Macromolecules **1998,** *31,* 5502−5506

Variational Approach to Necklace Formation in Polyelectrolytes

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Received December 3, 1997; Revised Manuscript Received May 4, 1998

ABSTRACT: By means of a variational approach we study the conditions under which a polyelectrolyte in a bad solvent will undergo a transition from a rodlike structure to a "necklace" structure in which the chain collapses into a series of globules joined by stretched chain segments.

1. Introduction

It is well established that in a salt-free environment and under good or Θ -solvent conditions, the electrostatic interaction between the monomers of a single polyelectrolyte chain induces a rodlike conformation, in which the overall size of the chain scales as its monomer number, $R \sim N$. In the presence of a small amount of salt, if the ions are homogeneously distributed such that their interaction with the chain is limited to screening the electrostatic interactions, a rodlike conformation is also expected. Even in this simple model, the introduction of a secondary interaction can lead to interesting structural modifications. Dobrynin et al.[1] have presented a scaling argument and computing evidence that by turning on an attractive interaction between the monomers, the standard rodlike conformation[2] is abandoned in favor of a "necklace" one. The necklace structure consists of highly stretched segments alternating with collapsed globules, the "beads" of the necklace. Another mean field calculation by Balazs et al.[3] also produced similar results. In this paper we further explore this possibility, by means of a variational approach. The techniques we use here are adapted to the case of long (effectively infinite) weakly charged polymers.

The necklace structure was first suggested by Kantor and Kardar[4] in their study of polyampholytes. This was argued on the basis of a similarity with the Rayleigh instability[6] that appears in charged fluids. Namely, a large charged droplet of fluid will split into smaller droplets to put the charges far away from each other and the splitting is only stopped at the increasing cost of surface energy. The droplets are kept together by cohesional molecular forces, which in the polymer case are replaced by the bonds between monomers. In this analogy the surface tension in the droplet is replaced by the interaction of the monomers with the bad solvent.

2. Variational Approach to Polyelectrolyte Conformation

The variational approach has been often used in the investigation of the structure of polyelectrolyte chains. This technique was first introduced in this context by de Gennes et al.[2] (Relevant work in this area by means of this and other techniques has been reviewed by Barrat and Joanny.[6])

The basic variational principle[7] states that given the Hamiltonian of the system H, and a family of simpler trial Hamiltonians H_t characterized by a set of parameters a, b, ..., the free energy of the system satisfies the inequality

$$F \leq F_t + \langle H - H_t \rangle_t \tag{1}$$

where F_t is the free energy of the trial Hamiltonian and the braces indicate averages with respect to the statistical ensemble associated with the trial Hamiltonian. From among the family of trial Hamiltonians one can then choose the one that gives the lowest upper bound for the true free energy. Approximations to the expectation values of observables of the system can be then taken to be those calculated by using the optimal trial Hamiltonian.

The usual problem with this method is that while the bound on the free energy is rigorously true, it might be useless and misleading if the family of Hamiltonians is not close enough (as operators in some space) to the true Hamiltonian. Solving this problem requires the use of general enough trial Hamiltonians with which practical calculations can still be done, and from a heuristic point of view, one can expect them to capture the essential features of the system. Further, a successful application of this method can be very instructive if the parameters that describe the trial Hamiltonians have a direct physical interpretation.

The model Hamiltonian of the polyelectrolyte chain that we consider is the well-established (continuum version) form,

$$H = \int \mathrm{d}n\, \frac{3kT}{2b^2} \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}n} \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}n} + \int \mathrm{d}n \int \mathrm{d}n'\, V(\mathbf{r}(n) - \mathbf{r}(n')) \tag{2}$$

with the usual entropic term and with the interaction potential between segments V modeled as having two parts: a hard-core interaction

$$V_{\mathrm{hc}} = \nu_0 \delta(\mathbf{r}) \tag{3}$$

that we will consider attractive (i.e., $\nu_0 < 0$), which corresponds to the immersion of the polymer in a bad solvent, and a screened electrostatic part

$$V_{\mathrm{e}} = f^2 e_0^{\,2} \frac{e^{-\kappa r}}{\epsilon r} \tag{4}$$

where f is the valence per monomer, e_0 is the electronic charge, and ϵ is the permittivity of the medium. We will consider only the case in which the charges are quenched in the polymer backbone.

S0024-9297(97)01767-1 CCC: $15.00

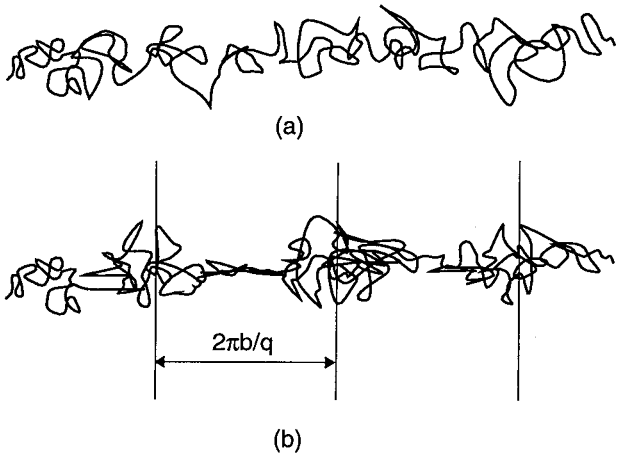

Figure 1. Typical configurations of the polyelectrolyte chain: (a) uniform stretching and (b) modulated stretching with wavelength $2\pi b/q$.

To observe the necklace conformation, the trial Hamiltonians must explicitly include the possibility of uniform and nonuniform stretching. We choose the following version of the stretched chain:

$$H = \int \mathrm{d}n \, \frac{3}{2b'^2} \left(\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}n} - \frac{\mathrm{d}\mathbf{r}_0}{\mathrm{d}n}\right)\left(\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}n} - \frac{\mathrm{d}\mathbf{r}_0}{\mathrm{d}n}\right) \tag{5}$$

This trial Hamiltonian incorporates Gaussian fluctuations around a background stretched conformation $\mathbf{r}_0$ with a renormalized Kuhn length b'. In the basic stretched-chain model, the conformation has uniform stretching but we will consider stretchings with further spatial dependence.

More precisely, we will consider background conformations of the form

$$\mathbf{r}_0(n) = \rho_0 n \hat{\mathbf{u}} + \epsilon \cos(qn)\hat{\mathbf{u}} \tag{6}$$

corresponding to a uniform unidirectional stretching modified by small modulations of the stretching along the same direction. This modulation in the average stretching $\boldsymbol{r}_0$ creates zones of accumulation and depletion of monomers along the basic rodlike conformation. We will show that for a range of values of the basic parameters of the problem, the minimum free energy with a uniform stretching is larger than if we include modulations at certain wavelengths; i.e., we will not find the optimal stretching but prove that the rod conformation is unstable against infinitesimal modulation. The wavelength of the most unstable mode thus predicts the spacing of the beads. Figure 1 illustrates this.

Bratko and Dawson[8] have considered the same model Hamiltonian and a similar variational principle that uses a general Gaussian matrix of correlation between monomers and a constraint on the allowed conformations that keeps the bond length fixed. This last constraint has also been incorporated in a variational approach by Ha and Thirumalai[9] in their discussion of the rigidity of a polyelectrolyte and, as discussed below, regularizes the behavior of the model in the strongly stretched and collapsed limits. In the previous study[8] of the polyelectrolyte in bad solvent a persistent stretching was not considered (i.e., $\mathrm{d}\boldsymbol{r}_0/\mathrm{d}n$ is set to 0) and the stretching of the chain was only observed through the large amplitudes of the fluctuations $\langle \mathbf{r}(n)\, \mathbf{r}(n')\rangle$. Instead, our approach takes the average stretched conformation $\mathbf{r}_0$ as the basic quantity describing the system.

The possibilities of uniform and nonuniform stretching have been properly considered by Jonsson et al.[10] when looking for the corrections to the stretching arising from the finite size of the polyelectrolyte. Their work, however, has not included consideration of further interactions beyond the electrostatic one.

3. Basic Rodlike Conformations

We start by looking at the minimum of the variational energy that can be obtained by considering only trial Hamiltonians with uniform background stretchings. Thus, we write

$$\rho(n) = \rho_0 \tag{7}$$

and the expressions in eq 1 are calculated as follows. First, the free energy for each of the springs associated with each pair of neighboring monomers is, up to a constant, $-3k_BT \ln b'$. Next, the average of the stretching energy per monomer (i.e., per unit length of the continuous chain) of the original chain in this ensemble has the forced background contribution $(3/2)k_B\rho^2$ and the basic random walk part $(3/2)(b'/b)^2 k_BT$.

The probability distribution for the position of two chain segments separated by n monomer units $G(\mathbf{r}(s + n),\mathbf{r}(s)) = G(\mathbf{r}(n) - \mathbf{r}(0))$, is just a Gaussian function with mean

$$\langle \mathbf{r}(n) - \mathbf{r}(0)\rangle = \rho_0 n \hat{\mathbf{u}} \tag{8}$$

and variance

$$\langle (\mathbf{r}(n) - \mathbf{f}_0 - \rho n \hat{\mathbf{u}})^2\rangle = b'^2 \tag{9}$$

Therefore, for an interaction potential $V(r)$, the averaged interaction energy per unit length is

$$\langle V\rangle = 2 \int_0^\infty \mathrm{d}s \int \mathrm{d}\mathbf{r}\; G(\mathbf{r}(s) - \mathbf{r}(0))\; V(|\mathbf{r}(s) - \mathbf{r}(0)|) \tag{10}$$

or using the potential's Fourier transform and the explicit form of the correlation between monomers:

$$\langle V\rangle = 2 \int_0^\infty \mathrm{d}s \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^{3/2}} \exp\left[-\frac{k^2 b'^2 s}{6} + i\mathbf{k}\cdot\hat{\mathbf{u}}\rho_0 s\right]\hat{V}(\mathbf{k}) \tag{11}$$

Integrals of this type that diverge on the $s \to 0$ limit, are regularized by the short distance cutoff $s_{\min} = 1$ (namely, one bond distance).

The final result of the evaluation of the averages is (in units of k_BT)

$$F = -3 \ln b' + \frac{3}{2}(b'^2 + \rho_0{}^2 - 1) + \frac{6z_B}{\rho_0} \ln\left(1 + \frac{6\rho_0}{b'^2\kappa}\right) + \frac{\nu}{b'^3}\left(\left(\frac{3}{2\pi}\right)^{3/2} - \frac{9}{4\pi}\frac{\rho}{b'}\right) \tag{12}$$

In this expression and in the rest of the paper, all distances are measured in Kuhn length units. We have also introduced the Bjerrum number $z_B = f^2e^2/k_BT\epsilon b$ and a dimensionless interaction prefactor $\nu = \nu_0 b^3/k_BT$.

Minimization of expression 12 with respect to ρ_0 and b' gives the basic stretched conformation as a function

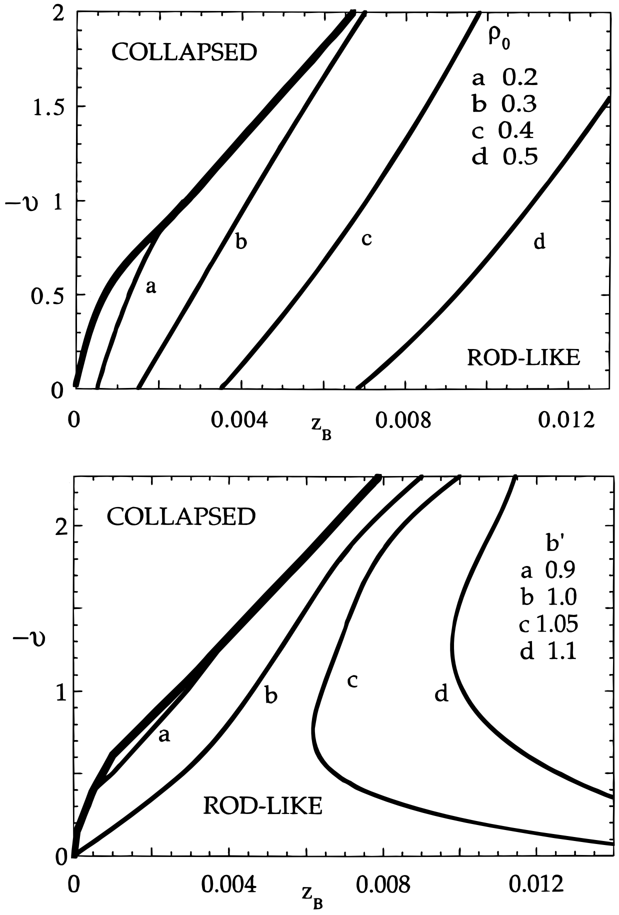

Figure 2. The $-\nu - z_B$ diagram for $\kappa = 10^{-4}$, where the thick lines mark the boundary between the collapsed and rodlike states. Within the rodlike region are shown (a) lines with constant values of the uniform stretching ρ_0 and (b) lines with constant values of the renormalized Kuhn length.

of the basic parameters, κ, z_B, and ν. In general, there exist two minima for this expression: one in the stretched region $\rho_0 \neq 0$ and another in which the chain is collapsed (or Gaussian) $\rho_0 \approx 0$. The present method and approximations, however, are suited to study only stretched conformations and cannot be reliably used to decide between the two states. For example, in our proposed variational family of Hamiltonians, the renormalized Kuhn length b' is intended to take values in the neighborhood of 1 (i.e., $b' \approx b$). Thus, to study the globule-like collapsed chain, it is necessary to modify the present variational principle and introduce a slightly different model Hamiltonian (by, for example, introducing a bond length constraint) that prevents the unphysical collapse $b' \to 0$. To a large extent, results concerning this collapsed regime can be found in the work of Bratko and Dawson[8] and Higgs et al.[11] Such a collapsed state is always present in the general phase diagram of the poleyelctrolyte since its formation requires only a suitable large first-order attractive virial. The possibility that a collapsed state might have a lower energy than the stretched state leads to modifications of our results that will be pointed out in the rest of the paper.

In finding the minimum of the evaluation of the averages, eq 12, we observe that for large values of the attractive interaction there is no local minimum with finite stretching. In Figure 2 we show a numerical example of the behavior of the stretching and the renormalized bond length, as functions of ν and z_B. According to the previous discussion, the real stretched region in the $\nu - z_B$ diagram is smaller than the one shown since the collapsed minimum will have a lower energy when the stretched minimum becomes unstable. In the examples provided, we use small values of the Bjerrum number, to keep the stretching consistent with our assumptions of Gaussian springs. Stretchings of order 1 should be treated with a suitable representation of the constraint of fixed bond length. Further, in the units we use, we look at regions of parameter space that correspond to fairly large hard core interactions but that still represent experimentally realizable conditions.

Finally, we point out that the criteria for the validity of these results in the case of finite size chains is as follows. The induced end to end stretching $\rho_0 N$ must be larger than the natural chain size $N^{1/2}$. Thus, our conclusion will be relevant for systems satisfying the condition

$$\rho_0 \geq N^{-1/2} \tag{13}$$

4. Stability of Rodlike Conformations

We will now determine the stability of the solutions found for uniform stretching. For this, we introduce a small perturbation on the background stretching, with a well-defined wavenumber q measured along the backbone:

$$\rho(s) = \rho_0 s + \rho_q \cos(qs) \tag{14}$$

with ρ_q being a small amplitude. The variational free energy per monomer associated with this stretching can be expanded in a power series in the amplitude ρ_q

$$f = f_0 + {\rho_q}^2 f_q + ... \tag{15}$$

Obviously, the uniformly stretched conformation does not have the minimum energy if f_q is negative. The true minimum can be found by minimization over all possible stretchings, but we will not attempt to solve this problem here. The results we obtain show that when the instability occurs, it does so in a particular range of wavelengths, indicating that the minimum energy is obtained in a regular necklace conformation, rather than in a randomly spaced one. There will be some amount of dispersion in the spacing of the "beads" but the dominant wavelength should appear clearly when looking at ensemble averages.

The linear stability analysis against small perturbations can also be carried out for perturbations that are transversal to the chain. These perturbations do not lead to instabilities, but their study is important in understanding the persistence length of polyelectrolyte chains[9,12,13] and will be studied elsewhere.[14]

The contribution to the free energy correction from the entropic Gaussian part of the model Hamiltonian is simply $(3/4)q^2{\rho_q}^2$. For the potential interaction part we write the contribution of a pair of monomers with labels t' and t ($t' > t$) as

$$\int \mathrm{d}\mathbf{k}(2\pi)^{-3/2} \exp[-6(t' - t)k^2/b'^2] \exp[i\mathbf{k}\cdot(\rho(t') - \rho(t))\hat{\mathbf{u}}]V(\mathbf{k}) \tag{16}$$

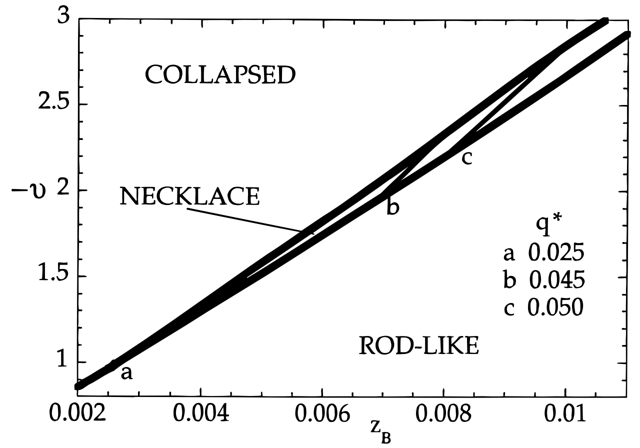

Figure 3. Region of necklace instability for $\kappa = 10^{-4}$ in the $-\nu - z_B$ diagram. Point a marks the limit of the necklace region, and lines b and c mark points of equal values of the most unstable wavenumbers q^*. Figure 4. Necklace unstable modes q for $\kappa = 10^{-4}$ and $z_B = 0.01$. The dashed line marks the most unstable mode for each value of ν.

We expand the exponential factor into

$$\exp[i\mathbf{k}\cdot(\rho(t') - \rho(t))\hat{\mathbf{u}}] = \exp[i\mathbf{k}\cdot\rho_0(t' - t)\hat{\mathbf{u}}]\Big(1 + i\mathbf{k}\cdot\hat{\mathbf{u}}\rho_q(\cos(qt') - \cos(qt)) - \frac{1}{2}{\rho_q}^2\mathbf{k}\cdot\hat{\mathbf{u}}^2(\cos(qt') - \cos(qt))^2\Big) + \ldots \quad (17)$$

This expansion is substituted into eq 16, a new variable $s = t' - t$ is introduced and the integration over t eliminates all oscillatory terms not depending on s only, to obtain the final result,

$$V_q{\rho_q}^2 = \frac{1}{2}{\rho_q}^2\int_0^\infty \mathrm{d}s \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}(\mathbf{k}\cdot\hat{\mathbf{u}})^2[-1 + \cos(qs)] \times \exp[i\mathbf{k}\cdot\rho_0\hat{\mathbf{u}}]\hat{V}(\mathbf{k}) \quad (18)$$

The criterion for instability is then

$$f_q = \frac{3}{4}q^2 + V_q < 0 \quad (19)$$

Concrete evaluation of eq 19 can be carried out for specific values of z_B, κ, and ν. The criteria is met for a bounded region of q values. Among the q values for which the system is unstable there will be one value q for which the determinant function f_q is most negative. We identify this wavenumber with the inverse of the most likely spacing between the beads of the necklace.

It is easier to discuss the results by keeping κ constant. For a given value of κ we can compute the region of stability in the $z_B-\nu$ plane and we present one such example in Figure 3. When κ is changed, the general morphology of the diagram is still the same as in Figure 3 and our results are consistent with those obtained by Dobrynin et al.[1] There are three main regions: the collapsed state that occurs for sufficiently large values of the attractive interaction discussed before, the rodlike conformation region in which the electrostatic interaction is dominant, and the more interesting part for our purposes, a narrow strip between them which is still rodlike but has undergone a finite wavelength modulation. In this last region, we have identified the points for which the value of the critical wavenumber q is the same. We also note that the instability region for necklaces starts always at a finite value of the Bjerrum number, since it is necessary for the system to have enough electrostatic energy to elongate the chain.

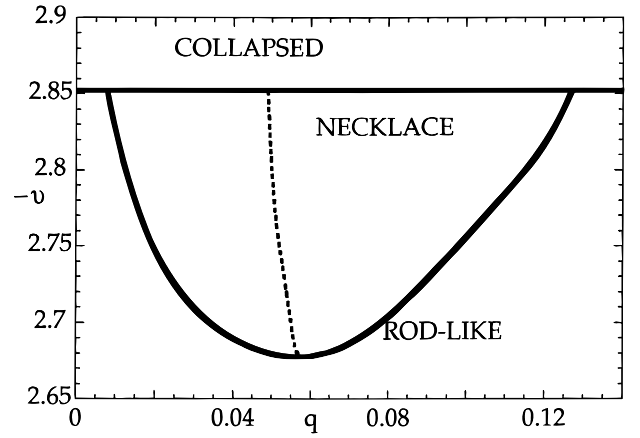

Figure 4. Necklace unstable modes q for $\kappa = 10^{-4}$ and $z_B = 0.01$. The dashed line marks the most unstable mode for each value of ν.

Different values of κ produce the same general results in that we always reach, first, a point of instability against collapse, and for sufficiently large charge, higher values of the attractive interaction, a necklace pattern. The main effect of a decreasing κ is to make the electrostatic interaction stronger, thus pushing the required values of ν for each instability ever higher. Higgs and Raphael[11] present the phase diagram of the polyelectrolyte in the $\nu-\kappa$ coordinates, and there this instability will show as a narrow strip between the collpased and rodlike states.

We add further detail to our example to illustrate another feature of the system. We have computed for $\kappa = 10^{-4}$ and $z_B = 0.001$ the region of instability and the region of unstable modes. The results appear in Figure 4. There, we confirm the different nature of the collapsed and the necklace states. The region in q space that is unstable is always finite. To obtain a smooth transition to the collapsed state, we would need this region to grow and touch large wavelength modes ($q \approx 0$) but this is not the case.

5. Conclusions

We confirm necklace formation in polyelectrolytes using the variational principle technique. In this calculational scheme we are limited to the regime in which the entropic free energy of the chain is still comparable with the energy scale imposed by the charge interaction, which leads to weak stretching. This calculation gives us not only insight into the onset region of the phenomena, but it also provides a concrete parameter space window for the experimental search of the transition, provinding an important refinement of scaling arguments. The present calculation can be refined in many ways. As we have mentioned before, it is important to consider the effects of a fixed bond length, and second, we can complicate the Gaussian correlations in the trial Hamiltonian so as to consider nonneighboring monomer correlations.

One reason the variational principle approach should provide accurate results for this problem is because it leads to a best fit for a few important parameters of the system at the expense of discarding further detail. In this case, for example, higher order correlations between monomers are ignored, while at the same time we explore a variety of overall shapes for the polyelectrolyte chain.

In the future it will be very important to determine the exact location of the transition between the collapsed and extended conformations. Since the region where the necklace formation is observed lies between these two states, it might happen that the collapsed state acquires the lowest energy before the onset of the finite wavelength instability. In that case the necklace cannot be observed. On the other hand, this scenario should not be true in general since our method can also underestimate the point at which the necklace transition occurs. Again, the physical onset of the necklace precedes the finite wavelength instability of the rodlike conformation.

Finally, we believe that the variational approach may be further exploited in the study of polymers and polyelectrolytes, since it provides a means to test the different structures arising in single and multiple chain systems. For example, one can study the case in which the charges are not quenched along the chain, a problem considered by Higgs and Joanny[15] and recently extended to include interchain interactions by Liu and Ha.[16]

Acknowledgment. We thank the National Science Foundation for financial support under grant number DMR9509838.

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MA971767N