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Effect of composition dependent Flory interaction parameter χ on polymer adsorption theory

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Abstract

Theories of polymer adsorption which neglect the functional dependence of Flory interaction parameter on polymer concentration may result in inconsistent predictions for the adsorption quantities. In this paper, the effect of variation of Flory interaction parameter χ with concentration on polymer adsorption at solid/solution interface is discussed. Comparison with the results for constant χ shows that this effect is significant and cannot be ignored.

1 Introduction

The interfacial phenomenon in polymer solution has attracted a wide variety of scientific interests both theoretically and experimentally due to its numerous industrial applications such as colloid suspension, adhesion, artificial organs and so on. Most existing theories[1–4] of polymer adsorption are based on a mean-field lattice model without the consideration of the dependence of the Flory interaction parameter χ on polymer concentration. However, it is well known that the Flory interaction parameter χ is strongly concentration dependent and therefore expected to be different at different position in the interfacial region. For example, in polystyrene- ethylbenzene solution, the χ value increases from 0.5 to over 1.0 at 35 $°C$ as the polystyrene concentration increases from near zero to 0.9. For solutions involving polar solvents, the situation can be more complicated since the interaction parameter may not be a monotonic function of concentration (displaying a maximum as conentration increases). In this case, the adsorption isotherm may not be the standard high affinity type. Hence, theories ignoring the concentration dependence of χ may lead to inconsistent predictions for the properties of polymer adsorption in most cases of interest becasue as long as the attractive force between the surface and polymer segments is not too small, the concentration gradient near the surface can be very high.

In this paper, we modified a lattice theory for polymer adsorption[5,6] by allowing χ to vary with concentration. The results are compared with those without such a consideration.

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2 Concentration dependence of χ

The interaction parameter χ was first introduced in the well known Flory-Huggins theory of polymer solution, which has been widely used to interpret thermodynamic properties of polymer solutions. The equation for free energy per lattice site is given by

$$\frac{\Delta F}{NkT} = \phi_1 \ln \phi_1 + \frac{1}{r}\phi_p \ln \phi_p + \chi \phi_1 \phi_p \tag{1}$$

where ϕ_1 and ϕ_p are the volume fraction of solvent and polymer segment,respectively; and N is the total number of polymer segments and solvent molecules in the system. In the classic Flory-Huggins theory, the interaction parameter χ was considered to be independent of concentration. This conclusion arises from the assumption that the probability of solvent contact with segments equals the volume fraction of polymer segments. In reality, the interaction parameter can be a strong function of polymer concentration. Although neglecting the concentration dependence of χ may not cause significant error for homogeneous polymer solutions, this is not the case for inhomogeneous systems. As mentioned earlier, when polymer solution is in contact with a solid wall with adsorbing potential, the concentration gradient can be extremely high near the wall, resulting in much difference in χ from point to point in the interfacial region. For nonpolar polymers in nonpolar solvents, the interaction parameter usually increases with polymer concentration. However, for polar solvents, the situation is very complicated. For instance, in the case of aqueous polymer solution, the χ increases slightly with ϕ_p at low concentration in some case, passes through a maximum and then decreases at higher concentration[8]. In other cases, χ parameter may increase or decreases with concentration monotonically. In this paper, we limit our discussion to the case of nonpolar polymer in nonpolar solvents. Several attempts have been made to account for the concentration dependence of χ on concentration[7-9]. Orofino and Flory have suggested that the interaction parameter can be written as the perturbation expansion form

$$\chi = \chi_1 + \chi_2 \phi_p + \chi_3 \phi_p^2 + \ldots \tag{2}$$

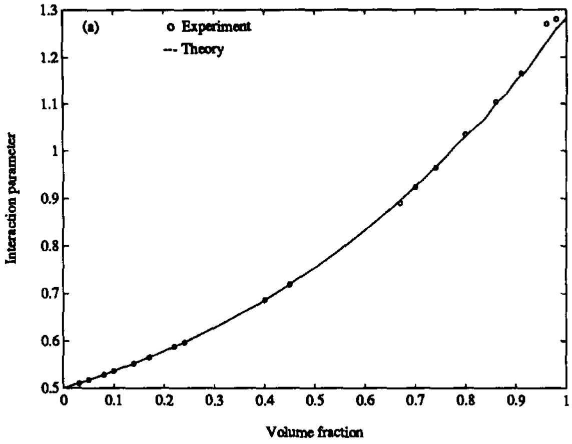
To use this equation, we need to determine the values for the higher order interaction parameters χ_i ($i = 2, 3, \ldots$), but this results in much difficulty. Evans and Napper[7] showed that when the interaction between polymer chains vanishes (in θ solvent), the variation of χ with concentration can be represented as equation 2 with $\chi_i = 1/(i+1)$ for all positive integral values of i. This suggests that near the θ point $\chi_1 = \frac{1}{2}$, $\chi_2 = \frac{1}{3} = \frac{2}{3}\chi_1$ and $\chi_3 = \frac{1}{4} = \frac{1}{2}\chi_1$. Therefore, we may adopt the following simplifying form for the interaction parameter

$$\chi = \chi_1 (1 + \frac{2}{3}\phi_p + \frac{1}{2}\phi_p^2) \tag{3}$$

Comparison of this equation against some experimental data shows that this simple equation is quite accurate over almost the entire concentration range(see Figure 1a).

Another suggestion is to use surface fraction instead of volume fraction as a measure of the molecular contact probability[8]. The surface fraction can be written in terms of volume fraction as

$$\Theta = \frac{1-\gamma}{1-\gamma\phi_p}\phi_p \tag{4}$$



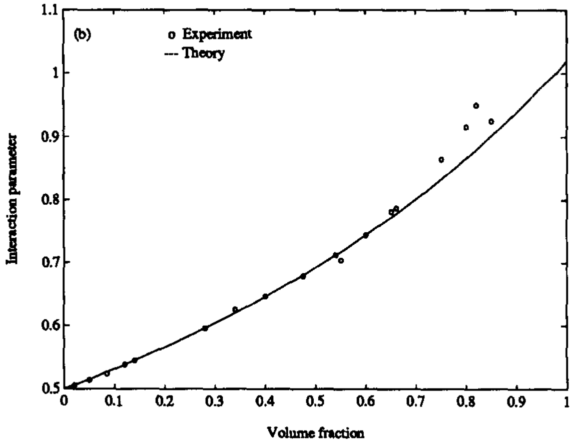


Figure 1: The concentration dependence of Flory interaction parameter χ: (a)comparison of the experimental points with equation (3) for poly(isobutylene) in benzene at 298K (ref.9).; (b) comparison of the experimental points with equation (5) for polystyrene in cyclohexane at 35°C (ref. 8).

where $\gamma = 2/Z$ in the lattice theory and $\gamma = 1 - \sigma_2/\sigma_1$ in the off-lattice model (σ_1 and σ_2 are surface area per unit volume of solvent molecules and polymer segments, respectively). In this case, the interaction parameter is found to be

$$\chi = \chi_0 \frac{1-\gamma}{(1-\gamma\phi_p)^2} \tag{5}$$

where χ_o is a constant. For polystyrene in cyclohexane, γ is found to be 0.3 experimentally, which is in agreement with the value calculated using $\gamma = 2/Z$ for simple cubic lattice (see Figure 1b).

3 Theory

Existing theories of polymer adsorption based on mean-field model yield similar predictions for macroscopic properties of adsorption such as concentration profiles, adsorbed amount and so on. In this paper, we use the theory first developed by Helfand[6] and modified later by the authors[5] as an example to illustrate the effect of incorporating the concentration dependence of χ. The theoretical derivation for the free energy of interfacial system[5,6] will not be reproduced here. The free energy expression can be written as follows

$$\begin{aligned}\frac{\Delta F^{mix}}{S_0 k_B T} &= \sum_i \sum_{s=1}^{r-1} \frac{\phi_p^i}{r} t(s,i) \cdot [m g_i^+ \ln g_i^+ + (1-2m) g_i^0 \ln g_i^0 + m g_i^- \ln g_i^-] \\ &\quad + \sum_i [\phi_1^i \ln \phi_1^i + \frac{1}{r} \phi_p^i t(1,i) \ln \phi_p^i t(1,i)] \\ &\quad + \sum_i^L \chi^i \phi_1^i [m \phi_p^{i+1} + (1-2m)\phi_p^i + m\phi_p^{i-1}] + \chi_{sp}\phi_p^1 + \chi_{s1}\phi_1^1\end{aligned} \tag{6}$$

where ϕ_p^i and ϕ_1^i are the concentrations of segments and solvent in layer i, respectively; S_0 is the number of lattice site in each layer and $t(s,i)$ is the relative contribution of segment s in a chain in layer i; and χ_{sp} and χ_{s1} are the adsorption energy of segment and solvent molecule, respectively; and g_i^+,g_i^0,g_i^- are anisotropic factors of layer i which account for the orientational preference of a segment toward layer $i+1$, i, and $i-1$, respectively; m is the fraction of nearest neighbors of any lattice site in its adjacent layer. The Flory-Huggins interaction parameter χ^i is written in terms of layer concentration ϕ_p^i(equation 3 or 5). For the sake of simplicity, we set $t(s,i) = 1$ for all s and i, this is equivalent to assuming that the ranking number of segments in a chain does not affect the adsorption probability. We believe that this will not influence our result significantly as far as the effect of χ is concerned.

There are two constraints on the anisotropic factors. The first one is the normalization condition

$$m g_i^+ + (1-2m) g_i^0 + m g_i^- = 1 \tag{7}$$

The second is the continuity requirement

$$\phi_p^i g_i^+ = \phi_p^{i+1} g_{i+1}^- \tag{8}$$

Now we can minimize the free energy with respect to ϕ_p^i and g_i^ν subject to the constraints 7 and 8 by assigning Lagrange multipliers to these constraints, i.e. α_i for equation 7 and β_i for equation 8. Minimization yields:

$$\begin{cases} g_i^+ = \exp(-\alpha_i - \beta_i) \\ g_i^0 = \exp(-\alpha_i) \\ g_i^- = \exp(-\alpha_i + \beta_{i-1}) \end{cases} \tag{9}$$

and

$$\begin{aligned} &-\alpha_i(1-\frac{1}{r}) - \ln(1-\phi_p^i) + \frac{1}{r}(\ln\phi_p^i + 1) \\ &< \chi\phi_p >^i - \chi^i < \phi_p >^i + (1-\phi_p^i) < \phi_p >^i \frac{d\chi^i}{d\phi_p^i} - \chi_s\delta(i-1) \\ &+ \ln(1-\phi_p^*) - \frac{\ln\phi_p^*}{r} + \chi(2\phi_p^* - 1) + \frac{d\chi^*}{d\phi_p^*} - \frac{1}{r} = 0 \quad i = 1, 2, ..., L \end{aligned} \tag{10}$$

where $\chi_s = \chi_{s1} - \chi_{sp}$ is the adsorption energy required to displace one adsorbed solvent molecule by one polymer segment, δ is the Kronecker delta function, ϕ_p^* and χ^* are concentration and interaction parameter for the bulk phase, respectively; $< \phi_p >^i = m\phi_p^{i+1} + (1-2m)\phi_p^i + m\phi_p^{i-1}$ and $< \chi\phi_p >^i = m\chi_{i+1}\phi_p^{i+1} + (1-2m)\chi_i\phi_p^i + m\chi_{i-1}\phi_p^{i-1}$.

4 Results of computation

Now we present some results for concentration profile, surface excess computed from the modified theory, and compare them against those for constant χ. The concentration profile is a plot of concentration against distance from the surface with the distance expressed in number of layers. The layer thickness is expected to be the size of segment length. The surface excess is defined by the following equation

$$\Gamma = \sum_{i=1}^{L}(\phi_p^i - \phi_p^*) \tag{11}$$

where ϕ_p^* is the bulk concentration. In the present calculation, our objective is to see how the concentration dependence of χ influences our predictions. Two set of calculations were performed. In the first set, χ in the interfacial region is assumed constant and equal to the bulk value evaluated using equation 3. In the second set, χ is allowed to vary with layer concentration according to the following equation

$$\chi^i = \chi_1(1 + \frac{2}{3}\phi_p^i + \frac{1}{2}(\phi_p^i)^2) \tag{12}$$

and its derivative is

$$\frac{d\chi^i}{d\phi_p^i} = \chi_1(\frac{2}{3} + \phi_p^i)$$

Inserting them in equation 10 and combining with equation 7-9, we can obtain the concentration profiles and layer anisotropic factors near the surface. In all the calculations, hexagonal lattice model ($m = 0.25$) is adopted.

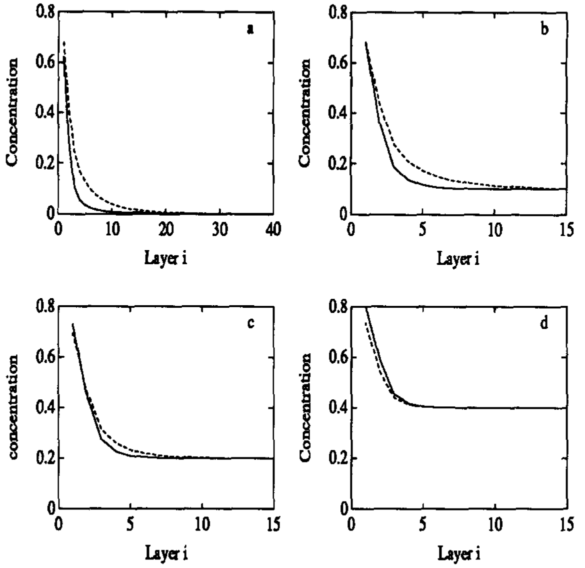


Figure 2: Plots of concentration profiles of polymer segments near solid surface at different bulk concentrations for $r = 1000$, $\chi_1 = 0.5$, $\chi_s = 1.0$. (a)$\phi_p^* = 0.001$, (b)$\phi_p^* = 0.1$, (c)$\phi_p^* = 0.2$ and (d)$\phi_p^* = 0.4$; – – – – constant χ(evaluated at ϕ_p^*),——— concentration dependent χ.

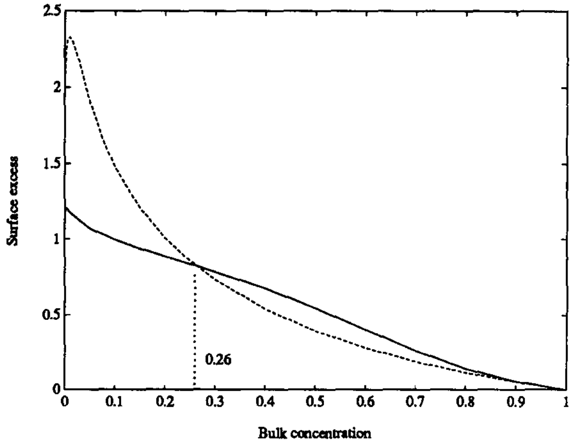


Figure 3: A plot of surface excess vs. bulk concentration for $r = 1000$, $\chi = 0.5$ and $\chi_s = 1.0$ (hexagonal lattice). – – – – for constant χ and ——— for concentration dependent χ_i

Figure 2 shows the concentration profiles of polymer segments near the surface for $r = 1000$, $\chi_1 = 0.5$ and $\chi_s = 1.0$ at four different ϕ_p^*. At the lower bulk concentration $\phi_p^* = 0.001$, it is shown that correction of concentration dependence of χ lead to lower concentration in the surface region(Fig 2a). However, at higher ϕ_p^* (Fig 2d), the situation is reversed. This can be explained as follows. Since equation 3 indicates that the interaction parameter χ is a monotonic function of concentration, incorporation of concentration dependence of χ increases the interaction or chemical potential of polymer segments in both bulk and interfacial region as ϕ_p^* increases from Figure 2a to Figure 2d. Therefore, the overall effect of incorporating a concentration dependent χ is determined by the balance between the amount of chemical potential increase in the regions. There exists a critical bulk concentration ϕ_p^{*c} (e.g. ϕ_p^{*c}=0.26 in Fig. 3) for every χ_1 at which variation of χ with concentration has no effect on adsorption. At lower ϕ_p^* ($\phi_p^* < \phi_p^{*c}$), the concentration in the interfacial region can be nevertheless very high; the amount of chemical potential increase in bulk due to correction of χ is smaller than that in the interfacial region, driving segments from interfacial region into the bulk phase, working against adsorption. The reverse is true at higher ϕ_p^* ($\phi_p^* > \phi_p^{*c}$). Here the amount of chemical potential increase in bulk due to correction of χ is larger than that in the interfacial region, thus favoring adsorption. This is illustrated in Figure 3.

5 Conclusion

From the results presented above, we can conclude that the concentration dependence of Flory interaction parameter cannot be neglected in the case of polymer adsorption from solution or in any nonuniform system with significant concentration gradient. Failure to take this into consideration may lead to erronous or inconsistent results for thermodynamic properties, such as adsorption isotherm, surface tensions, and so on. In addition to being concentration dependent, the interaction parameter χ can also be a function of concentration gradient when the concentration gradient is extremely high. Therefore for a nonuniform polymer solution system, χ can be written as

$$\chi = \chi(\phi_p, \nabla\phi_p, \nabla^2\phi_p, ...) \tag{13}$$

and the use of equation 12 alone would be inadequate. Unfortuately, there is no theory which can quantitatively describe this functional dependence of χ on both concentration and concentration gradient.

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