

approximated, $(A^E)_{T,p} \approx (G^E)_{T,p}$ [43], and eqn (1) can be written for the excess Gibbs free energy, G^E as:

$$\lim_{\sigma_i \rightarrow 0} \left(\frac{\partial G_{hs}^E / RT}{\partial \sigma_i} \right)_{T,P,x,\sigma_{j \neq i}} = \frac{\frac{\pi}{2} N_A \rho x_i x_j \sigma_j^2}{1 - \frac{\pi}{6} N_A \rho x_j \sigma_j^3} \quad (2)$$

The excess Gibbs free energy in Flory-Huggins theory, G_{FH}^E , is in the following form [44]:

$$\frac{G_{FH}^E}{RT} = x_1 \left[\ln \phi_1 + \left(1 - \frac{1}{r}\right) \phi_2 + \chi_{12} \phi_2^2 - \ln x_1 \right] + x_2 \left[\ln \phi_2 - (r-1) \phi_1 + \chi_{12} r \phi_1^2 - \ln x_2 \right] \quad (3)$$

where, ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively, and χ_{12} is the interaction parameter and r is the segment number. The segment number can be approximated as the ratio of molar volume of polymer (v_2) to molar volume of solvent (v_1) and can be represented as: $r = \frac{v_2}{v_1}$. Also, the following relation represents r as the ratio of molecular diameter of polymer (σ_2) to that of solvent (σ_1):

$$r = \frac{v_2}{v_1} = \frac{\frac{4}{3} \pi \left(\frac{\sigma_2}{2}\right)^3 N_0}{\frac{4}{3} \pi \left(\frac{\sigma_1}{2}\right)^3 N_0} = \left(\frac{\sigma_2}{\sigma_1}\right)^3 \quad (4)$$

where, N_0 is the Avogadro's number.

It can be shown that Flory-Huggins excess Gibbs function, as expressed by eqn (3), cannot satisfy the hard sphere limit required by eqn (2):

$$\lim_{\sigma_1 \rightarrow 0} \left(\frac{\partial G_{FH}^E / RT}{\partial \sigma_1} \right)_{T,P,x,\sigma_2} = 0 \quad (5)$$

It is obvious that the hard sphere limit of G_{FH}^E is in contrast with the non-zero limit predicted by eqn (2) and it needs an extension to satisfy this limit.

In the extension of Flory-Huggins excess Gibbs function for satisfying the hard sphere limit we take the advantage of perturbation theory approach and consider G_{FH}^E as a reference state and then add a ΔG^E as a perturbation term for the hard-sphere limit:

$$G^E = G_{FH}^E + \Delta G^E \quad (6)$$

where, G_{FH}^E is given by eqn (3) and the perturbation term ΔG^E will be obtained in the following manner:

For a binary mixture of solvent (1) and polymer (2) the hard-sphere limit of eqn (2) can be expressed in terms of packing fraction η_i as:

$$\lim_{\sigma_i \rightarrow 0} \left(\frac{\partial G^E / RT}{\partial \sigma_i} \right)_{T,P,x,\sigma_j} = \frac{3}{1-\eta_j} \left(\frac{\eta_j x_i}{\sigma_j} \right) \quad (7)$$

$i, j=1,2$ and $i \neq j$

where,

$$\eta_i \equiv \frac{\pi}{6} N_A \rho x_i \sigma_i^3 \quad (8)$$

is the packing fraction of component i and ρ is the density of the mixture.

To include the deviation of polymer chain from hard-sphere shape and adjust the limit represented by eqn (7) to a real chain, the perturbation term is $\frac{f \varepsilon_i}{RT} \left(\frac{\eta_j x_i}{\sigma_j} \right)$ introduced to the hard sphere limit and then

the final result will be:

$$\lim_{\sigma_i \rightarrow 0} \left(\frac{\partial G^E / RT}{\partial \sigma_i} \right)_{T,P,x,\sigma_j} = \frac{3}{1-\eta_j} \left(\frac{\eta_j x_i}{\sigma_j} \right) + \frac{f \varepsilon_i}{RT} \left(\frac{\eta_j x_i}{\sigma_j} \right) \quad (9)$$

where, ε_1 is the energy parameter, which is a measure of molecular interactions and f/RT has been included to consider both any deviation from the hard-sphere shape for molecules and also the effect of temperature on the molecular interactions. This factor satisfies the requirement that, as $T \rightarrow \infty$ the hard-sphere limit will be approached. It is worth noting that the factor $\eta_i x_i / \sigma_j$ has been introduced to take into account the effect of packing fraction as a measure of the molecular separations.

Integrating eqn (9) for the cases where $i=1$ and $j=2$:

$$\Delta(G^E / RT)_{T,P,x,\sigma_1} = \frac{3}{1-\eta_1} (\eta_1 x_2 s) + \frac{f \varepsilon_1}{RT} (\eta_1 x_2 s) + G(\eta_2, x_1) \quad (10)$$

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