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A closed-form, free-energy functional for a binary polymer mixture

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A new, closed-form, free-energy functional is derived for a binary polymer mixture. When the free-energy functional is expanded in series form around the mean concentration, the leading term in the expansion is the usual Flory-Huggins free energy. The Fourier transform of the coefficients of this expansion are approximate vertex functions $\bar{\Gamma}^{(n)}$. A useful and tractable form for $\bar{\Gamma}^{(n)}$ is obtained for all n which only depends on the magnitudes of the n wave vectors. It is shown that $\bar{\Gamma}^{(2)}$ is exact and $\bar{\Gamma}^{(3)}$ and $\bar{\Gamma}^{(4)}$ reduce to the correct limiting values in the small and large wave vector limits.

I. INTRODUCTION

The free energy of a binary polymer mixture is given by the well-known Flory-Huggins formula¹

$$f_{\text{FH}}/kT = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \phi_1 \phi_2 \chi, \quad (1)$$

where ϕ_i is the volume fraction and N_i is the degree of polymerization of component i ($i = 1$ or 2) and χ is the interaction parameter. In deriving this mean-field result the intrinsic connectivity of the polymer chains is completely ignored.² On size scales of the order of the radius of gyration of a polymer chain R connectivity produces concentration inhomogeneities which affect the free energy. De Gennes³ showed that the Fourier component of the second derivative of the free energy of an incompressible binary polymer mixture is given by

$$\left(\frac{d^2 f}{d\phi^2} \right)_q \equiv S^{-1}(q) = \frac{1}{N_1 \phi_1 D(q^2 R_1^2)} + \frac{1}{N_2 \phi_2 D(q^2 R_2^2)} - 2\chi, \quad (2)$$

where $D(x)$ is the well-known Debye static structure factor of a Gaussian chain:

$$D(x) = (2/x) [1 - (1 - e^{-x})/x] = 1 - \frac{x}{3} + \cdots, \quad (3)$$

where $x = (qR)^2 = q^2 Na^2/6$ and R is the radius of gyration of the chain and a is a statistical segment length. Although Eq. (2) is still a mean-field result, chain connectivity has been explicitly taken into account via a random phase approximation.

Using Eq. (2) de Gennes showed that the local free energy of a binary mixture is better represented by⁴

$$f/kT = f_{\text{FH}}/kT + \frac{1}{36} \left[\frac{a_1^2}{\phi} + \frac{a_2^2}{1-\phi} \right] |\nabla \phi|^2. \quad (4)$$

When $a_1 = a_2 = a$, the coefficient of the square gradient term, becomes the more familiar $a^2/[36\phi(1-\phi)]$. In deriving Eq. (4), de Gennes did not use the complete Debye functions in Eq. (2), but only its linear expansion $1 - x/3$. Thus, Eq. (4) is only valid for values of $qR \ll 1$, or equivalently, small values of the gradient $\nabla \phi$. In the generalization pre-

sented in this paper we use the complete Debye functions to arrive at a new and more complete representation of the free energy.

The presence of the gradient term in Eq. (4) means that the total (or extensive) free energy is given by a free-energy functional:

$$F/kT = \int d^3r \{ f_{\text{FH}}[\phi(\mathbf{r})]/kT + \frac{1}{36} \left[\frac{a_1^2}{\phi(\mathbf{r})} + \frac{a_2^2}{1-\phi(\mathbf{r})} \right] |\nabla \phi(\mathbf{r})|^2 \}, \quad (5)$$

i.e., the free energy is of the Landau-Ginsburg type

$$F = \int d^3r \{ f_0 + \kappa |\nabla \phi|^2 \}, \quad (6)$$

where f_0 is the homogeneous part of the free energy and κ scales the effect of concentration gradients on the free energy.

II. NEW RESULT

Instead of Eq. (6) we begin with a more general functional:

$$F/kT = \int d^3r \left\{ \phi_1 \phi_2 \chi + \sum_{i=1}^2 \kappa_i A_i(\nabla^2) \phi_i(\mathbf{r}) \right\}, \quad (7)$$

where κ_i is a function of $\phi_i(\mathbf{r})$ and $A_i(\nabla^2)$ is a linear operator of the form

$$A_i(\nabla^2) = 1 + \sum_{n=1}^{\infty} \alpha_{in} \nabla^{2n} \quad (8)$$

and the α_{in} are constants independent of concentration. Our choice of Eq. (7) is prompted by the form of Eq. (2) which can be rewritten as a sum of q -dependent and $q = 0$ (thermodynamic) contributions:

$$S^{-1}(q) = \sum_{i=1}^2 \frac{1}{N_i \phi_i} \{ 1 + [D^{-1}(q^2 R_i^2) - 1] \} - 2\chi. \quad (9)$$

When the components do not interact ($\chi = 0$) each component contributes independently to the free energy. Our task now is to determine κ_i and A_i .

Taking the functional derivative of Eq. (7) with respect to ϕ_2 and using $\phi_1 + \phi_2 = 1$, we obtain

$$\frac{\delta(F/kT)}{\delta\phi_2(\mathbf{r})} = \sum_{i=1}^2 (-1)^i [A_i(\nabla^2)\kappa_i + \kappa'_i A_i(\nabla^2)\phi_i] + (\phi_1 - \phi_2)\chi, \quad (10)$$

where $\kappa'_i \equiv d\kappa_i/d\phi_i$. Denoting the mean value of ϕ_i as $\bar{\phi}_i$ and making the substitution $\phi_i = \bar{\phi}_i + \delta\phi_i$, Eq. (10) can be linearized with the result (note that $\delta\phi_1 = -\delta\phi_2$):

$$\frac{\delta(F/kT)}{\delta\phi_2(\mathbf{r})} = \text{const} + \sum_{i=1}^2 [\bar{\phi}_i \kappa''_i(\bar{\phi}_i) + 2\kappa'_i(\bar{\phi}_i) A_i(\nabla^2)] \delta\phi_2 - 2\chi \delta\phi_2. \quad (11)$$

The term $\phi\kappa''(\bar{\phi})$ arises because $A\bar{\phi} = \bar{\phi}$. The coefficient of $\delta\phi_2$ is, of course, the second derivative of the free energy; in Fourier space it becomes

$$\sum_{i=1}^2 [\bar{\phi}_i \kappa''_i(\bar{\phi}_i) + 2\kappa'_i(\bar{\phi}_i) A_i(-q^2)], \quad (12)$$

where use has been made of the fact that the Fourier transform of $\nabla^2 \delta\phi$ equals $(-q^2) \delta\phi_q$. Comparing Eq. (12) with Eq. (9), we find that for $q = 0$,

$$\bar{\phi}_i \kappa''_i(\bar{\phi}_i) + 2\kappa'_i(\bar{\phi}_i) = \frac{1}{\bar{\phi}_i N_i} \quad (13a)$$

or

$$\frac{d}{d\phi_i} [\bar{\phi}_i^2 \kappa'_i(\bar{\phi}_i)] = \frac{1}{N_i} \quad (13b)$$

which yields

$$\kappa_i(\bar{\phi}_i) = \ln \bar{\phi}_i / N_i. \quad (14)$$

For $q \neq 0$, we have

$$A_i(-q^2) - 1 = \frac{1}{2} [d^{-1}(q^2 R_i^2) - 1] \quad (15a)$$

or

$$A_i(-q^2) = \frac{1}{2} [D^{-1}(q^2 R_i^2) + 1]. \quad (15b)$$

Thus, the generalized functional for the free energy can be written as

$$F/kT = \int d^3r \left[\frac{\ln \phi_1}{N_1} A_1(\nabla^2) \phi_1 + \frac{\ln \phi_2}{N_2} A_2(\nabla^2) \phi_2 + \phi_1 \phi_2 \chi \right] \quad (16)$$

which is our main result.

Note that if ϕ_i is replaced by its mean $\bar{\phi}_i$, the usual Flory-Huggins free energy, Eq. (1), is recovered. In the limit $qR_i \ll 1$, Eq. (15) becomes

$$A_i(-q^2) = \frac{1}{2} \left[\frac{1}{1 - (1/3)(qR_i)^2 + \dots} + 1 \right] = 1 + \frac{1}{6}(qR_i)^2 + \dots \quad (17a)$$

or

$$A_i(\nabla^2) = 1 - \frac{R_i^2}{6} \nabla^2 = 1 - \frac{N_i a_i^2}{36} \nabla^2. \quad (17b)$$

Substituting Eq. (17b) into Eq. (16) yields

$$F/kT = \int d^3r \left\{ f_{FH}/kT - \frac{1}{36} [a_1^2 \ln \phi_1 \nabla^2 \phi_1 + a_2^2 \ln \phi_2 \nabla^2 \phi_2] \right\}. \quad (18)$$

Assuming that $\nabla\phi = 0$ at the system boundaries, then

$$\int d^3r (\ln \phi \nabla^2 \phi) = - \int d^3r (|\nabla\phi|^2/\phi). \quad (19)$$

Substituting Eq. (19) into Eq. (18) yields the de Gennes result, Eq. (5).

III. FREE ENERGY EXPANSION

How accurate is the free-energy functional, Eq. (16)? To address this question we expand the free energy and compare the coefficients with exact results. As will be seen, in both the small and large q limits, the coefficients are correct up to at least fourth order.

As before let $\phi_i = \bar{\phi}_i + \delta\phi_i$; substituting into Eq. (16) yields

$$\Delta f \equiv F/V - f_{FH} = \int d^3r \left\{ \delta\phi_1 \delta\phi_2 \chi + \sum_{i=1}^2 \sum_{n=2}^{\infty} \left[\frac{(-1)^{n-1}}{N_i \bar{\phi}_i^{n-1}} \left(\frac{\delta\phi_i^n}{n} - \frac{\delta\phi_i^{n-1}}{n-1} A_i(\nabla^2) \delta\phi_i \right) \right] \right\} \quad (20)$$

and where we have used the mass conservation condition

$$\int d^3r \delta\phi_i = 0. \quad (21)$$

We want to express Δf in terms of the Fourier components of $\delta\phi_i$:

$$\delta\phi_i(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3q e^{i\mathbf{q}\cdot\mathbf{r}} \delta\phi_i(\mathbf{q}). \quad (22)$$

Substituting Eq. (22) into Eq. (20) and using the results

$$A_i(\nabla^2) e^{i\mathbf{q}\cdot\mathbf{r}} = A_i(-q^2) e^{i\mathbf{q}\cdot\mathbf{r}} \quad (23)$$

and

$$\int d^3r e^{i\mathbf{r}\cdot\left(\sum_{j=1}^n \mathbf{q}_j\right)} = (2\pi^3) \delta\left(\sum_{j=1}^n \mathbf{q}_j\right). \quad (24)$$

We obtain

$$\Delta f = \sum_{i=1}^2 \sum_{n=2}^{\infty} \frac{(-1)^{n-1}}{(2\pi)^{3(n-1)} N_i \bar{\phi}_i^{n-1}} \int \prod_{j=1}^n d^3q_j \delta\left(\sum_{j=1}^n \mathbf{q}_j\right) \times \left[\frac{1}{n} - \frac{1}{n-1} A_i(-q_n^2) \right] \delta\phi_i(\mathbf{q}_j) + \frac{\chi}{(2\pi)^3} \int d^3q \delta\phi_1(\mathbf{q}) \delta\phi_2(-\mathbf{q}). \quad (25)$$

$A_i(-q_n^2)$ in the integrand can be replaced by the symmetrical form

$$A_i(-q_n^2) \rightarrow \frac{1}{n} \sum_{j=1}^n A_i(-q_j^2)$$

and Eq. (25) can be written as

$$\Delta f = \sum_{i=1}^2 \sum_{n=2}^{\infty} \int \prod_{j=1}^n d^3 q_j \delta \phi_i(\mathbf{q}_j) \bar{\Gamma}_i^{(n)}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_n) + \frac{\chi}{(2\pi)^3} \int d^3 q \delta \phi_1(\mathbf{q}) \delta \phi_2(-\mathbf{q}), \quad (26)$$

where $\bar{\Gamma}_i^{(n)}$ are the vertex functions

$$\bar{\Gamma}_i^{(n)} = \frac{(-1)^{n-1}}{(2\pi)^{3(n-1)} n N_i \bar{\phi}_i^{n-1}} \delta\left(\sum_{j=1}^n \mathbf{q}_j\right) \times \left[1 - \frac{1}{n-1} \sum_{j=1}^n A_i(-q_j^2)\right] \quad (27a)$$

or in terms of Debye functions [see Eq. (15b)]

$$\bar{\Gamma}_i^{(n)} = \frac{(-1)^{n-1}}{N_i \bar{\phi}_i^{n-1}} \frac{(n-2)}{(2\pi)^{3(n-1)} 2n(n-1)} \delta\left(\sum_{j=1}^n \mathbf{q}_j\right) \times \left[1 - \frac{1}{n-2} \sum_{j=1}^n D^{-1}(q_j^2 R_i^2)\right]. \quad (27b)$$

Using the limiting values of the Debye function

$$D^{-1}(q^2 R_i^2) = \begin{cases} 1 + q^2 R_i^2/3, & q R_i \ll 1 \\ q^2 R_i^2/2, & q R_i \gg 1 \end{cases}, \quad (28)$$

in Eq. (27) yields

$$\bar{\Gamma}_i^{(n)} = \frac{(-1)^n}{(2\pi)^{3(n-1)} N_i \bar{\phi}_i^{n-1} n(n-1)} \times \delta\left(\sum_{j=1}^n \mathbf{q}_j\right) \begin{cases} 1 + \frac{r_i^2}{6} \sum_{j=1}^n q_j^2, & q_j R_i \ll 1 \\ \frac{R_i^2}{4} \sum_{j=1}^n q_j^2, & q_j R_i \gg 1 \end{cases}. \quad (29)$$

Now Hong and Noolandi⁵ have formally evaluated the vertex functions $\Gamma_i^{(n)}$ for a binary mixture up to fourth order. For two homopolymers, we have for each component⁶

$$\Gamma^{(2)}(\mathbf{q}_1, \mathbf{q}_2) = \frac{1}{2(2\pi)^3 N \bar{\phi}} \delta(\mathbf{q}_1 + \mathbf{q}_2) \frac{D^{-1}(X_1) + D^{-1}(X_2)}{2}, \quad (30)$$

$$\Gamma^{(3)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = -\frac{\delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)}{6(2\pi)^6 N \bar{\phi}^2 D(X_1) D(X_2) D(X_3)} \left[\frac{D(X_1) - D(X_2)}{X_2 - X_1} + \frac{D(X_2) - D(X_3)}{X_3 - X_2} + \frac{D(X_1) - D(X_3)}{X_3 - X_1} \right], \quad (31)$$

$$\Gamma^{(4)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) = \frac{\Pi_{j=1}^4 D^{-1}(X_j) \delta(\sum_{j=1}^4 \mathbf{q}_j)}{24(2\pi)^9 N \bar{\phi}^3} \{ 3D^{-1}(X_{12}) \times \left[\left(\frac{D(X_1) - D(X_2)}{X_2 - X_1} + \frac{D(X_1) - D(X_{12})}{X_{12} - X_1} + \frac{D(X_2) - D(X_{12})}{X_{12} - X_2} \right) \left(\frac{D(X_3) - D(X_4)}{X_4 - X_3} + \frac{D(X_3) - D(X_{34})}{X_{34} - X_3} + \frac{D(X_4) - D(X_{34})}{X_{34} - X_4} \right) - \frac{1}{2} \sum_P \left(\frac{D(X_{P_1})}{(X_{P_1, P_2} - X_{P_1})(X_{P_4} - X_{P_1})} + \frac{D(X_{P_1, P_2})}{(X_{P_1} - X_{P_1, P_2})(X_{P_4} - X_{P_1, P_2})} + \frac{D(X_{P_4})}{(X_{P_1} - X_{P_4})(X_{P_1, P_2} - X_{P_4})} \right) \right] \} + O(1/V), \quad (32)$$

where V is the system volume and

$$\begin{aligned} X_i &\equiv R^2 q_i^2, \\ X_{ij} &\equiv R^2 (\mathbf{q}_i + \mathbf{q}_j)^2, \\ X_{P_1, P_2} &\equiv R^2 (\mathbf{q}_{P_1} + \mathbf{q}_{P_2})^2, \end{aligned} \quad (33)$$

and where \sum_P means a sum of all permutations of the indices P_1, P_2, \dots, P_n ; for $n = 4$ this means that there are $4! = 24$ possible permutations.

Comparison of the exact values of the vertex functions $\Gamma^{(n)}$, Eqs. (30), (31), and (32), with the approximate ones, $\bar{\Gamma}^{(n)}$ given in Eq. (27) show that $\bar{\Gamma}^{(2)} = \Gamma^{(2)}$, but that $\bar{\Gamma}^{(3)} \neq \Gamma^{(3)}$ and $\bar{\Gamma}^{(4)} \neq \Gamma^{(4)}$.

However, the differences are not as severe as they may appear. It is straightforward to show that for small and large q_i , $\Gamma^{(3)}$ reduces to $\bar{\Gamma}^{(3)}$. With a significant amount of more algebra it can also be shown that $\Gamma^{(4)}$ reduces to $\bar{\Gamma}^{(4)}$ in the small and large q_i limits, i.e.,

$$\Gamma^{(3)} = \bar{\Gamma}^{(3)} = -\frac{\delta(\sum_{j=1}^3 \mathbf{q}_j)}{(2\pi)^6 6N \bar{\phi}^2} \begin{cases} 1 + \frac{R^2}{6} \sum_{j=1}^3 q_j^2, & q_j R^2 \ll 1 \\ \frac{R^2}{4} \sum_{j=1}^3 q_j^2, & q_j R^2 \gg 1 \end{cases}, \quad (34)$$

IV. SUMMARY

A new free-energy functional, Eq. (16) has been derived for a binary polymer mixture. Prior to this study, the well-known de Gennes free-energy functional, Eq. (5), has been the standard. However, it only correctly reproduces the second-order vertex function $\Gamma^{(2)}$ at small q values. Equation (16) correctly yields the Flory-Huggins free energy when the concentration is assumed to be spatially uniform, and correctly yields $\Gamma^{(2)}$ and values for $\Gamma^{(3)}$ and $\Gamma^{(4)}$ which have been shown to reduce to the correct limiting values in both small and large wave vector limits. This improvement has been achieved by allowing for terms such as $\nabla^{2n} \phi$ in the free energy to infinite order ($n \rightarrow \infty$) [see Eq. (8)]. In contrast the de Gennes formula only allows for a $\nabla^2 \phi$ term, or equivalently a $(\nabla \phi)^2$ term, in the free energy which is only valid for slow varying concentration inhomogeneities. The ap-

proximate vertex functions $\bar{\Gamma}^{(n)}$ will be useful in the nonlinear theory of spinodal decomposition in q space.

¹P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, NY, 1953).

²I. C. Sanchez, *Encyclopedia of Physical Science and Technology* (Aca-

demic, New York, 1987), Vol. XI.

³P. G. de Gennes, *J. Chem. Phys.* **72**, 4756 (1980).

⁴P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, NY, 1979).

⁵K. M. Hong and J. Noolandi, *Macromolecules* **16**, 1083 (1983).

⁶Since $\Gamma^{(3)}$ and $\Gamma^{(4)}$ are not explicitly displayed in Ref. 5, they are displayed here.