Continuum Description of a Condensation Process of a Multicomponent Fluid in a System of Fixed Mass and Fixed Volume

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

started: March 8, 2005
last updated: March 6, 2008

I. Problem Formulation

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 mass fraction of A in the liquid phase, $w_{A,L}$.

We begin our analysis with the overall mass balance. We define the system density to be

$$\rho = \frac{Nm}{V} \tag{1}$$

Since the system is closed and the volume is fixed, the density is constant

$$\frac{\partial \rho}{\partial t} = 0 \tag{2}$$

We can also examine a mass balance on component A. Again there is nothing moving in or out of the system and there is no generation of A, so we have the accumulation term equal to zero.

$$\frac{\partial \rho_A}{\partial t} = \frac{\partial \rho w_A}{\partial t} = 0 \tag{3}$$

Since the density is constant, the mass fraction of A is also constant.

We are going to define volume fractions as

$$\phi_L = \frac{V_L}{V} \qquad \text{and} \qquad \phi_V = \frac{V_V}{V} \tag{4}$$

where

$$1 = \phi_L + \phi_V \tag{5}$$

The volume of this system is constant,

$$V = V_L + V_V \tag{6}$$

The total mass of this system is constant

$$\begin{aligned} M &= M_L + M_V \\ &= \left(M_{A,L} + M_{B,L}\right) + \left(M_{A,V} + M_{B,V}\right) \\ &= \left(N_{A,L} m_A + N_{B,L} m_B\right) + \left(N_{A,V} m_A + N_{B,V} m_B\right) \end{aligned} \tag{7}$$

The mass of component A in this system is constant

$$M_A = M_{A,L} + M_{A,V} = N_{A,L} m_A + N_{A,V} m_A \tag{8}$$

The density of each of the phases is

$$\rho_L = \frac{M_L}{V_L} = \frac{N_{A,L} m_A + N_{B,L} m_B}{V_L} \qquad \text{and} \qquad \rho_V = \frac{M_V}{V_V} = \frac{N_{A,V} m_A + N_{B,V} m_B}{V_V} \tag{9}$$

The density of the components in each of the phases are

$$\begin{aligned} \rho_{A,L} &= w_{A,L}\rho_L = \frac{M_{A,L}}{V_L}, \qquad & \rho_{B,L} &= w_{B,L}\rho_L = \frac{M_{B,L}}{V_L}, \\ \rho_{A,V} &= w_{A,V}\rho_V = \frac{M_{A,V}}{V_V}, \qquad & \rho_{B,V} &= w_{B,V}\rho_V = \frac{M_{B,V}}{V_V}, \end{aligned} \tag{10}$$

Substituting equation (9) into equation (7) yields

$$M = V\rho = V_L \rho_L + V_V \rho_V \tag{11}$$

Substituting equations (4) and (5) into equation (11) yields

$$\rho = \phi_L \rho_L + \phi_V \rho_V = \left(1 - \phi_V\right)\rho_L + \phi_V \rho_V \tag{12}$$

Solving for the vapor fraction yields

$$\phi_V = \frac{\rho - \rho_L}{\rho_V - \rho_L} \tag{13}$$

We can now repeat these past few steps for component A. Substituting equation (10) into equation (8) yields

$$M_A = \rho_{A,L} V_L + \rho_{A,V} V_V \tag{14}$$

Substituting equations (4) and (5) into equation (14) yields

$$\rho_A = \rho_{A,L}\phi_L + \rho_{A,V}\phi_V = \rho_{A,L}(1-\phi_V) + \rho_{A,V}\phi_V \tag{15}$$

Solving for the vapor fraction yields

$$\phi_V = \frac{\rho_A - \rho_{A,L}}{\rho_{A,V} - \rho_{A,L}} \tag{16}$$

We will require a balance on the total mass of the vapor phase

$$\frac{\partial(\rho_V V_V)}{\partial t} = V\frac{\partial(\rho_V \phi_V)}{\partial t} = r_{vap} \tag{17}$$

where r_{vap} is the rate of vaporization with units of mass/time.

We will also require a balance on the mass of A in the vapor phase

$$\begin{aligned}\frac{\partial(\rho_{A,V} V_V)}{\partial t} &= V\frac{\partial(\rho_{A,V}\phi_V)}{\partial t} = V\frac{\partial(w_{A,V}\rho_V\phi_V)}{\partial t} = V\left[w_{A,V}\frac{\partial(\rho_V\phi_V)}{\partial t} + \rho_V\phi_V\frac{\partial w_{A,V}}{\partial t}\right]\\ &= V w_{A,V} r_{vap} + V\rho_V\phi_V\frac{\partial w_{A,V}}{\partial t}\end{aligned} \tag{18}$$

In equations (17) and (18) there are two unknown variables, r_{vap} and $\frac{\partial w_{A,V}}{\partial t}$. For the moment, we leave r_{vap} and $\frac{\partial w_{A,V}}{\partial t}$ as unknowns.

We will also require an energy balance,

$$\frac{\partial V\rho U}{\partial t} = -Q \tag{19}$$

where U is the specific internal energy of the entire system and ΔU_{vap} is the specific internal energy of vaporization. The internal energy U can be expressed as

$$U = \frac{N_L m}{Nm}U_L + \frac{N_V m}{Nm}U_V = \frac{\rho_L V_L U_L + \rho_V V_V U_V}{\rho_L V_L + \rho_V V_V} = \frac{\rho_L V_L U_L + \rho_V V_V U_V}{N_A m_A + N_B m_B} \tag{20}$$

where U_L and U_V are the specific internal energies of the liquid and vapor phases. Substituting equation (20) into equation (19) we have

$$\frac{\partial\left(\rho_L V_L U_L + \rho_V V_V U_V\right)}{\partial t} = -Q \tag{21}$$

Substitute in equation (12)

$$V\frac{\partial\left(\left(\rho - \rho_V \phi_V\right)U_L + \rho_V \phi_V U_V\right)}{\partial t} = -Q \tag{22}$$

Use the product rule to differentiate,

$$V\rho\frac{\partial U_L}{\partial t} + V\rho_V\phi_V\frac{\partial\left(U_V - U_L\right)}{\partial t} + V\left(U_V - U_L\right)\frac{\partial \rho_V\phi_V}{\partial t} = -Q \tag{23}$$

Substitute in equation (7) into equation (14)

$$V\rho\frac{\partial U_L}{\partial t} + V\rho_V\phi_V\frac{\partial\left(U_V - U_L\right)}{\partial t} + \left(U_V - U_L\right)r_{vap} = -Q \tag{24}$$

We recognize the presence of the internal energy of vaporization,

$$V\rho\frac{\partial U_L}{\partial t} + V\rho_V\phi_V\frac{\partial\left(U_V - U_L\right)}{\partial t} = -\Delta U_{vap}r_{vap} - Q \tag{25}$$

where the internal energy of vaporization is defined as $\Delta U_{vap} \equiv U_V - U_L$. Substitute in equation (11) into equation (25)

$$V\rho_L\phi_L\frac{\partial U_L}{\partial t} + V\rho_V\phi_V\frac{\partial U_V}{\partial t} = -\Delta U_{vap}r_{vap} - Q \tag{26}$$

At this point, this is precisely the same energy balance we had for the single component system.

Now, in a one-phase region of a binary mixture, we have three degrees of freedom and the internal energy is a function of temperature, density, and composition.

$$U = U\left(T, \rho, w_A\right) \tag{27}$$

Therefore, the time derivative is going to be written as

$$\frac{\partial U}{\partial t} = \left(\frac{\partial U}{\partial T}\right)_{\rho, w_A}\frac{\partial T}{\partial t} + \left(\frac{\partial U}{\partial \rho}\right)_{T, w_A}\frac{\partial \rho}{\partial t} + \left(\frac{\partial U}{\partial w_A}\right)_{T, \rho}\frac{\partial w_A}{\partial t} \tag{28}$$

The presence of the time derivative of the temperature is acceptable. We will use the energy balance to solve for the temperature as a function of time. The presence of the time derivatives of the density and the composition is a problem, since we have not yet presented a way to calculate those time derivatives. However, in a one-phase system, the density and the mass fraction of A are constants. Therefore

$$\frac{\partial U}{\partial t} = \left(\frac{\partial U}{\partial T}\right)_{\rho, w_A} \frac{\partial T}{\partial t} \quad \text{for closed, one-phase system with fixed volume} \tag{29}$$

So our energy balance in the one phase system is

$$\frac{\partial T}{\partial t} = \frac{-Q}{V\rho\left(\frac{\partial U}{\partial T}\right)_{\rho, w_A}} \tag{30}$$

Now when we have two phases in a binary system, we have two degrees of freedom and the internal energy is a function of temperature and density only

$$U_L = U_L\left(T, \rho_L, w_{A,L}(T, \rho_L)\right) \quad \text{and} \quad U_V = U_V\left(T, \rho_V, w_{A,V}(T, \rho_V)\right) \tag{31}$$

Therefore, the time derivative is going to be written as

$$\begin{aligned}
\frac{\partial U_L}{\partial t} &= \left(\frac{\partial U_L}{\partial T}\right)\bigg|_{sat,\rho_L} \frac{\partial T}{\partial t} + \left(\frac{\partial U_L}{\partial \rho_L}\right)\bigg|_{sat,T} \frac{\partial \rho_L}{\partial t} + \left(\frac{\partial U_L}{\partial w_A}\right)\bigg|_{sat} \frac{\partial w_A}{\partial t} \\
&= \left(\frac{\partial U_L}{\partial T}\right)\bigg|_{sat,\rho_L} \frac{\partial T}{\partial t} + \left(\frac{\partial U_L}{\partial \rho_L}\right)\bigg|_{sat,T} \frac{\partial \rho_L}{\partial t} + \left(\frac{\partial U_L}{\partial w_A}\right)\bigg|_{sat} \left(\left(\frac{\partial w_A}{\partial T}\right)\bigg|_{sat} \frac{\partial T}{\partial t} + \left(\frac{\partial w_A}{\partial \rho_L}\right)\bigg|_{sat} \frac{\partial \rho_L}{\partial t}\right) \\
&= \left[\left(\frac{\partial U_L}{\partial T}\right)\bigg|_{sat,\rho_L} + \left(\frac{\partial U_L}{\partial w_A}\right)\bigg|_{sat} \left(\frac{\partial w_A}{\partial T}\right)\bigg|_{sat}\right] \frac{\partial T}{\partial t} + \left[\left(\frac{\partial U_L}{\partial \rho_L}\right)\bigg|_{sat,T} + \left(\frac{\partial U_L}{\partial w_A}\right)\bigg|_{sat} \left(\frac{\partial w_A}{\partial \rho_L}\right)\bigg|_{sat}\right] \frac{\partial \rho_L}{\partial t}
\end{aligned}$$

$$\text{for a closed two-phase system with fixed volume} \tag{32}$$

This equation has a fundamental problem in that it includes a time derivative of the liquid density. We did not see this problem in the single component version of this solution because when we had only one component, there was only one degree of freedom in the system and that was the temperature. It was okay to have a time derivative of the temperature.

At this point we have to do something new to eliminate the presence of the time derivative of the liquid density in the simulation.

It is true that, due to the constraints imposed on our system by the fact that our system volume is constant, all the variables that we are going to determine from thermodynamic constraints (ϕ_V, ρ_V, ρ_L, $w_{A,L}$, and $w_{A,V}$) are determined once the temperature is known. In that sense, we can acknowledge that they are all functions of temperature, ie. $\rho_L(T)$, and if we differentiate this expression we have,

$$\frac{\partial \rho_L(T)}{\partial t} = \left(\frac{\partial \rho_L(T)}{\partial T}\right)_{M,V,M_A} \frac{\partial T}{\partial t} \tag{33}$$

However, the fundamental problem is that we do not know what this partial derivative looks like. We are having to solve for ρ_L at the same time that we solve for T, from the algebraic constraints imposed by thermodynamics. We have no differential equation for $\left(\frac{\partial \rho_L(T)}{\partial T}\right)_{M,V,M_A}$. The only equation we have that we have not used yet is equation (15).

$$\rho_A = \rho_{A,L}\phi_L + \rho_{A,V}\phi_V = \rho_{A,L}(1-\phi_V) + \rho_{A,V}\phi_V \tag{15}$$

One can think of this as an additional constraint that must be satisfied along with the thermodynamic criteria. If we conceptually move this material constraint into a thermodynamic constraint, then we have only one degree of freedom at VLE. In this case, we can write,

$$U_L = U_L\left(T, \rho_L(T), w_{A,L}(T)\right) \quad \text{and} \quad U_V = U_V\left(T, \rho_V(T), w_{A,V}(T)\right) \tag{34}$$

so that

$$\begin{aligned} \frac{\partial U_L}{\partial t} &= \left(\frac{\partial U_L}{\partial T}\right)_{\rho,w_A} \frac{\partial T}{\partial t} + \left(\frac{\partial U_L}{\partial \rho_L}\right)_{T,w_A} \frac{\partial \rho_L}{\partial t} + \left(\frac{\partial U_L}{\partial w_{A,L}}\right)_{\rho,T} \frac{\partial w_{A,L}}{\partial t} \\ &= \left(\frac{\partial U_L}{\partial T}\right)_{\rho,w_A} \frac{\partial T}{\partial t} + \left(\frac{\partial U_L}{\partial \rho_L}\right)_{T,w_A} \left.\left(\frac{\partial \rho_L}{\partial T}\right)\right|_{sat}^{*} \frac{\partial T}{\partial t} + \left(\frac{\partial U_L}{\partial w_{A,L}}\right)_{\rho,T} \left.\left(\frac{\partial w_{A,L}}{\partial T}\right)\right|_{sat}^{*} \frac{\partial T}{\partial t} \\ &= \left[\left(\frac{\partial U_L}{\partial T}\right)_{\rho,w_A} + \left(\frac{\partial U_L}{\partial \rho_L}\right)_{T,w_A} \left.\left(\frac{\partial \rho_L}{\partial T}\right)\right|_{sat}^{*} + \left(\frac{\partial U_L}{\partial w_{A,L}}\right)_{\rho,T} \left.\left(\frac{\partial w_{A,L}}{\partial T}\right)\right|_{sat}^{*}\right] \frac{\partial T}{\partial t} \end{aligned} \tag{35}$$

In this case our energy balance becomes of equation (26) becomes

$$V\rho_L\phi_L \frac{\partial U_L}{\partial t} + V\rho_V\phi_V \frac{\partial U_V}{\partial t} = -\Delta U_{vap} r_{vap} - Q \tag{26}$$

$$\frac{\partial T}{\partial t} = \frac{-\Delta U_{vap} r_{vap} - Q}{V\left\{ \begin{array}{l} \rho_L\phi_L\left[\left(\frac{\partial U_L}{\partial T}\right)_{\rho,w_A} + \left(\frac{\partial U_L}{\partial \rho_L}\right)_{T,w_A} \left.\left(\frac{\partial \rho_L}{\partial T}\right)\right|_{sat}^{*} + \left(\frac{\partial U_L}{\partial w_{A,L}}\right)_{\rho,T} \left.\left(\frac{\partial w_{A,L}}{\partial T}\right)\right|_{sat}^{*}\right]_L + \\ \rho_V\phi_V\left[\left(\frac{\partial U_V}{\partial T}\right)_{\rho,w_A} + \left(\frac{\partial U_V}{\partial \rho_V}\right)_{T,w_A} \left.\left(\frac{\partial \rho_V}{\partial T}\right)\right|_{sat}^{*} + \left(\frac{\partial U_V}{\partial w_{A,V}}\right)_{\rho,T} \left.\left(\frac{\partial w_{A,V}}{\partial T}\right)\right|_{sat}^{*}\right]_V \end{array} \right\}} \tag{36}$$

The asterisk indicates that equation (15) must also be considered as a constraint. The rate of vaporization that appears in equation (36) is given by equation (17)

$$V\frac{\partial\left(\rho_V\phi_V\right)}{\partial t}=r_{vap} \tag{17}$$

If we use the product rule and chain rule for differentiation we have

$$r_{vap}=V\frac{\partial\left(\rho_V\phi_V\right)}{\partial t}=V\left(\phi_V\frac{\partial\rho_V}{\partial t}+\rho_V\frac{\partial\phi_V}{\partial t}\right)=V\left(\phi_V\left.\left(\frac{\partial\rho_V}{\partial T}\right)\right|_{sat}\frac{\partial T}{\partial t}+\rho_V\frac{\partial\phi_V}{\partial t}\right) \tag{37}$$

The vapor fraction is related to the densities via equation (13), so that

$$\frac{\partial\phi_V}{\partial t}=\frac{1}{\rho_V-\rho_L}\left(\frac{\partial\rho}{\partial t}-\frac{\partial\rho_L}{\partial t}\right)-\frac{\rho-\rho_L}{\left(\rho_V-\rho_L\right)^2}\left(\frac{\partial\rho_V}{\partial t}-\frac{\partial\rho_L}{\partial t}\right) \tag{38}$$

which can be written as

$$\frac{\partial\phi_V}{\partial t}=\frac{1}{\rho_V-\rho_L}\frac{\partial\rho}{\partial t}-\left[\frac{1}{\rho_V-\rho_L}\left.\left(\frac{\partial\rho_L}{\partial T}\right)\right|_{sat}+\frac{\rho-\rho_L}{\left(\rho_V-\rho_L\right)^2}\left(\left.\left(\frac{\partial\rho_V}{\partial T}\right)\right|_{sat}-\left.\left(\frac{\partial\rho_L}{\partial T}\right)\right|_{sat}\right)\right]\frac{\partial T}{\partial t} \tag{39}$$

Thus the rate of vaporization is

$$r_{vap}=V\left(\left[\begin{array}{l}\phi_V\left.\left(\frac{\partial\rho_V}{\partial T}\right)\right|_{sat}-\frac{\rho_V}{\rho_V-\rho_L}\left.\left(\frac{\partial\rho_L}{\partial T}\right)\right|_{sat}\\-\frac{\rho_V\left(\rho-\rho_L\right)}{\left(\rho_V-\rho_L\right)^2}\left(\left.\left(\frac{\partial\rho_V}{\partial T}\right)\right|_{sat}-\left.\left(\frac{\partial\rho_L}{\partial T}\right)\right|_{sat}\right)\end{array}\right]\frac{\partial T}{\partial t}+\frac{\rho_V}{\rho_V-\rho_L}\frac{\partial\rho}{\partial t}\right) \tag{40}$$

This can be simplified as

$$r_{vap}=V\left(\left[\begin{array}{l}\left[\phi_V-\frac{\rho_V\left(\rho-\rho_L\right)}{\left(\rho_V-\rho_L\right)^2}\right]\left.\left(\frac{\partial\rho_V}{\partial T}\right)\right|_{sat}\\+\left[\frac{\rho_V\left(\rho-\rho_L\right)}{\left(\rho_V-\rho_L\right)^2}-\frac{\rho_V}{\rho_V-\rho_L}\right]\left.\left(\frac{\partial\rho_L}{\partial T}\right)\right|_{sat}\end{array}\right]\frac{\partial T}{\partial t}+\frac{\rho_V}{\rho_V-\rho_L}\frac{\partial\rho}{\partial t}\right) \tag{41}$$

or

$$r_{vap}=V\left(\left[\frac{-\rho_L\left(\rho-\rho_L\right)}{\left(\rho_V-\rho_L\right)^2}\left.\left(\frac{\partial\rho_V}{\partial T}\right)\right|_{sat}+\frac{\rho_V\left(\rho-\rho_V\right)}{\left(\rho_V-\rho_L\right)^2}\left.\left(\frac{\partial\rho_L}{\partial T}\right)\right|_{sat}\right]\frac{\partial T}{\partial t}+\frac{\rho_V}{\rho_V-\rho_L}\frac{\partial\rho}{\partial t}\right) \tag{42}$$

where we used the following relations,

$$\begin{aligned}
&\phi_V - \frac{\rho_V(\rho-\rho_L)}{(\rho_V-\rho_L)^2} = \frac{\rho-\rho_L}{\rho_V-\rho_L} - \frac{\rho_V(\rho-\rho_L)}{(\rho_V-\rho_L)^2} = \frac{(\rho-\rho_L)(\rho_V-\rho_L)}{(\rho_V-\rho_L)^2} - \frac{\rho_V(\rho-\rho_L)}{(\rho_V-\rho_L)^2} \\
&= \frac{(\rho-\rho_L)(\rho_V-\rho_L)-\rho_V(\rho-\rho_L)}{(\rho_V-\rho_L)^2} = \frac{\rho\rho_V - \rho\rho_L - \rho_L\rho_V + \rho_L{}^2 - \rho_V\rho + \rho_V\rho_L}{(\rho_V-\rho_L)^2} \\
&= \frac{-\rho\rho_L + \rho_L{}^2}{(\rho_V-\rho_L)^2} = \frac{-\rho_L(\rho-\rho_L)}{(\rho_V-\rho_L)^2}
\end{aligned} \tag{43}$$

and

$$\begin{aligned}
&\frac{\rho_V(\rho-\rho_L)}{(\rho_V-\rho_L)^2} - \frac{\rho_V}{\rho_V-\rho_L} = \frac{\rho_V(\rho-\rho_L)}{(\rho_V-\rho_L)^2} - \frac{\rho_V(\rho_V-\rho_L)}{(\rho_V-\rho_L)^2} = \frac{\rho_V(\rho-\rho_L)-\rho_V(\rho_V-\rho_L)}{(\rho_V-\rho_L)^2} = \\
&\frac{\rho_V\rho - \rho_V\rho_L - \rho_V\rho_V + \rho_V\rho_L}{(\rho_V-\rho_L)^2} = \frac{\rho_V\rho - \rho_V\rho_V}{(\rho_V-\rho_L)^2} = \frac{\rho_V(\rho-\rho_V)}{(\rho_V-\rho_L)^2}
\end{aligned} \tag{44}$$

Substituting equation (42) into the energy balance of equation (36) and solving for the time derivative of the temperature yields

$$\frac{\partial T}{\partial t} = \frac{-\Delta U_{vap} V \dfrac{\rho_V}{\rho_V-\rho_L}\dfrac{\partial \rho}{\partial t} - Q}{V\left\{\begin{aligned}
&\rho_L\phi_L\left[\left(\frac{\partial U_L}{\partial T}\right)_{\rho,w_A} + \left(\frac{\partial U_L}{\partial \rho_L}\right)_{T,w_A}\left(\frac{\partial \rho_L}{\partial T}\right)\bigg|_{sat}^{*} + \left(\frac{\partial U_L}{\partial w_{A,L}}\right)_{\rho,T}\left(\frac{\partial w_{A,L}}{\partial T}\right)\bigg|_{sat}^{*}\right]_L + \\
&\rho_V\phi_V\left[\left(\frac{\partial U_V}{\partial T}\right)_{\rho,w_A} + \left(\frac{\partial U_V}{\partial \rho_V}\right)_{T,w_A}\left(\frac{\partial \rho_V}{\partial T}\right)\bigg|_{sat}^{*} + \left(\frac{\partial U_V}{\partial w_{A,V}}\right)_{\rho,T}\left(\frac{\partial w_{A,V}}{\partial T}\right)\bigg|_{sat}^{*}\right]_V \\
&+ \Delta U_{vap}\left[\frac{-\rho_L(\rho-\rho_L)}{(\rho_V-\rho_L)^2}\left(\frac{\partial \rho_V}{\partial T}\right)\bigg|_{sat} + \frac{\rho_V(\rho-\rho_V)}{(\rho_V-\rho_L)^2}\left(\frac{\partial \rho_L}{\partial T}\right)\bigg|_{sat}\right]
\end{aligned}\right\}} \tag{45}$$

Our challenge now is to find the ten partial derivatives that appear in equation (45),

$$\begin{aligned}
&\left(\frac{\partial U_L}{\partial T}\right)_{\rho,w_A}, \left(\frac{\partial U_L}{\partial \rho}\right)_{T,w_A}, \left(\frac{\partial U_L}{\partial w_A}\right)_{T,\rho}, \left(\frac{\partial \rho_L}{\partial T}\right)\bigg|_{sat}^{*}, \left(\frac{\partial w_{A,L}}{\partial T}\right)\bigg|_{sat}^{*} \\
&\left(\frac{\partial U_V}{\partial T}\right)_{\rho,w_A}, \left(\frac{\partial U_V}{\partial \rho}\right)_{T,w_A}, \left(\frac{\partial U_V}{\partial w_A}\right)_{T,\rho}, \left(\frac{\partial \rho_V}{\partial T}\right)\bigg|_{sat}^{*}, \left(\frac{\partial w_{A,V}}{\partial T}\right)\bigg|_{sat}^{*}
\end{aligned}$$

from the combined thermodynamic constraints and equation (15).

II. General Thermodynamic Information

In an ordinary 2-phase VLE system, we have 2 degrees of freedom. Given, for example the temperature and the liquid density, we can find all of the other properties, including the vapor density and the composition in both phases. Thus we are finding three unknowns. We have three equations, namely mechanical equilibrium (pressures are equal)

$$p_L\left(T,\rho_L,w_{A,L}\right)=p_V\left(T,\rho_V,w_{A,V}\right) \tag{46}$$

and chemical equilibrium (chemical potentials of each component are equal)

$$\mu_{A,L}\left(T,\rho_L,w_{A,L}\right)=\mu_{A,V}\left(T,\rho_V,w_{A,V}\right) \tag{47}$$

$$\mu_{B,L}\left(T,\rho_L,w_{A,L}\right)=\mu_{B,V}\left(T,\rho_V,w_{A,V}\right) \tag{48}$$

Three equations and three unknowns: no problem. However, we are going to introduce another equation, which is equation (15) in which equation (13) has been used to eliminate the vapor fraction.

$$\rho_A=\rho_L w_{A,L}\frac{\rho_V-\rho}{\rho_V-\rho_L}+\rho_V w_{A,V}\frac{\rho-\rho_L}{\rho_V-\rho_L} \tag{49}$$

In this equation ρ and ρ_A are constants from the problem statement. This additional equation will be used to determine the liquid density. So now we have four equations and four unknowns: no problem. Now it is up to us to show how to get all the partial derivatives from equation (45).

We will differentiate all four of these equations with respect to temperature, so that we can obtain four partial derivatives.

$$\left.\left(\frac{\partial\rho_L}{\partial T}\right)\right|_{sat}^{*},\left.\left(\frac{\partial w_{A,L}}{\partial T}\right)\right|_{sat}^{*},\left.\left(\frac{\partial\rho_V}{\partial T}\right)\right|_{sat}^{*},\left.\left(\frac{\partial w_{A,V}}{\partial T}\right)\right|_{sat}^{*} \tag{50}$$

Finally, we will need a thermodynamic equation of state to obtain the remaining derivatives that we need:

$$\left(\frac{\partial U_L}{\partial T}\right)_{\rho,w_A},\left(\frac{\partial U_L}{\partial\rho}\right)_{T,w_A},\left(\frac{\partial U_L}{\partial w_A}\right)_{T,\rho},\left(\frac{\partial U_V}{\partial T}\right)_{\rho,w_A},\left(\frac{\partial U_V}{\partial\rho}\right)_{T,w_A},\left(\frac{\partial U_V}{\partial w_A}\right)_{T,\rho} \tag{51}$$

III. Derivation for the multicomponent van der Waals Equation of State

At this point we need an equation of state. We will proceed with the multicomponent van der Waals (vdW) equation of state (EOS), since it is the simplest EOS that allows for vapor liquid equilibrium (VLE).

The pressure for the vdW EOS for a mixture is given by

$$p = \frac{RT}{V_m - b_{mix}} - \frac{a_{mix}}{V_m^2} \tag{52}$$

where V_m is a molar volume, related to our density and composition via

$$V_m = \frac{x_A m_A + x_B m_B}{\rho} \tag{53}$$

and where the composition dependence of the fluid is contained in the mixture van der Waals size parameter, b_{mix},

$$b_{mix} = \sum_{j=1}^{N_c} x_j b_j \quad , \tag{54}$$

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

$$a_{mix} = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j a_{ij} \text{ ..,} \tag{55}$$

The specific internal energy of the vdW fluid is

$$U = \frac{1}{m}\left[\frac{3}{2}RT - \frac{a_{mix}}{V_m}\right] \tag{56}$$

The derivatives that we require in (41) and (42) have been obtained in another hand-out titled, “The Statistical Mechanical Derivation of the van der Waals Equation of State for a multicomponent fluid and its associated thermodynamic properties”. Here we summarize the results. The partial derivatives in equation (42) (written in terms of molar volume and mole fraction) are

$$\left(\frac{\partial U}{\partial T}\right)_{\rho, w_A} = C_p = \frac{1}{m}\left[\frac{3}{2}R + R\frac{1}{1 - 2\frac{a_{mix}\left(V_m - b_{mix}\right)^2}{RTV_m^3}}\right] \tag{57}$$

$$\left(\frac{\partial U_m}{\partial V_m}\right)_{T,N_i} = 2\frac{a_{mix}}{V_m^2} \tag{58}$$

$$\overline{U}_i = \left(\frac{\partial U}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \frac{3}{2}k_B T - \frac{2}{V_m}\sum_{j=1}^{N_c} x_j a_{ij} \tag{59}$$

These can be evaluated at either the liquid density and composition or the vapor density and composition to get the correct value for either phase. In order to convert from molar volume to density, use

$$\left(\frac{\partial \rho}{\partial V_m}\right)_{x_i} = -\frac{x_A m_A + x_B m_B}{V_m^2} \tag{60}$$

In order to convert from mole fraction to mass fraction use

$$\left(\frac{dw_A}{dx_A}\right) = \frac{w_A w_B}{x_A x_B} \tag{61}$$

Next, we need the partial derivatives in equation (41). They can be obtained from

$$\underline{\underline{A}}\,\underline{x} = \underline{b} \tag{62}$$

where

$$\underline{x} = \left[\left(\frac{\partial \rho_V}{\partial T}\right)^* \quad \left(\frac{\partial x_{A,V}}{\partial T}\right)^* \quad \left(\frac{\partial \rho_L}{\partial T}\right)^* \quad \left(\frac{\partial x_{A,L}}{\partial T}\right)^*\right]^T \tag{63}$$

$$\underline{b} = \begin{bmatrix} \left(\frac{\partial p_L}{\partial T}\right)_{\rho_L,x_A} - \left(\frac{\partial p_V}{\partial T}\right)_{\rho_V,x_A} \\ \left(\frac{\partial \mu_{A,L}}{\partial T}\right)_{\rho_L,x_A} - \left(\frac{\partial \mu_{A,V}}{\partial T}\right)_{\rho_V,x_A} \\ \left(\frac{\partial \mu_{B,L}}{\partial T}\right)_{\rho_L,x_A} - \left(\frac{\partial \mu_{B,V}}{\partial T}\right)_{\rho_V,x_A} \\ 0 \end{bmatrix} \tag{64}$$

and

$$\underline{\underline{A}}=\begin{bmatrix} \left(\frac{\partial p_V}{\partial \rho_V}\right)_{T,x_{A,V}} & \left(\frac{\partial p_V}{\partial x_{A,V}}\right)_{\rho_V,T} & \left(\frac{\partial p_L}{\partial \rho_L}\right)_{T,x_{A,L}} & \left(\frac{\partial p_L}{\partial x_{A,L}}\right)_{\rho_L,T} \\ \left(\frac{\partial \mu_{A,V}}{\partial \rho_V}\right)_{T,x_{A,V}} & \left(\frac{\partial \mu_{A,V}}{\partial x_{A,V}}\right)_{\rho_V,T} & \left(\frac{\partial \mu_{A,L}}{\partial \rho_L}\right)_{T,x_{A,L}} & \left(\frac{\partial \mu_{A,L}}{\partial x_{A,L}}\right)_{\rho_L,T} \\ \left(\frac{\partial \mu_{B,V}}{\partial \rho_V}\right)_{T,x_{A,V}} & \left(\frac{\partial \mu_{B,V}}{\partial x_{A,V}}\right)_{\rho_V,T} & \left(\frac{\partial \mu_{B,L}}{\partial \rho_L}\right)_{T,x_{A,L}} & \left(\frac{\partial \mu_{B,L}}{\partial x_{A,L}}\right)_{\rho_L,T} \\ \begin{bmatrix} -\rho_A+\rho_L w_{A,L} \\ +w_{A,V}\left(\rho-\rho_L\right) \end{bmatrix} & \rho_V\left(\rho-\rho_L\right)\left(\frac{dw_{A,V}}{dx_{A,V}}\right) & \begin{bmatrix} \rho_A-\rho_V w_{A,V} \\ +w_{A,L}\left(\rho_V-\rho\right) \end{bmatrix} & \rho_L\left(\rho_V-\rho\right)\left(\frac{dw_{A,L}}{dx_{A,L}}\right) \end{bmatrix} \tag{65}$$

All of the partial derivatives required in equation (56) are available in the other hand-out, “The Statistical Mechanical Derivation of the van der Waals Equation of State for a multicomponent fluid and its associated thermodynamic properties”.

III. The Solution Algorithm

The big picture is that we have one nonlinear ordinary differential equation: an energy balance. We know how to solve this numerically, using for example a Runge-Kutta method. We have one unknown, $T(t)$. In a one phase region, the energy balance reduces to

$$\frac{\partial T}{\partial t}=\frac{-Q}{V\rho\left(\frac{\partial U}{\partial T}\right)_{\rho,w_A}} \tag{29}$$

In the two phase region, our energy balance can be written as

$$\frac{\partial T}{\partial t}=\frac{-\Delta U_{vap}V\frac{\rho_V}{\rho_V-\rho_L}\frac{\partial \rho}{\partial t}-Q}{V\left\{\begin{array}{l} \rho_L\phi_L\left[\left(\frac{\partial U_L}{\partial T}\right)_{\rho,w_A}+\left(\frac{\partial U_L}{\partial \rho_L}\right)_{T,w_A}\left(\frac{\partial \rho_L}{\partial T}\right)\Bigg|_{sat}^{*}+\left(\frac{\partial U_L}{\partial w_{A,L}}\right)_{\rho,T}\left(\frac{\partial w_{A,L}}{\partial T}\right)\Bigg|_{sat}^{*}\right]_L+ \\ \rho_V\phi_V\left[\left(\frac{\partial U_V}{\partial T}\right)_{\rho,w_A}+\left(\frac{\partial U_V}{\partial \rho_V}\right)_{T,w_A}\left(\frac{\partial \rho_V}{\partial T}\right)\Bigg|_{sat}^{*}+\left(\frac{\partial U_V}{\partial w_{A,V}}\right)_{\rho,T}\left(\frac{\partial w_{A,V}}{\partial T}\right)\Bigg|_{sat}^{*}\right]_V \\ +\Delta U_{vap}\left[\frac{-\rho_L\left(\rho-\rho_L\right)}{\left(\rho_V-\rho_L\right)^2}\left(\frac{\partial \rho_V}{\partial T}\right)\Bigg|_{sat}+\frac{\rho_V\left(\rho-\rho_V\right)}{\left(\rho_V-\rho_L\right)^2}\left(\frac{\partial \rho_L}{\partial T}\right)\Bigg|_{sat}\right] \end{array}\right\}} \tag{45}$$

The ordinary differential equation is properly posed. All we need to solve it is an initial condition $T(t=t_o)=T_o$.

The only remaining issue is whether we have one phase or two phases, whether we use the energy balance in equation (29) or (45). This is an issue of thermodynamic stability. In the single component case, we could use a simplified graphical technique to determine the stability of the relative systems. If the total density of the 1-phase system fell between the densities of the liquid and vapor in the two phase system, then we had a two phase system. In the binary case, the phase diagram has an additional dimension for composition, so this simple prescription will not work. Instead, we can evaluate the Helmholtz free energy of the one-phase system and the two-phase system. Whichever system has the lower free energy is present. For a single-phase, the multicomponent Helmholtz free energy is

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

For two phases, this expression can be used twice using the molar volume and the compositions of each phase. The total Helmholtz free energy is then a weighted average of the liquid and vapor free energies.

$$A_m^{2\phi} = x^v A_m^v + x^l A_m^l$$

where x^v is the total mole fraction of the vapor phase (total moles in vapor over total moles in system).