A New Field Theory of Polymers

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高分子達は、粗視化すると、相互侵入可能な糸鞠（いとまり）集団と見なすことができる。この＜ソフトコロイド描像＞が、ここ数年リバイバルしている。その理由の一つとしては、近年関心の高い「コロイド・高分子の混合系」での有効性が挙げられる。そこで、本描像の中心量である重心密度場をモノマー濃度とは別変数として導入する、新しい場の理論的定式化法を開発した。得られた結果は、最近提唱されているブロック共重合体系の Uneyama-Doi 密度汎関数法 (Macromolecules **38** (2005) 196, 5817) への拡張が可能な汎関数積分形式となった。さらに本形式の多変数性を利用すると、**Flory-Huggins** 型自由エネルギーの最小密度がインプットされた新しい自己無撞着場方程式が導かれた。(***H.F.* J. Phys.: Condens. Mattter 17 (2005), L241.**)

1 Pagonabarraga–Cates free energy

Among the various density functionals of free energy for polymer solutions, I would like to describe a model functional $\mathcal{F}_{\rm PC}$ proposed by Pagonabarraga and Cates (PC) [1]. The PC's functional reflects the enlightening picture that polymers can be described mesoscopically by soft interpenetrating spheres, and thereby replaces all of entropic contributions by only the translational entropy of polymers as soft colloids: $-k_B^{-1}S\{c\} = \int d\mathbf{r} c(\mathbf{r}) \ln c(\mathbf{r}) - c(\mathbf{r})$ where $k_BT = 1$ and $c(\mathbf{r})$ is a polymer density. The PC free energy $\mathcal{F}_{\rm PC}$ then reads

$$\mathcal{F}_{\rm PC}\{\rho, c\} = U\{\rho\} - k_B^{-1}S\{c\} \qquad c_q = (Ns_0(q))^{-1/2}\,\rho_q \tag{1}$$

where $U\{\rho\}$ is a interaction energy functional, the Fourier-transformed quantity c_q is postulated to have the above relation with the monomer density ρ_q via the structure factor $s_0(q)$ of Gaussian chains. Noticeably, the PC functional is reduced to the Lifshitz–de Gennes form (with b the monomer length): $\mathcal{F}_{\rm LdG}\{\rho\} = U\{\rho\} - k_B^{-1}S\{\rho/N\} + b^2|\nabla\rho(\mathbf{r})|^2/\{36\rho(\mathbf{r})\}$ in the small–wave vector approximation $c(\mathbf{r}) \approx (1/N - b^2\nabla^2/36)\,\rho(\mathbf{r})$.

2 Outline

The PC's functional, $\mathcal{F}_{\rm PC}$ given by eq. (1), sheds light on how to develop a functional–integral formulation of soft polymeric colloids. The key procedures we have taken [2] are twofold: The

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first is to introduce a polymer concentration c in addition to the monomer density ρ. The second is to truncate the expansion of the intra–chain partition function at the first order. Consequently, we have obtained the functional integral, given below, whose exponent is similar to the PC's functional [1]. The differences from the PC's are that the c–ρ relation is represented not by the structure factor of Gaussian chains but by the form factor $\omega_{\rm cm}$ between the center of mass and monomer, and that the anomalous term is added. Furthermore, the new functional–integral representation not only has reproduced the classical Flory-Krigbaum effective potential between polymers, but also has provided an efficient SCF equation which preincludes the minimum of the Flory-Huggins functional as input.

3 Detailed Formulations of the functional integral [2]

To suppress an anomalous term of density functional, it is relevant to add the polymer order parameter $\psi(\mathbf{r})$ via the relation $\psi^2 = \rho$, eventually leading to

$$\Xi = \int D\rho\, Dc\, D\psi\, \det\Omega^{1/2} \prod_{\{\mathbf{r}\}} \delta(\psi^2 - \rho)\, \delta(\rho - \Omega c) \exp\left[-\mathcal{F}_{\rm PC}\{\rho, c\} + \mu \int d\mathbf{r}\, c(\mathbf{r}) \right]. \qquad (2)$$

The second Dirac delta functional implies that c and ρ are related each other through the operator Ω similarly to the PC's relation (1). The Fourier transform Ω_q, however, is not identical to eq. (1) but is proportional to the form factor, $\omega_{\rm cm}$, between the center of mass and monomer [3]:

$$\Omega_q = N\omega_{\rm cm}(x) = \frac{N\sqrt{\pi}}{x} e^{-x^2/12}\, {\rm erf}\left(\frac{x}{2}\right) \approx N e^{-x^2/6} \qquad x = qR_g, \qquad (3)$$

where R_g is the unperturbed radius-of-gyration of a chain given by $R_g^2 = Nb^2/6$ and erf denotes the error function. In spite of the different c–ρ relation from that of the PC's, it follows similarly that $\mathcal{F}_{\rm PC}$ reduces to $\mathcal{F}_{\rm LdG}$ in the small–wave vector expansion, $\Omega_q^{-1} \approx 1/N + b^2q^2/36 (\approx N^{-1}e^{q^2R_g^2/6})$.

Equation (2) is one of the main results and is extended straightforwardly to validate the formulations of blockcopolymers [4].

References

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