Order–disorder in binary substitutional alloys: a simple Ising approach

R. Krachler

Institut für Anorganische Chemie der Universität Wien, Währinger Strasse 42, A-1090 Wien (Austria)

Abstract

To gain insight to the nature of the order–disorder transformation in alloys, the Ising model with nearest-neighbour interactions is frequently used. The three-dimensional Ising model cannot be solved exactly, but modern approximation methods yield results which do not differ widely from exact solutions. Their mathematical derivations are complicated according to the fascinating physical features of the critical point. However, in the present study it could be shown that the Ising order–disorder temperatures of the simple cubic and b.c.c. lattices can be derived with sufficient accuracy from a simple graphical interpolation method. The specific heat *vs.* temperature curves are calculated. They show second-order transitions with rather high values of remaining short-range order at temperatures above the critical temperature.

1. Introduction

In alloys, in the case of substitutional ordering on a fixed lattice, the most important interactions are short ranged, *i.e.* a few interatomic distances at most, whereas long-range interactions are negligible. Short-range order as well as long-range order are thus consequences of local interactions.

Ordering in substitutional solid solutions means the special atomic arrangements characterized by higher than random probability of finding unlike atoms as nearest neighbours. When at high temperatures the disordering tendency of thermal agitation is high, any specific atom succeeds in surrounding itself with only a slightly greater than random number of unlike atoms. The atomic arrangements change with time, but if we were to "freeze in" an atomic distribution at any moment and count the numbers of like and unlike nearest-neighbour pairs, we should find the number of unlike pairs to be higher than for a random distribution. At lower temperatures the non-random correlations between the positions occupied by the different atomic species are higher in magnitude and effective over greater distances. Below the critical temperature long-range order appears. In this state it is possible to classify all the lattice sites in the crystal into sublattices, each of which tends to be occupied predominantly by one kind of atom. The symmetry of the lattice undergoes a step change during the order–disorder transition, whereas the internal energy changes continuously: the

order–disorder phenomena are second-order phase transitions [1]. They are members of the family of critical phenomena [2] which in principle can be described by one single theory. As the alloy is cooled, the long-range order parameter [3] remains zero until the critical temperature T_c is reached, and then the alloy abruptly becomes long-range ordered. If the temperature is reduced further, the value of the long-range order parameter increases smoothly.

To gain insight to the nature of critical phenomena, the Ising model is frequently used. The highlight in any discussion of the Ising model is Onsager's solution for the $H=0$ partition function for a two-dimensional lattice [4]. He has developed a method that can be carried through exactly in the cases of one- and two-dimensional lattices, but the application to real three-dimensional lattices is not possible. Figure 1 shows the specific heat of the two-dimensional Ising model as obtained from the exact solution of Onsager, compared with the Bethe approximation and the Kramers–Wannier and Kikuchi approximation [5–9]. Onsager was able to demonstrate that the specific heat possesses a logarithmic divergence at T_c when approached from either side of the transition.

2. Basic assumptions

In the Ising model used as a model of order–disorder [10], the energies E_{AA}, E_{BB} and E_{AB} associated with
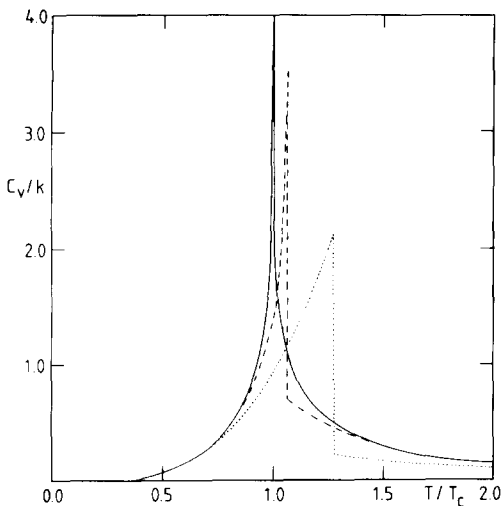
Fig. 1. Specific heat of the two-dimensional Ising model as obtained from the exact solution of Onsager (solid curve), from the Bethe approximation (dotted curve) and from the Kramers–Wannier and Kikuchi approximation (broken curve).

the A–A, B–B and A–B nearest-neighbour pairs are taken as constants irrespective of their environments and the temperature.

The total energy of the crystal is the sum of the pair energies:

$$E = n_{AA}E_{AA} + n_{BB}E_{BB} + n_{AB}E_{AB} \tag{1}$$

where n_{AA} (resp. n_{AB}, n_{BB}) is the number of A–A (resp. A–B, B–B) nearest-neighbour pairs.

Binary substitutional alloys with incompressible simple lattices are considered, simple cubic and b.c.c., in which cases all sites are equivalent. As an approximation it is assumed that the lattice vibrations are independent of the configurations of the atoms on the lattice sites. Empty lattice sites and atoms in interstitial positions are not considered.

The only parameter which enters the Ising model, the ordering energy v [11],

$$v = E_{AB} - 0.5(E_{AA} + E_{BB}) \tag{2}$$

is assumed to be negative according to a tendency for ordering.

Equation (1) gives an explicit expression of the energy as a function of the configuration of the system. As soon as the system is in thermal equilibrium, each configuration i has the usual statistical weight $\exp(-E_i/kT)$, where k is the Boltzmann constant and T is the absolute temperature [12]. Considering all the configurations corresponding to given concentrations of the alloy constituents, one generates the canonical statistical ensemble.

3. Statistical treatment

We fix the volume V, the temperature T, the numbers of atoms of the constituents, N_A and N_B, and the total number of sites, N, in our crystal. The energy E of the crystal is not fixed but depends at any moment on the particular arrangement of the atoms among the lattice sites (the configuration).

The probability of the configuration i depends solely on its own energy E_i and is given by

$$p_i = \frac{\exp(-E_i/kT)}{Z} \tag{3}$$

where Z is the partition function:

$$Z = \sum_i \exp\left(\frac{-E_i}{kT}\right)$$

The mean energy is

$$\bar{E} = \sum_i p_i E_i \tag{4}$$

The total number of nearest-neighbour bonds is given by

$$n_{AA} + n_{BB} + n_{AB} = N\frac{z}{2} \tag{5}$$

where z is the coordination number.

For an alloy with the exact stoichiometry AB, $n_{AA} = n_{BB}$ for all configurations. Therefore a certain value of n_{AA} corresponds to a certain value of the energy E (eqns. (1) and (5)).

The probability of E or the probability of n_{AA} is given by

$$p(n_{AA}) = \text{const} \times w(n_{AA}) \exp\left(\frac{-E(n_{AA})}{kT}\right) \tag{6}$$

where $w(n_{AA})$ is the number of configurations corresponding to n_{AA}.

$$E(n_{AA}) = -2vn_{AA} + N\frac{z}{2}E_{AB} \tag{6a}$$

for the stoichiometric composition AB.

For a crystal with a very large number of atoms, the peak of $p(n_{AA})$ vs. n_{AA} is extremely sharp. It follows that the crystal will spend by far the greater proportion of its time in configurations with n_{AA} very close to the most probable value and the average properties of the system will therefore correspond very closely to its properties when it is in configurations with the most probable n_{AA} value.

For a hypothetical crystal with small N the peak of $p(n_{AA})$ reduces to a flat maximum, still corresponding to the most probable n_{AA} value $n_{AA}(\text{equ})$. Provided that for a given composition

$$\frac{n_{AA}(\text{equ})}{N} = \text{const}(T) \qquad (7)$$

we can perform the extrapolation $N \rightarrow N_L$ and the equilibrium value of the energy can be determined from the maximum of $p(n_{AA})$.

$$E_{\text{equ}} = \frac{N_L}{N} [(E_{AA} + E_{BB})n_{AA}(\text{equ})$$

$$+ (N\frac{z}{2} - 2n_{AA}(\text{equ}))E_{AB}] \qquad (7a)$$

for the stoichiometric composition AB. N_L is Avogadro's number.

3.1. One-dimensional chain

In a hypothetical one-dimensional stoichiometric crystal AB the coordination number $z = 2$ and $N_A = N_B = N/2$. In order to produce periodic boundary conditions, the chain is closed: the first atom of the chain and the last one are nearest neighbours.

It can be shown that $w(n_{AA}, N)$ is given by

$$w = \begin{cases} \left(\dfrac{(N/2-1)!}{(N/2-n_{AA})!n_{AA}!}\right)^2 N\left(\dfrac{N}{2}-n_{AA}\right) & \text{for } n_{AA} > 0 \\ 2 & \text{for } n_{AA} = 0 \end{cases} \qquad (8)$$

where n_{AA} can take the values 0, 1, 2, 3, ..., $N/2-1$ and N is an even integer.

Using eqn. (8), the validity of eqn. (7) can be verified and the solution for the linear Ising lattice can be obtained in good agreement with the exact solution (4).

3.2. Three-dimensional lattices

Since the three-dimensional lattice consists of crossing one-dimensional chains, one may construct small closed three-dimensional arrangements of atoms representing the lattice type under consideration and count the number of A–A nearest-neighbour pairs for each configuration.

In the case where $N_A = N_B$ and $N = 8$ there exist

$$\frac{N!}{(N/2)!(N/2)!} = 70$$

distinct configurations.

Figure 2 shows the simple cubic and b.c.c. structures in the "$N = 8$" version. The complete set of nearest-neighbour pairs is listed in Fig. 2 in order to indicate the way of closing the three-dimensional arrangements. The maxima of the $p(n_{AA})$ curves are found by graphical interpolation (Fig. 3). From eqns. (1), (5) and (7a) the equilibrium energies were derived for a series of temperatures. The resulting C_v vs. T curves are shown in

linear chain:

	n_{AA}	$w(n_{AA})$
8 nearest-neighbor pairs	0	2
1-2,2-3,3-4,4-5,5-6,6-7,7-8,8-1	1	24
	2	36
	3	8

NaCl-type: $z = 6$

24 nearest-neighbor pairs

1-2,2-1,1-4,4-1,1-8,8-1,

2-3,3-2,2-7,7-2,3-4,4-3,

3-6,6-3,4-5,5-4,5-6,6-5,

5-8,8-5,6-7,7-6,7-8,8-7

n_{AA}	$w(n_{AA})$
0	2
4	30
6	32
8	6

CsCl-type: $z = 8$

32 nearest-neighbor pairs

1-5,5-1,1-6,6-1,1-7,7-1,1-8,8-1,

4-5,5-4,4-6,6-4,4-7,7-4,4-8,8-4,

5-2,2-5,5-3,3-5,6-2,2-6,6-3,3-6,

8-2,2-8,8-3,3-8,7-2,2-7,7-3,3-7

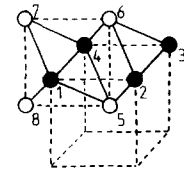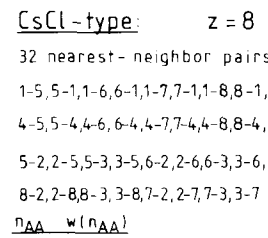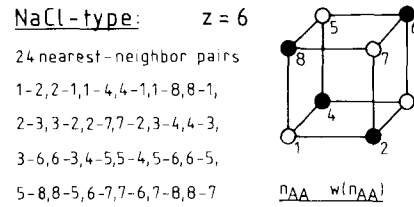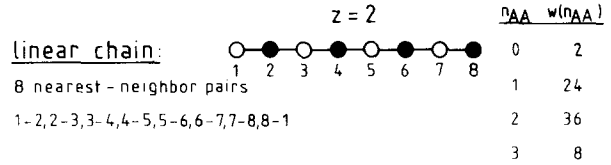| n_{AA}	$w(n_{AA})$
0	2
6	32
8	36

Fig. 2. Closed arrangements of eight atoms representing crystals with stoichiometric composition AB. White circles are A atoms, black circles are B atoms.

Figs. 4 and 5. They resemble Onsager's exact curve for the two-dimensional lattice (Fig. 1).

In Table 1 the resulting values for the critical temperature of order–disorder, T_c, are compared with the results of established methods [7, 13–20].

4. Discussion

The order–disorder transition in alloys is one of the cooperative phenomena. It is a process which depends upon the interplay of a large number of atoms.

How many atoms are needed in a statistical model in order to determine the critical properties?

Wilson [2] needs for the renormalization group theory about 10^6 lattice sites: "The array must be at least as large as the largest fluctuations at the temperature of interest".

The partition function needs the total macroscopic quantity of one mole of atoms because its use is based on the identity of the mean value and the most probable value of the energy.

The Monte Carlo method extrapolates from the behaviour of 1000 or 2000 atoms at least [20]. The proper choice of the system size N is very important in Monte
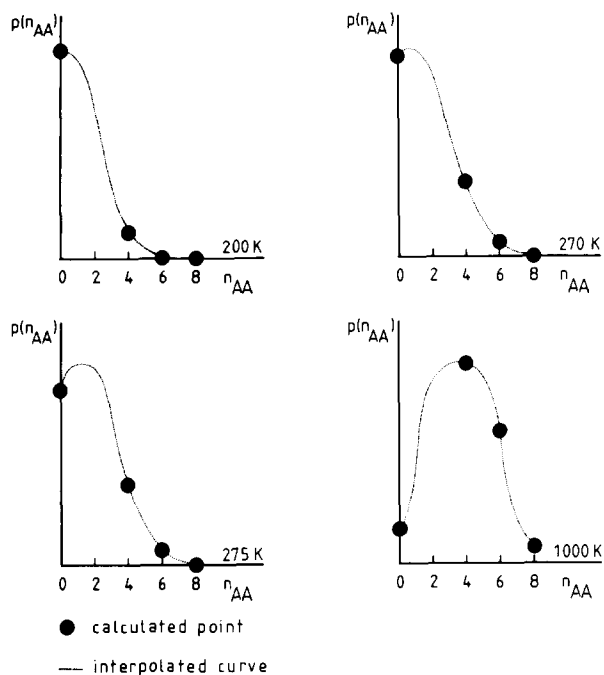
NaCl - type

Fig. 3. Probability of n_{AA} vs. n_{AA} at different temperatures for the eight-atom arrangement representing the NaCl-type structure. The ordering energy $v = -1000$ J mol^{-1}.
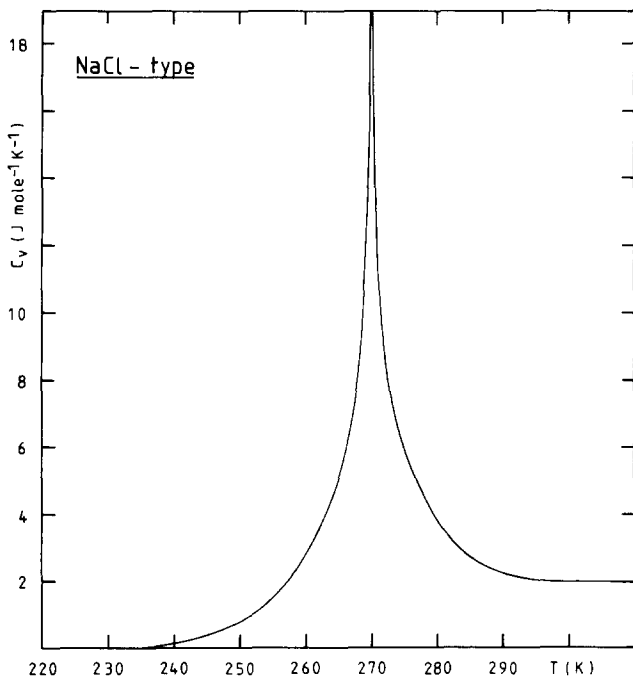

Fig. 4. Specific heat of the three-dimensional Ising model with coordination number six (NaCl type) as obtained from the present study. The ordering energy $v = -1000$ J mol^{-1}.

Carlo simulations. According to Binder [21], reliable information on the behaviour of the infinite system is obtained only if the linear dimension is much larger than the correlation length.
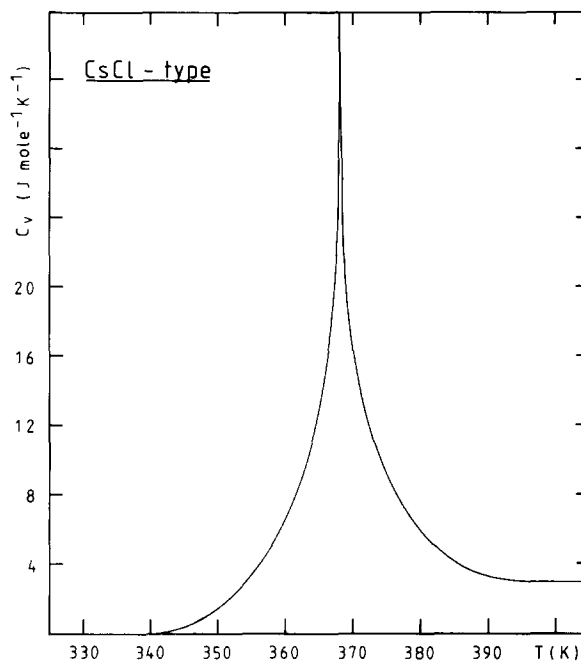

Fig. 5. Specific heat of the three-dimensional Ising model with coordination number eight (CsCl type) as obtained from the present study. The ordering energy $v = -1000$ J mol^{-1}.

TABLE 1. Order–disorder critical temperature values

Method	kT_c/v (NaCl type)	kT_c/v (CsCl type)	Reference(s)
Bragg–Williams	3	4	3, 11, 13
Quasi-chemical	2.465	3.48	5, 11, 13
Li	2.42	3.396	14
Kurata et al.	3.278		18
Fosdick–James	2.3145		17
Kikuchi	2.3049		7
Domb	2.181	3.076	16
Wakefield	2.25		15
Monte Carlo		3.05	20
"$N=8$"	2.245	3.060	Present study

However, in some cases the smallest possible arrangement of atoms that includes the complete information on the crystal structure may be sufficient. As could be shown above, the Ising order–disorder transition temperature of the simple cubic and b.c.c. lattices can be derived with sufficient accuracy from the variation in the positions of only eight atoms.

Acknowledgments

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