

Memo

Stability and critical points of mixtures

Thermotools

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1 Introduction

This memo is to present methods for calculating stability and critical points of mixture. Background information on stability of mixtures and the calculation of critical points is found in Reid and Beegle [4], Heidemann and Khalil [1], Michelsen [2] and Michelsen and Mollerup [3, Chap. 9].

2 Limit of stability formulated in temperature and pressure

The stability criterion for a mixture with composition z , formulated in temperature and pressure, is given by

$$\text{TPD}(\mathbf{w}) = \sum_i w_i (\mu_i(\mathbf{w}) - \mu_i(\mathbf{z})), \quad (1)$$

where TPD is the tangent plane distance function, and μ is the chemical potential. If looking at global stability, \mathbf{w} is any composition. In the case of local stability, \mathbf{w} is any perturbation of \mathbf{z} . If TPD is non-negative the mixture \mathbf{z} is stable.

A modified stability condition for a reduced tangent plane distance tpd , is given in Equation 2. tpd is evaluated using composition variables treated as mole numbers, \mathbf{Y} , instead of



composition, and have better properties and are easier to solve numerically than the *TPD* formulation.

$$\text{tpd}(\mathbf{Y}) = 1.0 + \sum_i Y_i (\ln Y_i + \ln \varphi_i(\mathbf{Y}) - \ln z_i - \ln \varphi_i(\mathbf{z})). \quad (2)$$

Here φ is the fugacity.

Differentiating Equation 2, we get

$$\mathbf{g} = \frac{\partial \text{tpd}}{\partial \mathbf{Y}} = \ln Y_i + \ln \varphi_i(\mathbf{Y}) - \ln z_i - \ln \varphi_i(\mathbf{z}), \quad (3)$$

$$H_{ij} = \frac{\partial^2 \text{tpd}}{\partial Y_i \partial Y_j} = \frac{\delta_{ij}}{Y_i} + \frac{\partial \ln \varphi_i(\mathbf{Y})}{Y_j}. \quad (4)$$

Looking at local stability of a mixture phase with composition \mathbf{z} , a perturbation of \mathbf{z} , $\mathbf{Y} = \mathbf{z} + \mathbf{e}$, for small \mathbf{e} must give a positive tpd. A Taylor series expansion from $\mathbf{Y} = \mathbf{z}$ yields,

$$\text{tpd}(\mathbf{Y}) = \text{tpd}(\mathbf{z}) + \left(\frac{\partial \text{tpd}}{\partial \mathbf{z}} \right)^\top \mathbf{e} + \frac{1}{2} \mathbf{e}^\top \left(\frac{\partial^2 \text{tpd}}{\partial \mathbf{z}^2} \right) \mathbf{e} + \dots \quad (5)$$

$$= \text{tpd} + \mathbf{g}^\top \mathbf{e} + \frac{1}{2} \mathbf{e}^\top \mathbf{H} \mathbf{e} + \dots \quad (6)$$

Since $\text{tpd}(\mathbf{z}) = 0$ and $\mathbf{g}(\mathbf{z}) = 0$, the local stability limit therefore becomes,

$$\det(\mathbf{H}) = 0, \quad (7)$$

or equivalent $\lambda_{\min} = 0$, where λ_{\min} is the minimum eigenvalue of \mathbf{H} .

To improve the scaling and the numerical properties of the problem, Michelsen [2] introduces a scaling of the composition variables,

$$X_i = \frac{Y_i - z_i}{\sqrt{z_i}}. \quad (8)$$

Further $X_i = su_i$, where \mathbf{u} is a normalized vector, $\mathbf{u}^\top \mathbf{u} = 1$. The perturbed composition then becomes,

$$Y_i = z_i + su_i \sqrt{z_i}. \quad (9)$$

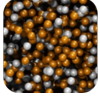
Differentiating Equation 2 with respect to X_i we get,

$$\frac{\partial \text{tpd}}{\partial X_i} = \sqrt{z_i} g_i, \quad (10)$$

$$\frac{\partial^2 \text{tpd}}{\partial X_i \partial X_j} = B_{ij} = \sqrt{z_i} \sqrt{z_j} H_{ij}. \quad (11)$$

Further, if we let \mathbf{u} be the eigenvector corresponding to the smallest eigenvalue, λ_{\min} , of \mathbf{B} , we have

$$b = \frac{1}{2} \mathbf{u}^\top \mathbf{B} \mathbf{u} = \frac{1}{2} \lambda_{\min}. \quad (12)$$



2.1 Numerical solver

Solving for $b = 0$ in Equation 12, for a specified pressure or temperature is complicated. The solution value (T or p) will lie near the value (T or p) where the underlying equation of state loses a density root (phase). A discontinuity will therefore be located close to the solution, excluding the possibility of using a bracketing solver, unless the position where the phase root disappears is known. If we are dealing with a cubic equation of state, the position where the model loses a density root can easily be determined, otherwise not. See Figure 1.

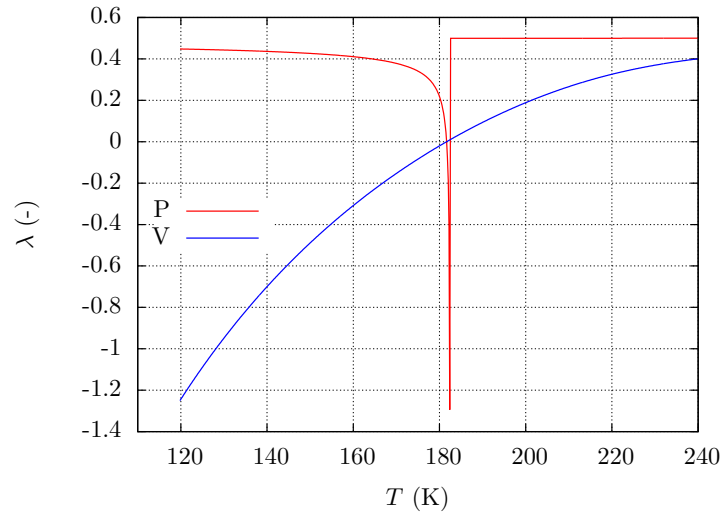


Figure 1: Minimum eigenvalue plotted as a function of T for given pressure, P and for given specific volume, V . The meta-stable limit is located at $T = 181.65$ K. The TP line has a discontinuity (phase disappears) located close to the meta-stable limit, while the TV line is monotonous. The plot is generated for a mixture of 90 % methane and 10 % ethane.

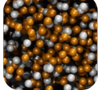
Specifying a pressure and solving for a temperature at the meta-stable limit, has been found possible for low pressures. The saturation temperature, when treating the fluid as a pure fluid, at low pressures, can be used as initial value of the search for a meta-stable limit of a gas/liquid. We then know that the solution will lie below (gas) and above (liquid) the initial guess. Using a Newton-Raphson (NR) solver we will take steps in a direction towards the solution, but with the possibility of overshooting the solution. Since the eigenvalue of the stability matrix, \mathbf{B} , changes abruptly when a phase disappears, and another phase is selected by the EOS density solver, a line search is used to back track if the search step becomes too large.

The NR solver must use numerical differentials since analytical differentials are difficult to derive in the general case.

For larger pressures, where the metastable limits of the gas and the liquid come close together, it has proven difficult to guarantee solution to the correct meta-stable limit. To overcome this problem, an alternative formulation is needed.

3 Alternative formulation

Michelsen and Heidemann [1] suggest that a formulation in the variables T and v is more robust than the P and T formulation. One reason for this is that following the meta stable



limit, the volume will be monotonous.

The Heidemann tangent plane distance for T and v are given as,

$$\text{TPD}(T, V, \mathbf{Y}) = A(T, V, \mathbf{Y}) - A(T, V_0, \mathbf{z}) + P(T, V_0, \mathbf{z})(V - V_0) - \sum_j \mu(T, V_0, \mathbf{z})(Y_j - z_j). \quad (13)$$

The Michelsen Michelsen and Mollerup [3, Chap. 9] reduced tangent plane distance for T and v are given as,

$$\text{tpd}(T, V, \mathbf{Y}) = \sum_j Y_j [\ln f_j(T, V, \mathbf{Y}) - \ln f_j(T, V_0, \mathbf{z})] - [P(T, V, \mathbf{Y}) - P_0] \frac{V}{RT}. \quad (14)$$

The Helmholtz energy can be written as follows,

$$A(T, V, \mathbf{Y}) = -P(T, V, \mathbf{Y})V + \sum_j Y_j \mu(T, V, \mathbf{Y}). \quad (15)$$

The fugacity coefficient definition

$$RT \ln f_j(T, V, \mathbf{Y}) = \frac{\partial A(T, V, \mathbf{Y})}{\partial Y_j} = \mu_j(T, V, \mathbf{Y}). \quad (16)$$

give the following relation:

$$A(T, V, \mathbf{Y}) = -P(T, V, \mathbf{Y})V + \sum_j Y_j \ln f_j(T, V, \mathbf{Y}). \quad (17)$$

Note that we are not working with the reduced Helmholtz energy, but the real Helmholtz energy.

Using Equations 15, 16 and 17, and $V = V_0$ it is seen that Equation 13 and Equation 14 represent the same stability criteria:

$$\text{tpd}(T, V, \mathbf{Y}) = \sum_j Y_j [\ln f_j(T, V, \mathbf{Y}) - \ln f_j(T, V_0, \mathbf{z})] - [P(T, V, \mathbf{Y}) - P_0] \frac{V}{RT}, \quad (18)$$

$$= \frac{1}{RT} \left(-P(T, V, \mathbf{Y})V + \sum_j Y_j \mu_j(T, V, \mathbf{Y}) \right) \quad (19)$$

$$- \frac{1}{RT} \left(-P_0 V_0 + P_0(V_0 - V) - \sum_j (Y_j - z_j + z_j) \mu_j(T, V_0, \mathbf{z}) \right), \quad (20)$$

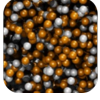
$$= \frac{1}{RT} \left(A(T, V, \mathbf{Y}) - A(T, V_0, \mathbf{z}) + P_0(V_0 - V) - \sum_j (Y_j - z_j) \mu_j(T, V_0, \mathbf{z}) \right), \quad (21)$$

Differentiating Equation 14 w.r.t. n_i , and using $V = V_0$ we get

$$g_i = \ln f_i(T, V_0, \mathbf{Y}) + \ln f_i(T, V_0, \mathbf{z}), \quad (22)$$

and

$$h_{ij} = \ln f_{ij}(T, V, \mathbf{Y}). \quad (23)$$



The same variable scaling is used for this formulation, as in the previous section (Equation 8). Using the temperature-pressure formulation to calculate an initial point, Section 2, for a low pressure, the entire meta-stable limit can be mapped using steps in the volume variable. Stepping with fixed increments in $\ln v$ was found optimal considering resolution of the line.

An example, plotting the meta-stable limit together with the phase envelope for a mixture of 90 % methane and 10 % ethane, is plotted in Figure 2.

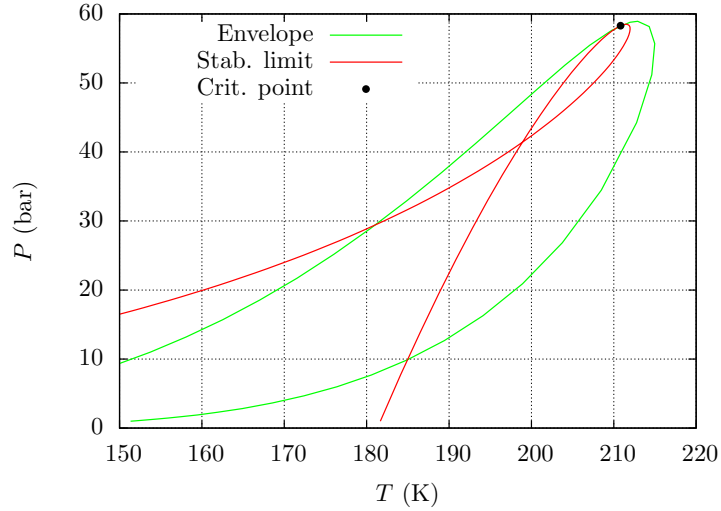


Figure 2: Phase envelope and meta-stable limit plotted for a mixture of 90 % methane and 10 % ethane. The critical point is plotted using a black dot.

3.1 Single component

The pure fluid stability limit is the well-known,

$$\left(\frac{\partial p}{\partial v}\right)_T = 0. \quad (24)$$

The mapping of the meta-stable limit for pure fluids currently use a solver for Equation 24. For robust and fast mapping, extrapolation of volume is performed between each step in temperature.

An example, plotting the meta-stable limit together with the saturation line for pure CO_2 , is plotted in Figure 3.

4 Critical point

“A critical point is a stable point which lies on the stability limit.” - Heidemann and Khalil [1]. The implications from this is that, if tpd is Taylor expanded, the cubic form must vanish. See [1] for more details.

4.1 Critical point solver

Since the third order differentials of tpd typically is difficult and time consuming to construct analytically, Michelsen [2] developed an approach to solve for a critical point numerically

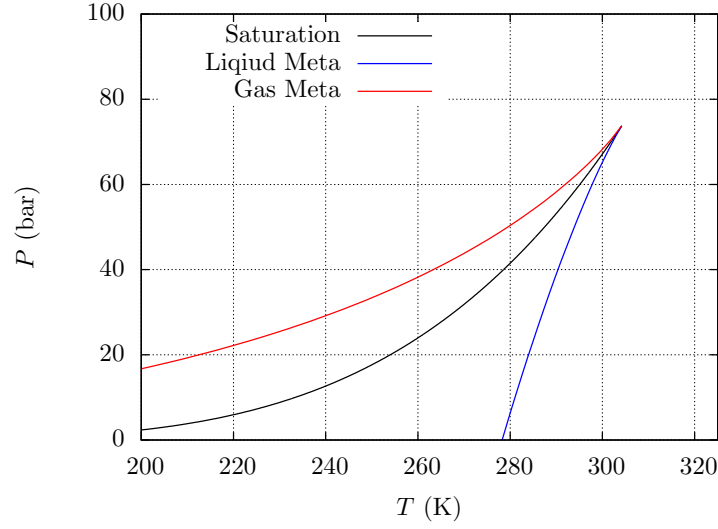


Figure 3: Saturation line and meta-stable limit plotted for pure CO₂. Peng-Robinson equation of state with van der Waals mixing rules are applied.

without calculating these differentials. The main components of this algorithm is given below for the formulation in temperature and volume. Using $F = \text{tpd}$, and Taylor expanding in s , we get

$$F(\mathbf{X} = s\mathbf{u}) = F_1(s) = \sum_{m=0}^{\infty} \left(\frac{s^m}{m!} \right) \left(\frac{\partial^m F_1}{\partial s^m} \right)_{s=0} = as + bs^2 + cs^3 + ds^4 + \mathcal{O}(s^5), \quad (25)$$

since $F_1(s=0) = 0$. Further, $a = (\partial F_1 / \partial s)_{s=0} = \sum_i \sqrt{z_i} u_i g_i(s=0) = 0$. For b we have,

$$b = \frac{1}{2} \sum_{i,j} B_{ij} u_i u_j = \frac{1}{2} \mathbf{u}^T \mathbf{B} \mathbf{u}, \quad (26)$$

identical to the definition in Equation 12. The smallest value of b is found by choosing \mathbf{u} to be the eigenvector corresponding to the minimum eigenvalue of \mathbf{B} . We then get,

$$\mathbf{B} \mathbf{u} = \lambda_{\min} \mathbf{u}, \mathbf{u}^T \mathbf{u} = 1 \quad (27)$$

For c we have,

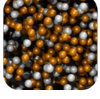
$$c = \frac{1}{6} \sum_{i,j,k} q_{ijk} u_i u_j u_k. \quad (28)$$

Differentiating Equation 25 with respect to s , we get,

$$\frac{\partial F_1}{\partial s} = 2bs + 3cs^2 + 4ds^3 + \mathcal{O}(s^4), \quad (29)$$

and this equals

$$\frac{\partial F_1}{\partial s} = \sum_i \frac{\partial F}{\partial Y_i} \frac{\partial Y_i}{\partial s} = \sum_i \sqrt{z_i} u_i g_i. \quad (30)$$



Evaluating at $s = \epsilon$ and $s = -\epsilon$, we get

$$\left(\frac{\partial F_1}{\partial s}\right)_\epsilon = 2b\epsilon + 3c\epsilon^2 + 4d\epsilon^3 + \mathcal{O}(\epsilon^4), \quad (31)$$

$$\left(\frac{\partial F_1}{\partial s}\right)_{-\epsilon} = -2b\epsilon + 3c\epsilon^2 - 4d\epsilon^3 + \mathcal{O}(\epsilon^4). \quad (32)$$

$$(33)$$

Adding the Equations above we get a Equation for c ,

$$c = \frac{1}{6\epsilon^2} \left(\left(\frac{\partial F_1}{\partial s}\right)_\epsilon + \left(\frac{\partial F_1}{\partial s}\right)_{-\epsilon} \right) + \mathcal{O}(\epsilon^2). \quad (34)$$

4.1.1 Critical point solver Jacobean

In order to construct a Newton-Raphson solver differentials for the Jaocobian is required. Differentiating Equation 27 with respect to temperature, we get the relation,

$$\mathbf{B}_T \mathbf{u} + \mathbf{B} \mathbf{u}_T = \lambda_T \mathbf{u} + \lambda_{\min} \mathbf{u}_T, \mathbf{u}^\top \mathbf{u}_T = 0 \quad (35)$$

Multiplying with \mathbf{u}^\top , and simplifying we get,

$$\mathbf{u}^\top \mathbf{B}_T \mathbf{u} + \mathbf{u}^\top \mathbf{B} \mathbf{u}_T = \lambda_T \mathbf{u}^\top \mathbf{u} + \lambda_{\min} \mathbf{u}^\top \mathbf{u}_T, \quad (36)$$

$$\mathbf{u}^\top \mathbf{B}_T \mathbf{u} = \lambda_T. \quad (37)$$

Rearranging Equation 35, we get

$$(\mathbf{B} - \lambda_{\min} I) \mathbf{u}_T = \lambda_T \mathbf{u} - \mathbf{B}_T \mathbf{u}. \quad (38)$$

We see that if $\mathbf{B}_T \mathbf{u}$ is known, it is possible to find \mathbf{u}_T . The elements of $\mathbf{B}_T \mathbf{u}$, is

$$(\mathbf{B}_T \mathbf{u})_i = \sqrt{z_i} \sum_j \sqrt{z_j} u_j \frac{\partial \ln f_{ij}}{\partial T} = \sqrt{z_i} \frac{\partial}{\partial s} \left(\frac{\partial \ln f_i}{\partial T} \right)_{s=0} \quad (39)$$

$$\approx \sqrt{z_i} \left(\frac{1}{2\epsilon} \right) \left[\left(\frac{\partial \ln f_i}{\partial T} \right)_{s=\epsilon} - \left(\frac{\partial \ln f_i}{\partial T} \right)_{s=-\epsilon} \right]. \quad (40)$$

Using $\mathbf{B}_T \mathbf{u}$, λ_T is determined, and further $b_T = \lambda_T/2$. To determine c_T , Equation 25 is used,

$$\frac{\partial F_1}{\partial T} = b_T s^2 + c_T s^3 + d_T s^4 + \mathcal{O}(s^5). \quad (41)$$

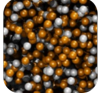
Further differentiating Equation 14, we get

$$\frac{\partial F_1}{\partial T} = \frac{\partial \text{tpd}}{\partial T} + \sum_j \frac{\partial \text{tpd}}{\partial Y_j} \frac{\partial Y_j}{\partial T}, \quad (42)$$

$$\frac{\partial \text{tpd}}{\partial T} = \sum_j Y_j [\ln f_{jT}(\mathbf{Y}) - \ln f_{jT}(\mathbf{z})] - [P_T(\mathbf{Y}) - P_T(\mathbf{z})] \frac{V}{RT} \quad (43)$$

$$+ [P(\mathbf{Y}) - P(\mathbf{z})] \frac{V}{RT^2} \quad (44)$$

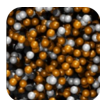
$$\frac{\partial \text{tpd}}{\partial Y_j} \frac{\partial Y_j}{\partial T} = g_j \sqrt{z_j} s(\mathbf{u}_T)_j \quad (45)$$



Evaluating equations 42 and 41 at ϵ and $-\epsilon$ and combining, we get,

$$c_T = \frac{1}{2\epsilon^3} \left(\left(\frac{\partial F_1}{\partial T} \right)_\epsilon - \left(\frac{\partial F_1}{\partial T} \right)_{-\epsilon} \right) + \mathcal{O}(\epsilon^2). \quad (46)$$

The differentials with respect to volume can be determined in the same manner.



References

- [1] Robert A. Heidemann and Ahmed M. Khalil. The calculation of critical points. *AIChE Journal*, 26(5):769–779, 1980. doi: 10.1002/aic.690260510.
- [2] Michael L. Michelsen. Calculation of critical points and phase boundaries in the critical region. *Fluid Phase Equilibria*, 16:57 – 76, 1984.
- [3] Michael L. Michelsen and Jørgen M. Møllerup. *Thermodynamic models: Fundamentals & computational aspects*. Tie-Line Publication, second edition, 2007.
- [4] Robert C. Reid and Bruce L. Beegle. Critical point criteria in legendre transform notation. *AIChE Journal*, 23(5):726–732, 1977. doi: 10.1002/aic.690230515.