Ans_FH Phase Boundary

(6) Equilibrium occurs when $\mu_1(\phi_2^\alpha) = \mu_1(\phi_2^\beta)$ AND $\mu_2(\phi_2^\alpha) = \mu_2(\phi_2^\beta)$

from problem 1 we get

$$\ln(1-\phi_2^\alpha) + (1-\phi_2^\alpha)\left(1-\frac{1}{\sigma}\right) + \chi\phi_2^{\alpha 2} = \ln(1-\phi_2^\beta) + (1-\phi_2^\beta)\left(1-\frac{1}{\sigma}\right) + \chi\phi_2^{\beta 2} \quad (A)$$

AND

$$\ln\phi_2^\alpha + (1-\sigma)(1-\phi_2^\alpha) - \chi\sigma(1-\phi_2^\alpha)^2 = \ln\phi_2^\beta + (1-\sigma)(1-\phi_2^\beta) - \chi\sigma(1-\phi_2^\beta)^2 \quad (B)$$

Solve (A) for χ. Call it

$$\chi_A = \frac{\ln\left(\frac{1-\phi_2^\beta}{1-\phi_2^\alpha}\right) + \left(1-\frac{1}{\sigma}\right)\left(\phi_2^\beta - \phi_2^\alpha\right)}{\phi_2^{\alpha 2} - \phi_2^{\beta 2}}$$

Solve (B) for χ. Call it

$$\chi_B = \frac{\ln\left(\phi_2^\beta/\phi_2^\alpha\right) + (1-\sigma)\left[\phi_2^\alpha - \phi_2^\beta\right]}{\sigma\left[(1-\phi_2^\alpha)^2 - (1-\phi_2^\beta)^2\right]}$$

Since $\chi = \frac{z\epsilon}{kT}$ it must be the same in both phases, since temp must be same.

Strategy: Set 1) $\chi_A = \chi_B$

2) Choose ϕ_2^β

3) Hunt for ϕ_2^α that make it work.

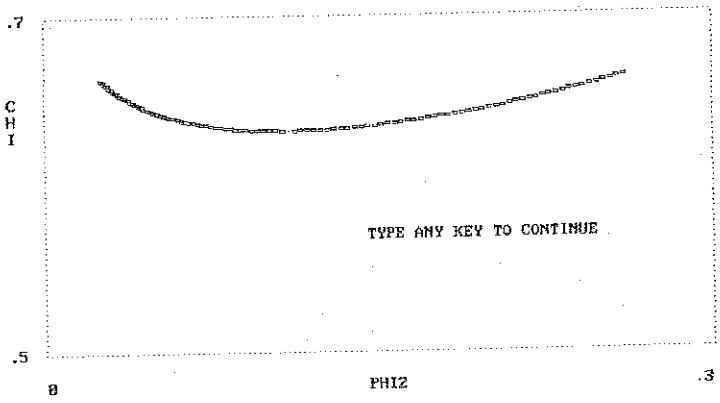
Before starting, consider where critical points are.

$$\chi_{crit} = \frac{(1+\sqrt{\sigma})^2}{2\sigma} \qquad \phi_{2,crit} = \frac{1}{1+\sqrt{\sigma}}$$

@ $\sigma = 65$, $\chi_{crit} = 0.632$ and $\phi_{2,crit} = 0.11$

The Basic Program provided solves the $\chi_A = \chi_B$ for progressively larger values of ϕ_2^β. It also makes a crude plot.

A MATH CAD page and EXCEL spreadsheet appear also. There are many alternative approaches.

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'COMPUTES FLORY-HUGGINS PHASE DIAGRAMS
'IDEA IS TO FIND PHI2CRIT AND CHICRIT FIRST.  THEN
'SELECT A PHI2B > PHI2CRIT AND GO SEARCHING FOR PHI2A AND
'THE CORRESPONDING CHI.  THE SEARCH IS TO MAKE TWO EQUATIONS
'DERIVED FOR CHI AND STEMMING FROM THE EQUILIBRIUM CONDITIONS (MU1A =
MU1B
'AND MU2A = MU2B) SIMULTANEOUSLY YIELD THE SAME VALUE OF CHI.
'
'THESE TWO EQUATIONS ARE 'A' AND 'B' IN THE HANDOUT.
'
'THE PROGRAM INCLUDES A VERY CRUDE PLOTTING ROUTINE.  IF YOU HAD TO DO
'THESE THINGS ALL DAY LONG, YOU WOULD FIND THIS PROGRAM FASTER THAN
'MATHCAD OR SIMILAR.  HOWEVER, YOU WOULD DEFINITELY WISH TO MAKE THE
'SEARCH MORE INTELLIGENT.
'
DIM ASTORE(100), BSTORE(100), CHISTORE(100)
CLS
INPUT "ENTER VALUE OF SIGMA:  ", SIGMA
CHICRIT = (1 + SQR(SIGMA)) ^ 2 / (2 * SIGMA)
PHI2CRIT = 1 / (1 + SQR(SIGMA))

PRINT "SIGMA:  "; SIGMA; "  CHI CRITICAL:  "; CHICRIT; "   PHI2 CRITICAL:  "; PHI2CRIT
BEEPROMPT:
PRINT "DO YOU WANT TO HEAR BEEP WHEN EACH SOLUTION IS FOUND?--Y/[N]"
SOUNDBEEP$ = UCASE$(INPUT$(1))
IF SOUNDBEEP$ = CHR$(13) OR SOUNDBEEP$ = " " THEN SOUNDBEEP$ = "N"
IF SOUNDBEEP$ <> "Y" AND SOUNDBEEP$ <> "N" THEN GOTO BEEPROMPT:
PRINT "HIT ANY KEY TO CONTINUE"; : JUNK$ = INPUT$(1)

BSTEP = .003   'LOOK FOR PHI2B POINTS AT PHI2CRIT + N*0.003 WHERE
               'N = INTEGER
ASTART = PHI2CRIT 'START SEARCHING "GOING LEFT" FROM CRIT POINT.
                  'THIS WILL BE CHANGED AFTER A SOLUTION HAS BEEN FOUND.
ASTEP = BSTEP / 100    'MY COMPUTER IS FAIRLY FAST, SO I CAN SEARCH
                       'CAREFULLY USING A SMALL STEP.


FOR NB = 1 TO 50
  PHI2B = PHI2CRIT + NB * BSTEP
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 LOWDIFF = 100    'SET THE DIFFERENCE FINDER TO SOMETHING HUGE
 FOR NA = 1 TO 10000
 PHI2A = ASTART - ASTEP * NA
   IF PHI2A <= 0 THEN
     IF SOUNDBEEP$ = "Y" THEN BEEP

     GOTO ENDA   'END LOOP WHEN PHI2A GOES NEGATIVE & STORE BEST VALUES
   END IF

   CHIE = (LOG((1 - PHI2B) / (1 - PHI2A)) + (1 - 1 / SIGMA) * (PHI2B - PHI2A)) / (PHI2A ^ 2 -
PHI2B ^ 2)
   CHIF = (LOG(PHI2B / PHI2A) + (1 - SIGMA) * (PHI2A - PHI2B)) / (SIGMA * ((1 - PHI2A) ^ 2 -
(1 - PHI2B) ^ 2))

   DIFF = ABS(CHIE - CHIF)
   IF DIFF < LOWDIFF THEN
      'BEEP: PRINT "NEW BEST FOUND"
      'PRINT PHI2B; PHI2A; DIFF
      LOWDIFF = DIFF
      BESTA = PHI2A
      BESTCHI = CHIE
   END IF
 NEXT NA
ENDA:
 ASTORE(NB) = BESTA
 BSTORE(NB) = PHI2B
 CHISTORE(NB) = BESTCHI
' PRINT "PHI2B:  "; BSTORE(NB); "PHI2A:  "; ASTORE(NB); "CHI:  "; CHISTORE(NB)
 SCREEN 9
 VIEW (40, 20)-(600, 300), , 1
 WINDOW (0, .7)-(.3, .5)  'SET UP A WINDOW TO LOOK AT PHASE DIAGRAM
                  'IN THE RANGE PHI2 = 0 TO 0.3 AND CHI = 0.5 TO 0.7
 LOCATE 2, 1: PRINT .7;
 LOCATE 22, 1: PRINT .5;
 LOCATE 7, 2: PRINT "C";
 LOCATE 8, 2: PRINT "H";
 LOCATE 9, 2: PRINT "I";
 LOCATE 24, 5: PRINT 0;
 LOCATE 24, 40: PRINT "PHI2";
 LOCATE 24, 73: PRINT .3;

 CIRCLE (BESTA, BESTCHI), .001: CIRCLE (PHI2B, BESTCHI), .001



 ASTART = BESTA
NEXT NB

PSET (PHI2CRIT, CHICRIT) 'PLOT THE CRITICAL POINT
LOCATE 15, 40: PRINT "TYPE ANY KEY TO CONTINUE"; : JUNK$ = INPUT$(1)

STOP
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Program Phase.MCD Paul Russo Chem. 4595

available on Website. Load into MathCad in library & try it!

$$\chi crit(\sigma) := \frac{\left(1+\sqrt{\sigma}\right)^2}{2\cdot\sigma} \qquad \sigma := 65 \qquad \phi 2crit(\sigma) := \frac{1}{1+\sqrt{\sigma}}$$

$\chi crit(\sigma) = 0.632$ $\qquad$ $\phi 2crit(\sigma) = 0.11$

$\phi\beta := .12, .14 .. .4$

$\phi\alpha := 0.005$ Initial guess

$$\chi A(\phi\beta, \phi\alpha) := \frac{\ln\left(\frac{1-\phi\beta}{1-\phi\alpha}\right) + \left(1-\frac{1}{\sigma}\right)\cdot(\phi\beta - \phi\alpha)}{\phi\alpha^2 - \phi\beta^2}$$

$$\chi B(\phi\beta, \phi\alpha) := \frac{\ln\left(\frac{\phi\beta}{\phi\alpha}\right) + (1-\sigma)\cdot(\phi\alpha - \phi\beta)}{\sigma\cdot\left[(1-\phi\alpha)^2 - (1-\phi\beta)^2\right]}$$

$Diff(\phi\beta, \phi\alpha) := \chi B(\phi\beta, \phi\alpha) - \chi A(\phi\beta, \phi\alpha)$

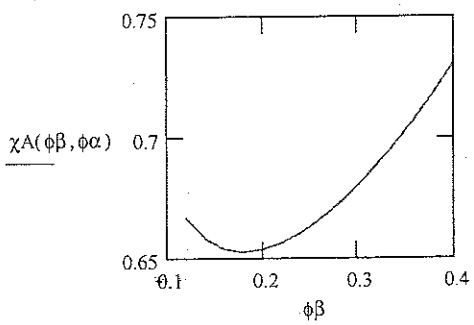
$a(\phi\beta) := root(Diff(\phi\beta, \phi\alpha), \phi\alpha)$ This is the phi2alpha value

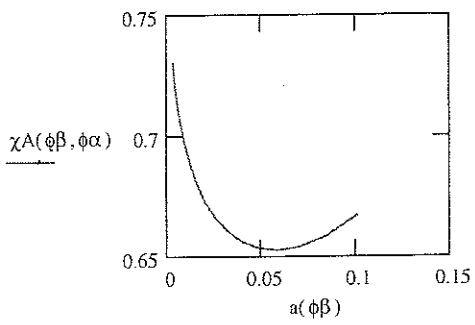
$\phi\beta$	$a(\phi\beta)$	$\chi A(\phi\beta,\phi\alpha)$	$\chi B(\phi\beta,\phi\alpha)$
0.12	0.101	0.667	0.752
0.14	0.084	0.658	0.736
0.16	0.07	0.654	0.724
0.18	0.058	0.653	0.716
0.2	0.048	0.654	0.711
0.22	0.039	0.656	0.707
0.24	0.032	0.661	0.705
0.26	0.026	0.666	0.705
0.28	0.021	0.673	0.705
0.3	0.016	0.68	0.707
0.32	0.013	0.689	0.709
0.34	$9.534\cdot10^{-3}$	0.698	0.712
0.36	$7.112\cdot10^{-3}$	0.708	0.716
0.38	$5.186\cdot10^{-3}$	0.719	0.72
0.4	$3.685\cdot10^{-3}$	0.731	0.724

This is not as accurate as I would like. Perhaps if I had more experience with MathCad.

The QuickBasic Program provided is much faster (for me) to write and gives answers of higher precision. But....I have spent lots of time with QuickBasic!

MathCad is cool considering how little I did to set this up.





You can download This from the web site and see how it was done

Sigma	65	Number of bonds
Phi2Crit	0.110347777	Critical Phi2 Value
ChiCrit	0.631727042	Critical Chi Value
DeltaPhi	0.008896522	Step Size for Search

To put new solutions in for the "index" Phi2B value, Click Tools...Solver. For the "target" select FIndex (e.g., F16 for the indicated cell) and click "solve" Accept the solution when it has been found.

Index	Phi2B Array Holding Phi2B's	Phi2A The variable to be scani the solver routine.	ChiA	ChiB
1	0.1192443	0.05	0.640205013	0.643298492
2	0.128140822	0.05	0.639034945	0.642148156
3	0.137037344	0.05	0.638375186	0.641397094
4	0.145933866	0.05	0.638165075	0.640990501
5	0.154830388	0.073703071	0.635281034	0.635281027
6	0.163726911	0.05	0.63890302	0.641042868
7	0.172623433	0.062511207	0.638312646	0.638312637
8	0.181519955	0.05	0.640943226	0.642041119
9	0.190416477	0.052823468	0.642084183	0.642084181
10	0.199313	0.05	0.644071611	0.64380388
11	0.208209522	0.05	0.645994319	0.644930194
12	0.217106044	0.05	0.64813547	0.646202377
13	0.226002566	0.05	0.650482493	0.647609659
14	0.234899088	0.05	0.653024697	0.649142744
15	0.243795611	0	0.662872256	#DIV/0!
16	0.252692133	0.05	0.658659676	0.652555122
17	0.261588655	0.05	0.661738246	0.654421277
18	0.270485177	0.05	0.664983251	0.656386674
19	0.2793817	0.05	0.668390165	0.658446611
20	0.288278222	0.05	0.671955283	0.660596953
21	0.297174744	0.05	0.675675631	0.662834064
22	0.306071266	0.05	0.679548897	0.665154741
23	0.314967789	0.05	0.683573363	0.667556161
24	0.323864311	0.05	0.687747863	0.670035839
25	0.332760833	0.05	0.692071729	0.672591589
26	0.341657355	0.05	0.696544764	0.675221491
27	0.350553877	0.05	0.701167207	0.677923861
28	0.3594504	0.05	0.705939714	0.68069723
29	0.368346922	0.05	0.710863334	0.683540323
30	0.377243444	0.05	0.715939494	0.686452036
31	0.386139966	0.05	0.721169991	0.689431427
32	0.395036489	0.05	0.726556981	0.692477696
33	0.403933011	0.05	0.732102975	0.695590175
34	0.412829533	0.05	0.737810837	0.69876832
35	0.421726055	0.05	0.743683783	0.702011697
36	0.430622577	0.05	0.749725386	0.705319977
37	0.4395191	0.05	0.755939579	0.708692927