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Volume Fluctuation Thermodynamics of Polymer Solutions

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ABSTRACT: The idea of "volume fluctuation thermodynamics" is formally developed to show in general terms how solution properties are affected by finite compressibility and by the mismatch in pure-component equation of state properties. For a binary solution, the intensive Gibbs free energy (g) is a function of its three canonical intensive variables: temperature (T), pressure (P), and composition (ϕ). However, an equivalent thermodynamic formulation is to treat g as a function of four independent variables (T, P, ϕ, and v) subject to a minimization condition that determines the equilibrium intensive volume, v. Alternatively, the formalism can be developed as a Legendre transform, which transforms g into itself with v replaced by a field variable that at equilibrium equals zero. This artifice allows the easy separation of constant volume (incompressible) and volume fluctuation (compressible) contributions to solution thermodynamic properties. It also provides convenient recipes for the calculation of thermodynamic properties for any statistical mechanical model. It is shown that the pressure composition coefficient, $(\partial P/\partial\phi)_{T,v}$, plays an important role in solution thermodynamics and reflects to a large degree the mismatch in pure-component equation of state properties. Contrary to popular belief, the magnitude of volume changes on mixing has little to do with equation of state effects on other thermodynamic properties. It is suggested that P-V-T measurements on solutions can be very effective in testing compressible molecular models. Multicomponent systems are also treated. A somewhat counterintuitive conclusion is that sometimes the more degrees of freedom a system has, the more difficult it is to achieve phase stability.

I. Introduction

The purpose of this paper is to show in general terms the contribution of "equation of state effects" to polymer solution thermodynamics. Prigogine and co-workers[1-3] in the 1950s, using corresponding states ideas, appear to have been the first to emphasize the importance of equation of state effects on solution thermodynamic properties. Later Patterson and co-workers[4-9] used and extended these corresponding states ideas to polymer solutions. In the 1960s and 1970s, molecular equation of state models[10-15] were developed and helped to clarify how equation of state contributions affected polymer solution properties. The latter have shown that the compressible nature of a polymer solution and differences in pure-component equation of state properties play an important role in polymer solution thermodynamics. For example, the incompressible classical theory, the Flory–Huggins theory, does not predict lower critical solution temperature behavior, whereas its compressible generalization does.[14-16] However, one does not have to appeal to corresponding states arguments or molecular models to see that finite compressibility and differences in pure-component properties affect solution properties. By use of what we term as "volume fluctuation thermodynamics", general thermodynamic equations will be developed to illustrate the effects of equation of state contributions on polymer solution thermodynamics.

II. Volume Fluctuation Thermodynamics

For the purposes of illustration, let us consider a binary solution of composition ϕ. The concentration variable ϕ may be any defined on [0,1] such as mole fraction (x), weight fraction (w), etc. The extensive Gibbs free energy (G) is in general a function of the temperature T, the pressure P, the total volume V, and the number of moles n_i of each component. However, the intensive Gibbs free energy (g) per mole, per unit mass, etc., of mixture is only a function of intensive variables T, P, v, and ϕ where v is an intensive volume such as the molar volume, specific volume, etc. The appropriate concentration variable is not arbitrary. It should be conjugate to g; i.e., if g is the free energy per mole, then ϕ is the mole fraction; if g is defined per unit volume, then ϕ is a volume fraction, etc. For a binary mixture the total differential of g is given by

$$\mathrm{d}g = \left(\frac{\partial g}{\partial T}\right)_{P,v,\phi} \mathrm{d}T + \left(\frac{\partial g}{\partial P}\right)_{T,v,\phi} \mathrm{d}P + \left(\frac{\partial g}{\partial v}\right)_{T,P,\phi} \mathrm{d}v + \left(\frac{\partial g}{\partial \phi}\right)_{T,P,v} \mathrm{d}\phi \qquad (1a)$$

or in a more compact notation

$$\mathrm{d}g = g_{\{T\}}\,\mathrm{d}T + g_{\{P\}}\,\mathrm{d}P + g_{\{v\}}\,\mathrm{d}v + g_{\{\phi\}}\,\mathrm{d}\phi \qquad (1b)$$

Now at equilibrium, T, P, v, and ϕ are constrained by $g_{\{v\}} = 0$ and thus

$$\mathrm{d}g = g_{\{T\}}\,\mathrm{d}T + g_{\{P\}}\,\mathrm{d}P + g_{\{\phi\}}\,\mathrm{d}\phi \qquad (1c)$$

From classical thermodynamics, we also have

$$\mathrm{d}g = g_T\,\mathrm{d}T + g_P\,\mathrm{d}P + g_\phi\,\mathrm{d}\phi \equiv -s\,\mathrm{d}T + v\,\mathrm{d}P + g_\phi\,\mathrm{d}\phi \qquad (1d)$$

where s is the intensive entropy of the solution. Equation 1c is consistent with the Gibbs phase rule that tells us that, for a two-component, one-phase system, there are only three independent intensive variables. However, the braced subscripts on g indicate that the derivative on g is taken holding three of the intensive variables of the set $\{T,P,v,\phi\}$ constant although only two are independent. Such derivatives on the free energy are termed *unconstrained* derivatives. The derivatives without braces are the ordinary *constrained* derivatives where only two of the variables from the canonical set $\{T,P,\phi\}$ are held constant. Equating eqs 1c and 1d yields

$$g_T \equiv g_{\{T\}} = -s \qquad (2a)$$

$$g_P \equiv g_{\{P\}} = v \qquad (2b)$$

$$g_\phi \equiv g_{\{\phi\}} = \mu_1 - \mu_2 \qquad (2c)$$

where μ_i is the chemical potential of component i.

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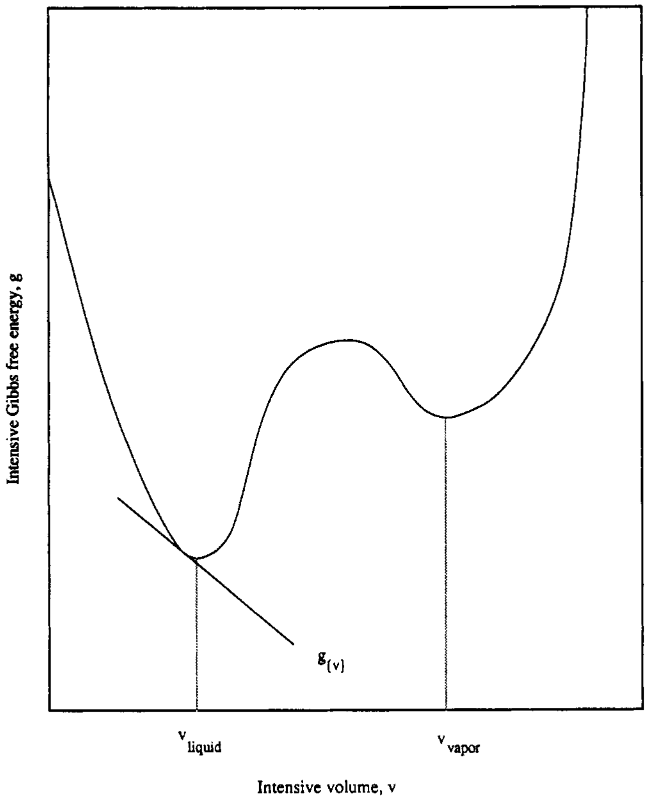

Figure 1. Schematic of the variation of the Gibbs free energy with volume at constant temperature, pressure, and composition. The slope $g_{\{v\}}$ in general does not equal zero. Here the liquid phase is more stable than the vapor phase.

Equation 2c is only obtained when $\phi = x_1$, the mole fraction of component 1.

In general $g_{\{v\}} \neq 0$ as illustrated in Figure 1; the liquid phase at the given T, P, and ϕ is more stable than the vapor phase of the same composition because it represents the global minimum in g. Since $g_{\{v\}} = 0$ defines a minimum in g, $\partial^2 g/\partial v^2)_{T,P,\phi} \equiv g_{\{vv\}}$ must be positive at the minumum. The deviation of the free energy from its equilibrium value, δg, is therefore

$$\delta g = \frac{1}{2} g_{vv} \delta v^2 + ... \tag{3}$$

and the probability of a volume fluctuation, $P(\delta v)$, is given by[17]

$$P(\delta v) \sim \exp(-\delta g/RT) \approx \exp(-g_{\{vv\}}\delta v^2/2RT) \tag{4}$$

This Gaussian form immediately indicates that the mean-square volume fluctuation, $\langle \delta v^2 \rangle$, is

$$\langle \delta v^2 \rangle = RT g_{\{vv\}}^{-1} \tag{5}$$

Below it will be shown that $g_{\{vv\}}^{-1} = v\beta$ where β is the isothermal compressibility.

At a fixed composition, there is a surface defined by $g_{\{v\}} = 0$ in T, P, and v space that defines the equilibrium values of v at given T, P, and ϕ (i.e., the equation of state). We can now look at the differential properties of this surface $g_{\{v\}}(T,P,v,\phi)$

$$\begin{aligned} \mathrm{d}g_{\{v\}} &= g_{\{vT\}}\,\mathrm{d}T + g_{\{vP\}}\,\mathrm{d}P + g_{\{vv\}}\,\mathrm{d}v + g_{\{v\phi\}}\,\mathrm{d}\phi \\ &= 0 \quad \text{on the equilibrium surface} \end{aligned} \tag{6}$$

The above equation is very important because it links various unconstrained second derivatives on the free energy where three variables from the set $\{T,P,v,\phi\}$ are held constant to the more familiar constrained second derivatives on the free energy where only two variables from the canonical set $\{T,P,\phi\}$ are held constant. For example, an important relation that immediately obtains from eq 6 is the variation of volume with composition under the usual laboratory conditions of constant temperature and pressure:

$$\left(\frac{\partial v}{\partial \phi}\right)_{T,P} = \left(\frac{\partial g_P}{\partial \phi}\right)_{T,P} \equiv g_{P\phi} \equiv -\frac{g_{\{v\phi\}}}{g_{\{vv\}}} \tag{7}$$

We also have from eq 6 that

$$\left(\frac{\partial v}{\partial P}\right)_{T,\phi} = -v\beta = g_{PP} \equiv -\frac{g_{\{vP\}}}{g_{\{vv\}}} \tag{8}$$

where β is the isothermal compressibility. Now $g_{\{vP\}}$ can be evaluated since, from eq 1, we have

$$v = g_P \equiv g_{\{P\}} \tag{9}$$

and thus

$$g_{\{Pv\}} = g_{\{vP\}} = 1 \tag{10}$$

The equality $g_{\{Pv\}} = g_{\{vP\}}$ follows because $\mathrm{d}g_{\{v\}}$ is an exact differential in the variables T, P, v, and ϕ and the order of differentiation is unimportant. However, note that $g_{vP} \neq g_{Pv} = 1$ because g_v could have been taken at constant P and ϕ, or P and T, or T and ϕ with different results. Since v is not one of the canonical variables for the Gibbs free energy, constrained derivatives with respect to v can be taken in three different ways (in contrast, there is only one unconstrained derivative). Substituting eq 10 into eq 8 yields the important relation

$$-g_{PP} = g_{\{vv\}}^{-1} = v\beta \tag{11}$$

Also from eqs 6 and 10, it follows that $g_{\{v\phi\}}$ is related to the *constant-volume, constant-temperature, composition coefficient of the pressure*:

$$\left(\frac{\partial P}{\partial \phi}\right)_{T,v} \equiv P_\phi = -\frac{\partial v/\partial \phi)_{T,P}}{\partial v/\partial P)_{T,\phi}} = -\frac{g_{P\phi}}{g_{PP}} \equiv -g_{\{v\phi\}} \tag{12}$$

Finally, from eqs 6 and 10 we also have

$$\left(\frac{\partial P}{\partial T}\right)_{v,\phi} = -\frac{g_{PT}}{g_{PP}} \equiv -g_{\{vT\}} = \alpha/\beta \tag{13}$$

where α is the thermal expansion coefficient. To summarize to this point, we can express the constrained second derivatives g_{PP}, g_{PT}, and $g_{P\phi}$ completely in terms of the unconstrained derivatives $g_{\{vv\}}$, $g_{\{vT\}}$, and $g_{\{v\phi\}}$ through eqs 11–13. This correspondence is also seen by forming the total differential of the pressure and using eq 6:

$$\begin{aligned} \mathrm{d}P = \left(\frac{\partial P}{\partial v}\right)_{T,\phi} \mathrm{d}v + \left(\frac{\partial P}{\partial T}\right)_{v,\phi} \mathrm{d}T + \left(\frac{\partial P}{\partial \phi}\right)_{T,v} \mathrm{d}\phi \equiv -(v\beta)^{-1}\,\mathrm{d}v + \\ \frac{\alpha}{\beta}\,\mathrm{d}T + P_\phi\,\mathrm{d}\phi \end{aligned} \tag{14a}$$

$$\begin{aligned} \mathrm{d}P \equiv g_{PP}^{-1}\,\mathrm{d}v - \frac{g_{PT}}{g_{PP}}\,\mathrm{d}T - \frac{g_{P\phi}}{g_{PP}}\,\mathrm{d}\phi \equiv -g_{\{vv\}}\,\mathrm{d}v - g_{\{vT\}}\,\mathrm{d}T - \\ g_{\{v\phi\}}\,\mathrm{d}\phi \end{aligned} \tag{14b}$$

However, to obtain the remaining three canonical second derivatives, g_{TT}, $g_{T\phi}$, and $g_{\phi\phi}$, in terms of unconstrained second derivatives, we must form the total differentials of g_T and g_ϕ:

$$\mathrm{d}g_T = \mathrm{d}g_{\{T\}} = g_{\{TT\}}\,\mathrm{d}T + g_{\{TP\}}\,\mathrm{d}P + g_{\{Tv\}}\,\mathrm{d}v + g_{\{T\phi\}}\,\mathrm{d}\phi \tag{15a}$$

$$\mathrm{d}g_\phi = \mathrm{d}g_{\{\phi\}} = g_{\{\phi T\}}\,\mathrm{d}T + g_{\{\phi P\}}\,\mathrm{d}P + g_{\{\phi v\}}\,\mathrm{d}v + g_{\{\phi\phi\}}\,\mathrm{d}\phi \tag{16a}$$

but

$$g_{\{TP\}} = g_{\{PT\}} \equiv \partial v/\partial T)_{v,P,\phi} = 0 \tag{17}$$

and similarly

$$g_{\{PP\}} = g_{\{\phi P\}} = g_{\{P\phi\}} = 0 \tag{18}$$

so that

$$\mathrm{d}g_T = \mathrm{d}g_{\{T\}} = g_{\{TT\}}\,\mathrm{d}T + g_{\{Tv\}}\,\mathrm{d}v + g_{\{T\phi\}}\,\mathrm{d}\phi \tag{15b}$$

and

$$\mathrm{d}g_\phi = \mathrm{d}g_{\{\phi\}} = g_{\{\phi T\}}\,\mathrm{d}T + g_{\{\phi v\}}\,\mathrm{d}v + g_{\{\phi\phi\}}\,\mathrm{d}\phi \tag{16b}$$

Note that eqs 10, 17, and 18 are consistent with the requirement that $\mathrm{d}g_P \equiv \mathrm{d}v$. Thus, g_{TT}, $g_{T\phi}$, and $g_{\phi\phi}$ are given by

$$g_{TT} = g_{\{TT\}} + g_{\{Tv\}}(\partial v/\partial T)_{P,\phi} = g_{\{TT\}} - g_{\{Tv\}}^{2} g_{\{vv\}} = g_{\{TT\}} - v\alpha^2/\beta \tag{19}$$

$$g_{T\phi} = g_{\{T\phi\}} + g_{\{Tv\}}(\partial v/\partial \phi)_{P,T} = g_{\{T\phi\}} - g_{\{Tv\}} g_{\{v\phi\}} g_{\{vv\}}^{-1} = g_{\{T\phi\}} - v\alpha P_\phi \tag{20}$$

$$g_{\phi\phi} = g_{\{\phi\phi\}} + g_{\{\phi v\}}(\partial v/\partial \phi)_{P,T} = g_{\{\phi\phi\}} - g_{\{v\phi\}}^{2} g_{\{vv\}}^{-1} = g_{\{\phi\phi\}} - v\beta P_\phi^{2} \tag{21}$$

Equation 20 was derived from eq 15, but it can also be obtained from eq 16 since $g_{T\phi} = g_{\phi T}$.

Now the constant pressure heat capacity, c_P, is related to the intensive enthalpy (h) and g_{TT} by

$$c_P \equiv \partial h/\partial T)_{P,\phi} = -Tg_{TT} = -Tg_{\{TT\}} + Tv\alpha^2/\beta \tag{22}$$

but we also have the well-known thermodynamic relationship

$$c_P = c_v + Tv\alpha^2/\beta \tag{23}$$

where c_v is the constant volume heat capacity. Comparison of eqs 22 and 23 indicates

$$c_v = -Tg_{\{TT\}} \tag{24}$$

As a check we can derive eq 24 directly from the definition of c_v

$$c_v \equiv \partial u/\partial T)_{v,\phi} = T\,\partial s/\partial T)_{v,\phi} = -T\,\partial g_T/\partial T)_{v,\phi} = -T\,\partial g_{\{T\}}/\partial T)_{v,\phi} = -Tg_{\{TT\}} \tag{25}$$

where u is the intensive internal energy and the last equality follows from eq 15b.

Similarly, the composition coefficients of the entropy, $\partial s/\partial\phi)_{T,P}$, and the enthalpy, $\partial h/\partial\phi)_{T,P}$, have "constant volume" contributions

$$\partial s/\partial\phi)_{T,P} = -g_{T\phi} = -[g_{\{T\phi\}} - g_{\{Tv\}} g_{\{v\phi\}} g_{\{vv\}}^{-1}] = -g_{\{T\phi\}} + v\alpha P_\phi \tag{26}$$

$$\partial h/\partial\phi)_{T,P} = g_{\{\phi\}} + T\,\partial s/\partial\phi)_{T,P} = g_{\{\phi\}} - Tg_{\{T\phi\}} + vT\alpha P_\phi \tag{27}$$

and the phase or diffusional stability condition, $g_{\phi\phi} > 0$, has a "constant volume" contribution as shown in eq 21.

Thus, the conditions of mechanical ($\beta > 0$), thermal ($c_v > 0$), and phase ($g_{\phi\phi} > 0$) stability for a binary solution can now be stated in terms of unconstrained second derivatives on the Gibbs free energy:

$$g_{\{vv\}} > 0 \quad \text{mechanical stability} \tag{28}$$

$$-g_{\{TT\}} > 0 \quad \text{thermal stability} \tag{29}$$

$$g_{\{\phi\phi\}} - g_{\{v\phi\}}^{2} g_{\{vv\}}^{-1} > 0 \quad \text{phase (diffusional) stability} \tag{30}$$

The conditions of equilibrium at constant T and P between two coexisting phases (fluid–fluid) of compositions ϕ' and ϕ'' are

$$g'_{\{v\}} = g''_{\{v\}} = 0 \quad T \text{ and } P \text{ equal in both phases} \tag{31}$$

$$g'_{\{\phi\}} = g''_{\{\phi\}} \quad \text{tangent construction} \tag{32}$$

$$g' - \phi' g'_{\{\phi\}} = g'' - \phi'' g''_{\{\phi\}} \quad \text{chemical potential equal in both phases} \tag{33}$$

These four equations define the four unknowns, ϕ', ϕ'', v', and v''.

III. Binary Solutions

A. Phase Stability. The conditions for diffusional or phase stability given in eq 30 can be expressed as

$$g_{\{\phi\phi\}} - v\beta P_\phi^{2} > 0 \tag{34}$$

The $g_{\{\phi\phi\}}$ term represents the constant volume or incompressible contribution to $g_{\phi\phi}$, whereas the negative $v\beta P_\phi^2$ term is the compressible and unfavorable contribution to phase stability. Using this formalism of volume fluctuation thermodynamics with its unconstrained free energy derivatives allows this separation of effects. It illustrates that the phase stability of a compressible solution is always less than the corresponding incompressible solution.

Why should a compressible solution be thermodynamically less stable than an incompressible solution? Contrary to intuition, sometimes the more degrees of freedom the system has, the more difficult it is to achieve phase stability. For example, a ternary solution of three polymers can phase separate even when all of the binary interaction parameters are negative and all three binary systems are completely miscible.[18] Allowing volume fluctuations is an additional degree of freedom that makes the stability requirements of a compressible solution always more stringent than those for an incompressible solution. An example of how this instability can occur is as follows: If the one-phase system is dense, then the most stable state might be a two-phase system in which the overall average density of the phase-separated system is smaller. Energetically the dense one-phase system is favorable, but it is entropically unfavorable (exceptions are possible, but they should be relatively rare). In statistical mechanical language, we would say that through volume fluctuations the system is able to explore other regions of configuration space corresponding to larger volumes and lower free energies in which the components are inhomogeneously distributed (phase separated). In contrast, the hypothetical incompressible solution samples a more restricted region of configuration space.

Consistent with the above qualitative comments is the thermodynamic requirement that phase separation at a lower critical solution temperature (LCST) is always entropically driven.[19,20] However, the entropic driving force does not have to be related to the aforementioned density effect. It is well-known that LCST behavior can obtain in incompressible models with specific interactions[21-23] where the incompressible $g_{\{\phi\phi\}}$ term has an entropic component that is unfavorable.

As can be seen also from eq 34, the constant-volume, constant-temperature, pressure composition coefficient, P_ϕ, plays an important role in phase stability. If two pure components had identical equation of state (P–V–T) properties and interacted neutrally with one another (no net attractive or repulsive interactions), P_ϕ would equal zero; i.e., the intensive volume of the solution would not change with composition and no change of pressure would be required to maintain the volume of the solution. Typically, for a polymer solution the magnitude of P_ϕ is of the order of 10^3 bar and it reflects to a large degree the mismatch in equation of state properties of polymer and solvent. In nonpolar polymer solutions where specific interactions are absent, the unfavorable $v\beta P_\phi{}^2$ term most likely dominates the phase instability at a LCST.

B. Partial Volumes. The partial molar volume, $\bar{v}_1$, of component 1 of a system of total volume V is defined as

$$\bar{v}_1 = (\partial V/\partial n_1)_{T,P,n_2} \tag{35}$$

which can easily be rewritten as

$$\bar{v}_1 = M_1[v + w_2(\partial v/\partial w_1)_{T,P}] \tag{36}$$

where v is the specific volume of the mixture and the w_is are weight fractions. The partial specific volume is obtained by dividing eq 36 by M_1. Using eqs 7, 11, and 12 in eq 36 yields the *partial specific volume* of component 1

$$\bar{v}_1 = v - w_2 g_{\{vv\}}{}^{-1} g_{\{vw_1\}} = v[1 + w_2\beta P_{w_1}] \tag{37}$$

and, of course, $\bar{v}_2$ is obtained easily by interchanging the indices.

Equation 37 suggests that pressure–volume–temperature (P–V–T) measurements of polymer solutions can be a very effective method for testing the various equation of state theories. For example, all theories could be placed on the same equal starting basis by choosing the equation of state parameters for polymer and solvent so that the pure-component liquid densities and compressibilities are correctly predicted at some convenient reference temperature. P–V–T measurements as a function of composition would then yield $\bar{v}$, $(\partial v/\partial w)_{T,P}$, and β data directly from which P_w could also be determined. The experimentally determined values of $\bar{v}$, P_w, and β could then be compared with those predicted by the various theories. In particular, the value of P_w, which plays an important role in determining chemical potentials (see next section), is a sensitive measure of a theory's accuracy.

C. Chemical Potentials. The chemical potential, μ_1, is defined as

$$\mu_1 = (\partial G/\partial n_1)_{T,P,n_2} \tag{38}$$

In terms of the intensive free energy and its associated intensive composition variable, we also have

$$\mu_1 = g + x_2(\partial g/\partial x_1)_{T,P} = M_1[g + w_2(\partial g/\partial w_1)_{T,P}] = v_1{}^0[g + \phi_2(\partial g/\partial \phi_1)_{T,P}] \tag{39}$$

where here (unlike above) $v_i{}^0$ is the *molar volume* of the pure component i. The units of $v_i{}^0$ and other intensive properties should be transparent from the context of how they are used. However, there can be some ambiguity about how the free energy density (free energy per unit volume) and the volume fractions (ϕ_i) are defined. In general for an m-component solution, we define g and ϕ_i as

$$g \equiv \frac{G}{\sum_{i=1}^{m} n_i v_i{}^0} \tag{40}$$

$$\phi_i \equiv \frac{n_i v_i{}^0}{\sum_{i=1}^{m} n_i v_i{}^0} \equiv \frac{w_i/\rho_i{}^0}{\sum_{i=1}^{m} w_i/\rho_i{}^0} \tag{41}$$

where the pure-component molar volumes ($v_i{}^0$) and mass densities ($\rho_i{}^0$) are determined at some convenient reference temperature and pressure (usually atmospheric). The important point is that the reference volume, $\sum_{i=1}^{m} n_i v_i{}^0$, and volume fractions ($\phi_i$) *are independent of temperature and pressure.* Thus, the reference molar volume $v_1{}^0$ that appears in eq 39 is independent of T and P.

In working with chemical potentials it is convenient to separate out the classical combinatorial contribution to the free energy (there is no loss of generality)

$$g = g^c + g^R \tag{42}$$

where g^c is the classical combinatorial free energy density

$$\frac{g^c}{RT} = \frac{\phi_1}{v_1{}^0}\ln\phi_1 + \frac{\phi_2}{v_2{}^0}\ln\phi_2 \tag{43}$$

and g^R is the residual free energy density. Now the chemical potential can be written as

$$\mu_1 = RT[\ln\phi_1 + (1 - v_1{}^0/v_2{}^0)\phi_2] + v_1{}^0[g^R + \phi_2 g_{\phi_1}{}^R] \tag{44}$$

Of course, if component 1 is the solvent in a polymer solution, then $v_1{}^0/v_2{}^0 \to 0$. Expanding g^R in a series around $\phi_2 = 0$, we obtain

$$\mu_1 = \mu_1{}^0 + RT[\ln\phi_1 + (1 - v_1{}^0/v_2{}^0)\phi_2] - \frac{1}{2}g_{\phi\phi}{}^{R_0}\phi_2{}^2 + \ldots \tag{45a}$$

where $\mu_1{}^0 \equiv v_1{}^0 g^R(\phi_1 = 1) \equiv v_1{}^0 g^{R_0}$ is the free energy of pure component 1; the superscript of zero in $g_{\phi\phi}{}^{R_0}$ means that the second derivative is evaluated at $\phi_2 = 0$. From eq 21, we have

$$g_{\phi\phi}{}^R = g_{\{\phi\phi\}}{}^R - \tilde{v}\beta P_\phi{}^2 \tag{46}$$

where $\tilde{v}$ is a *dimensionless* intensive volume defined by $\tilde{v} \equiv V/(n_1 v_1{}^0 + n_2 v_2{}^0)$. We have added the tilde above the v to remind us that this intensive volume ($\tilde{v}$) is dimensionless. Substituting eq 46 into eq 45a yields

$$\mu_1 = \mu_1{}^0 + RT[\ln\phi_1 + (1 - v_1{}^0/v_2{}^0)\phi_2] - \frac{1}{2}v_1{}^0[g_{\{\phi\phi\}}{}^{R_0} - \beta_1\tilde{v}_1(P_\phi{}^0)^2]\phi_2{}^2 + \ldots \tag{45b}$$

where $\beta_1 = \beta(\phi_1 = 1)$, $\tilde{v}_1 = \tilde{v}(\phi_1 = 1)$, and the superscript zero in $P_\phi{}^0$ means that P_ϕ is evaluated at $\phi_2 = 0$. Also note that

$$P_\phi = -g_{\{\tilde{v}\phi\}} = -g_{\{\tilde{v}\phi\}}{}^R \tag{47}$$

since g^c is independent of $\tilde{v}$. So to second order in polymer volume fraction, the solvent chemical potential depends on the solvent compressibility and the contribution is positive and unfavorable. If the residual free energy takes the classical incompressible form

$$g^{R} = \phi_1 g^{R}(\phi_1{=}1) + \phi_2 g^{R}(\phi_2{=}1) + RT\phi_1\phi_2\chi \tag{48}$$

where χ is a composition- and volume-independent interaction parameter, then $g_{\{\phi\phi\}}{}^{R} = -2RT\chi$, $P_\phi = -g_{\{\bar{v}\phi\}}{}^{R} = 0$, and eq 45b reduces to its familiar Flory–Huggins form:

$$\mu_1 - \mu_1{}^0 = RT[\ln \phi_1 + (1 - v_1{}^0/v_2{}^0)\phi_2 + v_1{}^0\chi\phi_2{}^2] \tag{49}$$

In the polymer literature the dimensionless product $v_1{}^0\chi$ is often designated as χ_1. Note that $RT\chi$ has units of energy density and is often approximated by $(\delta_1 - \delta_2)^2$ where δ_i is the solubility parameter (or the square root of the cohesive energy density) of component i.

If we require the experimental chemical potential always to satisfy an equation of the type

$$\mu_1 - \mu_1{}^0 = RT[\ln \phi_1 + (1 - v_1{}^0/v_2{}^0)\phi_2 + v_1{}^0\chi_{1\mu}\phi_2{}^2] \tag{50}$$

then $\chi_{1\mu}$ is given by

$$RT\phi_2{}^2\chi_{1\mu} = g^{R} - g^{R}(\phi_1{=}1) + \phi_2 g_{\phi_1}{}^{R} \tag{51}$$

The corresponding $\chi_{2\mu}$ associated with the polymer chemical potential is obtained by interchanging indices; in general, $\chi_{1\mu} \neq \chi_{2\mu}$ but are related to one another through a Gibbs–Duhem relationship.[24]

The variation of the chemical potential with composition depends explicitly on β and P_ϕ:

$$\left(\frac{\partial\mu_1}{\partial\phi_1}\right)_{T,P} = \phi_2 g_{\phi\phi} = v_1{}^0\phi_2\left\{RT\left[\frac{1}{v_1{}^0\phi_1} + \frac{1}{v_2{}^0\phi_2}\right] + g_{\{\phi\phi\}}{}^{R} - \bar{v}\beta P_\phi{}^2\right\} \tag{52}$$

Since $\partial\mu_1/\partial P)_{T,\phi} = \bar{v}_1$, the pressure dependence of μ_1 also depends explicitly on β and P_ϕ (see eq 37).

In the Appendix, volume fluctuation thermodynamics (VFT) is generalized to multicomponent systems.

IV. Discussion and Conclusions

The idea of volume fluctuation thermodynamics (VFT) has been formally developed to show in general terms how solution properties are affected by finite compressibility and by the mismatch in pure-component equation of state properties. The constant-volume, constant-temperature, pressure composition coefficient, $(\partial P/\partial\phi)_{T,v} \equiv P_\phi$, plays an important role in solution thermodynamics. If two pure components had identical equation of state (P–V–T) properties and interacted neutrally with one another (no net attractive or repulsive interactions), P_ϕ would equal zero; i.e., the intensive volume of the solution would not change with composition and no change of pressure would be required to maintain the volume of the solution. Typically, for a polymer solution the magnitude of P_ϕ is of the order of 10^3 bar and it reflects to a large degree the mismatch in equation of state properties of polymer and solvent. It has been suggested that pressure–volume–temperature (P–V–T) measurements of polymer solutions can be a very effective method for testing how well the various equation of state theories describe the thermodynamic properties of polymer solutions.

VFT has two advantages: The first is that constant volume (incompressible) and volume fluctuation (compressible) contributions to solution thermodynamic properties are easily separated. The second is that convenient recipes for multicomponent systems have been derived in terms of "unconstrained derivatives" on the Gibbs potential that can be used with any statistical mechanical model to calculate thermodynamic quantities. For example, the excess chemical potential of a component in a multicomponent mixture is given by eq A.12. All of the required derivatives in this expression are unconstrained derivatives, which are, in general, trivial to calculate. If the model potential is not the Gibbs potential, it can always be converted to the Gibbs potential by one or more Legendre transformations and then the recipes herein can be applied.

At first glance VFT looks like thermodynamic heresy with its four independent intensive variables for a binary mixture and its unconstrained derivatives holding three of these variables constant. However, it is not heresy but yet another way of manipulating thermodynamic relations. An alternative and more elegant (and possibly more palatable) development of VFT is to view it as a Legendre transform on $g(T,P,v,\phi)$ with respect to v, which transforms g into itself; i.e., $g \equiv g - vg_{\{v\}}$ where v is replaced by $g_{\{v\}}$ and then

$$\mathrm{d}g = g_{\{T\}}\,\mathrm{d}T + g_{\{P\}}\,\mathrm{d}P + g_{\{\phi\}}\,\mathrm{d}\phi - v\,\mathrm{d}g_{\{v\}} \tag{53}$$

The requirement that the transform equal itself (the identity transformation) requires that $g_{\{v\}} = 0$, $\mathrm{d}g_{\{v\}} = 0$, and eq 2 must hold. The equation $\mathrm{d}g_{\{v\}} = 0$ is the fundamental eq 6. Formally, the intensive *density* variable v has been replaced with the new intensive *field* variable $g_{\{v\}}$ that takes on the value of zero at equilibrium. Field variables (in contrast to density variables) have the property that they take on identical values for phases in equilibrium.[25] Temperature, pressure, and chemical potential are the usual field variables. In VFT, $g_{\{v\}} = 0$ in each phase determines the T, P, v, and ϕ relationship, i.e., the equation of state, in each phase (see eq 31). This equation is thermodynamically equivalent to the more familiar

$$\partial A/\partial V)_{T,\phi} + P = 0 \tag{54}$$

where A is the Helmholtz free energy.

From the canonical set $\{T,P,\phi\}$ there are six unique pairs and thus six canonical second derivatives on g. From the set $\{T,P,v,\phi\}$ there are 10 unique pairs and 10 unconstrained second derivatives on g; however, only six of these derivatives are nontrivial since $g_{\{PP\}} = g_{\{PT\}} = g_{\{P\phi\}} = 0$ and $g_{\{Pv\}} = 1$. Thus, the six nontrivial unconstrained derivatives are formed from the set $\{T,v,\phi\}$, which we note are the canonical variables for the Helmholtz free energy. The relationship between the canonical (or constrained) second derivatives and the unconstrained second derivatives is summarized below:

$$g_{PP} = -g_{\{vv\}}{}^{-1} \tag{55}$$

$$g_{Pz} = -g_{\{vz\}}/g_{\{vv\}} \qquad z = T \text{ or } \phi \tag{56}$$

$$g_{xy} = g_{\{xy\}} - g_{\{vx\}}g_{\{vy\}}/g_{\{vv\}} \qquad x, y = T \text{ or } \phi \tag{57}$$

The inverse relationships are obtained by interchanging braces, replacing P with v, and replacing v with $-P$. The latter replacement changes the sign in eq 56. These relationships among the second derivatives are formally identical with those obtained by the Legendre transform of the function $a(v,T,\phi)$ with respect to v to the transformed function $g(\partial a/\partial v,T,\phi) = a - va_v$,[26] i.e., the braced derivatives play the role of the Helmholtz free energy (a). *This leads us to the important conclusion that unconstrained second derivatives on the Gibbs free energy are equivalent to ordinary (constrained) second derivatives on the Helm-*

holtz energy; i.e.

$$g_{\{xy\}} = a_{xy} \qquad x, y = T, v, \text{ or } \phi \tag{58}$$

For a multicomponent system with m components, the above equation holds for $x, y = T, v, \phi_1, \phi_2, ..., \phi_{m-1}$.

The identity, Legendre transform approach suggests that "entropy fluctuation thermodynamics" could also be developed by assuming that g is a function of T, P, ϕ, and the intensive entropy, s. The extra density variable s could be eliminated by the identity, Legendre transform $g \equiv g - sg_{\{s\}}$, and adiabatic and nonadiabatic contributions could be easily separated from thermodynamic relations. However, model potentials do not usually adopt this functional form, and this does not seem to be a particularly useful extension of the concept. A more common situation is that model potentials are functions of one or more order parameters so that $g = g(T,P,\phi,z_1,z_2,...)$ where z_i are order parameters (see DiMarzio[27] for an example of this approach). The identity, Legendre transform

$$g \equiv g - \sum_i z_i g_{\{i\}} \tag{59}$$

where

$$g_{\{i\}} \equiv \partial g/\partial z_i)_{T,P,\phi,z_{j\neq i}} \tag{60}$$

would then require $g_{\{i\}} = 0$ and $\mathrm{d}g_{\{i\}} = 0$. Local stability with respect to the order parameter would also require $g_{\{ii\}} > 0$. Fluctuations in the order parameter would be governed by the analogue of eq 4

$$P(\delta z_i) \sim \exp(-g_{\{ii\}}\delta z_i^{\,2}/2RT) \tag{61}$$

if the order parameters are uncoupled ($g_{\{ij\}} = \delta_{ij}g_{\{ii\}}$). The set of simultaneous equations $g_{\{i\}} = 0$ ($i = 1, 2, ...$) determine the equations of state for the order parameters.

A misconception that seems to persist in the literature is that equation of state corrections to classical (incompressible) models are only necessary for systems where the volume of mixing, Δv, is nonzero. A corollary to this misconception is that the corrections become larger as the magnitude of Δv increases. In general, neither the compressibility (β) nor P_ϕ vanishes when $\Delta v = 0$; Δv is a first derivative property of the free energy [$\Delta v = \partial\Delta g/\partial P)_{T,\phi}$], whereas β and P_ϕ, which we have shown controls many of the equation of state contributions to thermodynamic properties, are second derivative properties of the free energy. A compressible solution can fortuitously have $\Delta v = 0$ but still exhibit large deviations from classical (incompressible) behavior in other thermodynamic properties. For example, the partial molar volume and entropy are second derivative properties that depend on the following composition derivatives

$$v_\phi = v\beta P_\phi$$
$$s_\phi = -g_{\{T\phi\}} + v\alpha P_\phi = -a_{T\phi} + v\alpha P_\phi \tag{62}$$

and the compositional dependence of the chemical potential is given by

$$\partial\mu_1/\partial\phi_1 = \phi_2[g_{\{\phi\phi\}} - v\beta P_\phi^{\,2}] = \phi_2[a_{\phi\phi} - v\beta P_\phi^{\,2}] \tag{63}$$

Note the explicit dependence of these properties on β and P_ϕ. From the viewpoint of causality, volume changes on mixing have little to do with equation of state effects on other thermodynamic properties. What is important are the magnitudes of β and P_ϕ. Equation of state effects are magnified in polymer solutions, especially polymer blends, because the combinatorial entropy contribution to the free energy in polymer systems is so small.

The phase stability of a compressible multicomponent solution is always less than that of the corresponding incompressible solution (see eq A.22). In statistical mechanical language, we would say that through volume fluctuations a system is able to explore other regions of configuration space corresponding to different volumes and lower free energies in which the components are inhomogeneously distributed (phase separated). In contrast, the hypothetical incompressible solution samples a more restricted region of configuration space. The instability caused by volume fluctuations is more clearly seen by using the result

$$\delta v = \sum_{i=1}^{m-1}\left(\frac{\partial v}{\partial\phi_i}\right)_{T,P,\phi}\delta\phi_i \equiv v\beta\sum_{i=1}^{m-1}P_i\,\delta\phi_i \tag{64}$$

in eq A.22 along with eqs 5 and 58 to obtain as the condition for phase stability

$$\delta^2 g = \sum_{i=1}^{m-1}\sum_{j=1}^{m-1}g_{\{ij\}}\,\delta\phi_i\,\delta\phi_j - RT\frac{\delta v^2}{\langle\delta v^2\rangle} =$$
$$\sum_{i=1}^{m-1}\sum_{j=1}^{m-1}a_{ij}\,\delta\phi_i\,\delta\phi_j - RT\frac{\delta v^2}{\langle\delta v^2\rangle} > 0 \tag{65a}$$

For a binary mixture, eq 65a reduces to

$$\delta^2 g = a_{\phi\phi}\,\delta\phi^2 - RT\frac{\delta v^2}{\langle\delta v^2\rangle} = (a_{\phi\phi} - v\beta P_\phi^{\,2})\,\delta\phi^2 > 0 \tag{65b}$$

This result reflects a somewhat counterintuitive fact; i.e., *sometimes the more degrees of freedom the system has, the more difficult it is to achieve phase stability.* Allowing the system volume fluctuations is an additional degree of freedom that always destabilizes the system. In a pseudo binary polymer/solvent system where the polymer is polydispersed in molecular weight, there are many additional degrees of freedom compared to the monodispersed polymer/solvent system. Here the polydispersed polymer/solvent system is less stable than the corresponding monodispersed polymer/solvent system whose molecular weight equals the number-average molecular weight of the polydispersed polymer. The spinodal condition is more stringent for the polydispersed system since it involves the weight-average molecular weight rather than the number average.[28] Stated another way, if the polydispersity index of a polymer is increased while maintaining its number-average molecular weight constant, the phase stability of the polymer/solvent system decreases.

Another example of destablization with increasing degrees of freedom is obtained by adding a third component to a binary system. This would not be surprising if the free energy increased, but it is surprising when the mixture free energy becomes more negative by adding the third component. To illustrate the latter, consider a "regular" binary solution with a free energy given by (terms linear in concentration are ignored)

$$g/RT = x_1\ln x_1 + x_2\ln x_2 + x_1x_2\chi \tag{66}$$

where the x_i are mole fractions and χ is a positive and dimensionless interaction parameter that varies inversely with T. Now add a third component to the system that interacts repulsively with component 1 ($\chi_{13} = \chi$) and attractively with component 2 ($\chi_{23} = -\chi$) so that the free energy of the ternary system becomes

$$g/RT = x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3 + (x_1x_2 + x_1x_3 - x_2x_3)\chi \quad (67)$$

Both the entropic and energetic terms for the ternary system are more negative than those for the binary system, and we might naively believe that the ternary system is more stable. However, using eq A.19, we have for the ternary system

$$g_{11} = \frac{1}{x_1} + \frac{1}{x_3} - 2\chi, \quad g_{12} = \chi + \frac{1}{x_3}, \quad g_{22} = \frac{1}{x_2} + \frac{1}{x_3} + 2\chi \quad (68)$$

so that phase stability requires (see eq A.22)

$$\left[\frac{1}{x_1} + \frac{1}{x_3} - 2\chi\right]\left[\frac{1}{x_2} + \frac{1}{x_3} + 2\chi\right] - \left(\chi + \frac{1}{x_3}\right)^2 > 0 \quad (69)$$

As is well-known, the binary solution is stable for all concentrations when $\chi < 2$. For the equimolar ternary ($x_1 = x_2 = x_3 = {}^1/_3$) the inequality eq 69 requires $\chi < {}^9/_5$ for stability of the equimolar ternary. This indicates that phase separation will occur at higher temperatures (since $\chi \sim 1/T$) for the ternary than for the binary; i.e., the ternary is less stable. The physics of what is going on here is relatively easy to understand. Asymmetry in the molecular interactions tends to destabilize the solution. Here the 2–3 interaction is energetically favorable. The solution tends to phase separate to form a phase rich in components 2 and 3 to maximize these favorable interactions. The associated entropy loss is offset by the lowering of the system potential energy.

The above example is contrary to our experience of solubilizing two immiscible polymers by adding a low molecular weight solvent. In this case the entropic gain in the entropy of mixing offsets any destabilizing effects caused by interaction asymmetries. However, in multicomponent solutions involving only polymers, the entropy of mixing is very small and interaction energy asymmetries dominate and destabilize the solution. For example, if the interaction asymmetries are large enough, a ternary solution of three polymers can phase separate even when all of the binary interaction parameters are negative and all three binary systems are completely miscible.[18]

How important are volume fluctuation (VF) contributions (a.k.a. "equation of state", "free volume", or "compressible" contributions) to polymer solution thermodynamics? With respect to phase stability, they are very significant. As is well-known, polymer solutions and blends tend to phase separate at elevated temperatures; VF effects play an important role in these phenomena. To see this more clearly, we can estimate the various contributions to the stability condition for a binary solution, eq 34. To my knowledge, P_ϕ has never been experimentally reported for a polymer solution, although it is easily obtained from partial molar volume and compressibility measurements (see eq 37). However, we can estimate P_ϕ from any equation of state model. When the lattice fluid model,[16] for example, is used, typical room-temperature calculated values for P_ϕ for a polymer/solvent system range from 1000 to 5000 atm. A typical compressibility is 1×10^{-4} atm^{-1} for a dilute polymer solution and 5×10^{-5} atm^{-1} for a very concentrated polymer solution. Thus, at room temperature and over a wide composition range we expect

$$50 \text{ atm} < \tilde{v}\beta P_\phi^{\,2} < 2500 \text{ atm}$$

(The dimensionless volume, $\tilde{v}$, is always near unity; see eq 46 and the discussion following.) Model calculations also predict that $\tilde{v}\beta P_\phi^{\,2}$ increases with temperature.

The constant-volume contribution to phase stability, $g_{|\phi\phi|}$, can be estimated from a classical Flory–Huggins type expression:

$$g_{|\phi\phi|} = RT\left[\frac{1}{v_1^{\,0}\phi_1} + \frac{1}{v_2^{\,0}\phi_2} - 2\chi\right] \quad (70)$$

For a polymer solution $v_2^0 \rightarrow \infty$ and except in very dilute solutions, $1/\phi_2 v_2^0 \approx 0$, and this term can be ignored. Thus

$$g_{|\phi\phi|} \approx \frac{RT}{v_1^{\,0}}\left[\frac{1}{\phi_1} - 2v_1^{\,0}\chi\right] \quad (71)$$

For a Θ solvent, $v_1^0\chi = 0.5$, and in a good solvent it is much smaller and can be ignored. Typical organic solvents have molar volumes of 50–100 cm^3/mol so that, at room temperature, and assuming $v_1^0\chi$ is small compared to unity, we have

$$250/\phi_1 \text{ atm} < g_{|\phi\phi|} < 500/\phi_1 \text{ atm}$$

What this exercise illustrates is that, even for a room-temperature polymer solution, VF effects can have important consequences for phase stability. For a binary polymer blend the effects are more consequential because both molar volumes (v_1^0 and v_2^0) are very large and $g_{|\phi\phi|} \approx 0$ over most of the composition range. The unfavorable VF term dominates, and immiscibility is the general rule unless the interaction term, χ, is negative. When χ is negative, $g_{|\phi\phi|} > 0$ and miscibility is possible. For the well-known miscible polystyrene/poly(phenylene oxide) blend, $RT\chi \approx -20$ J/cm^3 ≈ -200 atm. Since the lower critical solution temperature for this system is above 300 °C, $\tilde{v}\beta P_\phi^{\,2}$ must be smaller than 200 atm up to 300 °C. Values of $\tilde{v}\beta P_\phi^{\,2}$ in general tend to be smaller for polymer blends than for polymer/solvent systems because both β and P_ϕ tend to be smaller. The latter is true because P_ϕ is a measure of the dissimilarity between the equation of state properties of the components; two polymers will usually be more similar in their equation of state properties than a polymer and a solvent.

Dedication

In my last year of graduate school in 1969 I read a review paper, "Free Volume and Polymer Solubility: A Qualitative View" authored by D. Patterson.[7] I found this paper very interesting and wondered if this was a research area to which I could contribute. It was several years later before I actually began working in polymer solution thermodynamics. Unbeknownst to Professor Patterson, his review paper has had a profound influence on my professional career. In appreciation I wish to dedicate this paper to him.

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Appendix. Multicomponent Solutions

The equivalent of the fundamental eq 6 for an m-component solution is

$$\mathrm{d}g_{|v|} = g_{|vT|}\,\mathrm{d}T + \mathrm{d}P + g_{|vv|}\,\mathrm{d}v - \sum_{i=1}^{m-1} P_i\,\mathrm{d}\phi_i = 0 \quad (\text{A.1a})$$

where we have introduced the new compact notation

$$P_i \equiv -g_{\{vi\}} \equiv -\partial g_{\{v\}}/\partial\phi_i)_{T,P,v,\phi} \tag{A.2}$$

The subscript ϕ means that the derivative with respect to ϕ_i is taken holding all other concentration variables ($m - 2$) constant except ϕ_m ($\phi_i + \phi_m$ = constant). As is customary, we have only allowed $m - 1$ of the m concentration variables to be independent. The concentration variables are constrained by the usual $\sum_{i=1}^{m}\phi_i = 1$. An alternative and useful representation of eq A.1a is

$$\mathrm{d}g_{\{v\}} = g_{\{vT\}}\,\mathrm{d}T + \mathrm{d}P + g_{\{vv\}}\,\mathrm{d}v - \sum_{i=1}^{m} P_{[i]}\,\mathrm{d}\phi_i = 0 \tag{A.1b}$$

where all of the m concentration variables are treated as independent and

$$P_{[i]} \equiv -g_{\{v[i]\}} \equiv -\partial g_{\{v\}}/\partial\phi_i)_{T,P,v,[\phi]} \tag{A.3}$$

Here the subscript $[\phi]$ means that the derivative is taken holding the remaining $m - 1$ concentration variables constant. By equating eqs A.1a and A.1b, it is easily shown that the *constrained* P_i are related to the *unconstrained* $P_{[i]}$ by

$$P_i \equiv P_{[i]} - P_{[m]} \tag{A.4}$$

which is a general relationship applicable to any thermodynamic variable U; i.e., $U_i \equiv U_{[i]} - U_{[m]}$. An analogue of eq 7 is obtained from eq A.1b:

$$\partial v/\partial\phi_i)_{T,P,[\phi]} \equiv v_{[i]} = v\beta P_{[i]} \tag{A.5}$$

As a check for a binary solution

$$v_1 = v_{[1]} - v_{[2]} = v\beta(P_{[1]} - P_{[2]}) = v\beta P_1 = -g_{\{v\phi_1\}}/g_{\{vv\}} \tag{A.6}$$

and eq 7 is successfully recovered.

Partial Volumes. By use of the definition of the *partial specific volume* and weight fractions as the concentration variables, $\bar{v}_i$ is given by

$$\bar{v}_i \equiv \frac{1}{M_i}\left(\frac{\partial v}{\partial n_i}\right)_{T,P,n_{j\neq i}} = v + \frac{n_i}{w_i}\left(\frac{\partial v}{\partial n_i}\right)_{T,P,n_{j\neq i}} = v + \frac{n_i}{w_i}\sum_{j=1}^{m} v_{[j]}\left(\frac{\partial\phi_j}{\partial n_i}\right)_{n_{j\neq i}}$$

or

$$\bar{v}_i = v + \sum_{j=1}^{m}(\delta_{ij} - w_j)v_{[j]} = v + v_{[i]} - \sum_{j=1}^{m} w_j v_{[j]} \tag{A.7a}$$

where δ_{ij} is a Kronecker delta function:

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \tag{A.8}$$

Substituting eq A.5 into eq A.7a yields

$$\bar{v}_i = v\{1 + \beta[P_{[i]} - \sum_{j=1}^{m} w_j P_{[j]}]\} \tag{A.7b}$$

or in a more compact vector notation

$$\bar{v}_i = v\{1 + \beta(P_{[i]} - \mathbf{w}\cdot\mathbf{P}_{[w]})\} \tag{A.7c}$$

where $\mathbf{w}$ and $\mathbf{P}_{[w]}$ are the m-component vectors ($w_1, w_2, \ldots, w_m$) and ($P_{[1]}, P_{[2]}, \ldots P_{[m]}$), respectively. The reader can quickly verify that eq A.7 reduces to eq 37 for a binary solution.

The vector product $\mathbf{w}\cdot\mathbf{P}_{[w]}$ can be easily evaluated for a molecular model when the pressure P is a *homogeneous function* in the m concentration variables. For example, if P is a homogenous function of order n in the w_i, then by Euler's theorem

$$\mathbf{w}\cdot\mathbf{P}_{[w]} = nP \tag{A.9}$$

In practice, P must be decomposed into its various homogenous parts and then eq A.9 is applied to each part.

Chemical Potentials. The chemical potential, μ_i, of component i in an m-component solution is given by

$$\mu_i = v_i^0\{g + g_{[i]} - \sum_{j=1}^{m}\phi_j g_{[j]}\} \equiv v_i^0\{g + g_{[i]} - \phi\cdot\mathbf{g}_{[\phi]}\} \tag{A.10}$$

where we have used volume fractions as the concentration variables (see eqs 40 and 41) and algebraic operations similar to those used to derive $\bar{v}_i$ above. As before we separate g into its classical configurational and residual components so that

$$\mu_i = \mu_i^{\mathrm{c}} + \mu_i^{\mathrm{R}}$$

Applying eq A.10 to the configurational free energy, g^{c}, and residual free energy, g^{R}, we obtain

$$\mu_i^{\mathrm{c}} = RT\left[\ln\phi_i + 1 - v_i^0\sum_{j=1}^{m}\frac{\phi_j}{v_j^0}\right] \tag{A.11}$$

and

$$\mu_i^{\mathrm{R}} = v_i^0\{g^{\mathrm{R}} + (1 - \phi_i)g_{[i]}^{\mathrm{R}} - \sum_{j\neq i}^{m}\phi_j g_{[j]}^{\mathrm{R}}\} \tag{A.12a}$$

To obtain the equation analogous to eq 45b, eq A.12a is expanded around $\phi_i = 1$ and $\phi_{j\neq i} = 0$ at constant T and P and yields after some algebra

$$\mu_i^{\mathrm{R}} = \mu_i^0 - \frac{1}{2}v_i^0\sum_{j=1}^{m}\sum_{k=1}^{m} g_{[jk]}^{R_0}(\phi_j - \delta_{ij})(\phi_k - \delta_{ik}) + \ldots \tag{A.12b}$$

or

$$\mu_i^{\mathrm{R}} = \mu_i^0 - \frac{1}{2}v_i^0\{g_{[ii]}^{\mathrm{R}_0} - 2\sum_{j=1}^{m} g_{[ij]}^{\mathrm{R}_0}\phi_j + \sum_{j=1}^{m}\sum_{k=1}^{m} g_{[jk]}^{\mathrm{R}_0}\phi_j\phi_k\} + \ldots \tag{A.12c}$$

where $\mu_i^0 \equiv v_i^0 g^{\mathrm{R}}(\phi_i{=}1)$ and $g_{[jk]}^{\mathrm{R}_0} \equiv g_{[jk]}^{\mathrm{R}}(\phi_i{=}1)$. A quick check of the above equations is to assume that g^{R} has the following classical form:

$$g^{\mathrm{R}} = \sum_{j=1}^{m}\phi_j g^{\mathrm{R}}(\phi_j{=}1) + RT\sum_{j<k}^{m}\sum\phi_k\phi_j\chi_{kj} \tag{A.13}$$

Then $g_{[kj]}^{\mathrm{R}} = RT\chi_{kj}(1 - \delta_{kj})$, which when substituted into eq A.12c yields

$$\mu_i^{\mathrm{R}} = \mu_i^0 + v_i^0 RT[\sum_{j=1}^{m}\phi_j\chi_{ij} - \sum_{j<k}^{m}\sum\phi_k\phi_j\chi_{kj}] \tag{A.14}$$

the correct result for an m-component classical mixture.[29]

All of the second derivatives in eq A.12 are at fixed T and P; i.e.

$$g_{[jk]}^{\mathrm{R}} \equiv \partial g_{[j]}^{\mathrm{R}}/\partial\phi_k)_{T,P,[\phi]} \tag{A.15}$$

Thus (compare with eq 21)

$$g_{[jk]}{}^{\mathrm{R}} \equiv \partial g_{[j]}{}^{\mathrm{R}}/\partial\phi_k)_{T,P,\tilde{v},[\phi]} + \partial g_{[j]}{}^{\mathrm{R}}/\partial\tilde{v})_{T,P,\phi}\tilde{v}_{[k]} \equiv g_{\{[jk]\}}{}^{\mathrm{R}} - \tilde{v}\beta P_{[j]}P_{[k]} \quad (\mathrm{A.16})$$

Substituting eq A.16 into eq A.12 yields

$$\mu_i{}^{\mathrm{R}} = \mu_i{}^0 - \frac{1}{2}v_i{}^0\{g_{\{[ii]\}}{}^{\mathrm{R}_0} - \beta_i\tilde{v}_i(P_{[i]}{}^0)^2 - 2\sum_{j=1}^{m}[g_{\{[ij]\}}{}^{\mathrm{R}_0} - \beta_i\tilde{v}_iP_{[i]}{}^0P_{[j]}{}^0]\phi_j + \sum_{j=1}^{m}\sum_{k=1}^{m}[g_{\{[jk]\}}{}^{\mathrm{R}_0} - \beta_i\tilde{v}_iP_{[j]}{}^0P_{[k]}{}^0]\phi_j\phi_k\} + \ldots \quad (\mathrm{A.17})$$

where β_i is the compressibility of the pure component i and $\tilde{v}_i = \tilde{v}(\phi_i{=}1)$. Since

$$g_i = g_{[i]} - g_{[m]} \quad (\mathrm{A.18})$$

we also have

$$g_{ij} = g_{[i]j} - g_{[m]j} = g_{[ij]} - g_{[im]} - g_{[mj]} + g_{[mm]} \quad (\mathrm{A.19})$$

It can be verified that, for a binary solution, eq A.17 reduces to the residual part of eq 45b by using eqs A.18 and A.19.

The "constrained variation" of the chemical potential with composition at constant T and P is given by ($\phi_i + \phi_m$ = constant)

$$\left.\frac{\partial\mu_i}{\partial\phi_i}\right)_{T,P,\phi} = RTv_i{}^0(1-\phi_i)\left[\frac{1}{v_i{}^0\phi_i} + \frac{1}{v_m{}^0(1-\phi_i)}\right] + v_i{}^0\{g_{\{[i]i\}}{}^{\mathrm{R}} - \tilde{v}\beta P_{[i]}P_i - \sum_{j=1}^{m}\phi_j[g_{\{[j]i\}}{}^{\mathrm{R}} - \tilde{v}\beta P_{[j]}P_i]\} \quad (\mathrm{A.20})$$

where we have used the result

$$g_{[j]k}{}^{\mathrm{R}} = g_{[jk]}{}^{\mathrm{R}} - g_{[jm]}{}^{\mathrm{R}} = g_{\{[jk]\}}{}^{\mathrm{R}} - \tilde{v}\beta P_{[j]}P_{[k]} - \{g_{\{[jm]\}}{}^{\mathrm{R}} - \tilde{v}\beta P_{[j]}P_{[m]}\}$$

or

$$g_{[j]k}{}^{\mathrm{R}} = g_{\{[j]k\}}{}^{\mathrm{R}} - \tilde{v}\beta P_{[j]}P_k \quad (\mathrm{A.21})$$

It can be readily verified that, for a binary solution, eq A.20 reduces to eq 52. Equation A.20 would be useful in a pseudo ternary system with two solvents (components i and m) and a polydisperse polymer.

Phase Stability. For a multicomponent system the requirement for thermodynamic stability (or metastability) of a single homogeneous phase at constant T and P is that the second variation of the Gibbs free energy (δ^2g) is positive for arbitrary variations ($\delta\phi_i$) in composition:

$$\delta^2g = \sum_{i=1}^{m-1}\sum_{j=1}^{m-1}g_{ij}\,\delta\phi_i\,\delta\phi_j = \sum_{i=1}^{m-1}\sum_{j=1}^{m-1}g_{\{ij\}}\,\delta\phi_i\,\delta\phi_j - v\beta[\sum_{i=1}^{m-1}P_i\,\delta\phi_i]^2 > 0 \quad (\mathrm{A.22})$$

It is clear that the finite compressibility of the multicomponent solution makes the compressible solution less stable than the corresponding incompressible solution. Since eq A.22 is a quadratic form, the requirement that $\delta^2g > 0$ for arbitrary composition variations is satisfied when the matrix formed by the g_{ij} is positive definite. Two necessary conditions that must be satisfied for positive definiteness are that each diagonal element must be positive

$$g_{\{ii\}} - \tilde{v}\beta P_i{}^2 = \frac{1}{v_i{}^0\phi_i} + \frac{1}{v_m{}^0\phi_m} + g_{\{ii\}}{}^{\mathrm{R}} - \tilde{v}\beta P_i{}^2 > 0 \quad (\mathrm{A.23})$$

and the determinant of the $m{-}1 \times m - 1$ matrix g_{ij} must be positive

$$|g_{\{ij\}} - \tilde{v}\beta P_iP_j| > 0 \quad (\mathrm{A.24})$$

The spinodal is determined by setting the determinant equal to zero.[30]

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