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

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I. Problem Formulation

Consider N moles of a fluid with molecular weight m, initially above the critical temperature, T_c, 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, and the density of the liquid phase, ρ_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 are going to define volume fractions as

$$\phi_L = \frac{V_L}{V} \qquad \text{and} \qquad \phi_V = \frac{V_V}{V} \tag{3}$$

where

$$1 = \phi_L + \phi_V \tag{4}$$

The volume of this system is constant,

$$V = V_L + V_V \tag{5}$$

and the mass of this system is constant

$$M = M_L + M_V \tag{6}$$

The density of the individual phases are

$$\rho_L = \frac{M_L}{V_L} \qquad \text{and} \qquad \rho_V = \frac{M_V}{V_V} \tag{7}$$

Substituting equation (7) into equation (6) yields

$$M = V\rho = V_L\rho_L + V_V\rho_V \tag{8}$$

Substituting equations (3) and (4) into equation (8) yields

$$\rho = \phi_L\rho_L + \phi_V\rho_V = (1-\phi_V)\rho_L + \phi_V\rho_V \tag{9}$$

Solving for the vapor fraction yields

$$\phi_V = \frac{\rho - \rho_L}{\rho_V - \rho_L} \tag{10}$$

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

$$\frac{\partial(\rho_V V_V)}{\partial t} = V\frac{\partial(\rho_V \phi_V)}{\partial t} = r_{vap} \tag{11}$$

We will also require an energy balance,

$$\frac{\partial V\rho U}{\partial t} = -Q \tag{12}$$

where U is the specific internal energy of the entire system. Based upon an analogy with a reactive system, one might think that we are missing a generation term on the right hand side of the form, $-\Delta U_{vap} r_{vap}$, where ΔU_{vap} is the specific internal energy of vaporization, and r_{vap} is the rate of vaporization with units of mass/time. If the process we were modeling were a chemical reaction rather than the physical reaction of vaporization we would indeed require such a term. However, in a reactive system, this reaction term incorporates changes in the internal energy due to reaction aside from the kinetic and potential energy terms, such as changes in the internal energy of the molecule due to the formation or destruction of chemical bonds. In the case of a purely physical reaction, we do not require such a term.

The internal energy U can be expressed as

$$U = \frac{N_L m}{Nm}U_L + \frac{N_V m}{Nm}U_V = \frac{\rho_L V_L U_L + \rho_V V_V U_V}{\rho_L V_L + \rho_V V_V} = \frac{\rho_L V_L U_L + \rho_V V_V U_V}{Nm} \tag{13}$$

where U_L and U_V are the specific internal energies of the liquid and vapor phases. Substituting equation (13) into equation (12) we have

$$\frac{\partial\left(\rho_L V_L U_L + \rho_V V_V U_V\right)}{\partial t} = -Q \tag{14}$$

Substitute in equation (9)

$$V\frac{\partial\left(\left(\rho - \rho_V \phi_V\right)U_L + \rho_V \phi_V U_V\right)}{\partial t} = -Q \tag{15}$$

Use the product rule to differentiate,

$$V\rho\frac{\partial U_L}{\partial t} + V\rho_V\phi_V\frac{\partial\left(U_V - U_L\right)}{\partial t} + V\left(U_V - U_L\right)\frac{\partial\rho_V\phi_V}{\partial t} = -Q \tag{16}$$

Substitute in equation (11) into equation (16)

$$V\rho_L\phi_L\frac{\partial U_L}{\partial t} + V\rho_V\phi_V\frac{\partial U_V}{\partial t} = -\Delta U_{vap} r_{vap} - Q \tag{17}$$

It becomes very clear that we did not need to add the vaporization term in as a generation term. It appears naturally from the accumulation term. The problem is that we do not know the value of rvap. We will eventually have to solve this problem. For the time being, we hold off.

II. Functional Form of the Internal Energy

Now, in a one-phase region, we have two degrees of freedom and the internal energy is a function of both the density and temperature.

$$U_L = U_L\left(\rho_L, T\right) \qquad \text{and} \qquad U_V = U_V\left(\rho_V, T\right) \tag{18}$$

Therefore, the time derivative is going to be written as

$$\frac{\partial U_L}{\partial t} = \left(\frac{\partial U_L}{\partial T}\right)_{\rho_L}\frac{\partial T}{\partial t} + \left(\frac{\partial U_L}{\partial \rho_L}\right)_T\frac{\partial \rho_L}{\partial t} \tag{19}$$

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 derivative of the density is a problem, since we have not yet presented a way to calculate it. However, in a one-phase system, this is the total density and it is constant in this closed system of fixed volume. Therefore

$$\frac{\partial U_L}{\partial t} = \left(\frac{\partial U_L}{\partial T}\right)_{\rho_L}\frac{\partial T}{\partial t} \quad \text{for closed, one-phase system with fixed volume} \tag{20}$$

So, in a one phase system, our energy balance is simply

$$\frac{\partial T}{\partial t}=\frac{-Q}{V\rho\left(\frac{\partial U}{\partial T}\right)_{\rho}}=\frac{-Q}{V\rho C_V} \tag{21}$$

where we have recognized the presence of the specific constant volume heat capacity.

Now when we have two phases, we have one degree of freedom and the internal energy is a function of temperature only

$$U_L=U_L(\rho_L(T),T) \qquad \text{and} \qquad U_V=U_V(\rho_V(T),T) \tag{22}$$

Therefore, the time derivative is going to be written as

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

for a close two-phase system with fixed volume (23)

So, in order to solve this problem, we will need the thermodynamic partial derivatives that appear in equations (21) and (23). We require a specific equation of state to evaluate these partial derivatives. Without an equation of state the best we can do is substitute equation (23) into equation (17) to obtain

$$\frac{\partial T}{\partial t}=\frac{-\Delta U_{vap}r_{vap}-Q}{V\rho_L\phi_L\left[\left(\frac{\partial U_L}{\partial T}\right)_{\rho_L}+\left(\frac{\partial U_L}{\partial \rho_L}\right)_T\left(\frac{\partial \rho_L}{\partial T}\right)\Bigg|_{sat}\right]+V\rho_V\phi_V\left[\left(\frac{\partial U_V}{\partial T}\right)_{\rho_V}+\left(\frac{\partial U_V}{\partial \rho_V}\right)_T\left(\frac{\partial \rho_V}{\partial T}\right)\Bigg|_{sat}\right]} \tag{24}$$

The details of the partial derivatives in the denominator of the right hand side and the presence of r_{vap} in the numerator of the RHS, have yet to be determined.

The problem of rvap can be solved without resorting to a specific thermodynamic equation of state. If we assume that we know the thermodynamic derivatives in the denominator of equation (24), then we can write, via equation (11)

$$r_{vap}=V\frac{\partial(\rho_V\phi_V)}{\partial t}=V\left(\phi_V\frac{\partial \rho_V}{\partial t}+\rho_V\frac{\partial \phi_V}{\partial t}\right)=V\left(\phi_V\left(\frac{\partial \rho_V}{\partial T}\right)\Bigg|_{sat}\frac{\partial T}{\partial t}+\rho_V\frac{\partial \phi_V}{\partial t}\right) \tag{25}$$

The vapor fraction is related to the densities via equation (10), so that

$$\frac{\partial \phi_V}{\partial t}=\frac{1}{\rho_V-\rho_L}\left(\frac{\partial \rho}{\partial t}-\frac{\partial \rho_L}{\partial t}\right)-\frac{\rho-\rho_L}{(\rho_V-\rho_L)^2}\left(\frac{\partial \rho_V}{\partial t}-\frac{\partial \rho_L}{\partial t}\right) \tag{26}$$

which can be written as

$$\frac{\partial \phi_V}{\partial t} = \frac{1}{\rho_V - \rho_L}\frac{\partial \rho}{\partial t} - \left[\frac{1}{\rho_V - \rho_L}\left.\left(\frac{\partial \rho_L}{\partial T}\right)\right|_{sat} + \frac{\rho - \rho_L}{(\rho_V - \rho_L)^2}\left(\left.\left(\frac{\partial \rho_V}{\partial T}\right)\right|_{sat} - \left.\left(\frac{\partial \rho_L}{\partial T}\right)\right|_{sat} \right) \right] \frac{\partial T}{\partial t} \qquad (27)$$

We recognize that the first term on the right hand side of this equation is zero, for this system, because the total density doesn't change in time. The important point is that by subsituting equation (27) into equation (25), we have an expression for the rate of vaporization in terms of nothing but thermodynamic derivatives and the time derivative of the temperature. Substituting equations (25) and (27) into equation (24) yields

$$\frac{\partial T}{\partial t} = \frac{ -\Delta U_{vap} V \dfrac{\rho_V}{\rho_V - \rho_L}\dfrac{\partial \rho}{\partial t} - Q }{ \left\{ \begin{array}{l} V\rho_L\phi_L\left[\left(\dfrac{\partial U_L}{\partial T}\right)_{\rho_L} + \left(\dfrac{\partial U_L}{\partial \rho_L}\right)_T \left.\left(\dfrac{\partial \rho_L}{\partial T}\right)\right|_{sat} \right] + V\rho_V\phi_V\left[\left(\dfrac{\partial U_V}{\partial T}\right)_{\rho_V} + \left(\dfrac{\partial U_V}{\partial \rho_V}\right)_T \left.\left(\dfrac{\partial \rho_V}{\partial T}\right)\right|_{sat} \right] \\ \Delta U_{vap} V \left(\phi_V \left.\left(\dfrac{\partial \rho_V}{\partial T}\right)\right|_{sat} - \dfrac{\rho_V}{\rho_V - \rho_L}\left.\left(\dfrac{\partial \rho_L}{\partial T}\right)\right|_{sat} - \dfrac{\rho_V(\rho - \rho_L)}{(\rho_V - \rho_L)^2}\left(\left.\left(\dfrac{\partial \rho_V}{\partial T}\right)\right|_{sat} - \left.\left(\dfrac{\partial \rho_L}{\partial T}\right)\right|_{sat} \right) \right) \end{array} \right\} } \qquad (28)$$

This expression gives an ODE for temperature as a function of time purely in terms of known thermodynamic properties and thermodynamic partial derivatives. The time derivative of density in the first term of the numerator on the RHS will drop out in this specific problem since the total density is fixed.

The only remaining task is to evaluate the missing partial derivatives.

III. Derivation for van der Waals Equation of State

At this point we need an equation of state. We will proceed with the 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 is given by

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{29}$$

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

$$V_m = \frac{m}{\rho} \tag{30}$$

The specific internal energy of the vdW fluid is

$$U = \frac{1}{m}\left[\frac{3}{2}RT - \frac{a\rho}{m}\right] \tag{31}$$

In the one phase region,

$$\frac{\partial U_L}{\partial t} = \frac{1}{m}\frac{3}{2}R\frac{\partial T}{\partial t} = C_V\frac{\partial T}{\partial t} \tag{32}$$

where C_V is the specific constant volume heat capacity.

In a two phase system, we have

$$U_V = \frac{1}{m}\left[\frac{3}{2}RT - \frac{a\rho_V}{m}\right] \quad \text{and} \quad U_L = \frac{1}{m}\left[\frac{3}{2}RT - \frac{a\rho_L}{m}\right] \tag{33}$$

We require the derivatives of the internal energies.

$$\frac{\partial U_L}{\partial t} = \frac{1}{m}\left[\frac{3}{2}R\frac{\partial T}{\partial t} - \frac{a}{m}\frac{\partial \rho_L}{\partial t}\right] \quad \text{and} \quad \frac{\partial U_V}{\partial t} = \frac{1}{m}\left[\frac{3}{2}R\frac{\partial T}{\partial t} - \frac{a}{m}\frac{\partial \rho_V}{\partial t}\right] \tag{34}$$

$$\begin{aligned}\frac{\partial U_L}{\partial t} &= \frac{1}{m}\left[\frac{3}{2}R\frac{\partial T}{\partial t} - \frac{a}{m}\left(\frac{\partial \rho_L}{\partial T}\right)\bigg|_{sat}\frac{\partial T}{\partial t}\right] = \frac{1}{m}\left[\frac{3}{2}R - \frac{a}{m}\left(\frac{\partial \rho_L}{\partial T}\right)\bigg|_{sat}\right]\frac{\partial T}{\partial t} \\ \frac{\partial U_V}{\partial t} &= \frac{1}{m}\left[\frac{3}{2}R\frac{\partial T}{\partial t} - \frac{a}{m}\left(\frac{\partial \rho_V}{\partial T}\right)\bigg|_{sat}\frac{\partial T}{\partial t}\right] = \frac{1}{m}\left[\frac{3}{2}R - \frac{a}{m}\left(\frac{\partial \rho_V}{\partial T}\right)\bigg|_{sat}\right]\frac{\partial T}{\partial t}\end{aligned} \tag{35}$$

We have to obtain the partial of the phase densities with respect to pressure along the saturation line. The values of the densities themselves are obtained from a numerical solution of a set of two algebraic equations, namely the conditions of mechanical and chemical equilibrium.

$$p_L\left(\rho_L(T),T\right) = p_V\left(\rho_V(T),T\right) \tag{36}$$

and

$$\mu_L\left(\rho_L(T),T\right) = \mu_V\left(\rho_V(T),T\right) \tag{37}$$

For the van der Waals gas these equations are

$$\Delta\mu = \mu_V - \mu_L = k_B T\left[\ln\left(\frac{V_m^L - b}{V_m^V - b}\right) + \frac{b}{V_m^V - b} - \frac{b}{V_m^L - b}\right] - 2a\left(\frac{1}{V_m^V} - \frac{1}{V_m^L}\right) \tag{38}$$

$$\Delta p = p_V - p_L = \frac{k_B T}{V_m^V - b} - \frac{a}{{V_m^V}^2} - \frac{k_B T}{V_m^L - b} + \frac{a}{{V_m^L}^2} = 0 \tag{39}$$

We want to know the change in the molar volume as a function of temperature along the two-phase boundary of the phase diagram, also known as the saturation line. In order to obtain an analytical expression for this derivative, we must differentiate both equation (38) and (39) with respect to temperature. We will then obtain two derivatives, one for the liquid and one for the vapor. We will combine the two equations to solve for the two derivatives individually. We begin by differentiating equation (38) with respect to temperature along the saturation line.

$$\begin{aligned} &k_B T\left[\frac{1}{V_m^L - b}\frac{\partial V_m^L}{\partial T}\bigg|_{sat} - \frac{1}{V_m^V - b}\frac{\partial V_m^V}{\partial T}\bigg|_{sat} - \frac{b}{\left(V_m^V - b\right)^2}\frac{\partial V_m^V}{\partial T}\bigg|_{sat} + \frac{b}{\left(V_m^L - b\right)^2}\frac{\partial V_m^L}{\partial T}\bigg|_{sat}\right] \\ &+ k_B\left[\ln\left(\frac{V_m^L - b}{V_m^V - b}\right) + \frac{b}{V_m^V - b} - \frac{b}{V_m^L - b}\right] + 2a\left(\frac{1}{{V_m^V}^2}\frac{\partial V_m^V}{\partial T}\bigg|_{sat} - \frac{1}{{V_m^L}^2}\frac{\partial V_m^L}{\partial T}\bigg|_{sat}\right) = 0 \end{aligned} \tag{40}$$

Next we differentiate equation (39)

$$-\frac{k_B T}{\left(V_m^V - b\right)^2}\frac{\partial V_m^V}{\partial T}\bigg|_{sat} + \frac{k_B}{V_m^V - b} + 2\frac{a}{{V_m^V}^3}\frac{\partial V_m^V}{\partial T}\bigg|_{sat} + \frac{k_B T}{\left(V_m^L - b\right)^2}\frac{\partial V_m^L}{\partial T}\bigg|_{sat} - \frac{k_B}{V_m^L - b} - 2\frac{a}{{V_m^L}^3}\frac{\partial V_m^L}{\partial T}\bigg|_{sat} = 0 \tag{41}$$

Now we solve these two equations for the two partial derivatives. Take equation (41) and combine like terms.

$$\left(-\frac{k_B T}{\left(V_m^V - b\right)^2} + 2\frac{a}{{V_m^V}^3}\right)\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} + \left(\frac{k_B T}{\left(V_m^L - b\right)^2} - 2\frac{a}{{V_m^L}^3}\right)\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} = \frac{k_B}{V_m^L - b} - \frac{k_B}{V_m^V - b} \tag{42}$$

$$\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} = \frac{\dfrac{k_B}{V_m^L - b} - \dfrac{k_B}{V_m^V - b} + \left(\dfrac{k_B T}{\left(V_m^V - b\right)^2} - 2\dfrac{a}{{V_m^V}^3}\right)\left.\dfrac{\partial V_m^V}{\partial T}\right|_{sat}}{\left(\dfrac{k_B T}{\left(V_m^L - b\right)^2} - 2\dfrac{a}{{V_m^L}^3}\right)} \tag{43}$$

Next we combine terms in equation (40)

$$\begin{aligned}&\left(\frac{k_B T}{V_m^L - b} + \frac{k_B T b}{\left(V_m^L - b\right)^2} - \frac{2a}{{V_m^L}^2}\right)\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} - \left(\frac{k_B T}{V_m^V - b} + \frac{k_B T b}{\left(V_m^V - b\right)^2} - \frac{2a}{{V_m^V}^2}\right)\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} \\ &= -k_B\left[\ln\left(\frac{V_m^L - b}{V_m^V - b}\right) + \frac{b}{V_m^V - b} - \frac{b}{V_m^L - b}\right]\end{aligned} \tag{44}$$

$$\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} = \frac{-k_B\left[\ln\left(\dfrac{V_m^L - b}{V_m^V - b}\right) + \dfrac{b}{V_m^V - b} - \dfrac{b}{V_m^L - b}\right] + \left(\dfrac{k_B T}{V_m^V - b} + \dfrac{k_B T b}{\left(V_m^V - b\right)^2} - \dfrac{2a}{{V_m^V}^2}\right)\left.\dfrac{\partial V_m^V}{\partial T}\right|_{sat}}{\left(\dfrac{k_B T}{V_m^L - b} + \dfrac{k_B T b}{\left(V_m^L - b\right)^2} - \dfrac{2a}{{V_m^L}^2}\right)} \tag{45}$$

Now we equate (43) and (45) to obtain

$$\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} = \frac{\dfrac{\dfrac{k_B}{V_m^L - b} - \dfrac{k_B}{V_m^V - b}}{\left(\dfrac{k_B T}{\left(V_m^L - b\right)^2} - 2\dfrac{a}{{V_m^L}^3}\right)} + \dfrac{k_B\left[\ln\left(\dfrac{V_m^L - b}{V_m^V - b}\right) + \dfrac{b}{V_m^V - b} - \dfrac{b}{V_m^L - b}\right]}{\left(\dfrac{k_B T}{V_m^L - b} + \dfrac{k_B T b}{\left(V_m^L - b\right)^2} - \dfrac{2a}{{V_m^L}^2}\right)}}{\dfrac{\left(\dfrac{k_B T}{V_m^V - b} + \dfrac{k_B T b}{\left(V_m^V - b\right)^2} - \dfrac{2a}{{V_m^V}^2}\right)}{\left(\dfrac{k_B T}{V_m^L - b} + \dfrac{k_B T b}{\left(V_m^L - b\right)^2} - \dfrac{2a}{{V_m^L}^2}\right)} - \dfrac{\left(\dfrac{k_B T}{\left(V_m^V - b\right)^2} - 2\dfrac{a}{{V_m^V}^3}\right)}{\left(\dfrac{k_B T}{\left(V_m^L - b\right)^2} - 2\dfrac{a}{{V_m^L}^3}\right)}} \tag{46}$$

We can obtain the corresponding partial derivative for the liquid phase by substituting equation (46) into equation (43).

Differentiating equation (30) , we have

$$\frac{\partial \rho}{\partial T} = -\frac{\rho^2}{m}\frac{\partial V_m}{\partial T} \tag{42}$$

so we have the derivatives of the density that we require in the energy balance.

IV. The Solution Algorithm

The big picture is that we have one nonlinear ordinary differential equation that we wish to solve, namely the energy balance. We have one unknown, *T*(*t*). In a one phase region, the energy balance reduces to

$$\frac{\partial T}{\partial t} = \frac{-Q}{V\rho\left(\frac{\partial U}{\partial T}\right)_{\rho}} = \frac{-Q}{V\rho C_V} \tag{21}$$

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

$$\frac{\partial T}{\partial t} = \frac{-\Delta U_{vap} V \frac{\rho_V}{\rho_V - \rho_L}\frac{\partial \rho}{\partial t} - Q}{\left\{\begin{array}{l} V\rho_L\phi_L\left[\left(\frac{\partial U_L}{\partial T}\right)_{\rho_L} + \left(\frac{\partial U_L}{\partial \rho_L}\right)_T \left(\frac{\partial \rho_L}{\partial T}\right)\Big|_{sat}\right] + V\rho_V\phi_V\left[\left(\frac{\partial U_V}{\partial T}\right)_{\rho_V} + \left(\frac{\partial U_V}{\partial \rho_V}\right)_T \left(\frac{\partial \rho_V}{\partial T}\right)\Big|_{sat}\right] \\ \Delta U_{vap} V\left(\phi_V\left(\frac{\partial \rho_V}{\partial T}\right)\Big|_{sat} - \frac{\rho_V}{\rho_V - \rho_L}\left(\frac{\partial \rho_L}{\partial T}\right)\Big|_{sat} - \frac{\rho_V(\rho - \rho_L)}{(\rho_V - \rho_L)^2}\left(\left(\frac{\partial \rho_V}{\partial T}\right)\Big|_{sat} - \left(\frac{\partial \rho_L}{\partial T}\right)\Big|_{sat}\right)\right) \end{array}\right\}} \tag{28}$$

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

Let's assume that we start above the critical temperature. We then proceed to remove heat. It is true that at each step of the numerical solution of this ODE, we must check to see if we have one phase or two phases. In these two alternatives, one phase or two, only the temperature is the same. The molar volume in the one phase system will remain constant, since the total moles and the volume are constant. The pressure of the one phase system and the chemical potential of the one phase system can be evaluated. Then one can compute the vapor pressure, vapor and liquid phase densities, chemical potential, and vapor fraction of the two phase system. Note that the pressure of the one phase and two phase systems are not the same. Therefore, we cannot make the determination of whether we have a one phase or two phase system on the basis of the chemical potentials of the one and two phase systems. What we have done is simply to examine whether the one phase molar volume is between the vapor and liquid molar volumes from the two phase calculation. If it is, then the one phase system is in the two-phase envelope and we will have two phases. Otherwise, we have one phase. There are more rigorous ways to make this determination and perhaps we would be better suited to implement them. At this stage, however, we have implemented the decision making based on the molar volumes.

Once we have two phases, we must determine the equilibrium phase densities and the vapor pressure from the thermodynamic equilibrium constraints. Then we can use equation (3) to obtain the vapor fraction. We can also determine the necessary partial derivatives in equations (21) and (28). Then we are ready to take our next step through time.

V. An Example

I defined my van der Waals fluid with the following critical properties and molecular weights.

- T_c = 150 K
- p_c = 4.5e+6 Pa
- V_c = 7.49e-5 m^3/mol
- m = 0.0400 kg/mole

I place on kg of material in a box such that the molar volume was 1.03e-004 m^3/mol. The initial temperature was 1.01T_c. I removed heat at the rate of 100 J/sec.

Plots of the transient solution for the first 100 seconds follow.

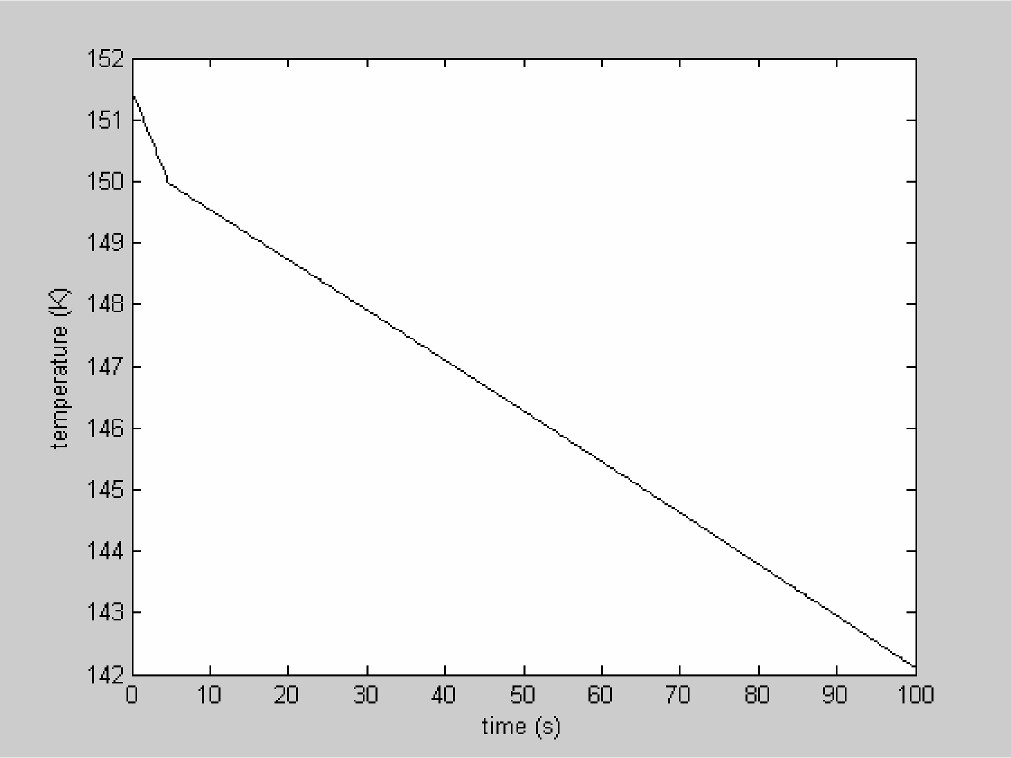

Figure 1. Temperature as a function of time.

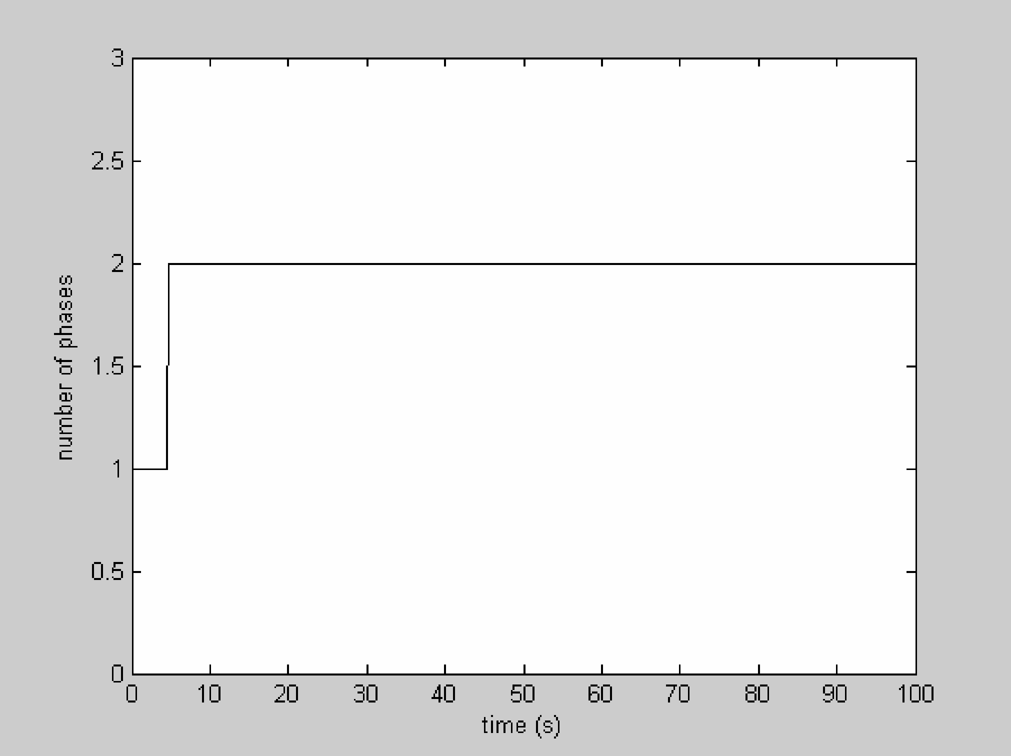

Figure 2. Number of phases as a function of time.

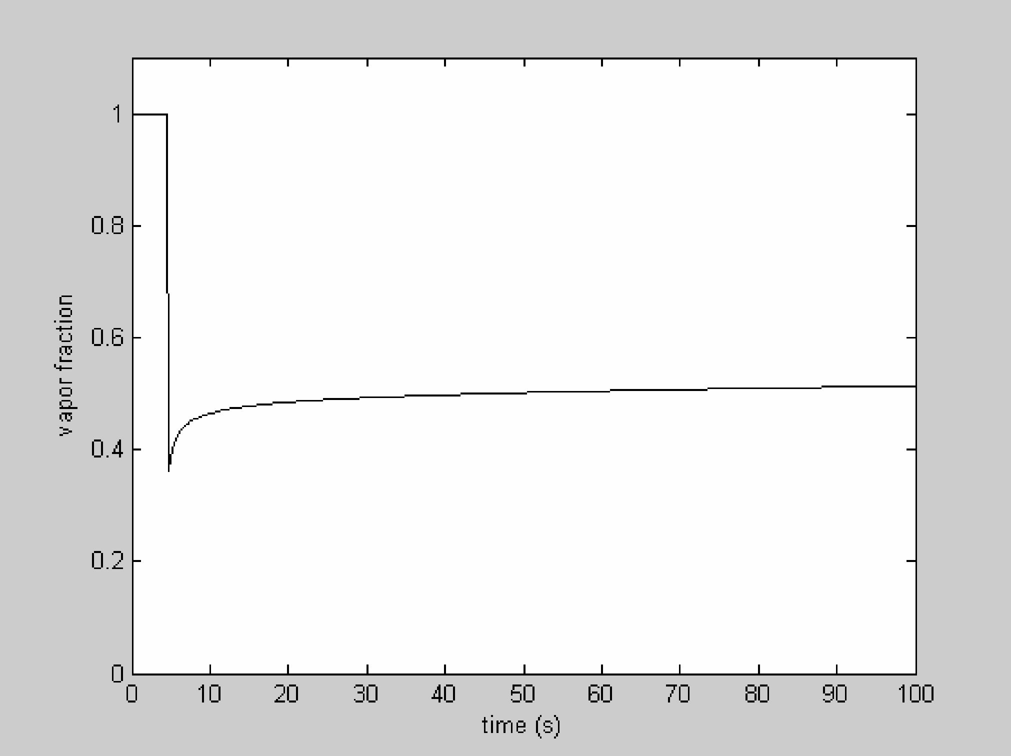

Figure 3. Vapor fraction as a function of time.

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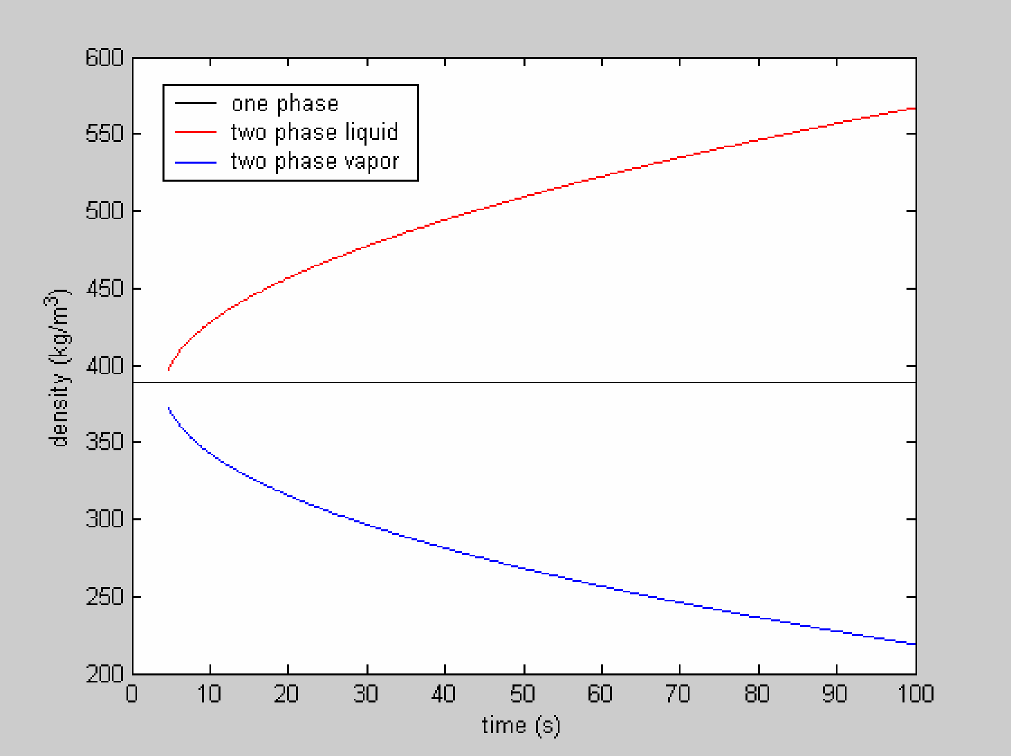

Figure 4. Density as a function of time.

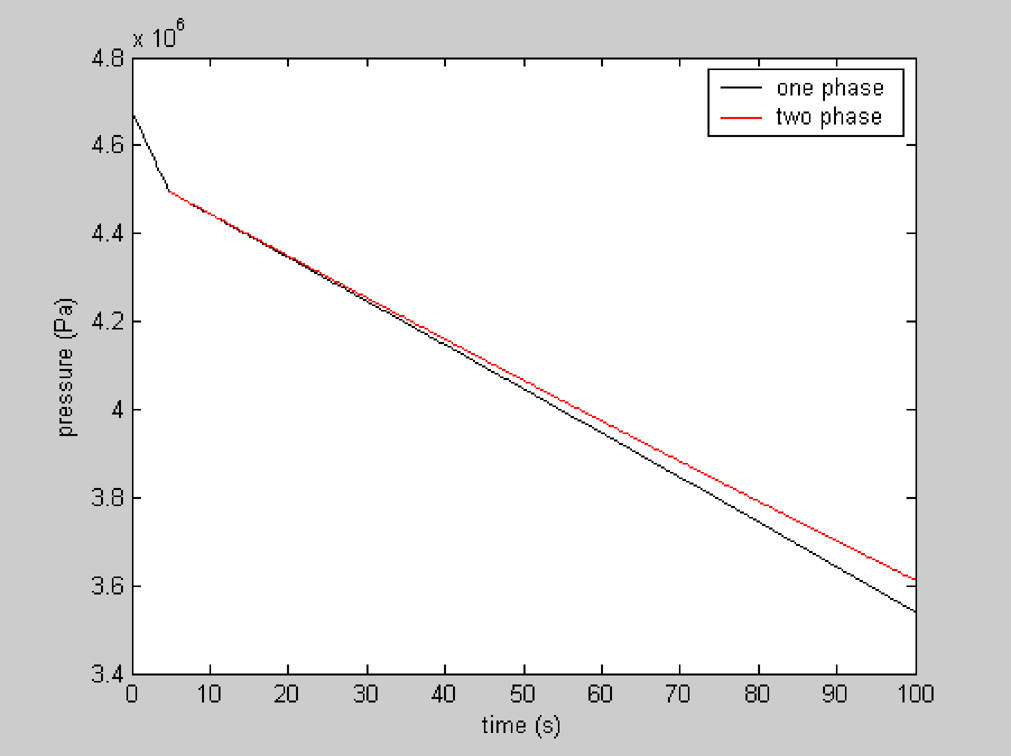

Figure 5. Pressure as a function of time.

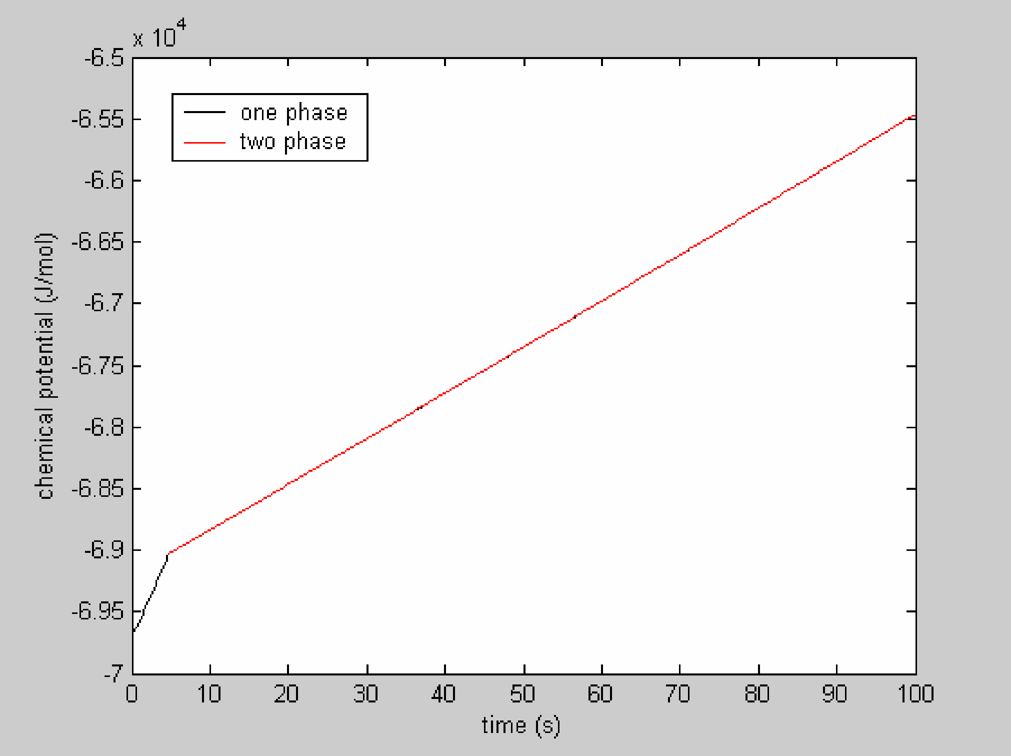

Figure 6. Chemical potential as a function of time.

VI. Codes

Attached are 4 Matlab codes used in the previous example.

- driver.m
- sysode.m
- sysodeinput.m
- newraph_md.m

driver.m starts the program. It calls sysode.m to solve the system of ordinary differential equations. (In this case there is only one ODE, the energy balance.) Sysode contains the Euler and classical fourth-order Runge-Kutta methods. The ODE is entered in sysodeinput.m. During the evaluation of the ODE, we must find out the vapor pressure and phase densities, which require an iterative solution. We use the newraph_nd.m, which uses the Newton-Raphon method with numerical derivatives. The function that we are solving, namely the constraint of chemical equilibria is located in the function at the end of newraph_md.

driver.m

```
clear all;
close all;
format long;
%
%  van der Waals two-phase closed system
%
% declare global variables
global a b Vol rho Cv m Tc tol h kB mm pi Vm R method_AE
global isave datamat i
% critical properties
Tc = 150; % K
pc = 4.5e+6;  % Pa
Vc =  7.49e-5; %m^3/mol
h = 6.62618e-34; % J*s
kB = 1.38066e-23; % J/K
Nav = 6.02205e+23; % molecules/mole
R = kB*Nav; % J/mole/K
pi = 2.0*asin(1); % pi=3.14...
a = 27*R^2*Tc^2/(64*pc);  % J*m^3/mol^2
b = R*Tc/(8*pc); % m^3/mol
m = 0.0400; % kg per mole
amu = 1.66056e-27; % kg/amu
mm = amu*m;
Cv = 3/2*R/m; % J/kg/K
%Vm = Vc; % m^3/mol
Vm = 1.03e-004; % m^3/mol
%  convert to per mass properties
rho = m/Vm;  % kg/m^3
%b = b/m; % m^3/kg
%a = a/m^2; % J*m^2/kg^2
% mass in the system
mass = 1; % kg
% specify system volume
Vol = mass/rho;
% specify initial conditions
To = 1.01*Tc;
% specify ODE solving parameters
method_ODE = 1; % Euler
method_AE = 3; % Newton-Raphson with Numerical Derivatives
isave = 0;
to=0;
tf= 20;
n= 100;
```

```
tol = 1.0e-8;
%  call sysode
[t,T]=sysode(method_ODE,n,to,tf,To);
% save results
isave = 1;
nT = max(size(T));
% datamat column 1:  number of phases
% datamat column 2:  1-phase density
% datamat column 3:  1-phase pressure
% datamat column 4:  1-phase chemical potential
% datamat column 5:  2-phase liquid density
% datamat column 6:  2-phase vapor density
% datamat column 7:  2-phase pressure
% datamat column 8:  2-phase chemical potential
% datamat column 9:  2-phase vapor fraction
datamat = zeros(nT,9);
p = R*T(1)/(Vm-b)-a/Vm^2;
for i = 1:1:nT
   f=sysodeinput(t(i),T(i));
end
% find where 2-phase region started
i2start = 0;
i = 0;
while (i2start == 0)
   i = i + 1;
   if (datamat(i,1) == 2)
      i2start = i;
   end
end
% plot results
figure(1)
plot(t,T,'k-');
xlabel('time (s)');
ylabel('temperature (K)');
% plot densities
figure(2)
plot(t,datamat(:,2),'k-');
hold on;
plot(t(i2start:nT),datamat(i2start:nT,5),'r-');
hold on;
plot(t(i2start:nT),datamat(i2start:nT,6),'b-');
hold off;
xlabel('time (s)');
ylabel('density (kg/m^3)');
legend('one phase', 'two phase liquid', 'two phase vapor');
% plot pressure
figure(3)
plot(t,datamat(:,3),'k-');
hold on;
plot(t(i2start:nT),datamat(i2start:nT,7),'r-');
hold off;
xlabel('time (s)');
ylabel('pressure (Pa)');
legend('one phase', 'two phase');
% plot chemical potentials
figure(4)
plot(t,datamat(:,4),'k-');
hold on;
plot(t(i2start:nT),datamat(i2start:nT,8),'r-');
hold off;
xlabel('time (s)');
ylabel('chemical potential (J/mol)');
legend('one phase', 'two phase');
% plot vapor fraction
figure(5)
plot(t,datamat(:,9),'k-');
xlabel('time (s)');
ylabel('vapor fraction');
axis([t(1) t(nT) 0 1.1]);
% plot number of phases
```

```
figure(6)
plot(t,datamat(:,1),'k-');
xlabel('time (s)');
ylabel('number of phases');
axis([t(1) t(nT) 0 3]);
```

sysode.m

```
function [x,y]=sysode(m,n,xo,xf,yo);
%  sysode(m,n,xo,xf,yo)
%  This routine solves one non-linear first-order ordinary differential
%  equation initial value problem.
%
%  m = 1 for Euler's method
%  m = 2 for Classical Runge-Kutta 4rth order method
%  n = number of steps
%  xo = starting value of x
%  xf = ending value of x
%  o = number of first order ordinary differential equations
%  yo = initial condition at xo
%
%  The differential equation must appear in the file 'sysodeinput.m'
%  This program creates an output data file 'sysode.out'
%
%  Author:  David Keffer   Date:  October 23, 1998
%

%
%  STEP ONE.  input parameters
%
if (nargin ~= 5)
   error('sysode requires 5 input arguments');
end
nsize=size(yo);
o=max(nsize(1),nsize(2));
%
%  STEP TWO DEFINE ODE and I
%
%  yo is the initial condition
%  the ode is defined in a file called odeivpn.m
%yo = zeros(1,o);
%
%  the vector nvec contains some info that can be passed
%  to sysodeinput (in case you need it)
%  nvec(1) = i, the iteration number
%  nvec(2) = n, the total number of iterations
%  nvec(3) = kk, the intra-iteration access number
%  nvec(4) = o, the number of first order ODEs
%  nvec(5) = m, the method used to solve
%
%  STEP THREE.  SOLVE THE ODE
%
h = (xf-xo)/n;
x = xo : h : xf;
if (m == 1)
   y = eulerevaln(x,h,n,o,yo);
else
   y = rk4evaln(x,h,n,o,yo);
end
%
%  STEP FOUR.  PLOT THE RESULT
%
iplot = 1;
if (iplot == 1)
for i = 1:o
  if (i==1)
     plot (x,y(:,i),'k-'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==2)
     plot (x,y(:,i),'r-'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==3)
     plot (x,y(:,i),'b-'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==4)
     plot (x,y(:,i),'g-'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==5)
     plot (x,y(:,i),'m-'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==6)
```

```
    plot (x,y(:,i),'k:'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==7)
    plot (x,y(:,i),'r:'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==8)
    plot (x,y(:,i),'b:'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==9)
    plot (x,y(:,i),'g:'), xlabel( 'x' ), ylabel ( 'y' )
  elseif (i==10)
    plot (x,y(:,i),'m:'), xlabel( 'x' ), ylabel ( 'y' )
 else
    plot (x,y(:,i),'k-'), xlabel( 'x' ), ylabel ( 'y' )
  end
  hold on
end
hold off
end
%
%  STEP FIVE.  WRITE THE RESULT TO sysode.out
%
op1=o+1;
fid = fopen('sysode.out','w');
if (op1 == 2)
  fprintf(fid,'x            y(1) \n');
  fprintf(fid,'%21.15e %21.15e   \n', [x;y']);
elseif (op1 == 3)
  fprintf(fid,'x            y(1)         y(2) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e  \n', [x;y']);
elseif (op1 == 4)
  fprintf(fid,'x            y(1)         y(2)         y(3) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e %13.7e \n', [x;y']);
elseif (op1 == 5)
  fprintf(fid,'x            y(1)         y(2)         y(3)         y(4) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e %13.7e %13.7e \n', [x;y']);
elseif (op1 == 6)
  fprintf(fid,'x            y(1)         y(2)         y(3)         y(4)         y(5) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e  %13.7e %13.7e %13.7e \n', [x;y']);
elseif (op1 == 7)
  fprintf(fid,'x            y(1)         y(2)         y(3)         y(4)         y(5)         y(6) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e  \n', [x;y']);
elseif (op1 == 8)
  fprintf(fid,'x            y(1)         y(2)         y(3)         y(4)         y(5)         y(6)         y(7) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e  \n', [x;y']);
elseif (op1 == 9)
  fprintf(fid,'x            y(1)         y(2)         y(3)         y(4)         y(5)         y(6)         y(7)         y(8) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e \n', [x;y']);
elseif (op1 == 10)
  fprintf(fid,'x            y(1)         y(2)         y(3)         y(4)         y(5)         y(6)         y(7)         y(8)         y(9) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e  \n', [x;y']);
elseif (op1 == 11)
  fprintf(fid,'x            y(1)         y(2)         y(3)         y(4)         y(5)         y(6)         y(7)         y(8)         y(9)         y(10) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e  %13.7e %13.7e \n', [x;y']);
else
  fprintf(fid,'x            y(1)         y(2)         y(3)         y(4)         y(5)         y(6)         y(7)         y(8)         y(9)         y(10)         y(11) \n');
  fprintf(fid,'%13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e %13.7e  \n', [x;y']);
end
fclose(fid);
%
%  If you want, interpolate to find a time at a particular value of y
%
interp = 0;
if (interp == 1)
   final_height = y(n+1)
   yf=2.54;
   time_at_h_1inch = INTERP1(y,x,yf,'linear')
end

%
%  multivariate classical fourth order Runge-Kutta
%
function y = rk4evaln(x,h,n,o,yo)
```

```
%
%  specify initial values of y
%
y = zeros(n+1,o);
dydt = zeros(1,o);
k1 = zeros(1,o);
k2 = zeros(1,o);
k3 = zeros(1,o);
k4 = zeros(1,o);
yt = zeros(o,1);
ytt = zeros(1,o);
%
for j = 1:o
   y(1,j) = yo(j);
end
%  solve new values of dydt and y
nvec =[0;n;1;o;2];
for i =  1:n
   nvec(1)=i;
   xt = x(i);
   ytt = y(i,:);
   yt = ytt;
   nvec(3)=1;
   k1 = sysodeinput(xt,yt,nvec);
   xt = x(i)+h/2;
   for j = 1:o
      yt(j) = ytt(j)+h/2*k1(j);
   end
   nvec(3)=2;
   k2 = sysodeinput(xt,yt,nvec);
   for j = 1:o
      yt(j) = ytt(j)+h/2*k2(j);
   end
   nvec(3)=3;
   k3 = sysodeinput(xt,yt,nvec);
   xt = x(i)+h;
   for j = 1:o
      yt(j) = ytt(j)+h*k3(j);
   end
   nvec(3)=4;
   k4 = sysodeinput(xt,yt,nvec);
   for j = 1:o
      y(i+1,j) = y(i,j)+h/6*(k1(j)+2*k2(j)+2*k3(j)+k4(j));
   end
end

%
%  multivariate Euler method
%
function y = eulerevaln(x,h,n,o,yo)
%  specify initial values of y
y = zeros(n+1,o);
dydt = zeros(1,o);
for j = 1:o
   y(1,j) = yo(j);
end
nvec =[0;n;1;o;1];
%  solve new values of dydt and y
for i =  1:n
   nvec(1) = i;
   dydt = sysodeinput(x(i),y(i,:),nvec);
   for j = 1:o
      y(i+1,j) = y(i,j)+h*dydt(j);
   end
end
```

sysodeinput.m

```
function dTdt = sysodeinput(t,T,nvec);
%
global a b Vol rho Cv m Tc tol h kB mm pi Vm R method_AE
global Tcurrent
global pold
global isave datamat i
% need Tcurrent to pass to AE solver
Tcurrent = T;
% thermal debroglie wavelength
   lambda = sqrt(h^2/(2*pi*mm*kB*T));
   lambda3 = lambda^3;
if (T >= Tc)
%   if you are above the critical point, you have one phase.
   nphase = 1;
   Vm1 = Vm;
   p1 = R*T/(Vm-b)-a/Vm^2; % Pa
   mu1 = -R*T*(log((Vm1-b)/lambda3) - b/(Vm1-b) + 2*a/(Vm1*R*T)); % J/mol
   p = p1;
   phiv = 1.0;
   fprintf(1,'1-phase:  p %e Vm %e \n',p, Vm);
else
%
% need to calculate the chemical potential for 1-phase and 2-phase
% systems in order to determine which one exists.
%
% one phase system
   Vm1 = Vm;
   p1 = R*T/(Vm-b)-a/Vm^2; % Pa
   mu1 = -R*T*(log((Vm1-b)/lambda3) - b/(Vm1-b) + 2*a/(Vm1*R*T)); % J/mol
   phiv = 1.0;
% two phase system
% iteratively determine vapor pressure
  %p2 = pold;
  [p2,err] = newraph_nd(pold);
  p2 = real(p2);
% compute molar volumes
  Vvec = roots([p2,(-b*p2-R*T),a,-a*b]);
  Vmv = max(real(Vvec)); %m^3/mol;
  Vml = min(real(Vvec)); %m^3/mol;
%   chemical potentials
   muv = -R*T*(log((Vmv-b)/lambda3) - b/(Vmv-b) + 2*a/(Vmv*R*T)); % J/mol
   mul = -R*T*(log((Vml-b)/lambda3) - b/(Vml-b) + 2*a/(Vml*R*T)); % J/mol
%   determine number of phases (based on chemical potential
%  find two densities
      rhov = m/Vmv; % kg/m^3
      rhol = m/Vml; % kg/m^3
% vapor fraction
      %xv = (Vm - Vml)/(Vmv-Vml);
      %phiv = xv*Vmv/(xv*Vmv + (1-xv)*Vml);
      phiv = (rho - rhol)/(rhov-rhol);
   if (Vm1 < Vml || Vm1 > Vmv)
      nphase = 1;
      p = p1; % Pa
   else
      nphase = 2;
% vapor pressure
      p = p2; % Pa
% thermo derivatives
      term1 = R/(Vml-b) - R/(Vmv-b);
      term2 = R*(log((Vml-b)/(Vmv-b)) + b/(Vmv-b) - b/(Vml-b));
      term3 = R*T/(Vml-b)^2 - 2*a/Vml^3;
      term4 = R*T/(Vml-b)+R*T*b/(Vml-b)^2 - 2*a/Vml^2;
      term5 = R*T/(Vmv-b)+R*T*b/(Vmv-b)^2 - 2*a/Vmv^2;
      term6 = R*T/(Vmv-b)^2 - 2*a/Vmv^3;
      dVmvdtsat = (term1/term3 + term2/term4) / (term5/term4 - term6/term3);
      dVmldtsat = ( term1 + term6*dVmvdtsat )/ term3;
      drhovdtsat = -rhov^2/m*dVmvdtsat; % kg/m^3/K
      drholdtsat = -rhol^2/m*dVmldtsat; % kg/m^3/K
```

```
    end
fprintf(1,'nphase: %i p1 %e Vm1 %e mu1 %e phiv %e p2 %e Vmv %e Vml %e muv %e \n',nphase, p1, Vm1, mu1, phiv, p2, Vmv, Vml, muv );
end
% heat loss
Q = 100; % J/sec
if (nphase == 1)
   dTdt = -Q/(Cv*Vol*rho); % K/sec
else
   phil = 1.0 - phiv;
   Ul = 1/m*(1.5*R*T - a/m*rhol);
   Uv = 1/m*(1.5*R*T - a/m*rhov);
   dUvap = Uv - Ul;
   dUdT_l = 1/m*1.5*R;
   dUdrho_l = -a/m^2;
   dUdT_v = 1/m*1.5*R;
   dUdrho_v = -a/m^2;
   drhodt = 0.0;
   EB_numerator_term1 = -Q;
   EB_numerator_term2 = -dUvap*Vol*rhov/(rhov-rhol)*drhodt;
   EB_numerator = EB_numerator_term1 + EB_numerator_term2;
   EB_denominator_term1 = Vol*rhol*phil*(dUdT_l + dUdrho_l*drholdtsat);
   EB_denominator_term2 = Vol*rhov*phiv*(dUdT_v + dUdrho_v*drhovdtsat);
   EB_denominator_term3a = phiv*drhovdtsat;
   EB_denominator_term3b = -rhov/(rhov-rhol)*drholdtsat;
   EB_denominator_term3c = -rhov*(rho-rhol)/(rhov-rhol)^2*(drhovdtsat - drholdtsat);
   EB_denominator_term3 = dUvap*Vol*(EB_denominator_term3a + ...
      EB_denominator_term3b + EB_denominator_term3c);
   EB_denominator = EB_denominator_term1 + EB_denominator_term2 + ...
      EB_denominator_term3;
   dTdt = EB_numerator / EB_denominator;
end

% save old value of pressure
pold = p;
if (isave == 1)
% datamat column 1:  number of phases
% datamat column 2:  1-phase density
% datamat column 3:  1-phase pressure
% datamat column 4:  1-phase chemical potential
% datamat column 5:  2-phase liquid density
% datamat column 6:  2-phase vapor density
% datamat column 7:  2-phase pressure
% datamat column 8:  2-phase chemical potential
% datamat column 9:  2-phase vapor fraction
    datamat(i,1) = nphase;
    datamat(i,2) = m/Vm1;
    datamat(i,3) = p1;
    datamat(i,4) = mu1;
    if (T <= Tc)
        datamat(i,5) = rhol;
        datamat(i,6) = rhov;
        datamat(i,7) = p2;
        datamat(i,8) = muv;
    end
    datamat(i,9) = phiv;
end
```

newraph_nd.m

```
%
%  Newton-Raphson method with numerical approximations to the derivative.
%
function [x0,err] = newraph_nd(x0);
maxit = 100;
tol = 1.0e-6;
err = 100.0;
icount = 0;
xold =x0;
while (err > tol & icount <= maxit)
   icount = icount + 1;
   f = funkeval(xold);
   h = min(0.01*xold,0.01);
   df = dfunkeval(xold,h);
   xnew = xold - f/df;
   if (icount > 1)
      err = abs((xnew - xold)/xnew);
   end
   %fprintf(1,'icount = %i xold = %e f = %e df = %e xnew = %e  err = %e \n',icount, xold, f, df, xnew, err);
   xold = xnew;
end
%
x0 = xnew;
if (icount >= maxit)
   % you ran out of iterations
   fprintf(1,'Sorry.  You did not converge in %i iterations.\n',maxit);
   fprintf(1,'The final value of x was %e \n', x0);
end

function df = dfunkeval(x,h)
fp = funkeval(x+h);
fn = funkeval(x-h);
df = (fp - fn)/(2*h);


function f = funkeval(p)
global a b Vol rho Cv m Tc tol h kB mm pi Vm R method_AE
global Tcurrent
T = Tcurrent;
% get molar volumes
Vvec = roots([p,(-b*p-R*T),a,-a*b]);
Vmv = max(Vvec); %m^3/mol;
Vml = min(Vvec); %m^3/mol;
% evaluate the function delta mu/RT
f = log((Vml-b)/(Vmv-b)) + b/(Vmv-b) - b/(Vml-b) - 2*a/(R*T)*(1/Vmv-1/Vml);
```