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Random Copolymers with Short-Range Interaction in the Equilibrium State: Mean Field Approximation and Numerical Studies

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We study macromolecules with quenched random charge disorder along the chain and short-range interactions between the monomers. Within a mean-field approach a collapse of a chain with increasing disorder is found, which becomes more pronounced for long chains. Molecular dynamics simulations reveal the same tendency, though the actual shape of the radius of gyration as a function of the disorder is different and reflects the finite length of a chain.

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Various concepts of the statistical mechanics of random systems, such as spin glasses [1] or neural networks [2], are used to describe the complex structural conformation of biological macromolecules. In spin glasses, the strength and the sign of the interaction between pairs of monomers are chosen at random [3,4] and we have the statistics of $N(N-1)/2$ different interacting pairs. In a neural network the interactions result from a learning process, using the information from known structures [2].

As an alternative, in this paper we investigate a "charge" model in which the interaction between two monomers is well defined by a function of characteristic parameters (charges) of the two monomers and a unique δ-like potential [5,6]. The randomness of the model consists in the disorder of the monomer charge sequences [7]

$$U_{ij}(\vec{r}_i - \vec{r}_j) = \delta(\vec{r}_i - \vec{r}_j)\left[v_0 + u_0(q_i + q_j) + q_i q_j\right]. \tag{1}$$

Here q_i behaves as an effective charge of the monomer i, which controls the interaction with the other monomers of the chain. The first term corresponds to a nonstochastic short-range interaction (for example, the excluded volume interaction). The influence of the second term is discussed in [7]. In case of charge inversion invariance ($q_i \rightarrow -q_i$), we get $u_0 = 0$. In the following we consider this situation, i.e., we will only discuss the influence of the random charge products $q_i q_j$. For vanishing excluded volume interaction a renormalization group study [6] shows a collapse regime for long chains and below the critical dimension $d_c = 2$. Short chains exhibit in $d < 2$ both a collapse regime and a swollen regime, depending on the strength of the charges. In the latter regime the characteristic lengths of the polymer molecule, e.g., the mean radius of gyration (see also the numerical results of [5]) exhibit the following dependence on the chain length: $R^2 \sim N^\nu$, with $\nu = 1 + (d_c - d)^2/8$. An analysis of the perturbation expansion in terms of Feynman diagrams [6] shows that the contribution from the quenched average over the charges becomes irrelevant for $d > d_c = 2$, i.e., the annealed average shows above $d_c = 2$ no essential deviation from the quenched average. Furthermore, for nonvanishing excluded volume effect and a dimension $2 < d < d_{c'} = 4$ ($d_{c'}$ is the critical dimension of the excluded volume effect) one can expect a swelling regime (for weak stochastic interaction in comparison to u_0) with a crossover to a collapse regime for strong interaction.

The aim of the present Letter is the analysis of these two regimes and the crossover between them for $2 < d < 4$. Because of the vanishing difference between quenched and annealed averages for $d > 2$, the free energy is determined by $\langle F \rangle = \langle \ln Z \rangle \approx \ln\langle Z \rangle$, where $\langle Z \rangle$ is the partition function averaged over all possible charge distributions. Z is a product of the nonstochastic part (free chain with excluded volume interaction, corresponding to the free energy of the well known Flory model)

$$\ln Z_0 = d \ln R - \frac{R^2}{N} - \bar{v}_0 \frac{N^2}{R^d} \tag{2}$$

and the annealed averaged contributions from the stochastic monomer interaction $\langle Z_{\mathrm{st}} \rangle = \langle \exp(-V_{\mathrm{st}}) \rangle$ with

$$V_{\mathrm{st}} = \sum_{i \neq j} q_i q_j \delta(\vec{r}_i - \vec{r}_j). \tag{3}$$

The Taylor expansion leads to

$$\langle Z_{\mathrm{st}} \rangle = \langle \exp(-V_{\mathrm{st}}) \rangle = \sum_{P=0}^{\infty} \frac{(-1)^P}{P!} \times \left\langle \left(\sum_{\imath \neg = j} q_i \delta(\vec{r}_i - \vec{r}_j) q_j \right)^P \right\rangle. \tag{4}$$

The averages in (4) can be calculated by usual mean-field arguments.Assuming a Gaussian distribution for the charges ($\langle q_i q_j \rangle = \Delta_0 \delta_{ij}$) one can write

$$\left\langle \left(\sum_{i \neq j} q_i \delta(\vec{r}_i - \vec{r}_j) q_j \right)^P \right\rangle = \sum_{i \neq j} \sum_{k \neq l} \cdots \langle (q_i \delta(\vec{r}_i - \vec{r}_j) q_j)(q_k \delta(\vec{r}_i - \vec{r}_j) q_l) \cdots \rangle. \tag{5}$$

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The value between two brackets $(\cdots)$ is defined as a pair, the average of two charges as a contraction. For the evaluation of (4) the following rules hold:

(i) A contraction within a pair $(q_i q_j)$ is forbidden.

(ii) Each contraction has the same value Δ_0 and cancels one summation (with P pairs follow therefore P contractions and P free summations).

(iii) If there is a cyclic connection from one pair over a set of I contractions back to this pair, we get a cycle of the length I. Each set of P contractions leads to a configuration $\{n_I\}$ of n_I cycles of the length I ($I = 2, 3, \ldots$).

(iv) The number of possibilities to construct the configuration $\{n_I\}$ is given by $\sum (I n_I)! / \prod [n_I! (I!)^{n_I}]$ (for $I \geq 2$).

(v) Each cycle of length I has $(I-1)! 2^{(I-1)}$ additional possibilities of the interior order for the contractions.

(vi) Each cycle of the length I contains also I functions $\delta(r_i - r_j)$ with the same cyclic connection

$$\sum_{i,j,\ldots} \delta(\vec{r}_i - \vec{r}_j) \delta(\vec{r}_j - \vec{r}_k) \cdots \delta(\vec{r}_{k'} - \vec{r}_i) \,. \tag{6}$$

Introducing the local monomer density $\sum_i \delta(\vec{r}_i - \vec{r}\,) = \rho(r)$ and replacing this value by the usual Flory approximation [$\rho(r) = N R^{-d}$ for $r < R$ and $\rho(r) = 0$ for $r \geq R$] leads to the contribution $(N R^{-d})^I R^d \delta(0)$, i.e., each pair contributes a factor $N R^{-d}$, each cycle an additional factor $R^d \delta(0)$. $\delta(0)$ is in the present model of the order l_0^{-3} (inverse effective monomer volume, l_0 is the effective segment length). Usually, R is determined in units of l_0, i.e., one can define $\delta(0) = 1$.

Finally, one gets the result

$$\begin{aligned} \langle Z_{\mathrm{st}} \rangle &= \sum_{\{n_I\}} \frac{1}{\prod_{I=2} n_I!} \prod_{I=2} \left[\frac{(-2R^{-d} \Delta_0 N)^I}{2 I R^{-d}} \right]^{n_I} \\ &= \exp\left[\Delta_0 N - \frac{1}{2} R^d \ln\left(1 + \frac{2\Delta_0 N}{R^d} \right) \right] . \end{aligned} \tag{7}$$

From (7) and (2) the total free energy F is obtained, which yields the (implicit) mean-field solution of R by determining the minimum of $F \rightarrow$ min!:

$$\frac{R^2}{N} - 1 = \frac{\bar{v} N^2}{R^d} - \frac{R^d}{2} \left[\ln\left(1 + \frac{2\Delta_0 N}{R^d} \right) - \frac{2\Delta_0 N}{R^d + 2\Delta_0 N} \right] . \tag{8}$$

Figure 1 shows the dependence of the averaged radius R on the disorder parameter for different chain lengths ($\bar{v} = 1$). The mean-field results are compared with molecular dynamics simulations.

In the molecular dynamics simulation we consider the chain to be comprised of mass points connected by rigid bonds of length l. Consequently, we employ the constraints $(\vec{r}_i - \vec{r}_{i-1})^2 = l^2$ in the united atoms dynamic. Nonbonded interactions between points separated by more than one bond are taken into account by the Lennard-Jones potential

$$V(\vec{r}_i - \vec{r}_j) = 4\epsilon \left(\frac{\sigma^{12}}{|\vec{r}_i - \vec{r}_j|^{12}} + \frac{q_i q_j \sigma^6}{|\vec{r}_i - \vec{r}_j|^6} \right) . \tag{9}$$

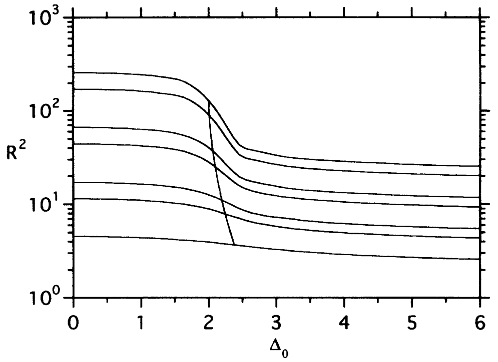

FIG. 1. Mean-field approximation of the averaged radius of gyration R as a function of the disorder parameter Δ_0 for different chain lengths ($N = 10\,000, 5000, 1000, 500, 100, 50, 10$ from top to bottom) and $\bar{v} = 1$.

The r^{-12} term accounts for the excluded volume of the atoms, whereas the r^{-6} term takes into account the screened, short-range interaction between charges at the atoms. Depending on the sign of the charges the interaction is attractive or repulsive, respectively. Similar to the mean-field calculations, we assume a Gaussian distribution of these charges. With the parameter $\sigma = l$ the potential prevents chain crossings. The equations of motion of the chain are given by

$$m_i \ddot{\vec{r}}_i = \vec{F}_i + \vec{F}_i' - \gamma m_i \dot{\vec{r}}_i + \vec{\Gamma}_i \,, \tag{10}$$

where $\vec{F}_i$ denotes the Lennard-Jones forces (9) and the vector $\vec{F}_i'$ the forces of constraint

$$\vec{F}_i' = \lambda_{i-1} (\vec{r}_i - \vec{r}_{i-1}) - \lambda_i (\vec{r}_{i+1} - \vec{r}_i) \,, \tag{11}$$

induced by the constant bond lengths. The λ_i are Lagrangian multipliers, for which $\lambda_0 = \lambda_N = 0$. The friction force, with the damping constant γ, and the stochastic force $\vec{\Gamma}_i$ ensures the simulation of a canonical ensemble, i.e., the temperature of our systems is fixed. The stochastic force is assumed to be a stationary, Gaussian white noise process

$$\left\langle \vec{\Gamma}_i(t) \right\rangle = 0 \,, \tag{12}$$

$$\langle \Gamma_{i\alpha}(t) \Gamma_{j\beta}(t') \rangle = 2 k_B T \gamma m_i \delta_{ij} \delta_{\alpha\beta} \delta(t - t') \,, \tag{13}$$

with T the temperature of the system. The indices α, β denote the Cartesian components (x, y, z) of the force.

The equations of motion were integrated using a method proposed by van Gunsteren and Berendsen [8,9] taking advantage of the fact that only nearest neighbors interact along the chain. In the integration we used a time step $h = 4 \times 10^{-3} \tau$ for small Δ_0 and $h = 2 \times 10^{-3} \tau$ for large Δ_0, where $\tau = (m\sigma^2/\epsilon)^{1/2}$. For the damping constant we chose $\gamma = 10/\tau$ and for the temperature $T = 4\epsilon/k_B$.

The numerical results presented in Fig. 2 show the collapse also found by the mean-field calculations, i.e., with

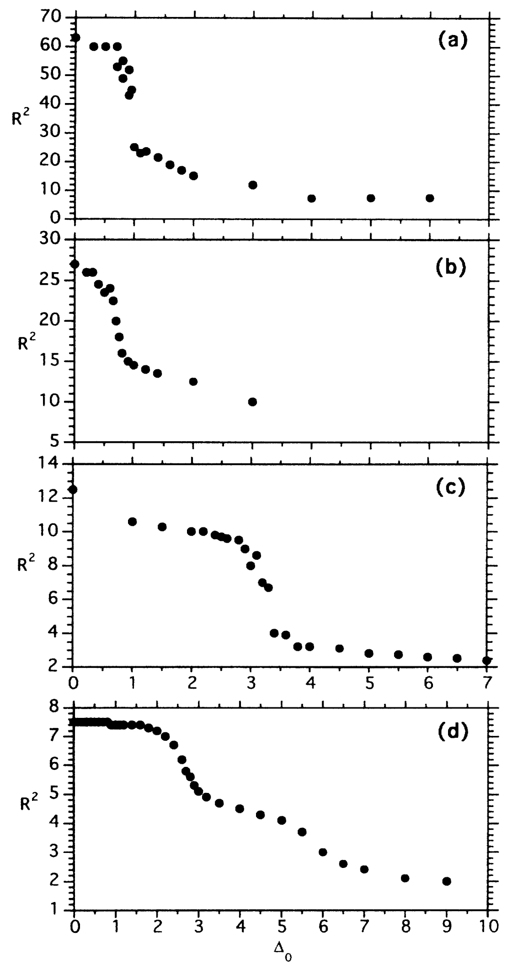

FIG. 2. Radius of gyration as a function of the disorder parameter Δ_0 for chains of various length calculated by molecular dynamics simulations. (a) $N = 100$, (b) $N = 50$, (c) $N = 30$, (d) $N = 20$.

respect to the collapse the two calculations exhibit the same qualitative behavior . Particularly for small values of the disorder parameter Δ_0 follows the characteristic swelling regime (excluded volume), whereas for sufficient large Δ_0 a collapse is observed. As expected, the numerical simulations show a marked influence of the finite (nonvanishing) volume of the monomers in comparison to the mean-field approximation, especially for short chains. (Note, the mean-field approximation leads for very large Δ_0 to the asymptotic behavior $R \sim N^{1/d}(\ln \Delta_0)^{-1/2}$ due to the repulsion term $N^2 R^{-d}$ [Eq. (2)], which cannot represent the hard-core-like structure of the monomers. But this effect is only important for large local densities in a strong collapsed regime.) On the other hand, the accuracy of the numerical results is mainly determined by the realization of a sufficient large number of equilibrium configurations. Because of the fact that the interior mobility of the chain decreases rapidly with increasing Δ_0 (in the collapse regime) this number (and therefore the accuracy of the numerical results) decreases very fast or one must increase the computation time considerably for a fixed accuracy, i.e., results for very large Δ_0 cannot be obtained by the used numerical simulation. However, the general scaling behavior for the collapse regime is given by $R \sim N^{1/d}$, on the other hand, the weakly Δ_0 dependent prefactor cannot be extracted reliably from the simulation for $\Delta_0 \rightarrow \infty$.

The crossover from the swelling to the collapse regime was realized in a relative small interval of the disorder parameter Δ_0. The Θ behavior (Gaussian behavior of the chain) corresponds to the turning point Δ_0^* of the $R(\Delta_0)$ curves and shows a weak dependence on the chain length N. The mean-field approximation predicts a monotonous decrease of Δ_0^* with increasing N, whereas from the numerical simulations a small deviation from this relation is found [as a result of the fact, that for small chain length the mean-field equations must be extended by additional terms of the order $O(L^{-1})$].

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