§22. The Effects of Periodicity on Multichain Coulomb Polymers (Polyampholytes)

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Electrically charged polymers are widely found in daily products and live organisms like DNA and RNA. In this study, an emphasis was placed on the effects of boundary conditions on the multichain polymers of random sequences.

We adopted periodic boundary conditions and the Ewald's PME method [1] to take infinite sums over the true and image charges for the long-range Coulomb force. The Coulomb force in the isolated system was calculated by

$$\mathbf{F}_{LR}^{(P)}(\mathbf{r}_i) = \sum_{j=1}^{N} \sum_{\mathbf{n}\in\mathbf{Z}}{}' Z_i Z_j e^2 \tilde{\mathbf{R}}_{ij} / \epsilon |\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|^2.$$

where $\tilde{\mathbf{R}}$ is a unit vector of $\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L$, with L the side length of periodicity, and $\mathbf{n}$ a three-dimensional integer vector. Because of the long-range nature of the Coulomb force, one has to adopt the following method to avoid practical difficulties of taking *infinite sums* over $\mathbf{n}$. Under the Ewald method, the Coulomb force is represented by

$$\mathbf{F}_{LR}^{(P)}(\mathbf{r}) = -q_i \nabla \Phi(\mathbf{r}) + \mathbf{F}^{(r)}(\mathbf{r}),$$

where the first term on RHS is the Fourier transform of the electrostatic potential of the form $\tilde{\Phi}(\mathbf{k}) = (4\pi/k^2)\exp(-k^2/4\alpha^2)\tilde{\rho}(\mathbf{k})$, and the second term is given by

$$\mathbf{F}^{(r)}(\mathbf{r}) = q_i \sum_{j=1}^{N} \sum_{\mathbf{n}\in\mathbf{Z}}{}' \left(\frac{2\alpha}{\sqrt{\pi}} \exp(-\alpha^2 R_{ij}^2)/R_{ij} + \mathrm{erfc}(\alpha R_{ij})/R_{ij}^2 \right) \hat{\mathbf{R}}_{ij}.$$

In Figure 1, a comparison of different boundary conditions is made, where the word "Isolated" corresponds to the run with a reflecting boundary condition, and "Periodic" to those with periodic boundary conditions. Both kind of gyration radii, $R_{g,sys}$ (of the total system) and R_{g1} (of each chain) are smaller in the periodic system at low temperature, indicating an occurrence of more compression in the continuous medium. However, at high temperature the chains are more homogeneously distributed in the periodic system; the chains tend to stay away from the boundary wall in the isolated system.

Detailed MD simulation results of multichain polyampholytes, including the effect of charge sequences, stiffness, the molecular weight and the number of the chains, the formation and stability of the globular state, under the wall boundary condition are described in a separate publication [3].

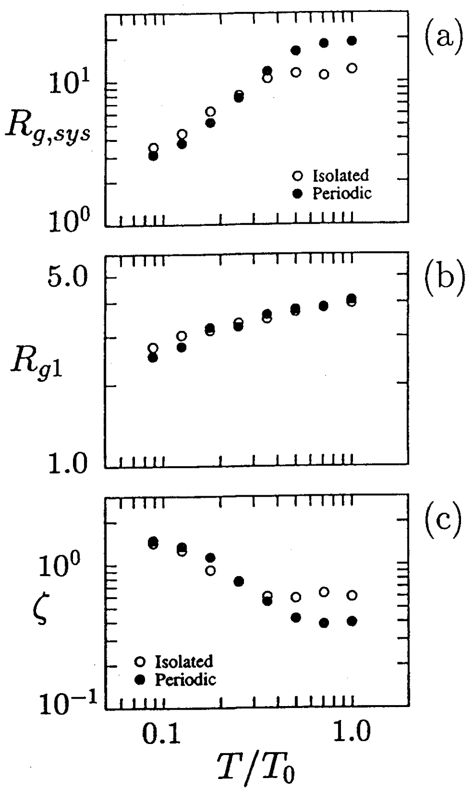

Fig.1 The effects of different boundary conditions are seen between the wall-bound and periodic systems.

References:
1. M.Deserno and C.Holm, *J.Chem.Phys.*, 109, 7678 (1998).
2. M.Tanaka, A.Yu Grosberg, and T.Tanaka, pp.599-606 *Slow Dynamics in Complex Systemsi*, edited by M.Tokuyama and I.Oppenheim, AIP CP469 (1999).
3. M.Tanaka, A.Yu Grosberg, and T.Tanaka, *Phys.Rev.*, E 56, 5798 (1997).