An interplay of electrostatic and excluded volume interactions in conformational behavior of a dipolar chain: Theory and Computer simulations

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Supporting information.

I. THEORY: FREE ENERGY OF A DIPOLAR POLYMER CHAIN

Within the theoretical model we consider a flexible polymer chain consisting of N monomer units. Each monomer unit is assumed to be a dipole. Namely, it is modelled as a hard sphere of the diameter σ_p and the charge e connected with a counterion of the diameter σ_c and the charge $-e$. The counterion can move freely around the monomer, remaining at the constant distance $d = (\sigma_p + \sigma_c)/2$ from the latter (see Figure 1). Thereby, all monomer units comprise freely rotating permanent dipoles, with the absolute value of the dipole moments equal to ed.

In order to describe the conformational behavior of the dipolar polymer chain, we construct the total free energy as a function of the chain gyration radius R_g:

$$F(R_g) = F_{conf}(R_g) + F_{vol}(R_g) + F_{el}(R_g), \tag{1}$$

where

$$F_{conf}(R_g) = \frac{9}{4} k_B T \left(\frac{6R_g^2}{Nl^2} + \frac{Nl^2}{6R_g^2} \right) \tag{2}$$

is the conformational free energy of the Gaussian polymer chain[1–3]. Since in the present study we do not discuss the chain stiffness effect, we fix the value of the bond length of the chain, assuming $l = \sigma_p$. Note that accounting for the stiffness effect will bring the additional length scale related to the chain persistence length, so that rather big values of the latter will lead to more complicated equilibrium chain conformations than shapeless coil/globule ones studied here.

The volume interactions contribution can be assessed within the virial expansion truncated at the third term:

$$F_{vol}(R_g) = Nk_B T \left(\frac{NB}{V_g} + \frac{N^2 C}{V_g^2} \right), \tag{3}$$

where $V_g = 4\pi R_g^3/3$ is the gyration volume, B and C are, respectively, the second and third virial coefficients of the volume interactions between monomers. The latter can be evaluated as the virial coefficients of hard dumbbells[4–7]:

$$B = v(1 + 3\alpha), \quad C = v^2(3\alpha^2 + 6\alpha + 1)/2, \tag{4}$$

where $v = \pi(\sigma_c^3 + \sigma_p^3)/6$ is the dumbbell volume and α is the non-sphericity parameter, $\alpha = R_c S_c / 3V_c$. The geometrical parameters R_c, S_c and V_c characterizing any convex body for the dumbbell can be written as follows[6,7]:

$$R_c = \frac{\sigma_p^2 + \sigma_c^2 + \sigma_p\sigma_c}{2(\sigma_p + \sigma_c)}, \; S_c = \frac{\pi}{2}\left(\sigma_p + \sigma_c\right)^2, \; V_c = \frac{\pi}{24}\left(\sigma_p + \sigma_c\right)^3, \tag{5}$$

so that the non-sphericity parameter is

$$\alpha = \frac{2\left(\sigma_p^2 + \sigma_c^2 + \sigma_p\sigma_c\right)}{\left(\sigma_p + \sigma_c\right)^2}. \tag{6}$$

In order to evaluate the contribution of the electrostatic interactions, $F_{el}(R_g)$, to the total free energy of the chain (eq.1), we neglect any coupling between the chain connectivity and the effect of electrostatic correlations of dipoles, calculating the electrostatic free energy within the modified random phase approximation (MRPA)[9–14] for the unbonded dipoles:

$$F_{el}(R_g) \simeq \frac{V_g k_B T}{2} \int\limits_{|\mathbf{q}|<\Lambda} \frac{d\mathbf{q}}{(2\pi)^3}\left(\ln\left(1 + \frac{\kappa^2(\mathbf{q})}{q^2}\right) - \frac{\kappa^2(\mathbf{q})}{q^2}\right), \tag{7}$$

where the screening function[15] for the unbonded dipoles takes the following form

$$\kappa^2(\mathbf{q}) = \kappa_D^2\left(1 - g_0(\mathbf{q})\right) \tag{8}$$

with the square of the inverse Debye screening radius being $\kappa_D^2 = 8\pi l_B \rho_p$, where $l_B = e^2/(4\pi\varepsilon k_B T)$ is the Bjerrum length; $k_B T$ is the thermal energy, ε is the solvent dielectric permittivity expressed in the SI constant ε_0 units. We assume the cut-off parameter being $\Lambda = 2\pi/r_s = (6\pi^2\rho_p)^{1/3}$, where $r_s = (3/4\pi\rho_p)^{1/3}$ is the Wigner-Seitz radius of the monomer unit[8] and $\rho_p = N/V_g$ is the concentration of monomers. It is worth noting, the cut-off excludes the nonphysical modes corresponding to the small distances between the dipoles from the summation over the vectors $\mathbf{q}$ of the reciprocal space. This extends significantly an applicability of the pure RPA relation: from the weak coupling regime, where the standard RPA can be successfully applied, to the strong coupling regime, where electrostatic interactions between charged species are strong[9]. Note, the similar cut-off, based on the condition of equality between the number of modes enumerated by the wave vectors $\mathbf{q}$ and the number of translational degrees of freedom of particles was used in works[9,11–14]. Further, using the following model structure function of dipoles $g_0(\mathbf{q}) = 1/\left(1+q^2d^2/6\right)$, bearing in mind the relation $\Lambda = (6\pi^2\rho_p)^{1/3}$, and taking the integral (7), we arrive at the following analytic relation for the electrostatic free energy in the approximation of unbonded dipoles

$$F_{el} = \frac{k_BTV_g}{d^3}\sigma(y,\theta), \tag{9}$$

where

$$\sigma(y,\theta) = \frac{\sqrt{6}}{2\pi^2}\theta^3 \ln\left(1+\frac{y}{1+\theta^2}\right) +$$

$$\frac{\sqrt{6}}{2\pi^2}\left((2+3y)\arctan\theta - 2(1+y)^{3/2}\arctan\left(\frac{\theta}{\sqrt{1+y}}\right) - \theta y\right) \tag{10}$$

with $y = \kappa_D^2 d^2/6 = l_B d^2 N/R_g^3$ and $\theta = \Lambda d/\sqrt{6} = (9\pi/2)^{1/3}N^{1/3}d/(\sqrt{6}R_g)$. It is instructive to note the limiting regimes following from the general relation (9):

$$\frac{F_{el}}{Vk_BT} \simeq \begin{cases} -\left(\frac{48}{\pi}\right)^{1/3} l_B\rho_p^{4/3}, 1 \ll \theta^2 \ll y \\ -\frac{\kappa_D^3}{12\pi}, 1 \ll y \ll \theta^2 \\ -\frac{\sqrt{6}\pi}{3}l_B^2 d\rho_p^2, y \ll 1,\ \theta^2 \gg 1. \end{cases} \tag{11}$$

The first regime describes the case, when the dipole length d is much bigger than the Wigner-Seitz radius r_s, which, in turn, is much bigger than the Debye screening length r_D ($r_D \ll r_s \ll d$). In that case we have an amorphous structure of the densely packed charged dipolar groups that behave as unbonded ions. The second regime is realized when $r_s \ll r_D \ll d$. In this case, as in the first regime, the charged dipolar groups can also be considered as free ions. However, in that regime the ionic groups should be organized as in rarefied electrolyte solution, so that the electrostatic free energy can be described by the classic Debye-Hueckel relation. The third regime corresponds to the condition $r_s \ll d \ll r_D$ at which the electrostatic correlations of monomers consist of the pairwise effective Keesom interaction of the dipolar particles. Despite the fact that in present study all considered limiting laws are not strictly realized, we can definitely claim that the described globular conformation of the dipolar chain is closer to the first regime, while the coil conformation – to the third regime.

II. NUMERICAL SETUP

Following the theoretical model, we simulate a flexible dipolar chain as 256 spherical backbone beads, each bearing the charge e, linked by springs. An oppositely charged bead (a counterion) is connected to every backbone bead by a spring, thus, being able to freely rotate. The absolute values of the charges on the chain beads and counterions are equal to each other. Thus, every chain bead together with the counterion comprises a dipole of an arbitrary direction.

The dipolar chain is placed in a cubic cell of the length $L = 300$ and the periodic boundary conditions are applied. The chosen box size guarantees that the stretched chain has no intersections with its periodic image. The polyelectrolyte chain with side charged groups is assumed to be in a medium of uniform dielectric constant ϵ. The total potential energy of the system accounts for excluded volume and electrostatic interactions between all the beads, as well as the connectivity of the consecutive backbone charged beads and the connectivity between the backbone ions with the corresponding counterions into dipoles.

The excluded volume interactions are described by purely repulsive Lennard-Jones potential:

$$U_{LJ}(r_{ij}) = \begin{cases} 4\epsilon_{LJ}\left[\left(\dfrac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\dfrac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \epsilon_{LJ} & , r_{ij} \le R^c_{ij} \\ 0 & , r_{ij} > R^c_{ij} \end{cases} \tag{12}$$

where r_{ij} is the distance between the centers of ith and jth beads, $\epsilon_{LJ} = 1.0$ is the strength, and R^c_{ij} is the cutoff distance that depends on the size of a certain bead. We set $R^c_{ij} = 2^{1/6}\sigma_{ij}$ for each pair of particles, mimicing good solvent conditions for all the species present in the system. The hard core distance σ_{ij} between two beads is determined by the bead types, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, where σ_i and σ_j are the diameters of either backbone ions σ_p or counterions σ_c. In our simulations, we fix the backbone ion diameter and use it as a unit length, i.e. $\sigma_p = 1.0$ while the diameter σ_c of the counterions is varied.

The connectivity between neighboring beads along the polymer backbone, $U_{FENE}(r)$, is given by the FENE potential

$$U_{FENE}(r) = -\frac{1}{2}k_{FENE}R_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right) \tag{13}$$

where k_{FENE} is the spring constant and R_0 is the maximum extension of the bond. We set $k_{FENE} = 20.0$ and $R_0 = 2.0$ providing the equilibrium length of the bonds equal to unity.

The average length of the dipoles is determined by a combination of the FENE and Lennard-Jones potentials between the corresponding particles:

$$U_{bond}(r) = -\frac{1}{2}k_{FENE}R_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right) + 4\epsilon_{LJ}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \epsilon_{LJ} \tag{14}$$

where $\epsilon_{LJ} = 1.0$, $k_{FENE} = 100.0$ for all pairs, the parameters σ and R_0 are varied to simulate dipolar chains with various equilibrium values of the dipole length.

The electrostatic interaction between charged particles at the distance r is given by the Coulomb potential

$$U_{c,ij}(r) = \frac{Z_i Z_j l_B}{r} \tag{15}$$

where $Z_{i,j} = \pm 1$ are the valencies of the ionic groups.

The equations of motion are integrated in time within the LAMMPS package. The Nose-Hoover thermostat is used to maintain the constant temperature $T = 1.0$ of the system. The particle-particle/particle-mesh (PPPM) technique with the accuracy of 10^{-4} is applied to calculate the long range Coulomb interactions. The time step of integration is equal to 0.005. A random elongated conformation of the chain is taken as a starting state, the charge neutrality is ensured. The simulation runs are divided into an equilibration run (5×10^6 steps), followed by a production run (15×10^6 steps). All the data shown in the plots are obtained via averaging over the production run.

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