Phase equilibria of polydisperse hydrocarbons: moment free energy method analysis

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Abstract

We analyze the phase equilibria of systems of polydisperse hydrocarbons by means of the recently introduced moment method. Hydrocarbons are modelled with the Soave-Redlick-Kwong and Peng-Robinson equations of states. Numerical results show no particular qualitative difference between the two equations of states. Furthermore, in general the moment method proves to be an excellent method for solving phase equilibria of polydisperse systems, showing excellent agreement with previous results and allowing a great improvement in generality of the numerical scheme and speed of computation.

1 Introduction

In this paper we analyze the phase behaviour of a mixture of hydrocarbons, by means of the moment method [7, 8]. This method allows to reduce the number of degrees of freedom of the free energy, which normally depends on the concentration of each specie in the mixture, to a smaller number of moments of the density distribution which already appear in the excess part of the free energy. By doing this, one is able is reduce the number of equations needed to analyze the phase equilibria and, at the same time, by projecting the free energy onto the space generated by the moments only, to check for global and local stability of the phases [8].

The approximation made when introducing the moment free energy can be efficiently controlled and minimized by means of the adaptive method of choice of extra moments [11], which allows to reduce the deviation of the moment method solution from the exact solution, by simply retaining two extra moments, beyond the ones appearing in the excess free energy. This iterative method, which it can be proven, converges to the exact solution, as long as it converges at all, shows to represent an excellent compromise between approximation, which
can easily be reduced to an error smaller than 0.01%, and computational speed. Furthermore, the resulting algorithm turns out to be stable and to be very little affected by the number of species in the mixture. In fact, as the number of unknowns is not increased by the increase of the number of species, the computation is hardly affected at all, with just a small influence on its global speed of computation, while no relevant error is introduced.

The numerical results agree very well with the results obtained with a widely diffused commercial program in different points of the phase diagram. The concentration of each component in the coexisting phases and the density of both phases are evaluated correctly. Cloud point is detected exactly. Furthermore, the introduction of heavy species, up to n-C15, even present in very small amount, does not compromise either numerical results or computation.

2 Polydisperse hydrocarbons

In order to analyze the phase equilibria of hydrocarbons, we will refer to the two equations of state most widely used to describe them, i.e., the Soave-Redlick-Kwong (SRK) [6] equation of state and the Peng-Robinson (PR) [5] equation of state. Both are cubic equations of state and thus are able to predict gas-liquid phase transitions. Although originally introduced for pure systems, as we will see, they are both easily extended to describe multicomponent, i.e., polydisperse systems. As we will show, given the polydisperse form of two equations of state, one can easily obtain the Gibbs and Helmholtz free energies, by Legendre transforming, and therefore obtain the phase equilibrium equations that are to be solved, in order to fully analyze the phase behaviour of the system.

The SRK equation of state is generally written as

$$P = \frac{N\kappa_BT}{V-b} - \frac{N^2\alpha(T)a_C}{V(V+b)}$$

where $N$ is the total number of particles, $V$ the total volume, $\kappa_B$ the Boltzman constant and the parameters $a$, $b$ and $\alpha(T)$ depend on the critical temperature and pressure, shape and size of the molecules etc., of the specific hydrocarbon.

The extension of the equation above to the case of polydisperse system is rather straightforward, if one introduces a set of parameters $a_{C,i}$, $b_i$, $\alpha_i(T)$ for each specie $i$ and defines new global parameters $B$ and $D$ as follows

$$B = \sum_i N_i b_i$$

and

$$D(T) = \sum_{i,j} N_i N_j a_{ij}(T)$$

where

$$a_{ij}(T) = \sqrt{a_{C,i}a_{C,j}\alpha_i(T)\alpha_j(T)}$$
In this way, the polydisperse version of Eq. (11) is

\[ P = \frac{N \kappa B T}{V - B} - \frac{D}{V(V + B)} \]  \hspace{1cm} (5)

where \( N = \sum_i N_i \) is the total number of particles of the system.

The Helmholtz free energy can now be obtained simply by solving the equation

\[ P = -\frac{\partial F}{\partial V} \]

and by introducing \( F_{id} \), the ideal part of the free energy, i.e., the free energy of a mixture of ideal gas

\[ F_{id} = \kappa B T \sum_i N_i \left( \ln \frac{N_i}{V} - 1 \right) \]  \hspace{1cm} (6)

The free energy then turns out to be

\[ F(n, V, T) = F_{id} + N \kappa B T \ln \frac{V}{V - B} - \frac{D}{B} \ln \frac{V + B}{V} \]  \hspace{1cm} (7)

The above quantity is extensive, one can therefore define an intensive “free energy density” \( f = F/Vol \). Introducing a density distribution \( \rho(k) = N_k/V \) and multiplying by \( \beta = 1/\kappa B T \), the free energy density turns out to be

\[ \beta f[\rho(k), T] = \beta f_{id} - \rho \ln(1 - \tilde{B}) - \frac{\tilde{D}}{B} \ln(1 + \tilde{B}) \]  \hspace{1cm} (8)

where the ideal part is just

\[ f_{id} = \kappa B T \sum_k \rho(k) \ln \rho(k) - 1 \]  \hspace{1cm} (9)

and we have defined two new parameters \( \tilde{B} \) and \( \tilde{D} \), by rescaling \( B \) and \( D \) with the volume

\[ \tilde{B} = \frac{B}{V} = \sum_k b_k \rho(k) \]  \hspace{1cm} (10)

\[ \tilde{D} = \frac{\beta D}{V^2} = \sum_{k,j} \beta a_{k,j}(T) \rho(k) \rho(j) \]  \hspace{1cm} (11)

The non-ideal part of the free energy in Eq. (8) is called excess free energy \( \tilde{f} \) and contains the terms due to the interaction between the particles in a non-ideal gas.

The Gibbs free energy can now be obtained from the expressions above, simply by Legendre transforming \( F \) as \( G(N, P, T) = \min_V \{ F(N, V, T) + PV \} \).
We now introduce a Gibbs free energy per particle \( g = G/N \) and divide again the resulting function into the ideal part

\[
\beta g_{id}[x(k), P, T] = \frac{\beta G_{id}}{N} = \sum_k x(k) \ln x(k) + \ln \beta P
\]  

(12)

and the excess part

\[
\beta \tilde{g}[x(k), P, T] = \frac{\beta \tilde{G}}{N} = -\sum_k x(k) \left[ \ln \beta PV + 1 \right] + \frac{\beta \tilde{f}}{\rho} + \frac{\beta P}{\rho}
\]  

(13)

where the number fraction \( x(k) \) of the specie \( k \) is just \( x(k) = N_k/N = \rho(k)/\rho \), with \( \rho = \sum_k \rho(k) = N/V \) the overall density.

From the above equations (12,13) we can now derive the phase equilibrium equations \( \mu_a = \mu_b \) for the coexisting phases \( a \) and \( b \), and each specie \( k \) as \( \mu_k = \partial G/\partial N_k = \partial g/\partial x(k) \). For a system of \( M \) species, dividing in \( P \) phases, the phase equilibrium is therefore fully analyzed by solving a system of \((P-1)M\) equations, plus the \( M \) equations given by the conservation of the total number of particles, i.e., \( \sum_a x^a(k) = x^{(0)}(k) \), where \( x^{(0)}(k) \) is the number density of the \( k \)th specie of the parent, in the \( MP \) unknowns \( x^a(k) \). The values of \( P \) and \( T \) are set as external parameters.

As far as the Peng-Robinson equation of state is concerned, not much change is needed in the equations above. The PR equation is generally written as

\[
P = \frac{N_k \kappa B}{V - B} - \frac{D}{V(V + B) + B(V - B)}
\]  

(14)

where \( B \) and \( D \) differ from the SRK case in the numerical coefficients of \( b_k \) and \( a_{C,k} \). Once again, from the equation above one gets the excess part of Helmholtz free energy as

\[
\beta \tilde{f} = \rho \ln \frac{V}{V - B} + \frac{\sqrt{2}}{4} \frac{D}{BV} \ln \left( \frac{V + (1 - \sqrt{2})B}{V + (1 + \sqrt{2})B} \right)
\]  

(15)

Similarly, the excess part of the Gibbs free energy per particle turns out to be

\[
\beta \tilde{g} = -\sum_k x(k) \left[ \ln \beta PV + 1 \right] + \frac{\beta \tilde{f}}{\rho} + \frac{\beta P}{\rho}
\]  

(16)

2.1 Truncatable systems

A polydisperse system is said to be truncatable when the excess part of its free energy, say the Helmholtz free energy, is a function a limited number of moments \( \rho_i \) of the density distribution \( \rho(k) \)

\[
\rho_i = \sum_k w_i(k) \rho(k)
\]  

(17)
with given weight functions $w_i(k)$. In other words, the Helmholtz free energy of a truncatable system is

$$f[ρ(k), T] = \sum_k ρ(k) [\ln ρ(k) - 1] + \tilde{f}(ρ_i)$$

For a truncatable system one has

$$βμ(k) = β [\tilde{f}(ρ_i)] = \frac{∂(βf)}{∂ρ(k)} = \ln ρ(k) + \sum_i w_i(k) \tilde{μ}_i$$

where the excess moment chemical potentials $\tilde{μ}_i = \frac{∂\tilde{f}}{ρ_i}$. By imposing the equality of the chemical potentials in all the coexisting phases, one gets that the density distribution of the coexisting phases must have the form

$$ρ^a(k) = R(k) \exp[-β] \sum_i \tilde{μ}_i^a w_i(k)] (18)$$

By imposing the lever rule, i.e., the conservation of the total number of particles per specie, $\sum_a v^a ρ^a(k) = ρ^{(0)}(k)$ ($ρ^{(0)}(k)$ is the density of the parent and $v^a = V^a/V$ is the volume occupied by the phase) one finds that the function $R(k)$ has the form

$$R(k) = \frac{ρ^{(0)}(k)}{\sum_a v^a \exp[-β] \tilde{μ}_a^a]} = \frac{ρ^{(0)}(k)}{\sum_a v^a \exp[-β] \sum_i \tilde{μ}_i^a w_i(k)]} (19)$$

Although formally solved through the two equations above, an actual numerical solution of the system is not easily found. Eq. (18) actually represents a set of, say, $M$ (for $M$ species of particles) self consistent all strongly coupled through the denominator of Eq. (19). The problem is that, although the excess free energy is a function just of the moments $ρ_i$, usually a much smaller number than the number of species, the ideal part of the free energy is still function of the whole density distribution $ρ(k)$. Ideally, one would like to reduce the problem to a smaller number of degrees of freedom, by expressing also the ideal part of the free energy as a function of the moments only. While this argument will be treated in the next section, here we will show that both the SRK and the PR equations of state are in fact truncatable.

In fact, it is rather easy to show that the equations of state generate two truncatable systems if one introduces two moments of the density distribution $ρ_1$ and $ρ_2$ as follows

$$ρ_1 = \tilde{B} = \sum_k b_k ρ(k)$$

$$ρ_2 = \sum_k d_k ρ(k)$$

where, from Eq. (4), $d_k = \sqrt{βa_{C_k}α_k(T)}$. From the definition above and Eq. (3), we get that $\tilde{D} = ρ_2^2$. Plugging (20,21) into Eq. (3), we therefore get, for the
SRK equation of states

\[
\beta \tilde{f}(\rho, \rho_1, \rho_2) = -\rho \ln(1 - \rho_1) - \frac{\rho_2^2}{\rho_1} \ln(1 + \rho_1)
\] (22)

Note that in the above expression, the overall density \( \rho \) is itself a moment of the density distribution, with weight function \( w_0(k) = 1 \), as \( \rho = \rho_0 = \sum_k \rho(k) \).

In other words, the excess part of the free energy is fully described by the knowledge of only three moments of the density distribution \( \rho_0, \rho_1, \rho_2 \) and not on the whole distribution \( \rho(k) \) itself.

For the PR equation of state the argument is again similar to the case of the SRK equation of states. Introducing again the three moments \( \rho_0, \rho_1 \) and \( \rho_2 \), we get that the excess part of the Helmholtz free energy is just

\[
\beta \tilde{f}(\rho_0, \rho_1, \rho_2) = -\rho \ln(1 - \rho_1) - \frac{\sqrt{2} \rho_2^2}{4 \rho_1} \ln \left( \frac{1 + (1 - \sqrt{2})\rho_1}{1 + (1 + \sqrt{2})\rho_1} \right)
\] (23)

As far as the Gibbs free energy is concerned, it is easy to show [8] that the Gibbs free energy inherits its moment structure from the Helmholtz free energy. However, this time, one usually introduces normalized moments \( m_i \) of the number density distribution \( x(k) \) defined as

\[
m_i = \sum_k w_i(k) x(k) = \frac{\rho_i}{\rho_0}
\] (24)

Clearly this time \( m_0 = \sum_k x(k) = 1 \), thus, since \( \tilde{f} \) depends on three moments, \( \rho_0, \rho_1, \rho_2 \), the Gibbs free energy depends itself on the overall density, which, however, is obtained from the equation of state, as a function of \( P, m_1 \) and \( m_2 \).

In other words, the Gibbs free energy turns out to have one degree of freedom less than the Helmholtz free energy.

In any case, with the definitions above, one gets that the excess part of the Gibbs free energy for the SRK equation of states is just

\[
\beta \tilde{g}(m_1, m_2) = \ln \frac{\rho_0}{\beta P} - 1 + \beta \frac{P}{\rho_0} - \ln(1 - \rho_0 m_1) - \frac{m_2^2}{m_1} \ln(1 + \rho_0 m_1)
\] (25)

Similarly, for the PR equation of state, we get

\[
\beta \tilde{g}(m_1, m_2) = \ln \frac{\rho_0}{\beta P} - 1 + \beta \frac{P}{\rho_0} - \ln(1 - \rho_0 m_1) + \frac{\sqrt{2} m_2^2}{4 m_1} \ln \left( \frac{1 + (1 - \sqrt{2})\rho_0 m_1}{1 + (1 + \sqrt{2})\rho_0 m_2} \right)
\] (26)

Note that in the two equations above we have omitted the dependence of \( \tilde{g} \) on \( P \) and \( T \).

3 The moment method

Truncatable systems allow to express the excess free energy as a function of a small, say \( M \), number of moments only. However, as we saw in the previous
section, the difficulty of solving the phase coexistence equations remains largely unaltered, as the ideal part of the free energy is still function of the full density (or number) distribution. Ideally, one would like to express the ideal free energy too, as a function of the moments only. This is in fact possible, by means of the moment method \[1, 7, 8\]. While the following description will refer mostly to the Helmoltz free energy, similar considerations can be made for the Gibbs free energy \[8\], with the introduction of the normalized moments and the number density distribution.

The moment method arises from the hypothesis, in fact verified in different works \[1, 7, 11, 10\], that the excess free energy is mostly responsible for the phase behaviour of the whole system. This is in fact not surprising, as the ideal free energy is overall convex, and thus does not allow for phase separation. With this in mind, the moment free energy is constructed as follows. We subtract from the actual free energy a term \(\rho(k) \ln \rho^0(k)\), where \(\rho^0(k)\) is the density distribution of the parent. This term, as linear in the density \(\rho(k)\), does not affect the phase behaviour, as it adds just a constant to the chemical potential \(\mu(k) = \partial f/\partial \rho(k)\). The resulting function is then minimized with respect to \(\rho(k)\) with the \(M\) moments appearing in the excess part as constraints (2 in the two previous cases). The minimum value of the resulting free energy is then found to be

\[
f_{\text{mom}}(\rho) = \sum_{i}^{M} \lambda_{i} \rho_{i} - \rho_{0} + \tilde{f}(\rho) \tag{27}
\]

where \(\rho\) is just a vector having the moments \(\rho_i\) as components and the \(\lambda\)s are the \(M\) Lagrange multipliers. The minimum value of the free energy is reached for a density distribution from the family

\[
\rho_{\text{mom}}(k) = \rho^{(0)}(k) \exp \left( \sum_{i}^{M} \lambda_{i} w_{i}(k) \right) \tag{28}
\]

From the moment free energy (27), one can also define the moment chemical potentials \(\mu_i\), as \(\mu_i = \partial f_{\text{mom}}/\partial \rho_i = \lambda_i + \tilde{\mu}_i\). The pressure is obtained from the Gibbs-Duhem relation as

\[
P = \sum_{k} \mu(k) \rho(k) - f = \sum_{i} \mu_i \rho_i - f
\]

It is easy to show that the above expression obtained from the moment free energy is in fact identical to the one obtained from the exact free energy \[8\]. Furthermore, it is easy to show that the moment free energy correctly detects the onset of phase coexistence. In other words, one can show \[8, 9\] that any two phases coexist for the full system, if and only if, they coexist for the moment free energy, thus, \(\mu^a(k) = \mu^b(k) \Leftrightarrow \mu^a_i = \mu^b_i\). Thus, at least up to the onset of the phase coexistence, the full solution in Eq. (18) actually belongs to the family in Eq. (28). Cloud point and shadow phases are then correctly detected by the moment free energy solution above. Furthermore, spinodals and critical/tricritical points are found exactly \[8\].
The enforcement of the lever rule only for the moments is in fact the only approximation we make in using the moment method, as this does not ensure the satisfaction of the complete lever rule, while, as mentioned earlier, equality of pressure and chemical potentials are ensured. However, as shown in details in [11, 10], the approximation can be reduced efficiently by retaining extra moments and, in particular, by means of the adaptive method of choice of extra weight functions which allows to obtain a solution as close as wanted to the exact one, by retaining only two extra moments.

In order to give a more precise insight of the actual problem one has to solve in the case of the two equations of state mentioned earlier, let us sketch the resulting system of equations, obtained within the moment method approach. As mentioned, since we have \( P \) and \( T \) as external parameters, we move on to the Gibbs formalism. Thus we evaluate the gibbs free energy and from that, we calculate the moment chemical potentials as \( \mu_i = \frac{\partial g_{\text{mom}}}{\partial m_i} \), where \( m_i \) are the normalized moments. Let us now assume we have a Gas-Liquid demixing and let us call \( \phi^a = N^a/N^{(0)} \) the fraction of particles in each phase (G or L). The phase coexistence is then fully solved by enforcing the equality of the moment chemical potentials and of the quantity \( \Pi = g_{\text{mom}} - \ln P - \sum_{i \neq 0} m_i \mu_i \), which is a sort of Legendre transform of the pressure [8], in all the coexisting phases. We must also enforce the conservation of the total number of particles, i.e., \( \sum_a N_a(k) = N^{(0)}(k) \). If we multiply by \( w_i(k) \) on both sides and sum over \( k \), we get, after rearranging, the lever rule for the normalized moments \( \sum_a \phi^a m_i^a = m_i^{(0)} \), which is the condition we actually enforce. Thus, for the two equations of state, the system of equations we have to solve turns out to be

\[
\begin{align*}
\mu_1^G &= \mu_1^L \\
\mu_2^G &= \mu_2^L \\
\Pi^G &= \Pi^L \\
m_1^{(0)} &= \phi^G m_1^G + (1-\phi^G)m_1^L \\
m_2^{(0)} &= \phi^G m_2^G + (1-\phi^G)m_2^L \\
P &= P(\rho_0^G, m_1^G, m_2^G)
\end{align*}
\]

i.e., 7 equations in the 7 unknowns \( \lambda_1^G, \lambda_1^L, \lambda_2^L, \rho_0^G, \rho_0^L, \phi^G \). The moment chemical potentials and the pressure are then for the SRK equation of state:

\[
\beta \mu_1 = \beta \lambda_1 + \frac{\rho_0}{1 - \rho_0 m_1} - \frac{\rho_0 m_2^2}{m_1(1 + \rho_0 m_1)} + \frac{m_2^2}{m_1^2} \ln (1 + \rho_0 m_1)
\]

\[
\beta \mu_2 = \beta \lambda_2 - 2 \frac{m_2^2}{m_1} \ln (1 + \rho_0 m_1)
\]

\[
\beta P = \frac{\rho_0}{1 - \rho_0 m_1} - \frac{\rho_0^2 m_2^2}{1 + \rho_0 m_1}
\]

For the PR equation of state, the calculations are just slightly more complicated,
as now we get:

\[ \beta \mu_1 = \beta \lambda_1 + \frac{\rho_0}{1 - \rho_0 m_1} - \frac{\rho_0 m_2^2}{m_1 (1 + 2 \rho_0 m_1 - \rho_0^2 m_2^2)} - \frac{\sqrt{2}}{4} \frac{m_2^2}{m_1^2} \ln \left[ \frac{1 + (1 - \sqrt{2}) \rho_0 m_1}{1 + (1 + \sqrt{2}) \rho_0 m_1} \right] \]

\[ \beta \mu_2 = \beta \lambda_2 + \frac{\sqrt{2}}{2} \frac{m_2}{m_1} \ln \left[ \frac{1 + (1 - \sqrt{2}) \rho_0 m_1}{1 + (1 + \sqrt{2}) \rho_0 m_1} \right] \]

\[ \beta P = \frac{\rho_0}{1 - \rho_0 m_1} - \frac{\rho_0^3 m_2^2}{1 + 2 \rho_0 m_1 - \rho_0^2 m_1^2} \]

4 Numerical results

As a way of example, in order to show the potential of the method described in the previous section, in this section we will show some numerical results obtained by applying it to a real case-study. We solve the phase equilibria for a mixture of 24 hydrocarbons, up to nC15, along a straight line crossing the \((P, T)\) phase diagram. The calculations are done using the SRK equation of state, although no relevant difference is observed when using the PR equation of state. Our numerical results are compared with the results obtained with a commercial program (PVTsim), licensed to Snamprogetti s.p.a. (that provided the results). In Fig. 4 we plot the concentration in mole % of C1 (methane), in the two coexisting phases, against the temperature. Our result agrees very well with the points obtained with PVTsim. The concentration of both phases is evaluated correctly. Furthermore, the cloud point, i.e., the point at which the liquid phase appears, is detected exactly on the phase envelope shown by PVTsim.

In Fig. 4 we show again the same case. Now we plot the concentration of n-C4 against the pressure. As the pressure-temperature path enters the coexistence region, liquid is found. This time the component represents less than 1% of the total composition of the gas, while it is about 10% of the total composition of the liquid. Again, even with a heavier hydrocarbon, our numerical results are in excellent agreement with the ones obtained with PVTsim.

5 Conclusion

We have applied the moment method to the analysis of phase equilibria of mixture of hydrocarbons, using the SRK and PR equations of state. Our results show that not only the moment method is applicable as it correctly detects gas-liquid phase coexistence. Even with a large number of components in the mixture, our algorithm remains robust and numerical calculation fast. Furthermore, our numerical results agree quantitatively very well with the results obtained using a widely used commercial program (PVTsim). No further demixing, beyond the G-L coexistence is observed, however, it is not yet clear whether this depends on the equations of state used, or rather to the choice of the mixture of hydrocarbons. It may be possible to have the coexistence of more than
two (G and L) phases, e.g., more than one different liquid and/or gas phases, using a wider distribution of hydrocarbons.

As far as future developments are concerned, one could proceed to the analysis of a fully polydisperse case, i.e., by introducing a continuous distribution of species. Clearly the two equations should first be extended to the continuous case, e.g., by introducing a continuous dependence of the acentric factor on the size of particles. It is possible that further demixing appears using different distributions. The extension to the continuous case should not have any impact on our method. Clearly, the computation may be slightly slower, as in that case the moments have to be evaluated by integration rather than summation over a finite number of species; however, no formal or substantial adjustment is needed.

Finally, further applications of the moment method could be tried. For instance, one could try to apply it to metallurgy or other cases of industrial interest. Clearly, when solid phases appear, one would have to extend the analysis introducing spatial and/or orientational degrees of freedom. However, as previous results already show [1, 2, 3, 4, 11, 10] this should not represent a limitation for the method.
Figure 2: Concentration in mole % of n-C4 against pressure across the phase diagram. As pressure and temperature drop enough to enter the phase coexistence region, the liquid phase is found. The concentration the element in both phases are in excellent agreement with the ones obtained with PVTsim. Again, it is not clear whether the small deviations inside the coexistence region are due to our method, or rather to approximations and truncations introduced by PVTsim.

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