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A Field-Space Conformal Solution Method[1]

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We propose a radical extension of the principle of corresponding states to mixtures. All previous methods of which we are aware are based upon the application of "mixing rules" which are explicit in the compositions of the resultant, or target, mixture. In the present development these relations are functions of field variables alone, specifically the activities of the reference system. This has a profound effect upon the basic machinery of the transformations. For example, when the new method is used to map the properties of a binary fluid mixture onto those of a pure fluid (and in contrast to the description of a mixture by one-fluid theory with van der Waals mixing rules), the dew–bubble-point surface of the mixture is mapped onto the vapor pressure curve of the pure fluid, and the critical line of the mixture is mapped onto the critical point of the pure fluid. Thus, there is no separate "pseudocritical" locus. The principal technical advantage of such a development is numerical; calculation of the location of vapor–liquid coexistence and critical manifolds is enormously simplified. The most important theoretical aspect associated with the new method is that if the reference system is described by an equation of state which obeys the critical scaling laws, then the entire critical manifold of the target system will also exhibit critical scaling.

KEY WORDS: binary mixture; conformal solution; corresponding states; critical phenomena; equation of state; field space; mixtures.

1. INTRODUCTION

In an earlier publication [1], Fox introduced the notion of field-space corresponding-states transformations and proposed this class of thermo-

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dynamic transformations as the basis of a new method for describing the properties of fluid mixtures. In this paper we present two new primitive transformations and construct a "one-fluid" version of the theory; that is, we describe the properties of mixtures through reference to the properties of a pure fluid.

The present development is meant to be directly compared to one-fluid conformal-solution theories of conventional form and, in particular, to the van der Waals one-fluid theory. We demonstrate that the new method can satisfy the simplest useful technical test: to fit the liquid–vapor phase equilibria of some "conformal" binary mixtures.

The motivation for our work comes from a number of diverse considerations; primary among them is an apparent fault in the structure of corresponding-states theories as they are presently implemented. This fault manifests itself when the reference pure fluid or fluids used in the corresponding states description of a mixture is of nonclassical type, i.e., displays scaling behavior in the region around the critical point.

In Fig. 1, the typical mapping between reference pure fluid and target binary mixture is indicated schematically. States on the dew- and bubble-point manifolds of the mixture (here shown at a single representative composition) are mapped by the transformation to states in the one-phase region of the reference fluid's phase diagram. The pure-fluid critical point and the region around it are mapped by the reverse transformation into the physically inaccessible interior of the mixture two-phase region. Thus the

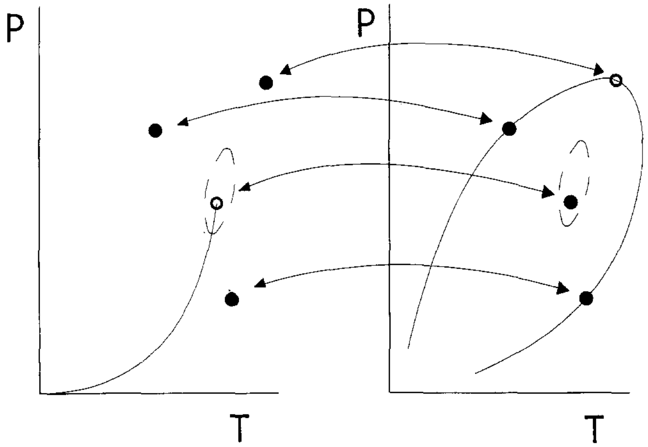

Fig. 1. Mapping of states between pure-fluid reference system and target mixture (shown at one representative composition). All dew- and bubble-state points, including the critical point of the mixture, are mapped into the one-phase region of the pure-fluid reference system.

peculiar scaling behavior of thermodynamic quantities in the neighborhood of the critical point of a pure fluid will certainly not be reflected as an appropriate mixture critical scaling behavior. In fact the nonclassical aspect of the reference system is, excepting certain special cases, completely lost, and thermodynamic behavior near the critical line of the mixture is entirely classical.

A further and related difficulty involved in this marriage of nonclassical and corresponding-states structures is apparent when one considers the predicted shape of the critical line (in the case of a binary mixture) in the dilute regime approaching the critical point of one of the component pure fluids. As Levelt Sengers *et al.* have shown [2], the termination of a classical critical line upon a pure-fluid critical point, described by this structure to be fully nonclassical, results in an anomalous shape for that critical line which stands in sharp contrast to the experimental evidence. Levelt Sengers *et al.* predict that this anomaly will occur even when the reference system is classical, provided that the behavior in the critical region is sufficiently like that of a scaling-law system.

We deduce that these difficulties stem from the structure of the corresponding-states transformation, relying in part upon the existence of a separate body of theory which yields a transformation mechanism free of these problems. We refer to this second class of transformations as "field-space corresponding-states" transformations.

The mapping of target mixture states onto pure-fluid reference states characteristic of a field-space one-fluid transformation is indicated schematically in Fig. 2. In this case the states along the dew- and bubble-point curves (shown again at a representative constant-composition section of the mixture) map onto the vapor-pressure curve of the pure fluid, and the critical point of the mixture maps onto the critical point of the pure fluid. A region around the critical point of the pure fluid is mapped by the reverse transformation into a region of one-phase points about the critical point of the mixture. Clearly, in this type of mapping, the scaling behavior of a nonclassical pure-fluid reference system will be manifested, in some form, near the critical line of the mixture.

The principal defining property that we associate with field-space transformations is that the fields of the target system are smooth (analytic) and convexity-preserving functions of the independent fields of the reference system. The term "fields" is used, in the sense introduced by Griffiths and Wheeler [3], to mean those intensive thermodynamic variables which are always equal in coexisting phases, such as the pressure, temperature, chemical potentials, and activities. The remainder of the intensive variables, for example, the molar densities, the entropy density, and the molar energy, are called "densities" and may be recognized as

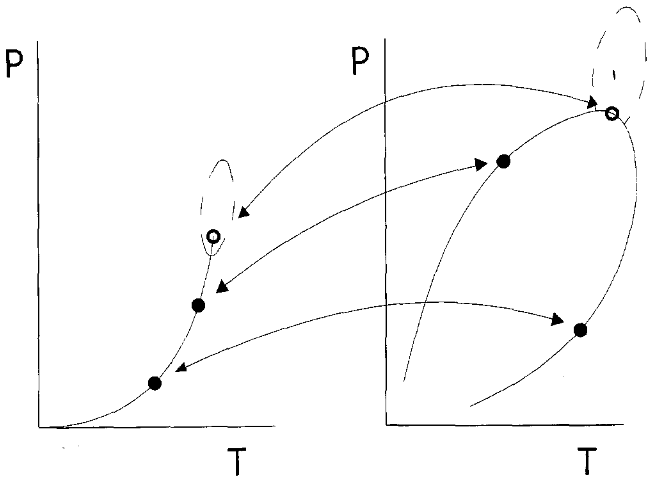

Fig. 2. Mapping characteristic of a field-space transformation. The critical point (line) of the mixture is mapped onto the critical point of the reference pure fluid and the dew–bubble curve (surface) is mapped onto the pure fluid vapor–pressure curve.

ratios of extensive quantities, and therefore generally take different values in coexisting phases. By "convexity preserving" we mean that the thermodynamic stability of a state point of the reference system, which may be expressed mathematically as convexity relations among the field variables, is preserved at the transformed point in the target system.

As indicated in Ref. 1 there are a number of exact calculations in statistical mechanics that result in transformations of the field-space type and also describe mixtures in terms of pure-fluid reference systems. The primary examples are the decorated lattice-gas transformations [4, 5] which, in some implementations, map the properties of energetically simple fluid mixtures onto the properties of the one-component lattice gas or Ising model.

By purely thermodynamic construction, Leung and Griffiths [6] have developed a field-space "two-fluid" model; that is, the mixture properties are smoothly interpolated from a reference system composed of fitted fundamental equations for each of the pure fluid components. Moldover and Gallagher [7] and, more recently, Rainwater et al. [8, 9] have used flexible modifications of this model to correlate the liquid–vapor equilibria of a large number of binary mixtures in a range from about half of the critical pressure of the more volatile component up to the critical line. This model, which has always been used with nonclassical reference functions, has proved to be a very valuable vehicle for the elucidation of nonclassical critical effects in mixtures. The primary limitation of the Leung–Griffiths model is that it takes the form of an expansion about the critical line of the mixture and therefore can describe only a part of the phase diagram.

While we think that neither the decorated lattice-gas calculations nor the Leung–Griffiths approach can be generalized into an acceptable replacement theory for the van der Waals one-fluid theory and its derivatives, the fact of an exact calculation in the one case and apparently excellent correlative ability in the other have encouraged us to pursue a separate path toward a field-space transform method.

2. ONE-FLUID FIELD-SPACE TRANSFORM

Two pure fluids are said to be conformal if their interparticle potential functions differ only by two scale factors, one a ratio of potential energies and the other a ratio of interaction lengths. A statistical-mechanical treatment [10] (which invokes the usual approximation of independent degrees of freedom) shows that volumetric behavior of one of the fluids may be expressed through reference only to the volumetric behavior of the other fluid.This is typically expressed as a relation between pressures,

$$p'(\rho', T') = (f/h)\, p(\rho, T); \qquad \rho = h\rho'; \qquad T = T'/f \tag{1}$$

where p' is the pressure, T' the temperature, and ρ' the molar density of the "target" fluid. These quantities are expressed as functions of the "reference" fluid pressure p, temperature T, density ρ, and constant scale factors f and h.

The expressions for a binary mixture, in the one-fluid form of the conformal solution theory, are

$$p'(\rho_1', \rho_2', T') = (f/h)\, p(\rho/T); \quad \rho = h(\rho_1' + \rho_2') = h\rho'; \quad T = T'/f \tag{2}$$

where p' is now the pressure, ρ_1' and ρ_2' are the component molar densities of the target mixture, and the scale factors f and h are simple functions of $x_1' = \rho_1'/(\rho_1' + \rho_2')$. Various approximations have been used to specify the forms of f and h; Ref. 11 provides a review of popular forms. This structure embodies the idea of van der Waals that a binary mixture at constant composition has the properties of a pure fluid.

In the case of the field-space variant of the same theory, the equivalent expressions are

$$p'(z_1', z_2', T') = (f/h)\, p(z, T); \qquad z = z_1' + z_2'; \qquad T = T'/f \tag{3}$$

where z is the activity of the pure fluid, and z_1' and z_2' are the activities of the components of the binary mixture. The scale factors f and h are simple functions of $\eta \equiv z'_1/(z'_1 + z'_2)$. This form embodies the hypothesis of Griffiths and Wheeler [3] that a binary mixture at a constant field (for example, at constant η) has the properties of a pure fluid.

In order to calculate the target densities it is convenient to introduce the Gibbs–Duhem equation appropriate to this choice of variables:

$$dp = \left(\frac{p+\varepsilon}{T}\right) dT + RT \sum_{i=1}^{m} \frac{\rho_i}{z_i} dz_i \tag{4}$$

where ε is the internal energy density U/V, m the number of chemical components, and R the gas constant. The calculation of target molar densities ρ_1 and ρ_2 proceeds directly from their definitions:

$$\begin{aligned}
\rho'_1 &\equiv \frac{z'_1}{RT'}\left(\frac{\partial p'}{\partial z'_1}\right)_{z'_2, T'} = \frac{z'_1}{RT'}\left(\frac{\partial (fp/h)}{\partial z'_1}\right)_{z'_2, T'} \\
&= \frac{z'_1}{RT'}\left\{\frac{p}{h}\left(\frac{\partial f}{\partial z'_1}\right)_{z'_2} - \frac{fp}{h^2}\left(\frac{\partial h}{\partial z'_1}\right)_{z'_2}\right. \\
&\quad \left. + \frac{f}{h}\left[\left(\frac{\partial p}{\partial z}\right)_T \left(\frac{\partial z}{\partial z'_1}\right)_{z'_2} + \left(\frac{\partial p}{\partial T}\right)_z \left(\frac{\partial T}{\partial z'_1}\right)_{z'_2, T'}\right]\right\} \\
&= \frac{z'_1}{RT'}\left\{\frac{p}{h}\left(\frac{\partial f}{\partial z'_1}\right)_{z'_2} - \frac{fp}{h^2}\left(\frac{\partial h}{\partial z'_1}\right)_{z'_2}\right. \\
&\quad \left. + \frac{f}{h}\left[\frac{\rho RT}{z} - \frac{T'}{f^2}\left(\frac{p+\varepsilon}{T}\right)\left(\frac{\partial f}{\partial z'_1}\right)_{z'_2}\right]\right\}
\end{aligned} \tag{5}$$

If we define $f_\eta \equiv df/d\eta$ and $h_\eta \equiv dh/d\eta$, the resulting expression for the density is

$$\rho'_1 = \frac{1}{h}\left\{\eta\rho - \left[\frac{p}{RT}\frac{h_\eta}{h} + \frac{\varepsilon}{RT}\frac{f_\eta}{f}\right](\eta - \eta^2)\right\} \tag{6}$$

A similar calculation for ρ'_2 yields

$$\rho'_2 = \frac{1}{h}\left\{(1-\eta)\rho + \left[\frac{p}{RT}\frac{h_\eta}{h} + \frac{\varepsilon}{RT}\frac{f_\eta}{f}\right](\eta - \eta^2)\right\} \tag{7}$$

and thus the total density of the target system is

$$\rho' = \rho'_1 + \rho'_2 = \rho/h \tag{8}$$

The relation for the target composition variable x'_1 is then

$$x'_1 = \frac{\rho'_1}{\rho'} = \eta - \left[\frac{p}{\rho RT}\frac{h_\eta}{h} + \frac{u}{RT}\frac{f_\eta}{f}\right](\eta - \eta^2) \tag{9}$$

where u is the molar internal energy U/n of the reference system. The remaining independent density, the internal energy density, is also easily calculated:

$$\left(\frac{p'+\varepsilon'}{T'}\right) \equiv \left(\frac{\partial p'}{\partial T'}\right)_{z'_1, z'_2} = \left(\frac{\partial (fp/h)}{\partial (fT)}\right)_{z'_1, z'_2}$$

$$= \frac{1}{h}\left(\frac{\partial p}{\partial T}\right)_z = \frac{1}{h}\left(\frac{p+\varepsilon}{T}\right) \tag{10}$$

$$\Rightarrow \varepsilon' = \frac{f}{h}\varepsilon \Rightarrow \frac{u'}{RT'} = \frac{u}{RT} \tag{11}$$

3. IMPLEMENTATION WITH A CUBIC EQUATION OF STATE

The primary technical application for a one-fluid theory is in the correlation, and ultimately in the prediction, of liquid–vapor equilibria in mixtures. Fortunately, it is also in that application that the field-space transformations, due to their structure, develop important advantages over conventional methods. As is perhaps clear from the mapping indicated in Fig. 2, the method describes all mixture phase equilibria through reference to the properties of a pure fluid along its vapor pressure curve. Hence only a correlation or tabulation of certain saturation properties of the reference system is required, rather than a complete description of the one-phase region, as is the usual case. Second, since all the reference states lie on a one-dimensional manifold, rather than on a two-dimensional manifold as in the conventional theory, many types of numerical calculations, which involve searching for solutions over states of the reference system, can in principle be much simpler in the field-space case. The location of the critical line is made particularly simple since it maps to a single reference state.

These advantages would be lost, however, if no implementation of the method which correlates mixtures of interest could be found. In this section, we show for the functions $f(\eta)$ and $h(\eta)$ preliminary choices which involve one adjustable parameter. We find it necessary to introduce a second adjustable mixture parameter elsewhere. We choose for a reference system the Berthelot equation of state, together with a compatible choice for the molar energy. We regard the Berthelot form as the simplest equation of state with an acceptable vapor pressure curve; it is

$$p = \frac{\rho RT}{1-\rho b} - \frac{a}{T}\rho^2 \tag{12}$$

$$u = CRT - \int_0^{\rho} \left[T\left(\frac{\partial p}{\partial T}\right)_{\rho} - p \right] \frac{d\rho}{\rho^2} = CRT - \frac{2a\rho}{T} \tag{13}$$

where a, b, and C are constants. We choose for the functions $f(\eta)$ and $h(\eta)$ the inverse polynomials

$$f(\eta) = (f_0 + f_1\eta)^{-1} \tag{14}$$

$$h(\eta) = (h_0 + h_1\eta + h_2\eta^2)^{-1} \tag{15}$$

with the h_i and the f_i all constants. Since a and b may be adjusted to fit the Berthelot critical pressure and temperature to those of the pure fluid 2, the constants f_0 and h_0 are redundant and we set them equal to 1. Two additional constants (the sums $1 + h_1 + h_2$ and $1 + f_1$) are fixed by constraining the other end of the critical line to terminate at the critical temperature and pressure of pure component 1. That leaves only the heat-capacity-like parameter C and the binary-interaction parameter h_2 as free parameters to be determined by the properties of the mixture. The shape of the critical line in the pressure–temperature plane is determined by h_2, with $h_2 = 0$ a straight line.

Figures 3, 4, and 5 are fits of the dew–bubble surface, in the $p - T - x$ space, of n-butane + n-pentane, n-butane + n-hexane, and n-butane + n-octane, respectively. The experimental data are from the work of Kay et al. [12, 13]. In a companion paper [14] we test the effect of using improved reference equations of state and show the density behavior of these same systems.

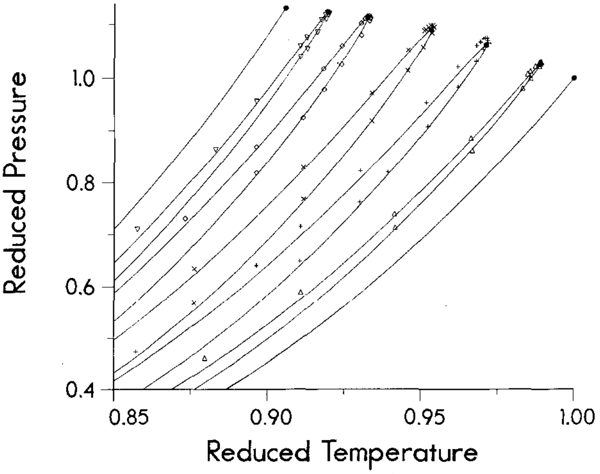

Fig. 3. The pTx diagram for the system n-butane + n-pentane fitted with the parameters $h_2 = -0.104$ and $C = 4.3$. The data are reduced by the critical pressure and temperature of the component with higher critical temperature (in our notation, component 2).

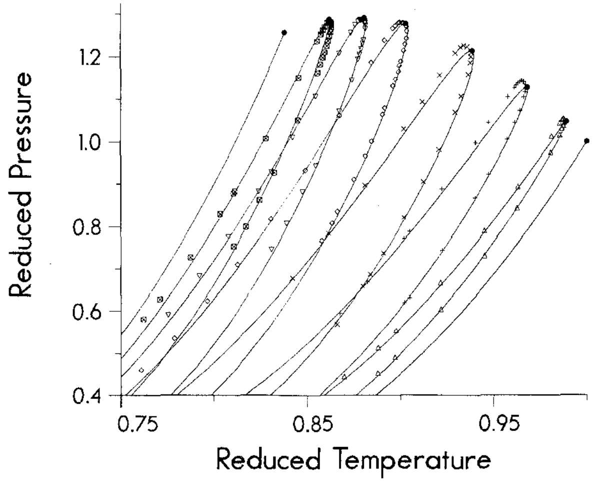

Fig. 4. The pTx diagram for the system n-butane + n-hexane fitted with the parameters $h_2 = -0.55$ and $C = 4.95$.

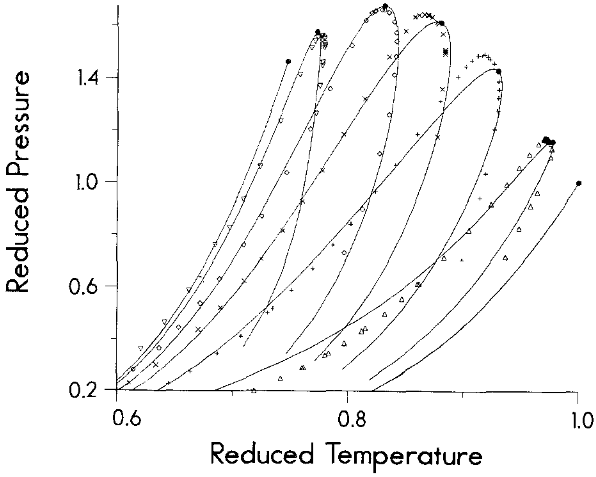

Fig. 5. The pTx diagram for the system n-butane + n-octane fitted with the parameters $h_2 = -1.842$ and $C = 5.1$.

4. CONCLUDING DISCUSSION AND FUTURE DIRECTION

The transformation method we have presented in this report may be useful in high-pressure liquid–vapor equilibrium calculations in its present form, but we hope to significantly improve it in the near-future. While we have concentrated here on implementation and application of the method, there are still a number of theoretical questions regarding the structure of the transformation which ultimately must be addressed. Readers familiar with the statistical-mechanical basis of the conformal solution theory will no doubt be disturbed at the presence of the ideal-gas heat capacity parameter C in our definition of the internal energy, since it is not a configurational property. It is, however, an important fitting parameter, and although we might have contrived to hide its relationship with the energy in various ways, we cannot now do reasonable fitting without it. During the preparation of this report, we discovered that if the relationship between reference and target activities is defined as $z = h(z'_1 + z'_2)$ instead of the form we have been using, a number of annoying problems with the low-density limit disappear. It will certainly be important to implement this form of the transformation, and we hope to be able to do so using only the configurational properties of the reference system.

The principal technical problem is the failure to predict accurately liquid densities, as indicated in the companion paper [14]. This problem is probably due to the transformation structure rather than to our implementation, with the fact that the critical compressibility factor is constrained to be constant along the entire critical line being a related symptom. We believe that this problem can be corrected using a version of the background-transformation technique developed in Ref. 1.

The thermodynamic transformation introduced in this report may be decomposed into two primitive transformations; one scales the temperature, and the other scales the pressure-temperature ratio. The total transformation is then constructed by serially applying the primitive transformations in either order (that is, they are commutative). Reference 1 introduced six other primitive transformations. We think that this factoring into primitives may be the most useful way to both use and develop these methods, and we plan to follow this approach in our future work.

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REFERENCES

1. J. R. Fox, *Fluid Phase Equil.* **37**:123 (1987).
2. J. M. H. Levent Sengers, R. F. Chang, and G. Morrison, in *Equations of State—Theories and Applications,* ACS Symposium Series 300, K. C. Chao and R. L. Robinson, eds. (1986), Chap. 5.
3. R. B. Griffiths and J. C. Wheeler, *Phys. Rev.* **A2**:1047 (1970).
4. J. C. Wheeler, *Annu. Rev. Phys. Chem.* **28**:411 (1977).
5. G. R. Andersen and J. C. Wheeler, *J. Chem. Phys.* **70**:1326 (1979).
6. S. S. Leung and R. B. Griffiths, *Phys. Rev. A* **8**:2670 (1973).
7. M. R. Moldover and J. S. Gallagher, *AIChE J.* **24**:267 (1978).
8. J. C. Rainwater and F. R. Williamson, *Int. J. Thermophys.* **7**:65 (1986).
9. J. C. Rainwater and R. T. Jacobsen, *Cryogenics* **28**:22 (1988).
10. J. S. Rowlinson and I. D. Watson, *Chem. Eng. Sci.* **24**:1565 (1969).
11. G. A. Mansoori, in *Equations of State—Theories and Applications,* ACS Symposium Series 300, K. C. Chao and R. L. Robinson, eds. (1986), Chap. 15.
12. R. L. Hoffman, M.S. thesis (Ohio State University, 1962); O. L. Davies, M.S. thesis (Ohio State University, 1962). Most of the data appeared in W. B. Kay, R. L. Hoffman, and O. L. Davies, *J. Chem. Eng. Data* **20**:333 (1975).
13. D. A. Fichtner, M.S. thesis, (Ohio State University, 1962). Most of the data appeared in W. B. Kay, J. Genco, and D. A. Fichtner, *J. Chem. Eng. Data* **19**:275 (1974).
14. T. S. Storvick and J. R. Fox, *Int. J. Thermophys.* **11**:61 (1990).