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Theta Point Calculation of a Polymer Chain with Electric Dipole Moments: Monte Carlo Simulation

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Abstract

Monte Carlo simulations are used to simulate a single polymer chain in a more generalized model. The more generalized model differs from the simpler models by including dipole-dipole interactions. The polymer chain is modeled as a freely rotating chain where the neighboring beads are connected by harmonic spring. Excluded volume effects are included employing modified Lennard-Jones potential. As the extension in this work, each monomer unit carries permanently a freely-rotating electric dipole moment. After getting the system equilibrated the average values are measured and Θ-temperature of the system is determined. The effects of the presence of the dipole moments to the Θ-temperature of the system are investigated. The results are analyzed in comparison with a bare model.

Keywords: Polymer Chain, Theta Temperature, Monte Carlo, Dipole-dipole interaction

1. INTRODUCTION

Polymers are large molecules and composed of many repeating units and very complex systems. Polymers play many important roles in our daily life. Both synthetic and natural polymers are of high interest [1, 2]. For polymeric systems many theoretical approximations have been developed and also many experiments have been carried out. Despite many outgoing pieces of research of today, frequently it is not easy to have a direct comparison between theory and experiments. Therefore, computer simulations are very common way to perceive the details of polymeric systems [3]. In a polymeric system, the chains are essentially very long. Especially polymeric systems carrying electric charges, which are called polyelectrolytes (PELs), are of high interest in science and technology. PELs are so important in technology because they are seen in many modern applications. In PELs one examines the clash between different interactions, on the one hand, the interactions emerging from the presence of electric charges, while on the other hand the

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ones emerging from solvent effects [4-6]. In a polymeric or polyelectrolyte system, the solvent is allocated as good, poor (or bad) and theta (Θ) solvent. The general behavior of a polymer chain or a charged one is quite different in these different solvent regimes. The critical solvent regime can be seen as the theta (Θ) solvent because it splits the good solvent regime and poor solvent regime. The determination of the Θ solvent could be very crucial when one needs to understand the solvent effects. The determination of Θ point for polymeric systems is widely worked essentially, but in this current work the polymer system is modeled in a more generalized way: That is, each unit along polymer chain carries one freely-rotating electric dipole. Utilizing Monte Carlo (MC) simulations, the effects of the presence of electric dipoles to the Θ point of the system are investigated. The paper is outlined: In the next section we give the details of the solvent effects for polymeric systems, next we describe our model and method to distinguish the effects of having permanent dipole moments. Afterward we display our results and finally make our conclusion.

1.1. Solvent Effects in Polymeric Systems

In a dilute solution, the interaction between polymer chains can be neglected, because the chains are far apart from each other. This fact enables us to start with a single polymer chain. However, monomer units along the same chain can interact with each other. The simplest model in polymer physics is "ideal chain", where no interaction is considered between the monomer units. But the interactions between monomers are so important because they determine if the polymer dissolves in the solution. Because of this fact real polymers are modeled as a self-avoiding walk, opposite to a random walk of an ideal chain. It means that one physical space can be occupied by only one polymer subunit. This is called "excluded-volume effect". This makes the chain more expanded.

In a simple mean-field approach due to Flory [7], the size of polymer chain can be calculated at different solvent qualities. In a "good" solvent case, effective interaction between monomer subunits is repulsive; that is, interactions between solvent molecules and polymer molecules are more important than interactions between the polymer molecules. As a result, polymer chain is found in an expanded form. This repulsive effect makes the polymer chain swollen. In a poor (or bad) solvent, interactions between monomer subunits are more important than interactions between solvent and polymer subunits. In this case, polymer collapses into a compact globular structure. At very poor solvents polymer chain can be even separated from the solution.

Between these solvent regimes, Θ solvent regime lies. In this regime, both competing attractive and repulsive interactions are equal and cancel each other and the chain is said to be at the Θ point. Θ chains are amazing because it is a transition structure. The change of polymer structure as the solvent quality changes is called "coil-globule" transition. At Θ point the chain is found as exhibiting the characteristics of an ideal polymer chain. This is interesting because it is the case of an imaginary chain where monomer subunits are allowed to overlap each other. That is, there is no interaction between monomers or solvent molecules. These kinds of polymers are not present in reality. Θ chains are very important concerning the fact that they are often used as starting steps in understanding the properties of real polymers (neutral or charged). Coil-globule transition has been worked extensively because of its importance. For instance, protein is found in a globular structure (biologically active). But when heated it forms into a looser coil (stopping its activity). In the scaling theory [5], the end-to-end distance R for an ideal and Θ polymer chain is written as

$$R \cong bN^{1/2} \tag{1}$$

in the case of a neutral polymer chain with excluded volume effect,

$$R \cong bN^{3/5} \tag{2}$$

but in a poor solvent case,

$$R \cong b(N/\tau)^{1/2} \tag{3}$$

where b is the typical segment length and N is the total number of the segments. τ is the scaled temperature from the Θ temperature as given by

$$\tau = \frac{\Theta - T}{\Theta} \tag{4}$$

where T is the temperature of the solvent. The solvent effects mentioned above can be also schematically drawn like in Figure 1.

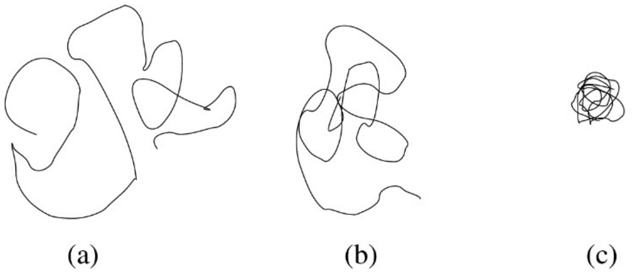

Figure 1 A single polymer chain in different solvents: (a) in a good solvent, (b) in a Θ solvent and, (c) in a poor solvent

In many simulation works the Θ point of the system to be investigated is required to be known [see 8, 9]. In many of these studies, only the basic interactions are included. In [10] the authors studied the effects of residual interactions on polymer properties near its Θ point. In that work, the physical measurables of the system are obtained by perturbation calculations. This theoretical work has shown that through including binary and ternary excluded volume interactions experimental and simulation data could be explained and the conflicts of mean-field and perturbation theories could be removed. Further to this work, Cherayil *et al.* investigated the effects including higher moments and also compared the results with the results of Monte Carlo simulations [11]. In another relatively old work [12] for various solvents, Θ temperatures were studied. This analytical work included first-order calculations in the density of vacancies and showed the changes in Θ temperatures. A molecular dynamics work by Zhou and Daivis [13] simulates polymer chains versus solvent quality. The coarse-grained simulation approach, model and the determination of Θ of the system are similar to our Monte Carlo simulation. But our work aims to investigate the effects of higher interactions to Θ point of the system. Apart from these works, our current work presents a clear picture of the effects of these higher interactions to the Θ point of the polymer system and the work aims to investigate the changes in the Θ point of the system.

2. MODEL AND METHOD

The polymer chain is of freely jointed beads, harmonic springs between neighboring monomers, so that the interaction potential between neighboring monomers is

$$U_{bond}(r) = \frac{3}{2} k_B T \frac{r^2}{b_0^2}, \tag{5}$$

where $r_{nm} = |\mathbf{r}_m - \mathbf{r}_n|$ is the distance between beads n and m and b_0 being the (bare) average bond length. Furthermore, monomer-monomer and monomer-solvent interactions are taken into account by a modified Lennard-Jones potential

$$U_{LJ}(r) = \begin{cases} 4\epsilon\{m(r) + s(r)\} & , if\ r \le r_c \\ 0 & , if\ r > r_c \end{cases} \tag{6}$$

where

$$m(r) = \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right], \tag{7}$$

and

$$s(r) = \beta \left[cos \frac{2\pi r}{r_c} - 1\right]. \tag{8}$$

The cut-off distance in this interaction potential can be taken as $r_c = 2^{1/6}\sigma$ [13]. This cut-off distance is shorter than the one of the standard Lennard-Jones potential, so that the simulation has an advantage over the simulation time. The solvent effects are taken into account by the second term, $s(r)$, where β parameter tunes the solvent quality, namely from good solvent to poor solvent through Θ point. The solvent quality is being hidden in the parameter of β. A sketch of this potential for a few β values is given in Figure 2.

Besides, the monomer units are modeled as having electric dipoles. The interaction between two electric dipoles (that is, between any monomers pairs here), while they are rotating freely when they are separated and shielded in a medium with high dielectric constant follows as [15]

$$U_{d-d}(r) = -\frac{u_1^2 u_2^2}{3 k_B T r^6} \tag{9}$$

where the orientation between two dipoles is not constant, freely rotating by the random thermal motions of molecules, so that thermal averaging can be taken implementing Boltzmann distribution to compute the averages over all possible orientations.

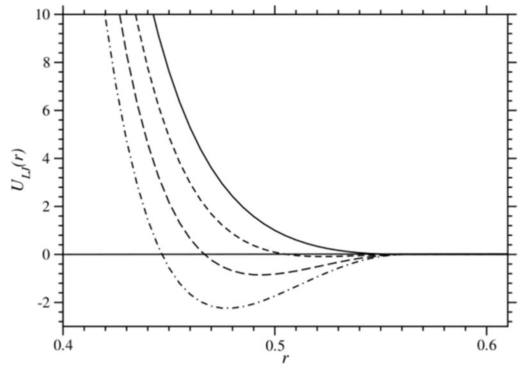

Figure 2 Modified Lennard-Jones potential at various β's: solid line for β=0.0, the dashed line for 1.0, the long-dashed line for 2.0 and the dot-dashed line for 3.0

Modeling the system with identical electric dipole moments $u_1 = u_2 = ed$ (e being the elementary electric charge and d the distance between two charges), this equation can be reduced to the following:

$$U_{d-d}(r) = -\frac{\lambda_B^2 d^4 k_B T}{3r^6}, \tag{10}$$

where λ_B is the Bjerrum length.

In the work, b_0 is used as the unit of length, ϵ as the unit of energy and the monomer mass m as the unit of mass. The simulations are carried out at $k_B T = 1.2$. σ is set to 1/2, to ensure that the length distribution will be only weakly perturbed by the short-range interaction, but remains almost Gaussian. ϵ is set to unity and λ_B is set to b_0.

This polymer chain is simulated by applying the standard Metropolis Monte Carlo (MC) method [16]. Three different MC moves are done in the simulations, which are local move, pivot move, and reptation move. The local move means that one single monomer unit is selected randomly and then given a random displacement. In the pivot move, one monomer unit is again selected randomly and then one hand of the chain is rotated as a rigid body at a random orientation. The reptation move selects randomly one end of the chain and then attaches it to the opposite end at a random orientation. During the simulations the acceptance rates of these moves are monitored, a tuning in the frequency of these moves can be needed, especially for the maximum displacement amount of the local move. As mentioned already in some works [17, 18], depending on the type of starting configuration different mixing of the elementary MC moves is necessary. In particular, the acceptance rate of the pivot one becomes very low for compact structures. After assuring equilibrated structures we measure the averages of physical quantities on the system. The ergodicity of the simulation is confirmed by running the simulations with different starting configurations.

2. RESULTS AND DISCUSSION

The Θ point of the system is resolved at various d values in Eq. 10. As d raises, the side effects of dipole-dipole interaction increase, making the comprehensive interaction more attractive. The case where no dipole-dipole interaction exists was given in the literature [18]. In this current paper, the determination of the Θ point will be given in detail for various d values. To determine the Θ point of the modeled system, the parameter β in Eq.8 is varied, since this parameter indicates varying the solvent quality. At $d = 0.05\lambda_B$, the short-ranged attractive interactions compensate the repulsive interactions, therefore the chain evinces the features of an ideal chain, $R \cong N^{1/2}b$. For $\beta < \beta_\Theta$, resembling a good solvent case, the chain turns into a swollen coil, $R \cong N^{3/2}b$, while in the poor solvent regime $\beta > \beta_\Theta$ the chain collapses into a globule, $R \cong N^{1/3}b$. The determination of the Θ point was done through the simulations of the neutral chains of length N=4, 8, 16, 32, 64, 128, 256 at different β's. In Figure 3 $\langle R^2 \rangle/(Nb^2)$ versus $1/N$ is plotted. At $\beta = \beta_\Theta$ the curve straightens at larger N's. The determined $\beta = \beta_\Theta$ can be confirmed in several ways. One way can be to plot the scaled end-to-end distance (R^2/bN) versus β. For larger lengths of the chains, the curves merge at the value of $\beta = \beta_\Theta$ [19]. For this d value, the determination of θ value is confirmed in Figure 4.

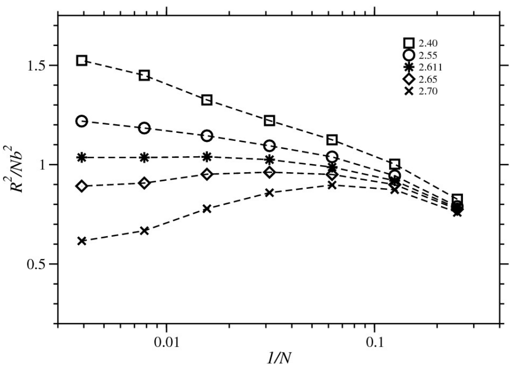

Figure 3 For $d = 0.05\lambda_B$, the chain length dependence of the normalized mean square end-to-end distance of an uncharged chain at different values of the parameter β of the modified Lennard-Jones potential: β=2.40 (squares), 2.55 (circles), 2.611 (stars), 2.65 (diamonds), 2.70 (crosses). Error bars are less than symbol size

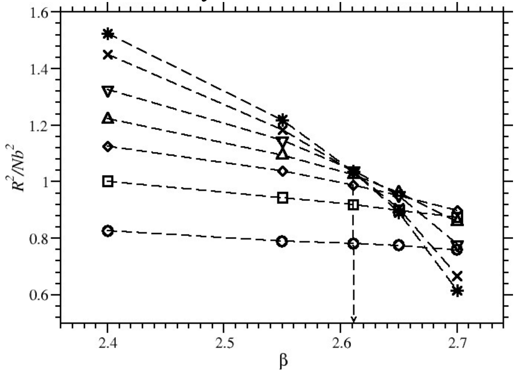

Figure 4 For $d = 0.05\lambda_B$, the scaled end-to-end distance versus β. N=4 (circles), 8 (squares), 16 (diamonds), 32 (triangle-ups), 64 (triangle-downs), 128 (crosses) and 256 (stars). The arrow points the $\beta = \beta_\Theta$ point. Error bars are less than symbol size

For a more detailed examination of the structure at all length scales, the spherically averaged form factor $S(q)$ can be measured;

$$S(q) = \left\langle \left\langle \frac{1}{N+1} \left| \sum_{j=0}^{N} \exp(i\vec{q}.\vec{r}_j) \right|^2 \right\rangle_{|q|} \right\rangle, \qquad (7)$$

where r_j is the position vector of monomer j [20, 21]. In Figure 5, for $d = 0.05\lambda_B$, this single chain structure factors calculated at three different β values are plotted. In this plot, one sees that the asymptotic behavior of the chain at the $\beta_\Theta = 2.611$ is identical to an ideal polymer chain.

The other β_Θ points determined at the different d values are displayed in Table 1. The second row of the table is the β_Θ value determined for the case without dipole moments [18].

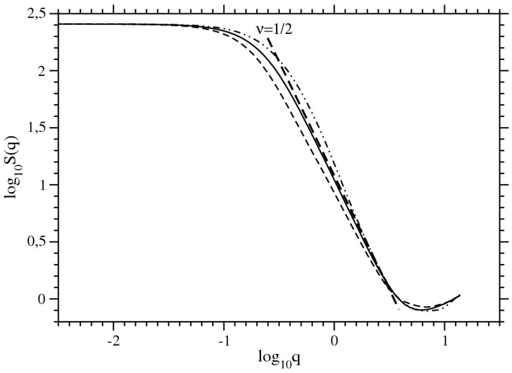

Figure 5 For $d = 0.05\lambda_B$, the spherically averaged structure factors are shown for β=2.40 (dashed), 2.611 (solid) and 2.70 (dot-dashed curve). The dashed line shows the asymptotic behavior for an ideal chain

Table 1
The determined β_Θ values at various d values

d	β_Θ
No dipole	2.615
$0.05\lambda_B$	2.611
$0.10\lambda_B$	2.606
$0.20\lambda_B$	2.600
$0.30\lambda_B$	2.520
$0.40\lambda_B$	2.454
$0.50\lambda_B$	1.973

Looking at the table, we observe that the presence of the dipole moments increases the overall attraction inside the system. This effect lets the Θ point of the system appear at lower values. The shift in β_Θ value for the very small d values is quite small, especially for the first two ones. To understand it, we can look at the contribution of the dipole-dipole interaction potential to the overall potential of the system. In Table 2, the average (absolute) proportions of dipole-dipole interaction potential to the total energy are given at τ=0.0. Also in the same table, the average bond lengths are given. In this table, we see that the average bond lengths are almost the same at these τ=0.0 cases. But we see that the contribution is (almost) zero at small d values. When the contribution increases, the shift in β_Θ (or Θ) points becomes larger.

Table 2
At various d values and τ=0.0, the average absolute portion of the dipole-dipole energy to the total energy (second row) and the average bond length values (third row)

d	$\left\|\frac{E_{d-d}}{E_{total}}\right\|$	$\langle b \rangle$
$0.05\lambda_B$	0.0000	1.040
$0.10\lambda_B$	0.0000	1.038
$0.20\lambda_B$	0.0007	1.032
$0.30\lambda_B$	0.0065	1.032
$0.40\lambda_B$	0.0411	1.038
$0.50\lambda_B$	0.1351	1.030

3. CONCLUSIONS AND OUTLOOK

Performing standard Metropolis Monte Carlo simulations of a polymer chain whose monomers carrying freely rotating electric dipole moments, in agreement with the theoretical expression [15], it has been shown that the effect of the presence of electric dipole moments decreases the overall interaction potential energy of the system. This effect is figured out by determining Θ point of the system into consideration. Comparing the determined corresponding Θ point for the system with the one determined previously [18], the shift to the smaller values is presented. The results are also analyzed by the structure factors of the system. On the other hand, due to the small contribution of this dipole-dipole interaction, the shift is in small quantity, as can be predicted theoretically. When the contribution of the dipole-dipole interactions to the total energy grows, the effect is seen more clearly.

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