1.0

4.5
2.8 2.5

3.2 2.2

3.6

4.0 2.0

1.1

1.8

1.25 1.4 1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 2	2. GOVT ACCESSION NO. AD-A089246	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Spinodal Decomposition in Binary Mixtures of Strongly Anisotropic Molecules.		5. TYPE OF REPORT & PERIOD COVERED Technical Report.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Paul H. E. Meijer Erik Bodegom		8. CONTRACT OR GRANT NUMBER(s) ONR-N00014-78-C-0518
9. PERFORMING ORGANIZATION NAME AND ADDRESS Physics Department The Catholic University of America Washington, D. C. 20064		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		12. REPORT DATE August, 1980
		13. NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Spinodal decomposition, Supercooling, Phase diagram

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We determine the phase separation and the spinodal of binary liquids with anisotropic interaction between the molecules. The results show the influence of the anisotropy parameters on the position of the spinodal curve. The model is interpreted as a decorated lattice transformation of the Bethe-Peierls solution.

80 9 12 017

AD A089246

DDC FILE COPY

Technical Report No. 2

Spinodal Decomposition

in Binary Mixture of

Strongly Anisotropic Molecules

by

Paul Meijer

and

Erik Bodegom

Physics Department

The Catholic University of America

Abstract

We determine the phase separation and the spinodal of binary liquids with anisotropic interaction between the molecules. The results show the influence of the anisotropy parameters on the position of the spinodal curve. The model is interpreted as a decorated lattice transformation of the Bethe-Peierls solution.

Since supercooling is most easily obtained in glasses and organic liquids such as alcohols, we try to establish the influence of anisotropic interaction between molecules. One of the simplest ways to introduce anisotropy is to assume that molecules have a finite number of contact points, some of these are strongly adhering to similar points on other molecules and other points are not strongly adhering. The last points may even have a repulsive interaction. In order to give meaning to the model we assume that special adherence is associated with H-bonding , non-special adherence with van der Waals forces and repulsion may be due to protruding parts of the molecule.

This model was proposed some time ago by Barker and Fock to explain the lower critical point that occurs in the phase separation in binary liquids.

In this note we point out that about the same solution of the problem as was obtained by Barker and Fock, can be found by a different method. The method enables us to map the solution on a standard Bethe-Peierls solution.

On the basis of this we compute the spinodal and find that anisotropy seems to "retract" this curve closer to the center. If the number of repulsive contact points dominates the spinodal will behave similar to a isotropic binary phase separation. Barker and Fock[1] assume that a molecule has two kinds of contact points. For the time being we will assume that there is one contact point of one kind (hereafter called the "special" contact point) and all the other contact points of the other type (the "normal" ones).

The interaction energies between two different types of molecules will depend on which of the contact points is involved in forming the "bond".

Let us denote the two types of molecules by A and B each of which can be oriented in n directions (absolute directions in space). This can conveniently be described by an arrow, where the tip of the arrow denotes the special contact point.

Thus for A molecules: ↑ ↗ → etc.

B molecules: ↑ ↗ →→ etc.

Barker and Fock took for n the coordination number (γ) of the underlying lattice. However n could also be larger than γ (See: Andersen and Wheeler[3]). In both cases the coordination number was six (simple cubic lattice). We will restrict ourselves also to the simple cubic lattice.

Now one can imagine two kinds of possible solutions:

a) The concentrations of the A molecules in the n different ("absolute") directions are all equal and similarly for the B molecules or

b) The concentrations of the A molecules in the different absolute orientations are not equal (similarly for the B molecules), i.e. there is a net orientation of the molecules (liquid crystals).

For the time being we will only consider the first case (isotropic solutions) in the pair approximation.

Basic equations

The point probabilities (i=1, . . . , n) are all equal since we are dealing with the isotropic solution.

Thus:

$$x_i^A = \frac{x_A}{n}$$

where x_A is the concentration of the A molecules. A similar expression holds for the

B molecules, with the normalization:

$$n \left(\frac{X_A}{n} + \frac{X_B}{n} \right) = 1$$

The pair probabilities are given by (in the isotropic solution):

Variable (y_i)	Bond		Weight factor (g_i)	Energy (E_i)
y_1	↑ ↑	any pair of A molecules	n^2	0
y_2	↑ ↕	No arrows pointing towards the other molecules	$2(n-1)^2$	U_1
y_3	↑ ←—	A not pointing towards the B molecule	$2(n-1)$	U_2
y_4	—→ ↕	B not pointing towards the A molecule	$2(n-1)$	U_3
y_5	—→←—		2	U_4
y_6	↕ ↕	any pair of B molecules	n^2	0

Normalization:

$$\sum_{i=1}^{6} g_i\, y_i = 1$$

Energies can be represented by the matrix $\begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}$; for example $\begin{bmatrix} 1 & 2 \\ 2 & 2 \end{bmatrix}$ means that U_1 is different from $U_2 = U_3 = U_4$.

Relations between point and pair probabilities are:

$$X_A = n^2 y_1 + (n-1)^2 y_2 + (n-1) y_3 + (n-1) y_4 + y_5$$

$$X_B = (n-1)^2 y_2 + (n-1) y_3 + (n-1) y_4 + y_5 + n^2 y_6$$

It is clear that here all different $x_i{}^A$ are equal to each other. However the ratio of the special contact point to the sum of special and normal contact points for each type of molecule (which should be less or equal to $1/\gamma$ depending on the value of n) might not be conserved. This will be discussed later on.

Φ $\quad(=\beta f$; where f is the free energy per molecule and $\beta = 1/kT$) is then given by[2]:

$$\Phi = \frac{\gamma}{2} \sum_{i=1}^{6} \beta \epsilon_i g_i y_i - (\gamma-1)\left\{ x_A \ln \frac{x_A}{n} + x_B \ln \frac{x_B}{n} \right\} +$$

$$+ \frac{\gamma}{2} \sum_{i=1}^{6} g_i y_i \ln y_i + \beta\lambda\left(1 - \sum_{i=1}^{6} g_i y_i \right)$$

where λ the Lagrange multiplier for the normalization of the probabilities. Minimizing Φ with respect to y_i leads to:

$$y_1 = \exp\left(\frac{2}{\gamma}\beta\lambda\right)(x_A x_A)^{\frac{\gamma-1}{\gamma}} \quad , \quad y_4 = \exp\left(\frac{2}{\gamma}\beta\lambda\right)(x_A x_B)^{\frac{\gamma-1}{\gamma}} \exp(-\beta u_3)$$

$$y_2 = \exp\left(\frac{2}{\gamma}\beta\lambda\right)(x_A x_B)^{\frac{\gamma-1}{\gamma}} \exp(-\beta u_1) \quad , \quad y_5 = \exp\left(\frac{2}{\gamma}\beta\lambda\right)(x_A x_B)^{\frac{\gamma-1}{\gamma}} \exp(-\beta u_4)$$

$$y_3 = \exp\left(\frac{2}{\gamma}\beta\lambda\right)(x_A x_B)^{\frac{\gamma-1}{\gamma}} \exp(-\beta u_2) \quad , \quad y_6 = \exp\left(\frac{2}{\gamma}\beta\lambda\right)(x_B x_B)^{\frac{\gamma-1}{\gamma}}$$

Now replacing:

$$(n-1)^2 y_2 + (n-1) y_3 + (n-1) y_4 + y_5 = n^2 y_2'$$

and putting:

$$y_2' = \exp\left(\frac{2}{\gamma}\beta\lambda\right)(x_A x_B)^{\frac{\gamma-1}{\gamma}} \exp(-k)$$

where K represents the effective interaction energy between A and B molecules times β. It follows immediately that K has to satisfy:

$$n^2 e^{-K} = (n-1)^2 e^{-\beta u_1} + (n-1) e^{-\beta u_2} + (n-1) e^{-\beta u_3} + e^{-\beta u_4}$$

It can be shown that this system is now entirely analogous to a magnetic spin- 1/2 system with K/2 replacing $\beta\epsilon$. Phase separation is determined by the following equation (for $\theta \neq 0$)[2]:

$$e^{K} = \frac{\sinh\left(\frac{\gamma}{2}\theta\right)}{\sinh\left(\frac{\gamma}{2}-1\right)\theta}$$

where θ is given by:

$$\frac{x_A}{x_B} = e^{\gamma \theta}$$

The critical points are determined by:

$$K_c = \ln\left(\frac{\gamma}{\gamma - 2}\right)$$

Phase separation occurs when $K > K_c$. Figures 1 to 4 give the phase diagrams for certain specific cases. Since the phase diagrams are symmetric around $x_A = .5$ only one half of the diagrams is plotted. Also plotted in these figures are the spinodal lines (denoted by s).

Discussion

Consider the original Barker and Fock solution. They put constraints on the different pair probabilities such that ratio of special to all contact points is conserved.

In our case this ratio is not necessarily conserved. To see whether this ratio deviates much from the exact ratio, a plot is made (fig. 5) of this ratio (R divided by the exact ratio, $R^* = 1/6$) vs temperature for two cases (corresponding to fig. 1 and fig. 2). The maximum deviation is seen to be approximately 20%, which is, considering that only the pair approximation is used, not so bad.

However our solution does not give "unphysical" phase diagrams like in their case: $\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix}$ for which a phase diagram is given in fig. 6.

Furthermore, the isotropic solution also has closed loop phase diagrams for the fcc lattice i.e. $\gamma = 12$, whereas in Barker and Fock the closed loop phase diagrams are only obtained for γ given by:

$$4 - 2\sqrt{2} < \gamma < 4 + 2\sqrt{2}$$

in the case of $\boxed{\begin{smallmatrix} 1 & 2 \\ 2 & 2 \end{smallmatrix}}$.

In comparing the isotropic model with Andersen and Wheeler's model three main differences can be observed.

I. In their decorated lattice model the decorated (or secondary) lattice points are also occupied by molecules.

II. In their model only the orientation of the molecules on the decorated lattice is of importance (i.e. no orientation of molecules on the primary lattice.)

III. Because of these two features of their model they are able to map their model on the spin-1/2 Ising model, for which the "exact" solution is known. It can be shown that in the cluster variation method an increase in cluster of the phase diagrams. This is illustrated in figure 7, where the phase diagrams of Ising systems with only repulsive energies between unlike spins are plotted versus the reduced temperature in the first three approximations.

It is highly probable that in the decorated model, this widening has also occured because the model is mapped on the Ising model for which they use the exact solution (and not a lower order approximation).

Figure Captions

Fig. 1 Phase diagram with n=6 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix}$, U_1=1, U_2=-.25 and U_3=0

Fig. 2 Phase diagram with n=6 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 2 \end{bmatrix}$, U_1=1 and U_2=-.25

Fig. 3 Phase diagram with n=5001 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix}$, U_1=1, U_2=-1 and U_3=-10

Fig. 4 Phase diagram with n=5001 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 2 \end{bmatrix}$, U_1=1 and U_2=-1

In the above figures s denotes the spinodal.

Fig. 5a Ratio of special contact point to all contact points of A molecules normalized by the exact value (R*= 1/6) corresponding to fig. 1.

Fig. 5b Idem, but corresponding to fig. 2.

Fig. 6 Phase diagram with n=6 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix}$, U_1=1, U_2=.0 and U_3=-.25 (Barker and Fock solution)

Fig. 7 Phase diagrams in different approximations

1. Mean field (T_c=3)

2. pair approximation (T_c=2.4663)

3. 4 - cluster approximation (T_c=2.3049)

Figure Captions

Fig. 1 Phase diagram with n=6 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix}$, $U_1=1$, $U_2=-.25$ and $U_3=0$

Fig. 2 Phase diagram with n=6 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 2 \end{bmatrix}$, $U_1=1$ and $U_2=-.25$

Fig. 3 Phase diagram with n=5001 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix}$, $U_1=1$, $U_2=-1$ and $U_3=-10$

Fig. 4 Phase diagram with n=5001 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 2 \end{bmatrix}$, $U_1=1$ and $U_2=-1$

In the above figures s denotes the spinodal.

Fig. 5a Ratio of special contact point to all contact points of A molecules normalized by the exact value ($R^*= 1/6$) corresponding to fig. 1.

Fig. 5b Idem, but corresponding to fig. 2.

Fig. 6 Phase diagram with n=6 and energies given by $\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix}$, $U_1=1$, $U_2=.0$ and $U_3=-.25$ (Barker and Fock solution)

Fig. 7 Phase diagrams in different approximations

      1. Mean field ($T_c=3$)

      2. pair approximation ($T_c=2.4663$)

      3. 4 - cluster approximation ($T_c=2.3049$)

References

1.   J.A. Barker and W. Fock, Discussions Faraday Soc., 15 (1953) 180 (See also: J.A. Barker, J. Chem. Phys, 20 (1952)1526)

2.   "Crystal Statistics" by R. Kikuchi, Lecture notes, Hughes Research Lab (1979).

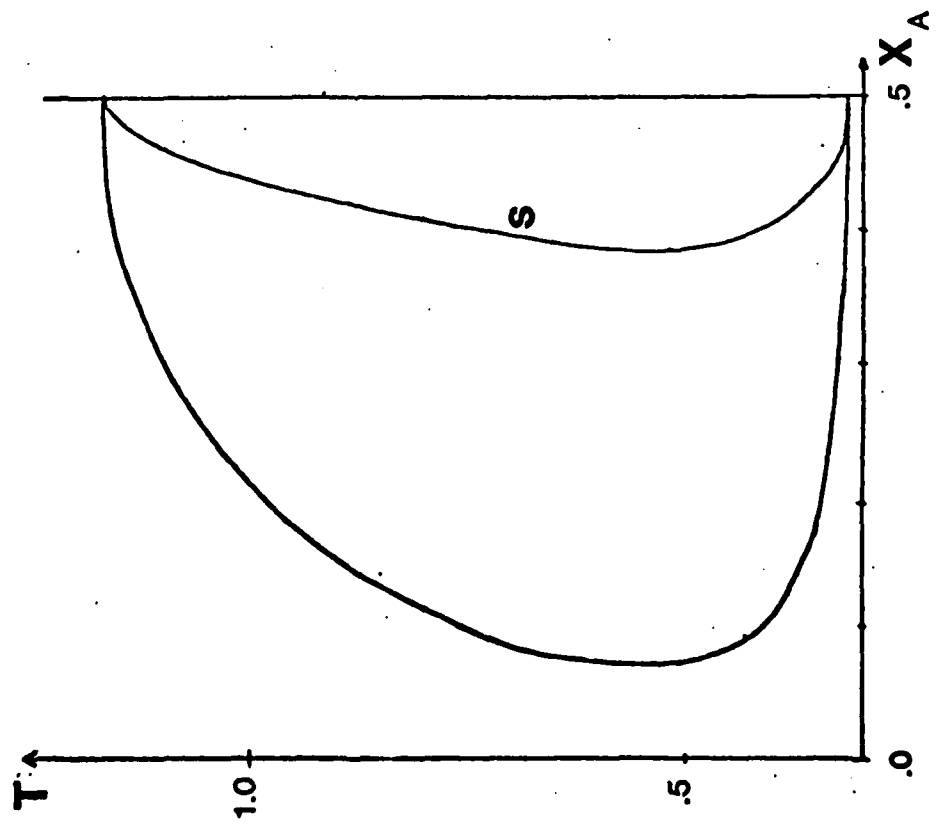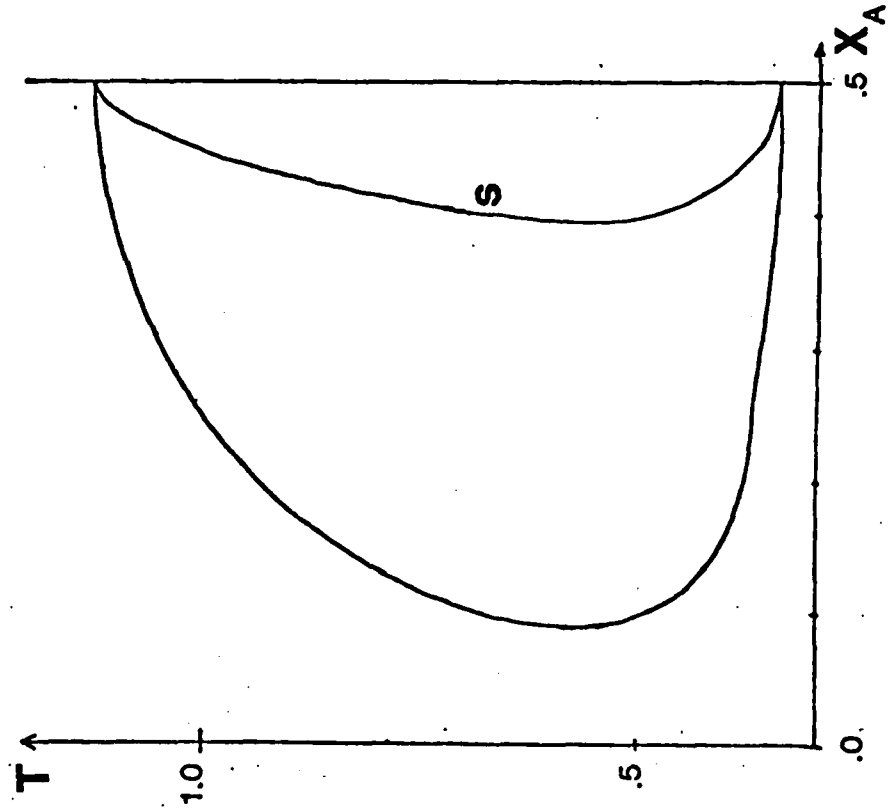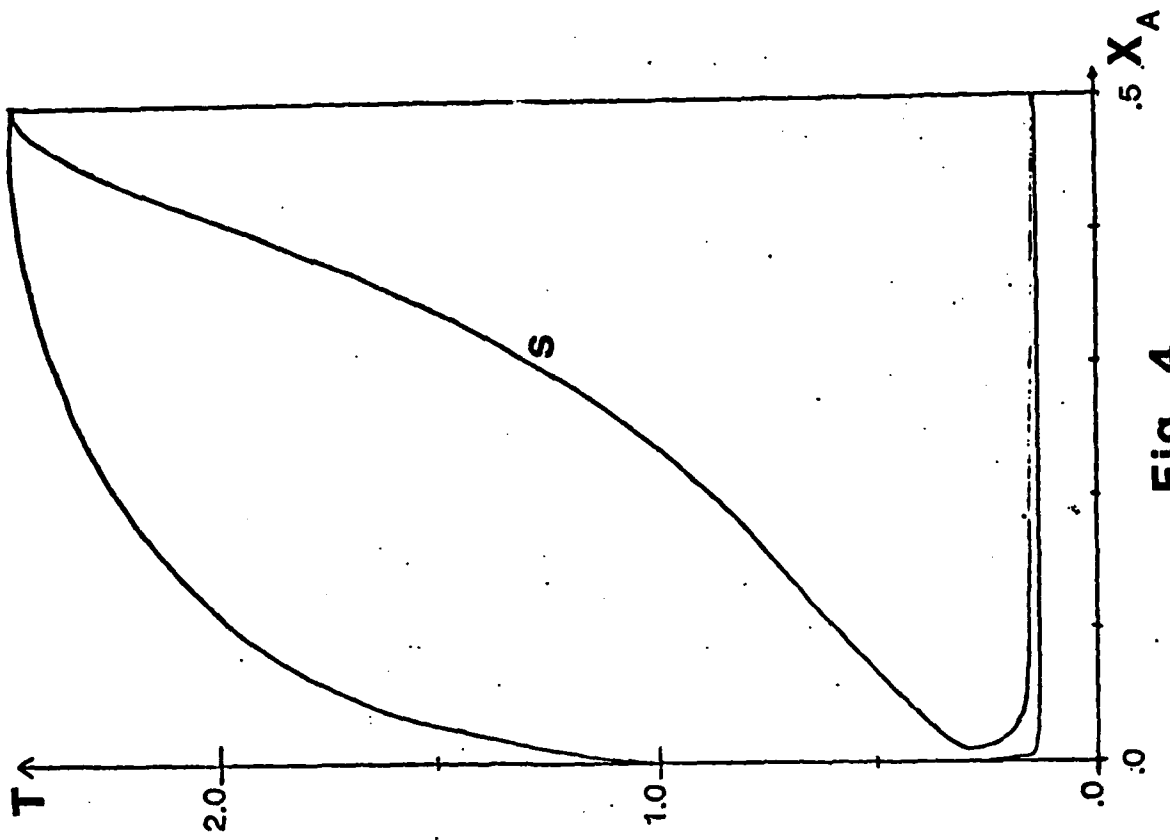3.   G. R. Andersen and J. C. Wheeler, J. Chem. Phys 69 (1978) 2082,3403
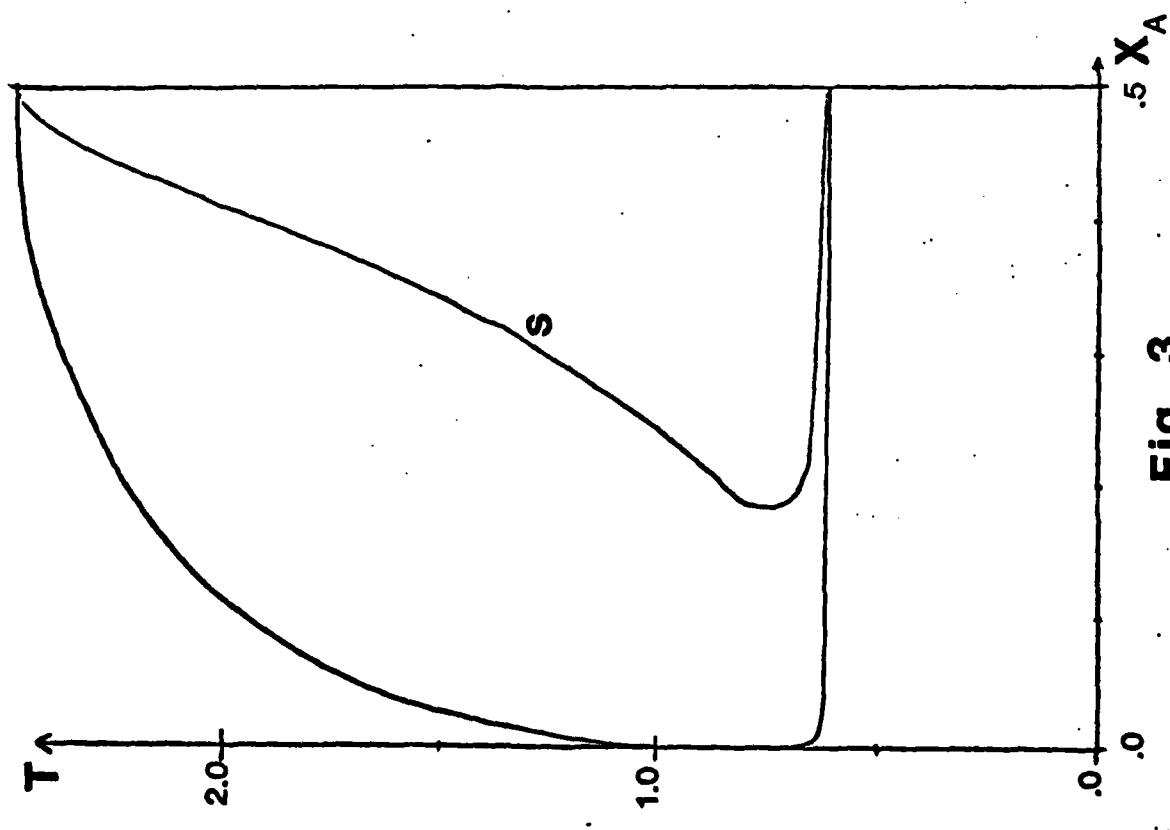
Fig. 2

Fig. 1

Fig. 3

Fig. 4

Fig. 6

(a)

(b)
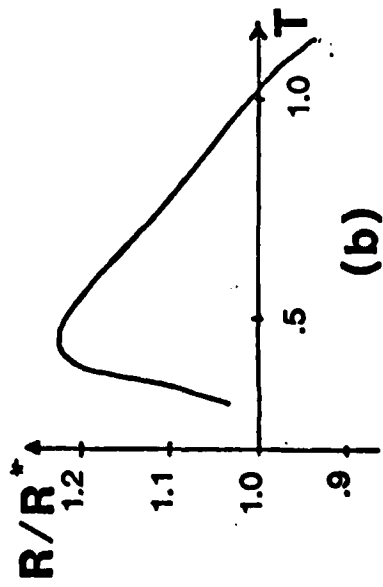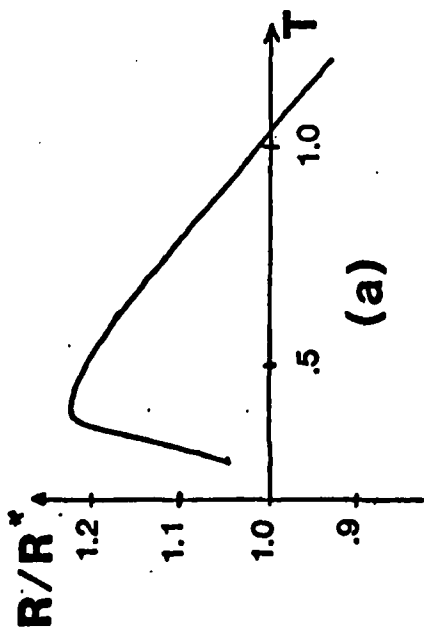
Fig. 5
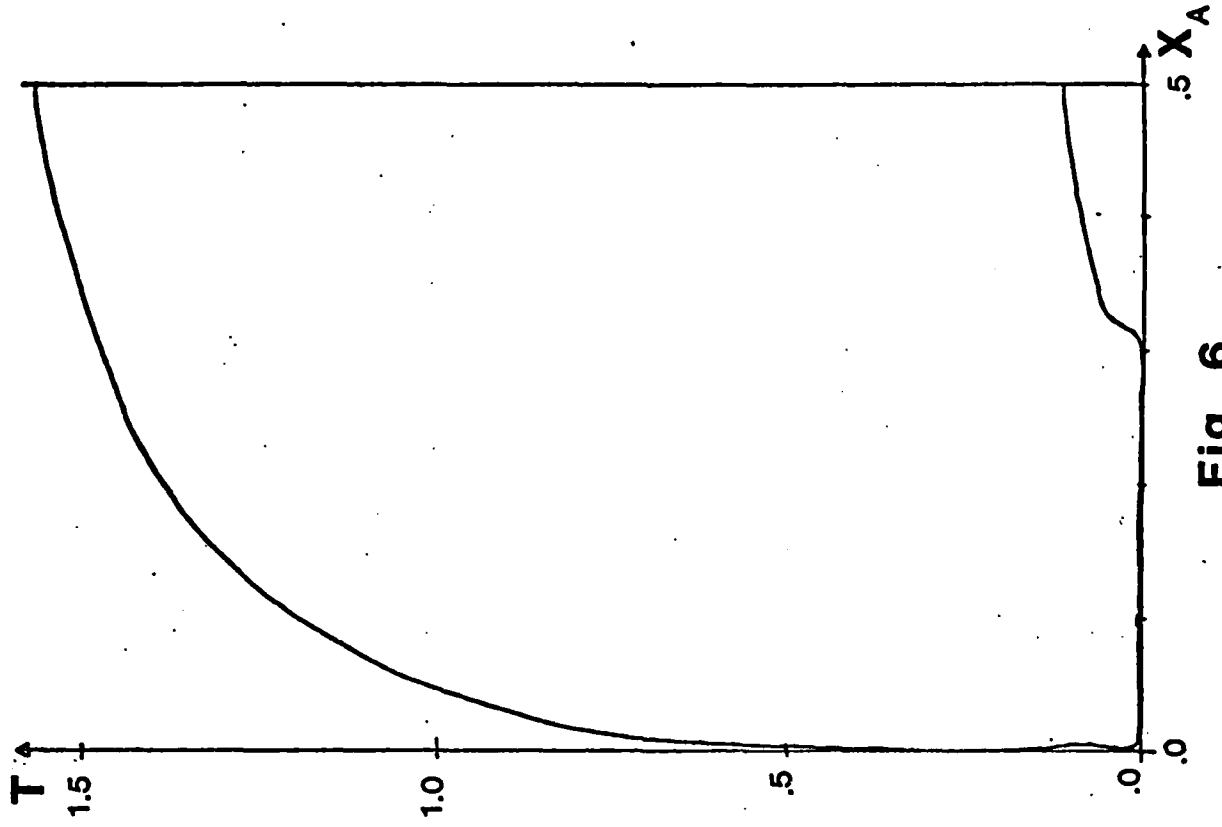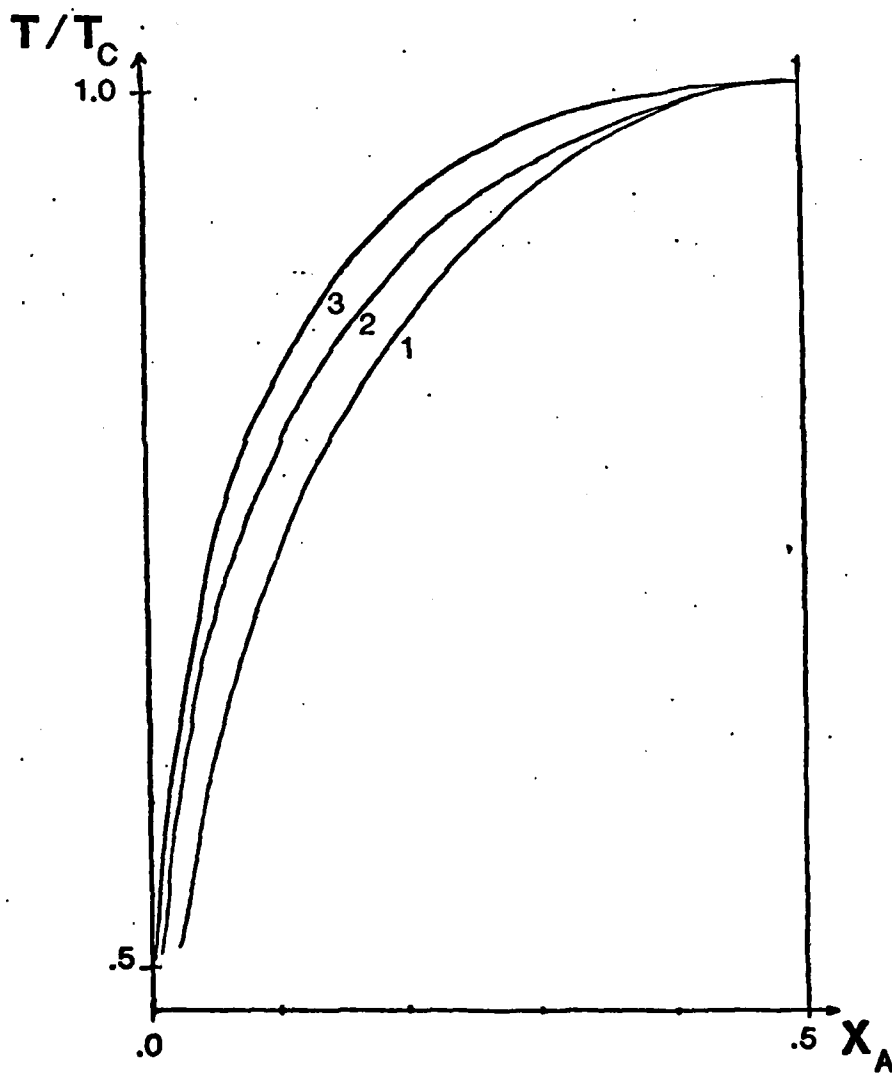
Fig. 7

END

DATE
FILMED

10-80

DTIC