The Statistical Mechanical Derivation of the van der Waals Equation of State for a multicomponent fluid and its associated thermodynamic properties

David Keffer
Department of Chemical Engineering
The University of Tennessee, Knoxville
dkeffer@utk.edu

started: March 3, 2005
last updated: March 9, 2005

I. Formulation of the partition function

We will perform our derivation in the canonical ensemble, where we specify the number of molecules, *N*, the volume, *V*, and the temperature *T*. We will briefly revisit the derivation of the single-component van der Waals partition function because following the analogous procedure will guide us to the appropriate partition function in the multicomponent case.

For a monatomic single-component van der Waals fluid, we have previously derived the partition function. It has three components. A configurational contribution, a translational contribution, and a mean-field potential energy contribution.

$$Q_{vdw}(N,V,T)=\Omega(N)Q_{trans}(N,V,T)Q_{pot}(N,V,T) \quad . \tag{1}$$

The configurational contribution to the partition function is simply

$$\Omega=\frac{1}{N!} \quad . \tag{2}$$

The translational contribution to the partition function is

$$Q_{trans}=\left(\frac{V-Nb}{\Lambda^3}\right)^N \quad . \tag{3}$$

where b is the van der Waals volume of the molecule and the thermal deBroglie wavelength is defined as

$$\Lambda=\sqrt{\frac{h^2}{2\pi m k_B T}} \quad , \tag{4}$$

where *h* is Planck's constant, k_B is Boltzmann's constant, and *m* is the mass of the molecule. The mean-field potential energy contribution to the partition function is

$$Q_{pot}=\exp\left(-\frac{NE_{vdw}}{k_B T}\right) \quad . \tag{5}$$

where the potential energy per particle due to particle interactions, E_{vdw}, is

$$E_{vdw} = -a\frac{N}{V} \quad , \tag{6}$$

where a is the van der Waals energetic parameter. These contribution result in the van der Waals partition function,

$$Q_{vdw}\left(N,V,T\right) = \frac{1}{N!}\left(\frac{V-Nb}{\Lambda^3}\right)^N \exp\left(\frac{N^2 a}{Vk_B T}\right) \quad . \tag{7}$$

Before we jump straight into formulating the binary van der Waals partition function, it is also useful to examine the relationship between the single-component and binary ideal gas partition functions. The single component ideal gas partition function has only configurational and translational components.

$$Q_{IG}\left(N,V,T\right) = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \quad . \tag{8}$$

The binary ideal gas partition function is a straight forward extension,

$$Q_{IG}\left(N_1,N_2,V,T\right) = \frac{1}{N_1!N_2!}\left(\frac{V}{\Lambda_1^3}\right)^{N_1}\left(\frac{V}{\Lambda_2^3}\right)^{N_2} \quad . \tag{9}$$

For a multicomponent ideal gas with N_c components, we have

$$Q_{IG}\left(N_1,N_2\ldots N_{N_c},V,T\right) = \prod_{i=1}^{N_c} Q_{IG,i}\left(N_i,V,T\right) \quad , \tag{10}$$

where the partition function of component i is

$$Q_{IG,i}\left(N_i,V,T\right) = \frac{1}{N_i!}\left(\frac{V}{\Lambda_i^3}\right)^{N_i} \quad , \tag{11}$$

and where the thermal de Broglie wavelength for component i is defined as

$$\Lambda_i = \sqrt{\frac{h^2}{2\pi m_i k_B T}} \quad . \tag{12}$$

For a multicomponent van der Waals fluid we will have a molecular volume, b_i, for each component. We will also have a mean-field interaction potential for each pair of components, a_{ij}. Clearly, it makes sense that when the two components are the same, they have the pure component interaction potential, namely

$$a_{ii} = a_i \quad . \tag{13}$$

When the two components are not the same, a_{ij} is an independent parameter. Frequently, people use the mixing rule that

$$a_{ij} = a_{ji} = \sqrt{a_i a_j}\left(1 - k_{ij}\right) \quad , \tag{14}$$

where k_{ij} is an empirical "binary interaction parameter", which is zero unless there is experimental data that indicates that it should be otherwise. However, a mixing rule such as equation (13) is not essential for the statistical mechanical development in this work. As such, we will leave a_{ij} as an independent parameter, which can be reduce to equation (13) or some other form at a later date. However, there is no reason not to assume the symmetry of the interaction parameter, so we will assume $a_{ji} = a_{ij}$.

The partition function for the van der Waals equation of state for a multicomponent mixture can be written as

$$Q_{vdw}\left(N_1, N_2 \ldots N_{N_c}, V, T\right) = \prod_{i=1}^{N_c} Q_{vdw,i}\left(N_1, N_2 \ldots N_{N_c}, V, T\right) \quad . \tag{15}$$

where $Q_{vdw,i}$ is the contribution from component i. It is worthwhile noting that each component's partition function is a function of all of the number of molecules, in constrast to the partition function for the multicomponent ideal gas. The partition function for component i can be written as

$$Q_{vdw,i}\left(N_1, N_2 \ldots N_{N_c}, V, T\right) = \Omega_i\left(N_i\right) Q_{trans,i}\left(N_1, N_2 \ldots N_{N_c}, V, T\right) Q_{pot,i}\left(N_1, N_2 \ldots N_{N_c}, V, T\right) \quad . \tag{16}$$

The configurational contribution to the partition function is simply

$$\Omega_i\left(N_i\right) = \frac{1}{N_i!} \quad . \tag{17}$$

The translational contribution to the partition function is

$$Q_{trans,i}\left(N_1, N_2 \ldots N_{N_c}, V, T\right) = \left(\frac{V - \sum_{j=1}^{N_c} N_j b_j}{\Lambda_i^3} \right)^{N_i} \quad . \tag{18}$$

The total molecular volume to the presence of all the molecules of every component must be substracted from the total volume to obtain the accessible volume. The mean-field potential energy contribution to the partition function is

$$Q_{pot,i} = \exp\left(-\frac{N_i E_{vdw,i}}{k_B T}\right) \quad . \tag{19}$$

where the potential energy for component *i* has contributions from all molecules of every component,

$$E_{vdw} = -\frac{1}{V}\sum_{j=1}^{N_c} N_j a_{ij} \quad . \tag{20}$$

Assembling all of the pieces produces the multicomponent van der Waals partition function,

$$Q_{vdw}\left(N_1, N_2 \ldots N_{N_c}, V, T\right) = \prod_{i=1}^{N_c} \frac{1}{N_i!}\left(\frac{V - \sum_{j=1}^{N_c} N_j b_j}{\Lambda_i^{\,3}}\right)^{N_i} \exp\left(\frac{N_i}{V k_B T}\sum_{j=1}^{N_c} N_j a_{ij}\right) \quad , \tag{21}$$

which for a binary mixture reduces to

$$Q_{vdw}\left(N_1, N_2, V, T\right) = \frac{1}{N_1! N_2!}\frac{\left(V - N_1 b_1 - N_2 b_2\right)^{N_1+N_2}}{\Lambda_1^{\,3N_1}\Lambda_2^{\,3N_2}} \exp\left(\frac{N_1^2 a_{11} + 2N_1 N_2 a_{12} + N_2^2 a_{22}}{V k_B T}\right) \quad .(22)$$

II. Derivation of Thermodynamic Properties

As always, we require the natural log of the partition function

$$\ln\left(Q_{vdw}\right) = \sum_{i=1}^{N_c}\left[-\ln\left(N_i!\right) + N_i \ln\left(\frac{V - \sum_{j=1}^{N_c} N_j b_j}{\Lambda_i^{\,3}}\right) + \frac{N_i}{V k_B T}\sum_{j=1}^{N_c} N_j a_{ij}\right] \tag{23}$$

We use Stirling's approximation for the natural log of the factorial of a large number

$$\ln(Q_{vdw}) = \sum_{i=1}^{N_c}\left[-N_i \ln(N_i) + N_i + N_i \ln\left(\frac{V - \sum_{j=1}^{N_c} N_j b_j}{\Lambda_i^{\,3}}\right) + \frac{N_i}{Vk_BT}\sum_{j=1}^{N_c} N_j a_{ij}\right] \tag{24}$$

The first thermodynamic property that we will calculate is the pressure because that is what everyone associates with the van der Waals equation of state.

$$p = k_BT\left(\frac{\partial \ln(Q)}{\partial V}\right)_{\mathbf{N},T} = k_BT\sum_{i=1}^{N_c}\left[\frac{N_i}{V - \sum_{j=1}^{N_c} N_j b_j} - \frac{N_i}{V^2 k_BT}\sum_{j=1}^{N_c} N_j a_{ij}\right] \tag{25}$$

where we have introduced the notation **N**, which is a vector of all N_i. If we introduce four additional variables, a mole fraction defined as

$$x_i \equiv \frac{N_i}{\sum_{j=1}^{N_c} N_j} = \frac{N_i}{N} \tag{26}$$

a molecular volume, V_m, defined as

$$V_m \equiv \frac{V}{N} \quad , \tag{27}$$

a mixture van der Waals size paramater, b_{mix},

$$b_{mix} = \sum_{j=1}^{N_c} x_j b_j \quad , \tag{28}$$

and a mixture van der Waals interaction parameter, a_{mix},

$$a_{mix} = \sum_{i=1}^{N_c}\sum_{j=1}^{N_c} x_i x_j a_{ij} \;.., \tag{29}$$

then we can rewrite the van der Waals equation of state in a very familiar form,

$$p = \frac{k_BT}{V_m - b_{mix}} - \frac{a_{mix}}{V_m^2} \tag{30}$$

This expression for the pressure provides the confirmation that our partition function in equation (21) is correct.

Now let's derive other thermodynamic functions. We will start with the Helmholtz free energy, *A*,

$$A = -k_B T \ln(Q) = -k_B T \sum_{i=1}^{N_c} \left[-N_i \ln(N_i) + N_i + N_i \ln\left(\frac{V - \sum_{j=1}^{N_c} N_j b_j}{\Lambda_i^3} \right) + \frac{N_i}{V k_B T} \sum_{j=1}^{N_c} N_j a_{ij} \right] \quad (31)$$

On a per molecule basis, we can write

$$A_m = \frac{A}{N} = k_B T \sum_{i=1}^{N_c} x_i \ln(x_i) - k_B T - k_B T \sum_{i=1}^{N_c} x_i \ln\left(\frac{V_m - b_{mix}}{\Lambda_i^3} \right) - \frac{1}{V_m} a_{mix} \quad (32)$$

The internal energy is

$$U = k_B T^2 \left(\frac{\partial \ln(Q)}{\partial T} \right)_{\mathbf{N},V} = \frac{3}{2} k_B T \sum_{j=1}^{N_c} N_j - \frac{1}{V} \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} N_i N_j a_{ij} \quad (33)$$

On a per molecule basis, we can write

$$U_m = \frac{U}{N} = \frac{3}{2} k_B T - \frac{a_{mix}}{V_m} \quad (34)$$

The chemical potential of component *i* is

$$\mu_i = -k_B T \left(\frac{\partial \ln(Q)}{\partial N_i} \right)_{T,V,N_{j \neq i}} = k_B T \ln(N_i)$$
$$- k_B T \left[\ln\left(\frac{V - \sum_{j=1}^{N_c} N_j b_j}{\Lambda_i^3} \right) - \frac{b_i}{V - \sum_{j=1}^{N_c} N_j b_j} \sum_{j=1}^{N_c} N_j + \frac{2}{V k_B T} \sum_{j=1}^{N_c} N_j a_{ij} \right] \quad (35)$$

In terms of the macroscopic variables, the chemical potential can be written as

$$\mu_i = -k_B T \ln\left(\frac{V_m - b_{mix}}{x_i \Lambda_i^3} \right) + \frac{k_B T b_i}{V_m - b_{mix}} - \frac{2}{V_m} \sum_{j=1}^{N_c} x_j a_{ij} \quad (36)$$

It is also useful to write this as

$$\mu_i = -k_B T \ln\left(\frac{V_m - b_{mix}}{x_i \Lambda_i^3}\right) + \frac{k_B T}{V_m - b_{mix}}\left(\frac{\partial b_{mix}}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} - \frac{1}{V_m}\left(\frac{\partial a_{mix}}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} \tag{37}$$

where we see have used the fact that if we want to express derivatives in terms of mole fractions (rather than number of molecules) then we have to hold constant the ratios of all other mole fractions (rather than the number of all the other molecules), namely

$$\left(\frac{\partial b_{mix}(x_i)}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} = \left(\frac{\partial b_{mix}(N_i)}{\partial N_i}\right)_{T,V,N_{j\neq i}} \tag{38}$$

Equation (38) is useful when a macroscopic mixing rule is given in terms of the mole fractions. Equation (37) is useful from a macroscopic point of view because it shows explicitly that, aside from an ideal gas-like contribution to the chemical potential, all of the remaining terms are dictated by the choice of mixing rules for the parameters.

The entropy is

$$S = \frac{U - A}{T} = k_B\left[\frac{5}{2}N + \sum_{i=1}^{N_c} N_i \ln\left(\frac{V - \sum_{j=1}^{N_c} N_j b_j}{\Lambda_i^3}\right) - \sum_{i=1}^{N_c} N_i \ln(N_i)\right] \tag{39}$$

The molecular entropy is

$$S_m = \frac{S}{N} = k_B\left[\frac{5}{2} + \sum_{i=1}^{N_c} x_i \ln\left(\frac{V_m - b_{mix}}{\Lambda_i^3}\right) - \sum_{i=1}^{N_c} x_i \ln(x_i)\right] \tag{40}$$

The enthalpy is

$$H = U + PV = \frac{3}{2}k_B TN - \frac{2}{V}\sum_{i=1}^{N_c}\sum_{j=1}^{N_c} N_i N_j a_{ij} + \frac{k_B TVN}{V - \sum_{j=1}^{N_c} N_j b_j} \tag{41}$$

The molecular enthalpy is

$$H_m = \frac{H}{N} = \frac{3}{2}k_B T - \frac{2a_{mix}}{V_m} + \frac{k_B TV_m}{V_m - b_{mix}} \tag{42}$$

The Gibbs free energy is

$$G = H - TS = -k_B T N - \frac{2}{V}\sum_{i=1}^{N_c}\sum_{j=1}^{N_c} N_i N_j a_{ij} + \frac{k_B T V N}{V - \sum_{j=1}^{N_c} N_j b_j}$$

$$- k_B T\left[\sum_{i=1}^{N_c} N_i \ln\left(\frac{V - \sum_{j=1}^{N_c} N_j b_j}{\Lambda_i^3}\right) - \sum_{i=1}^{N_c} N_i \ln(N_i)\right] \tag{43}$$

The molecular Gibbs free energy is

$$G_m = \frac{G}{N} = -k_B T\left[1 - \frac{V_m}{V_m - b_{mix}} + \left[\sum_{i=1}^{N_c} x_i \ln\left(\frac{V_m - b_{mix}}{\Lambda_i^3}\right) - \sum_{i=1}^{N_c} x_i \ln(x_i)\right]\right] - \frac{2a_{mix}}{V_m} \tag{44}$$

In addition to the basic thermodynamic properties, we can also calculate a variety of thermodynamic properties from the partial derivatives. We shall start with derivatives of the pressure.

$$\left(\frac{\partial p}{\partial T}\right)_{V_m, N_i} = \frac{k_B}{V_m - b_{mix}} \tag{45}$$

$$\left(\frac{\partial p}{\partial V_m}\right)_{T, N_i} = -\frac{k_B T}{(V_m - b_{mix})^2} + 2\frac{a_{mix}}{V_m^3} \tag{46}$$

$$\left(\frac{\partial V_m}{\partial T}\right)_{p, N_i} = -\frac{\left(\frac{\partial p}{\partial T}\right)_{V_m, N_i}}{\left(\frac{\partial p}{\partial V_m}\right)_{T, N_i}} = \frac{1}{\frac{T}{V_m - b_{mix}} - 2\frac{a_{mix}(V_m - b_{mix})}{k_B V_m^3}} \tag{47}$$

$$\left(\frac{\partial p}{\partial N_i}\right)_{T, V, N_{j\neq i}} = -\frac{k_B T b_i}{\left(V - \sum_{j=1}^{N_c} N_j b_j\right)^2}\sum_{k=1}^{N_c} N_k + \frac{k_B T}{V - \sum_{j=1}^{N_c} N_j b_j} - \frac{2}{V^2}\sum_{j=1}^{N_c} N_j a_{ij} \tag{48}$$

Equation (48) can also be written as

$$\left(\frac{\partial p}{\partial N_i}\right)_{T, V, N_{j\neq i}} = \frac{1}{N}\left[-\frac{k_B T b_i}{(V_m - b_{mix})^2} + \frac{k_B T}{V_m - b_{mix}} - \frac{2}{V_m^2}\sum_{j=1}^{N_c} x_j a_{ij}\right] \tag{49}$$

as well as

$$\left(\frac{\partial p(x_i)}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} = \frac{1}{N}\left[-\frac{k_B T}{(V_m - b_{mix})^2}\left(\frac{\partial b_{mix}(x_i)}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} + \frac{k_B T}{V_m - b_{mix}} - \frac{1}{V_m^2}\left(\frac{\partial a_{mix}(x_i)}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}}\right] \quad (50)$$

Next we can take derivatives of the internal energy. The molecular constant volume-heat capacity is

$$C_v = \left(\frac{\partial U_m}{\partial T}\right)_{V_m,N_i} = \frac{3}{2}k_B \quad (52)$$

The molecular constant-pressure heat capacity is

$$C_p = \left(\frac{\partial H_m}{\partial T}\right)_{p,N_i} = \left(\frac{\partial U_m}{\partial T}\right)_{p,N_i} + p\left(\frac{\partial V_m}{\partial T}\right)_{p,N_i} \quad (53)$$

Now we need, the first term on the RHS. Going to the Tables of P.W. Bridgman, we have

$$\left(\frac{\partial U_m}{\partial T}\right)_{p,N_i} = C_V + T\left(\frac{\partial p}{\partial T}\right)_{V_m,N_i}\left(\frac{\partial V_m}{\partial T}\right)_{p,N_i} - p\left(\frac{\partial V_m}{\partial T}\right)_{p,N_i} \quad (54)$$

Substituting equation (20) into equation (19) yields

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_{V_m,N_i}\left(\frac{\partial V_m}{\partial T}\right)_{p,N_i} = \frac{3}{2}k_B + k_B\frac{1}{1-2\frac{a_{mix}(V_m - b_{mix})^2}{k_B T V_m^3}} \quad (55)$$

The derivative of the internal energy with respect to the volume is

$$\left(\frac{\partial U_m}{\partial V_m}\right)_{T,N_i} = 2\frac{a_{mix}}{V_m^2} \quad (56)$$

The partial molar internal energy is

$$\overline{U_i} = \left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \frac{3}{2}k_B T - \frac{2}{V}\sum_{j=1}^{N_c} N_j a_{ij} \quad (57)$$

$$\overline{U_i} = \left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \frac{3}{2}k_B T - \frac{2}{V_m}\sum_{j=1}^{N_c} x_j a_{ij} = \frac{3}{2}k_B T - \frac{1}{V_m}\left(\frac{\partial a_{mix}(x_i)}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} \quad (58)$$

The derivative of the enthalpy with respect to the volume is

$$\left(\frac{\partial H_m}{\partial V_m}\right)_{T,N_i} = \frac{4a_{mix}}{V_m^2} + \frac{k_B T}{V_m - b_{mix}} - \frac{k_B T V_m}{\left(V_m - b_{mix}\right)^2} \tag{59}$$

The partial molar enthalpy is

$$\overline{H}_i = \left(\frac{\partial H}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \frac{3}{2}k_B T - \frac{4}{V}\sum_{j=1}^{N_c} N_j a_{ij} + \frac{k_B T V}{V - \sum_{j=1}^{N_c} N_j b_j} - \frac{b_i k_B T V N}{\left(V - \sum_{j=1}^{N_c} N_j b_j\right)^2} \tag{60}$$

$$\overline{H}_i = \frac{3}{2}k_B T - \frac{4}{V_m}\sum_{j=1}^{N_c} x_j a_{ij} + \frac{k_B T V_m}{V_m - b_{mix}} - \frac{b_i k_B T V_m}{\left(V_m - b_{mix}\right)^2} \tag{61}$$

$$\overline{H}_i = \frac{3}{2}k_B T - \frac{2}{V_m}\left(\frac{\partial a_{mix}(x_i)}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} + \frac{k_B T V_m}{V_m - b_{mix}} - \frac{k_B T V_m}{\left(V_m - b_{mix}\right)^2}\left(\frac{\partial b_{mix}(x_i)}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} \tag{62}$$

Now, we move on to derivatives of the chemical potential, which we shall also shortly require.

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{V_m,x_i} = -k_B \ln\left(\frac{V_m - b_{mix}}{x_i \Lambda_i^3}\right) - \frac{3k_B}{2}\left(\ \right) + \frac{k_B}{V_m - b_{mix}}\left(\frac{\partial b_{mix}}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} \tag{63}$$

$$\left(\frac{\partial \mu_i}{\partial V_m}\right)_{T,x_i} = \frac{-k_B T}{V_m - b_{mix}} - \frac{k_B T}{\left(V_m - b_{mix}\right)^2}\left(\frac{\partial b_{mix}}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} + \frac{1}{V_m^2}\left(\frac{\partial a_{mix}}{\partial x_i}\right)_{T,V,\frac{x_{j\neq i}}{x_{k\neq i}}} \tag{64}$$

$$\begin{aligned}\left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,V_m} &= \frac{k_B T}{x_j}\delta_{ij} + \frac{k_B T}{V_m - b_{mix}}\left[\left(\frac{\partial b_{mix}}{\partial x_j}\right)_{T,V,\frac{x_{m\neq j}}{x_{k\neq j}}} + \left(\frac{\partial b_{mix}}{\partial x_i}\right)_{T,V,\frac{x_{m\neq i}}{x_{k\neq i}}}\right] \\ &+ \frac{k_B T}{\left(V_m - b_{mix}\right)^2}\left(\frac{\partial b_{mix}}{\partial x_j}\right)_{T,V,\frac{x_{m\neq j}}{x_{k\neq j}}}\left(\frac{\partial b_{mix}}{\partial x_i}\right)_{T,V,\frac{x_{m\neq i}}{x_{k\neq i}}} - \frac{1}{V_m}\left(\frac{\partial}{\partial x_j}\left(\frac{\partial a_{mix}}{\partial x_i}\right)_{T,V,\frac{x_{m\neq i}}{x_{k\neq i}}}\right)_{T,V,\frac{x_{m\neq j}}{x_{k\neq j}}}\end{aligned} \tag{65}$$

For the van der Waals fluid, this becomes

$$\left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,V_m} = \frac{k_B T}{x_j}\delta_{ij} + \frac{k_B T\left(b_i + b_j\right)}{V_m - b_{mix}} + \frac{k_B T b_i b_j}{\left(V_m - b_{mix}\right)^2} - \frac{2a_{ij}}{V_m} \tag{66}$$

III. Vapor-Liquid Equilibrium

In a mixture of N_c components, the phase rule tells us that at vapor-liquid equilibrium we have N_c degrees of freedom.

$$DOF = C - \phi + 2 = N_c - 2 + 2 = N_c \tag{67}$$

So in a binary mixture, we have two degrees of freedom, meaning that we can arbitrary specify two variables, fixing all other variables.

At equilibrium, we have the following constraints. We have thermal equilibrium, in which the temperature of the two phases are equal,

$$\Delta T = T_V - T_L = 0 \tag{68}$$

We have mechanical equilibrium, in which the pressure of the two phases are equal,

$$\Delta p = p_V - p_L = 0 \tag{69}$$

We have chemical equilibrium, in which the chemical potential of each component in the two phases are equal,

$$\Delta \mu = \mu_{i,V} - \mu_{i,L} = 0 \qquad \text{for all i} \tag{70}$$

Consider a binary mixture. Let’s suppose that, in choosing our two degrees of freedom, we fix the temperature and the density of the liquid phase. In this case, we have three remaining unknowns, ρ_V, $w_{A,L}$, and $w_{A,V}$. Conveniently, we have three equations to solve for these three unknowns, equation (69) and equation (70) for i = 1 and i=2.

This set of three equations and three unknowns must be solved using an iterative, numerical procedure. Once the densities and compositions are known, the vapor pressure can be calculated using equation (30) for either the liquid phase or the vapor phase.

IV. Constrained Vapor-Liquid Equilibrium

Consider a fluid containing N_A moles of component A with molecular weight m_A and N_B moles of component B with molecular weight m_B, initially above the critical temperature of the mixture, $T_{c,mix}$, in a closed volume, V. We remove heat at a constant rate, Q, causing the temperature to drop. Eventually the system will fall into the two phase region and phase separate. We want to describe the time dependence of the system. Specifically, we want the following variables as a function of time: the temperature, T, the pressure, p, the vapor fraction, ϕ_V, the density of the vapor phase, ρ_V, the density of the liquid phase, ρ_L., the mass fraction of A in the vapor phase, $w_{A,V}$, and the the mass fraction of A in the liquid phase, $w_{A,L}$.

In this case, there is only degree of freedom, namely the temperature. The other degree of freedom has been lost to the fact that the volume and the mass are constants in time. This constraint can be written as

$$\rho_A = \rho_L w_{A,L} \frac{\rho_V - \rho}{\rho_V - \rho_L} + \rho_V w_{A,V} \frac{\rho - \rho_L}{\rho_V - \rho_L} \tag{71}$$

where ρ is a constant equal to the total mass of the system over the total volume of the system,

$$\rho = \rho_A + \rho_B = \frac{N_A m_A + N_B m_B}{V} \tag{72}$$

So, now if we have four unknowns ρ_L, ρ_V, $w_{A,L}$, and $w_{A,V}$. Conveniently, we now have four equations to solve for these four unknowns, equation (69), equation (70) for i = 1 and i=2, and equation (71). Life is good. If we want the steady-state solution to this equilibrium, we have only to solve these four equations.

However, if we want to know the transient behavior of the system, then we have to write the mass, momentum, and energy balances that describe this system. We won't write these equations in this hand-out. However, in their formulation, we discover that we require some partial derivatives that we have not yet obtained.

We require

$$\left.\left(\frac{\partial V_{m,L}}{\partial T}\right)\right|_{sat}^{*}, \left.\left(\frac{\partial x_{A,L}}{\partial T}\right)\right|_{sat}^{*}, \left.\left(\frac{\partial V_{m,V}}{\partial T}\right)\right|_{sat}^{*}, \left.\left(\frac{\partial x_{A,V}}{\partial T}\right)\right|_{sat}^{*} \tag{73}$$

where the asterisk indicates that these partial derivatives are evaluated along the saturation (two-phase) line where all four of the constraints (including equation (71)) are satisified. We now demonstrate how to obtain these partial derivatives.

We begin by differentiating all of the constraints with respect to temerature.

$$dp_V - dp_L = 0 \tag{74}$$

The pressure, as we have written it, is a function of T, ρ, and x_A. Therefore,

$$dp = \left(\frac{\partial p}{\partial T}\right)_{\rho, x_A} dT + \left(\frac{\partial p}{\partial \rho}\right)_{T, x_A} d\rho + \left(\frac{\partial p}{\partial x_A}\right)_{\rho, T} dx_A \tag{75}$$

In the constrained system, ρ and x_A. are functions of T, so we can write

$$\begin{aligned} dp &= \left(\frac{\partial p}{\partial T}\right)_{\rho,x_A} dT + \left(\frac{\partial p}{\partial \rho}\right)_{T,x_A} \left(\frac{\partial \rho}{\partial T}\right)^{*} dT + \left(\frac{\partial p}{\partial x_A}\right)_{\rho,T} \left(\frac{\partial x_A}{\partial T}\right)^{*} dT \\ &= \left[\left(\frac{\partial p}{\partial T}\right)_{\rho,x_A} + \left(\frac{\partial p}{\partial \rho}\right)_{T,x_A} \left(\frac{\partial \rho}{\partial T}\right)^{*} + \left(\frac{\partial p}{\partial x_A}\right)_{\rho,T} \left(\frac{\partial x_A}{\partial T}\right)^{*}\right] dT \end{aligned} \tag{76}$$

Substituting equation (76) into equation (74) yields

$$\begin{aligned} &\left[\left(\frac{\partial p_V}{\partial T}\right)_{\rho_V,x_A} + \left(\frac{\partial p_V}{\partial \rho_V}\right)_{T,x_{A,V}} \left(\frac{\partial \rho_V}{\partial T}\right)^{*} + \left(\frac{\partial p_V}{\partial x_{A,V}}\right)_{\rho_V,T} \left(\frac{\partial x_{A,V}}{\partial T}\right)^{*}\right] \\ &= \left[\left(\frac{\partial p_L}{\partial T}\right)_{\rho_L,x_A} + \left(\frac{\partial p_L}{\partial \rho_L}\right)_{T,x_{A,L}} \left(\frac{\partial \rho_L}{\partial T}\right)^{*} + \left(\frac{\partial p_L}{\partial x_{A,L}}\right)_{\rho_L,T} \left(\frac{\partial x_{A,L}}{\partial T}\right)^{*}\right] \end{aligned} \tag{77}$$

By differentiating equation (70) in a similar manner, equivalent equations can be written, where we replace the pressure with the chemical potential of each species. Finally, we differentiate equation (71)

$$\begin{aligned} \left(\left(\frac{\partial \rho_V}{\partial T}\right)^{*} - \left(\frac{\partial \rho_L}{\partial T}\right)^{*}\right)\rho_A &= \left(\frac{\partial \rho_L}{\partial T}\right)^{*} w_{A,L}(\rho_V - \rho) + \rho_L \left(\frac{\partial w_{A,L}}{\partial T}\right)^{*} (\rho_V - \rho) + \rho_L w_{A,L} \left(\frac{\partial \rho_V}{\partial T}\right)^{*} \\ &+ \left(\frac{\partial \rho_V}{\partial T}\right)^{*} w_{A,V}(\rho - \rho_L) + \rho_V \left(\frac{\partial w_{A,V}}{\partial T}\right)^{*} (\rho - \rho_L) - \rho_V w_{A,V} \left(\frac{\partial \rho_L}{\partial T}\right)^{*} \end{aligned} \tag{78.a}$$

$$\begin{aligned} 0 &= \left[-\rho_A + \rho_L w_{A,L} + w_{A,V}(\rho - \rho_L)\right]\left(\frac{\partial \rho_V}{\partial T}\right)^{*} + \left[\rho_A + w_{A,L}(\rho_V - \rho) - \rho_V w_{A,V}\right]\left(\frac{\partial \rho_L}{\partial T}\right)^{*} \\ &+ \rho_L(\rho_V - \rho)\left(\frac{\partial w_{A,L}}{\partial T}\right)^{*} + \rho_V(\rho - \rho_L)\left(\frac{\partial w_{A,V}}{\partial T}\right)^{*} \end{aligned} \tag{78}$$

Equation (78) is in terms of densities and mass fractions, rather than molar volumes and mole fractions. We can convert from mass fraction to mole fraction.

$$w_A = \frac{x_A m_A}{x_A m_A + x_B m_B} = \frac{x_A m_A}{x_A m_A + (1 - x_A) m_B} \tag{79}$$

$$\begin{aligned} \left(\frac{dw_A}{dx_A}\right) &= \frac{m_A}{x_A m_A + (1 - x_A) m_B} - \frac{x_A m_A (m_A - m_B)}{(x_A m_A + (1 - x_A) m_B)^2} \\ &= \frac{m_A m_B}{(x_A m_A + (1 - x_A) m_B)^2} = \frac{w_A w_B}{x_A x_B} \end{aligned} \tag{80}$$

We can also convert from densities to molar volumes

$$\rho = \frac{x_A m_A + x_B m_B}{V_m} \tag{81}$$

$$\left(\frac{\partial \rho}{\partial V_m}\right)_{x_i} = -\frac{x_A m_A + x_B m_B}{V_m^2} \tag{82}$$

With these equations, we can rewrite equation (78) as

$$\begin{aligned} 0 = {} & \left[-\rho_A + \rho_L w_{A,L} + w_{A,V}(\rho - \rho_L)\right]\left(\frac{\partial \rho_V}{\partial V_m^V}\right)\left(\frac{\partial V_m^V}{\partial T}\right)^* \\ & + \left[\rho_A + w_{A,L}(\rho_V - \rho) - \rho_V w_{A,V}\right]\left(\frac{\partial \rho_L}{\partial V_m^L}\right)\left(\frac{\partial V_m^L}{\partial T}\right)^* \\ & + \rho_L(\rho_V - \rho)\left(\frac{dw_{A,L}}{dx_{A,L}}\right)\left(\frac{\partial x_{A,L}}{\partial T}\right)^* + \rho_V(\rho - \rho_L)\left(\frac{dw_{A,V}}{dx_{A,V}}\right)\left(\frac{\partial x_{A,V}}{\partial T}\right)^* \end{aligned} \tag{83}$$

Our four equations ((77), (77) for μ_A and μ_B, and (83)) are all linear in the four unknown derivatives of equation (73), therefore they can be solved using linear algebra for the four derivatives.

$$\underline{\underline{A}}\,\underline{x} = \underline{b} \tag{84}$$

where

$$\underline{x} = \left[\left(\frac{\partial \rho_V}{\partial T}\right)^* \quad \left(\frac{\partial x_{A,V}}{\partial T}\right)^* \quad \left(\frac{\partial \rho_L}{\partial T}\right)^* \quad \left(\frac{\partial x_{A,L}}{\partial T}\right)^*\right]^T \tag{85}$$

$$\underline{b} = \begin{bmatrix} \left(\frac{\partial p_L}{\partial T}\right)_{\rho_L, x_A} - \left(\frac{\partial p_V}{\partial T}\right)_{\rho_V, x_A} \\ \left(\frac{\partial \mu_{A,L}}{\partial T}\right)_{\rho_L, x_A} - \left(\frac{\partial \mu_{A,V}}{\partial T}\right)_{\rho_V, x_A} \\ \left(\frac{\partial \mu_{B,L}}{\partial T}\right)_{\rho_L, x_A} - \left(\frac{\partial \mu_{B,V}}{\partial T}\right)_{\rho_V, x_A} \\ 0 \end{bmatrix} \tag{86}$$

and

$$\underline{\underline{A}} = \begin{bmatrix} \left(\frac{\partial p_V}{\partial \rho_V}\right)_{T,x_{A,V}} & \left(\frac{\partial p_V}{\partial x_{A,V}}\right)_{\rho_V,T} & \left(\frac{\partial p_L}{\partial \rho_L}\right)_{T,x_{A,L}} & \left(\frac{\partial p_L}{\partial x_{A,L}}\right)_{\rho_L,T} \\ \left(\frac{\partial \mu_{A,V}}{\partial \rho_V}\right)_{T,x_{A,V}} & \left(\frac{\partial \mu_{A,V}}{\partial x_{A,V}}\right)_{\rho_V,T} & \left(\frac{\partial \mu_{A,L}}{\partial \rho_L}\right)_{T,x_{A,L}} & \left(\frac{\partial \mu_{A,L}}{\partial x_{A,L}}\right)_{\rho_L,T} \\ \left(\frac{\partial \mu_{B,V}}{\partial \rho_V}\right)_{T,x_{A,V}} & \left(\frac{\partial \mu_{B,V}}{\partial x_{A,V}}\right)_{\rho_V,T} & \left(\frac{\partial \mu_{B,L}}{\partial \rho_L}\right)_{T,x_{A,L}} & \left(\frac{\partial \mu_{B,L}}{\partial x_{A,L}}\right)_{\rho_L,T} \\ \begin{bmatrix} -\rho_A + \rho_L w_{A,L} \\ + w_{A,V}(\rho - \rho_L) \end{bmatrix} & \rho_V(\rho - \rho_L)\left(\frac{dw_{A,V}}{dx_{A,V}}\right) & \begin{bmatrix} \rho_A - \rho_V w_{A,V} \\ + w_{A,L}(\rho_V - \rho) \end{bmatrix} & \rho_L(\rho_V - \rho)\left(\frac{dw_{A,L}}{dx_{A,L}}\right) \end{bmatrix} \tag{84}$$

All of the terms that appear in A and B, we can first solve for. Once we know those terms, we can solve equation (84) for the remaining unknown derivatives.