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A perturbation correction of the Flory-Huggins polymer solution theory

G.A.Mansoori*

University of Illinois at Chicago,
810 S. Clinton Street, Chicago,
IL 60607–7000 USA

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A perturbation theory modification of the Flory-Huggins polymer solution theory is presented. The proposed perturbation equation utilizes the results by Tukur et al [J. Chem. Phys. 110 (7), 3463, 1999] for hard-sphere binary mixture at infinite size ratio. The resulting perturbation theory equations are used to predict properties of three different polymers with different molecular weights in different solvents. Comparison of the proposed perturbation calculations with those of the Flory-Huggins theory and the experimental data indicate that the proposed perturbation method appreciably improves the prediction of polymer solution properties especially at large polymer/solvent size ratios.

Key words: *perturbation theory, Flory-Huggins theory, hard-sphere equation*

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1. Introduction

Various statistical mechanical theories of polymer solutions have been developed during the last half a century. The original and one of the best known of these theories is the Flory-Huggins theory [1,2]. It is shown that the Flory-Huggins theory is a rather crude approximation for polymer solutions when the polymer to solvent size ratio increases [3]. There have been several attempts to improve the predictive capability of the Flory-Huggins theory [4–9] by empirical modification of its interaction parameter (χ). In the perturbation modification of the Flory-Huggins theory presented here the original expression of the polymer solution theory and

*E-mail: mansoori@uic.edu

its interaction parameter are retained. However, additional terms are added to the Flory-Huggins equation correcting its asymptotic value at infinite size ratio and at infinite temperature.

According to the Flory-Huggins theory [10] for the mixture of a polymer and a solvent the following expression holds for the Gibbs free energy of mixing ΔG_{M}:

$$\Delta G_{\mathrm{M}}^{\mathrm{FH}} = RT\left(n_1 \ln\varphi_1 + n_2 \ln\varphi_2 + \chi_1 n_1 \varphi_2\right), \tag{1}$$

where n_i and φ_i are number of moles and volume fraction of component i, respectively, and χ_1 is the Flory-Huggins interaction parameter. According to equation (1), the expressions for activities of solvent (1) and polymer (2) are as follows:

$$\ln a_1^{\mathrm{FH}} = \ln\varphi_1 + \left(1 - \frac{1}{r}\right)\varphi_2 + \chi_1\varphi_2^2, \tag{2}$$

$$\ln a_2^{\mathrm{FH}} = \ln\varphi_2 - (r-1)(1-\varphi_2) + \chi_1 r(1-\varphi_2)^2. \tag{3}$$

In the above equations a_i^{FH} and φ_i are activity and volume fraction of component i, *respectively*, and r is segment fraction which is the ratio of molecular volume of polymer to molecular volume of solvent i.e. :

$$r \equiv (\nu_2/\nu_1) = (\sigma_2/\sigma_1)^3, \tag{4}$$

where, ν_1, ν_2 are molecular volume and σ_1 and σ_2 are molecular diameters of solvent and polymer, respectively. The Flory-Huggins interaction parameter (χ_1) has the following definition:

$$\chi_1 \equiv z\Delta w_{12} x_1/kT, \tag{5}$$

which is a dimensionless quantity [10] that characterizes the interaction energy per solvent molecule divided by kT. In equation (5) z is coordination number and Δw_{12} is interchange energy.

From the expressions of the activities, equations (2) and (3), the following equations for the excess Gibbs free energy over an ideal solution, entropy of dilution and enthalpy of dilution of the polymer and solvent for the binary polymer plus solvent mixture are derived:

$$\begin{aligned} \frac{G_{\mathrm{FH}}^{\mathrm{E}}}{RT} &= x_1\left[\ln\varphi_1 + \left(1-\frac{1}{r}\right)\varphi_2 + \chi_1\varphi_2^2 - \ln x_1\right] \\ &\quad + x_2\left[\ln\varphi_2 + (r-1)\varphi_1 + \chi_1 r\varphi_1^2 - \ln x_2\right]. \end{aligned} \tag{6}$$

According to equations (2), (3) and (5) :

$$\Delta\bar{S}_1^{\mathrm{FH}} = -R\left[\ln\varphi_1 + \left(1-\frac{1}{r}\right)\varphi_2\right], \tag{7}$$

$$\Delta\bar{S}_2^{\mathrm{FH}} = -R\left[\ln\varphi_2 - (r-1)\varphi_1\right] \tag{8}$$

and also:

$$\Delta \bar{H}_1^{\mathrm{FH}} = RT\varphi_2^2\chi_1\,, \tag{9}$$

$$\Delta \bar{H}_2^{\mathrm{FH}} = RTr\varphi_1^2\chi_1\,. \tag{10}$$

In the above equations $\Delta \bar{S}_i^{\mathrm{FH}}$ and $\Delta \bar{H}_i^{\mathrm{FH}}$ are entropy of dilution and enthalpy of dilution of component i.

Considering the equation (1) it can be shown that:

$$\lim_{\sigma_i \to 0} \left(\frac{\partial G_{\mathrm{FH}}^{\mathrm{E}}/RT}{\partial \sigma_i} \right)_{T,P,\sigma_{j \neq i}} = 0. \tag{11}$$

This equation indicates that according to the Flory-Huggins theory the partial derivative of the excess Gibbs free energy of the mixture at the hard sphere limit ($T \to \infty$) and at infinite size ratio limit ($\sigma_i \to 0$) diminishes.

Recently Tukur et al [11] showed that for a binary hard sphere mixture of infinite size difference the following expression is rigorously valid for partial derivative of the excess Helmholtz free energy, A^{E}, of the polymer+solvent mixture with respect to the molecular diameter of solvent when the solvent diameter approaches zero:

$$\lim_{\sigma_i \to 0} \left(\frac{\partial A_{\mathrm{hs}}^{\mathrm{E}}/RT}{\partial \sigma_i} \right)_{T,V,\sigma_{j \neq i}} = \frac{\pi/2 \cdot N_{\mathrm{A}} \rho x_i x_j \sigma_j^2}{1 - \pi/6 \cdot N_{\mathrm{A}} \rho x_j \sigma_j^3}\,, \tag{12}$$

where ρ, N_{A}, x_i, σ_i and T are mixture density, Avogadro's number, mole fraction of component i, molecular size of component i and absolute temperature, respectively. This expression can be applied for the excess Gibbs free energy, G^{E}, assuming the excess volume of the mixture is negligible, i.e.

$$\lim_{\sigma_i \to 0} \left(\frac{\partial G_{\mathrm{hs}}^{\mathrm{E}}/RT}{\partial \sigma_i} \right)_{T,P,\sigma_{j \neq i}} = \frac{\pi/2 \cdot N_{\mathrm{A}} \rho x_i x_j \sigma_j^2}{1 - \pi/6 \cdot N_{\mathrm{A}} \rho x_j \sigma_j^3} \qquad \text{for} \quad \nu^{\mathrm{E}} = 0. \tag{13}$$

In the following section we utilize equation (13) in a perturbation correction of the Flory-Huggins theory of polymer solutions.

2. Perturbation modification of the Flory-Huggins theory

Considering that the infinite temperature limit is practically equivalent to the hard-sphere limit and comparing equations (11) and (13) it is obvious that the hard-sphere limit ($T \to \infty$) at the infinite size ratio ($\sigma_1 \to 0$) as predicted by the Flory-Huggins equation is not correct. This indicates that the Flory-Huggins expression for excess Gibbs is the first term of the double perturbation expansion of excess Gibbs with respect to powers of (σ_1) and ($1/T$),

$$\frac{G^{\mathrm{E}}}{RT} = \frac{G_{\mathrm{FH}}^{\mathrm{E}}}{RT} + \left(\frac{\partial \left(\frac{G_{\mathrm{FH}}^{\mathrm{E}}}{RT} \right)}{\partial \sigma_1} \right)_{\sigma_1 = 0} \cdot \sigma_1 + \left(\frac{\partial \left(\frac{G_{\mathrm{FH}}^{\mathrm{E}}}{RT} \right)}{\partial \left(\frac{1}{T} \right)} \right)_{T = \infty} \cdot \left(\frac{1}{T} \right) + \text{higher order terms.} \tag{14}$$

Now, by integrating equation (13) with respect to σ_1 and $(1/T)$ and replacing for the second and third terms in equation (14) and neglecting the higher order terms, of the orders of $O[\sigma_1]^2$, $O[\sigma_1(1/T)]$, $O[1/T]^2$ and higher, the following expression for the perturbation modification of the Flory-Huggins excess Gibbs free energy will be derived [12,13]:

$$\begin{aligned}\frac{G^{\mathrm{E}}}{RT} &= \frac{G^{\mathrm{E}}_{\mathrm{FH}}}{RT} + \Big\{ 3\left[(\eta_1/(1-\eta_1))(s-1)/x_1 + (\eta_2/(1-\eta_2))(s^{-1}-1)/x_2\right] \\ &\quad + \left[\alpha(\eta_1(Es-1)/x_1 + \eta_2(s^{-1}-1)/x_2)\right]\frac{1}{RT}\Big\} x_1 x_2 \,. \end{aligned} \tag{15}$$

In this equation

$$\alpha = f\varepsilon_2\,, \qquad E = \varepsilon_2/\varepsilon_1\,. \tag{16}$$

s represents the ratio of molecular diameters of polymer to solvent, i.e.

$$s \equiv \sigma_2/\varrho_1 = r^{1/3} \equiv (\nu_2/\nu_1)^{1/3}\,, \tag{17}$$

and η_i is the packing fraction of component i in the mixture,

$$\eta_i \equiv \frac{\pi}{6} N_{\mathrm{A}} \rho x_i \sigma_i^3, \tag{18}$$

equation (15) can predict the exact asymptotic value given by equation (13). In what follows equation (15) is used to calculate the properties of various polymer solutions with different polymer/solvent size ratios and comparisons are made with the Flory-Huggins theory. It is shown that the proposed perturbation expression is capable of predicting polymer solution properties more accurately than the Flory-Huggins theory when the size difference between the polymer and solvent increases. Starting with equation (15), expressions for the other thermodynamic properties of polymer solution can be derived:

The expressions for the activity of solvent, $a_1 = x_1\gamma_1$, and activity of polymer, $a_2 = x_2\gamma_2$, are derived as follows [12]:

$$\begin{aligned}\ln a_1 &= \ln a_1^{\mathrm{FH}} + \Big\{ 3\left(\frac{\eta_1/x_1(s-1)}{(1-\eta_1)^2} + \frac{\eta_2/x_2(s^{-1}-1)(1-\eta_2/x_2)}{(1-\eta_2)^2}\right) \\ &\quad \times \frac{\alpha}{RT}\left(\eta_1/x_1(Es-1) + (s^{-1}-1)\eta_2/x_2\right)\Big\} x_2^2 \end{aligned} \tag{19}$$

and

$$\begin{aligned}\ln a_2 &= \ln a_1^{\mathrm{FH}} + \Big\{ 3\left(\frac{\eta_1/x_1(1-\eta_1/x_1)(s-1)}{(1-\eta_1)^2} + \frac{\eta_2/x_2(s^{-1}-1)}{(1-\eta_2)^2}\right) \\ &\quad \times \frac{\alpha}{RT}\left(\eta_1(Es-1)/x_1 + \eta_2(s^{-1}-1)/x_2\right)\Big\} x_1^2 \end{aligned} \tag{20}$$

since $\ln\gamma_i = \left(\partial\left(nG^{\mathrm{E}}/RT\right)/\partial n_i\right)_{T,P,n_{j\neq i}}$ and $a_i = x_i\gamma_i$. In these equations a_1^{FH} and a_2^{FH} are the Flory-Huggins solvent and polymer activities, respectively as given by equations (2) and (3). Expressions for activities of solvent and polymer and equation (5), can be used to derive the following equation for the entropy of dilution, $\Delta S_i = -R\left[\partial(T\ln a_i)/\partial T\right]_{P,\varphi_2}$ of solvent due to addition of the polymer:

$$\Delta\bar{S}_1 = \Delta\bar{S}_1^{\mathrm{FH}} - 3R\left(\frac{\eta_1/x_1(s-1)}{(1-\eta_1)^2} + \frac{\eta_2/x_2(1/s-1)(1-\eta_2/x_2)}{(1-\eta_2)^2}\right)x_2^2 \tag{21}$$

and

$$\Delta\bar{S}_2 = \Delta\bar{S}_2^{\mathrm{FH}} - 3R\left(\frac{\eta_1/x_1(1-\eta_1/x_1)(s-1)}{(1-\eta_1)^2} + \frac{\eta_2/x_2(1/s-1)}{(1-\eta_2)^2}\right)x_2^2\,. \tag{22}$$

Also from the expressions for the activities the following equations for the heat of dilutions, $\Delta\bar{H}_i = -RT^2\left(\partial\ln a_i/\partial T\right)_{P,\varphi_2}$, are derived:

$$\Delta\bar{H}_1 = \Delta\bar{H}_1^{\mathrm{FH}} + \alpha\left[(1/s-1)\eta_2/x_2 + (Es-1)\eta_1/x_1\right]x_2^2 \tag{23}$$

and

$$\Delta\bar{H}_2 = \Delta\bar{H}_2^{\mathrm{FH}} + \alpha\left[(1/s-1)\eta_2/x_2 + (Es-1)\eta_1/x_1\right]x_1^2\,. \tag{24}$$

In the following section, the above equations are used to calculate properties of various polymer solutions and the results are compared with the calculations based on the Flory-Huggins relations and experimental data.

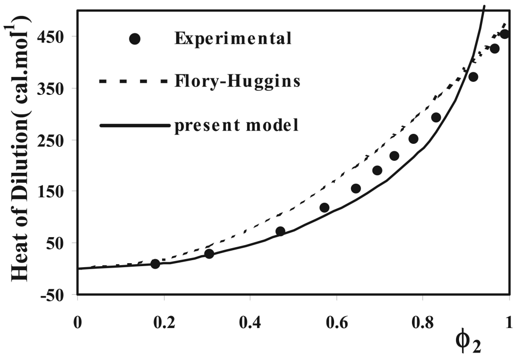

Figure 1. Solvent (1) heat of dilution versus volume fraction of polymer (2) for the solution of benzene (solvent) in PDMS3,850 (polymer) at 25°C. The solid circles are the experimental data [12], the dashed lines are the calculations based on the Flory-Huggins theory and the solid lines are the calculations based on the present perturbation model.

3. Calculations and discussions

In order to test the present perturbation theory model three different polymer+solvent systems with various (solvent/polymer) size ratios, for which experimental data are available [14–16], are used. These systems (Benzene+PDMS3,850,

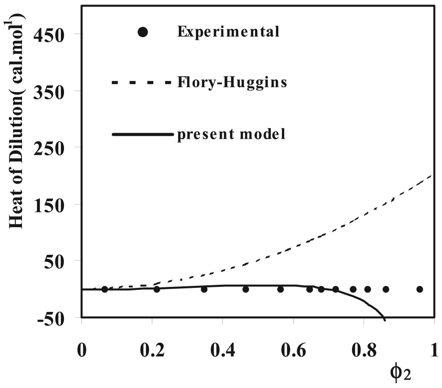

Figure 2. The same as figure 1 but for the system toluene (solvent) in PS290,000 (polymer) and the experimental data is taken from [12].

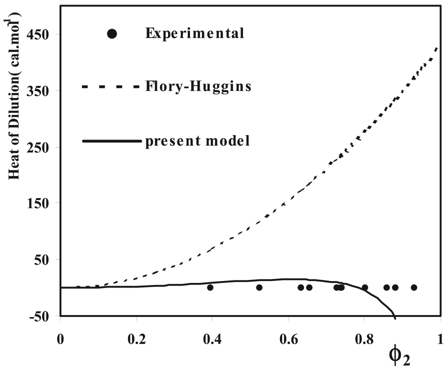

Figure 3. The same as figure 1 but for the system MEK (solvent) in PS290,000 (polymer) and the experimental data is taken from [12].

Table 1. Parameters used for the present study.

system	group-cont. method σ_1 [nm]	E[–]	Flory-Huggins σ_2 [nm]	χ_1 [–]	Perturbation model σ_2 [nm]	χ_1 [–]	α[J/mol] $\times 10^{-3}$
Benzene+PDMS 3,850	0.535	1.620	1.895	0.809	1.500	0.426	–36.271
Toluene+PS 290,000	0.574	1.602	7.797	0.343	6.300	0.114	806.077
MEK+PS 290,000	0.539	1.480	7.732	0.725	6.800	0.149	693.142

Toluene+PS290,000 and MEK+PS290,000) are identical to those used in the original paper of Flory [10]. In the first stage parameters E and η_1 of the polymers are calculated [12] using a group contribution method [17,18]. Parameters χ_1, σ_1 and α are determined [12] using experimental solvent activity data using equation (19). Similarly parameters χ_1 and σ_2 of the Flory-Huggins theory are calculated from the experimental activity data. Numerical values of all these parameters for the three polymer-solvent mixtures are reported in table 1.

The enthalpy of dilution of the solvents in polymer solution systems are calculated using equations (9) and (23). The results of calculations are shown in figures 1–3. According to these figures the proposed perturbation modification generally improves the predictions. As the size difference between polymer and solvent increases, the improved predictions by the perturbation model are more pronounced.

The entropy of dilution of solvents in polymers of the same three systems are predicted and the results are reported in figure 4 based on the present perturbation model and the Flory-Huggins theory. According to this figure, the entropy of dilutions predicted by the Flory-Huggins equation is not in agreement with the

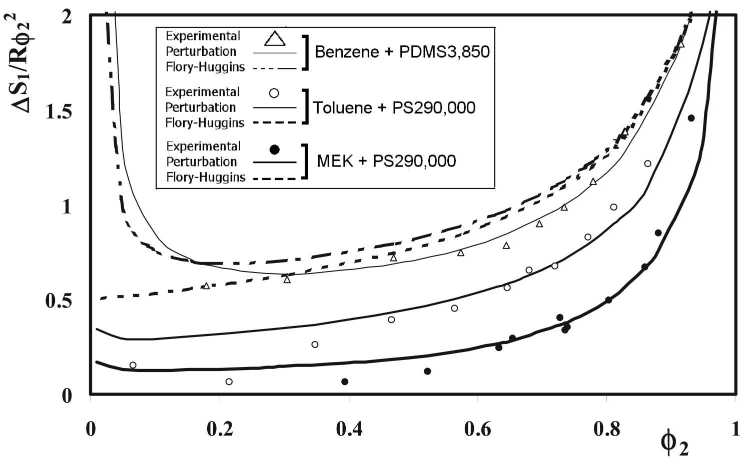

Figure 4. Solvent (1) entropy of dilution versus volume fraction of polymer (2) for three different solvent+polymer mixtures (Benzene+PDMS3,850, Toluene+PS290,000 and MEK+PS290,000) at 25°C. In this figure predictions by the present perturbation model are compare with the Flory-Huggins theory and the experimental data [12,13].

experimental data specially for high molecular weight polymers while the calculations by the perturbation model are in very good agreement with the experimental data both for low and high molecular weight polymers. The entropy of dilutions predicted by the Flory-Huggins theory, for high molecular weight polymer solutions (Toluene+PS290,000 and MEK+PS290,000) are in error, nearly constant, and independent of the polymer under consideration.

The results reported in this paper demonstrate the major improvement in predicting polymer solution properties using the proposed perturbation modification of the Flory-Huggins theory. The improvement becomes more appreciable for polymer solutions with large size difference between the polymer and solvent.

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Покращення на основі теорії збурень теорії Флорі-Хаггінса для полімерних розчинів

Г.А.Мансурі

Ілінойський університет Чикаго, Чикаго, США

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Представлено покращення теорії полімерних розчинів Флорі-Хаггінса на основі теорії збурень. Запропоноване рівняння збурення використовує результати Тукур та ін. [J. Chem. Phys. 110 (7), 3463, 1999] для бінарної суміші твердих сфер для безмежно великого співвідношення розмірів. Отримані рівняння теорії збурень використовуються для передбачення властивостей трьох різних полімерів з різною молекулярною вагою і у різних розчинниках. Порівняння отриманих результатів я результатами теорії Флорі-Хаггінса і експериментальними даними показує, що запропонований метод збурень суттєво покращує розрахунок властивостей полімерних розчинів, особливо у випадку великих співвідношень розмірів полімера і розчинника.

Ключові слова: *теорія збурень, теорія Флорі-Хаггінса, рівняння твердих сфер*

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