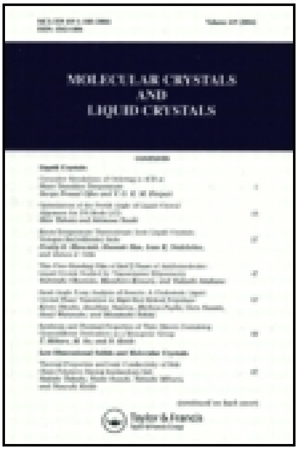

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INTERFACES IN HIGHER ORDER PHASE CHANGE MODELS

P. DELANO HAGAN-VON DREELE AND P. H. VON DREELE^{+}

A previously described combinatorial degeneracy factor can be used in a partition function from which the thermodynamic properties F/k and Cp/k can be calculated at various temperatures throughout a phase transition or phase separation. This combinatorial approach results in a distinction between the probability of occurrence of an A-B interface ($P_{AB} = \nu X_A X_B$) and the mole fraction of A-B interfaces (X_{AB}) in a particular configuration. For a one dimensional system $P_{AB} = X_{AB}$; however, for two and higher dimensional systems $P_{AB} \neq X_{AB}$. The equations for computing X_{AB} are shown along with the temperature dependence of P_{AB} and X_{AB} through a phase change. From the composition and the number of interfaces, a lower bound of the average size of the ordered region can be estimated.

1. INTRODUCTION

Liquid crystals and ordered fluids are often characterized by a regular arrangement of the component species which is changed or randomized upon heating. Such higher order phase transitions and phase separations have been followed calorimetrically and spectroscopically. Theoretical models for these systems have been developed to fit the data and to permit calculation from the model of quantities which cannot presently be measured experimentally. The Lenz-

Ising model is one of the most popular models for higher order transitions. It was solved completely for the one dimensional system for both the cases of $H_o = 0$ and of $H_o \neq 0$ in 1925 and then in 1944 Onsager provided a solution for the two-dimensional system with $H_o = 0$. The two dimensional system with $H_o \neq 0$ and the three-dimensional system with $H_o = 0$ and with $H_o \neq 0$ have not been solved exactly.

The present paper uses a combinatorial method of statistical mechanics to compute the partition function and the thermodynamic properties F/k and Cp/k at various temperatures throughtout a phase change. The difference between the probability of an A-B interface and the mole fraction of A-B interfaces which are equal for one dimensional systems and not equal for two-dimensional systems is emphasized. From the mole fraction of interfaces and the composition of the system it is possible to estimate the minimum average size of the ordered region.

2. A COMBINATORIAL METHOD FOR THE ISING MODEL WITH $H_o = 0$ THAT CAN BE USED TO MODEL PHASE CHANGES.

The Ising model has a lattice of two kinds of species, A and B, which completely occupy the sites. Between these sites there is a nearest neighbor pairwise interaction energy whose value can be E_{AA} or E_{BB} if the species at the adjacent site is the same as that at the origin site or it can be E_{BA} or E_{AB} if the species at the adjacent site is different from that at the origin site. For each total lattice energy there are a number of different configurations possible denoted by a degeneracy factor, γ. The partition function, Q, is written as in equation 1.

$$Q = \Sigma \gamma \exp((\text{pairwise energy})/kT) \qquad (1)$$

For a one dimensional system the degeneracy factor and pairwise energy are given in equation 2 and equation 3, respectively.

$$\gamma = \frac{N_A! \qquad N_B!}{N_{AA}!\, N_{AB}!\, N_{BB}!\, N_{BA}!}^{\,1/N} \qquad (2)$$

$$= \frac{X_A^{X_A} \qquad X_B^{X_B}}{X_{AA}^{X_{AA}} \quad X_{AB}^{X_{AB}} \quad X_{BB}^{X_{BB}} \quad X_{BA}^{X_{BA}}}$$

$$\text{pairwise energy} = \Sigma\, N_{ij}E_{ij} \qquad (3)$$

$$= N_{AA}E_{AA} + N_{AB}E_{AB} + N_{BB}E_{BB} + N_{BA}E_{BA}$$

$$= N_A E_{AA} + N_B E_{BB} + N_{AB}E_{non} \quad \text{when } N_{AB} = N_{BA}$$

$$\text{and } E_{non} = 2E_{AB} - E_{AA} - E_{BB}$$

$$= N\,(E_{AA} + 2\,P_{AB}(E_{AB} - E_{AA})) \text{ when } E_{AA} = E_{BB}$$

$$= N\,(1 - \nu)\,E \text{ when } X_A = X_B;\ E_{AA} = E_{BB} = +E;\ E_{AB} = -E$$

In these expressions $P_{AB} = \nu X_A X_B$ where ν is a nonideality parameter and $X_{AA} = X_A - X_{AB}$. The Onsager solution of the two-dimensional problem is an elliptic integral in E and T and Prigogine has obtained from this solution an expression for γ which is also a function of E and T. Prigogine proposed a combinatorial γ which is within 10% of γ_{Onsager} and the present author has proposed one that is within 1%

of γ_{Onsager}. This latter combinatorial is shown in eqn. 4.

$$\gamma = \left[\frac{N_A! \qquad N_B!}{N_{AAA}!N_{AAB}!N_{BAA}!N_{BAB}!N_{BBB}!N_{BBA}!N_{ABB}!N_{ABA}!}\right]^{\frac{1}{2N}}$$

in which $N_{AAB} = \nu N_A X_A X_B$, $N_{BAB} = \nu^2 N_B X_A X_B$, $N_{AAA} = N_A - 2N_{BAA} - N_{BAB}$. (4)

There are two different ways to express the pairwise energy only one of which will be discussed here and it is shown in equation 5.

$$\begin{aligned} \text{Pairwise energy} &= 2\,\Sigma\, N_{ij}E_{ij} \\ &= 2\,(N_{AA}E_{AA} + N_{AB}E_{AB} + N_{BB}E_{BB} + N_{BA}E_{BA}) \qquad (5) \\ &= 2\,(1-\nu)\,N\,E \end{aligned}$$

Hence, the partition function is now a function of ν, E, and T since when $H_o = 0$, $X_A = X_B = 0.5$.

3. TEMPERATURE DEPENDENCE OF THERMODYNAMIC PROPERTIES ACCOMPANYING HIGHER ORDER PHASE TRANSITIONS AND SEPARATIONS.

The free energy per site, F/k, can be calculated from the partition function, Q, using eqn. 6.

$$F/k = -T \lim_{N\to\alpha} \ln Q^{1/N} \qquad (6)$$

The specific heat, Cp/k, is derived from F/k as shown in equation 7.

$$Cp/k = -T\,\frac{d^2(F/k)}{d\,T^2} \qquad (7)$$

In the Ising model it is customary to fix E/k at +1 which corresponds to a repulsive A-B force that causes a decrease in A-B pairs and an increase in A-A and B-B pairs. With X_A and E fixed, for a given T the F/k value is a function only of ν and has a single minimum which corresponds to the maximum term in the partition function, Q. For values of T in the range from 0 to 6, the maximum term approximation was used to locate F/k and the results are plotted in Figure 1. As can be seen, F/k is a continuous function of T becoming more negative as T is increased with a change in slope near T = 2. The Onsager values for F/k which were obtained by numerical integration were found to be within 1% of F/k(combinatorial) for the range of temperatures shown.

The specific heat was calculated by numerical differentiation of F/k using a step size of 0.001 to 0.025 degrees. Values using the combinatorial method were calculated at T = 0.5, 1.0, 1.5, 1.75, 2.0, 2.2, 2.3, 2.5, 3.0, 3.5, and 4.0 and the smoothed values are plotted in Figure 2. Also shown are the Cp/k(Onsager) values at T = 1.5, 2.0, 2.5, and 3.0. As can be seen, the Cp/k(comb) do not agree exactly with Cp/k(Ons); however, the agreement is better than any of the previous approaches (Bragg-Williams, quasichemical, Kramers-Wannier, or Cavallotti). Thus, an extremely good approximation of the very difficult Onsager solution has been found. Further, the combinatorial method has a γ which is readily extended to higher dimensions and Q(comb) can be easily generalized to the $H_o \neq 0$ case by multiplying it by $\exp(NMH_o/(kT))$ where $M = X_B - X_A$.

4. DISTINCTION BETWEEN PROBABILITY OF AN A-B INTERFACE AND THE MOLE FRACTION OF A-B INTERFACES.

4.1 Counting Pairwise Interactions

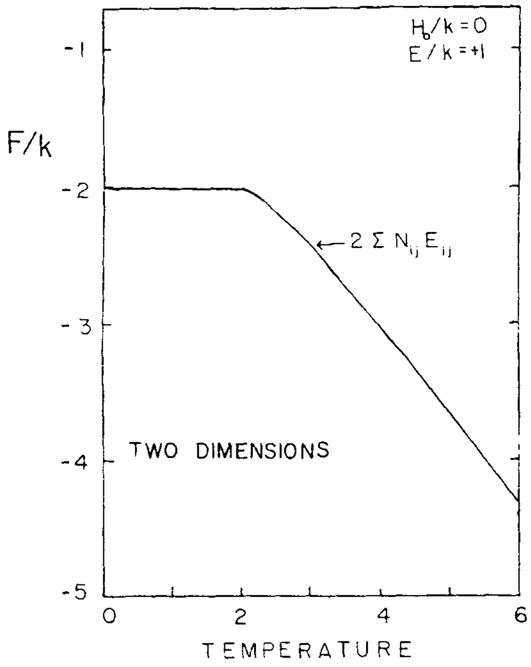

FIGURE 1 F/k versus Temperature

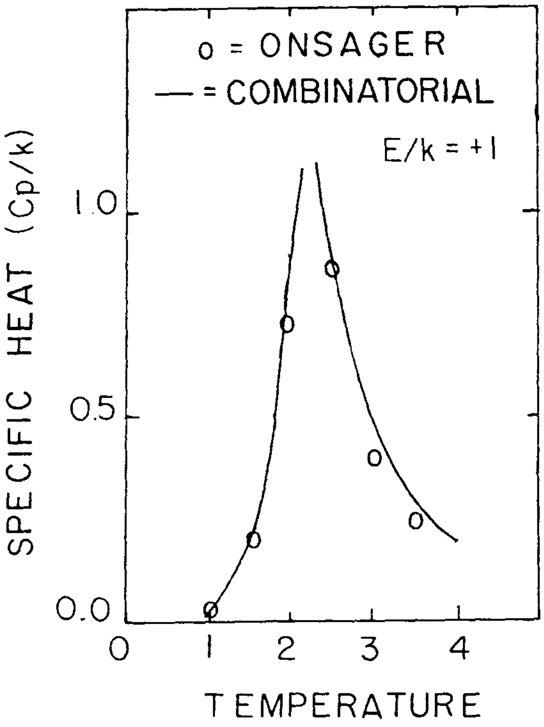

FIGURE 2 Cp/k versus T

The Ising model has a lattice of A and B species with nearest neighbor interactions between adjacent sites. For the square planar lattice, the number of nearest neighbors to each site, Z, is four (north, east, south, and west). If one wishes to count all of the pairs bonds between the sites without overcounting them, then for each site one can count only two unique bonds say north and east. The south bond is counted uniquely as the north bond from the site to the south of the origin site and the west bond is counted uniquely as the east bond from the site to the west of the origin site. Similarly, for a one dimensional system Z = 2, but the number of unique bonds to each lattice site is one.

4.2 Distinguishability of Species and Existence of A(1..m) Moieties.

The A and B species when they occupy sites on the lattice may become distinguishable from other A and B species. In the one-dimensional system, an A species at an origin whose unique neighboring site is occupied by an A, i.e. A(A) can be distinguished from an A species with a B neighbor A(B). In the combinatorial of equation 2, it is these groups of distinguishable kinds of A species ($N_{AA}!$ and $N_{AB}!$) which are divided out of the total number of configurations possible if all N_A were distinguishable ($N_A!$). In the two-dimensional systems an A species at an origin site has two unique neighboring sites which can be occupied by A or B species so there are 2^m or 2^2 or 4 possible distinguishable A moieties: A(AA), A(AB), A(BA), A(BB). Again in the combinatorial of equation 4, these moieties are divided out of $N_A!$ (P. Von Dreele, submitted).

4.3 Probability and Mole Fraction of A(1..m) Moieties.

Each moiety has a probability of its occurrence ($P_{A(AA)}$, $P_{A(AB)}$, $P_{A(BA)}$, and $P_{A(BB)}$) which can be constructed and they are shown in equation 8.

$$
\begin{aligned}
P_{A(AB)} &= X_A P_{AB} = \nu X_A X_A X_B = X_{A(AB)} \\
P_{A(BA)} &= X_A P_{AB} = \nu X_A X_B X_A = X_{A(BA)} \qquad (8) \\
P_{A(BB)} &= \nu X_B P_{AB} = \nu^2 X_A X_B X_B = X_{A(BB)} \\
P_{A(AA)} &= X_A - P_{A(AB)} - P_{A(AB)} - P_{A(BB)} = X_{A(AA)}
\end{aligned}
$$

The mole fraction of the A(1..m) moieties is the same as the probability of occurrence of the moiety as is shown in equation 8. However, if one wishes to count the number of pairwise bonds of a particular kind such as X_{AA}, X_{AB}, X_{BA}, or X_{BB}, then the result obtained depends upon the dimension of the lattice. For the one dimensional lattice $X_{AB} = P_{AB}$ and similarly for all other kinds of pairwise bonds. For the two dimensional lattice, $X_{AB} \neq P_{AB} = \nu X_A X_B$. To count a particular pairwise bond, one adds the mole fractions of each of the kinds of moieties weighted for the number of the pairwise bonds of interest present in each moiety. This is shown in equation 9 for X_{AB} and X_{AA}. Division by m is necessary to have $\Sigma X_{ij} = 1$.

$$
\begin{aligned}
X_{AB} = (&0X_{A(AA)} + 1X_{A(AB)} + 1X_{A(BA)} + 2X_{A(BB)} \\
&+ 0X_{B(AA)} + 0X_{B(AB)} + 0X_{B(BA)} + 0X_{B(BB)})/m \qquad (9) \\
X_{AA} = (&2X_{A(AA)} + 1X_{A(AB)} + 1X_{A(BA)} + 0X_{A(BB)} \\
&+ 0X_{B(AA)} + 0X_{B(AB)} + 0X_{B(BA)} + 0X_{B(BB)})/m
\end{aligned}
$$

A graphical representation of the relationship between X_{AB} and P_{AB} for one and two dimensions is shown in Figure 3 where $X_A = X_B = 0.5$. P_{AB} is linear in ν and coincident with P_{AB} for one dimension but X_{AB} is not linear in ν for two-dimensions. In comparing theoretical and experimental results, it is important to remember this distinction. One should know the dimensionality of the system on which one has collected experimental data by chemical cross-linking or other methods as it determines the amounts of the different kinds of pairwise bonds.

5. VARIATION OF P_{AB} AND X_{AB} DURING TEMPERATURE INDUCED PHASE CHANGES.

The ν values which correspond to the maximum term in the partition function for the systems shown in Figures 1 and 2 have been converted to P_{AB} and X_{AB} using equations 8 and 9. These quantities are plotted versus temperature over the phase change which occurs at about $T_{change} = 2.2$ to 2.3 and are shown in Figure 4. As can be seen, since this is a two dimensional system P_{AB} and X_{AB} are not equal. On heating, both quantities increase continuously and the maximum rate of increase is near T_{change}. This behavior differs from that of a system undergoing a thermally induced phase change characterized by a latent heat.

6. THEORETICAL ESTIMATION OF THE SIZE OF THE ORDERED REGION.

Calculating an averge size for the ordered region in dimensions higher than one is difficult due to the presence of invaginations in the boundary and small inclusions within a larger ordered region. For this reason attention is focused on a configuration which can be defined and studied. The quantity which will be estimated is the domain size if all the domains were uniform in size

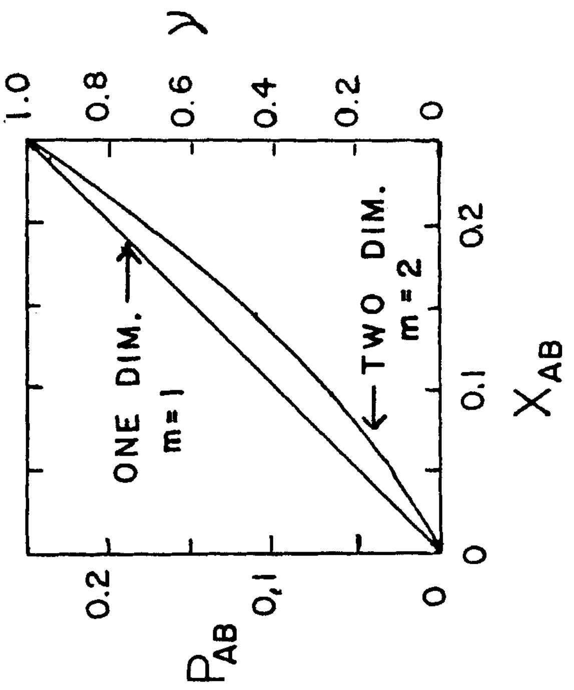

FIGURE 3 P_{AB} versus X_{AB}

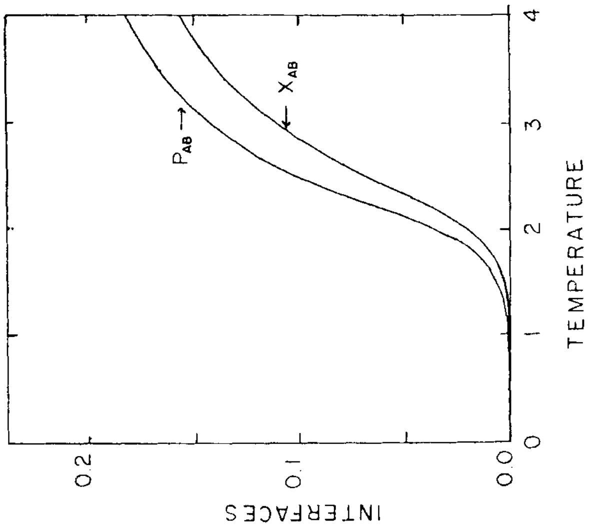

FIGURE 4 P_{AB} and X_{AB} versus Temperature when the interfacial region is minimized. In the square planar model the domains will be square and for the A species they will be of size Dom_A with a side of length $Side_A$. The number of domains of A is $NDom_A$. From these definitions equation 10 follows

$$Dom_A = (Side_A)^2 = \frac{N_A}{N_{domA}} \qquad (10)$$

Now $N_{AB} = 2\ N\ X_{AB}$ since there are 2N unique bonds in the lattice although $\Sigma\ X_{ij} = 1$. Further, the A species in the perimeter of the domain will have bonds to adjacent A and adjacent B species for each domain. One half of the A species in the perimeter (2 $Side_A$) will have a unique countable bond to a B species; hence, equation 11 can be constructed.

$$\begin{aligned} L_{AB} &= 2\ N\ X_{AB} = N_{domA}\ 2\ Side_A \\ &= 2\ N\left(\frac{\nu + \nu^2}{8}\right) \quad \text{for } \nu < 1 \end{aligned} \qquad (11)$$

For ν greater than 1, one should use the full expression for X_{AB} from eqn. 9 and adjust the mole fractions to satisfy material balance. On combining eqns. 10 and 11 one obtains eqn. 12.

$$Dom_A = \left(\frac{4}{\nu + \nu^2}\right)^2 \qquad (12)$$

For ν less than or equal to 1, this provides an estimate of the size of the ordered region when $H_o = 0$ or $X_A = X_B = 0.5$.

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[+] This work was completed in part while the author was a student at New York University and at Harvard University Extension.