

## In Search of the Griffiths Shield Region

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The van der Waals equation of state for binary mixtures has been used to determine the location and shape of the Griffiths shield region (where three tricritical lines intersect). If one takes the geometric mean for  $a_{12}$ , the arithmetic mean for  $b_{12}$ , and the configurational free energy as ideal, the center of the Griffiths shield region is found only when the ratio of molecular sizes is infinite. When the Flory equation for the configurational free energy for mixtures of chain molecules is substituted for the ideal form, the results appear to be somewhat different. However, for all the cases studied, with systems which approach geometric mean behavior one finds the shield region only when the ratio of molecular size is very large and when the internal pressure of the small molecule is very much greater than that of the long-chain molecule.

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**KEY WORDS:** Tricritical lines; Griffiths shield region; binary mixtures; molecular size differences; van der Waals equation of state; Flory configurational free energy.

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### 1. INTRODUCTION

Twenty years ago in this laboratory, van Konynenburg<sup>(1)</sup> made a detailed computer study of the types of phase diagrams that could be derived from the van der Waals equation for binary mixtures. Most of the calculations were made for molecules of equal size (van der Waals  $b_1 = b_2$ ), although a few calculations were made for the case  $b_2 = 3b_1$ . The global phase diagrams were classified into five types according to the connectivity of the critical lines; these include all but one of the major types of binary-mixture phase diagrams known to chemists and chemical engineers. (The exception, now known<sup>(2)</sup> as type VI, shows a low-temperature lower critical tem-

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This paper is dedicated to our colleague Howard Reiss on the occasion of his 66th birthday.

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perature and requires a nonrandom ordering not included in the van der Waals formulation.)

In their treatment of van der Waals phase diagrams<sup>(1,3,4)</sup> van Konynenburg and Scott introduced three reduced parameters to describe the binary interactions:

$$\xi = (b_2 - b_1)/(b_2 + b_1) = (V_{c2} - V_{c1})/(V_{c2} + V_{c1}) \quad (1)$$

$$\begin{aligned} \zeta &= (a_{22}/b_2^2 - a_{11}/b_1^2)/(a_{22}/b_2^2 + a_{11}/b_1^2) \\ &= (p_{c2} - p_{c1})/(p_{c2} + p_{c1}) \end{aligned} \quad (2)$$

$$A = (a_{22}/b_2^2 - 2a_{12}/b_1 b_2 + a_{11}/b_1^2)/(a_{22}/b_2^2 + a_{11}/b_1^2) \quad (3)$$

where  $b_1$  and  $b_2$  are the van der Waals intrinsic volume parameters, while  $a_{11}$ ,  $a_{12}$ , and  $a_{22}$  are the attraction parameters for like and unlike pairs in the binary mixture. For van der Waals and van der Waals-like equations, the parameter  $\xi$  measures the relative difference in size of the two molecules and is related to the difference in critical volumes  $V_{c1}$  and  $V_{c2}$  of the two pure-fluid components; similarly, the parameter  $\zeta$  measures the relative difference in "internal pressure" and is related to the difference in critical pressures  $p_{c1}$  and  $p_{c2}$  of the two fluids. The parameter  $A$  is a measure of the (low-temperature, high-density) enthalpy of mixing; it determines (for an ideal configurational entropy) the magnitude of the deviation from ideal-solution behavior at low temperatures and high densities.

Figure 1 shows what we have called the "master diagram" for mixtures of molecules of equal size ( $\xi = 0$ ). This is *not* the original van Konynenburg diagram, for he had missed the small triangular region in the center. This was first discovered by Furman *et al.*<sup>(5)</sup> in a three-component system and later found by Furman and Griffiths<sup>(6)</sup> for a van der Waals binary mixture. This "Griffiths shield region" occurs around the intersection of three tricritical lines that form the boundaries between types, and is characterized by phase diagrams with critical lines and three-phase lines in addition to those found in adjacent regions outside the shield. This complex behavior does not correspond to any presently known binary phase diagrams, presumably because most known systems are found not far from the locus (shown dashed in Fig. 1) of the geometric mean approximation,

$$a_{12} = (a_{11} a_{22})^{1/2} \quad (4)$$

The question then arises: if one goes to systems where the molecules have very different sizes, will the shield region move closer to the geometric mean line? A partial answer is given by some previously reported results<sup>(3)</sup> for geometric-mean systems. If Eq. (4) is valid, the parameter  $A$  is a function of  $\zeta$ :

$$A = 1 - (1 - \zeta^2)^{1/2} \quad (5)$$

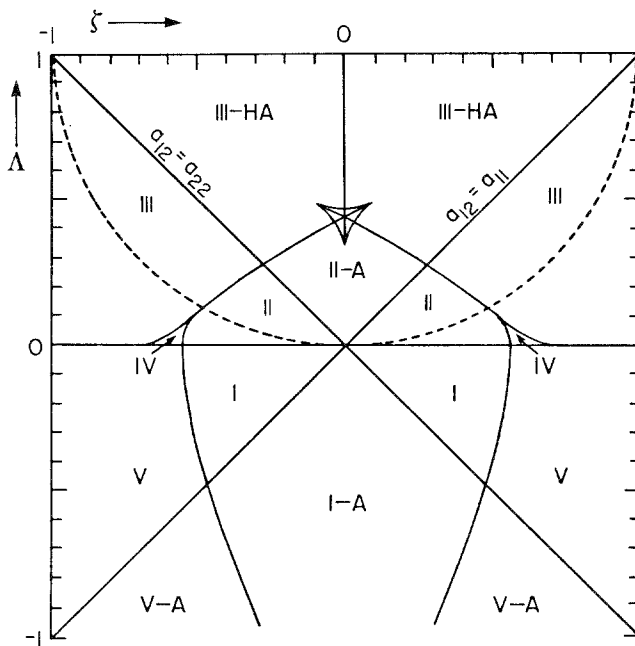


Fig. 1. Master diagram for van der Waals mixtures of molecules of equal size ( $\xi = 0$ ). The shield region is at the upper center around the point where the three tricritical lines intersect. The geometric mean [Eqs. (4) and (5)] is shown by the dashed line. The diagram is divided into five principal regions and is further subdivided by the two diagonal straight lines that indicate the presence or absence of azeotropes. For details see ref. 4. (Reproduced by permission from ref. 12.)

so that a single  $\zeta$ ,  $\xi$  diagram can be constructed (Fig. 2; the corresponding figure in ref. 2 has several lines plotted incorrectly). The two tricritical lines (corresponding to the vanishing of three-phase kinks in critical lines starting from the critical points of the two pure fluids) start from  $\zeta = 0.48514$  and  $-0.48514$  at  $\xi = 0$ , and do not intersect until  $\zeta = -0.80$  at  $\xi = 1$  (corresponding to the limit at which the ratio  $b_2/b_1$  becomes infinite). However, further calculations were required to determine how close to the geometric mean the shield region gets for finite ratios. We now report some of these results.

## 2. PROCEDURE

We start with a generalized van der Waals equation for a binary mixture:

$$pV_m/RT = 1 + cf(b/V_m) - a/(RTV_m) \quad (6)$$

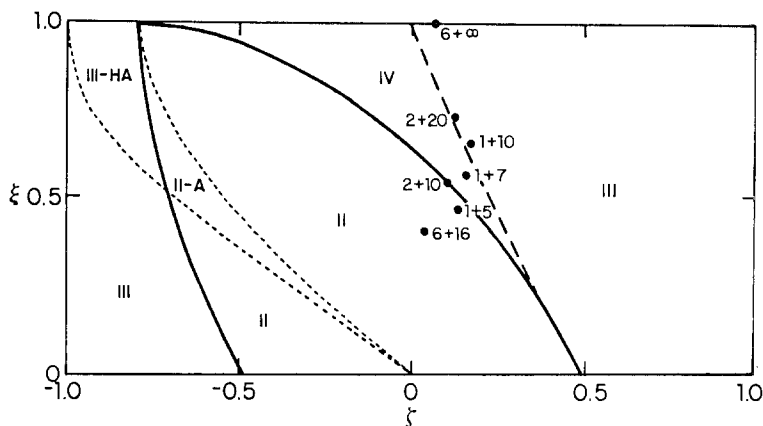


Fig. 2. Types of phase equilibria for van der Waals mixtures obeying the geometric mean for  $a_{12}$ . Negative values of  $\xi$  are not shown because the origin is a center of symmetry.  $\xi$  and  $\zeta$  coordinates are shown for a few binary mixtures of  $n$ -alkanes. This is a corrected version of Fig. 2 in ref. 3 (where some of the lines were misplotted).

The parameters  $a$  and  $b$  have the usual van der Waals meaning, except that for mixtures they are quadratic functions of the mole fractions:

$$a = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} \quad (7)$$

$$b = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22} \quad (8)$$

The parameter  $c$ , first introduced by Prigogine<sup>(7)</sup> but appearing here in a form first introduced by Beret and Prausnitz,<sup>(8)</sup> adds a third dimension to a corresponding-states treatment; it allows for the entropy differences produced by a chain molecule with internal degrees of freedom. The function  $f(b/V_m)$  is the free volume function, which for the van der Waals equation itself is  $b/(V_m - b)$ .

The pressure equation can be integrated to yield the Helmholtz free energy; one then adds the entropy of ideal mixing to obtain an equation for the Helmholtz free energy  $A_m$  of a binary mixture:

$$\begin{aligned} A_m(T, V_m, x) - x_1 A_m^0(T, V_m^0) - x_2 A_m^0(T, V_m^0) \\ = -RT \ln(V_m/V_m^0) - RTcg(b/V_m) - a/V_m + RT(x_1 \ln x_1 + x_2 \ln x_2) \end{aligned} \quad (9)$$

Here  $A_1^0$  and  $A_2^0$  are the molar Helmholtz free energies of the pure fluids in their ideal-gas state at reference molar volume  $V_m^0$ , and the function  $g(b/V_m)$  arises from integration of the function  $f$  in Eq. (6). The final term

in Eq. (5) is the combinatorial free energy of ideal mixing. An alternative for this in the dense fluid mixture would be the simple Flory<sup>(9)</sup> expression for mixing chains of different length; this is done by adding to Eq. (9) the extra term  $RT[x_1 \ln b_1 + x_2 \ln b_2 - \ln(x_1 b_1 + x_2 b_2)]$ .

Two of the simplest forms for  $g(b/V_m)$  are that of the original van der Waals equation and a modification that Scott<sup>(10)</sup> suggested some years ago. A third is that derived from the widely used equation of Carnahan and Starling.<sup>(11)</sup> They are most easily expressed in terms of a new variable,  $y = b/(4V_m)$ :

$$\text{van der Waals:} \quad g = \ln(1 - 4y) \quad (10a)$$

$$\text{Scott:} \quad g = 2 \ln(1 - 2y) \quad (10b)$$

$$\text{Carnahan and Starling:} \quad g = 4y(1 - 3y/4)/(1 - y)^2 \quad (10c)$$

The computer programs that we have written permit a variety of choices: among the various forms of  $g$ , between the van der Waals and Lorentz combining rules for  $b_{12}$ , between ideal and Flory mixing, and for choices of  $c$  other than 1. In fact, we have largely restricted our calculations to the van der Waals or Scott forms for  $g$ , to  $c = 1$ , and to the van der Waals combining rule [the arithmetic mean  $b_{12} = (b_{11} + b_{22})$ ], which seems more appropriate for chain molecules and reduces to a linear expression for  $b$ :

$$b = x_1 b_1 + x_2 b_2 \quad (11)$$

Most of our calculations involve three kinds of Fortran computer programs:

1. CRLN, a program for generating critical lines [with determination of  $(\partial^4 G_m / \partial x^4)_{T,p}$  to distinguish between stable and unstable critical lines].

2. CEP, a program for determining critical end points by constructing the tangent plane to the free energy surface at a critical point and determining whether the plane cuts the free energy surface anywhere else; this determines whether the critical point is stable or only metastable.

3. Various programs to determine two- and three-phase coexistence curves.

For positive values of  $A$  there are three major critical lines, two that start from the gas-liquid critical points of the two pure components (labeled  $C_1$  and  $C_2$ ) and a third ( $C_m$ ) that starts from the liquid-liquid critical solution point of the close-packed mixture ( $V_m = b$ ); these may be examined by plotting them on a  $y, x$  graph for various choices of the parameters  $\xi$ ,  $\zeta$ , and  $A$ . These critical lines may or may not be connected

by a continuous set of critical points; if all the intervening points are stable (as distinct from metastable or unstable), this defines the type of the phase diagram. However, some parts of the critical lines pass through unstable regions or regions of negative pressure (metastable or unstable), and different parts may not connect at all.

Some typical  $y, x$  graphs are sketched in Fig. 3, where the solid lines represent stable parts of the critical lines (terminating at critical end points), while the dashed lines and dotted lines represent metastable and unstable parts, respectively. The first graph (Fig. 3a) is the very symmetrical  $y, x$  plot one obtains at the exact center of the shield region for

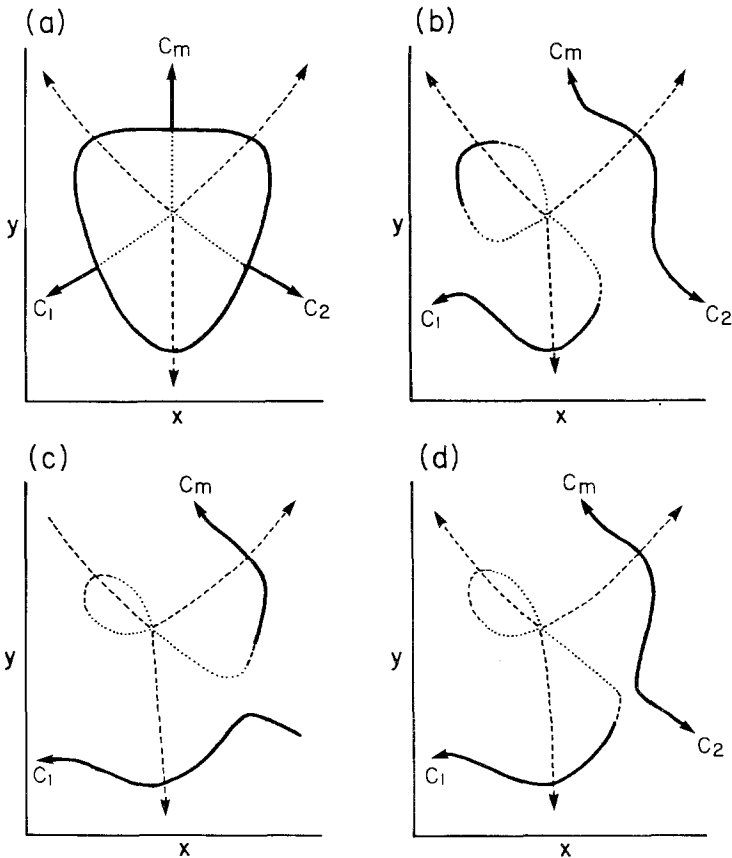


Fig. 3. Some typical  $y, x$  graphs (sketched, not to scale): (a) a system at the center of the shield region for the symmetrical  $\xi = 0$  master diagram (Fig. 1); (b) a system inside the shield region, showing a third stable critical line; (c, d) two systems outside the shield region, but near a double point. The solid lines are stable critical lines, the dashed lines metastable ones, and the dotted lines unstable ones (see text).

$\xi = 0$ ; qualitatively the diagram can be described as consisting of a distorted circle and three intersecting nearly straight lines. Any change in  $\zeta$  or  $A$  destroys part of the symmetry and part of the connectivity and distorts the  $y, x$  graph. A point where parts of the critical lines change connectivity (exchange ends), as shown in the difference between Figs. 3c and 3d, is a mathematical double point. Where residual parts of what was originally the "circle" form detached stable critical lines (as in Fig. 3b), the system lies within the shield region; otherwise (as in Figs. 3c and 3d), the system lies outside. (Except for this difference, Figs. 3b and 3d are quite similar, although the latter is closer to the double point.)

The first and easiest step in determining the topology of a master diagram is to locate the double points. Frequently, but not always, a tricritical line lies extremely close to the double-point line; where the boundaries between types II and III are shown in Fig. 1, the tricritical line lies so close to the double-point line that the intervening region (which has been called<sup>(12)</sup> type IV\*) is narrower than the width of the printed line. However, where a substantial type IV region exists between types II and III, the double-point line runs down the middle of the type IV region; the II–IV boundary is then a tricritical line, while the IV–III boundary occurs where two detached critical lines coalesce (i.e., where two critical-endpoint lines join smoothly).

While, in principle, some of these points could be determined by complicated analytic procedures, in practice we have proceeded empirically by calculating critical lines for selected values of the system parameters. Examination of the computer output can distinguish between stable (or metastable) and unstable regions of the critical lines and the range of parameters within which the double points must lie. One can then, while keeping two parameters constant (normally  $\xi$  and one of the other two), vary systematically the third and determine the double point as precisely as desired.

The next step is to determine the tricritical point, again by varying a parameter systematically until a small unstable region of the critical line (which shows up as a kink in the  $T, p$  graph) has decreased in length to the vanishing point. The lengthiest task is that of determining critical end points with CEP; this is necessary to determine the boundaries of the shield region and the nontricritical boundary of type IV regions.

### 3. RESULTS

Most of the early calculations were made with the assumptions of an ideal configurational free energy and of the van der Waals combining rule for  $b_{12}$  [i.e., Eq. (11)], even though there is an inconsistency between the

two assumptions, since the former is more nearly appropriate for mixtures of large and small spheres and the latter for mixtures of chain molecules. The shapes of the shield regions for  $\xi = 0.0, 0.5, 0.75,$  and  $0.9$  with these assumptions and the simple van der Waals form of  $g(y)$  [Eq. (10a)] are shown in Fig. 4. They move progressively left on the master diagram into regions of negative  $\zeta$  and become increasingly distorted. Although the breaking of the symmetry means that the three tricritical lines are no longer required to intersect at exactly the same place, the intersections are remarkably close together. Figure 5 shows the movement of the "center" of the shield region (i.e., the point of intersection) with increasing  $\xi$  for both the van der Waals and Scott  $g(y)$ . The two curves are very similar, except that the Scott form does in fact reach the geometric-mean line at about  $\xi = 0.9$ .

More recently calculations have been made using the more nearly consistent assumptions of the van der Waals additive  $b_{12}$  and the Flory configurational free energy for mixing chain molecules. For these systems the intersections of the tricritical lines also move to the left to more and more negative  $\zeta$ 's, but there are important other differences that we have

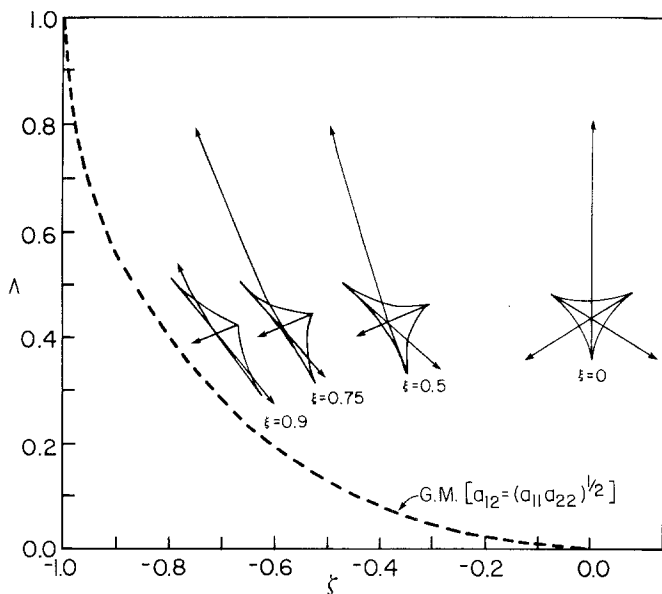


Fig. 4. Tricritical lines and the shield region for systems following the van der Waals  $g(y)$ , the ideal configurational free energy, and the van der Waals  $b_{12}$ . The diagrams for  $\xi = 0.0, 0.5, 0.75,$  and  $0.9$  are shown.



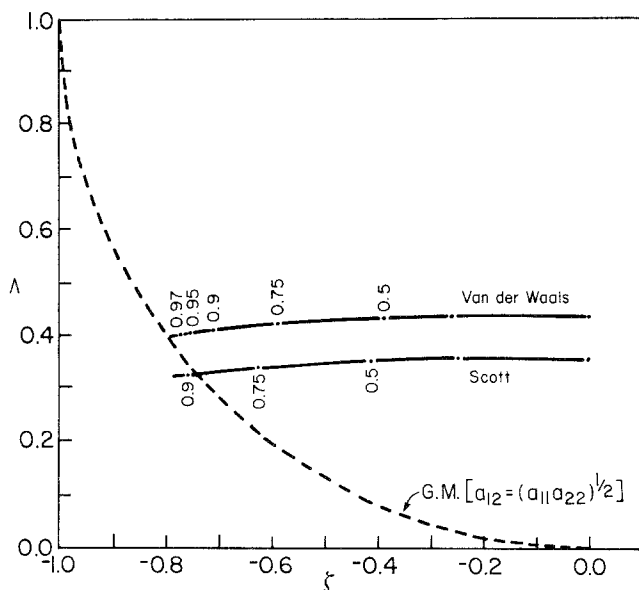


Fig. 5. Locus of the "center" of the shield region (the almost common intersection of the three tricritical lines) for systems with the ideal configurational free energy, the van der Waals  $b_{12}$ , and either (a) the van der Waals  $g(y)$  or (b) the Scott  $g(y)$ . Numbers attached to points on the lines are values of  $\xi$ .

not yet adequately explored. However, some preliminary observations can be made:

1. For large values of  $\xi$  (e.g.,  $\xi = 0.98$ , corresponding to a chain length ratio  $r = 100$ ), there are four tricritical lines, not three.
2. Three of these tricritical lines intersect almost at a common point, as in the case of ideal configurational free energy, and this intersection appears to move in such a way as to reach the geometric mean line by  $\xi = 1.0$ .
3. The intersections of the fourth tricritical line with the others are quite significantly separated, and it appears likely that they will never reach the geometric-mean line.
4. For large values of  $\xi$ , some (but not all) of the tricritical lines seem to be fairly insensitive to the precise value of  $\xi$ ; this suggests that parts of a master diagram for high polymer solutions ( $r > 100$ ) should be reasonably independent of  $r$ .

We have not yet searched for critical end points with systems corresponding to this Flory chain-molecule model, so we cannot yet

produce an equivalent of Fig. 4. Since there are now four critical lines, we suspect that there may be new kinds of phase behavior in the new master diagrams.

We conclude on a discouraging note. Even if our future calculations show a shield region near the geometric-mean line for solution of chain molecules, the prospects of finding such systems experimentally seem poor. Such systems will surely lie in regions of the master diagram beyond  $A = 0.2$  and  $\zeta = -0.7$ . The combination of large, positive  $\xi$ 's with large, negative  $\zeta$ 's requires a long-chain polymer with weak interactions between segments (low internal pressure or "solubility parameter") dissolved in a low-molecular-weight solvent with very strong intermolecular interactions (high internal pressure or solubility parameter. It would not be too great an exaggeration to represent such systems as being like the system polytetrafluoroethylene + mercury.

## ACKNOWLEDGMENT

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