Journal of Statistical Physics, Vol. 66, Nos. 3/4, 1992

Evaluation and Comparison of Critical Lines for Various Models of Gas–Liquid Binary Systems

Mustafa Keskin,[1] Mustafa Gençaslan,[1] and Paul H. E. Meijer[2]

Received November 23, 1990; final August 30, 1991

Critical lines of a two-component gas–liquid system can be plotted as a function of temperature and pressure, as is usually done with experimental results, and also as a function of the density coordinates. In the latter representation the mathematical double points can be found with higher precision. The existence of such a point depends on the values of the energy parameters, and the locus of these parameter values giving rise to double points maps the boundary between the different kinds of phase diagram. We show how the double point, which in the case of the lattice gas is due to an accidental symmetry, can be regained in various other, less symmetrical models by adjustment of the interaction parameters.

KEY WORDS: Binary systems; gas–liquid systems; Tompa model; lattice gas; van der Waals equation.

1. INTRODUCTION

The critical lines for a two-component system form the infrastructure for the complete phase behavior (i.e., the equation of state, its regions of coexisting phases, the tricritical points, etc.) of the binary gas–liquid systems for each given set of the interaction parameters. Critical lines refer to the locus of critical points. These lines can be used to find impending gas–liquid, liquid–gas, or even gas–gas separations, as well as intermediate states of the above. The critical lines have segments that are actually unstable, and hence do not represent physically observable states, since

[1] Physics Department, Erciyes University, 38039 Kayseri, Turkey.
[2] Physics Department, Catholic University of America, Washington, D.C. 20064.

0022-4715/92/0200-0885$06.50/0

systems go into a three-phase state which usually lies close to the unstable critical line coordinates. We do not take this option into account, except in the calculations done in the last two cases, where we indicate at what point the critical line will become unstable.

For each set of energy parameters, i.e., for each point in the master diagram, one finds a different structure of critical lines. Each kind of phase diagram, as classified by the connectivities of the phase lines, corresponds to a given area in the master diagram. The boundaries between these regions can be found by looking for the existence of double points in the critical line diagram, that is, if a double point occurs in the critical line diagram, the corresponding energy parameters represent a point in the master diagram which is a boundary point between two regions. This procedure is trivial for the lattice gas, since this model has a very high "accidental" symmetry. This is also true, but to a lesser extent, for the extended Tompa model as described below. In the more general cases we show how the double points can be established by trial and error. It is of great practical importance that these adjustment are done in the density–density diagram, since the branches that form the double points in the p–T diagrams are all tangent to each other, which makes the point less visible in these plots.

The variety of critical lines plotted in density space have in common that, provided the unstable parts are also incorporated, they all have four rather trivial "anchor" points.[1] In exceptional cases there may be additional closed loops.[2] The anchor points are: (1) the critical point of the pure 1 component, (2) the critical point of the pure 2 component, (3) the critical point associated with jamming, and (4) the unstable point at zero temperature. The various ways to connect these points together make up the ensemble of critical lines for each given set of interaction parameter values. Density space consists of a two-dimensional plot using the coordinates x_1 and x_2, the density of component one (resp. two) as a fraction of the volume occupied. Since $0 < x_1 < 1$ and $0 < x_2 < 1$ as well as $(x_1 + x_2) < 1$, the allowed values for the coordinates lie inside a triangle. It is convenient to introduce a third coordinate: $x_0 = 1 - x_1 - x_2$, which, in the case of the lattice gas, can be interpreted as the density of the unoccupied sites: the holes.

To illustrate what we have in mind, consider the possible connection between the following four anchor points on the border of the triangle: C_1, the critical point of the pure 1 system (coordinates $x_1 \neq 0$, $x_2 = 0$); C_2, the critical point of the pure 2 system (coordinates $x_1 = 0$, $x_2 \neq 0$); C_0, the critical point of the jammed system $(x_1 + x_2 = 1)$; and the unstable critical point C_u $(x_1 = x_2 = 0)$. These four points may be connected in two different ways: C_1 connected to C_2 and C_0 to C_u, called type II by Scott and van

Konynenburg,[3] or one might connect C_1 to C_2 and C_2 to C_0 as in type III. The two remaining corners ($x_1 = 0$, $x_2 = 1$ and $x_1 = 1$, $x_2 = 0$) are connected with each other by an entirely unstable line and hence are ignored in this example. Under special circumstances, i.e., certain combinations of energy parameter values, all these four anchor points are connected to a vertex which is a double point (DP). We call this the van Laar point[4] if the double point is also a tricritical point. In the case of a lattice gas such DPs are easy to find; they occur when two of the three energy parameters are equal.

Projecting the x_1, x_2 critical lines as a p–T plot can be done in two different ways, depending on the choice of coordinates for the holes. Returning to the special case that two energy parameters are equal, we may associate the holes with the unequal energy parameter, which leads to a symmetric p–T plot, or we may associate the unequal parameter with one of the two components. In this case we deal with the permuted symmetric case. In the first case the points C_1 and C_2 coincide; in the second case one of the critical temperatures is equal to the critical temperature at which the pressure goes to infinity. We let C_2 correspond to C_0 and C_1 to the weak interaction, since this label refers traditionally to the solvent molecules. The second case was dealt with by Schouten *et al.*[5] As shown in the work of Furman and Griffiths,[6] the van der Waals equation is in most cases rather close to the symmetric permuted case. We refer to Fig. 9 in Furman and Griffiths' paper.[6] This is also seen near the van Laar point.[7] If one "deforms" the van der Waals case back into the lattice gas, the points 0, 0 and 0, 1 become interchangeable if the energies of the second particle (U_2) and of the holes (U_0) are equal. In this case one branch of the critical line is a straight line from C_2 (now at 0, 1/2) to the point C_u and we obtain the permuted lattice gas. In the van Laar case this line is almost straight from C_2 at (0, 1/3) to C_u at (1, 0). We show elsewhere that this branch cannot be factorized out as is the case in the lattice gas.

Since the coordinates in the master diagram that give rise to a double point in the critical line structure play the role of separators between the different types, we illustrate how these points can be established through adjustment of parameters in a number of models different from the simple lattice gas: the extended Tompa model, the intermediate model (intermediate between the lattice gas and the van der Waals equation for binary mixtures), and a combination of the Tompa model and van der Waals equation.

The Tompa modification of the lattice gas[8] reverts to the Flory–Huggins model for chain molecules[9] if one deals with solvent and solute only, i.e., if the holes are ignored. Although the parameter N (the number of links in the chain molecule) was supposed to be very large in the original

application of the model, we employ this parameter to express the difference in size of the molecules of each component of the mixture; hence, values in the neighborhood of one will be used.

2. CALCULATION OF THE CRITICAL LINES

The free energy per unit volume V_0 of the generalized lattice gas is given by[10]

$$\frac{F}{V_0} = -(w_1 x_1^2 + w_{12} x_1 x_2 + w_2 x_2^2) - \mu_1 x_1 - \mu_2 x_2 + T\left[x_1 \ln x_1 + \frac{x_2}{N} \ln x_2 + (x_0 - \sigma) \ln x_0 \right] \tag{1}$$

where T is the temperature, σ is a parameter ($\sigma = 0$ given the lattice gas and $\sigma = 1$ the van der Waals binary mixture equation), and N is an another parameter which expresses the "length" of the second type of molecule with respect to the first. The remaining variables are the chemical potentials μ_1 and μ_2, the energy interaction parameters between like molecules w_1 and w_2, the interaction between different types of molecules w_{12}, and the density x_1 and x_2 of species of type 1 and type 2, respectively.

The total density is given by $\rho = x_1 + x_2$ and the concentration by $c = x_2/(x_1 + x_2)$. The resulting equation of state is

$$pV_0 + w_1 x_1^2 + w_{12} x_1 x_2 + w_2 x^2 = T\left[(\sigma - 1) \ln x_0 + \frac{x_1 + x_2}{x_0} \sigma + \frac{x_2}{N} - x_2 \right] \tag{2}$$

where V_0 is a constant which describes the volume occupied by a molecule of type 1. The volume occupied by a molecule of type 2 is approximately NV_0.

In order to obtain the critical line, the second and third derivatives of the free energy with respect to x_1 and x_2 are needed to calculate the density derivatives at constant concentration. The condition for the limit of stability in the coexisting phases is given by the Hessian:

$$\alpha_1 \alpha_0 + \alpha_2 \alpha_0 + \alpha_1 \alpha_2 = 0 \tag{3}$$

with

$$\alpha_1 = T/x_1 - U_1 \tag{4a}$$

$$\alpha_2 = T/Nx_2 - U_2 \tag{4b}$$

$$\alpha_0 = [(1 + \sigma/x_0)/x_0]\, T - U_0 \tag{4c}$$

with

$$U_1 = 2w_1 - w_{12}, \qquad U_2 = 2w_2 - w_{12}, \qquad U_0 = w_{12}$$

The coordinate $x_0 = 1 - x_1 - x_2$ represents the holes in the case of the lattice gas ($\sigma = 0$); otherwise it is just a coordinate of convenience. If, in addition, $N = 1$, the model is permutationally symmetric. Note that the spinodal can be expressed as $T(x_1, x_2)$, where the spinodal temperature is the solution of the second-order equation (3). Often, but not always, one root leads to a negative temperature. The next higher derivative at constant T can be expressed either in a symmetrical way[10,11] or directly as follows:

$$\chi = s_1'(\alpha_2 + \alpha_0) + s_2'(\alpha_1 + \alpha_0)\,\alpha_1 - s_0'(\alpha_1 + \alpha_2)^2 \tag{5}$$

which has the practical advantage that the resulting expression is again of the second order in the temperature. s_i stands for the second derivatives of the entropy with respect to the corresponding variables:

$$s_1 = 1/x_1; \qquad s_2 = 1/Nx_1; \qquad s_0 = (1 + \sigma/x_0)/x_0 \tag{5'}$$

From the above equations we can establish the critical line as follows: Eq. (3) expresses the spinodal temperature as function of x_1 and x_2 for each given set of parameters U_1, U_2, and U_0, since x_0 is determined by x_1 and x_2. This temperature is inserted in Eq. (5), which depends on T, x_1, and x_2. In other words, solving (3) and (5), i.e., eliminating the temperature T, leads to a curve in x_1 and x_2 space for given set of values of the energy parameters. Although it is possible, after a considerable number of algebraic manipulations, to obtain a polynomial in x_1 and x_2 for the critical line, our results were obtained by a numerical solution of the above equations using the program of the CMLIB of the NIST (the National Institute of Standards and Technology) which were transported on the tape to the Data General machine at Erciyes University in Kayseri. The subroutine used was called SNLS1E or SNSQE.

After the critical line was established as a function of x_1 and x_2, the data were translated into pressure and temperature values using Eqs. (3) and (2). Some sections of these critical lines may be unstable and are indicated by dashed lines in the figures.

3. RESULTS

The results are given in three groups of figures. Figures 1–4 are used to discuss the pure lattice gas for energy parameters at, and near, the double point. The first two figures show the need for permutation, the last

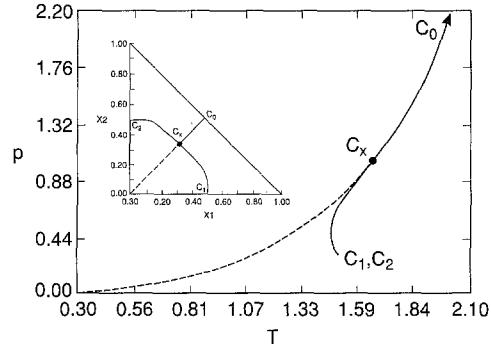

Fig. 1. Critical pressure p as a function of the critical temperature T for a lattice gas with equal energy parameters: $w_1 = w_2 = 3$ and $w_0 = 5$. The insert is the corresponding x_1–x_2 plot. C_x is the double point.

two show the effect of small deviations. The second set, Figs. 5–6, describes the result of symmetry breaking of the lattice gas model, spectacular in the unpermuted case, less spectacular in the permuted case. Figs. 7–9 show the existence of double points for two different "mixed" models: Fig. 7 shows an intermediate model between the lattice gas and the van der Waals equation for binary liquids, and Figs. 8 and 9 are used to compare the van Laar double point with the double point obtained in a mixed Tompa–van der Waals model.

Figure 1 gives the p–T critical line for the lattice gas with symmetrical parameters: $w_1 = w_2 = 3$, $w_0 = 5$ ($w_0 = w_1 + w_2 - w_{12}$). At the crossing point C_x the four branches C_x–C_0, C_x–C_1, C_x–C_2, and C_x–C_u meet and have a common tangent. The branches C_x–C_1 and C_x–C_2 coincide. The branch C_x–C_0 has a vertical tangent at $T = 2.5$, which corresponds to the critical

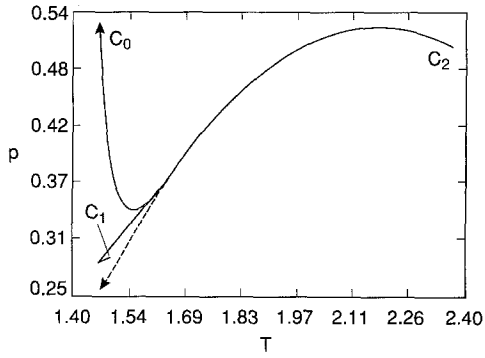

Fig. 2. Same energy parameters as in Fig. 1 with permutation of x_2 into x_0: $w_1 = w_0 = 3$ and $w_2 = 5$.

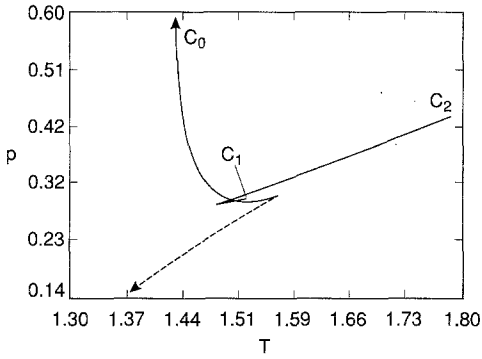

Fig. 3. Disappearance of the double point through modified energy parameters: $w_1 = 3 + \Delta$, $w_2 = 5$, and $w_0 = 3 - \Delta$, with $\Delta = 0.05$.

point of consolution for the fully occupied lattice (jamming). In this particular model the double point is also a tricritical point. This is due to the symmetry of the model[12] and this property usually disappears when the symmetry is broken.

The same data for x_1 and x_2 are used to plot Fig. 2, but the coordinate x_2 is permuted with $x_0 = 1 - x_1 - x_2$. This case corresponds to the calculations performed by Schouten *et al.*[5]. The resulting figure shows the same behavior; C_1 and C_0 (formerly C_2) are separated in pressure, but remain almost at the same temperature $T = 1.5$. Compared to experimental plots of this type, the lattice gas has the drawback that the critical pressure p_2 lies much higher than the critical pressure p_1, which is not always the case; they may be more or less equal, sometimes even reversed in order. The permuted symmetric case is somewhat similar to the van der Waals case at the van Laar point, as found by Deiters and Pegg,[13] as referred to by Meijer.[14]

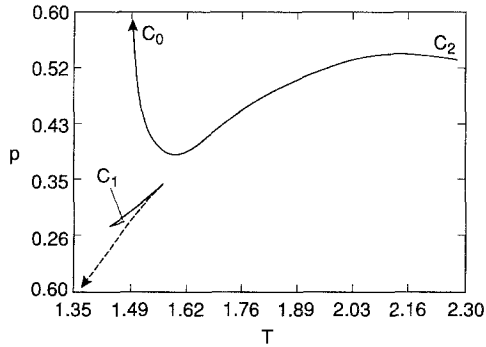

Fig. 4. Change in connectivity if $\Delta = -0.05$.

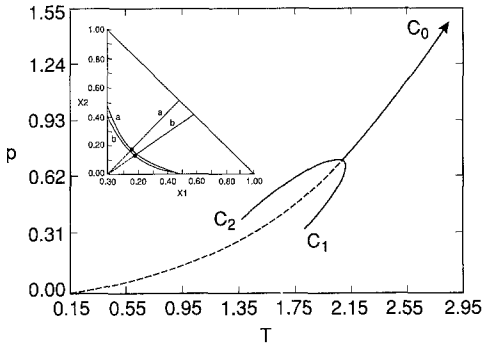

Fig. 5. Symmetry breaking of case 1, due to $N \neq 1$: Tompa model with $N = 2$: $w_1 = 3.656854$, $w_2 = 2.0$, and $w_0 = 9.656854$. Insert contains the corresponding x_1–x_2 plots: (a) for $N = 1$; (b) for $N = 2$.

Slightly unequal values of the parameters w_1 and w_0 lead to figures in which the branches are disconnected. Depending on the sign of the deviation, the unstable point C_u may be connected with C_0 (Fig. 3) or with C_1 (Fig. 4). In both cases, the cusp which was originally situated at the tricritical point remains, but no longer coincides with the other branch. It can be shown that this cusp is the point at which the critical line becomes either metastable or stable, depending on nonlocal conditions. The secondary cusp near C_1 is not associated with this transition; it is purely due to the projection and disappears for different values of the energy parameters. Also, the crossing of the lines in Fig. 3 is due to the projection; these points belong to different densities and concentrations. As explained in ref. 15, the relation between Fig. 3 and Fig. 4 is easy to see if an x_1–x_2 plot is used. For equal parameters the double point is a true crossing point

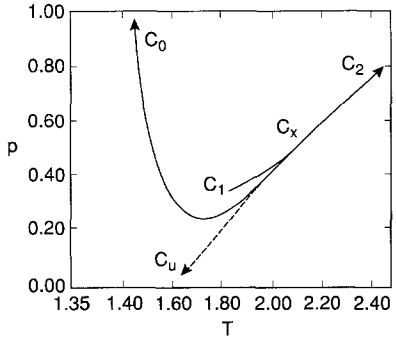

Fig. 6. Tompa model with permutation: $N = 2$; $w_1 = 3.656854$, $w_2 = 9.656854$, and $w_0 = 2.0$.

and is also a tricritical point, and any deviation from equality that makes this point breaks open.

We will now discuss various other ways in which the symmetry of the lattices gas can be broken, aside from introducing unequal energy parameters. They are: the Tompa model, the intermediate van der Waals model, and a combination of these two.

The coincidence of C_1 and C_2 in Fig. 1 can be lifted by introducing a value of $N>1$ (Tompa model), as is shown in Fig. 5. The insert shows the corresponding x_1–x_2 curve (labeled b). No permutation was used in this figure. The crossing point is again a true double point, as shown,[16] but no longer a tricritical point. The crossing point for the lattice gas ($N=1$ and $\sigma=0$) occurs when two of the energy parameters, for instance, w_1 and w_2, are equal, which implies $U_1=U_2$. In ref. 1 it was shown that the crossing point remains present when $U_1=N^{1/2}U_2$ in the Tompa model. We now will use $w_1=2(2\sqrt{N}-1)$, $w_2=2$, and $w_0=4(\sqrt{N}+1)$, with $N=2$. For $N=1$ this corresponds to case d of Fig. 1 of ref. 1 ($w_1=w_2=2$, $w_0=8$) and this critical line is shown as curve a in the insert. This is different from the choice used in Fig. 1: $w_1=w_2=3$, $w_0=5$; the general shape of the $N=1$ figures is rather similar. Not surprisingly, the $N\neq 1$ looks drastically different. The dependence of $T(C_2)$ on N is given in the Appendix; $T(C_1)$ remains the same: $w_1/2$. Higher values of N will fold the curve between C_1 and C_2 more and more open.

The permuted Tompa model leads to p–T plots given in Fig. 6. The crossing point C_x is connected to C_1, C_2, and C_u as was the case in Fig. 1, but the branch towards C_0 goes through a deeper minimum, which eventually, for larger values of N, leads to a negative pressure.

A different variation on the lattice model is the intermediate model used for Fig. 7. Intermediate means a value for σ in Eq. (1) between the

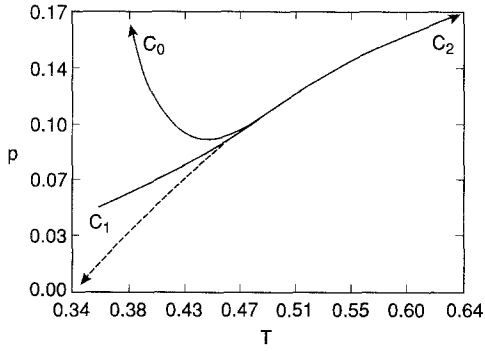

Fig. 7. Intermediate model under double point conditions: $N=1$, $\sigma=0.5$; $w_1=1.0$, $w_2=3.234549$, and $w_0=0.637579$.

lattice gas value ($\sigma = 0$) and the van der Waals value ($\sigma = 1$). In the last case the four branches of the critical lines meet each other if the van Laar condition is fulfilled (the van Laar point is a specific point in energy space[13]). If σ is lowered and the energy parameters are kept the same, the branches will disconnect. For $\sigma = 1/2$ we adjusted the energy parameter w_2 so that crossing is obtained again. The value for Δw which makes the crossing point reappear was taken from Fig. 6b in ref. 1 to be 0.35625. The resulting p–T plot in this case looks rather similar to the plot of the lattice gas in Fig. 2. However, the crossing point is no longer necessarily a tricritical point.

Finally, we combined the Tompa model with the van der Waals equation near the van Laar point. The idea for using the Tompa model is that for $N \neq 1$ the model expresses the unequal size of the molecules. The energy parameters corresponding to the van Laar point in the master diagram of the van der Waals equation lead to a critical line structure with a double point that is at the same time a tricritical point, as shown in ref. 1. In the same paper it was illustrated that a small deviation from zero of the k factor, as given in $w_{12} = 2(1-k)(w_1 w_2)^{1/2}$, leads to an opening up of the double point (ref. 1, Fig. 6).

Starting again with the van Laar condition as given in ref. 12, we now introduce $N = 1.05$ and find, as expected, a similar opening up of the critical line near the crossing point as was found in the previous case when the parameters were $N = 1$ and $k = 0.01$. However, one can also close the gap by adjusting the potential parameters (in this case w_2) as it were to com-

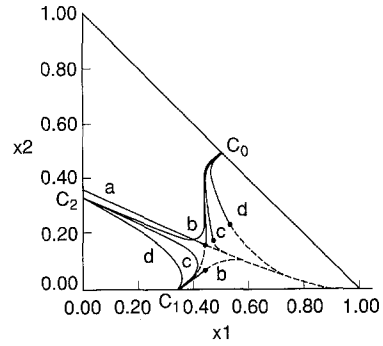

Fig. 8. Combined Tompa and van der Waals ($\sigma = 1$, $N \neq 1$) model: the critical lines in the x_1–x_2 plane. Solid lines are the stable and the dashed lines are the unstable parts of the critical lines. The dots give the limits of stability. (a) The van der Waals case at the van Laar point, given for reference purposes: $N = 1$, $w_1 = 1.0$, $w_2 = 2.884549 = (w_2)_{vL}$, and $w_0 = w_1 + w_2 - 2(w_1 w_2)^{1/2} \equiv w_{geom}$. (b) $N = 1.05$, $w_1 = 1.0$, $w_2 = (w_2)_{vL}$, $w_0 = w_{geom}$. (c) $N = 1.05$, $w_1 = 1.0$, $w_2 = (w_2)_{vL} + \Delta w$, with $\Delta w = -0.1$, $w_0 = w_{geom}$. (d) Same as (c), with $\Delta w = -0.5$.

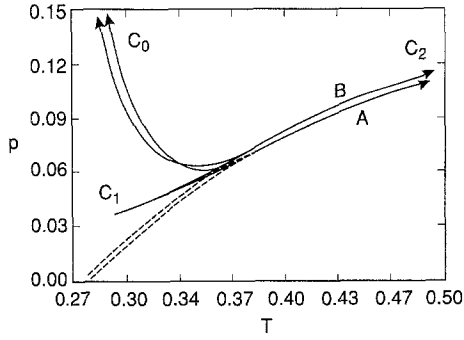

Fig. 9. The critical lines in the p–T plane: (A) van der Waals at the van Laar point: $\sigma = 1$, $N = 1$. (B) $\sigma = 1$, $N = 1.05$; $w_1 = 1.0$, $\Delta w = -0.0579$, and $w_0 = w_{\text{geom}}$.

pensate for the effect of the nonunit value of N. The value $\Delta w = -0.1$ (case (c)) clearly overshoots this goal. In this fashion the double point is restored, using $\Delta w = -0.0519$, but this point is no longer a tricritical point. This is illustrated in Fig. 8. The resulting p–T critical line is given in Fig. 9. Despite the fact that the x_1–x_2 plot is different from the van Laar case, we found that the p–T curves are almost identical except for a small displacement. It is often observed that the pressure–temperature results are rather insensitive to the underlying choice of densities. This insensitivity also plays a role in interpreting data in the form of equations of state, since most data are given as pressure and temperature information. Again, it may be worthwhile to mention that solid lines are the stable and the dashed lines are the unstable parts of the critical lines in the figures.

From the last part we conclude that the van der Waals–Tompa expression shows that it is possible to construct a van Laar-like p–T plot, which is based on a crossing point in the x_1–x_2 coordinates that is not tricritical and that this p–T plot is barely different from the actual van Laar plot, which does have a tricritical point. This implies that it is very difficult to extract basic parameters from experimental critical lines of this kind on the basis of critical lines alone.

APPENDIX

The positions of the three anchor points C_1, C_2, and C_0 for the van der Waals–Tompa model are given by the following equations.

The coordinates of the point C_1 are independent of the value of N, but depend on σ. The position is given by[1] the following coordinate values:

$$x_1 = \{[9 + 8(\sigma - 1)]^{1/2} - 3\}/4(\sigma - 1); \qquad x_2 = 0 \tag{A1}$$

The point C_0 is independent of σ, but is dependent on N; its position is given by

$$x_1 = N^{1/2}/(1+N^{1/2}); \qquad x_2 = 1/(1+N^{1/2}) \tag{A2}$$

The coordinates of the third anchor point C_2 depend both on N and on σ and cannot be given explicitly since they are the roots of an equation of the third degree (except when either $N=1$ or when $\sigma=0$). The equation expressed with the help of x_0 is given by

$$2(1-x_0)^2\,\sigma + x_0(1-2x_0) = x_0^3\left(\frac{1}{N}-1\right) \tag{A3}$$

from which one can determine $x_1 = 1-x_0$ and $x_2 = 0$.

ACKNOWLEDGMENTS

We thank Dr. R. Boisvert of NIST for helping us establish the CMLIB in Kayseri. One of us (P.H.E.M.) thanks the Physics Department of Erciyes University for their hospilality. This work was supported by NATO Grant 86/708. We thank Dr. I. L. Pegg for many stimulating discussions.

REFERENCES

1. P. H. E. Meijer, M. Keskin, and I. L. Pegg, *J. Chem. Phys.* **88**:1976 (1988); Erratum, *J. Chem. Phys.* **90**:3408 (1989), M. Gençaslan, M. Sc. Thesis, Erciyes University (1990).
2. L. Z. Boshkov, *Doklady Akad. Nauk SSSR* **294**(4):901 (1987).
3. R. L. Scott and P. H. van Konynenburg, *Disc. Faraday Soc.* **49**:87 (1970); P. H. van Konynenburg and R. L. Scott, *Phil. Trans. R. Soc.* **298**:495 (1980).
4. J. J. van Laar, *Proc. Sect. Sci. Kon. Ned. Akad. Wet.* 7:646 (1905); **8**:33 (1905).
5. J. A. Schouten, C. A. ten Seldam, and N. J. Trappeniers, *Physica* **73**:556 (1974).
6. D. Furman and R. B. Griffiths, *Phys. Rev. A* **17**:1139 (1978).
7. P. H. E. Meijer, *Physica A* **152**:359 (1989).
8. H. Tompa, *Trans. Faraday Soc.* **45**:1142 (1949).
9. P. J. Flory, *Principles of Polymer Chemistry* (Cornel University Press, Ithaca, New York, 1953).
10. P. H. E. Meijer, *J. Stat. Phys.* **53**:543 (1988).
11. S. Krinksy and D. Mukamel, *Phys. Rev. B* **11**:399 (1975).
12. P. H. E. Meijer and M. Napiorkowski, *J. Chem. Phys.* **86**:5771 (1987).
13. U. K. Deiters and I. L. Pegg, *J. Chem. Phys.* **90**:6632 (1989).
14. P. H. E. Meijer, *J. Chem. Phys.* **90**:448 (1989).
15. P. H. E. Meijer, Binary gas–liquid system classification, in *International Symposium on Supercritical Fluids, 1988, Nice*, M. Perrut, ed. (Société Française de Chemie), Vol. 1, pp. 239–244.
16. P. H. E. Meijer, I. L. Pegg, J. Aronson, and M. Keskin, *Fluid Phase Equilibria* **58**:65 (1990).