Regular Article

Polarizable polymer chain under external electric field: Effects of many-body electrostatic dipole correlations

Yu.A. Budkov[1,a] and A.L. Kolesnikov[2,b]

[1] Department of Applied Mathematics, National Research University Higher School of Economics, Moscow, Russia
[2] Institut für Nichtklassische Chemie e.V., Universität Leipzig - Leipzig, Germany

Abstract. We present a new simple self-consistent field theory of a polarizable flexible polymer chain under an external constant electric field with account for the many-body electrostatic dipole correlations. We show the effects of electrostatic dipole correlations on the electric-field-induced globule-coil transition. We demonstrate that only when the polymer chain is in the coil conformation, the electrostatic dipole correlations of monomers can be considered as pairwise. However, when the polymer chain is in a collapsed state, the dipole correlations have to be considered at the many-body level.

1 Introduction

Nowadays statistical thermodynamics of dielectric polymers is one of the most unexplored areas of polymer physics. Indeed, till now only several theoretical works have been published, where thermodynamic and structural properties of dielectric polymers in the bulk solution [1–5] and under external electric field [6] have been discussed. In ref. [1] Podgornik investigated, within the path integrals formalism, the renormalized persistence length of semi-flexible polymer chain whose segments interact via a screened Debye-Hückel dipolar interaction potential. In ref. [2] Kumar *et al.*, within the Edwards-Singh method, calculated the mean-square radius of gyration of polyzwitterionic molecules in aqueous solutions as a function of the chain length, electrostatic interaction strength, added salt concentration, dipole moment, and degree of ionization of the zwitterionic monomers. In ref. [3] Dean *et al.* showed that, taking into account the polarizing many-body correlations at the level of random phase approximation (RPA) can lead to ordering of the semi-flexible anisotropic polymer chains in the solution. In ref. [4] Kumar *et al.* showed, within the field-theoretic formalism, that dipolar interactions in polymer blends can significantly enhance the phase segregation. Lu *et al.*, within the field-theoretic formalism, analyzed the van der Waals interactions between two rigid polymers polarizable along their backbone [5].

In our recent work [6] we investigated the conformational behavior of the polarizable flexible polymer chain under the external electric field within the Flory-type mean-field theory [7]. We showed that, regardless the polymer chain conformation (coil or globule) an electric field increase causes swelling of the polymer chain. We also showed that, increasing the electric field in the regime of poor solvent can provoke the globule-coil transition. However, we fully neglected the many-body electrostatic correlations between monomers related to their molecular polarizability which cannot be accounted for at the level of pure mean-field theory [3]. These polarizing correlations, related to the fluctuations of the local electrostatic potential, could be accounted for via the fluctuation corrections to the mean-field approximation. It is evident in advance that contribution of the latter effects to the total free energy must be important at enough large monomer polarizability. Thus, a natural question appears: *How can the electrostatic many-body correlations of monomers change the polarizable polymer chain conformational behavior under the external electric field?*

2 Theory

Let us consider a polarizable flexible polymer chain immersed in a dielectric solvent which we model as a continuous dielectric medium with the dielectric permittivity ε_s. Let the polymer chain have a degree of polymerization N and each monomer have a molecular polarizability γ. The monomer polarizability may be related to the electronic polarizability of monomers as well as to the orientational polarizability of their permanent dipoles. The first case can be realized for the synthetic glassy polymers. The second case of permanent monomer dipoles is possible for the weak polyelectrolytes in the regime of counterion

a e-mail: ybudkov@hse.ru
b e-mail: bancocker@mail.ru

condensation, when the counterions and monomers form the strongly bound ion pairs. We consider only the case of isotropic dielectric response for simplicity. We also assume that the polymer chain is under the homogeneous electric field **E**. To study the conformations of the polymer chain in the external electric field, we use the simple Flory-type [7] mean-field theory, considering the radius of gyration R_g as a single order parameter. Therefore, we assume that the polymer chain occupies the volume which can be estimated by the gyration volume $V_g = 4\pi R_g^3/3$. Using all the above-mentioned model assumptions, one can write a total free energy of the polymer chain in the following form:

$$\mathcal{F}(R_g) = \mathcal{F}_{\text{conf}}(R_g) + \mathcal{F}_{\text{vol}}(R_g) + \mathcal{F}_{\text{el}}(R_g), \qquad (1)$$

where $\mathcal{F}_{\text{conf}}(R_g)$ is the free energy of the ideal polymer chain which can be calculated by the following interpolation formula [8–14]:

$$\mathcal{F}_{\text{conf}}(R_g) = \frac{9}{4}k_B T \left(\alpha^2 + \frac{1}{\alpha^2} \right), \qquad (2)$$

where $\alpha = R_g/R_{0g}$ is the expansion factor, $R_{0g}^2 = Nb^2/6$ is the mean-square radius of gyration of the Gaussian polymer chain, b is the Kuhn length, k_B is the Boltzmann constant, T is the temperature; the contribution of pairwise interactions of monomers to the total free energy can be accounted for simplicity via the standard virial series as follows:

$$\mathcal{F}_{\text{vol}}(R_g) = k_B T \left(\frac{N^2 B}{2V_g} + \frac{N^3 C}{6V_g^2} \right), \qquad (3)$$

where B and C are the second and third virial coefficients, respectively; the electrostatic contribution can be written as a sum of two contributions

$$\mathcal{F}_{\text{el}}(R_g) = \mathcal{F}_{\text{el}}^{(\text{MF})}(R_g) + \mathcal{F}_{\text{el}}^{(\text{fl})}(R_g), \qquad (4)$$

where first term is a mean-field approximation for the electrostatic free energy which can be estimated as the free energy of the dielectric sphere [15]

$$\mathcal{F}_{\text{el}}^{(\text{MF})}(R_g) = -\frac{V_g E^2}{8\pi}\frac{3\varepsilon_s(\varepsilon_p - \varepsilon_s)}{2\varepsilon_s + \varepsilon_p} = -\frac{3N\varepsilon_s\gamma E^2}{2\left(3\varepsilon_s + \frac{4\pi\gamma N}{V_g}\right)}, \qquad (5)$$

where the effective dielectric permittivity inside the polymer volume $\varepsilon_p = \varepsilon_s + 4\pi\gamma N/V_g$ in the mean-field approximation is introduced [6,16]; γ is the molecular polarizability of monomers, and $E = |\mathbf{E}|$ is the absolute value of the external electric field. The second term in eq. (4) determines the contribution of correlations between fluctuating dipoles. This contribution can be assessed for the enough large polymer volume within the formalism proposed in [3] at the level of random phase approximation (RPA) for the case of isotropic dielectric response:

$$\mathcal{F}_{\text{el}}^{(\text{fl})} \simeq \frac{V_g k_B T}{2} \int_{|\mathbf{k}|<\Lambda} \frac{d\mathbf{k}}{(2\pi)^3} \ln\left(\frac{V_s(\mathbf{k})}{V_p(\mathbf{k})} \right)$$
$$= \frac{2\pi V_g k_B T}{3b^3} \ln\left(1 + \frac{4\pi\gamma}{\varepsilon_s}\frac{N}{V_g} \right), \qquad (6)$$

where $V_p(\mathbf{k}) = 4\pi/(\varepsilon_p\mathbf{k}^2)$ and $V_s(\mathbf{k}) = 4\pi/(\varepsilon_s\mathbf{k}^2)$ is the Fourier images of Coulomb potentials inside the polymer volume and in the pure solvent, respectively; $\Lambda = 2\pi/b$ is the parameter of ultraviolet cut-off. The choice of such value of the cut-off parameter Λ is due to the fact that at the scales $\sim b$ fluctuations of the electrostatic potential related to the dipoles fluctuations are absent [3].

Collecting together all the above-mentioned expressions, we arrive at the following result for the total free energy of the polymer chain in the solution under external electric field:

$$\frac{\mathcal{F}}{k_B T} = \frac{9}{4}\left(\alpha^2 + \frac{1}{\alpha^2} \right) + \frac{N^2 B}{2V_g} + \frac{N^3 C}{6V_g^2}$$
$$- \frac{3N\varepsilon_s\gamma E^2}{2k_B T\left(3\varepsilon_s + \frac{4\pi\gamma N}{V_g}\right)} + \frac{2\pi V_g}{3b^3}\ln\left(1 + \frac{4\pi\gamma}{\varepsilon_s}\frac{N}{V_g} \right). \qquad (7)$$

We would like to stress that in our previous work [6] we have estimated the mean-field electrostatic contribution as the free energy of dielectric plate, whereas here we use more appropriate relation for the free energy of dielectric sphere.

3 Numerical results and discussions

To further perform some analytical estimates and numerical calculations, it is convenient to introduce the following dimensionless variables: $\tilde{E} = E\sqrt{\varepsilon_s b^3/k_B T}$, $\tilde{B} = Bb^{-3}$, $\tilde{C} = Cb^{-6}$, and $\tilde{\gamma} = \gamma b^{-3}/\varepsilon_s$.

Moreover, minimizing the total free energy (7) with respect to the expansion factor α, after some algebra we arrive at the equation in dimensionless form:

$$\alpha^5 - \alpha = \frac{3\sqrt{6}}{2\pi}\tilde{B}\sqrt{N} + \frac{27\tilde{C}}{\pi^2\alpha^3} + \frac{2\sqrt{6}\tilde{\gamma}^2\sqrt{N}\tilde{E}^2}{\left(1 + \frac{6\sqrt{6}\tilde{\gamma}}{\alpha^3\sqrt{N}}\right)^2}$$
$$- \frac{4\sqrt{6}\pi^2 N^{3/2}\alpha^6}{243}\left(\ln\left(1 + \frac{18\sqrt{6}\tilde{\gamma}}{\alpha^3\sqrt{N}} \right) - \frac{\frac{18\sqrt{6}\tilde{\gamma}}{\alpha^3\sqrt{N}}}{1 + \frac{18\sqrt{6}\tilde{\gamma}}{\alpha^3\sqrt{N}}} \right). \qquad (8)$$

The first and second terms on the right-hand side of eq. (8) determine the effect of volume interactions. The third term determines the influence of the interactions of induced dipoles with the applied electric field on the polymer swelling. As is seen, the latter always leads to swelling of the polymer chain that is related to the well-known electrostriction phenomena [15]. The fourth term determines the effect of many-body correlations of the fluctuating dipoles on the polymer swelling.

To understand how the electrostatic dipole correlations can affect the polymer conformation, at first we consider the case of repulsive volume interactions ($\tilde{B} > 0$), when the polymer chain is in the conformation of expanded coil ($\alpha \gg 1$). Thus in this limit we get

$$\alpha^5 - \alpha \simeq \frac{3\sqrt{6}}{2\pi}\sqrt{N}\left(\tilde{B} + \frac{4\pi}{3}\tilde{\gamma}^2\tilde{E}^2 - \frac{32\pi^3}{3}\tilde{\gamma}^2 \right). \qquad (9)$$

Equation (9) means that correlations between fluctuating dipoles in the coil state lead to an effective decreasing in the second virial coefficient. At zero electric field, in the case when the monomer polarizability is attributed to the orientational polarizability of permanent dipoles, *i.e.*, when $\gamma = p^2/(3k_BT)$ (where p is a permanent dipole), we get the following equation for the expansion factor in physical units:

$$\alpha^5 - \alpha \simeq \frac{3\sqrt{6}}{2\pi b^3}\sqrt{N}\left(B - \frac{32\pi^3 p^4}{27(k_BT)^2\varepsilon_s^2 b^3}\right). \quad (10)$$

It should be noted that eq. (10) is similar to that was obtained for the weak polyelectrolyte chain in the regime of counterion condensation [17]. The latter equation means that when the polymer chain is in the coil conformation, the electrostatic dipole correlations can be considered as pairwise. However, when the polymer chain adopts a collapsed state, the higher dipole correlations become important. In other words, when the polymer chain is in the globule state, polarizing dipole correlations have to be accounted for at the many-body level. In order to elucidate the role of the many-body dipole correlations in the polymer chain conformational behaviour, let us consider the dependence of the expansion factor on the monomer polarizability $\tilde{\gamma}$ at zero electric field. We assume in this case that the volume interactions are repulsive, *i.e.*, that $\tilde{B} > 0$. In fig. 1 the dependences of the expansion factor on the monomer polarizability at the different second virial coefficients $\tilde{B}$ are depicted. As is seen, increasing the monomer polarizability leads to a dramatic decrease in the expansion factor. The latter result means that the enough strong electrostatic many-body correlations of monomers can provoke the coil-globule transition. It is worth noting that in the theory (see, for instance, ref. [17]), where the monomer dipole correlations were considered as pairwise, to compensate the attraction of the dipoles, it is needed to take into account the repulsive volume interactions up to the third term of the virial expansion. However, accounting for the dipole correlations at the many-body level, as is seen from fig. 1, allows to compensate the attraction of the dipoles taking into account the repulsive volume interactions even at the level of the second virial coefficient.

It should be noted that this effect is quite similar to the coil-globule transition of polyelectrolyte chain induced by correlations of charges [18–24].

As one can see from eq. (8), the presence of the electric field inside the polymer coil, oppositely, leads to an effective increase in the second virial coefficient. In the case of strong electric field ($\tilde{E} \gg 1$), we get the limiting laws for the expansion factor and the radius of gyration:

$$\alpha \sim \tilde{\gamma}^{2/5}\tilde{E}^{2/5}N^{1/10}, \qquad R_g/b \sim \tilde{\gamma}^{2/5}\tilde{E}^{2/5}N^{3/5}, \quad (11)$$

which were first obtained (up to numerical prefactors) and discussed in ref. [6].

Now let us pass to the discussion of how the many-body electrostatic correlations of the fluctuating dipoles can change the conformation behavior of the polymer chain under the external electric field compared to the
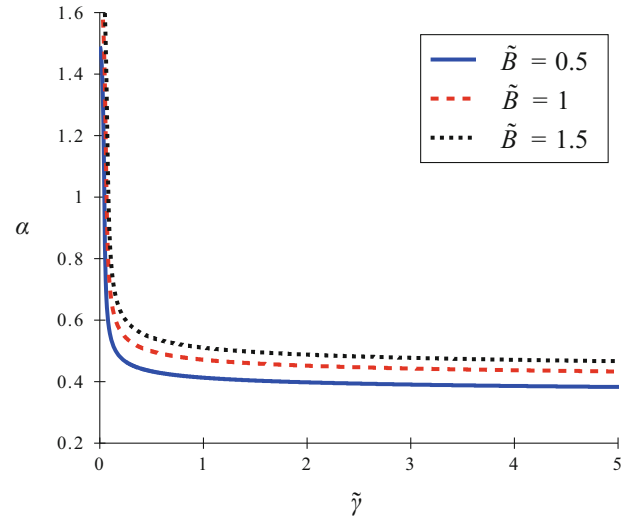

Fig. 1. The expansion factor α as a function of the monomer polarizability at the different second virial coefficients $\tilde{B}$. The data are shown for $N = 100$, $\tilde{E} = 0$, $\tilde{C} = 0$.

pure mean-field theory. Especially, we would like to focus on the influence of the electrostatic correlations of monomers on the *electric-field-induced globule-coil transition* which was in detail discussed in ref. [6] in the framework of mean-field theory. We assume that $\tilde{B} = -0.25$ and $\tilde{C} = 0.1$, so that the polymer chain is in the globule state even at $\tilde{\gamma} = 0$. Figure 2 demonstrates the expansion factor as a function of the electric field at a different monomer polarizability $\tilde{\gamma}$ obtained within a) the pure mean-field theory and b) the present theory on accounting for the many-body electrostatic dipole correlations. As is seen, in both cases applying the electric field exceeding some threshold value induces the globule-coil transition. Nevertheless, accounting for the electrostatic correlations shifts this transition to larger electric fields. It is worth noting that in the region of small electric fields, when the polymer chain is in a collapsed state, electrostatic correlations lead to smaller values of the expansion factor than what predicted by the mean-field theory. Thereby this phenomenon is reminiscent of the globule-coil transition of the polyelectrolyte chain caused by the electic field [23,24]. It should be noted that in the region of sufficiently large monomer polarizability in both theories, globule-coil transition occurs as a first-order phase transition, *i.e.*, as an abrupt increase in the expansion factor.

4 Conclusion

In conclusion, we have formulated the simple Flory-type self-consistent field theory of the polarizable polymer chain under an external electric field accounting for the many-body dipole electrostatic correlations. We have shown that when the polymer chain is in the coil state, while the monomer polarizability is small, the electrostatic dipole correlations can be considered as pairwise. In this case their effect consists of a decrease in the second virial
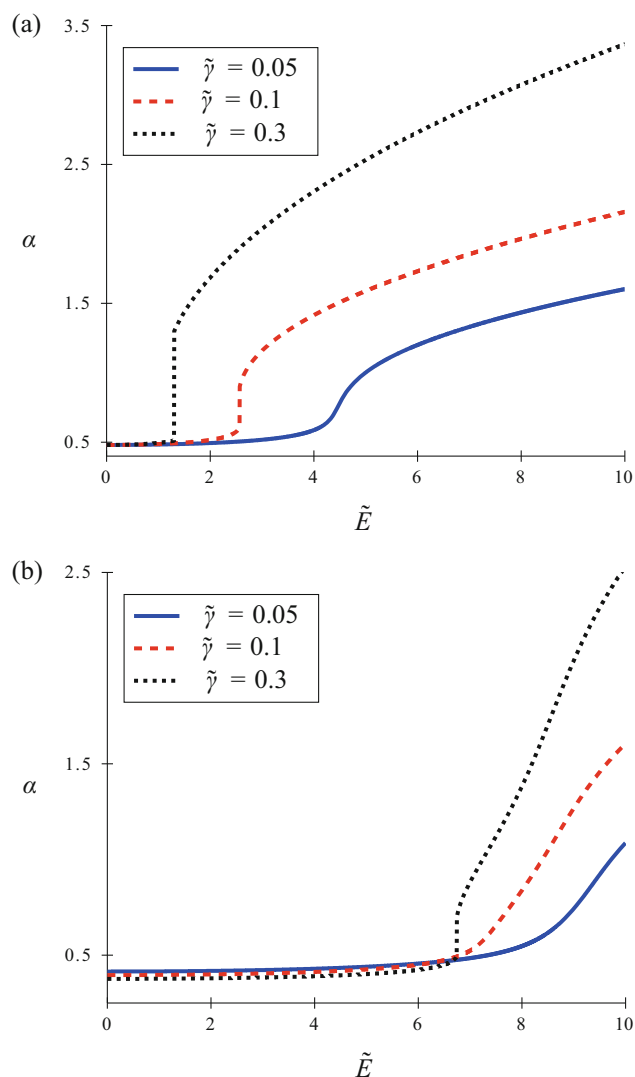
(a)

(b)

Fig. 2. The expansion factor α as a function of the electric field $\tilde{E}$ is calculated by the (a) mean-field theory and (b) theory with account for the electrostatic dipole correlations at different monomer polarizabilities $\tilde{\gamma}$. The data are shown for $N = 100$, $\tilde{B} = -0.25$, $\tilde{C} = 0.1$.

coefficient of monomer-monomer interaction. However, at a strong enough monomer polarizability, electrostatic dipole correlations can cause the coil-globule transition. When the polymer chain is in the globule state, electrostatic dipole correlations have to be considered at the many-body level. We have also shown that the account for the many-body electrostatic dipole correlations does not qualitatively change the main result of our previous pure mean-field theory [6]: *the electric-field-induced globule-coil transition*. However, in the present theory the electric field, at which the globule-coil transition takes

place, shifts to higher values. Such trend is related to the fact that the availability of the polarizability on the polymer backbone leads to an additional effective attraction between monomers. So a stronger electric field needs to be applied to disjoin the polymer globule.

References

1. Rudi Podgornik, Phys. Rev. E **70**, 031801 (2004).
2. Rajeev Kumar, Glenn H. Fredrickson, J. Chem. Phys. **131**, 104901 (2009).
3. David S. Dean, Rudolf Podgornik, J. Chem. Phys. **136**, 154905 (2012).
4. Rajeev Kumar, Bobby G. Sumpter, M. Muthukumar, Macromolecules **47**, 6491 (2014).
5. Bing-Sui Lu, Ali Naji, Rudolf Podgornik, J. Chem. Phys. **142**, 214904 (2015).
6. Yu.A. Budkov, A.L. Kolesnikov, M.G. Kiselev, J. Chem. Phys. **143**, 201102 (2015).
7. P. Flory *Statistical Mechanics of Chain Molecules* (Wiley-Interscience, New York, 1969).
8. M. Fixman, J. Chem. Phys. **36**, 306 (1962).
9. Yu.A. Budkov, A.L. Kolesnikov, J. Stat. Mech. **2016**, 103211 (2016).
10. A.Yu. Grosberg, D.V. Kuznetsov, Macromolecules **25**, 1970 (1992).
11. Yu.A. Budkov, A.L. Kolesnikov, N. Georgi, M.G. Kiselev, J. Chem. Phys. **141**, 014902 (2014).
12. Yu.A. Budkov, A.L. Kolesnikov, N. Georgi, M.G. Kiselev, EPL **109**, 36005 (2015).
13. Yu.A. Budkov, A.L. Kolesnikov, M.G. Kiselev, J. Chem. Phys. **143**, 201102 (2015).
14. Yu.A. Budkov, A.L. Kolesnikov, N.N. Kalikin, M.G. Kiselev, EPL **114**, 46004 (2016).
15. L.D. Landau, E.M. Lifshitz, *Electrodynamics of Continuous Media*, Vol. **8**, *A Course of Theoretical Physics* (Pergamon Press, Oxford, 1960).
16. Yu.A. Budkov, A.L. Kolesnikov, M.G. Kiselev, EPL **111**, 28002 (2015).
17. Prasanta Kundu, Arti Dua, J. Stat. Mech. **2014**, 07023 (2014).
18. Francisco J. Solisa, Monica Olvera de la Cruz, J. Chem. Phys. **112**, 2030 (2000).
19. N.V. Brilliantov, D.V. Kuznetsov, R. Klein, Phys. Rev. Lett. **81**, 1433 (1998).
20. Anvy Moly Tom, Satyavani Vemparala, R. Rajesh, Nikolai V. Brilliantov, Phys. Rev. Lett. **117**, 147801 (2016).
21. H. Schiessel, P. Pincus, Macromolecules **31**, 7953 (1998).
22. A.G. Cherstvy, J. Phys. Chem. B **114**, 5241 (2010).
23. R.R. Netz, J. Phys. Chem. B **107**, 8208 (2003).
24. R.R. Netz, Phys. Rev. Lett. **90**, 128104 (2003).