaction terms for repulsive monomers, i.e. $\rho_{\mathrm{A}}(\mathbf{r})\rho_{\mathrm{A}}(\mathbf{r})$ or $\rho_{\mathrm{A}}(\mathbf{r})\rho_{\mathrm{B}}(\mathbf{r})$, for example.

## 3. Field Theoretic Formulation, Pair Fields

To set up an appropriate field theory for this problem, the well-known polymer magnet analogy can be used. To be more specific, we use here the propagator representation over soft spin fields, which is the usual $O(n)$ theory, rather than the direct hard spin version.[4,13] To begin with, we start form the Laplace–de Gennes transformation of the polymer propagator $G(\mathbf{R},N)$

$$G(\mathbf{R},\mu) = \int_0^\infty \mathrm{d}N \exp(-\mu N)\, G(\mathbf{R},N) \quad (14)$$

and the usual $O(n)$ $\varphi^4$ Hamiltonian in the theory of phase transitions

$$\mathcal{L}[\varphi] = \int \mathrm{d}\mathbf{r} \left\{\varphi(\mathbf{r})\left(\mu - \frac{l^2}{6}\frac{\partial^2}{\partial \mathbf{r}^2}\right)\varphi^*(\mathbf{r}) + u(\varphi(\mathbf{r})\varphi^*(\mathbf{r}))^2\right\} \quad (15)$$

Here $\varphi$ is an $n$-component complex order parameter field, and the original Green function $G(\mathbf{R},N)$ is represented by an $n = 0$ field theory of the form[12,13]

$$G(\mathbf{R},\mu) = \lim_{n\to 0} \int \prod_{\alpha=1}^{n} \mathrm{d}\{\varphi_\alpha(\mathbf{r})\}\, \mathrm{d}\{\varphi_\alpha^*(\mathbf{r})\}\, \varphi_1(\mathbf{R})\varphi_1^*(\mathbf{0}) \times \exp\{-\mathcal{L}[\varphi]\} \quad (16)$$

The use of the generating functional

$$Z[\mathbf{h},\mathbf{h}^*] = \int \mathrm{d}\{\varphi\}\, \mathrm{d}\{\varphi^*\} \exp\{-\mathcal{L}[\varphi] - \int \mathrm{d}\mathbf{r}\, [\mathbf{h}^*(\mathbf{r})\varphi(\mathbf{r}) + \mathbf{h}(\mathbf{r})\varphi^*(\mathbf{r})]\} \quad (17)$$

yields the correlation function in the form

$$G(\mathbf{R},\mu) = \left.\frac{\delta^2 Z[\mathbf{h},\mathbf{h}^*]}{\delta h_1(\mathbf{R})\delta h_1^*(\mathbf{0})}\right|_{\mathbf{h}\to \mathbf{0}} \quad (18)$$

The comparison with usual field theories of critical phenomena when $n > 0$ yields for the mass $\mu$ the correspondence $\mu \equiv (T - T_{\mathrm{c}})/T_{\mathrm{c}}$. The main interest in this paper is not in the first instance the critically in terms of vanishing mass but in the physical behavior of the system around the vanishing coupling constant $u \propto (f_* - f)/f_*$ (or similar for the case of complex formation $u \propto (c - c_*)c_*$ for the total interaction of the polymer system). In ref 10 it has been already shown that the only use of the order parameter $\varphi$ does not lead to relevant new physical insight for the problem studied in this paper. Instead of the field $\varphi$ it is essential to use now a new (complex) pair field $\Delta$

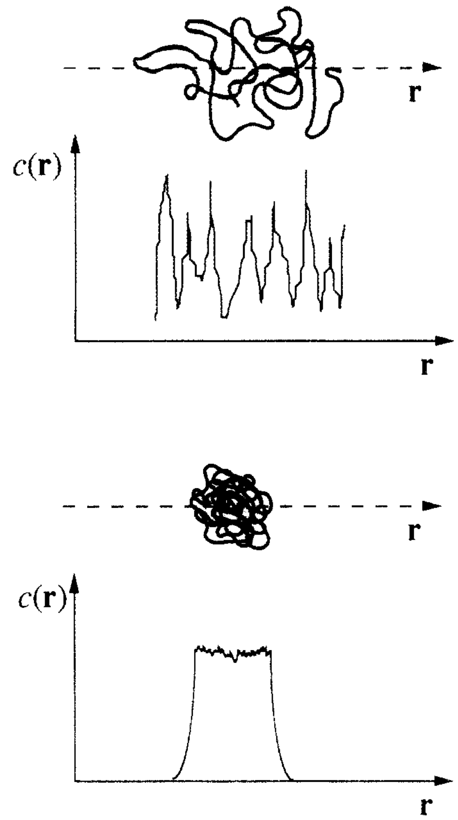

**Figure 2.** Globular state containing much less fluctuations as the swollen state, as shown in this intuitive figure. This justifies the Gaussian approximation in the pair field Hamiltonian.

which reads at the mean-field level

$$\Delta(\mathbf{r}) = u\varphi(\mathbf{r})\varphi(\mathbf{r}) \tag{19}$$

The latter step is quite analogous to the case of the BCS theory of superconductivity and has been extensively studied in great detail in ref 14. It is important to notice that this step is an extension of the usual polymer random phase approximation. The conventional RPA for polymers uses density fields only. The use of such density fields is appropriate for repulsive systems and cannot be extended to attractive systems. Pair fields are very useful to account for the properties of different pairs of monomers and their behavior as a unit.

From the demonstration in Appendix A it can be seen that the generating functional can be written in terms of the pair field

$$Z[\mathbf{h},\mathbf{h}^*] = Z_0\mathcal{N}^{-1}\int d\{\Delta\}\, d\{\Delta^*\} \exp\left\{-\mathcal{H}[\Delta,\Delta^*] - \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' \begin{pmatrix}\mathbf{h}(\mathbf{r})\\ \mathbf{h}^*(\mathbf{r})\end{pmatrix} \mathbf{G}_\Delta(\mathbf{r},\mathbf{r}') \begin{pmatrix}\mathbf{h}^*(\mathbf{r}')\\ \mathbf{h}(\mathbf{r}')\end{pmatrix}\right\} \tag{20}$$

where $Z_0$ is the partition function of the noninteracting system, i.e. $u = 0$. Moreover the Green function $\mathbf{G}_\Delta(\mathbf{r},\mathbf{r}')$ reads

$$\delta(\mathbf{r}-\mathbf{r}')\begin{pmatrix}\delta_{\alpha\beta}\left(\mu - \dfrac{l^2}{6}\dfrac{\partial^2}{\partial\mathbf{r}^2}\right)^{-1} & \Delta^*(\mathbf{r})\\ \Delta(\mathbf{r}) & \delta_{\alpha\beta}\left(\mu - \dfrac{l^2}{6}\dfrac{\partial^2}{\partial\mathbf{r}^2}\right)^{-1}\end{pmatrix} \tag{21}$$

The Hamiltonian $\mathcal{H}$ depends on infinitely many higher order terms for various reasons. Firstly, the globule is a dense object and fluctuations can be safely negelected (see Figure 2 for an illustration). Secondly, the result which will be derived below justifies this approximation itself. Thirdly, this situation is closely related to the derivation of the Lifshitz theory[3] from the $O(n)$ model for collapsed polymers.[19] There it is shown that the collapsed state contains less fluctuation as the swollen polymer. This situation is quite obvious but expresses itself directly in the theory. It has also to be realized that the Landau expansion in the pair field contains more information as the corresponding theory for the densities. However, the Gaussian approximation for the pair fields has a higher range of validity, as does the Gaussian approximation for polymer melts, especially when collapse problems are studied. This can be seen by the following argument. Kholodenko and Freed[16] studied the collapse problem (polymer in bad solvent) using a $\phi^6$ theory. When the excluded volume term becomes negative, the symmetry of the problem is broken. As a result a finite polymer (globule) concentration appears. In technical terms this means that the mean value of the field $\varphi$ is no longer zero but develops a finite value. As can be seen in Appendix A, the pair field has already a non-zero mean value. Thus the Gaussian approximation in the pair field theory already contains the broken symmetry implicitly.

Nevertheless higher order terms have to be investigated in separate works. Note further that the new order parameter pair field $\Delta$ describes the physics of pairing effects quite analogously to the case of Cooper pair formation in the BCS theory of superconductivity. The pairing effects produce dense systems, and fluctuations are small and can be neglected. Therefore we expect a Gaussian approximation to the Hamiltonian to be appropriate. Hence the lowest order Hamiltonian in **k** space is given by

$$\mathcal{H}_{\mathrm{RPA}} = -\left(\frac{3}{2\pi\mu l^2}\left(\frac{3\mu}{l^2}\right)^{1/2} + \frac{1}{u}\right)\int_{\mathbf{k}}|\Delta|^2 + \frac{1}{96\pi\mu^2}\left(\frac{3\mu}{l^2}\right)^{1/2}\int_{\mathbf{k}}\mathbf{k}^2|\Delta|^2 \tag{22}$$

where we have used the short hand notation $\int_{\mathbf{k}} = \int d\mathbf{k}/(2\pi)^3$.

In the next section a physical interpretation of this result is put forward. It is shown that the physical meaning of the mass term $\mu$ of the field theory is a chemical potential, as it must be since $\mu$ is the Laplace conjugate to the degree of polymerization $N$. Hence $\mu$ has to be real, and because of the appearance of $\mu^{1/2}$ the property $\mu \geq 0$ is necessary. It is easy to see that for coupling constants (total interactions) $u \geq 0$ the RPA Hamiltonian is unstable; i.e. $\mathcal{H}_{\mathrm{RPA}}$ is not bound from below as soon as $u \geq 0$. Therefore we use in the following $u = -|u|$. It has to be stressed once more that the Hamiltonian for the pair field does only make sense for attractive systems. The negative value of the total interaction $u$ in all expressions above is thus essential.

We must add another very important remark: In the starting equations we ignored the three body interaction, although we have considered negative two body forces (attracting chains). This point is contradictory, and the system becomes completely ustable; i.e. the polymer chain will collapse to a point. The problem will be analyzed qualitatively below in a Flory type argument. Moreover we can show that the model we discuss is valid only for very small attraction forces. When strong attraction forces are present, our theory becomes modified. In practice one can argue technically as follows. A small factor that makes the partition function convergent for all wave vectors can be added. This yields unphysically and physically relevant terms. It can be shown that the physically relevant results are equivalent to those presented above.[20]

## 4. Conformational Statistics at the Onset of the Phase Change

Although the swollen single coil has a very small monomer concentration compared to dense systems, we can assign the globule a finite monomer concentration and indeed the globule can be considered as a thermodynamic object on its own. This becomes valid when the number of monomers in the polymer becomes very large. Let $Z$ be the partition function which is defined by $\mathbf{h} \rightarrow 0$ from eq 20. The corresponding grand potential (in units of the thermal energy $k_BT$) is then given by[1]

$$\Omega - \Omega_0 = -\log Z/Z_0 \tag{23}$$

The monomer concentration inside the globule is then given by

$$\rho_G = \frac{\partial}{\partial\mu}\left(\frac{\Omega - \Omega_0}{V}\right) \tag{24}$$

where $V$ is the volume of the system. From eq 23 follows the grand potential[18] (see Appendix B)

$$\frac{\Omega - \Omega_0}{V} = \frac{n^2}{V}\log\left(\frac{1}{|u|} - \frac{3}{2\pi\mu l^2}\left(\frac{3\mu}{l^2}\right)^{1/2}\right) + \frac{n^2}{2\pi^2}\int_0^{1/l} \mathrm{d}k\, k^2 \times \log\left[\left(\frac{1}{|u|} - \frac{3}{2\pi\mu l^2}\left(\frac{3\mu}{l^2}\right)^{1/2}\right) + \frac{1}{96\pi\mu^2}\left(\frac{3\mu}{l^2}\right)^{1/2} k^2\right] \tag{25}$$

In eq 25 the $k = 0$ part has been calculated separately, and in the $k$ integration a large momentum cutoff $1/l$ has been used. Application of eq 24 yields, in the polymer limit $n \rightarrow 0$, a nonvanishing globule density of the form

$$\rho_G = \frac{n^2}{V}\frac{|u|3(3)^{1/2}}{2\mu}\frac{1}{2\pi l^3\mu^{1/2} - |u|3(3)^{1/2}} \tag{26}$$

whenever for $n \rightarrow 0$ or $V \rightarrow \infty$ if the right hand side of eq 26 contains a pole. Therefore we find for the chemical potential of the globule (in units of the thermal energy $k_BT$)

$$\mu_G = 12\left(\frac{|u|}{{}^4/_3\pi l^3}\right)^2 \tag{27}$$

The monomer–monomer correlation function, i.e. the radial density distribution, can be calculated according to des Cloizeaux[1] as follows

$$\langle\rho_G(\mathbf{k})\rho_G(-\mathbf{k})\rangle = \rho^2_G\langle\varphi_1(\mathbf{k})\varphi_1(-\mathbf{k})\rangle \tag{28}$$

where $\rho_G$ is the density of the globule. The right hand side of eq 28 can be calculated by means of eqs 18 and 20. A detailed analysis[18] shows that the computation to zeroth order in $\Delta$ is sufficient. The more physical reason is that near the transition the expectation value $\langle\Delta\rangle$ becomes zero. The correlation function is then given by

$$\langle\rho_G(\mathbf{k})\rho_G(-\mathbf{k})\rangle = \frac{\rho^2_G}{\mu_G + \frac{l^2}{6}\mathbf{k}^2} \tag{29}$$

The corresponding correlation length $\xi$ reads

$$\xi^2 = -\frac{3\frac{\partial^2}{\partial\mathbf{k}^2}\langle\rho_G(\mathbf{k})\rho_G(-\mathbf{k})\rangle\Big|_{\mathbf{k}=0}}{\langle\rho_G(\mathbf{k}=0)\rho_G(-\mathbf{k}=-0)\rangle} \tag{30}$$

and with eqs 27, 29, and 30 the general result in terms of the coupling constant $u$ (the total energy)

$$\xi^2 = \frac{l^2}{\mu_G} = \frac{l^2}{12}\left(\frac{|u|}{{}^4/_3\pi l^3}\right)^{-2} \tag{31}$$

can be found. This result makes physical sense. If the total energy is very large (strong attraction), the correlation length is small. When $u$ approaches zero, critical behavior can be found; i.e., the globule dissolves.

To be more specific to the problem of collapse or single chain complex formation, we can use eqs 12 and 13 which yield

$$\xi^2 \propto l^2\left(\frac{f_* - f}{f_*}\right)^{-2} \tag{32}$$

and

$$\xi^2 \propto l^2\left(\frac{c - c_*}{c_*}\right)^{-2} \tag{33}$$

It is interesting to note that the divergence of the correlation length is very strong, i.e. with the power of −2. The possible reason for this strong divergence for zero coupling constant lies in the strong attraction of the polymer corresponding segments. Finite size effects for finite (contour length) $L$ have to be taken into account, when $f \rightarrow f_*$ and $c \rightarrow c_*$, but will not be discussed in detail in this paper.

For the discussion of conformational statistics of the globule the inverse Laplace transformation of the propagator

$$G(\mathbf{k},N) = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} \mathrm{d}\mu\, \exp(\mu N)G(\mathbf{k},\mu) \tag{34}$$

can be used. To determine $G$, it is sufficient (in analogy to eq 29) to set in the matrix of (21) $\Delta$ to zero. Equations 18 and 20 yield immediately

$$G(\mathbf{k},\mu) = \frac{Z/Z_0}{\mu + \frac{l^2}{6}\mathbf{k}^2} \tag{35}$$

Equation 23, i.e. $Z/Z_0 = \exp(\Omega_0 - \Omega)$, yields in the exponent of eq 34 a very pronounced saddle point. Indeed, the saddle point approximation produces for $n \rightarrow 0$, $\mu_{sp} = \mu_G$.[18] Note that $\mu_G$ is taken from eq 27. For an infinite degree of polymerization, i.e. $N \rightarrow \infty$, we find

$$G(\mathbf{k},N) = \frac{\exp(\mu_G N)}{\mu_G + \frac{l^2}{6}\mathbf{k}^2} \tag{36}$$

and in real space

$$G(\mathbf{R},N) = \frac{9}{8}\frac{1}{{}^3/_4\pi l^3}\frac{\exp(\mu_G N)\exp(-(6\mu_G)^{1/2}|\mathbf{R}|/l)}{|\mathbf{R}|/l} \tag{37}$$

A qualitative comparison shows very good agreement with the result given by Grosberg *et al.*[21] for the range $R \geq \langle\mathbf{R}^2\rangle^{1/2}$, i.e. close to the critical point. The microscopic model presented in this paper breaks down, when $R \ll$

$\langle \mathbf{R}^2\rangle^{1/2}$, and the reason is quite obvious: This theory does not contain the third virial coefficient, which stabilizes the density deep in the collapsed state, i.e., for very negative values of $u$.

The calculation of the mean size of the chain at the onset of the collapse transition can be carried out, i.e. $\langle \mathbf{R}^2\rangle$ and according to eq 8 (compare eq 31).

$$\langle \mathbf{R}^2\rangle = \xi^2 \tag{38}$$

## 5. Flory Argument

Let us now compare the field theoretical computations to a simple Flory type estimate of the corresponding free energies. Indeed, similar results (apart from prefactors) can be found also be a simple Flory type argument. These arguments are often too simple but have been used many times to get rough estimates of the physical behavior in the scaling limit. Moreover the crude arguments will provide also some statements of the validity of the results obtained above. In this brief section it is shown that such arguments lead to results similar to those derived above, when the total interaction $u$ approaches the value zero from below. In section 2 it has been noticed that the Hamiltonian consists of an entropic and an energetic part. Both parts of the Hamiltonian should be balanced. For the case of the repulsive interaction, i.e. $u > 0$, the polymer tends to swell, whereas the elastic entropic part of the Hamiltonian tends to shrink the polymer due to the entropic penalty of swelling. As a result the Flory value of the self-avoiding walk exponent is obtained.

In the case of the attractive interaction, i.e. $u < 0$, the situation is more complicated and a simple estimate of an exponent is not possible, but nevertheless a range of validity of the field theoretic results can be discussed. The reasons are the following: The elastic part prevents the polymer from collapsing to a point, as compression of the coil costs an entropy penalty. The elastic part now takes the form of confinement of the polymer in a box. Starting from eqs 5 and 10, the interaction part of the Hamiltonian can be approximated as[1,2,4]

$$\frac{E_{\mathrm{int}}(\mathbf{R})}{k_{\mathrm{B}}T} = -\frac{1}{2}|u|\frac{N^2}{|\mathbf{R}|^3} \tag{39}$$

Near the transition from the globular state to the Gaussian state the chain length $N$ can be replaced in eq 39 by $N = l^{-2}R^2$, and we find

$$\frac{E_{\mathrm{int}}(\mathbf{R})}{k_{\mathrm{B}}T} = -\frac{1}{2}|u|l^{-4}|\mathbf{R}| \tag{40}$$

Then the energy $-E_{\mathrm{int}}/k_{\mathrm{B}}T$ or $^1/_2|u|l^{-4}|\mathbf{R}|$ is the confinement potential.

Now the entropic part has to be estimated near the transition from the globular to the Gaussian state in a useful way. For distances $|\mathbf{R}|$ less than the ideal end-to-end distance $R_0$, i.e. $R_0^2 = l^2N$, we can use[4]

$$\frac{E_{\mathrm{entropic}}}{k_{\mathrm{B}}T} = \mathrm{const}\left(\frac{|\mathbf{R}|}{R_0}\right)^{-2} \tag{41}$$

where const is an unimportant positive number. Near the critical point $u = 0$ we have $|\mathbf{R}| \approx R_0$, and eq 41 can be written

$$\frac{E_{\mathrm{entropic}}}{k_{\mathrm{B}}T} = \mathrm{const} - 2\mathrm{const}\,\log(|\mathbf{R}|/R_0) \tag{42}$$

The free energy of the corresponding Hamiltonian can be estimated as

$$\frac{F_{\mathrm{globul}}}{k_{\mathrm{B}}T} = \mathrm{const} - 2\mathrm{const}\,\log(|\mathbf{R}|/R_0) + \frac{1}{2}|u|l^{-4}|\mathbf{R}| \tag{43}$$

Minimization of eq 43 with respect to the size $|\mathbf{R}|$ yields

$$|\mathbf{R}|^2 = 16\mathrm{const}^2 l^2\left(\frac{|u|}{l^3}\right)^{-2} \tag{44}$$

It is remarkable that the simple Flory argument leads to the same result (apart from constants) as the more formal theory, i.e. eq 32 or 38.

The apparent contradiction that from the assumption $|\mathbf{R}| \approx R_0$ near the globule-to-coil transition a result has been concluded which shows no $N$ dependence in eq 44 has its basis in the asymptotic limit $N \to \infty$. Therefore eq 44 is valid also only in the asymptotic limit $|u| \to 0$.

This Flory type argument differs naturally from that usually used for the coil–globule transition, where the balance of attractive two body interactions are balanced with the repulsive three body interactions

$$\frac{E_{\mathrm{int}_3}(\mathbf{R})}{k_{\mathrm{B}}T} = \frac{1}{6}w\frac{N^3}{|\mathbf{R}|^6} \tag{45}$$

with strength $w$ to give the natural globular size of the chain with the density limitation. To illustrate this latter point, we mention that in the globular state the elastic contribution is no longer important but the (negative) two body interaction and the (positive) three body interaction balance each other to give the globule density

$$c = \left(\frac{w}{|u|}\right)^{1/3} \tag{46}$$

We are now in the position to discuss the range of validity. First it is easily demonstrated that the Flory estimate is not of the usual quality; the free energy is highly fluctuating and still large. This is here natural due to the assumptions made above, i.e. $|u| \approx 0$ and consequently $R \approx R_0$. The system is close to its collapse (from above) or decollapse (from below). Therefore large fluctuations are present. If these results are used to compare the two body forces to the three body forces, it is shown that the condition $w \ll l^6$ emerges. This is the crucial point. In the field theoretic part we concluded that the calculations are valid for very small values of the three body energy prefactor $w$. The Flory approximation and the field theory yield similar conclusions. These are also in accord with the results presented by Kholondenko and Freed.[16] In this reference an expansion around the symmetry broken (collapsed) phase has been performed. In fact we have to require that all interactions are small to make the Gaussian approximation valid. Compared to ref 16 we have used a different route: The starting point was the globule, and the transition to the coil has been investigated near the vanishing attractive interaction. At this point the three body forces are not expected to play the dominant role. This is obvious since the three body forces determine the concentration of the globule, which becomes approximately zero near the globule–coil transition. Therefore the more important contribution is the entropy penalty due to the confinement of the chain. This statement is closely related to the Gaussian approximation in the Landau expansion for the pair field. These two different Flory arguments show also the similarity between the pair field method and the symmetry breaking of the standard field theory.[16]

The standard field theory, both types of Flory arguments, and the pair field method yield, however, the same answer for the size of the chain.

## 6. Conclusions

In this paper we have presented a theory of the onset of the collapse transition for chains that contain several attractive monomers placed anywhere along the contour. In the way the theory was formulated originally with the Edwards Hamiltonian it can already be seen that if the fraction of attractive monomers becomes larger than a critical value $f_*$, the chain collapses on itself. An interesting application of this theory is the behavior of polyampholytes in polar solvent. Polyampholytes are polymer chains containing positive and negative charges. When the salt concentration becomes large, the electrostatic interactions are screened out completely and the polymer just faces excluded volume interactions. When the salt concentration is lowered, the Coulomb interaction becomes long ranged and the chain forms a collapsed state. Many other interpretations of experiments with polyelectrolytes are imaginable but not specifically mentioned here (see also ref 10).

The Hamiltonian in this paper is formulated in the way the usual polyelectrolyte theories are formulated: The attractive units (or charges) are smeared out along the chain, and the parameter relevant for their number is the fraction $f$. To continue the problem with the use of a standard RPA does not lead to nontrivial conclusions.

The basic step for a new formulation of this problem was to transform it into a field theoretic formulation. This enables us to use a special definition of a pair field which accounts for properties of pair monomers; i.e. the pair field is designed to study pairing effects. Another difficulty is that this theory indicates a phase change with vanishing coupling constant. We have analyzed the simple model of attractive chains, i.e. a smeared out attractive interaction along the polymer. In preliminary computations on realistic systems, such as ionomers or random copolymers, it can be shown that the theory developed above yields also—subject to alterations—sensible results. For ionomers the present formulation has to be modified, as the present model in terms of pair fields provides only informations of duplets; the interpretation of the results can be put forward to find multiplets, i.e. clustering of more than two attractive monomers. Such discussions are especially important for the more detailed theory of ionomers. A first phenomenological step in this direction has been put forward by Khokhlov,[7] but a microscopic formulation starting from a chain Hamiltonian for such a problem has not been given yet.

The theory was given only in Gaussian approximation, but it can be argued that in the globule the fluctuations are small and the Gaussian theory is sufficient. This point has to be studied in detail further, especially the influence of the third virial coefficient. Another important point is the study of these molecules when the attractive monomers are not distributed uniformly along the chain but are placed in random positions along the chain contour. Such a problem requires more complicate mathematics since quenched distributions are present. The replica theory has to be used for these problems and will be considered in a separate work.

## Appendix A

To introduce a theory for attractive systems, other methods must be used, as in the familiar case of repulsive systems. The starting point is the interaction term in the field theoretic formulation of the $O(n)$ model. Repulsive systems can be treated quite successfully by the use of a random field that decouples two different monomers (Edwards transformation). This is exactly not what is required for the case of attractive systems. Therefore the interaction term is treated in a different way. A pair field is introduced to couple two different monomers and two different replicas. This is outlined in the following.

Starting from $\Delta_{\alpha\beta}(\mathbf{r}) = \Delta_{\beta\alpha}(\mathbf{r})$, a new symmetric field may be defined according to

$$\omega_{\alpha\beta}(\mathbf{r}) = \Delta_{\alpha\beta}(\mathbf{r}) - u\varphi_\alpha(\mathbf{r})\varphi_\beta(\mathbf{r}) \tag{47}$$

then the identity

$$\mathrm{d}\{\omega_{\alpha\beta}\} = \mathrm{d}\{\Delta_{\alpha\beta}\} \tag{48}$$

holds. It follows from eq 47

$$\frac{1}{u}\int \mathrm{d}\mathbf{r}\, |\omega_{\alpha\beta}(\mathbf{r})|^2 = \frac{1}{u}\int \mathrm{d}\mathbf{r}\, |\Delta_{\alpha\beta}(\mathbf{r})|^2 + u\int \mathrm{d}\mathbf{r}\, \varphi_\alpha(\mathbf{r})\varphi_\alpha^*(\mathbf{r})\varphi_\beta(\mathbf{r})\varphi_\beta^*(\mathbf{r}) - \int \mathrm{d}\mathbf{r}\, \varphi_\alpha(\mathbf{r})\Delta_{\alpha\beta}^*(\mathbf{r})\varphi_\beta(\mathbf{r}) - \int \mathrm{d}\mathbf{r}\, \varphi_\alpha^*(\mathbf{r})\Delta_{\alpha\beta}(\mathbf{r})\varphi_\beta^*(\mathbf{r}) \tag{49}$$

The normalization $\mathcal{N}$ is given by

$$\mathcal{N} = \int \prod_{\alpha,\beta=1}^{n} \mathrm{d}\{\Delta_{\alpha\beta}(\mathbf{r})\}\, \mathrm{d}\{\Delta_{\alpha\beta}^*(\mathbf{r})\} \times \exp\left\{\frac{1}{u}\sum_{\alpha,\beta=1}^{n}\int \mathrm{d}\mathbf{r}\, |\Delta_{\alpha\beta}(\mathbf{r})|^2\right\} \tag{50}$$

This can be given with a simplified notation using eq 48

$$\exp\{-u\int \mathrm{d}\mathbf{r}\, (\varphi(\mathbf{r})\varphi^*(\mathbf{r}))^2\} = \mathcal{N}^{-1}\int \mathrm{d}\{\Delta\}\, \mathrm{d}\{\Delta^*\} \times \exp\left\{\frac{1}{u}\int \mathrm{d}\mathbf{r}\, |\Delta|^2 - \int \mathrm{d}\mathbf{r} \begin{pmatrix}\varphi \\ \varphi^*\end{pmatrix}\begin{pmatrix}0 & \Delta^* \\ \Delta & 0\end{pmatrix}\begin{pmatrix}\varphi^* \\ \varphi\end{pmatrix}\right\} \tag{51}$$

When eq 51 is used in eq 17 and the Gaussian integration over $\varphi$ fields is performed, eq 20 is finally given.

## Appendix B

In this appendix we derive eq 25. Equation 25 is via eq 23 related to the partition function $Z$. Together with eq 20 we can write for the partition function for vanishing fields $\mathbf{h}$ and $\mathbf{h}^*$

$$Z = Z_0\mathcal{N}^{-1}\int \mathrm{d}\{\Delta\}\, \mathrm{d}\{\Delta^*\}\exp\{-\mathcal{H}[\Delta,\Delta^*]\} \tag{52}$$

In the Gaussian RPA we may in eq 52 replace $\mathcal{H}$ by $\mathcal{H}_{\mathrm{RPA}}$. According to eq 22 $\mathcal{H}_{\mathrm{RPA}}$ can be viewed as follows

$$\mathcal{H}_{\mathrm{RPA}} = a\int_{\mathbf{k}}|\Delta|^2 + b\int_{\mathbf{k}}\mathbf{k}^2|\Delta|^2 \tag{53}$$

with the abbreviations

$$a = \frac{1}{|u|} - \frac{3}{2\pi\mu l^2}\left(\frac{3\mu}{l^2}\right)^{1/2} \tag{54}$$

and

$$b = \frac{1}{96\pi\mu^2}\left(\frac{3\mu}{l^2}\right)^{1/2} \tag{55}$$

Thus $Z$ is given by

$$Z/Z_0 = \mathcal{N}^{-1}\int \mathrm{d}\{\Delta\}\, \mathrm{d}\{\Delta^*\}\exp\{-a\int_{\mathbf{k}}|\Delta|^2 - b\int_{\mathbf{k}}\mathbf{k}^2|\Delta|^2\} \tag{56}$$

Equation 56 represents a Gaussian integral which can be calculated straight forwardly. This yields an irrelevant additive term

$$-\log Z/Z_0 = n^2 \sum_{|k|<1/l} \log (a + b\mathbf{k}^2) \tag{57}$$

where a cutoff of $1/l$ regularizes the unphysical short distance behavior. The summation in eq 57 can be replaced by an integral via $\sum \rightarrow V\int$. The $k = 0$ term has to be treated separately. This integral representation is identical with eq 25.

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