

SCATTERING FUNCTION OF POLYMER BLENDS*

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Abstract For a system of flexible polymer molecules, the concepts of two concentrations, namely the segmental and the molecular concentrations, have been proposed in this paper. The former is equivalent to the volume fraction. The latter can be defined as the number of the gravity centers of macromolecules in a unit volume. The two concentrations should be correlated with each other by the conformational function of the polymer chain and should be discussed in different thermodynamic equations. On the basis of these concepts it has been proved that the Flory-Huggins entropy of mixing should be the result of the mixing “ideal gases of the gravity centers of macromolecules”. The general correlation between the free energy of mixing and the scattering function (structural factor) of polymer blends has been studied based on the general fluctuation theory. When the Flory-Huggins free energy of mixing is adopted, the de Gennes scattering function of a polymer blend can be derived.

Keywords Segmental concentration, Molecular concentration, Scattering function

INTRODUCTION

A fundamental feature of polymer systems is the connectivity of segments comprising the macromolecule. It exerts an important influence on the thermodynamic properties of polymer solutions. Flory and Huggins have proposed a formula for the free energy for mixing of polymer blends^[1]

$$\frac{F}{kT} = \frac{\Phi_1}{N_1} \ln \Phi_1 + \frac{\Phi_2}{N_2} \ln \Phi_2 + \chi \Phi_1 \Phi_2 \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, Φ_1, Φ_2, N_1 and N_2 are the volume fractions and the chain lengths for the two polymer components, respectively, and χ is the Flory-Huggins interaction parameter. This formula has been subjected to much criticism due to the mean field assumption, and some improved theories were proposed^[2–6]. An important task of theoretical studies is to overcome the boundaries of the mean field method of macromolecules in statistical mechanics. In this work we try to propose a new physical concept for a polymer system.

TRANSLATIONAL AND CONFORMATIONAL DEGREES OF FREEDOM OF A SYSTEM OF MACROMOLECULES

As is well known, for particles of ideal gases with no internal structure, only translational degrees of freedom are to be considered. For complex molecules the free energy will comprise a translational part and an internal part. A set of variables, some corresponding to the translational state and some to the internal state, will be considered.

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For a polymer blend, two thermodynamic variables are necessary: one describes the translational degree of freedom of the center of gravity of the macromolecule, and the other is the conformational degree of freedom describing the flexibility of the polymer chain. For a thermodynamic treatment of a polymer blend, two concentrations are needed, that is, the segmental concentration and the molecular concentration.

The segmental concentration can be defined as the number of the segments in unit volume. For convenience the segmental volume is taken as unity, so the segmental concentrations of a polymer blend are exactly equivalent to the volume fractions Φ_1 and Φ_2 for the polymer components 1 and 2 of the blend, respectively.

Now we introduce a molecular concentration. First we should define the position of a macromolecule. Generally, it is easy to understand that the center of gravity of a macromolecule can be taken as the position of the molecule. The random thermal motion of centers of gravity can be considered to represent translational degree of freedom of polymer chains. Therefore the molecular concentration can be defined as the number of centers of gravity of each component of the blend in unit volume, which can be denoted as c_1 and c_2 , respectively.

Moreover, it should be pointed out that both of the two concentrations are of true importance. In fact, in different thermodynamic equations or phenomena maybe only one of the concentrations can be used and not the other concentration. For example, in the scattering experiments, the segments will act as the scattering center, therefore the scattering function should be the mean square fluctuation of the segment concentration; the incompressibility condition which represents the exclusive volume effect should be satisfied by the segment concentration too; the heat of mixing is proportional to the contact points between the segments of the two component polymers, it should be proportional to the product of the two local segment concentrations. On the other hand, polymer binary blend is a mixture of two groups of different macromolecules, and is not a mixture of two groups of dispersed segments, therefore the entropy of mixing should be a function of the molecular concentrations of the two polymer components; the spinodal decomposition of two polymers is a phase separation behavior of two polymers, it should be described by the molecular concentration too. So, we should carefully distinguish the two kinds of concentration in thermodynamic treatments of polymer systems.

RELATIONSHIP BETWEEN SEGMENTAL AND MOLECULAR CONCENTRATIONS

The relation between the average segmental and the molecular concentrations of a solution is very simple:

$$\bar{\Phi}_1 = N_1 \bar{c}_1, \quad \bar{\Phi}_2 = N_2 \bar{c}_2 \quad (2)$$

When only the average concentrations are considered, the molecular concentration can be represented by the segmental concentration. Generally the segmental and the molecular concentrations should be correlated by means of a conformational function for the macromolecular chain. For a polymer blend,

$$\Phi_1(\bar{r}) = \int c_1(\bar{R}) G_1(\bar{r}, \bar{R}) d\bar{R}, \quad \Phi_2(\bar{r}) = \int c_2(\bar{R}) G_2(\bar{r}, \bar{R}) d\bar{R} \quad (3)$$

where $G_1(\bar{r}, \bar{R})$ and $G_2(\bar{r}, \bar{R})$ are the conformational functions which represent the number concentration of the segments of a macromolecule of 1 and 2 species, which are at position $\bar{r}$ with its center of gravity being at position $\bar{R}$. The integral should be performed over the whole space. By this method we can directly introduce the conformational model reflecting the flexibility or rigidity of the polymer chain into the thermodynamic formulas of polymer systems.

TRANSLATIONAL ENTROPY OF POLYMER BLENDS

Now we discuss the translational entropy of a binary blend using the above-mentioned concepts. Let us take n_1 polymer molecules of chain length N_1 in a volume $V_1 = n_1 N_1$. Because the polymer chains are very long, the concentration of their center of gravity is very small, its thermodynamic behavior will correspond to that of a rarefied gas described as a homogeneous ideal gas. Consequently we can write its entropy using the formula of an ideal gas as

$$S_1 = kn_1 \ln \frac{V_1}{n_1} \quad (4)$$

and similarly for the second component:

$$S_2 = kn_2 \ln \frac{V_2}{n_2} \quad (5)$$

After mixing, the total volume of the system is $V = V_1 + V_2$. The total entropy is given by

$$S_{\text{total}} = k \left(n_1 \ln \frac{V_1 + V_2}{n_1} + n_2 \ln \frac{V_1 + V_2}{n_2} \right) \quad (6)$$

Before mixing, the volumes of the two components should be $V_1 = n_1 N_1$ and $V_2 = n_2 N_2$, respectively. If the conformational entropy does not change during mixing, the entropy of mixing per unit volume is easily obtained as

$$S_{\text{mix}} = \frac{S_{\text{total}} - S_1 - S_2}{V_1 + V_2} = -k \left[\bar{c}_1 \ln(\bar{c}_1 N_1) + \bar{c}_2 \ln(\bar{c}_2 N_2) \right] \quad (7)$$

where $\bar{c}_1$ and $\bar{c}_2$ are the molecular concentrations of the two components, respectively, defined as the number of molecules per unit (segmental) volume:

$$\bar{c}_1 = \frac{n_1}{V_1 + V_2}, \quad \bar{c}_2 = \frac{n_2}{V_1 + V_2} \quad (8)$$

It is obvious that Eq. (7) has neglected the effect of the conformational entropy of polymer chains in the mixing process.

According to Flory's assumption, the local heat of mixing can be regarded as proportional to the product of Φ_1 and Φ_2 . The heat of mixing of the solution should be written as

$$H_{\text{mix}} / kT = \chi \bar{\Phi}_1 \bar{\Phi}_2 \quad (9)$$

Combining Eq. (7) and (9), we have the free energy of mixing in statistical thermodynamic terms:

$$F_{\text{mix}} / kT = \bar{c}_1 \ln(\bar{c}_1 N_1) + \bar{c}_2 \ln(\bar{c}_2 N_2) + \chi \bar{\Phi}_1 \bar{\Phi}_2 \quad (10)$$

Replace of $\bar{c}_1$ and $\bar{c}_2$ according to Eq. (2) gives

$$\frac{F_{\text{mix}}}{kT} = \frac{\bar{\Phi}_1}{N_1} \ln \bar{\Phi}_1 + \frac{\bar{\Phi}_2}{N_2} \ln \bar{\Phi}_2 + \chi \bar{\Phi}_1 \bar{\Phi}_2 \quad (11)$$

It can be seen that if

$$\bar{\Phi}_1 \bar{\Phi}_2 = \bar{\Phi}_1 \cdot \bar{\Phi}_2 \quad (12)$$

then the free energy of mixing formula Eq. (11) will be the same as Eq. (1). This means that the Flory-Huggins free energy of mixing equation implies two hypotheses: First, they only considered the translational entropy and ignored the contribution of the conformational entropy during mixing. Secondly, their heat of mixing involves the mean field assumption *i.e.* Eq. (12). However, Eq. (12) is generally not valid for polymer systems, since a polymer solution could not be treated as a homogeneous system due to the coil structure of the polymer chains. These two hypotheses are the shortcomings of Flory's mean field theory for a polymer system.

Fluctuation in Polymer Blend

According to the above-mentioned concepts, we can establish a general method for calculating the scattering function (structural factor) of a binary polymer blend from its free energy of mixing. Because the heat of mixing of a polymer blend should be a function of the segmental concentrations of the two components, and the entropy

of mixing should be a function of the molecular concentrations, the general form of the local heat of mixing and entropy should be as follows:

$$H_{\text{mix}} = H_{\text{mix}}(\Phi_1, \Phi_2), S_{\text{mix}} = S_{\text{mix}}(c_1, c_2) \quad (13)$$

The structural factor should be the Fourier components of the mean square fluctuation of the concentration^[7]. The fluctuation probability ω will be proportional to the following term

$$\omega \propto \exp[-(\Delta H - T\Delta S)/kT] \quad (14)$$

where ΔS and ΔH are the average deviations of the total entropy of mixing and the heat of mixing from their mean (equilibrium) values, respectively:

$$\Delta H = (1/V) \int [H_{\text{mix}}(\Phi_1, \Phi_2) - H_{\text{mix}}(\bar{\Phi}_1, \bar{\Phi}_2)] dV \quad (15)$$

$$\Delta S = (1/V) \int [S_{\text{mix}}(c_1, c_2) - S_{\text{mix}}(\bar{c}_1, \bar{c}_2)] dV \quad (16)$$

In order to calculate them we shall expand the entropy of mixing and the heat of mixing in power series of the deviation between the local and the equilibrium concentrations near the equilibrium state. The mean square value is a measure of the strength of the fluctuation. If the higher moments are neglected, we have

$$\Delta H = \frac{1}{2V} \int \left[\frac{\partial^2 H_{\text{mix}}}{\partial \Phi_1^2} (\delta \Phi_1)^2 + 2 \frac{\partial^2 H_{\text{mix}}}{\partial \Phi_1 \partial \Phi_2} \delta \Phi_1 \delta \Phi_2 + \frac{\partial^2 H_{\text{mix}}}{\partial \Phi_2^2} (\delta \Phi_2)^2 \right] dV \quad (17)$$

$$\Delta S = \frac{1}{2V} \int \left[\frac{\partial^2 S_{\text{mix}}}{\partial c_1^2} (\delta c_1)^2 + 2 \frac{\partial^2 S_{\text{mix}}}{\partial c_1 \partial c_2} \delta c_1 \delta c_2 + \frac{\partial^2 S_{\text{mix}}}{\partial c_2^2} (\delta c_2)^2 \right] dV \quad (18)$$

where

$$\delta \Phi_1 = \Phi_1 - \bar{\Phi}_1, \quad \delta \Phi_2 = \Phi_2 - \bar{\Phi}_2, \quad \delta c_1 = c_1 - \bar{c}_1, \quad \delta c_2 = c_2 - \bar{c}_2 \quad (19)$$

are the differences of the concentrations from their mean (equilibrium) values. Expanding them in the Fourier series we have

$$\begin{aligned} \delta \Phi_1 &= \sum_{\vec{q}} \delta \Phi_{1\vec{q}} \exp(i\vec{q}\vec{r}), \quad \delta \Phi_2 = \sum_{\vec{q}} \delta \Phi_{2\vec{q}} \exp(i\vec{q}\vec{r}) \\ \delta c_1 &= \sum_{\vec{q}} \delta c_{1\vec{q}} \exp(i\vec{q}\vec{r}), \quad \delta c_2 = \sum_{\vec{q}} \delta c_{2\vec{q}} \exp(i\vec{q}\vec{r}) \end{aligned} \quad (20)$$

Substituting Eq. (20) into Eq. (17) and (18), we obtain

$$\Delta H = \frac{1}{2} \sum_{\vec{q}} \left[\frac{\partial^2 H_{\text{mix}}}{\partial \Phi_1^2} (\delta \Phi_{1\vec{q}})^2 + 2 \frac{\partial^2 H_{\text{mix}}}{\partial \Phi_1 \partial \Phi_2} \delta \Phi_{1\vec{q}} \delta \Phi_{2\vec{q}} + \frac{\partial^2 H_{\text{mix}}}{\partial \Phi_2^2} (\delta \Phi_{2\vec{q}})^2 \right] \quad (21)$$

$$\Delta S = \frac{1}{2} \sum_{\vec{q}} \left[\frac{\partial^2 S_{\text{mix}}}{\partial c_1^2} (\delta c_{1\vec{q}})^2 + 2 \frac{\partial^2 S_{\text{mix}}}{\partial c_1 \partial c_2} \delta c_{1\vec{q}} \delta c_{2\vec{q}} + \frac{\partial^2 S_{\text{mix}}}{\partial c_2^2} (\delta c_{2\vec{q}})^2 \right] \quad (22)$$

Under the incompressibility condition $\Phi_1 + \Phi_2 = 1$, we have:

$$\delta \Phi_{1\vec{q}} + \delta \Phi_{2\vec{q}} = 0 \quad (23)$$

then Eq. (17) becomes

$$\Delta H = \frac{1}{2} \sum_{\bar{q}} \left(\frac{\partial^2 H_{\text{mix}}}{\partial \Phi_1^2} - 2 \frac{\partial^2 H_{\text{mix}}}{\partial \Phi_1 \partial \Phi_2} + \frac{\partial^2 H_{\text{mix}}}{\partial \Phi_2^2} \right) (\delta \Phi_{1\bar{q}})^2 \quad (24)$$

First, in a polymer blend we should consider the relationships between the fluctuation quantities $\delta c_{1\bar{q}}$, $\delta c_{2\bar{q}}$, and $\delta \Phi_{1\bar{q}}$, $\delta \Phi_{2\bar{q}}$ by using Eq. (3). Here we propose that there are two kinds of fluctuations in a polymer blend. One is the deviation of the molecular concentration from its equilibrium value, which corresponds to the fluctuation of the molecular concentration $c_1(\bar{R})$ and $c_2(\bar{R})$ in Eq. (3); the other is the deviation of the macromolecular conformation from its equilibrium state related to the fluctuation of $G_1(\bar{r}, \bar{R})$ and $G_2(\bar{r}, \bar{R})$ in Eq. (3). When the conformational fluctuations are to be considered, the functions $G_1(\bar{r}, \bar{R})$ and $G_2(\bar{r}, \bar{R})$ will depend on both $\bar{r}$ and $\bar{R}$. If the conformational fluctuations are ignored, the conformational functions will be dependent only on the combination variable $\bar{r} - \bar{R}$, then they would be independent on the spatial positions of the gravity centers of polymer chains of the blend. In this case the conformational functions can be denoted by $G_1(\bar{r} - \bar{R})$ and $G_2(\bar{r} - \bar{R})$ for the two components respectively.

$$\Phi_1(\bar{r}) = \int c_1(\bar{R}) G_1(\bar{r} - \bar{R}) dV, \quad \Phi_2(\bar{r}) = \int c_2(\bar{R}) G_2(\bar{r} - \bar{R}) dV \quad (25)$$

Their Fourier components could be written as

$$\delta \Phi_{1\bar{q}} = G_{1\bar{q}} \delta c_{1\bar{q}}, \quad \delta \Phi_{2\bar{q}} = G_{2\bar{q}} \delta c_{2\bar{q}} \quad (26)$$

We define the structural factors of the components themselves as follows

$$S_{1\bar{q}} = \frac{G_{1\bar{q}}^2}{N_1^2}, \quad S_{2\bar{q}} = \frac{G_{2\bar{q}}^2}{N_2^2} \quad (27)$$

So the mean square fluctuation of the segmental concentration can be written directly.

DE GENNES FORMULA

According to the above discussion, if the change of the conformational entropy during mixing is ignored, the local entropy of mixing and the local heat of mixing will be:

$$S_{\text{mix}}/k = -c_1 \ln c_1 N_1 - c_2 \ln c_2 N_2, \quad H_{\text{mix}}/kT = \chi \Phi_1 \Phi_2 \quad (28)$$

Substituting them into Eq. (24) and (22) we have

$$\frac{\Delta H - T\Delta S}{kT} = \sum_{\bar{q}} \frac{1}{2} \left(\frac{\delta c_{1\bar{q}}^2}{c_1} + \frac{\delta c_{2\bar{q}}^2}{c_2} - 2\chi \delta \Phi_{1\bar{q}} \delta \Phi_{2\bar{q}} \right) \quad (29)$$

Putting Eq. (2) and (27) into (29), and using the incompressibility condition, we get the Fourier component of the free energy fluctuation as:

$$\frac{\Delta H - T\Delta S}{kT} = \frac{1}{2} \sum_{\bar{q}} \left(\frac{1}{N_1 \Phi_1 S_{1\bar{q}}} + \frac{1}{N_2 \Phi_2 S_{2\bar{q}}} - 2\chi \right) \delta \Phi_{1\bar{q}}^2 \quad (30)$$

Substituting it into Eq. (14), we have

$$\omega \propto \exp \left[-\frac{1}{2} \sum_{\bar{q}} \left(\frac{1}{N_1 S_{1\bar{q}} \Phi_1} + \frac{1}{N_2 S_{2\bar{q}} \Phi_2} - 2\chi \right) \delta \Phi_{1\bar{q}}^2 \right] \quad (31)$$

the mean square fluctuation $\overline{\delta \Phi_{1\bar{q}}^2}$ is the reciprocal of the term in the bracket.

$$\frac{1}{\overline{\delta\Phi_{1\bar{q}}^2}} = \frac{1}{N_1 S_1(\bar{q}) \Phi_1} + \frac{1}{N_2 S_2(\bar{q}) \Phi_2} - 2\chi \quad (32)$$

Using $S(\bar{q}) \equiv \text{const} \cdot \overline{\delta\Phi_{1\bar{q}}^2}$, we get the de Gennes scattering function^[8] for polymer blends,

$$\frac{1}{S(\bar{q})} = \frac{1}{N_1 S_1(\bar{q}) \Phi_1} + \frac{1}{N_2 S_2(\bar{q}) \Phi_2} - 2\chi \quad (33)$$

Due to the importance of this formula, several derivations have been proposed^[9–13]. But the advantage of our derivation is to show its connection with the general thermodynamic fluctuation theory and the relation between the structural factor and the free energy of mixing. Special assumptions and models are unnecessary. On the basis of these results the fluctuation theory of a polymer blend could be further developed.

REFERENCES

- 1 Flory, P.J., "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, New York, 1953, p.509
- 2 Nies, E., Wang, S.J., Janssen, R.H.C. and Cifra, P., *Macromolecules*, 1999, 32: 2016
- 3 Dudowitz, J., Fleed, K.F. and Madder, W.G., *Macromolecules*, 1990, 23: 4803
- 4 Schweiger, K.S. and Curro, J.G., *J. Chem. Phys.*, 1989, 91: 5059
- 5 Li, X.Y. and Zhao, D.L., *Acta Polymerica Sinica* (in Chinese), 2003, 21(4): 581
- 6 Li, X.Y. and Zhao, D.L., *J. Chem. Phys.*, 2003, 119(7): 3996
- 7 Landau, L.D. and Lifschitz, E.M., "Statistical Physics, Part 1, 3rd", Pergamon Press, Oxford, 1986, p.333
- 8 de Gennes, P. G., "Scaling Concepts in Polymer Physics", Cornell Univ. Press, Ithaca, New York, 1979, p.109
- 9 Benoit, H. and Benmouna, M., *Macromolecules*, 1984, 17: 535
- 10 Shibayama, M., Yang, H., Stein, R.S. and Han, C.C., *Macromolecules*, 1985, 18: 2179
- 11 Bingder, K., *J. Chem. Phys.*, 1983, 79: 6387
- 12 Curro, J.G. and Schweizer, K.S., *Macromolecules*, 1991, 24: 6736
- 13 Bawendi, M.G. and Freed, K.F., *J. Chem. Phys.*, 1988, 88: 2741