

# 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 formula<sup>1</sup>

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

where  $\phi_i$  is the volume fraction and  $N_i$  is the degree of polymerization of component  $i$  ( $i = 1$  or  $2$ ) and  $\chi$  is the interaction parameter. In deriving this mean-field result the intrinsic connectivity of the polymer chains is completely ignored.<sup>2</sup> 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 Gennes<sup>3</sup> 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:

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

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 by<sup>4</sup>

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

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:

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

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  $\kappa$  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  $\kappa_i$  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  $\alpha_{in}$  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  $\kappa_i$  and  $A_i$ .

Taking the functional derivative of Eq. (7) with respect to  $\phi_2$  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  $\phi_i$  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  $\nabla^{2n}\delta\phi$  equals  $(-q^2)^n \delta\phi_q$ . 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

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

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

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

which is our main result.

Note that if  $\phi_i$  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  $\Delta f$  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

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

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 Noolandi<sup>5</sup> have formally evaluated the vertex functions  $\Gamma_i^{(n)}$  for a binary mixture up to fourth order. For two homopolymers, we have for each component<sup>6</sup>

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

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

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

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.,

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

$$\Gamma^{(4)} = \bar{\Gamma}^{(4)} = \frac{\delta(\sum_{j=1}^4 \mathbf{q}_j)}{(2\pi)^9 12N \bar{\phi}^3} \begin{cases} 1 + \frac{R^2}{6} \sum_{j=1}^4 q_j^2, & q_j^2 R^2 \ll 1 \\ \frac{R^2}{4} \sum_{j=1}^4 q_j^2, & q_j R^2 \gg 1 \end{cases}. \quad (35)$$

#### 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.

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

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

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

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

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

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

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