A FRAMEWORK FOR SIMULATING THE PARTIALLY MISCIBLE MULTI-COMPONENT HYDROCARBON FLUIDS IN POROUS MEDIA VIA THE PSEUDO-POTENTIAL LATTICE BOLTZMANN MODEL

Zhicheng W. Wang[1] (iD); Cheng Peng[2] (iD); Luis F. Ayala[3] (iD); Seyyed A. Hosseini[1] (iD)

[1]Bureau of Economic Geology, The University of Texas at Austin, Austin, TX, USA; [2]School of Mechanical Engineering, Shandong University, Jinan, Shandong Province, China; [3]Department of Energy and Mineral Engineering, The Pennsylvania State University, University Park, PA; USA

APPENDIX A: EOS OF PARTIALLY-MISCIBLE MCMP FLUIDS

The volumetric behavior of the multi-component multiphase (MCMP) fluids system can be described by the cubic equation of state (EOS). The Peng-Robinson EOS (PR-EOS) is selected in this present work, which is more rigorous and accurate in modeling the hydrocarbon fluid pressure thermodynamic behaviors. For multi-component (MC) hydrocarbons, the PR-EOS, which is an analytical expression that provides functional relationships PVT of a fluid system, is proposed as (6) (**Eq. A1**):

$$p_{EOS}(\tilde{\rho}) = \frac{\tilde{\rho}RT}{1 - b_m\tilde{\rho}} - \frac{[a\alpha(T)]_m\tilde{\rho}^2}{1 + 2b_m\tilde{\rho} - b_m^2\tilde{\rho}^2} \tag{A1}$$

where $\tilde{\rho}$ is the molar density of the phase, which can be mathematically related to the mass density of the phase ρ as (**Eq. A2**):

$$\tilde{\rho} = \frac{\rho}{\sum_i c_i M_i} \tag{A2}$$

c_i and M_i are the molar fraction and molar mass of the ith component in the mixture, respectively. R is the universal gas constant, T is the temperature, and $[a\alpha(T)]_m$ and b_m are the attraction and co-volume coefficients of the mixture, which are defined as (6) (**Eq. A3**):

$$[a\alpha(T)]_m = \sum_i^{n_c} \sum_j^{n_c} c_i\, c_j \sqrt{[a_i\alpha_i(T)][a_j\alpha_j(T)]}(1 - \zeta_{ij}) \tag{A3}$$

$$b_m = \sum_i^{n_c} c_i\, b_i$$

where c_i, c_j are the local molar fraction of ith component and jth component in the mixture. ζ_{ij} is the binary interaction coefficient between the ith and jth components. For hydrocarbon mixtures, since all components are essentially miscible in each phase, $\zeta_{ij} = 0$ (1). a_i, $\alpha_i(T)$, b_i are (**Eq. A4**):

$$a_i = \Omega_{ai}^o \frac{R^2 T_{ci}^2}{p_{ci}} \qquad\qquad b_i = \Omega_{bi}^o \frac{R T_{ci}}{p_{ci}} \qquad\qquad\qquad (A4)$$

$$\alpha_i(T) = \left[1 + m_i\left(1 - \sqrt{T/T_{ci}}\right)\right]^2$$

where T_{ci}, p_{ci} are the critical temperature, and critical pressure of the ith component, $\Omega_{ai}^o = 0.45724$ and $\Omega_{bi}^o = 0.0778$ are constants (4, 5). Finally, m_i is a function of the Pitzer's acentric factor ω_i (6) (**Eq. A5**):

$$m_i = \begin{cases} 0.374640 + 1.54226\omega_i - 0.26992\omega_i^2, & \omega_i \le 0.49 \\ 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3, & \omega_i > 0.49 \end{cases} \qquad (A5)$$

Through defining a compressibility factor $Z = p/(\tilde{\rho} R T)$, the PR-EOS in **Equation A1** can be recast as a cubic equation (**Eq. A6**):

$$Z^3 + (B - 1)Z^2 + (A - 2B^2 - 2B)Z - (AB - B^2 - B) = 0 \qquad\qquad\qquad (A6)$$

where (**Eq. A7**):

$$A = \sum_i^{n_c} \sum_j^{n_c} c_i c_j A_{ij} \qquad\qquad A_{ij} = \sqrt{A_i A_j}\left(1 - \zeta_{ij}\right) \qquad\qquad (A7)$$

$$A_i = \Omega_{ai}^o \frac{p_{ri}}{T_{ri}}\left[1 + m_i\left(1 - \sqrt{T_{ri}}\right)\right]^2 \qquad B = \sum_i^i c_i B_i \qquad\qquad B_i = \Omega_{bi}^o \frac{p_{ri}}{T_{ri}}$$

$p_{ri} = p/p_{ci}$, $T_{ri} = T/T_{ci}$ are the reduced pressure and reduced temperature of the ith component, respectively. This form is used more frequently in lattice Boltzmann (LB) implementation. For example, when imposing the pressure boundary condition, with a given pressure p^*, a constant prevailing temperature T, and a known molar composition c_i, the compressibility factor Z can be solved from the cubic (**Eq. A6**). The results could end in either one real root or as many as three real roots of Z. In the latter case, the middle root is always discarded, and the remaining root that results in the smaller Gibbs energy is picked. The Gibbs energy difference dG between the largest root Z_{max} and the smallest root Z_{min} is computed as (**Eq. A8**).

$$\frac{dG}{RT} = (Z_{max} - Z_{min}) + \ln\left(\frac{Z_{min} - B}{Z_{max} - B}\right) + \frac{A}{2\sqrt{2}B}\ln\left\{\frac{\left[Z_{min} + (1 + \sqrt{2})B\right]\left[Z_{max} + (1 - \sqrt{2})B\right]}{\left[Z_{min} + (1 - \sqrt{2})B\right]\left[Z_{max} + (1 + \sqrt{2})B\right]}\right\} \qquad (A8)$$

When $dG > 0$, Z_{max} is selected, otherwise Z_{min} is selected. With the selected compressibility factor, the molar density of the phase $\tilde{\rho}$, the phase mass density ρ and the cell-volume densities $\bar{\rho}_i$ of the ith component are related as shown in **Equation A9**.

$$\tilde{\rho} = \frac{p}{ZRT} \qquad\qquad \rho = \tilde{\rho}\sum_i c_i M_i \qquad\qquad \bar{\rho}_i = \rho\frac{c_i M_i}{\sum_i c_i M_i} \qquad (A9)$$

APPENDIX B: DERIVATION OF THE FORCE-SPLIT COEFFICIENT AT SINGLE-PHASE CONDITION

To derive the force-split coefficient at single-phase condition, recall the hydrostatic balance for each component, such that (**Eq. B1**):

$$-\nabla(c_s^2 \bar{\rho}_i) + \kappa_i \boldsymbol{F} = 0 \qquad\qquad\qquad (B1)$$

Therefore, the ratio of force split coefficients κ_i in **Equation B1** is equal to the ratio of derivatives of cell-volume densities (**Eq. B2**):

$$\frac{\kappa_1}{\kappa_2} = \frac{\partial \bar{\rho}_1}{\partial \bar{\rho}_2} \tag{B2}$$

For the single-phase region, compositions c_1 and c_2 can be assumed to be uniform. The fractions in **Equation 8** (main text) are therefore constant for both components. Accordingly, when taking derivatives in **Equation B2**, the ratio between κ_1 and κ_2 is calculated as follows (**Eq. B3**):

$$\frac{\kappa_1}{\kappa_2} = \frac{c_1 M_1}{c_2 M_2} \tag{B3}$$

combined with the last equation in **Equation 6** (original text), which means (**Eq. B4**):

$$\kappa_1 = \frac{c_1 M_1}{c_1 M_1 + c_2 M_2} \qquad\qquad \kappa_2 = \frac{c_2 M_2}{c_1 M_1 + c_2 M_2} \tag{B4}$$

This is essentially equivalent to $\gamma_1 = \gamma_2 = 1$, which means the components have the same tendency to escape from the current phase and to form the other phase. The definition of κ_i takes similar forms under single-phase and multiphase conditions. Grouping these two scenarios, the generic piecewise definition of γ_i can then be obtained, such that (**Eq. B5**):

$$\gamma_1 = \begin{cases} 1 & single\ phase \\ \dfrac{ln(\tilde{\rho}_i/\tilde{\rho}_v) - lnK_1}{ln(\tilde{\rho}_i/\tilde{\rho}_v) - lnK_2} & multiphase \end{cases} \tag{B5}$$

$$\gamma_2 = 1$$

APPENDIX C: THE SCALING SYSTEM OF MCMP AT THE PORE SCALE VIA LBM

To establish thermodynamically correct scales in LB simulations, it essentially involves determining five fundamental independent units. These units correspond to length (L), time (t), temperature (T), mass (M), and amount of substance (N). To ensure each unit has its unique scale between LB and physical, five independent physical variables in the LB simulation need to be selected for scaling. The following five variables can be considered: three parameters in the EOS, which are the attraction parameter $a\alpha$, co-volume parameter b (defined in **Eq. A4**), and universal gas constant R; the molecular weight MW of the component; and the interfacial tension (IFT, or σ) (3). Li & Luo (2) proposed a scheme to tune the IFT value in LB units, and this scheme can be therefore leveraged to control the scaling system (7).

Five aforementioned independent physical variables, if represented by the combinations of χ_M, χ_L, χ_t, χ_N, χ_T are formulated as **Equation C1**:

$$\chi_a = (\chi_M)(\chi_L)^5(\chi_t)^{-2}(\chi_N)^{-2} \tag{C1}$$
$$\chi_b = (\chi_L)^3(\chi_N)^{-1}$$
$$\chi_R = (\chi_M)(\chi_L)^2(\chi_t)^{-2}(\chi_T)^{-1}(\chi_N)^{-1}$$
$$\chi_{MW} = (\chi_M)(\chi_N)^{-1}$$
$$\chi_\sigma = (\chi_M)(\chi_t)^{-2}$$

In the scales, χ is defined as the ration between variables in physical units and in LB units. Therefore, for the random variable ξ, the scale is defined as such (**Eq. C2**):

$$\chi_\xi = \frac{\xi_{phy}}{\xi_{LB}} \tag{C2}$$

Equation C3 can be obtained by rewriting **Equation C1**. The process essentially involves solving a system of equations of five unknowns. The scaling system is calculated as:

$$\chi_L = (\chi_\sigma)(\chi_b)^2(\chi_a)^{-1} \tag{C3}$$

$$\chi_t = (\chi_{MW})^{\frac{1}{2}}(\chi_\sigma)(\chi_b)^{\frac{5}{2}}(\chi_a)^{-\frac{3}{2}}$$

$$\chi_M = (\chi_{MW})(\chi_\sigma)^3(\chi_b)^5(\chi_a)^{-3}$$

$$\chi_N = (\chi_\sigma)^3(\chi_b)^5(\chi_a)^{-3}$$

$$\chi_T = (\chi_R)^{-1}(\chi_b)^{-1}(\chi_a)$$

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