Supporting information to Communication on "Molecular theory of electrostatic collapse of dipolar polymer gels" by Yury A. Budkov, Nikolai N. Kalikin, and Andrei L. Kolesnikov

I. SCREENING FUNCTION

Here we demonstrate a derivation of the screening function of the dipolar polymer gel within the random phase approximation (RPA)[1]. The screening function within such approach can be calculated as follows[1]

$$\kappa^2(\mathbf{k}) = \frac{4\pi}{\varepsilon k_B T} C(\mathbf{k}), \tag{1}$$

where $C(\mathbf{k})$ is the Fourier-image of the charge density correlation function

$$C(\mathbf{r}-\mathbf{r}') = \left\langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}')\right\rangle, \tag{2}$$

where $\langle (...) \rangle$ means averaging over statistics of the polymer subchains without dipoles. Taking into account that the microscopic charge density is determined by the following expression

$$\hat{\rho}(\mathbf{r}) = q\sum_{i=1}^{n}\sum_{\alpha_i=1}^{m}\left(\delta(\mathbf{r}-\mathbf{r}_i^{\alpha_i}) - \delta(\mathbf{r}-\mathbf{r}_i^{\alpha_i}-\xi_i^{\alpha_i})\right), \tag{3}$$

we obtain

$$C(\mathbf{r}-\mathbf{r}') = q^2\sum_{i,j}\sum_{\alpha_i,\gamma_j}\left\langle \left(\delta(\mathbf{r}-\mathbf{r}_i^{\alpha_i}) - \delta(\mathbf{r}-\mathbf{r}_i^{\alpha_i}-\xi_i^{\alpha_i})\right)\left(\delta(\mathbf{r}'-\mathbf{r}_j^{\gamma_j}) - \delta(\mathbf{r}'-\mathbf{r}_j^{\gamma_j}-\xi_j^{\gamma_j})\right)\right\rangle =$$

$$q^2\sum_{i,j}\sum_{\alpha_i,\gamma_j}\int\frac{d\mathbf{k}}{(2\pi)^3}\int\frac{d\mathbf{p}}{(2\pi)^3}\left\langle e^{-i\mathbf{k}\mathbf{r}_i^{\alpha_i}-i\mathbf{k}\mathbf{r}_j^{\gamma_j}}\right\rangle_r\left\langle\left(e^{-i\mathbf{k}\xi_i^{\alpha_i}}-1\right)\left(e^{-i\mathbf{p}\xi_j^{\gamma_j}}-1\right)\right\rangle_\xi e^{i\mathbf{k}\mathbf{r}+i\mathbf{p}\mathbf{r}'}, \tag{4}$$

where indices (i,j) enumerate the subchains, while (α_i,γ_j) – their monomer units. We have also used the Fourier-representation of the Dirac delta-function

$$\delta(\mathbf{x}) = \int\frac{d\mathbf{k}}{(2\pi)^3}e^{i\mathbf{k}\mathbf{x}}. \tag{5}$$

Using the identity[1]

$$\left\langle e^{-i\mathbf{k}\mathbf{r}_i^{\alpha_i}-i\mathbf{p}\mathbf{r}_j^{\gamma_j}}\right\rangle_r = \frac{(2\pi)^3}{V}\delta(\mathbf{k}+\mathbf{p})\left\langle e^{-i\mathbf{k}(\mathbf{r}_i^{\alpha_i}-\mathbf{r}_j^{\gamma_j})}\right\rangle_r, \tag{6}$$

we arrive at

$$C(\mathbf{r}-\mathbf{r}') = \frac{q^2}{V}\sum_{i,j}\sum_{\alpha_i,\gamma_j}\int\frac{d\mathbf{k}}{(2\pi)^3}e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\left\langle e^{-i\mathbf{k}(\mathbf{r}_i^{\alpha_i}-\mathbf{r}_j^{\gamma_j})}\right\rangle_r\left\langle\left(e^{-i\mathbf{k}\xi_i^{\alpha_i}}-1\right)\left(e^{i\mathbf{k}\xi_j^{\gamma_j}}-1\right)\right\rangle_\xi =$$

$$\frac{q^2 nm}{V}\int\frac{d\mathbf{k}}{(2\pi)^3}e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\left(2-\omega(\mathbf{k})-\omega(-\mathbf{k})\right)+$$

$$\frac{q^2}{V}\sum_{i,j}\sum_{\alpha_i\neq\gamma_i,\gamma_j}\int\frac{d\mathbf{k}}{(2\pi)^3}e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\left\langle e^{-i\mathbf{k}(\mathbf{r}_i^{\alpha_i}-\mathbf{r}_j^{\gamma_j})}\right\rangle_r|1-\omega(\mathbf{k})|^2, \tag{7}$$

where we extracted averaging over the monomer units coordinates $\mathbf{r}_i^{\alpha_i}$ and displacements $\xi_i^{\alpha_i}$ of the grafted charged centers and took into account that $\omega(\mathbf{k})=\left\langle e^{i\mathbf{k}\xi_i^{\alpha_i}}\right\rangle_\xi$. Further, using the definition of the structure factor[2]

$$S(\mathbf{k})=1+\frac{1}{nm}\sum_{i,j}\sum_{\alpha_i\neq\gamma_i,\gamma_j}\left\langle e^{-i\mathbf{k}(\mathbf{r}_i^{\alpha_i}-\mathbf{r}_j^{\gamma_j})}\right\rangle_r, \tag{8}$$

we obtain

$$C(\mathbf{r}-\mathbf{r}')=\int\frac{d\mathbf{k}}{(2\pi)^3}e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}C(\mathbf{k}), \tag{9}$$

where

$$C(\mathbf{k})=2q^2c\left(1-Re(\omega(\mathbf{k}))+\frac{1}{2}\left(S(\mathbf{k})-1\right)|1-\omega(\mathbf{k})|^2\right) \tag{10}$$

with the monomer unit concentration $c=mn/V$. Therefore, according to eq. (1), the screening function takes the following form

$$\kappa^2(\mathbf{k})=\frac{8\pi q^2c}{\varepsilon k_BT}\left(1-Re(\omega(\mathbf{k}))+\frac{1}{2}\left(S(\mathbf{k})-1\right)|1-\omega(\mathbf{k})|^2\right), \tag{11}$$

where $Re(\omega(\mathbf{k}))$ is the real part of the complex function, $\omega(\mathbf{k})$. In the case of a spherically symmetric distribution function, for which $\omega(-\mathbf{k})=\omega(\mathbf{k})$ and $Re(\omega(\mathbf{k}))=\omega(\mathbf{k})$, we obtain eq. (5), written in the main text. In the absence of chain connectivity, when $S(\mathbf{k})=1$, the screening function transforms into the expression for the solution of low-molecular weight dipolar molecules obtained earlier[1]. For the case of the unbound charged sites ($\omega(\mathbf{k})=0$), the screening function transforms into the expression for salt-free polyelectrolyte solutions obtained for the first time in paper[3].

II. ELECTROSTATIC FREE ENERGY

In this section, we derive the electrostatic free energy of the dipolar gel within the RPA[1,3]. Using the approximation of independent subchains, the electrostatic (corrrelation) free energy can be written as follows[3]

$$F_{cor}=\frac{Vk_BT}{2}\int\frac{d\mathbf{k}}{(2\pi)^3}\left(\ln\left(1+\frac{\kappa^2(\mathbf{k})}{k^2}\right)-\frac{\kappa^2(\mathbf{k})}{k^2}\right), \tag{12}$$

where the screening for spherically symmetric probability distribution function $\omega(r)$ takes the form

$$\kappa^2(\mathbf{k}) = \kappa_D^2(1-\omega(\mathbf{k}))\left(1+\frac{1}{2}\left(S(\mathbf{k})-1\right)\left(1-\omega(\mathbf{k})\right)\right). \tag{13}$$

The reference structure factor of the subchain for $m \gg 1$ is approximated by the well-known Debye structure factor $S(\mathbf{k}) \approx 1 + 12/(k^2b^2)$ of the Gaussian chain, where b is the Kuhn's length. Using the ansatz for the characteristic function $\omega(\mathbf{k}) = (1 + k^2l^2/6)^{-1}$, where l is the dipole length, we arrive at

$$F_{cor} = F_{cor}^{(d)} + F_{cor}^{(ch)}, \tag{14}$$

where the first term is the electrostatic free energy of the unbound dipolar monomers, determined by the expression[1]

$$F_{cor}^{(d)} = -\frac{Vk_BT}{l^3}\sigma(y), \tag{15}$$

with the strength of the electrostatic interactions $y = 4\pi p^2 c/(3k_BT\varepsilon)$ ($p = ql$ is the dipole moment) and auxiliary function

$$\sigma(y) = \frac{\sqrt{6}}{4\pi}\left(2(1+y)^{3/2} - 2 - 3y\right). \tag{16}$$

The second term determines the effect of the chain connectivity on the electrostatic free energy and can be written in the following form

$$F_{cor}^{(ch)} = -\frac{Vk_BT}{l^3}\delta(y,\gamma), \tag{17}$$

with a geometric parameter $\gamma = l^2/b^2$ and the auxiliary functions

$$\delta(y,\gamma) = \delta_1(y,\gamma) + \delta_2(y,\gamma), \tag{18}$$

$$\delta_1(y,\gamma) = \frac{3\sqrt{6}}{4\pi}\left(1+\frac{y}{2}-\sqrt{1+y}\right)\gamma, \tag{19}$$

$$\delta_2(y,\gamma) = \frac{\sqrt{6}\gamma^2y^2}{4\pi(y-\gamma(1+y))^2}\Bigg[1-(2y+5)\sqrt{1+y}-\frac{3\gamma(1+y)(1-\sqrt{1+y})}{y}+ \\ \frac{1}{\sqrt{2}}\left(\left(2+y+\sqrt{y^2+4y-4\gamma(1+y)}\right)^{3/2}+\left(2+y-\sqrt{y^2+4y-4\gamma(1+y)}\right)^{3/2}\right)\Bigg]. \tag{20}$$

III. DISCUSSION OF THE DIPOLE NONLOCALITY EFFECT

We would like to note that the condition $\gamma \approx 1$ can be realized for zwitterionic polymers, such as polyesters, polyphosphazenes, and polyphosphobetaines[4]. For the polyelectrolyte chains, immersed in the low-polar solvents[5,6], where the monomer units and counterions usually form solvent-separated ionic pairs with a fluctuating mutual distance, γ can be greater than unity. It is also worth noting that at sufficiently small γ ($l \ll b$), the contribution of the electrostatic interactions between the dipolar monomer units can be described with good accuracy by the electrostatic free energy of the freely moving dipolar particles (see, eq.(15)). Note that we have discussed this limiting regime earlier in the context of the conformational behavior of a single dipolar polymer chain with point-like dipoles on its monomer units[7]. However, for the subchains with $\gamma \sim 1$, the contribution (17) to the electrostatic free energy becomes considerable. In other words, when the dipole length is comparable with the Kunh length, the approximation of disconnected monomers, used for different condensed polymer systems with the short-range volume interactions[8,9], gives a large discrepancy.

Now we would like to discuss the parameters of the real polymers, for which one can expect to observe experimentally the discussed above transition. For instance, the dipole moment of monomer units of the polybetaines can reach $\approx 24 - 34\ D$ (see[10] and references therein). Thus, the dipole length, $l = p/e$, where e is the elementary charge, for these polymers is in range $\approx 0.5 - 0.7\ nm$. For the polymer chains with dipole moment $p = 24\ D$, immersed in water at $T = 300\ K$ ($\varepsilon \approx 78$) we obtain the coupling parameter $\lambda \approx 6$ which is in the region of the collapsed gel, depicted on Fig. 3 in the main text for $\Phi_0 = 10^{-3}$. In order to avoid the collapse, in this case, it is necessary to enhance significantly the reference volume fraction, Φ_0, of the monomer units.

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