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Statistical model of polymer like chains of ionic groups linked by
double hydrogen bonds

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Статистична модель ланцюжків іонних груп полімерного типу, з'єднаних подвійними водневими зв'язками

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Анотація. Запропоновано квантово - статистичну модель для опису процесів полімеризації комплексів уранілу $UO_2[(OH)_2UO_2]_n^{2+}$ з врахуванням статистичного характеру розподілу протонів на водневих зв'язках. Враховано ефективну короткодійчу взаємодію між протонами, далекодіючу електростатичну протон - протонну взаємодію а також граничні ефекти для опису всіх можливих конфігурацій іонних груп на кінцях полімерного комплексу. При певних граничних умовах досліджено залежності вільної енергії і хімічного потенціалу іонної групи від числа іонних груп в полімерному ланцюжку. Обговорено умови формування комплексів різної довжини.

Statistical model of polymer like chains of ionic groups linked by double hydrogen bonds

I.V.Stasyuk, T.V.Golubets'

Abstract. The quantum - statistical model for the description of polymerization process of uranile complexes $UO_2[(OH)_2UO_2]_n^{2+}$ are proposed allowing for the statistical character of distribution protons on the hydrogen bonds. The effective short - range configurational interaction between protons, long - range electrostatic proton - proton interactions as well as boundary effects with the description of all configurations of ionic groups on the ends of polymer complex are considered. At the certain boundary conditions the dependences on the number of ionic groups in polymer chain are investigated. The conditions of complex formations of various lengths are discussed.

1. Object of studies.

The object of our study are polymer complexes $UO_2[(OH)_2UO_2]_n^{2+}$ of uranile with sheet-like double bridges of ionic groups OH^- (Fig. 1) [1,2]. Objects of such a type are formed under the influence of hydrolysis and radiolysis of electrolytic water solutions.

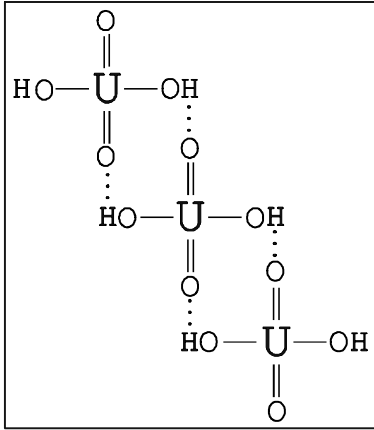


Figure 1. The schematic structure of polymer complex of uranile.

account effective short-range configurational interactions between protons surrounding an intermediate ionic groups, long-range electrostatic proton-proton interactions as well as boundary effects with the description of all configurations of ionic groups on the ends of polymer complex.

For this intention, we formulate quantum - statistical model and provide calculation of the free energy of polymer complex and chemical potential of ionic group. Their dependences on the number of ionic groups in polymer chain at the certain boundary conditions are investigated. The stability of complexes of various lengths is considered.

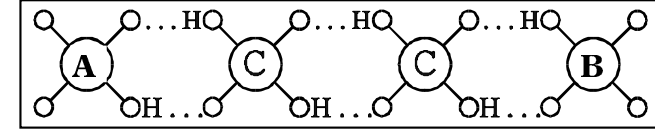
2. Model of polymer chain.

The structure, shown at (Fig. 1), can be presented as a molecular complex, where pairs of hydrogen bonds join in series ionic groups. A case is considered, when the groups (A) and (B) at the ends of a polymer are the same as to their properties as intermediate ionic groups (C).

Strong dependence [3–5] of a complex formation on the pH level of environment, metal ion concentration, and temperature is a characteristic feature of uranile ions' behaviour UO_2^{2+} in electrolytic water solutions. The description of the influence of afore-said factors on the process of polymerization of such objects with the participation of hydrogen bonds from the microscopic point of view is an actual problem.

The main purpose of this work is the investigation of thermodynamics of the polymerization process allowing for the statistical character of distribution protons on hydrogen bonds. We take into

Let's introduce the basis of 4^N states $|l\rangle = ||1, l_1\rangle \otimes \dots \otimes ||k, l_k\rangle \otimes \dots \otimes ||N, l_N\rangle$



($l_k = 1 \dots 4$), where $||k, l_k\rangle = |k; S_{k1}^z, S_{k2}^z\rangle$ are single-site states which are determined by possible values $S_{kr}^z = \pm 1/2$ of a pseudospin component for r hydrogen bond ($r = 1$ – “upper”, $r = 2$ – “lower”) on k double bridge and N is a total number of pairs of hydrogen bonds.

Effective short-range configurational interaction between protons belonging to an intermediate ionic group we shall present as follows:

$$H_{k,k+1} = w'_1 \hat{X}_k^{11} \hat{X}_{k+1}^{44} + w' \left(\hat{X}_k^{11} \hat{X}_{k+1}^{22} + \hat{X}_k^{11} \hat{X}_{k+1}^{33} + \hat{X}_k^{33} \hat{X}_{k+1}^{44} + \hat{X}_k^{22} \hat{X}_{k+1}^{44} \right) + \varepsilon_1 \left(\hat{X}_k^{22} \hat{X}_{k+1}^{22} + \hat{X}_k^{33} \hat{X}_{k+1}^{33} \right) + \varepsilon \left(\hat{X}_k^{11} \hat{X}_{k+1}^{11} + \hat{X}_k^{44} \hat{X}_{k+1}^{44} \right) + \varepsilon_2 \left(\hat{X}_k^{22} \hat{X}_{k+1}^{33} + \hat{X}_k^{33} \hat{X}_{k+1}^{22} \right) + w \left(\hat{X}_k^{44} \hat{X}_{k+1}^{22} + \hat{X}_k^{44} \hat{X}_{k+1}^{33} + \hat{X}_k^{33} \hat{X}_{k+1}^{11} + \hat{X}_k^{22} \hat{X}_{k+1}^{11} \right) + w_1 \hat{X}_k^{44} \hat{X}_{k+1}^{11}$$

ε	w'	w'	w'
w	ε_1	ε_2	w'
w	ε_2	ε_1	w'
w_1	w	w	ε

Figure 2. Energies of proton configurations.

where w'_1 , w_1 , w' , w , ε_1 , ε_2 , ε are energies of proton configurations (Fig. 2) in a potential minima near ionic group and $\hat{X}_k^{pq} = |k; p\rangle \langle k; q|$ - Hubbard operators.

Hamiltonian of a proton subsystem consists of two parts $\hat{H} = \hat{H}_S + \hat{H}_L$, where

$$\hat{H}_m^S = (m+2)\varepsilon + \sum_{k=1}^m \sum_{pq} B^{pq} \times \hat{X}_k^{pp} \hat{X}_{k+1}^{qq} + \hat{H}_1^A + \hat{H}_{m+1}^B$$

stands for the short - range configurational interaction, and

$$\hat{H}_m^L = -\frac{a^2 (Ze)^2}{c^3} \sum_{\substack{l, l'=1 \\ (l \neq l')}}^{m+1} \frac{(\hat{X}_l^{11} - \hat{X}_l^{44})(\hat{X}_{l'}^{11} - \hat{X}_{l'}^{44})}{|l - l'|^3} \quad (1)$$

is an electrostatic dipole - dipole long - range part. Here $m = N - 1$ is the number of intermediate ionic groups, Ze – effective charge of proton, a –

distance between potential minimums of protons on the hydrogen bond, c – distance between centres of ionic groups and B^{pq} ($p, q = 1 \dots 4$) is a square matrix:

$$\{B^{pq}\} = \begin{pmatrix} 0 & \frac{w'+w}{2} - \varepsilon & \frac{w'+w}{2} - \varepsilon & w'_1 - \varepsilon - 2\delta \\ \frac{w'+w}{2} - \varepsilon & \varepsilon_1 - \varepsilon & \varepsilon_2 - \varepsilon & \frac{w'+w}{2} - \varepsilon \\ \frac{w'+w}{2} - \varepsilon & \varepsilon_2 - \varepsilon & \varepsilon_1 - \varepsilon & \frac{w'+w}{2} - \varepsilon \\ w_1 - \varepsilon + 2\delta & \frac{w'+w}{2} - \varepsilon & \frac{w'+w}{2} - \varepsilon & 0 \end{pmatrix} \quad (2)$$

Boundary effects are described by the terms $\hat{H}_1^A = \sum_p \alpha_{Ap} \hat{X}_1^{pp}$ (“left” end group) and $\hat{H}_{m+1}^B = \sum_q \alpha_{Bq} \hat{X}_{m+1}^{qq}$ (“right” end group) which are included in a general expression (see eq. (2)) for model Hamiltonian

$$\begin{aligned} \alpha_{A1} &= \alpha_A - \varepsilon + \delta & \alpha_{A2} &= \mu_A^1 - \varepsilon & \alpha_{A3} &= \mu_A^2 - \varepsilon & \alpha_{A4} &= \alpha'_A - \varepsilon - \delta \\ \alpha_{B1} &= \alpha'_B - \varepsilon - \delta & \alpha_{B2} &= \mu_B^1 - \varepsilon & \alpha_{B3} &= \mu_B^2 - \varepsilon & \alpha_{B4} &= \alpha_B - \varepsilon + \delta \end{aligned} \quad (3)$$

where $\delta = (w' - w)/2$ and $\alpha'_i, \alpha_j, \mu_k^l$ ($i, j, k = A, B; l = 1, 2$) are quantities which can take values of configuration energies from the set of possible ones (Fig. 2) depending on the number of protons joined outside to the boundary ionic groups (A) and (B).

3. Transfer matrix approach.

At the calculation of the free energy of a proton subsystem we use an expression

$$F_m = -\frac{1}{\beta} \ln Z_m \quad \text{where} \quad Z_m = Z_m^S \langle e^{-\beta \hat{H}_m^L} \rangle_S \quad (4)$$

where $Z_m^S = Sp [e^{-\beta \hat{H}_m^S}]$ is partition function of the system with the short - range interactions only and

$$\langle e^{-\beta \hat{H}_m^L} \rangle_S = \frac{1}{Sp [e^{-\beta \hat{H}_m^S}]} Sp [e^{-\beta \hat{H}_m^L} e^{-\beta \hat{H}_m^S}] \quad (5)$$

denotes the statistical average on the initial basis with Hamiltonian \hat{H}_m^S .

We shall calculate trace in Z_m^S using a transfer - matrix method [6]. By introducing auxiliary diagonal matrices $\hat{A} = \sum_p e^{-\beta \alpha_{Ap}} \hat{X}^{pp}$; $\hat{D} = \sum_q e^{-\beta \alpha_{Bq}} \hat{X}^{qq}$ (see section 2, eq. (3)), and using properties of direct product of matrices as well as commutation relation $[X_k^{pp}, X_{k+1}^{qq}] = 0$ for projecting operators, we shall obtain a formula for evaluation of partition

function:

$$\begin{aligned} Z_m^S &= e^{-\beta(m+2)\varepsilon} Sp \left[e^{-\beta \hat{H}_1^A} e^{-\beta \sum_{k=1}^m \sum_{pq} B^{pq} \hat{X}_k^{pp} \hat{X}_{k+1}^{qq}} e^{-\beta \hat{H}_{m+1}^B} \right] = \\ &= e^{-\beta(m+2)\varepsilon} \tilde{\Sigma} \hat{A} [e^{-\beta \hat{B}}]^m \hat{D} \end{aligned} \quad (6)$$

here $\tilde{\Sigma}[\dots]$ is the sum of all elements of the product of matrices $\hat{A} [e^{-\beta \hat{B}}]^m \hat{D}$ and $[e^{-\beta \hat{B}}]_{pq} = e^{-\beta B^{pq}}$ is a transfer-matrix of the system.

The transfer-matrix is given by the following expression:

$$[e^{-\beta \hat{B}}]_{pq} = \begin{pmatrix} 1 & e^{-\beta(\frac{w'+w}{2}-\varepsilon)} & e^{-\beta(\frac{w'+w}{2}-\varepsilon)} & e^{-2\beta\delta} e^{-\beta(w'_1-\varepsilon)} \\ e^{-\beta(\frac{w'+w}{2}-\varepsilon)} & e^{-\beta(\varepsilon_1-\varepsilon)} & e^{-\beta(\varepsilon_2-\varepsilon)} & e^{-\beta(\frac{w'+w}{2}-\varepsilon)} \\ e^{-\beta(\frac{w'+w}{2}-\varepsilon)} & e^{-\beta(\varepsilon_2-\varepsilon)} & e^{-\beta(\varepsilon_1-\varepsilon)} & e^{-\beta(\frac{w'+w}{2}-\varepsilon)} \\ e^{2\beta\delta} e^{-\beta(w_1-\varepsilon)} & e^{-\beta(\frac{w'+w}{2}-\varepsilon)} & e^{-\beta(\frac{w'+w}{2}-\varepsilon)} & 1 \end{pmatrix} \quad (7)$$

The next step is to use a unitary transformation $\hat{U}^{-1} e^{-\beta \hat{B}} \hat{U}$ which will put the transfer-matrix (7) to a diagonal form. This allows to present $[e^{-\beta \hat{B}}]^m = \hat{U} \hat{\Lambda}^m \hat{U}^{-1}$, where $\hat{\Lambda}$ is a diagonal matrix ($\hat{U}^{-1} e^{-\beta \hat{B}} \hat{U} = \hat{\Lambda}$) with eigenvalues λ_k .

4. Free energy.

We consider the case when the most probable among various proton configurations near ionic group are the two-proton ones (that corresponds to the chemical formulae $[UO_2(OH)_2]^{2+}$), and the proton configurations with four or zero protons (energies w'_1 and w_1 , see Fig. 2) are practically absent. A great number of works testifies to this fact [8,9], where configuration interaction mechanism as used not only for description of molecular systems, but also for crystals with hydrogen bonds. Further on we use this fact, putting w'_1 and $w_1 \rightarrow \infty$. In this case at finite values of the parameter $\delta = (w' - w)/2$ it is easy to see that the eigenvalues of the transfer - matrix (7) are the following:

$$\begin{aligned} \lambda_1 &= \frac{1}{2} (\gamma_1 + \gamma_2 + 1) + \frac{1}{2} \sqrt{(\gamma_1 + \gamma_2 - 1)^2 + 4\eta^2} & \lambda_3 &= \gamma_1 - \gamma_2 \\ \lambda_2 &= \frac{1}{2} (\gamma_1 + \gamma_2 + 1) - \frac{1}{2} \sqrt{(\gamma_1 + \gamma_2 - 1)^2 + 4\eta^2} & \lambda_4 &= 1 \end{aligned}$$

where

$$\gamma_1 = e^{-\beta(\varepsilon_1-\varepsilon)} \quad \gamma_2 = e^{-\beta(\varepsilon_2-\varepsilon)} \quad \eta = 2e^{-\beta(\frac{w'+w}{2}-\varepsilon)}$$

Correspondingly, we obtain a configurational contribution to the partition function of the system:

$$Z_m^S = \frac{1}{4} (\lambda_1^m + \lambda_2^m) (\nu_A^+ \nu_B^+ + \rho_A^+ \rho_B^+) + \frac{1}{4} (\lambda_1^m - \lambda_2^m) \left[\frac{1}{\sqrt{\varphi^2 + 1}} (\nu_A^+ \rho_B^+ + \nu_B^+ \rho_A^+) - \frac{\varphi}{\sqrt{\varphi^2 + 1}} (\nu_A^+ \nu_B^+ + \rho_A^+ \rho_B^+) \right] + \frac{(\gamma_1 - \gamma_2)^m}{2} \rho_A^- \rho_B^- - \frac{1}{2} \nu_A^- \nu_B^- \quad (8)$$

here notations are introduced ($\varphi = \frac{\gamma_1 + \gamma_2 - 1}{2\eta}$):

$$\begin{aligned} \nu_A^\pm &= e^{-\beta(\alpha_A - \varepsilon + \delta)} \pm e^{-\beta(\alpha'_A - \varepsilon - \delta)} & \nu_B^\pm &= e^{-\beta(\alpha_B - \varepsilon + \delta)} \pm e^{-\beta(\alpha'_B - \varepsilon - \delta)} \\ \rho_A^\pm &= e^{-\beta(\mu_A^1 - \varepsilon)} \pm e^{-\beta(\mu_A^2 - \varepsilon)} & \rho_B^\pm &= e^{-\beta(\mu_B^1 - \varepsilon)} \pm e^{-\beta(\mu_B^2 - \varepsilon)} \end{aligned}$$

We calculate the full partition function of system using the expressions (4) and (5) with the help of the cumulant expansion of a statistical mean value $\langle e^{-\beta \hat{H}_m^L} \rangle_S$.

Let's introduce a notation $\lambda = -\frac{\beta a^2 (Ze)^2}{c^3}$ ($\beta = 1/kT$); then $\langle e^{-\beta \hat{U}_m} \rangle_S = \langle e^{-\lambda \hat{R}_m} \rangle_S$, where

$$\hat{R}_m = \sum_{l, l'=1}^{m+1} \frac{(\hat{X}_l^{11} - \hat{X}_l^{44})(\hat{X}_{l'}^{11} - \hat{X}_{l'}^{44})}{|l - l'|^3} \quad (l \neq l') \quad (9)$$

We will take into account a small values of λ parameter that corresponds to high - temperature expansion. Then, when the terms up to the second order are taken into account, we obtain the following expression for free energy:

$$F(m) = \varepsilon(m+2) - \frac{1}{\beta} \left[\ln \left(Sp \left[e^{-\beta \hat{H}_m^S} \right] \right) - \lambda \langle \hat{R}_m \rangle_S + \frac{\lambda^2}{2} \left[\langle (\hat{R}_m)^2 \rangle_S - \langle \hat{R}_m \rangle_S^2 \right] \right] \quad (10)$$

where mean value $\langle \hat{R}_m \rangle_S$ and dispersion $\langle (\hat{R}_m)^2 \rangle_S - \langle \hat{R}_m \rangle_S^2$ can be calculated using the relation (9).

5. Averages.

We demonstrate the scheme of calculating of $\langle \hat{X}_{i_1}^{p_1 p_1} \dots \hat{X}_{i_n}^{p_n p_n} \rangle_S$ averages appearing at this stage on the example of pair correlation function $\langle \hat{X}_l^{rr} \hat{X}_{l'}^{ss} \rangle_S$.

Using (6) we have

$$\langle \hat{X}_l^{rr} \hat{X}_{l'}^{ss} \rangle_S = \gamma \sum_{n_1, n_2, \dots, n_{m+1}} \delta_{r n_l} \delta_{s n_{l'}} e^{-\beta A(n_1)} e^{-\beta B^{n_1 n_2}} e^{-\beta B^{n_2 n_3}} \dots \dots e^{-\beta B^{n_m n_{m+1}}} e^{-\beta D(n_{m+1})}, \text{ where } \gamma = e^{-\beta(m+2)\varepsilon} / Sp \left[e^{-\beta \hat{H}_m^S} \right] \quad (11)$$

Using a notation $V^{pq} = e^{-\beta B^{pq}}$ for transfer - matrix we obtain from (11) a following four alternatives ($l' > l$):

Variant I ($1 < l < l' < m+1$)

$$\langle \hat{X}_l^{pp} \hat{X}_{l'}^{qq} \rangle_S = \gamma \sum_{n_1, n_{m+1}} e^{-\beta A(n_1)} \langle n_1 | \hat{V}^{l-1} | p \rangle \langle p | \hat{V}^{l'-l} | q \rangle \times \langle q | \hat{V}^{m-l'+1} | n_{m+1} \rangle e^{-\beta D(n_{m+1})}$$

Variant II ($1 < l < m+1$ and $l = m+1$)

$$\langle \hat{X}_l^{pp} \hat{X}_{l'}^{qq} \rangle_S = \gamma \sum_{n_1} e^{-\beta A(n_1)} \langle n_1 | \hat{V}^{l-1} | p \rangle \langle p | \hat{V}^{m-l+1} | q \rangle e^{-\beta D(q)}$$

Variant III ($l = 1$ and $1 < l' < m+1$)

$$\langle \hat{X}_l^{pp} \hat{X}_{l'}^{qq} \rangle_S = \gamma \sum_{n_{m+1}} e^{-\beta A(p)} \langle p | \hat{V}^{l'-1} | q \rangle \langle q | \hat{V}^{m-l'+1} | n_{m+1} \rangle e^{-\beta D(n_{m+1})}$$

Variant IV ($l = 1$ and $l' = m+1$)

$$\langle \hat{X}_l^{pp} \hat{X}_{l'}^{qq} \rangle_S = \gamma e^{-\beta A(p)} \langle p | \hat{V}^m | q \rangle e^{-\beta D(q)}.$$

6. Summary

The results presented below are obtained by means of numerical calculations. They show the dependences of free energy $F(m)$ on the length of polymer chain (number of intermediate ionic groups m) for the different boundary conditions at various temperatures.

We have used the values for energies of proton configuration interaction: ε_1 and ε_2 in the range $100 \dots 150 \text{ cm}^{-1}$; w and w' in the range $600 \dots 800 \text{ cm}^{-1}$ ($Ze = 1/4e$). These values are characteristic for the systems [8,9] with hydrogen bonds.

The parameters a and c we took from structural data [7] ($a = 0.5 \text{ \AA}$ and $c = 6.064 \text{ \AA}$). These distances are specific of hydrogen-bonded crystalline compounds with uranile ($\lambda_{T=298K} = -0,08$). The second order term in cumulant expansion (5) gives a contribution no greater than 25-30 % of the linear one. The main results can be summarized as follows:

1. In the context of accepted approach for the proposed model we observe the effect of linear dependence of the chain free energy on number of links at increasing of m . In this case the free energy per one ionic group goes into saturation. Taking into account the long - range interaction do not cause essential changes. The one exception is shown in the Fig. 3(b) that corresponds to lower temperature. This is a result of using of high - temperature expansion approximation at the consideration of the long - range interaction.
2. We can elucidate the role of deviation of the $F(m)$ dependence from the linear one by constructing corresponding dependences for derivative $\partial F/\partial m = \mu$. This quantity plays the role of chemical potential of ionic group UO_2^{2+} in the polymer chain. The equilibrium state of chain in the surrounding medium (electrolytic solution) can be determined by the condition $\mu = \tilde{\mu}$, where $\tilde{\mu}$ is chemical potential of ionic group in surrounding medium. At $\mu < \tilde{\mu}$ preferable is the association of the ionic groups into chains. Whereas at $\mu > \tilde{\mu}$ the state with ionic group in solution is more stable.
3. As it is evident from graphs in Fig. 4, we can separate three regions (I,II,III) of possible values of chemical potential $\tilde{\mu}$. It corresponds to essentially different behaviour of investigated system. In the region I ($\tilde{\mu} > \mu$) the formation of chain with arbitrary length takes place. In the region III ($\mu > \tilde{\mu}$) a chain falls to pieces. Of special interest is a case when $\tilde{\mu}$ is situated in area II. The chain is unstable for decreasing dependence $\mu(m)$ at $m < m^*$ (see Figs. 4(a), 4(b)), where m^* is defined by condition $\mu(m^*) = \tilde{\mu}(m^*)$. Whereas, at $m > m^*$ the creation of chains with a large number of links leads to more stable states. Here m^* plays a role of lowest critical size of chain. When μ is increasing with m (Fig. 4(c)), the states with $m < m^*$ are stable. In this case short chains are preferable. Nonmonotonic dependence of $\mu(m)$ (Fig. 4(b)) can lead to existence of chains with some definite length which can be obtained from condition of minimal value of $\mu(m)$. Such a behaviour takes place when $\tilde{\mu}$ is situated in region II.
4. The graphs represented in Fig. 3 and Fig. 4 correspond to complexes with different proton configurations at their ends. As it is evident from the beforesaid, the chains stability depend critically on the boundary conditions. The realisation of the certain boundary proton configurations has a statistical character. That is why the more consistent description of this effect should use a great

canonical ensemble at the description of proton subsystem. It gives a possibility of closer examination of the surrounding medium role in the uranile polymer complex formation.

7. Acknowledgement

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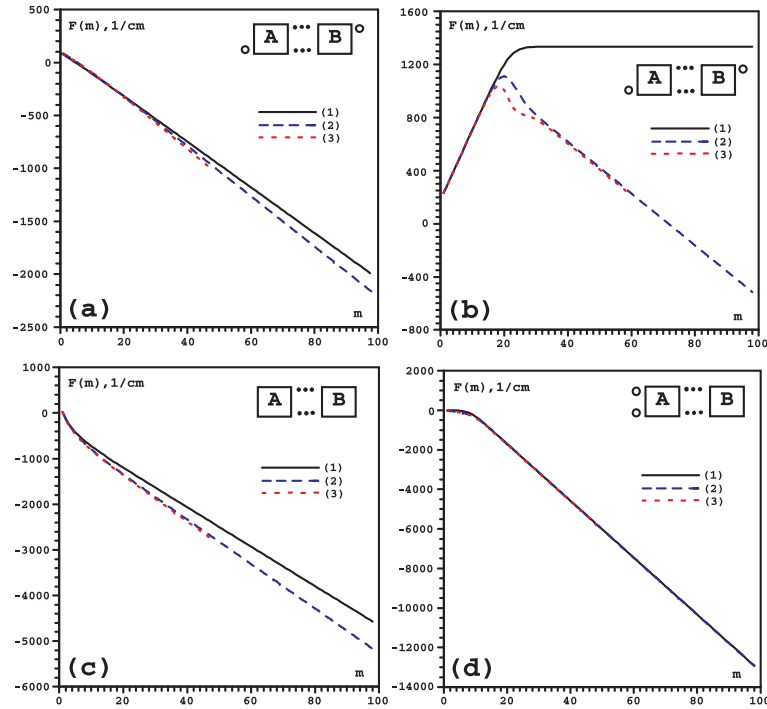


Figure 3. Free energy $F(m)$ of polymer chain as a function of number of ionic groups m with an account for: (1) – the short-range configuration interaction only, (2) and (3) – the short - range interaction and the long - range one in the first and second orders of cumulant expansion respectively. Temperature and energies of proton configuration ($\varepsilon = 0$): (a) – $T = 298K$, $\varepsilon_1 = \varepsilon_2 = 125cm^{-1}$, $w' = w = 800cm^{-1}$ ($\alpha_A = \alpha_B = w$, $\mu_A^1 = \mu_B^1 = \varepsilon_1$, $\mu_A^2 = \mu_B^2 = \varepsilon_2$, $\alpha'_A = \alpha'_B = w'$); (b) – $T = 150K$, $\varepsilon_1 = \varepsilon_2 = 125cm^{-1}$, $w' = w = 800cm^{-1}$ ($\alpha_A = \alpha_B = w$, $\mu_A^1 = \mu_B^1 = \varepsilon_1$, $\mu_A^2 = \mu_B^2 = \varepsilon_2$, $\alpha'_A = \alpha'_B = w'$); (c) – $T = 298K$, $\varepsilon_1 = \varepsilon_2 = 125cm^{-1}$, $w' = 200cm^{-1}$, $w = 800cm^{-1}$ ($\alpha_A = \alpha_B = \varepsilon$, $\mu_A^1 = \mu_A^2 = \mu_B^1 = \mu_B^2 = w'$, $\alpha'_A = \alpha'_B = \infty$); (d) – $T = 298K$, $\varepsilon_1 = \varepsilon_2 = 0cm^{-1}$, $w' = w = 800cm^{-1}$ ($\alpha_A = \alpha'_B = \infty$, $\mu_A^1 = \mu_A^2 = w$, $\mu_B^1 = \mu_B^2 = w'$, $\alpha'_A = \alpha_B = \varepsilon$);

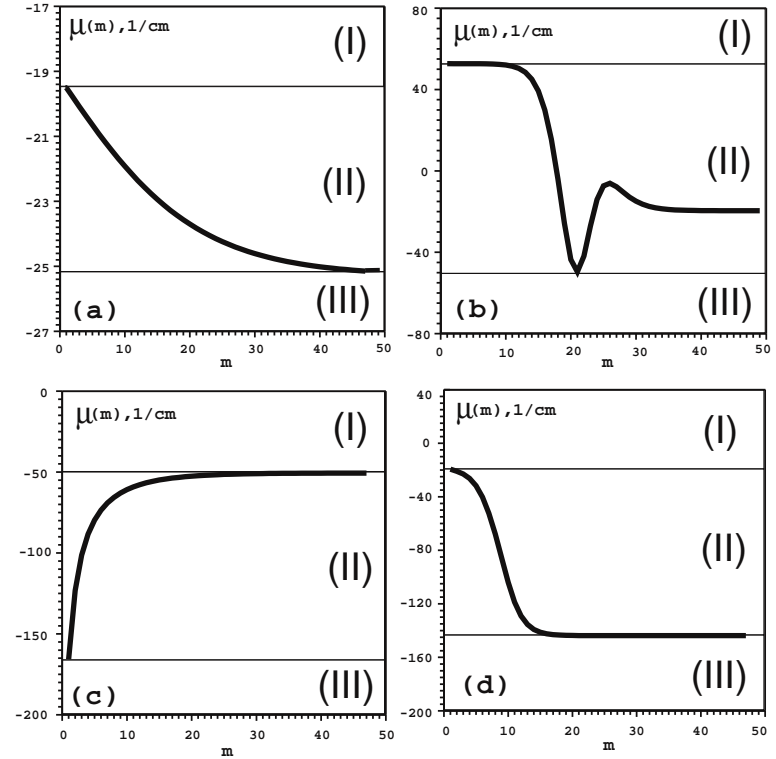


Figure 4. The chemical potential $\mu(m)$ as a function of number of ionic group m calculated allowing for the short - range and long - range interaction between protons (Temperature and energies of proton configurations are the same as in Figure 3 in the cases (a)-(d)).

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