A multi-phase, multi-component critical equation of state

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Abstract. Realistic equations of state valid in the whole state space of a multi-component mixture should satisfy at least three important constraints:
(i) The Gibbs phase rule holds.
(ii) At low densities, one can deduce a virial equation of state with the correct multi-component structure.
(iii) Close to critical points, plait points, and consolute points, the correct universality and scaling behavior is guaranteed.

This paper discusses semiempirical equations of state for mixtures that express the pressure as an explicit function of temperature and the chemical potentials. In the first part, expressions are derived for the most important thermodynamic quantities. The main result of the second part is the construction of a large family of equations of state with the properties (i)–(iii).

Keywords: activity equation of state, critical points, grand canonical ensemble, scaling fields, universality, vapor-liquid-liquid equilibrium (VLLE), virial equation of state
1 Activity equations of state

We consider mixtures with $C$ pure components $i = 1, \ldots, C$. Their equilibrium is characterized by constant temperature $T$, pressure $P$, and chemical potentials $\mu_i$ ($i = 1, \ldots, C$), whereas the various thermodynamic densities and concentrations are piece-wise constant only, with jumps at phase boundaries. We write $n_i$ for the mole number of component $i$ and $V$ for the total volume of the mixture; in each phase, the density $n_i/V$ of component $i$ is determined by temperature, pressure, and chemical potentials. $R$ denotes the universal gas constant. The theory of thermodynamics describes and derives the rules that relate these quantities; the axioms of thermodynamics (see Appendix A) itself can be derived by means of statistical mechanics from the dynamics of the molecules making up the mixture. For a rigorous and self-contained derivation see, e.g., Neumaier [29, Part II].

It is well-known (see, e.g., Callen [9]) that in the zero density limit, a mixture behaves like an ideal gas, characterized by chemical potentials\footnote{The thermodynamic formalism specifies each chemical potential $\mu_i$ only up to a term $\mu_U + T\mu_S$ with arbitrary constants $\mu_U$ and $\mu_S$. These constants depend on the values of internal energy $U$ and entropy $S$ (where only differences are observable) at some fixed reference point. The $\gamma_i(T)$ inherit this ambiguity as the combined expression $\mu_i/RT - \gamma_i(T)$ is observable and hence unambiguous.} of the form

$$\mu_i = RT \left( \gamma_i(T) + \log \frac{V_0n_i}{V} \right) \quad \text{for} \quad \frac{V_0n_i}{V} \to 0,$$

with a fixed reference volume $V_0 > 0$ and suitable functions $\gamma_i$ of $T$, and an equation of state of the form

$$\frac{PV}{RT} = n_1 + \ldots + n_C.$$
We shall work with dimensionless reduced quantities, using a fixed reference temperature \(T_0 > 0\) and a fixed reference pressure \(P_0 > 0\) satisfying
\[
P_0 V_0 = RT_0,
\]
and formulate our results in terms of the **reduced temperature**
\[
\tau := \log \frac{T}{T_0},
\]
the temperature-scaled **reduced pressure**
\[
\pi := \frac{PT_0}{P_0 T},
\]
the **reduced activities**
\[
z_i := \exp \left( \frac{\mu_i}{RT} - \gamma_i(T) \right),
\]
which we collect together in a \(C\)-dimensional **activity vector** \(z\), and the **reduced densities**
\[
\rho_i := \frac{V_0}{V} n_i \quad (i = 1, \ldots, C). \tag{1}
\]
It is also conventional to use the **total molar number**
\[
n := \sum_i n_i
\]
and the **mole fractions**
\[
x_i := \frac{n_i}{n} = \frac{\rho_i}{\rho} \quad (i = 1, \ldots, C),
\]
where
\[
\rho = \sum_i \rho_i
\]
is the **total reduced density**. Clearly
\[
\sum_i x_i = 1, \quad x_i \geq 0 \quad (i = 1, \ldots, C).
\]

The original variables can be easily recovered from the reduced quantities and the total volume \(V\):
\[
T = T_0 e^\tau, \quad P = \frac{P_0 T}{T_0} \pi, \quad \mu_i = RT(c_i(\tau) + \log z_i), \quad n_i = \frac{V}{V_0} \rho_i, \tag{2}
\]
where
\[
c_i(\tau) := \gamma_i(T_0 e^\tau) = \gamma_i(T).
\]

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2To aid the reader, we use := to indicate that a term on the left is defined by the right hand side.

3This choice, while somewhat unconventional, gives the simplest formulas in Section 2, and was used already by Vidler & Tennyson [39] for highly accurate fits to ideal gas properties of water.
The ideal gas law takes the simple form

\[ \pi = \sum_i z_i, \quad \rho_i = z_i \quad (i = 1, \ldots, C). \]  

(3)

In a general mixture, the intrinsic meaning of \( \pi, \tau, z \), visible only in non-equilibrium situations, is that of **thermodynamic force fields** with a distinguished meaning whose spatial gradients induce changes in various densities. Equilibrium is characterized by the absence of these forces, i.e., the constancy of the corresponding force fields throughout the mixture. \( \tau, \pi \) and the \( z_i \) are nonnegative, and a (reduced) activity \( z_i \) is zero (corresponding to \( \mu_i = -\infty \)) precisely when a substance is not present. In particular, pure substances are the limiting case of mixtures where only a single component of \( z \) is nonzero. Intuitively, the reduced activities are a kind of effective densities (the name derives from the now outdated terminology "active number densities"), but with a force field character.

Since the thermodynamic state space is only \((C + 1)\)-dimensional, there is always an algebraic relation between \( \pi, \tau, z \) generalizing (3), which we shall call an **activity equation of state** (activity EOS). In some sense, an activity EOS is the most fundamental formulation of equilibrium thermodynamics. Indeed, everything else in thermodynamics can be derived by assuming a few properties of an activity EOS only; see Section 2. Many phenomena find their simplest description when formulated in terms of the variables \( \tau, \pi, \) and \( z \); cf. the discussion in Fisher [11].

In statistical mechanics (see, e.g., Reichl [36]), one derives from the grand canonical ensemble in the thermodynamic limit an activity EOS of the pressure-explicit form

\[ \pi = \pi(\tau, z), \]  

(4)

and proves that the pressure can be written for small \( z \) as a power series in \( z \),

\[ \pi(\tau, z) = \sum_{k_1, \ldots, k_C=0}^{\infty} \pi_{k_1, \ldots, k_C}(\tau)z_1^{k_1} \cdots z_C^{k_C} \]  

(5)

with smooth functions \( \pi_{k_1, \ldots, k_C}(\tau) \) of \( \tau \) that are (at least in principle) computable from microscopic information. The way we defined the reduced variables implies that for small \( z \) we have \( \pi(\tau, z) = \sum z_i + O(z^2) \), hence \( \pi_{k_1, \ldots, k_C}(\tau) = 0 \) if all \( k_i \) vanish, and \( \pi_{k_1, \ldots, k_C}(\tau) = 0 \) if all \( k_i \) but one vanish and the remaining takes the value 1.

Therefore we shall take an equation with these properties as our starting point. However, we do not assume that \( \pi(\tau, z) \) is derived from statistical mechanics but take it as an

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4The following is taken from the text after (2.2): “... the "forces" or "fields" rather than the "densities", are the more basic and simpler variables in terms of which to describe a statistical system undergoing a phase transition. The validity of this general philosophy is confirmed by nearly all solved problems in statistical mechanics; the greater simplicity of the grand canonical formulation for so many purposes, particularly for the derivation of fluctuation formulae or sum rules, is a familiar illustration of the point. A further explicit demonstration will be provided by the soluble models of systems displaying critical behavior [...] At a fundamental level the preferred status of the forces seems to correspond rather directly to the completely convex character of the corresponding thermodynamic potentials, alluded to above. Convexity in all the forces together means in effect that the various local densities can fluctuate freely with, at fixed fields, no over-all constraints.”
appropriate semiempirical expression whose form must be determined from constraints from a combination of theoretical considerations and matching to experimental data. The main goal of this paper is to propose in Section 5 a particular class of activity equations of state with the properties stated in the abstract. EOSs from this class therefore have the potential to cover the whole state space. However, to relate the activity EOS (4) to more well-known forms of the EOS, we first discuss in Sections 2–3 more or less well-known consequences of (4) and (5), rederiving the most important formulas in a concise way. Section 4 discusses the additional issues introduced by multiple phases.

2 Free energies

In this section, we derive from the activity EOS formulas for mole numbers, entropy, various free energies, and their reduced versions. At a given volume $V$, these and everything else may be computed from the expression

$$P(T, \mu) := \frac{P_0 T}{T_0} \pi(\tau, z), \quad \tau = \log \frac{T}{T_0}, \quad z_i = \exp \left( \frac{\mu_i}{RT} - c_i(\tau) \right),$$

for $P$ at fixed $T$ and $\mu$, deduced from (2). An activity EOS is thermodynamically consistent whenever $P(T, \mu)$ is jointly convex in $(T, \mu)$ and a strictly increasing function of each $\mu_i$ when the other variables are held constant; cf. Appendix A.

Fixing $T$ and all but one of the variables $\mu_1, \ldots, \mu_C$ in the Gibbs–Duhem relation

$$V dP = SdT + \sum_i n_i d\mu_i,$$

(6)

where $S$ denotes the entropy, gives

$$\frac{dP(T, \mu)}{d\mu_i} = \frac{n_i}{V} = \frac{\rho_i}{V_0},$$

(7)

$$\rho_i = \frac{V_0}{V} n_i = \frac{V_0}{V_0} \frac{dP(T, \mu)}{d\mu_i} = \frac{V_0 P_0 T}{T_0} \frac{d\pi}{d\mu_i} = RT \frac{d\pi}{dz_i} \frac{dz_i}{d\mu_i} = \frac{z_i}{d\pi} \frac{d\pi}{dz_i}.$$  

We conclude that

$$\rho_i = \frac{z_i}{d\pi} \frac{d\pi}{dz_i} \quad \text{for} \quad i = 1, \ldots, C.$$  

(8)

Since the $\rho_i$ are nonnegative, $\pi(\tau, z)$ must be a strictly increasing function of each $z_i$ when the remaining variables are held constant. We describe the Gibbs free energy

$$G := \sum_i \mu_i n_i = \frac{RTV}{V_0} g$$

and the Helmholtz free energy

$$A := G - PV = \frac{RTV}{V_0} f$$
in terms of the dimensionless reduced Gibbs free energy $g$ and the dimensionless reduced Helmholtz free energy $f$. A simple substitution gives

$$g = \sum_i \rho_i (c_i + \log z_i), \quad f = g - \pi. \quad (9)$$

The internal energy

$$U := A + TS = \frac{RTV}{V_0} \varepsilon$$

and the enthalpy

$$H := G + TS = \frac{RTV}{V_0} h$$

are described in terms of the dimensionless reduced internal energy $\varepsilon$, and the dimensionless reduced enthalpy $h$. Substitution now gives

$$\varepsilon = f + s, \quad h = g + s \quad (10)$$

with the dimensionless reduced entropy $s = \frac{V_0 S}{RV}$, which implies

$$S = \frac{RV}{V_0} s. \quad (11)$$

Fixing all variables $\mu_1, \ldots, \mu_C$ in (6) gives

$$\frac{dP(T, \mu)}{dT} = \frac{S}{V} = \frac{Rs}{V_0}, \quad (12)$$

$$s = \frac{V_0 S}{RV} = \frac{V_0}{R} \frac{dP(T, \mu)}{dT} = \frac{V_0 P_0}{RT_0} \frac{d(T \pi)}{dT} = \frac{d(T \pi)}{dT} = \pi + T \frac{d\pi}{dT}$$

$$= \pi + T \left( \frac{d\pi}{dT} \frac{dT}{dT} + \sum_i \frac{d\pi}{dz_i} \frac{dz_i}{dT} \right) = \pi + \frac{d\pi}{dT} \frac{dT}{dT} - \sum_i \frac{d\pi}{dz_i} z_i \left( \frac{dc_i}{dT} + c_i + \log z_i \right)$$

since

$$\frac{dz_i}{dT} = z_i \left( -\frac{\mu_i}{RT^2} - \frac{dc_i}{dT} \frac{1}{T} \right) = -\frac{z_i}{T} \left( \frac{dc_i}{dT} + \frac{\mu_i}{RT} \right) = -\frac{z_i}{T} \left( \frac{dc_i}{dT} + c_i + \log z_i \right).$$

Therefore

$$s = \pi + \frac{d\pi}{dT} - \sum_i \rho_i \left( \frac{dc_i}{dT} + c_i + \log z_i \right), \quad (13)$$

$$h = g + s = \pi + \frac{d\pi}{dT} - \sum_i \rho_i \frac{dc_i}{dT}, \quad (14)$$

and since $\varepsilon = f + s = g - \pi + s = h - \pi$, we find that

$$\varepsilon = \frac{d\pi(\tau, z)}{dT} - \sum_i \rho_i \frac{dc_i(\tau)}{dT}. \quad (15)$$
Looking at (2), (8), (9), (13), (14), and (15), we see that the activity EOS (4) encodes all thermodynamic information about the mixture. In particular, one can also compute thermodynamic response functions such as the (volume-based) molar heat capacity

\[ c_V(T) := \left( \frac{dU}{n\,dT} \right)_{V,n} = \frac{R}{\rho} \left( \frac{dT\,\varepsilon}{dT} \right)_\rho = \frac{R}{\rho} \left( \varepsilon + \frac{d\varepsilon}{d\tau} \right)_\rho. \]

In engineering practice, one usually works in terms of densities or composition rather than activities. To determine \( z = z(\tau, \rho_1, \ldots, \rho_C) \) as a function of reduced temperature and densities, one must solve the nonlinear system of equations (8). Often, (8) is uniquely solvable for the \( \rho_i \), but if there are multiple solutions, the solution with largest reduced Helmholtz free energy \( f \) is the correct one. If we substitute this into the activity EOS (4), we find an EOS

\[ \pi = \pi(\tau, z(\tau, \rho_1, \ldots, \rho_C)) \] for the reduced pressure in terms of reduced temperature and densities. We also find (with \( \tau = \log(T/T_0) \)) the isochoric form

\[ f(T, \rho_1, \ldots, \rho_C) = \sum_i \rho_i \left( c_i(\tau) + \log z_i(\tau, \rho_1, \ldots, \rho_C) \right) - \pi(\tau, z(\tau, \rho_1, \ldots, \rho_C)) \]

of the reduced Helmholtz free energy as discussed, e.g., by Sengers & Levelt Sengers [37] and Quiñones-Cisneros & Deiters [33].

3 Ideal gas and virial equation of state

Specializing the preceding formulas to the case of a pure ideal gas with the single component \( i \), we find

\[ \pi = z_i = \rho_i, \]

\[ g = \rho_i(c_i + \log \rho_i), \quad f = g - \pi = \rho_i(c_i - 1 + \log \rho_i), \]

\[ \varepsilon = -\rho_i \frac{dc_i}{d\tau}, \quad h = \rho_i \left( 1 - \frac{dc_i}{d\tau} \right), \quad s = h - g = \rho_i \left( 1 - \frac{dc_i}{d\tau} - c_i - \log \rho_i \right). \]

\[ c_V(T) = -RT \frac{d^2(Tc_i)}{dT^2} = -R \left( \frac{dc_i}{d\tau} + \frac{d^2c_i}{d\tau^2} \right). \]

In particular, one can calculate \( c_i(\tau) \) from zero density heat capacities by numerical integration.\(^5\) Real gases behave like an ideal gas only in the limit of zero densities. At low densities, the behavior of mixtures is governed by the multi-component virial equation of state, an expansion of the pressure as a multivariate power series in densities with temperature-dependent coefficient, first derived by Fuchs [13] in statistical mechanics terms. But the virial expansion may be obtained from (16) without reference to statistical mechanics by a multivariate Taylor expansion. Given an activity EOS (4) satisfying (5)

\(^5\)The different ways of fixing the ambiguities in the definition of the \( \mu_i \) mentioned in footnote 1 correspond to the different possible choices of the integration constants.
and reducing to $\pi = \sum z_i$ in the zero density limit, we may write (5) at low reduced densities $\rho_i$ as

$$\pi = \sum_i z_i + \frac{1}{2} \sum_{i,j} G_{ij} z_i z_j + O(z^3),$$

leaving implicit the temperature dependence of the coefficients

$$G_{ij}(\tau) = \frac{d^2 \pi}{d z_i d z_j} (\tau, 0)$$

that determine the second order deviations from the ideal gas law. At low densities, the system of equations (8) for $i = 1, \ldots, C$ can be solved uniquely for $z_i = \rho_i + O(\rho^2)$ by successive substitution. Since

$$z_i = \frac{\rho_i}{d\pi/dz_i} = \frac{\rho_i}{1 + \sum_j G_{ij} z_j + O(z^2)} = \rho_i \left( 1 - \sum_j G_{ij} \rho_j + O(\rho^2) \right),$$

we have

$$\pi = \sum_i \rho_i \left( 1 - \sum_j G_{ij} \rho_j + O(\rho^2) \right)$$

This gives to second order the reduced virial equation of state

$$\pi = \sum_i \rho_i - \frac{1}{2} \sum_{i,j} G_{ij}(\tau) \rho_i \rho_j + O(\rho^3) = \rho - \frac{\rho^2}{2} \sum_{i,j} G_{ij}(\tau) x_i x_j + O(\rho^3). \quad (18)$$

Using (2), we may compare this with the traditional, unreduced form

$$\frac{P}{RT} = \frac{n}{V} + B_2(T, x) \left( \frac{n}{V} \right)^2 + O\left( \left( \frac{n}{V} \right)^3 \right)$$

defining the second virial coefficient $B_2(T, x)$. We find that

$$B_2(T, x) = -\frac{T_0 R}{2P_0} \sum_{i,j} G_{ij} \left( \log \frac{T_0}{T} \right) x_i x_j.$$

Higher order terms in the virial equation of state may be derived in a similar fashion.

4 Phase equilibrium

In a mixture that exists in multiple phases, $\pi(\tau, z)$ is nondifferentiable along the coexistence manifold, defined as the set of states $(\tau, z)$ for which arbitrarily small neighborhoods contain points corresponding to two different phases. Each phase $s$ has its own
three times\textsuperscript{6} continuously differentiable activity EOS

\[ \pi = \pi_s(\tau, z). \]

In each single phase region, only one of these equations holds, while on the coexistence manifold, two or more of these equations are satisfied simultaneously. For an \( m \)-phase equilibrium involving the phases \( s_1, \ldots, s_m \), we have \( m \) independent equations

\[ \pi = \pi_s(\tau, z) \quad (s = s_1, \ldots, s_m). \]

Generically, these define a \( (C + 2 - m) \)-dimensional manifold, which is the well-known Gibbs phase rule. In particular, the number of coexistent phases is generically at most \( C + 2 \).

Rigorous results from statistical mechanics (cf. Langer \cite{23}, Penrose & Lebowitz \cite{32}, Isakov \cite{16}, Friedli & Pfister \cite{12}) imply that any EOS has essential singularities\textsuperscript{7} everywhere along the coexistence manifold. These are absent only in an approximate mean field treatment and in semiempirical models, where each \( \pi_s(\tau, z) \) is usually three continuously differentiable in some region beyond the coexistence boundaries, until singularities are reached at another boundary defining the spinodal manifold. In the region between the coexistence and the spinodal manifold, the phase activity EOS then describes a metastable state. These states are strictly speaking not governed by equilibrium thermodynamics, but as long as the relaxation times to the stable state are sufficiently long, an approximate equilibrium description is possible, and it is accurate close to the coexistence manifold. In any case, the stable state is the state of maximal pressure\textsuperscript{8} and satisfies the multiphase activity EOS

\[ \pi = \pi(\tau, z) := \max_s \pi_s(\tau, z), \tag{19} \]

where at each \((\tau, z)\) the maximum is taken over all possible phases \( s \), using the value \(-\infty\) at states beyond the spinodal where some \( \pi_s(\tau, z) \) is undefined.

Modeling phases by means of (19) has the advantage compared to models based on a Helmholtz free energy that the model cannot have any accidental unwanted phases. Coexistent phases are characterized by common values of \( \pi, \tau, \) and \( z \). In particular, stable coexistent phases exist precisely at the states in which several of the functions \( \pi_s(\tau, z) \) have coinciding values.

To derive the composition of each phase at fixed \( \pi, \tau, \) and total composition \( x \) in stable

\textsuperscript{6}In theory, we have infinite differentiability away from the coexistence manifold. However for practical modeling, it is sufficient to require three times continuous differentiability. Then all thermodynamic quantities of interest, being obtainable from \( \pi(\tau, z) \) and its first two derivatives, have a continuously differentiable dependence on \( \tau \) and \( z \), which is sufficiently smooth for practical applications.

\textsuperscript{7}An essential singularity is a point at which the Taylor series expansion has zero convergence radius.

\textsuperscript{8}For example, consider a \((P, \mu)\) diagram for two phases of a pure substance at fixed temperature. Here \( \mu \) is essentially the Gibbs free energy; therefore the stable phase consists of the branches with the smallest value of \( \mu \) at fixed \( P \). The drawing then implies that \( P \) has the largest value at fixed \( \mu \).
equilibrium, one must solve the constrained optimization problem:

$$\max_z \sum_i x_i \log z_i$$

subject to:

$$\pi_s(\tau, z) \leq \pi$$  for all possible phases \(s\).

By general results from optimization theory, any solution of this optimization problem must satisfy the **optimality conditions**

$$x_i = \sum_s \lambda_s \rho_{si}, \quad \rho_{si} = z_i \frac{d\pi_s(\tau, z)}{dz_i}, \quad (20)$$

where the \(\lambda_s\) are Lagrange multipliers satisfying the **complementarity conditions**

$$\min(\lambda_s, \pi - \pi_s(\tau, z)) = 0 \quad \text{for all possible phases} \ s. \quad (21)$$

Should the optimality conditions have multiple solutions, the correct solution is given by the global maximum. The reduced density \(\rho_s\) of phase \(s\) and the mole fractions \(x_{si}\) of component \(i\) in phase \(s\) are then given by

$$\rho_s = \sum_i \rho_{si}, \quad x_{si} = \frac{\rho_{si}}{\rho_s}. \quad (21)$$

Compared with the optimization problems arising in the conventional Helmholtz or Gibbs formulations, there are two important differences:

(i) A solution of the optimization problem is automatically a stable equilibrium; to obtain a metastable phase equilibrium one must solve instead an alternative optimization problem in which the constraints corresponding to the more stable competing phases are dropped.

(ii) The complementarity conditions automatically determine the phases actually present as they imply \(\lambda_s = 0\) if \(\pi_s(\tau, z) < \pi\).

To generalize this to reacting mixtures, we consider an initial composition and the final equilibrium state resulting if the mixture is left to reach both chemical and phase equilibrium. As any chemical reaction changes the mole numbers of some of the components, the composition and the total number of moles changes until equilibrium is reached. The phase equilibrium problem in the presence of chemical reactions is therefore obtained by solving the constrained optimization problem

$$\max_{\xi, z} \sum_i \left( n_i^{\text{init}} + (N\xi)_i \right) \log z_i$$

subject to:

$$\pi_s(\tau, z) \leq \pi \quad \text{for all phases} \ s,$$

$$0 \leq n_i^{\text{init}} + (N\xi)_i \quad (i = 1 \ldots, C).$$

Here \(n_i^{\text{init}}\) is the initial mole number of component \(i\), \(\xi\) is a vector of extent of reaction coordinates, and \(n_i = n_i^{\text{init}} + (N\xi)_i\) the equilibrium mole number of component \(i\). \(N\) is the

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9 The formulation as a maximization problem is due to thermodynamic stability; see Appendix A. It is similar to the maximization occurring in the definition of Legendre transforms and in the definition of the Gibbs potential in Neumaier [30].
matrix of stoichiometric coefficients of the allowed chemical reactions, each column of $N$

Traditionally, the semiempirical view is microscopically supported by an approximate mean

field treatment in terms of an analytic Helmholtz free energy. In this case the state

functions in different phases are connected by analytic continuation using so-called van
der Waals loops, which contain besides the metastable regions also spurious unphysical

states. As a consequence of the van der Waals construction, the $\pi_s(\tau, z)$ are located on
different sheets of the same analytic function. However, when presented in the form of an
activity EOS (19), the $\pi_s(\tau, z)$ for different phases of the same mixture may be completely
unrelated. Such a heterogenous approach is common practice for the joint modeling of
fluid and solid phases, though there are frameworks in which one can give a joint Helmholtz
description of all phases; see, e.g., Lomonosov [26].

However, if some of the phases are not well separated everywhere in the state space then a
more sophisticated joint description must exist. This is the case precisely when a coexis-
tence boundary contains a critical point, i.e., a point on the boundary of the coexistence
manifold (Griffiths & Wheeler [15]). In this case, the joint description is constrained
by nontrivial scaling laws near the critical points, which will be discussed next.

5 A multiphase critical equation of state

Equations of state valid over the whole state space must account for the existence of critical
points (for pure fluids a liquid-vapor critical point, for mixtures plait points at liquid-vapor
 equilibrium and consolute points at liquid-liquid equilibrium) and of the universal, i.e.,
substance independent power laws with which certain thermodynamic quantities scale near
the critical point; cf. the fairly recent survey by Sengers & Shanks [38].

The form of any globally valid equation of state (EOS) is strongly restricted by renormal-
ization group arguments. An exposition of the results in a form most useful for multi-
component mixtures is given in Neumaier [31], where a new and general analytic form
of an EOS accommodating all critical properties was derived. In a renormalization group
setting, the critical behavior of mixtures is characterized by the existence of several scaling fields, the strong scaling field $\Sigma$ the thermal scaling field $\Theta$, the dependent scaling field $D$, and a number of scaling correction fields $I_k$ ($k = 1, 2, \ldots$); here the term field just means a smooth function of $\pi, \tau, z$. The form of the analytic scaling EOS in [31] is

$$D^{-2a/e\Sigma^2} = \Gamma(D^{-1/e\Theta}, D^{-e_1/e I_1}, D^{-e_2/e I_2}, \ldots),$$

(22)

where $\Gamma$ is a universal, substance-independent analytic function of its arguments; the only nonanalytic behavior is in the powers of $D$, involving the critical exponents

$$e > a > 1 > 0 > e_1 \geq e_2 \geq \ldots.$$  

(23)

10Since the renormalization group technique works rigorously in terms of thermodynamic force fields only, the variables $\tau, \pi$, and $z$ are the most natural thermodynamic variables for a multi-component equation of state near the critical point.
The critical exponents are also universal; the first few values are approximately given by
\[ a \approx 1.56383(34), \quad e \approx 1.89036(48), \quad e_1 \approx -0.52(3), \quad e_2 \approx -1.05(8), \quad e_3 \approx -1.5(3). \] (24)

Much is known about the universal function \( \Gamma \); see [31].

The strong scaling field \( \Sigma \) and the thermal scaling field \( \Theta \) have a clear physical meaning: For \( \Theta \leq 0 \), the system is in a lower density phase if \( \Sigma > 0 \) and in a higher density phase if \( \Sigma < 0 \). If \( \Sigma = 0 \), the system has two coexistent lower and higher density phases. At \( \Theta < 0 = \Sigma \), we have a first-order phase transition, i.e., some thermodynamic response functions possess a jump discontinuity. The inequality \( \Theta > 0 \) defines a low density part of the phase space, connected very smoothly to the low density phase at \( \Sigma > 0 > \Theta \). However, at \( \Theta = 0 > \Sigma \), there is a higher-order phase transition between high density states and low density states, with continuous but nonanalytic thermodynamic response functions.

Near the vapor-liquid critical point, the condition \( \Theta > 0 > \Sigma \) corresponds approximately to the conventional definition of supercritical, which in an engineering context means that both pressure and temperature are above the pressure and temperature at the critical point. This justifies to call the states with \( \Theta > 0 > \Sigma \) supercritical in a theoretically more justified sense. Critical points are characterized by \( \Sigma = \Theta = 0 \). Genericly, for mixtures with \( C \) components, they form a manifold of dimension \( C - 1 \) in the \((C + 1)\)-dimensional thermodynamic state space.

The above is referred to as the complete scaling setting. Much of the work on critical EOS has been done in the more restrictive, simplified setting of revised scaling. The latter means that \( D \) has the special form
\[ D(\pi, \tau, z) = \pi_{\text{reg}}(\tau, z) - \pi \]
with a smooth function \( \pi_{\text{reg}} \) of \( \tau \) and \( z \), and that the remaining scaling fields \( \Sigma, \Theta \) and the \( I_k \) are independent of \( \pi \). In the resulting activity EOS
\[ \pi = \pi_{\text{reg}}(\tau, z) - \tilde{D}(\tau, z), \]
where in the present context \( \tilde{D}(\tau, z) \) is obtained from (22) by solving for \( D \), one interprets \( \pi_{\text{reg}}(\tau, z) \) as a classical, regular part and \( \tilde{D}(\tau, z) \) as a singular crossover term to critical behavior.

In the first paper modeling (binary) mixtures with correct scaling properties close to the critical point, LEUNG & GRIFFITHS [25] express everything in terms of force field variables. For industrial applications, multicomponent formulations in a cubic EOS, Helmholtz or Gibbs free energy framework are desirable, so that the composition can be kept constant. A number of such formulations were presented in the literature; see, e.g., [1, 5, 10, 17, 19, 20, 21, 35]. However, formulations at fixed composition cannot match exactly the singularities; indeed WHEELER & GRIFFITHS [40] prove that when some mole fractions are held constant, curves of plait points have bounded heat capacity, while the heat capacity at the critical point of a pure substance diverges. A more detailed analysis leads to additional renormalization phenomena (FISHER [11]). Ignoring these, as often done in these formulations, therefore requires additional approximations which may
result in artifacts very close to the critical point (Kiselev & Friend [20]). Other papers (e.g., [7, 8]) implement the renormalization group approach more directly, resulting in an iterative definition of an equation of state that in the limit of infinitely many iterations satisfies the correct scaling laws. A thorough discussion of many practically relevant issues is given in the surveys by Anisimov & Sengers [2] and Behnejad et al. [4].

Most previous critical EOS are limited in several different ways:

- Frequently, the thermal scaling field $\Theta$ is taken to be linear in the temperature. However, linearity in $T$ limits the EOS to a narrow range of temperatures. Scaling fields with a more favorable temperature dependence such as one linear in $T^{-1}$ or $\tanh(T_0/T)$ extrapolate much better to the high temperature regime; see, e.g., Lundow & Campbell [27].
- Almost all studies attempting to go beyond the immediate neighborhood of the critical point work in the simplified setting of revised scaling. However, this setting does not account for all observable fluid behavior; see, e.g., Bertrand et al. [6]. The only previous EOS not restricted to revised scaling is the crossover EOS of Bakhshandeh & Behnejad [3], which employs complete scaling, with scaling fields linear in $P$, $T$, and $\mu$.
- All noniterative equations of state with correct critical scaling are currently based on an implicit representation in terms of a Schofield type parameterization.
- Most papers discuss the two-phase case only. The only exception is Rainwater [34], who attempts to cover vapor-liquid-liquid equilibrium. The main reason for this lack of generality seems to be that (as Rainwater’s paper shows) a crossover mechanism in terms of a Schofield type parameterization is very difficult to extend to the multiphase case, since the Schofield parameters have no clear meaning far from the critical point and tend to introduce unphysical artifacts such as two coexisting vapor phases.

The new analytic scaling EOS (22) leads to a large family of implicit or explicit activity equations of state that, by their very form, automatically have the following properties:

(i) The Gibbs phase rule holds.

(ii) At low densities, one can deduce a virial equation of state with the correct multi-component structure.

(iii) Close to critical points, plait points, and consolute points, the correct universality and scaling behavior is guaranteed.

To find the most general form of an EOS with these properties, we partition the phases into groups $g$ completely separated by a phase space boundary, while the phases within each group may be connected with each other by paths in phase space not crossing the coexistence manifold. One of these groups consists of all fluid phases; for solid phases, the groups may consist of a single phase only or (as, e.g., for $\beta$-brass, cf. Lamers & Schweika [22]) may contain several phases related by a critical point. The phases within each group are described by common, substance-specific scaling fields $\Theta_g(\pi, \tau, z)$, $\Sigma_g(\pi, \tau, z)$, and $D_g(\pi, \tau, z)$, one for each phase group $g$. As discussed above, the critical behavior is correctly modelled if the EOS for each phase group takes the form

$$D_g^{-2\alpha/e} \Sigma_g^2 = \Gamma(D_g^{-1/e} \Theta_g, D_g^{\alpha_1/e} I_{g1}, D_g^{\alpha_2/e} I_{g2}, \ldots) \quad (25)$$

with a universal, substance-independent function $\Gamma$; here the arguments $(\pi, \tau, z)$ were suppressed for easy readability. For given $\tau$ and $z$, the stable phase is determined by finding for each phase group $g$ the solutions $\pi$ of the equations (25), and taking – according
to Section 4 – the one with largest $\pi$. In case of ties, multiple phases from different phase groups coexist.

Since the group $f$ of fluid phases contains the vapor phase, we require for this phase group additional properties that ensure a proper ideal gas limit ($\pi$ and $z$ small). We require four conditions; the first condition makes sure that for small $\pi$ and $z$, we only have a single phase. The second condition allows us to write the EOS in the pressure-explicit form (4) of an activity EOS. The third condition embodies the ideal gas law, and the final condition produces the virial equation of state:

- (25) holds identically for arguments $(\pi, \tau, z) = (0, \tau, 0)$ with
  \[ \Theta_f(0, \tau, 0) \geq 1 \quad \text{for all } \tau > 0. \]  

This guarantees that $\Theta_f > 0$ for small $\pi$ and $z$, so that we are in the single-phase case.

- The nondegeneracy condition
  \[ \frac{dD_f(0, \tau, 0)}{d\pi} \neq 0 \]  

holds. This condition ensures that for small $\pi$ and $z$ we may uniquely solve the equation $D_f(\pi, \tau, z) = D$ for $\pi = \pi_f(D, \tau, z)$.

- A condition on the derivative of (25) at $(\pi, \tau, z) = (0, \tau, 0)$ that guarantees that (25) is consistent with (and hence implies) $\pi_f(D, \tau, z) = \sum z_i + O(z^2)$.

- $D_f, \Theta_f,$ and $\Sigma_f$ have a multivariate power series expansion in $z$. This condition allow one to write $\pi_f(D, \tau, z)$ has a power series expansion in $z$.

As shown in Section 3, these conditions together imply the virial equation of state and hence the correct low density behavior.

Whenever all requirements discussed in this section are satisfied (which is easy to achieve), (25) is a global multi-component EOS with correct critical scaling and a correct low density limit. For binary mixtures, a global crossover EOS with these properties was first derived by Kiselev & Friend [20], using the Schofield parameterization. The present approach is more general, needs no parameterization, and works for arbitrarily many components and phases. The fact that we use essentially the multiphase activity EOS (19) from Section 4 automatically ensures the Gibbs phase rule.

Thus we satisfied the desired properties (i)–(iii). The requirements discussed above still leave very much freedom for detailed modeling. For example, we may make the $\Theta_g$, and $\Sigma_g$ independent of $\pi$ and choose the $D_g$ linear in $\pi$, thus staying within the realm of the assumption of revised scaling. However, this would not be adequate for many real fluids; so more general choices are advisable.

To model vapor-liquid-liquid equilibrium (VLLE), the simpler revised scaling setting is indeed not sufficient. The vapor-liquid equilibrium is described by a coexistence equation relating $\tau$ and $z$, which we may write conceptually in the form $\tau = \tau_{VL}(z)$. The degree of freedom lost by enforcing this coexistence relation reappears as an order parameter specifying the relative proportion of the vapor and liquid phases. Similarly, liquid-liquid equilibrium is described by a coexistence equation $\tau = \tau_{LL}(z)$, and an order parameter specifying the relative proportion of the two liquid phases. When the two coexistence surfaces meet, i.e., if $\tau = \tau_{VL}(z) = \tau_{LL}(z)$, we have exchanged two lost degrees of freedom
by two order parameters specifying the relative proportion of the vapor and the two liquid phases. Now both the VL and the LL branch of the coexistence manifold must satisfy the equation \( \Sigma(\pi, \tau, z) = 0 \). This is possible only if \( \Sigma \) is nonlinear; cf. Anisimov et al. [1]. However, in revised scaling, \( \Sigma \) is independent of \( \pi \), and \( \pi \) is uniquely determined by \( \tau \) and \( z \) [31]. This implies that in revised scaling only two simultaneous phases within the same phase group are possible, which excludes VLLE. However, already allowing \( \Sigma(\pi, \tau, z) \) to be quadratic in \( \pi \) removes this obstacle.

For practical applications, it remains to be seen which particular analytic choices for the scaling fields account for the behavior of mixtures in the whole state space. To be able to fit experimental data, one needs to choose particular forms for the scaling fields \( \Theta \) and \( \Sigma \) and the various coefficient functions. The strong scaling field \( \Sigma_g \) of each group \( g \) of phases is more or less determined by the requirement that it vanishes precisely on the coexistence curve, which allows it to be fitted directly to experimental coexistence data. Constraints for \( \Sigma_f, \Theta_f \) and \( D_f \) for the group \( f \) of fluid phases are obtained by (26) and by matching its \( z = 0 \) expansion to the virial equation of state. Each thermal scaling field \( \Theta_g \) is also constrained by the requirement that \( \Theta_g \) vanishes on the critical manifold. Close to the critical manifold, the universal function \( \Gamma \) is constrained by the known asymptotic results, summarized in [31]. Universality gives further constraints when data for different mixtures are available, as the universal function \( \Gamma \) must be independent of the particular mixture. The freedom remaining must be determined from experimental information. To exploit the available freedom without incurring artifacts due to excessive parameter sensitivity, fitting procedures may make use of all techniques available for the construction of modern, accurate multiparameter equations of state, as reviewed, e.g., in Lemmon & Span [24].

A Axioms for equilibrium thermodynamics

The theory of thermodynamics makes essential use of the concept of convexity. A set \( X \subseteq \mathbb{R}^n \) is called convex if \( tx + (1 - t)y \in X \) for all \( x, y \in X \) and all \( t \in [0, 1] \). A real-valued function \( \Phi \) is called convex on the convex set \( X \subseteq \mathbb{R}^n \) if \( \Phi \) is defined on \( X \) and, for all \( x, y \in X \),

\[
\Phi(tx + (1 - t)y) \leq t\Phi(x) + (1 - t)\Phi(y) \quad \text{for } 0 \leq t \leq 1.
\]

If \( x \) is written explicitly as several arguments (such as \( T, P, \mu \) below), one says that \( \Phi \) is jointly convex in these arguments. Clearly, \( \Phi \) is convex iff for all \( x, y \in X \), the function \( f : [0, 1] \to \mathbb{R} \) defined by

\[
f(t) := \Phi(x + t(y - x))
\]

is convex. It is well-known that, for twice continuously differentiable \( \Phi \), this is the case iff the second derivative \( f''(t) \) is nonnegative for sufficiently small \( t \geq 0 \).

Neumaier [30] shows that the assumptions in the following list of axioms are sufficient to deduce all general results of phenomenological thermodynamics of a single phase, including the extremal principles.
**A.1 Definition. (Phenomenological thermodynamics)**

(i) Temperature $T$ and volume $V$ are positive, entropy $S$ and mole numbers $n_i$ are nonnegative. The **extensive variables** $U, S, V, n_i$ are additive under the composition of disjoint subsystems.

(ii) The **intensive variables** $T, P, \mu$ are related by the **equation of state**

$$\Delta(T, P, \mu) = 0.$$  \hfill (27)

The **system function** $\Delta$ appearing in the equation of state is jointly convex in $T, P, \mu$ and decreasing in $P$. The set of $(T, P, \mu)$ satisfying $T > 0$ and the equation of state is called the **state space**.

(iii) The internal energy $U$ satisfies the **Euler inequality**

$$U \geq TS - PV + \sum_i \mu_i n_i$$  \hfill (28)

for all $(T, P, \mu)$ in the state space.

(iv) **Equilibrium states** have well-defined intensive and extensive variables satisfying equality in (28). A system is in **equilibrium** if it is completely characterized by an equilibrium state.

It is proved in [30] that, as a consequence, in any equilibrium state, the extensive variables are given by

$$S = \Omega \frac{\partial \Delta}{\partial T}(T, P, \mu), \quad V = -\Omega \frac{\partial \Delta}{\partial P}(T, P, \mu), \quad n_i = \Omega \frac{\partial \Delta}{\partial \mu_i}(T, P, \mu),$$  \hfill (29)

and the **Euler equation**

$$U = TS - PV + \sum_i \mu_i n_i,$$  \hfill (30)

the case of equality in (28). Here $\Omega$ is a positive number independent of $T$, $P$, and $\mu$, called the **system size**.

The system function $\Delta$ is not uniquely determined by a thermodynamic system, as multiplication by a nonzero function does not change the equation of state. Within a single phase $s$, this freedom may be used to bring the system equation into the pressure-explicit form

$$\Delta(T, P, \mu) = P_s(T, \mu) - P$$

with a suitable function $P_s(T, \mu)$. In this case, the system size is the volume, $\Omega = V$, and the requirements that $P_s(T, \mu)$ is jointly convex in $(T, \mu)$ and

$$\frac{\partial P_s}{\partial \mu_i}(T, P, \mu) = \frac{n_i}{V} \geq 0$$

are sufficient to satisfy the remaining conditions in the above axioms with the equation of state

$$P = P_s(T, \mu).$$  \hfill (31)
The equation of state for the most stable phases is given by $P = P(T, \mu)$ with the function

$$P(T, \mu) := \max_s P_s(T, \mu),$$

which is automatically convex when all $P_s(T, \mu)$ are convex. The coexistence region consists of the states $(T, \mu)$ for which the maximum is attained for two or more phases $s$ simultaneously.

In terms of the reduced force fields $\pi$, $\tau$, and $z$, (31) is just an activity EOS with

$$\pi(\tau, z) := \frac{\tau}{P_0} P_s(T, \mu), \quad T = \frac{T_0}{\tau}, \quad \mu_i = \frac{RT_0}{\tau} \log \frac{z_i}{c_i(\tau)},$$

(32)

Conversely, one can get from any activity EOS (4) an equation of state $P = P_s(T, \mu)$ with the definition

$$P_s(T, \mu) := \frac{P_0 T}{T_0} \pi(\tau, z), \quad \tau = \frac{T_0}{T}, \quad z_i := c_i(T_0/T)e^{\mu_i/RT},$$

(33)

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