Mixing

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In what follows, all quantities are unitless and extensive quantities are normalised by the number of particles.

Free Energy of Mixing

The free energy of mixing, ΔG_m , in a fluid solution comprising particles A and B can be written as,

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1}$$

where ΔH_m is the enthalpy of mixing, T is the temperature and ΔS_m is the entropy of mixing. A regular solution is the simplest, non-ideal solution model which assumes random mixing of particles in the fluid phase. For a regular solution, ΔS_m is assumed to equal ΔS_m^{ideal} , which is the entropy of mixing in an ideal solution and can be calculated according to,

$$\Delta S_m^{ideal} = \frac{-k_{\rm B}}{(n_A + n_B)} (n_A \ln x_A + n_B \ln x_B)$$

$$= -k_{\rm B} (x_A \ln x_A + x_B \ln x_B)$$
(2)

In the above equation, n and x are the total numbers and number fractions (e.g $x_A = n_A/(n_A + n_B)$) of particles A and B in the fluid.

In an ideal solution $\Delta H_m^{ideal}=0$; however, particle–particle interactions lead to deviations from ideal behaviour in a regular solution. Assuming random mixing of particles A and B in the fluid, the total number of B particles in contact with A particles is $x_A Z n_B$, where Z is the average first-sphere coordination number. Similarly, $x_B Z n_A$ particles of A are in contact with B particles on average. Also

assuming a negligible contribution of the $p\Delta V_m$ term to the enthalpy of mixing, we can determine this quantity according to,

$$\Delta H_m = \frac{1}{2(n_A + n_B)} \left\{ x_A Z n_B (\epsilon_{AB} - \epsilon_{BB}) + x_B Z n_A (\epsilon_{AB} - \epsilon_{AA}) \right\}$$

$$= \frac{Z n_A n_B}{2(n_A + n_B)^2} (2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})$$

$$= \omega x_A x_B$$
(3)

where the factor of one half is introduced to avoid double counting of the pairwise particle interactions, and ϵ are the energies of interaction between a pair of particles with types indicated by the subscript notation. Here we introduce the interaction parameter, $\omega = Z(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})/2$.

Taking these assumptions in the regular solution model, the free energy of mixing can be reformulated:

$$\Delta G_m = \omega x_A x_B + k_B T (x_A \ln x_A + x_B \ln x_B) \tag{4}$$

Only ω in the above equation is unknown. This can be estimated by simulating bulk fluids, with varying x_A and x_B , in the NpT ensemble. Figure 1 shows $\Delta H_m = H(x_B) - H(x_B = 0)$ as a function of x_B from simulations where the Hamaker constant in the colloid pair potential between particles A and B was 55ϵ . A quadratic function was fitted to the data which reveals that $\omega = -3\epsilon$. Also shown in the Figure are curves for ΔS_m and ΔG_m calculated according to Equations 2 and 4 for the case when T=2.

Chemical Potential and Activities

The chemical potential of an ideal solution can be written according to,

$$\mu_{A}^{ideal} = \mu_{A}^{\varnothing} + \mu_{A}^{mixing}$$

$$= \mu_{A}^{\varnothing} + \left(\frac{\partial \Delta G_{m}^{ideal}}{\partial n_{A}}\right)_{T,P,n_{B}}$$

$$= \mu_{A}^{\varnothing} + k_{B}T \frac{\partial}{\partial n_{A}} \left\{ n_{A} \ln \left(\frac{n_{A}}{n_{A} + n_{B}}\right) + n_{B} \ln \left(\frac{n_{B}}{n_{A} + n_{B}}\right) \right\}$$

$$= \mu_{A}^{\varnothing} + k_{B}T \ln x_{A}$$

$$(5)$$

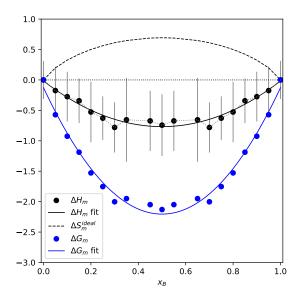


Figure 1: $\Delta H_m = H(x_B) - H(x_B = 0)$ as a function of the number fraction of B particles, x_B , (black points) calculated from simulations in the NpT ensemble containing varying numbers of n_A and n_B and with constant $n_A + n_B$, where T=2 and p=0.0008. Uncertainties of one standard deviation are shown by the error bars. A quadratic fit to the data with functional form $3x_B^2 - 3x_B - 0.02$ is shown by the sold black line. The black dashed line represents the enthalpy of mixing for an ideal solution, ΔS_m^{ideal} , calculated according to Equation 2. The blue points provide $\Delta G_m = \Delta H_m - T\Delta S_m^{ideal}$ and the blue solid line is a fit to this data set with functional form $8.3x_B^2 - 8.3x_B - 0.13$.

where μ_A^{\varnothing} is the chemical potential of a liquid composed purely of A. In the regular solution model, this is modified to include and additional term, $F(x_A)$, which accounts for the chemical interactions between particles,

$$F(x_A) = \left(\frac{\partial \Delta H_m}{\partial n_A}\right)_{T,P,n_B}$$

$$= \omega \frac{\partial}{\partial n_A} \left\{\frac{n_A n_B}{n_A + n_B}\right\}$$

$$= \omega \left(\frac{n_B}{n_A + n_B} - \frac{n_A n_B}{(n_A + n_B)^2}\right)$$

$$= \omega x_B^2$$
(6)

For a regular solution, therefore, the chemical potential is,

$$\mu_A = \mu_A^{\varnothing} + k_{\rm B} T \ln x_A + \omega x_B^2 \tag{7}$$

By defining the activities of A particles as $a_A = x_A f_A$, where $f_A = \exp\left(\frac{\omega x_B^2}{k_B T}\right)$ and is the activity coefficient, the familiar equation results,

$$\mu_A = \mu_A^{\varnothing} + k_{\rm B} T \ln a_A \tag{8}$$

Fluid Demixing and the Phase Diagram

The free energy of mixing profile displayed in Figure 1 indicates a favourable complete mixing of particles A and B in the fluid. This results from the fact that, in the regular solution model, ΔS_m^{ideal} is always positive within the limits $x_A = 0, 1; x_B = 1, 0$ and because $\epsilon_{AB} > \epsilon_{AA} = \epsilon_{BB}$, i.e. $\omega < 0$. As ω is increased and becomes positive, the potential energy of interaction between particles A and B becomes less favourable than the interaction between particles of the same type and ΔH_m is positive, as shown in Figure 2.

Should the contribution of a positive $\Delta H_m(x_A)$ to $\Delta G_m(x_A)$ exceed $-T\Delta S_m^{ideal}(x_A)$, then demixing of the fluid into dense A and B regions occurs. Figure 2 provides ΔH_m and ΔG_m for a range of ω values. As the interaction parameter is increased, two minima emerge in the free energy profiles indicating that the fluids A and B are only partially miscible and with a free energy barrier around $x_A=0.5$ to complete mixing. The average x_A and x_B in the dense A and B regions in the resulting fluids are indicated by the two minima in the ΔG_m profiles when $\omega \geq 4.5\epsilon$. When $\omega = 4.5\epsilon$, the phase separation region, bounded by the values of x_A at the minima, is relatively narrow compared to the case when $\omega = 7.5\epsilon$. Note that increasing T will lead to a narrowing of the phase separation regions, and, when T is sufficiently high, the ΔG_m curve for complete mixing of A and B will result.

The first order derivative of ΔG_m with respect to x_A can be calculated as follows.

$$\frac{d\Delta G_m}{dx_A} = \frac{d}{dx_A} \left\{ \omega x_A (1 - x_A) + k_B T (x_A \ln x_A + (1 - x_A) \ln (1 - x_A)) \right\}
= \omega (1 - 2x_A) + k_B T (\ln x_A - \ln (1 - x_A))$$
(9)

Figure 2 provides the curves resulting from evaluation of the above equation with varying ω . When $\omega < 4.5\epsilon$, $d\Delta G_m/dx_A$ increases monotonically as a function of x_A . The curves for higher values of ω show inflection points and three

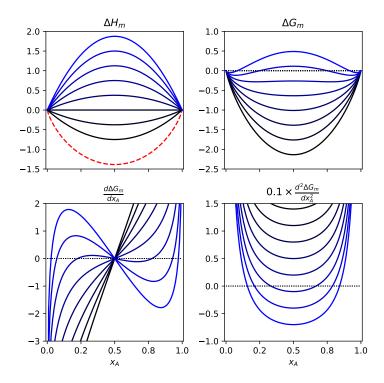


Figure 2: ΔH_m , ΔG_m , $d\Delta G_m/dx_A$ and $d^2\Delta G_m/dx_A^2$ as a function of x_A calculated according to Equations 3, 4, 9 and 10, respectively, and with varying values of ω from -3ϵ to $+7.5\epsilon$ in 1.5 ϵ increments shown by the solid lines with the black—blue colour scale indicating increasing ω . Also provided in the top left panel is $-T\Delta S_m^{ideal}$ shown by the red dashed line and which was calculated using Equation 2. The curves for $d^2\Delta G_m/dx_A^2$ have been scaled by a factor of 0.1.

roots to Equation 9 which provide important information about the T, x_A phase diagram. Between the bounds of $d\Delta G_m/dx_A=0$ around the point $x_A=0.5$ (which correspond to the minima in $\Delta G_m(x_A)$), the system is *metastable* with respect to more stable fluids rich in A and B particles. These points mark the, so-called, binodal points of a binodal curve in the T, x_A phase diagram where phase separation becomes likely. This curve, for the case when $\omega=6\epsilon$, is shown in Figure 3. The average compositions of the resulting fluids at a given T correspond to the values of x_A and $(1-x_A)$ at these points.

Further information about the T, x_A phase diagram can be gained by taking the second order derivative of ΔG_m with respect to x_A :

$$\frac{d^2 \Delta G_m}{dx_A^2} = k_{\rm B} T(x_A^{-1} + (1 - x_A)^{-1}) - 2\omega$$
 (10)

The curves calculated using the above equation are also provided in Figure 2. The minima of the curves when $\omega \geq 4.5\epsilon$ are all below $d^2\Delta G_m/dx_A^2=0$. Indeed, the roots of the equation are called the spinodal points, which mark the boundary of the spinodal region in the T, x_A phase diagram, as highlighted in Figure 3. In this region, the mixed fluid is thermodynamically unstable and will spontaneously phase separate into fluids rich in A and B. Equation 10 can be solved to determine the critical temperature for phase separation, T_c :

$$T_c = \frac{\omega}{2k_{\rm B}} \tag{11}$$

Therefore, at T=2, any AB mixture with $\omega > 4\epsilon$ can be termed 'sub-critical'.

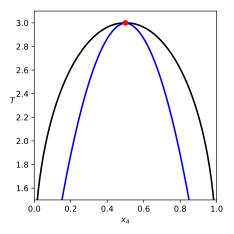


Figure 3: The T, x_A phase diagram for a system of A and B particles with $\omega = 6\epsilon$. The black binodal line marks the boundary of the immiscible region where phase separation occurs. This envelopes the blue spinodal curve marking the region where the mixture is unstable and phase separation is spontaneous. The red point is the critical temperature, T_c .

The spinodal curve lies within the immiscible region—marked by the binodal curve—in the T, x_A phase diagram (see Figure 3). In the immiscible region phase separation becomes likely but not inevitable over short timescales, due to the fact that this is an activated process (outside of the unstable region) with an energy barrier, ΔG^* , to phase separation. ΔG^* can be estimated by drawing a tangent, $f(x_A)$, on the $\Delta G_m(x_A)$ curve at a position, x_A , in the metastable region; ΔG^* is then approximated as the difference in $\Delta G_m(x_A)$ between $f(x_A)$

and a parallel tangent, $f^{||}(x_A)$, drawn around the maximum in $\Delta G_m(x_A)$. The driving force for nucleation is $\Delta \Delta G_m = \Delta G_m(x_A) - \min(\Delta G_m(x_A))$. One can easily see that as x_A is increased towards 0.5 in the metastable region, $\Delta \Delta G_m$ becomes more negative and ΔG^* decreases; this makes nucleation more probable and decreases the rate of phase separation according to classical nucleation theory.

As x_A is further increased, and if nucleation in the metastable region of the phase diagram is not achieved, eventually the system reaches the composition where $d^2\Delta G_m/dx_A^2\approx 0$. Using the above geometrical interpretation of ΔG^* , the barrier to phase separation here is zero. Beyond this point, infinitesimal fluctuations in particle densities will lead to a reduction $\Delta\Delta G_m$. The wavelength of these fluctuations is determined by the diffusivity of particles, and, over time, the amplitude of the density fluctuations increases. Eventually, coarsening via Ostwald ripening leads to two fluid regions with compositions corresponding to the minima in $\Delta G_m(x_A)$.