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## Short-range order in a 1D substitutional solid solution

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**Abstract.** A new combinatorial approach is proposed to calculate configurational entropy, and an exact expression for the dimensional distribution function of impurity microclusters is obtained for the 1D Ising model of substitutional solid solution for any impurity concentration. The method can be applied to determine the thermodynamic behaviour of the finite Ising chain as well as of one with not only nearest-neighbour interaction.

Short-range order in a solid solution is important for its thermodynamic as well as electronic (for semiconductor compounds) properties. Using a thermodynamic treatment one faces the problem of entropy calculation even in the configurational approximation. Usually, the regular alloy approximation or the quasichemical approximation is used [1–3]. The latter takes into consideration pair correlations in atom arrangement.

It should be noted that the 1D Ising problem can be solved exactly, as Kramers and Wannier first showed [4]. This work is reviewed in [2, 3], where one can also find some alternative derivations of the final expression for the statistical sum. Moreover, the quasichemical approximation appears to be exact in this case. However, these approaches do not give complete information about the short-range order. In particular, it is difficult to obtain the dimensional distribution function of impurity microclusters, which is of considerable interest in such problems as the description of solid solution spinodal decay and the calculation of electron and vibrational properties. In fact, only the pair correlation function was obtained for  $c = 0.5$  [3]. Recently [5] a similar problem of clustering in a 1D random walk was considered, but these results also can be applied only to the Ising model of an alloy of 50:50 composition.

In the present paper we propose a new combinatorial method of configurational entropy calculation and obtain an exact expression for the dimensional distribution function for a 1D alloy of any impurity concentration.

Let us consider a chain which consists of  $N$  atoms of two sorts: 1 (impurity) and 2 (matrix atoms). The Hamiltonian of the chain with nearest-neighbour interactions is:

$$H = E_0 + \frac{(\varepsilon_{11} - \varepsilon_{22})}{2} \sum_i S_i + \frac{E_m}{2} \sum_{(i,j)} S_i S_j \quad (1)$$

where  $\varepsilon_{11}$ ,  $\varepsilon_{22}$  and  $\varepsilon_{12}$  are the bond energies,

$$S_i = \begin{cases} +1 & \text{if position } i \text{ is occupied by atom 1} \\ -1 & \text{if position } i \text{ is occupied by atom 2} \end{cases} \quad E_m = \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) - \varepsilon_{12}$$

and  $E_0$  is independent of  $S_i$ . The sum in the last term of (1) has taken over all pairs of

sites  $(i, j)$ . A number of unique ways of atom arrangement leading to the same eigenvalue of  $H$  can be obtained by the approach considered below, which is also able to provide us with more detailed information about the thermodynamic state of the chain.

We begin by discussing a simple example in order to show the essence of the method. In the identity

$$(x - y)^N = \sum_s^N \binom{N}{s} x^s y^{N-s}$$

let  $x$  and  $y$  be atoms of type 1 and 2 respectively. It is not difficult to see that the coefficient in this expansion with  $s = N_1$  is the number of unique ways of arranging  $N_1$  impurity atoms in  $N$  positions with concentration  $c = N_1/N$  fixed. Moreover, for the system with Hamiltonian (1) it is sufficient to find the number of unique atom arrangements with  $N$ ,  $N_1$ , and  $N_{12}$  fixed ( $N_{12}$  is the number of pairs of different atoms) in order to find the configurational entropy. Denote the cluster which consists of an initial type 2 atom followed by  $q$  type 1 atoms as  $yx^q$ . We can obtain this number  $\Gamma(N, N_1, N_{12})$  using the identity

$$\sum_{q=0}^{\infty} x^q (y + yx + \dots + yx^q + \dots)^{N-N_1} = y^{N-N_1} \frac{1}{1-x} \sum_{s=0}^{N-N_1} \binom{N-N_1}{s} \left[ \frac{x}{1-x} \right]^s. \quad (2)$$

It is equal to the coefficient of  $x^{N_1}$  in the  $s = N_{12}/2$  term in the right-hand side of (2). Thus,

$$\begin{aligned} \Gamma(N, N_1, N_{12}) &= \binom{N-N_1}{N_{12}/2} \frac{1}{(N_1 - N_{12}/2)!} \frac{\partial^{N_1 - N_{12}/2}}{\partial x^{N_1 - N_{12}/2}} \left[ \frac{1}{(1-x)^{N_{12}/2+1}} \right] \Big|_{x=0} \\ &= \binom{N-N_1}{N_{12}/2} \binom{N_1}{N_{12}/2}. \end{aligned} \quad (3)$$

This formula together with the expression for the Helmholtz potential

$$F = E - TS = \varepsilon_{11}N_1 + \varepsilon_{22}(N - N_1) - E_m N_{12} - kT \ln \Gamma(N, N_1, N_{12}) \quad (4)$$

gives the thermodynamics of the finite chain. If  $N$  tends to infinity, we find from (3), (4)

$$\begin{aligned} f(c, p) = F/N &= \varepsilon_{11}c + \varepsilon_{22}(1 - c) - 2E_m p - kT \{ (1 - c) \ln(1 - c) \\ &+ c \ln c - (1 - c - p) \ln(1 - c - p) - (c - p) \ln(c - p) - 2p \ln p \} \end{aligned} \quad (5)$$

where  $p = N_{12}/(2N)$ . Minimizing (5) with  $c = \text{const}$  gives:

$$(1 - c - p)(c - p)/p^2 = \exp(-2E_m/kT) \quad (6)$$

which is the equation of the quasichemical approach (see, for example, [2]).

The calculation of the number of unique arrangements considered above enables us to get more detailed information about short-range order. Multiplying the terms which

contain  $x^n$  for a particular  $n$  by a parameter  $z$  the right-hand side of identity (2) takes the form:

$$y^{N-N_1} \sum_{s=0}^{N-N_1} \binom{N-N_1}{s} x^s \left( \frac{1}{1-x} + x^{n-1}(z-1) \right)^{s+1}.$$

Denote the coefficient of  $x^{N_1}$  in term  $s = N_{12}/2$  here as  $T_n(z)$ . In the same way as above it is not difficult to obtain that

$$T_n(z) = \binom{N-N_1}{N_{12}/2} \sum_{r=0}^{r_{\max}} \binom{N_{12}/2+1}{r} \binom{N_1-nr}{N_{12}/2-r} (z-1)^r \quad (7)$$

where  $r_{\max} = \min\{N_{12}/2+1, [(N_1 - N_{12}/2)/(n-1)]\}$  and  $[X]$  denotes the integer part of  $X$ . Using this function  $T_n(z)$  defined by (7) one can get additional information concerning short-range clustering. Thus, it is clear that  $T_n(1) \equiv \Gamma(N, N_1, N_{12})$ . Then, it is possible to express  $\Gamma(N, N_1, N_{12}, t_n)$ —the number of unique arrangements with fixed  $N, N_1, N_{12}$  and  $t_n$  ( $t_n$  is the number of clusters consisting of  $n$  adjacent type 1 atoms)—by means of this function:

$$\begin{aligned} \Gamma(N, N_1, N_{12}, t_n) &= \frac{1}{t_n!} \frac{\partial^{t_n}}{\partial z^{t_n}} T_n(z) \Big|_{z=0} \\ &= \binom{N-N_1}{N_{12}/2} \sum_{r=t_n}^{r_{\max}} (-1)^{r-t_n} \binom{N_{12}/2+1}{r} \binom{N_1-nr}{N_{12}/2+r} \binom{r}{t_n} \end{aligned} \quad (8)$$

as well as an average value of all powers of  $t_n$ :

$$\begin{aligned} \overline{t_n^p} &= \frac{1}{T_n(1)} \left( z \frac{\partial}{\partial z} \right)^p T_n(z) \Big|_{z=0} \\ &= \binom{N_1}{N_{12}/2}^{-1} \sum_{r=1}^p \binom{N_{12}/2+1}{r} \binom{N_1-nr}{N_{12}/2+r} \left( z \frac{\partial}{\partial z} \right)^p (z-1)^r \Big|_{z=1}. \end{aligned} \quad (9)$$

By the way, it is obvious from (9) that  $\overline{\exp(at_n)} = T_n(\exp a)/T_n(1)$ . It follows from (9) that for a very long Ising chain ( $N$  tends to infinity)

$$\overline{t_n} = \binom{N_{12}/2+1}{1} \binom{N_1-n}{N_{12}/2-1} / \binom{N_1}{N_{12}/2} \approx (N_{12}/2)(p/c)(1-(p/c))^{n-1} \quad (10)$$

$$\begin{aligned} \overline{(\Delta t_n)^2} &= \overline{t_n^2} - (\overline{t_n})^2 = \overline{t_n} [1 - 2(p/c)(1-(p/c))^{n-1} \\ &\quad + n^2(p/c)^2(1-(p/c))^{n-1} - (n-1)^2(p/c)^2(1-(p/c))^{n-2}]. \end{aligned} \quad (11)$$

Formula (10), which gives the appearance frequency for microclusters of different length, provides together with equation (6) full information about short-range clustering in the Ising chain.

Let us consider some particular cases.

(i) *Ordering solution* ( $E_m > 0$ ). Solving (6) gives:

$$p = \begin{cases} c - c^2/(1 - 2c) \exp(-2E_m/kT) & c < \frac{1}{2} \\ (1 - c) - (1 - c)^2/(1 - 2c) \exp(-2E_m/kT) & c > \frac{1}{2} \\ \frac{1}{2} - \exp(-E_m/kT) & c = \frac{1}{2} \end{cases}$$

and the dimensional distribution function for impurity clusters is

$$W_n = 2\bar{r}_n/N_{12} = [c/(1 - 2c) \exp(-2E_m/kT)]^{n-1}. \quad (12)$$

As expected, the overwhelming majority of impurity atoms are surrounded by matrix atoms.

(ii) *Ideal solution* ( $|E_m|/kT \ll 1$ ). We have simply

$$p = c(1 - c) \quad W_n = c^{n-1}(1 - c)$$

(iii) *Decaying solution* ( $E_m < 0$ ). It follows from (6) for the concentration range  $c(1 - c) > \exp(2E_m/kT)$  that:

$$p = \sqrt{c(1 - c)} \exp(E_m/kT) \\ W_n = \sqrt{(1 - c)/c} \exp(E_m/kT) (1 - \sqrt{(1 - c)/c} \exp(E_m/kT))^{n-1}. \quad (13)$$

Though this probability peaks at  $n = 1$  (in accordance with [5]), it is easy to see that the largest number of impurity atoms is included in clusters of length  $\bar{n} = \sqrt{c/(1 - c)} \exp(-E_m/kT)$ , since this corresponds to a maximum of  $nW_n$ .

Such 'optimal' clusters can be rather big ( $\bar{n} \gg 1$ ) unless the impurity concentration is very small. Thus, one can expect significant features in the vibrational spectrum of the chain.

The results obtained above can be presented in another way, if we calculate the sort-range order parameters and spatial correlation function. By definition, the former are [6]:

$$\alpha_i = (p_i - c)/(1 - c) \quad (14)$$

where  $p_i$  is the conditional probability of an impurity atom appearing as the  $i$ th neighbour of another impurity atom. Let

$$p_i = p'_i + p''_i$$

where the first term corresponds to the situation when both atoms belong to the same cluster and the second to the opposite. Taking into account that  $nW_n/(\sum_n nW_n)$  is the probability of an impurity atom belonging to a cluster of length  $n$  we have:

$$p'_i = p/c \sum_{n=i+1}^{\infty} (n - i)W_n = (1 - (p/c))^i \quad p''_i = c(1 - p'_{i-1}) \quad (15)$$

Putting (15) into (14) we obtain:

$$\alpha_i = (\xi^i - c\xi^{i-1})/(1 - c) \quad \alpha_0 = 1 \quad (16)$$

where  $\xi = 1 - p/c$ . For an ideal solution we have from (16)

$$\alpha_i = \begin{cases} 1 & i = 0 \\ 0 & i \neq 0 \end{cases}$$

as expected.

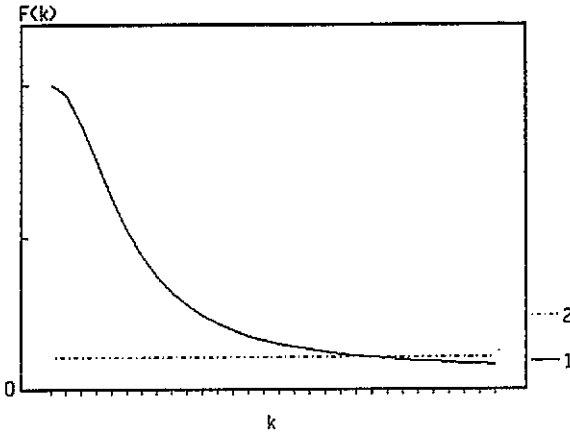


Figure 1. Dependence on wavenumber of the averaged square of the Fourier component of composition fluctuations  $F(k) = N\langle |c_k|^2 \rangle / (c(1-c))$  for decaying (1) and ideal (2) solutions.

Instead of short-range order parameters one can use the pair correlation function which is defined as follows:

$$K(r_j) = \alpha_j (c(1-c)) = \langle c_0 c_j \rangle - c^2$$

where

$$c_j = \begin{cases} 1 & \text{if position } j \text{ is occupied by atom 1} \\ 0 & \text{if position } j \text{ is occupied by atom 2.} \end{cases}$$

If  $c = \frac{1}{2}$ , the expression for  $K$ , which follows immediately from (16), coincides with that obtained in [3]. If necessary, the higher order correlation functions can be obtained in a similar way.

Finally, we have for the Fourier components of composition fluctuations

$$c_k = \frac{1}{N} \sum_{n=0}^{N-1} (c_n - c) \exp(ikn)$$

the following formula valid for  $p/c \ll 1$  (i.e. for a decaying solution) and  $k \ll 1$ :

$$\langle |c_k|^2 \rangle = \frac{c(1-c)}{N} \frac{p/c + k^2/2}{(p/c)^2 + k^2}. \quad (17)$$

This value can be measured experimentally [6]. The dependence (17) is shown in figure 1.

In conclusion, the approach presented above can be generalized for the case of more extended pairwise interaction between atoms in the chain. Instead of equation (6) one obtains a system of equations which contain a set of mixing energies for different

shells. For example, in the case of next-nearest-neighbour (nnn) interactions with corresponding energies  $\bar{\epsilon}_{11}$ ,  $\bar{\epsilon}_{22}$ ,  $\bar{\epsilon}_{12}$  and  $\bar{E}_m$  the term

$$E = N(\bar{\epsilon}_{11}c + \bar{\epsilon}_{22}(1 - c)) - \bar{E}_m Q_{12}$$

must be added to the Helmholtz potential (4), where  $Q_{12}$  is the number of nnn unlike atoms. The entropy should be taken as

$$kT \ln \Gamma(N, N_1, N_{12}, Q_{22})$$

which can be obtained from the identity

$$\begin{aligned} (y + yx + yx^2 + \dots + yx^{N_1})^{N-N_1} &= \sum_{s=0}^{N-N_1} \binom{N-N_1}{s} y^{N-N_1} (x + \dots + x^{N_1})^s \\ &= \sum_{s=0}^{N-N_1} \binom{N-N_1}{s} y^{N-N_1} \sum_{q=0}^s \binom{s}{q} x^q (x^2 + \dots + x^{N_1})^{s-q} \end{aligned}$$

and is given by

$$\Gamma(N, N_1, N_{12}, Q_{22}) = \binom{N-N_1}{N_{12}/2} \binom{N_{12}/2}{Q_{22}} \binom{N_1 - N_{12}/2}{N_{12}/2 - Q_{22}}.$$

Since  $Q_{22} + Q_{12} = 1 - c$ , we have a system of two equations like (6) for the parameters  $p$  and  $Q_{22}$ .

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