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LETTER TO THE EDITOR

A functional-integral formulation for polymer colloids: Pagonabarraga–Cates free energy revisited

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Abstract

We have formulated a new functional-integral representation with respect to both polymer and monomer densities, along the lines of the current picture treating polymers as soft colloids. Comparison between the resulting form and a model free energy functional of Pagonabarraga and Cates (PC 2001 *Europhys. Lett.* **55** 348) indicates that the PC relation between monomer and polymer concentrations is to be modified, and that further insertion of the order parameter defined by the square of monomer density is indispensable for regularizing a divergent term absent in the PC functional. Moreover, the saddle-point approximation to our functional integral leads to a self-consistent equation which efficiently preincludes the minimum of the Flory–Huggins-type local free energy as input.

1. Introduction

Since the seminal work of Edwards [1], functional-integral formulations have played a central role in developing mesoscopic theories of polymer melts and solutions [2–4]. The field-theoretic approaches have usually started with taking the collective variables of both monomer density $\rho(\mathbf{r})$ and its conjugate potential field $\varphi(\mathbf{r})$. Correspondingly, previous coarse-grained theories are classified into two types, potential and density forms, eliminating the other field in some ways [3, 5].

The former is readily available, since we have no difficulty in Gaussian-integrating out the ρ-variable with the potential φ retained [2]. The saddle point approximation to the potential form, known as self-consistent field (SCF) theory, has been remarkably successful in explaining a variety of mesostructures experimentally observed in block copolymers and polymer alloys [2, 6]. More recently, the SCF equation has been devised for discovering novel ordered phases [2, 7] and for considering fluctuations [2, 8].

In formulating the latter density forms, on the other hand, approximations have been involved. First, eliminating the φ-field itself requires the steepest descent approximation of the φ-integral at a given density. Moreover, the solution of the saddle point equation with ρ fixed has been expressed in perturbative forms; otherwise the full mean field theory (or the non-perturbative saddle point approximation both to φ and ρ fields) is formally identical to the above SCF theory [3, 5][1].

To derive the approximate density functional, much use has been made of the cumulant expansion [4, 9]. The resulting forms are hence represented by the vertex functions, similarly to the effective action in the standard field theory [10]. The perturbative but illuminating functionals have offered superiority both in exploring new mesostructures [11] and in taking systematic account of composition fluctuations [12].

An alternative expansion has also been proposed by Tang and Freed [13], and has since been applied to liquid crystals [14] as well as semiflexible polymers [15]. The method takes the gradient expansion of the potential field about the centre of mass (c.m.) of polymer chains, which yields [13] the Lifshitz–de Gennes (LdG) functional [17],

$$\mathcal{F}_{\mathrm{LdG}}\{\rho\} = U\{\rho\} - k_{\mathrm{B}}^{-1}S\{\rho/N\} + \frac{\alpha b^2}{4}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} = \mathcal{F}_{\mathrm{FH}}\{\rho\} + \frac{\alpha b^2}{4}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}, \tag{1}$$

without collecting power series in the density deviation from the smeared value $\overline{\rho}$ like the cumulant expansion method [16]. In equation (1), the symbols denote the following: the constant N is the polymerization degree, the functionals of interaction energy U and entropic contribution $-k_{\mathrm{B}}^{-1}S$ in the unit of thermal energy $k_{\mathrm{B}}T$ are given respectively as $U\{m\} = (v/2)\,m\cdot m + m\cdot J$ and $-k_{\mathrm{B}}^{-1}S\{m\} = \int \mathrm{d}\mathbf{r}\, m(\mathbf{r})\ln m(\mathbf{r}) - m(\mathbf{r})$ (where we have introduced the notation $f\cdot g = \int \mathrm{d}\mathbf{r}\, f(\mathbf{r})\, g(\mathbf{r})$, excluded volume v and an external field J), the constant α is equal to $1/6$ (Lifshitz) or $1/9$ (de Gennes) [17], b is the monomer length of polymers and $\mathcal{F}_{\mathrm{FH}} = U - k_{\mathrm{B}}^{-1}S$ corresponds to the Flory–Huggins-type functional.

When we set $\psi^2 = \rho$, ignore the logarithmic entropy term, and add the chemical potential μ of the polymer, the stationary condition $\delta\mathcal{F}_{\mathrm{LdG}}/\delta\rho = \mu/N$ of the above LdG functional (1) leads to [18]

$$\alpha b^2\nabla^2\psi(\mathbf{r}) = [v\psi^2(\mathbf{r}) - \mu/N + J(\mathbf{r})]\,\psi(\mathbf{r}). \tag{2}$$

Equation (2) agrees with the SCF equation in the ground state dominance approximation and has been useful particularly in studying adsorptions of long polymers or polyelectrolytes [18]; in the last case, J in equation (2) denotes the electrostatic potential produced by ions. Worthy of special mention in recent years is the successful extension of the LdG approach, or the set of equations (1) and (2), to block copolymers [19].

Among the various density forms, this letter will focus on a model functional $\mathcal{F}_{\mathrm{PC}}$ proposed by Pagonabarraga and Cates (PC) [20]. The PC functional reflects the enlightening picture that polymers can be described mesoscopically by soft interpenetrating spheres [21], and thereby replaces all of entropic contributions by only the translational entropy of polymers as soft colloids [20]:

$$\mathcal{F}_{\mathrm{PC}}\{\rho, c\} = U\{\rho\} - k_{\mathrm{B}}^{-1}S\{c\} \qquad c_q = (Ns_0(q))^{-1/2}\,\rho_q \tag{3}$$

where $c(\mathbf{r})$ is a polymer density and 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. While too much simplicity of the PC form (3) contrasts with the density functional theory in a narrow sense [22] (the so-called DFT in liquid state physics [23]), the PC functional is noticeably reduced to the LdG form (1) in the small-wavevector approximation $c(\mathbf{r}) \approx (1/N - b^2\nabla^2/36)\,\rho(\mathbf{r})$, namely $\mathcal{F}_{\mathrm{PC}} \approx U\{\rho\} - k_{\mathrm{B}}^{-1}S\{\rho/N - b^2\nabla^2\rho/36\} = \mathcal{F}_{\mathrm{LdG}}\{\rho\}$, and hence is of practical use.

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[1] However, the computational advantage of the density form has been suggested in [5].

2. Strategy

Motivated by the PC proposal [20], we will add a new variable, polymer density $c(\mathbf{r})$, into the conventional functional integral of monomer concentration $\rho(\mathbf{r})$ (see equation (19) below) and will evaluate the functional integrals of potential fields conjugate to both polymer and monomer densities. A noteworthy step is the non-perturbative saddle-point approximation of the potential field $h(\mathbf{r})$ coupled to the present polymer concentration $c(\mathbf{r})$ (see ($\mathcal{D}3$) below); for the prescription yields the logarithmic entropy term, $-k_{\mathrm{B}}^{-1}S\{c\}$, as well as the density functional-integral form of simple fluids [24].

3. Results

Before presenting more details of the formulations, we would like to state the benefits which the above redoubling of density variables brings as follows. ($\mathcal{R}1$) With the help of the polymer concentration, a modified PC functional is verified conditionally. ($\mathcal{R}2$) Minimal account of chain connectivity, also taken in the first result, reproduces the Flory–Krigbaum potential [25] for the effective interaction between polymers. ($\mathcal{R}3$) Our formalism provides an efficient SCF equation suitable for exploring new assemblies.

($\mathcal{R}1$) *Functional integral forms*. From the evaluations which will be detailed in ($\mathcal{D}3$) and ($\mathcal{D}4$), we get the grand partition function Ξ expressed by functional integrals with respect to the monomer and polymer densities, ρ and c:

$$\Xi = \int \mathrm{D}\rho\, \mathrm{D}c \prod_{\{\mathbf{r}\}} \delta[\rho(\mathbf{r}) - \Omega c(\mathbf{r})] \exp\left[-\mathcal{F}_{\mathrm{PC}}\{\rho, c\} + \mathcal{A}\{c\} + \mu \int \mathrm{d}\mathbf{r}\, c(\mathbf{r})\right]. \tag{4}$$

The above Dirac delta functional implies that c and ρ are related to each other through the operator Ω similarly to the PC relation (3). The Fourier transform Ω_q, however, is not identical to equation (3) but is proportional to the form factor, $\omega_{\mathrm{c.m.}}$, between c.m. and monomer [26]:

$$\Omega_q = N\omega_{\mathrm{c.m.}}(x) = \frac{N\sqrt{\pi}}{x}\,\mathrm{e}^{-x^2/12}\,\mathrm{erf}\left(\frac{x}{2}\right) \approx N\mathrm{e}^{-x^2/6} \qquad x = qR_{\mathrm{g}}, \tag{5}$$

where R_{g} is the unperturbed radius of gyration of a chain given by $R_{\mathrm{g}}^2 = Nb^2/6$ and erf denotes the error function. In spite of the different c–ρ relation from that of the PC, it follows similarly that

$$\mathcal{F}_{\mathrm{PC}}\{\rho, c = \Omega^{-1}\rho\} \approx \mathcal{F}_{\mathrm{PC}}\left\{\rho, c = (1/N - b^2\nabla^2/36)\rho\right\} = \mathcal{F}_{\mathrm{LdG}}\{\rho\} \tag{6}$$

in the small-wavevector expansion, $\Omega_q^{-1} \approx 1/N + b^2q^2/36(\approx N^{-1}\,\mathrm{e}^{q^2R_{\mathrm{g}}^2/6})$.

The PC proposal thus far receives only a modification of the operator Ω. More crucially, equation (4) has the exponent $\mathcal{A}\{c\}$ given by

$$\exp(\mathcal{A}\{c\}) = \prod_{\{\mathbf{r}\}} \sqrt{\frac{2\pi}{c(\mathbf{r})}} = \lim_{\epsilon\to 0} \exp\left(\frac{1}{2\epsilon}\int \mathrm{d}\mathbf{r}\, \ln\frac{2\pi}{c(\mathbf{r})}\right). \tag{7}$$

The last representation manifests the divergent behaviour to be regularized somehow, and the presence of this density functional term is what we have meant by the above 'conditional verification'.

To suppress the anomaly (7), it is relevant to add the polymer order parameter $\psi(\mathbf{r})$ via the relation $\psi^2 = \rho$. As shown in ($\mathcal{D}5$), the ψ-integral transforms equation (4) to

$$\Xi = \int \mathrm{D}\rho\, \mathrm{D}c\, \mathrm{D}\psi\, \det\Omega^{1/2} \prod_{\{\mathbf{r}\}} \delta(\psi^2 - \rho)\delta(\rho - \Omega c) \exp\left[-\mathcal{F}_{\mathrm{PC}} + \mu\int \mathrm{d}\mathbf{r}\, c(\mathbf{r})\right], \tag{8}$$

where the divergent term $\mathcal{A}\{c\}$ disappears but the determinant of the operator $\Omega^{1/2}$ emerges instead. The functional-integral form (8) is the main result of this letter.

($\mathcal{R}2$) *Effective interaction.* One of the central issues in regarding polymers as soft colloids is to evaluate the effective interaction V_{eff} between polymers, and much progress in this direction has been made [25, 27]. We then would like to see the correspondence between previous results and ours, expressing the interaction energy functional $U\{\rho\}$ by polymer density c:

$$U\{\rho_q \approx N\, c_q\, \mathrm{e}^{-q^2R_{\mathrm{g}}^2/6}\} = \frac{N^2 v}{2}\sum_{\mathbf{q}} c_q^2 \exp\left(-\frac{q^2R_{\mathrm{g}}^2}{3}\right)$$
$$= \frac{N^2 v}{2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\left(\frac{3}{4\pi R_{\mathrm{g}}^2}\right)^{3/2} \exp\left(-\frac{3(\mathbf{r}-\mathbf{r}')^2}{4R_{\mathrm{g}}^2}\right)c(\mathbf{r})c(\mathbf{r}'). \tag{9}$$

From this, one finds that $V_{\mathrm{eff}}(\mathbf{r}) = N^2 v(3/4\pi R_{\mathrm{g}}^2)^{3/2}\exp(-3\mathbf{r}^2/4R_{\mathrm{g}}^2)$ in agreement with the Gaussian effective interaction proposed by Flory and Krigbaum [25]. In other words, our first approximation of chain correlations reproduces the primitive result correctly.

($\mathcal{R}3$) *A new SCF equation.* Lastly, we wish to point out that not only does the PC functional $\mathcal{F}_{\mathrm{PC}}$ encompass the LdG one $\mathcal{F}_{\mathrm{LdG}}$ as described in equation (6), but also our functional integral (8) goes beyond the LdG approach where equation (2) has been derived from equation (1) somewhat heuristically [18, 19].

It is readily found that the saddle point approximation to the ψ-integral in equation (8) verifies the SCF equation (2) and forms the basis of the LdG approach as follows: let us again set $\rho = \psi^2$ and neglect the logarithmic entropy term to get $\mathcal{F}_{\mathrm{PC}}\{\rho = \psi^2, c = \Omega^{-1}\psi^2\} \approx U\{\psi^2\} + (b^2/9)\int \mathrm{d}\mathbf{r}\,|\nabla\psi(\mathbf{r})|^2$. Using the expression for $\mathcal{F}_{\mathrm{PC}}\{\psi\}$, the saddle-point approximation of the ψ-integral, $\delta\mathcal{F}_{\mathrm{PC}}/\delta\psi = 2\mu\psi$, reads as the present equation (2).

The above derivation, however, makes no use of the multivariable form of equation (8). We then demonstrate below that combination of ψ- and ρ-integrals provides a new SCF equation, starting with the transform of the functional integral (8):

$$\Xi = \int \mathrm{D}\rho\,\mathrm{D}\psi\,\mathrm{D}\kappa\,\det\Omega^{-1/2}$$
$$\times\exp\left[-\mathcal{F}_{\mathrm{FH}}\{\rho\} - \frac{b^2}{9}\int \mathrm{d}\mathbf{r}\,|\nabla\psi|^2 + \mathrm{i}\kappa\cdot(\psi^2-\rho) + \mu\int \mathrm{d}\mathbf{r}\,\frac{\rho}{N}\right]. \tag{10}$$

Here the c-field in equation (8) has been integrated out as

$$\int \mathrm{D}c\,\det\Omega^{1/2}\prod_{\{\mathbf{r}\}}\delta(\rho-\Omega c) = \det\Omega^{1/2}\det\Omega^{-1} = \det\Omega^{-1/2}, \tag{11}$$

due to both the relation $\delta(\rho-\Omega c) = \delta(\Omega c-\rho)$ and the representation $\mathcal{F}_{\mathrm{PC}}\{\rho, c\}+\mu\int \mathrm{d}\mathbf{r}\,c(\mathbf{r}) \approx \mathcal{F}_{\mathrm{FH}}\{\rho\} + (b^2/9)\int \mathrm{d}\mathbf{r}\,|\nabla\psi|^2 + \mu\int \mathrm{d}\mathbf{r}\,\rho(\mathbf{r})/N$, and the delta functional in equation (8), $\prod_{\{\mathbf{r}\}}\delta[\psi^2(\mathbf{r})-\rho(\mathbf{r})]$, has been exponentiated: $\prod_{\{\mathbf{r}\}}\delta[\psi^2(\mathbf{r})-\rho(\mathbf{r})] = \int \mathrm{D}\kappa\,\exp\big(\mathrm{i}\psi^2\cdot\kappa - \mathrm{i}\rho\cdot\kappa\big)$.

To evaluate the ρ-integral in equation (10), we select a trial density ρ_t satisfying the stability condition, $\delta\mathcal{F}_{\mathrm{FH}}/\delta\rho|_{\rho=\rho_t} = \mu/N$, for the local free energy of Flory–Huggins type, and expand the exponent of equation (10) around the trial density ρ_t to get

$$\begin{aligned}&\mathcal{F}_{\mathrm{FH}}\{\rho\} + \mathrm{i}\kappa\cdot\rho \approx \mathcal{F}_{\mathrm{FH}}\{\rho_t\} + \mathrm{i}\kappa\cdot\rho_t + \mathrm{i}\,\kappa\cdot\Delta\rho + \tfrac{1}{2}\int \mathrm{d}\mathbf{r}\,\mathcal{F}_{\mathrm{FH}}^{(2)}\{\rho_t\}\Delta\rho(\mathbf{r})^2\\ &\rho_t(\mathbf{r})/N = \mathrm{e}^{\mu}\exp[-Nv\,\rho_t(\mathbf{r}) - NJ(\mathbf{r})],\end{aligned} \tag{12}$$

where $\Delta\rho = \rho - \rho_t$ and $\mathcal{F}_{\mathrm{FH}}^{(2)}$ denotes the second functional derivative, $\mathcal{F}_{\mathrm{FH}}^{(2)}\{\rho_t\} \equiv \delta^2\mathcal{F}_{\mathrm{FH}}/\delta\rho^2|_{\{\rho_t\}} = v + [N\rho_t(\mathbf{r})]^{-1}$. It is now possible to carry out the Gaussian integration over both $\Delta\rho$- and κ-fields in equation (10), amounting to

$$\Xi = \mathrm{e}^{-\mathcal{F}_{\mathrm{FH}}\{\rho_t\}+\mu\int \mathrm{d}\mathbf{r}\,\rho_t/N}\det\Omega^{-1/2}$$
$$\times\int \mathrm{D}\psi\,\exp\left[-\int \mathrm{d}\mathbf{r}\,\frac{b^2}{9}|\nabla\psi|^2 - \int \mathrm{d}\mathbf{r}\,\frac{1}{2}\mathcal{F}^{(2)}_{\mathrm{FH}}\{\rho_t\}(\psi^2-\rho_t)^2\right]. \qquad (13)$$

The saddle-point condition for the ψ-integral leads to

$$\frac{b^2}{9}\nabla^2\psi(\mathbf{r}) = \mathcal{F}^{(2)}_{\mathrm{FH}}\{\rho_t\}[\psi^2(\mathbf{r})-\rho_t(\mathbf{r})]\psi(\mathbf{r}), \qquad (14)$$

which is our SCF equation. Good correspondence between equations (14) and (2) is seen for $v \neq 0$ and $J = 0$. In this case, the previous equation (2) is reduced to $(b^2/9)\nabla^2\psi = v(\psi^2-\overline{\rho})\psi$ due to $\mu = Nv\overline{\rho}$ with the neglect of the logarithmic entropy term, and then agrees with equation (14) in the approximation $\mathcal{F}^{(2)}_{\mathrm{FH}} \approx v$ and $\rho_t(\mathbf{r}) \approx \overline{\rho}$.

Comparison between equations (2) and (14) reveals at the same time the predominance of our SCF equation (14). To see this, let us drop the Laplacian terms on the left sides of equations (2) and (14) without considering conformational entropy. The local equations give, respectively, the previous solution $\psi_0^2 = \overline{\rho}$ in the above case ($v \neq 0$ and $J = 0$) and $\psi_0^2 = \rho_t$ in ours, implying that the new SCF equation (14) preincludes the minimum of the Flory–Huggins-type free energy through the input density $\rho_t(\mathbf{r})$, in contrast to conventional SCF theories, which search the solutions of inhomogeneous density distribution in the full range, relying solely on the self-consistency.

The above feature of equation (14) should be efficient for discovering new assemblies of polymers, because the detailed modulation of monomer density is not investigated before finding the extent of polymer segregation, or the trial density $\rho_t(\mathbf{r})$, due to attractive interactions and/or external fields.

4. Details

Let us now turn our attention to mathematical manipulations. The following descriptions consist of five steps which are further grouped into three parts. In the first part, we set up the problem by ($\mathcal{D}1$) writing down the configurational integral representations and by ($\mathcal{D}2$) introducing functional integrals of both monomer and polymer concentrations, ρ and c. Next, we will ($\mathcal{D}3$) perform the Gaussian approximation for the integral with respect to the conjugate field of polymer density and will ($\mathcal{D}4$) take a first approximation of intramolecular correlation; consequently, while the former step ($\mathcal{D}3$) provides the exponent of equation (4), the latter ($\mathcal{D}4$) provides the delta functional of equation (4). In the final part ($\mathcal{D}5$), we show that an anomalous density functional given by (7) is suppressed by adding the polymer order parameter ψ.

($\mathcal{D}1$) *Configurational integral representation*. Let us consider a solution of M polymer chains with its volume V. We represent polymers by continuous space curves $\mathbf{R}^i$, where $i = 1, \ldots, M$ indexes the different polymers and s is a contour length variable running from zero to unity. The grand partition function Ξ is expressed by path integrals with the Wiener measure $\widetilde{D}\mathbf{R}^i(s)$ [1]:

$$\Xi = \sum_{M=0}^{\infty}\frac{\mathrm{e}^{\mu M}}{M!}\int\prod_{i=1}^{M}\widetilde{D}\mathbf{R}^i(s)\,\exp(-U\{\hat{\rho}\})$$
$$\widetilde{D}\mathbf{R}^i(s) \equiv D\mathbf{R}^i(s)\exp\left(-\frac{1}{4R_{\mathrm{g}}^2}\int_0^1 \mathrm{d}s\left|\frac{\mathrm{d}\mathbf{R}^i(s)}{\mathrm{d}s}\right|^2\right), \qquad (15)$$

where the interaction energy $U\{\hat{\rho}\} = (v/2)\hat{\rho}\cdot\hat{\rho} + \hat{\rho}\cdot J$ is the functional of microscopic representation for monomer density, $\hat{\rho}(\mathbf{r}) = N\sum_{i=1}^{M}\int_0^1 \mathrm{d}s\,\delta[\mathbf{r}-\mathbf{R}^i(s)]$.

($\mathcal{D}2$) *Introducing two density fields*. As usual, we first constrain the monomer density field $\rho(\mathbf{r})$ to the microscopic one $\hat{\rho}(\mathbf{r})$ by the identity

$$1 = \int \mathrm{D}\rho \prod_{\{\mathbf{r}\}} \delta[\rho(\mathbf{r}) - \hat{\rho}(\mathbf{r})] = \int \mathrm{D}\rho\, \mathrm{D}\varphi \exp[\mathrm{i}(\rho - \hat{\rho}) \cdot \varphi]. \tag{16}$$

Moreover, we wish to introduce a polymer density field $c(\mathbf{r})$ as another integration variable through a microscopic concentration,

$$\hat{c}(\mathbf{r}) = \sum_{i=1}^{M} \delta[\mathbf{r} - \mathbf{R}^i_{\mathrm{c.m.}}]\, \delta\left[\mathbf{R}^i_{\mathrm{c.m.}} - \int_0^1 \mathrm{d}s\, \mathbf{R}^i(s)\right], \tag{17}$$

where $\mathbf{R}^i_{\mathrm{c.m.}}$ denotes the position of the centre of mass (c.m.) of the ith polymer, therefore $\hat{c}(\mathbf{r})$ corresponds to the number density of the c.m. of polymers. As before we equate the polymer density field $c(\mathbf{r})$ with the microscopic quantity $\hat{c}(\mathbf{r})$:

$$1 = \int \mathrm{D}c \prod_{\{\mathbf{r}\}} \delta[c(\mathbf{r}) - \hat{c}(\mathbf{r})] = \int \mathrm{D}c\, \mathrm{D}h \exp\big[\mathrm{i}(c - \hat{c}) \cdot h\big]. \tag{18}$$

Inserting the two identities (16) and (18) into the partition function (15), we have

$$\begin{aligned} \Xi &= \int \mathrm{D}\rho\, \mathrm{D}\varphi\, \mathrm{D}c\, \mathrm{D}h\ \exp(-U\{\rho\} + \mathrm{i}\rho \cdot \varphi + \mathrm{i}c \cdot h + \mathrm{e}^{\mu} Q\{h,\ \varphi\}) \\ Q\{h,\ \varphi\} &= \int \widetilde{D}\mathbf{R}(s) \exp\left(-\mathrm{i}h(\mathbf{R}_{\mathrm{c.m.}}) - \mathrm{i}N \int_0^1 \mathrm{d}s\, \varphi[\mathbf{R}(s)]\right), \end{aligned} \tag{19}$$

which are the starting forms of functional integrals. To be noted in the second line of the above equations, the position vector $\mathbf{R}_{\mathrm{c.m.}}$ of the h-field is dependent on configurations of the continuous curve, $\{\mathbf{R}(s)\}$, via the relation $\mathbf{R}_{\mathrm{c.m.}} = \int_0^1 \mathrm{d}s\, \mathbf{R}(s)$.

($\mathcal{D}3$) *Gaussian approximation to the conjugate field h*. We would like to integrate out the h-field in equation (19) exploiting the saddle-point equation, $\mathrm{i}c(\mathbf{r}) + \mathrm{e}^{\mu}(\delta Q/\delta h)\big|_{\{h^*\}} = 0$, or

$$c(\mathbf{r}) = \exp[\mu - \mathrm{i}h^*(\mathbf{r})] Z_{\mathrm{intra}}(\mathbf{r}) \tag{20}$$

$$Z_{\mathrm{intra}}(\mathbf{r};\{\varphi\}) = \int \widetilde{D}\mathbf{R}(s)\, \delta[\mathbf{r} - \mathbf{R}_{\mathrm{c.m.}}] \exp\left[-\mathrm{i}N \int_0^1 \mathrm{d}s\, \varphi\{\mathbf{R}(s)\}\right]. \tag{21}$$

Here we use the subscript 'intra' since $Z_{\mathrm{intra}}(\mathbf{r};\{\varphi\})$ corresponds to the intra-chain partition function performing the path-integral over all the chain configurations with the position of the c.m., $\mathbf{R}_{\mathrm{c.m.}}$, fixed at $\mathbf{r}$. Considering only quadratic fluctuations around the saddle point field $\{h^*(\mathbf{r})\}$, we obtain

$$\begin{aligned} &\int \mathrm{D}h \exp[\mathrm{i}c \cdot h + \mathrm{e}^{\mu} Q\{h,\ \varphi\}] \\ &\quad = \int \mathrm{D}(\Delta h) \exp\left[\mathrm{i}c \cdot h^* + \mathrm{e}^{\mu} Q\{h^*,\ \varphi\} + \int \mathrm{d}\mathbf{r} \frac{\mathrm{e}^{\mu} Q^{(2)}\{h^*,\ \varphi\}}{2} \Delta h(\mathbf{r})^2\right] \\ &\quad = \exp\left(k_{\mathrm{B}}^{-1} S\{c\} + \int \mathrm{d}\mathbf{r}\, c(\mathbf{r}) \ln[Z_{\mathrm{intra}}(\mathbf{r};\{\varphi\})] + \mathcal{A}\{c\} + \mu \int \mathrm{d}\mathbf{r}\, c(\mathbf{r})\right), \end{aligned} \tag{22}$$

where the anomalous term $\mathcal{A}\{c\}$ is due to the Gaussian integration over the fluctuating field $\{\Delta h\}$. Since the second derivative of $Q\{h,\ \varphi\}$ with respect to h, denoted by $Q^{(2)}$, satisfies $\mathrm{e}^{\mu} Q^{(2)}\{h^*,\ \varphi\} = -c(\mathbf{r})$ at the saddle-point path h^*, we get the anomaly $\mathcal{A}\{c\}$ of equation (7).

($\mathcal{D}$4) *Minimal consideration of intramolecular correlation.* Let us go on to take minimal account of the connectivity of polymers, by expanding $Z_{\mathrm{intra}}(\mathbf{r};\ \{\varphi\})$ only to the lowest order in φ:

$$\begin{aligned} Z_{\mathrm{intra}}(\mathbf{r};\{\varphi\}) &\approx Z_{\mathrm{intra}}(\mathbf{r};\varphi\equiv 0) - \mathrm{i}N\int \mathrm{d}\mathbf{r}'\,G(\mathbf{r}-\mathbf{r}')\,\varphi(\mathbf{r}') \\ G(\mathbf{r}-\mathbf{r}') &= \int_0^1 \mathrm{d}s\int \widetilde{D}\mathbf{R}\;\delta[\mathbf{r}-\mathbf{R}_{\mathrm{c.m.}}]\,\delta[\mathbf{r}'-\mathbf{R}(\mathbf{s})], \end{aligned} \tag{23}$$

where the intra-chain partition function $Z_{\mathrm{intra}}(\mathbf{r};\ \varphi\equiv 0)$ in the absence of external field $\varphi = 0$ is nothing but the partition function of a Gaussian chain and is equal to unity, $Z_{\mathrm{intra}}(\mathbf{r};\ \varphi\equiv 0) = 1$, by definition of the Wiener measure $\widetilde{D}\mathbf{R}$ [1] because it is possible to explore the full space of the tangent vector $\mathrm{d}\mathbf{R}(s)/\mathrm{d}s$ in equation (15) without moving the centre of mass as mentioned before.

Therefore, in the approximation (23), the logarithm of Z_{intra} appearing in the exponent of the last line in equation (22) reads

$$\ln[Z_{\mathrm{intra}}(\mathbf{r};\{\varphi\})] \approx -\mathrm{i}N\int \mathrm{d}\mathbf{r}'\,G(\mathbf{r}-\mathbf{r}')\,\varphi(\mathbf{r}'), \tag{24}$$

and the φ-integral yields

$$\begin{aligned} \int D\varphi\,\mathrm{e}^{\mathrm{i}\rho\cdot\varphi + c\cdot\ln Z_{\mathrm{intra}}} &= \int D\varphi\;\exp\left[\int \mathrm{d}\mathbf{r}\,\mathrm{i}\varphi(\mathbf{r})\left\{\rho(\mathbf{r}) - N\int \mathrm{d}\mathbf{r}'\,G(\mathbf{r}-\mathbf{r}')\,c(\mathbf{r})\right\}\right] \\ &= \prod_{\{\mathbf{r}\}}\delta[\rho(\mathbf{r}) - \Omega\,c(\mathbf{r})], \end{aligned} \tag{25}$$

noting that the kernel $G(\mathbf{r}-\mathbf{r}')$ given in equation (23) is expressed by the c.m.–monomer form factor $\omega_{\mathrm{c.m.}}$ (see also the definition (5)):

$$N\int \mathrm{d}\mathbf{r}'\,G(\mathbf{r}-\mathbf{r}')\,c(\mathbf{r}') = N\int \mathrm{d}\mathbf{r}'\,\omega_{\mathrm{c.m.}}(R_{\mathrm{g}}\nabla)\,\delta(\mathbf{r}-\mathbf{r}')\,c(\mathbf{r}') = \Omega\,c(\mathbf{r}). \tag{26}$$

Combining equations (19), (22) and (25), namely the h- and φ-integrations of equation (19), amounts to the results (4) and (5).

($\mathcal{D}$5) *Why is the polymer order parameter ψ to be added?* Because the third time insertion of the identity

$$1 = \int D\psi\;\det\left\{\frac{\delta\psi^2}{\delta\psi}\right\}\prod_{\{\mathbf{r}\}}\delta[\psi^2(\mathbf{r}) - \Omega\,c(\mathbf{r})] = \det(4\Omega c)^{1/2}\int D\psi\prod_{\{\mathbf{r}\}}\delta(\psi^2-\Omega\,c), \tag{27}$$

suppresses the anomaly given by equation (7) as follows:

$$\begin{aligned} \mathrm{e}^{\mathcal{A}\{c\}} &= \lim_{\epsilon\to 0}\exp\left[\frac{1}{2\epsilon}\int \mathrm{d}\mathbf{r}\,\ln\left(\frac{2\pi}{c}\right) + \ln(4\Omega\,c)\right]\int D\psi\prod_{\{\mathbf{r}\}}\delta(\psi^2-\Omega\,c) \\ &= \det(8\pi\Omega)^{1/2}\int D\psi\prod_{\{\mathbf{r}\}}\delta(\psi^2-\Omega\,c). \end{aligned} \tag{28}$$

Equation (4) with (28) leads to the regularized form (8), absorbing the constant $\det(8\pi)^{1/2}$ into an integral measure formally.

5. Concluding remarks

The PC functional, $\mathcal{F}_{\mathrm{PC}}$, given by equation (3), has thus shed light on how to develop a functional-integral formulation of soft polymeric colloids. The key procedures are twofold.

The first, the set of equations (17) and (18), is to introduce a polymer concentration c in addition to the monomer density ρ. The second, equation (23), is to truncate at $\mathcal{O}(\varphi)$ the expansion of the intra-chain partition function, Z_{intra}, given by (21). Consequently, as described in ($\mathcal{R}1$), we have obtained equation (4), whose exponent is similar to the PC functional [20]. The differences from the PC are that the c–ρ relation is represented not by the structure factor of Gaussian chains but by the form factor $\omega_{\mathrm{c.m.}}$ given in (5), and that the anomalous term (7) is added. Furthermore, as shown in ($\mathcal{R}2$) and ($\mathcal{R}3$), the new functional-integral representation, (4) or (8), not only has reproduced the classical Flory–Krigbaum effective potential (9) between polymers, but also has provided an efficient SCF equation (14) which preincludes the stability condition of the Flory–Huggins functional through the trial density (12).

Finally, we should note that the present functional-integral representation is extended straightforwardly to validate the formulations of block copolymers [19], and also has the advantage of systematic improvements on the following approximations: the saddle-point approximation in deriving equation (14), and the minimal consideration (23) of intramolecular correlation in evaluating the intra-chain partition function Z_{intra}. Beyond the former mean-field theory, density fluctuations can be readily taken into account along the conventional lines [12]. The latter extension, on the other hand, not only relaxes the strict constraint on the c–ρ relation but also produces the coupling between the monomer–monomer and c.m.–monomer correlations, suggesting the relevance of our field-theoretic approach to current issues in describing polymers as soft colloids: effective interaction between polymers [25, 27], the relationship between the measurable monomer–monomer structure factor and the c.m. structure factor [28] and so on.

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