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Kyoto University
A New Field Theory of Polymers

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1 Pagonabarraga-Cates free energy

Among the various density functionals of free energy for polymer solutions, I would like to describe a model functional \( \mathcal{F}_{\text{PC}} \) 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: 

\[ -k_B T \frac{1}{2} S\{c\} = \int dr c(r) \ln c(r) - c(r) \]

where \( k_B T = 1 \) and \( c(r) \) is a polymer density. The PC free energy \( \mathcal{F}_{\text{PC}} \) then reads

\[ \mathcal{F}_{\text{PC}} (\rho, c) = U(\rho) - k_B T \frac{1}{2} S\{c\} \quad c_q = (N s_0(q))^{-1/2} \rho_q \]  

(1)

where \( U(\rho) \) is an interaction energy functional, the Fourier-transformed quantity \( c_q \) is postulated to have the above relation with the monomer density \( \rho_q \) 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):

\[ \mathcal{F}_{\text{LdG}} (\rho) = U(\rho) - k_B T \frac{1}{2} S\{\rho/N\} + b^2 |\nabla \rho(r)|^2 / \{36 \rho(r)\} \]

in the small–wave vector approximation \( c(r) \approx (1/N - b^2 \nabla^2 / 36) \rho(r) \).

2 Outline

The PC's functional, \( \mathcal{F}_{\text{PC}} \) 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 $\rho$. 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 $c-\rho$ relation is represented not by the structure factor of Gaussian chains but by the form factor $\omega_{cm}$ 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 $\psi(r)$ via the relation $\psi^2 = \rho$, eventually leading to

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

(2)

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

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

(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 $c-\rho$ relation from that of the PC’s, it follows similarly that $\mathcal{F}_{\text{PC}}$ reduces to $\mathcal{F}_{\text{LdG}}$ in the small-wave vector expansion, $\Omega_q^{-1} \approx 1/N + b^2 q^2/36(\approx N^{-1} e^{q^2 R_g^2/6})$.

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

References


