Supporting Information
Thermodynamically-stable two-phase equilibrium calculation of hydrocarbon mixtures with capillary pressure

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Thermodynamic stability of the numerical algorithm

The second law of thermodynamics indicates the entropy increment is nonnegative over the time. According to the relation $\mathrm{d}S = -\mathrm{d}F/T - p_c\mathrm{d}V_1/T$ that is the eq (8) in the article, we can derive

$$\frac{\mathrm{d}F}{\mathrm{d}t} + p_c\frac{\mathrm{d}V_1}{\mathrm{d}t} \leq 0 \tag{1}$$

with $\mathrm{d}S/\mathrm{d}t \geq 0$. By integrating the inequality (1) over the time interval $\left(t^k, t^{k+1}\right]$, it becomes

$$F^{k+1} - F^k + \widehat{p}_c\left(V_1^{k+1} - V_1^k\right) \leq 0 \tag{2}$$

with $\widehat{p_c} = p_c^k$ or $\widehat{p_c} = p_c^{k+1}$. It is considered the numerical algorithm is thermodynamically stable if the inequality (2) is satisfied for each time step.

By multiplying $\left(\mu_{i,1}^{k+1} - \mu_{i,2}^{k+1}\right)$ on the both sides of mole evolution equation, the summation over all components yields

$$\begin{aligned} \sum_{i=1}^{M} \left(\mu_{i,1}^{k+1} - \mu_{i,2}^{k+1}\right) \frac{N_{i,1}^{k+1} - N_{i,1}^{k}}{\delta t} = & \sum_{i=1}^{M} \left(\mu_{i,1}^{k+1} - \mu_{i,2}^{k+1}\right) \sum_{j=1}^{M} \psi_{i,j} \left(\mu_{j,2}^{k+1} - \mu_{j,1}^{k+1}\right) \\ & + \sum_{i=1}^{M} \left(\mu_{i,1}^{k+1} - \mu_{i,2}^{k+1}\right) \psi_{i,M+1} \left(p_1^{k+1} - p_2^{k+1} - p_c^{k+1}\right) \end{aligned} \tag{3}$$

Applying the convex-concave splitting of chemical potential, the left-hand side of the above equation is expanded as follows

$$\begin{aligned} \sum_{i=1}^{M} \left(\mu_{i,1}^{k+1} - \mu_{i,2}^{k+1}\right) \frac{N_{i,1}^{k+1} - N_{i,1}^{k}}{\delta t} = & \sum_{i=1}^{M} \left(\mu_i^{\text{convex}}\left(\mathbf{n}_1^{k+1}\right) + \mu_i^{\text{concave}}\left(\mathbf{n}_1^{k}\right)\right) \frac{N_{i,1}^{k+1} - N_{i,1}^{k}}{\delta t} \\ & + \sum_{i=1}^{M} \left(\mu_i^{\text{convex}}\left(\mathbf{n}_2^{k+1}\right) + \mu_i^{\text{concave}}\left(\mathbf{n}_2^{k+1}\right)\right) \frac{N_{i,2}^{k+1} - N_{i,2}^{k}}{\delta t} \end{aligned} \tag{4}$$

Due to the property of the convex function and concave function, the following inequalities are satisfied

$$F_1^{\text{convex}}\left(\mathbf{n}_1^{k+1}\right) - F_1^{\text{convex}}\left(\mathbf{n}_1^{k}\right) \leq \sum_{i=1}^{M} \mu_i^{\text{convex}}\left(\mathbf{n}_1^{k+1}\right)\left(N_{i,1}^{k+1} - N_{i,1}^{k}\right)$$
$$F_1^{\text{concave}}\left(\mathbf{n}_1^{k+1}\right) - F_1^{\text{concave}}\left(\mathbf{n}_1^{k}\right) \leq \sum_{i=1}^{M} \mu_i^{\text{concave}}\left(\mathbf{n}_1^{k}\right)\left(N_{i,1}^{k+1} - N_{i,1}^{k}\right)$$
$$F_2^{\text{convex}}\left(\mathbf{n}_2^{k+1}\right) - F_2^{\text{convex}}\left(\mathbf{n}_2^{k}\right) \leq \sum_{i=1}^{M} \mu_i^{\text{convex}}\left(\mathbf{n}_2^{k+1}\right)\left(N_{i,2}^{k+1} - N_{i,2}^{k}\right)$$
$$F_2^{\text{concave}}\left(\mathbf{n}_2^{k+1}\right) - F_2^{\text{concave}}\left(\mathbf{n}_2^{k}\right) \leq \sum_{i=1}^{M} \mu_i^{\text{concave}}\left(\mathbf{n}_2^{k}\right)\left(N_{i,2}^{k+1} - N_{i,2}^{k}\right)$$

and we can derive

$$\frac{F_1^{k+1}-F_1^k}{\delta t} \le \sum_{i=1}^{M}\Big(\mu_i^{\text{convex}}\left(\mathbf{n}_1^{k+1}\right)+\mu_i^{\text{concave}}\left(\mathbf{n}_1^{k}\right)\Big)\frac{N_{i,1}^{k+1}-N_{i,1}^{k}}{\delta t} \tag{5}$$

$$\frac{F_2^{k+1}-F_2^k}{\delta t} \le \sum_{i=1}^{M}\Big(\mu_i^{\text{convex}}\left(\mathbf{n}_2^{k+1}\right)+\mu_i^{\text{concave}}\left(\mathbf{n}_2^{k}\right)\Big)\frac{N_{i,2}^{k+1}-N_{i,2}^{k}}{\delta t} \tag{6}$$

Finally, the following inequality is obtained

$$\begin{aligned}\frac{F^{k+1}-F^k}{\delta t} &= \frac{\left(F_1^{k+1}+F_2^{k+1}\right)-\left(F_1^{k}+F_2^{k}\right)}{\delta t}\\ &\le \sum_{i=1}^{M}\left(\mu_{i,1}^{k+1}-\mu_{i,2}^{k+1}\right)\frac{N_{i,1}^{k+1}-N_{i,1}^{k}}{\delta t}\\ &= \sum_{i=1}^{M}\left(\mu_{i,1}^{k+1}-\mu_{i,2}^{k+1}\right)\sum_{j=1}^{M}\psi_{i,j}\left(\mu_{j,2}^{k+1}-\mu_{j,1}^{k+1}\right)\\ &\quad+\sum_{i=1}^{M}\left(\mu_{i,1}^{k+1}-\mu_{i,2}^{k+1}\right)\psi_{i,M+1}\left(p_1^{k+1}-p_2^{k+1}-p_c^{k+1}\right)\end{aligned} \tag{7}$$

Similarly, multiplying the volume evolution equation by $\left(p_2^{k+1}-p_1^{k+1}+p_c^{k+1}\right)$ yields

$$\begin{aligned}\left(p_2^{k+1}-p_1^{k+1}+p_c^{k+1}\right)\frac{V_1^{k+1}-V_1^k}{\delta t} &= \left(p_2^{k+1}-p_1^{k+1}+p_c^{k+1}\right)\sum_{j=1}^{M}\psi_{M+1,j}\left(\mu_{j,2}^{k+1}-\mu_{j,1}^{k+1}\right)\\ &\quad+\left(p_2^{k+1}-p_1^{k+1}+p_c^{k+1}\right)\psi_{M+1,M+1}\left(p_1^{k+1}-p_2^{k+1}-p_c^{k+1}\right)\end{aligned} \tag{8}$$

The left-hand side of the above equation is expanded as

$$\left(p_2^{k+1}-p_1^{k+1}+p_c^{k+1}\right)\frac{V_1^{k+1}-V_1^k}{\delta t} = -\,p_2^{k+1}\frac{V_2^{k+1}-V_2^k}{\delta t} - p_1^{k+1}\frac{V_1^{k+1}-V_1^k}{\delta t} + p_c^{k+1}\frac{V_1^{k+1}-V_1^k}{\delta t} \tag{9}$$

Applying the convex-concave property, we can derive the inequalities as follows

$$
\begin{aligned}
F_1^{\text{convex}}\left(\mathbf{n}_1^{k+1}\right) - F_1^{\text{convex}}\left(\mathbf{n}_1^{k}\right) &\leq \left[-\sum_{i=1}^{M} n_{i,1}^{k+1}\mu_i^{\text{convex}}\left(\mathbf{n}_1^{k+1}\right) + f_1^{\text{convex}}\left(\mathbf{n}_1^{k+1}\right)\right]\left(V_1^{k+1} - V_1^{k}\right) \\
F_1^{\text{concave}}\left(\mathbf{n}_1^{k+1}\right) - F_1^{\text{concave}}\left(\mathbf{n}_1^{k}\right) &\leq \left[-\sum_{i=1}^{M} n_{i,1}^{k}\mu_i^{\text{concave}}\left(\mathbf{n}_1^{k}\right) + f_1^{\text{concave}}\left(\mathbf{n}_1^{k}\right)\right]\left(V_1^{k+1} - V_1^{k}\right) \\
F_2^{\text{convex}}\left(\mathbf{n}_2^{k+1}\right) - F_2^{\text{convex}}\left(\mathbf{n}_2^{k}\right) &\leq \left[-\sum_{i=1}^{M} n_{i,2}^{k+1}\mu_i^{\text{convex}}\left(\mathbf{n}_2^{k+1}\right) + f_2^{\text{convex}}\left(\mathbf{n}_2^{k+1}\right)\right]\left(V_2^{k+1} - V_2^{k}\right) \\
F_2^{\text{concave}}\left(\mathbf{n}_2^{k+1}\right) - F_2^{\text{concave}}\left(\mathbf{n}_2^{k}\right) &\leq \left[-\sum_{i=1}^{M} n_{i,2}^{k}\mu_i^{\text{concave}}\left(\mathbf{n}_2^{k}\right) + f_2^{\text{concave}}\left(\mathbf{n}_2^{k}\right)\right]\left(V_2^{k+1} - V_2^{k}\right)
\end{aligned}
$$

By combination of the above inequalities, the following inequality holds

$$
F^{k+1} - F^{k} \leq \left(p_2^{k+1} - p_1^{k+1}\right)\left(V_1^{k+1} - V_1^{k}\right) \tag{10}
$$

With eq (7), eq (8) and eq (10), it can be derived

$$
\begin{aligned}
\frac{F^{k+1} - F^{k} + p_c^{k+1}\left(V_1^{k+1} - V_1^{k}\right)}{\delta t} \leq &\sum_{i=1}^{M}\left(\mu_{i,1}^{k+1} - \mu_{i,2}^{k+1}\right)\sum_{j=1}^{M}\psi_{i,j}\left(\mu_{j,2}^{k+1} - \mu_{j,1}^{k+1}\right) \\
&+ \sum_{i=1}^{M}\left(\mu_{i,1}^{k+1} - \mu_{i,2}^{k+1}\right)\psi_{i,M+1}\left(p_1^{k+1} - p_2^{k+1} - p_c^{k+1}\right) \\
&+ \left(p_2^{k+1} - p_1^{k+1} + p_c^{k+1}\right)\sum_{j=1}^{M}\psi_{M+1,j}\left(\mu_{j,2}^{k+1} - \mu_{j,1}^{k+1}\right) \\
&+ \left(p_2^{k+1} - p_1^{k+1} + p_c^{k+1}\right)\psi_{M+1,M+1}\left(p_1^{k+1} - p_2^{k+1} - p_c^{k+1}\right)
\end{aligned} \tag{11}
$$

The right-hand side of the above inequality can be reduced into a more concise vector-matrix form

$$
-\begin{bmatrix} \sum_{i=1}^{M}\left(\mu_{i,2}^{k+1} - \mu_{i,1}^{k+1}\right) \\ p_1^{k+1} - p_2^{k+1} - p_c^{k+1} \end{bmatrix}^T \begin{bmatrix} \psi_{i,j} & \psi_{i,M+1} \\ \psi_{M+1,j} & \psi_{M+1,M+1} \end{bmatrix} \begin{bmatrix} \sum_{i=1}^{M}\left(\mu_{i,2}^{k+1} - \mu_{i,1}^{k+1}\right) \\ p_1^{k+1} - p_2^{k+1} - p_c^{k+1} \end{bmatrix} \leq 0 \tag{12}
$$

with the coefficient matrix

$$\boldsymbol{\Psi} = \begin{bmatrix} \psi_{i,j} & \psi_{i,M+1} \\ \psi_{M+1,j} & \psi_{M+1,M+1} \end{bmatrix}$$

being positive definite. At the end, we can derive

$$F^{k+1} - F^{k} + p_c^{k+1} \left(V_1^{k+1} - V_1^{k} \right) \leq 0. \tag{13}$$

It has been proved the proposed numerical algorithm is thermodynamically stable. Equation (13) can be extended to the case where capillary pressure p_c is treated explicitly.