

## Estimation of the Equilibrium Properties of the Simple *AB* Alloy

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### *Abstract*

Simulation estimates are presented for the equilibrium values of energy, long-range order and particle concentration as functions of temperature and chemical potential for the *AB* alloy set on a simple square lattice. The simulation was based on a simple Markov process with transitions defined in terms of particle exchange between nearest-neighbour lattice sites. An ensemble mode of relaxation, employing an ensemble of five  $32 \times 32$ -particle samples from the alloy, was used in order to reduce the level of the fluctuations. The usual periodic boundary conditions were replaced by probability boundary conditions where the states of the external lattice site were estimated using probability distribution functions whose lower moments were equal to the running moments of the sample. These boundary conditions allowed particles to move in and out of the sample region, so that the relative numbers of *A* and *B* particles could adjust to accommodate the difference in chemical potential between the two particle-species.

### 1. Introduction

Computer simulation has been used extensively to examine various aspects of the behaviour of statistical models which exhibit order–disorder transitions, with much of the effort being directed toward the study of kinetic Ising models of ferromagnetism or alloy models which are isomorphic to them (see e.g. Ehrmann *et al.* 1960; Yang 1963; Ogita *et al.* 1969; Binder 1974). In almost all of these investigations, the simulation has been based on the ‘Monte Carlo’ prescription given in 1953 by Metropolis *et al.* while studying hard disc systems. In general terms, the computer simulation of a statistical mechanical system is based on simulated sampling over the set of configurations of a finite subsystem or sample taken from the infinite system, the sample statistics providing estimates for the appropriate quantities describing the infinite system. The sample particles are not independent of the rest of the infinite system and, since the interaction between the two systems will contribute to the energy of the sample particles, a satisfactory means of describing this interaction must be found. Recently (Johnson 1978), we discussed modifications to the conventional simulation process, as applied to Ising systems, where the interaction is estimated using probability distribution functions whose lower moments are equal to the running sample moments (correlations) obtained from the simulation. In the present paper we apply these ideas to the study of the equilibrium behaviour of the simple *AB* alloy and in particular consider the estimation of equilibrium thermodynamic properties, such as long-range order and the relative concentrations of *A*

and  $B$  particles, as functions of the temperature and volume and of the relative chemical potentials of the two species of particles.

In studying the behaviour of kinetic Ising systems, the simulation process is usually regarded as a realization of the actual physical process which controls the behaviour of the system. In physical terms, the system of Ising particles is assumed to interact with a large thermal reservoir which can induce in the system transitions allowing particles to change from one configuration to another. It follows that, if the system is initially in thermodynamic equilibrium at a given reservoir temperature, and if this temperature is suddenly changed, the reservoir will reach equilibrium at the new temperature very rapidly, since its relaxation time is, by definition, very short. The Ising system, on the other hand, over a very much longer time, will pass to equilibrium at the new temperature through a sequence of configurations determined by a stochastic process whose probability field is defined in terms of the coupling between the Ising system and the thermal reservoir and the nature of the interaction between the particles. If the coupling between the Ising system and the reservoir is weak, the stochastic process may be approximated by a Markov process which is such that each transition probability is a function only of the energy of the transition and does not depend explicitly on the particle configuration immediately prior to the transition. This Markov property can be seen as a consequence of the requirements that detailed balance for the transition process holds at and very near to equilibrium. It would therefore appear that using the Markov process in the simulation of the approach to equilibrium is really only justified when the system is already sufficiently close to the required equilibrium. In all other cases a more general stochastic process should be used. However, if we are interested only in the equilibrium properties of the particle system, and not in the time approach to equilibrium, it does not matter how the approach is made so long as the system is able to reach equilibrium and to stay there. This last condition would appear to be guaranteed by the nature of the Markov process as it is usually set up.

In the course of the simulation, the sample particles will interact with each other and with those outside. The states of the external particles are unknown and must be estimated, preferably using the sample statistics, in order to calculate the interaction with these particles. For an Ising system with nearest-neighbour influence only, this interaction can be described in terms of 'boundary conditions' applied at the edge of the sample. This will, in effect, impose conditions on the particles immediately outside the sample, these being the only external particles that matter on account of the short range of the interaction. In the Ising model the particles are set at the node points of a lattice, and assigning boundary conditions thus provides a means of estimating the spin states of the particles on the nearest-neighbour external sites in the case of a spin system, or a means of estimating the particle occupancy of these sites in the case of an alloy. The conventional method of assigning the boundary conditions is to replicate the (instantaneous) sample over all space, thus setting up a periodic structure. The inner particles interact with each other in a known way since their states are known, while their interaction with the outer particles is estimated by assuming the states of these particles to be those of the equivalent inner particles. However, these 'periodic boundary conditions' are not really satisfactory for reasons related to critical phenomena (Johnson 1978) and, from a simulation point of view, work reasonably well only when the sample is large enough so that

boundary effects are small compared with bulk effects. Further, they do not allow any level of continuity in the local correlations to be maintained across the sample boundary. This continuity is essential since the sample may be taken from anywhere within the infinite system and the particles outside the sample must accordingly behave in the same way as those inside. For alloy systems, periodic boundary conditions have the added disadvantage that, in the course of the simulation, particles are unable to move across the sample boundary and so allow the particle-species concentrations to adjust in order to accommodate any difference in chemical potential. For an alloy system with periodic boundary conditions the chemical potentials can play no role in the determination of equilibrium since, if there is no particle creation, the particle numbers cannot change and hence the system cannot reach the lowest possible free-energy state. For the  $AB$  alloy with periodic boundary conditions, the lowest possible energy state is reached only for the 50:50 alloy and this implies that the particles have the same chemical potential. If there are vacancies present, and these take part in the transitions, there are effectively three particle types and it is difficult to see how periodic boundary conditions can ever be satisfactory.

From the above discussion, it is clear that for the alloy problem the occupancies of the lattice sites outside the sample must be assigned in such a way that particles are able to enter and leave the sample region, thus making the sample truly representative of the infinite system. This movement must accommodate not only differences in chemical potential but must also be in accord with the fluctuations that must occur in the simulation. If the particle numbers are free to change then the equilibrium state found in the course of the simulation will be the proper thermodynamic equilibrium state, that is, the state with the lowest possible free energy, and it can therefore be interpreted in terms of a grand canonical probability distribution. Of course, if the chemical potentials are correctly chosen functions of temperature, as well as of volume and concentration, the particle concentrations will remain constant with temperature.

Following the method of the earlier paper (Johnson 1978), we assign the occupancy of each external site using probability distribution functions whose lower moments are equal to the running moments, which are the lattice site correlation functions obtained from the simulation. The occupancy of each external site is thus not fixed but will vary in a way determined by the statistical behaviour of the sample particles, that is, the external particles will behave, statistically at least, in the same way as the internal particles. In implementing these probability boundary conditions, we use transitions based on particle interchange between nearest-neighbour lattice sites, which are similar to the spin exchange transitions first introduced by Kawasaki (1966). The probability boundary conditions are clearly consistent with the transition process, particles moving in and out of the sample region by means of the exchange process. Furthermore, using these boundary conditions provides a self-consistent means of computing the sample moments, that is, the lattice site correlation functions, and hence the particle numbers.

In this paper we consider the simulation of an  $AB$  alloy set on the simple square lattice with all the sites occupied either by  $A$  particles or by  $B$  particles. We restrict ourselves to probability boundary conditions using only first moments, that is, the long-range order functions. Specifically, we determine the equilibrium state of a  $32 \times 32$ -particle sample for a range of temperatures and chemical potentials and, in

a particular case, give the variation in relative chemical potential so that the particle numbers in the sample region remain constant. The numerical results show the existence of a phase transition at temperatures consistent with the Onsager value of  $2.2\dots$  for the equivalent ferromagnetic system in zero field. However, the actual temperature is difficult to locate precisely on account of the fluctuations. A larger sample would probably enable the fluctuations to be reduced but a feature of the present simulation is the use of an ensemble mode of relaxation, where an ensemble of  $32 \times 32$  alloy samples is allowed to relax simultaneously, cycle by cycle, using ensemble-averaged moments in the probability boundary conditions. The fluctuations are certainly less than they would have been had the ensemble members been allowed to relax independently, but the proper way to reduce the fluctuations is either to increase  $N$ , to which there is a practical limit, or to introduce higher moments into the boundary conditions (Johnson 1978). However, this would increase the computational time considerably and better computational and programming techniques would have to be developed for this to be done.

## 2. Alloy Simulation

Let  $L$  be the simple two-dimensional infinite square lattice with site coordination number  $z = 4$  and with the same fixed uniform lattice spacing in each lattice direction.  $L$  is a superlattice composed of two sublattices  $L_\alpha$  and  $L_\beta$  such that every  $\alpha$ -site is surrounded by  $z$   $\beta$ -sites and every  $\beta$ -site is surrounded by  $z$   $\alpha$ -sites. Let every site of  $L$  be occupied either by an  $A$  particle or by a  $B$  particle, with the number of  $A$  particles not necessarily equal to the number of  $B$  particles. There are thus no vacant lattice sites and no interlattice particles. We shall refer to this system of particles on the superlattice  $L$  as the  $AB$  alloy, with a particular distribution of  $A$  and  $B$  particles on  $L$  constituting a configuration of the alloy. This alloy system is assumed to interact with a thermal reservoir at a given fixed temperature thereby inducing in the alloy transitions which cause the particles to change from one configuration to another. In the course of a sequence of configurations generated in this way, particles will move from one sublattice to the other, so that we may consider the system of particles on  $L$  to consist of two subsystems of particles, the one set on  $L_\alpha$  and the other set on  $L_\beta$ , which can interact by exchange of particles. If the alloy is initially in thermodynamic equilibrium with the reservoir at a particular temperature and this temperature is then changed, the reservoir, by definition, will reach equilibrium at the new temperature in 'zero time', while the alloy will, in the course of a long time, pass from those configurations characteristic of equilibrium at the initial temperature to those characteristic of equilibrium at the new temperature. These 'equilibrium configurations' are characteristic in the sense that they are the most likely ones at the given temperature. We now wish to develop the computer simulation of the passage of the alloy from equilibrium at one temperature towards equilibrium at a new temperature in terms of a stochastic process in which particle configurations are generated sequentially according to a well-defined transition process. The stochastic process will also operate when the alloy is in the equilibrium state, so that when, in a statistical sense, the alloy is sufficiently close to equilibrium the time sequence of configurations will be stationary and we may collect running averages of configuration-dependent quantities which may later be interpreted in terms of the variables defining the thermodynamic state of the system.

We proceed within the context of the simple Ising model and ascribe to each lattice site  $i \in L$  a state variable  $s_i$ , which describes the occupancy of the site and is defined by

$$s_i = +1 \quad \text{if site } i \text{ is occupied by an } A \text{ particle,} \quad (1a)$$

$$s_i = -1 \quad \text{if site } i \text{ is occupied by a } B \text{ particle.} \quad (1b)$$

If the potential energy can be represented as the sum of pairwise-additive potentials over nearest neighbours, we may write this energy as

$$V(\mathbf{s}) = \frac{1}{4} \sum_{\langle ij \rangle} [\varepsilon_{AA}(1+s_i)(1+s_j) + \varepsilon_{BB}(1-s_i)(1-s_j) + \varepsilon_{AB}\{(1+s_i)(1-s_j) + (1-s_i)(1+s_j)\}]. \quad (2)$$

Here  $\mathbf{s}$  is the configuration vector  $(s_1, s_2, s_3, \dots)$  and the summation is over nearest-neighbour pairs. Also  $\varepsilon_{AB}$  is the potential energy for unlike particles and  $\varepsilon_{AA}$  and  $\varepsilon_{BB}$  are the potential energies for like particles. Rewriting equation (2) we have

$$V(\mathbf{s}) = \frac{1}{4} \sum_{\langle ij \rangle} \{(\varepsilon_{AA} - \varepsilon_{AB}) + (\varepsilon_{BB} - \varepsilon_{AB})\} s_i s_j + \frac{1}{2}(\varepsilon_{AA} - \varepsilon_{BB}) \sum_i s_i + \frac{1}{4}N(\varepsilon_{AA} + \varepsilon_{BB} + 2\varepsilon_{AB}),$$

where  $N$  is the number of particles involved. If we assume that at very low temperatures the most likely configuration is that in which every site of  $L_\alpha$  is occupied by an  $A$  particle and every site of  $L_\beta$  is occupied by a  $B$  particle, then we have  $\varepsilon_{AA} > \varepsilon_{AB}$  and  $\varepsilon_{BB} > \varepsilon_{AB}$ , so that

$$(\varepsilon_{AA} - \varepsilon_{AB}) + (\varepsilon_{BB} - \varepsilon_{AB}) > 0$$

and we can write

$$V(\mathbf{s}) = J \sum_{\langle ij \rangle} s_i s_j + \gamma \sum_i s_i + E_0, \quad (3)$$

where

$$J = \frac{1}{4}\{(\varepsilon_{AA} - \varepsilon_{AB}) + (\varepsilon_{BB} - \varepsilon_{AB})\} > 0, \quad (4a)$$

$$\gamma = \frac{1}{2}(\varepsilon_{AA} - \varepsilon_{BB}) \geq 0, \quad (4b)$$

$$E_0 = \frac{1}{4}N(\varepsilon_{AA} + \varepsilon_{BB} + 2\varepsilon_{AB}) < 0. \quad (4c)$$

For  $J > 0$  it is known that an order-disorder transition will occur at a nonzero temperature (Domb 1974).

In general,  $N_A$  and  $N_B$ , the number of  $A$  and  $B$  particles respectively, will not be constant, although any change in the number of  $A$  particles will be matched by the negative of this change in the number of  $B$  particles. Accordingly, the equilibrium statistical mechanics of the alloy system will be described by the grand canonical partition function  $\Xi$  defined by

$$\begin{aligned} \Xi &\equiv \Xi(T, V, \mu_A, \mu_B) \\ &= \sum_{N_A=0}^N \sum_{\mathbf{s}} \exp\left\{\beta\left(-V(\mathbf{s}) + \frac{1}{2} \sum_i \{\mu_A(1+s_i) + \mu_B(1-s_i)\}\right)\right\}, \end{aligned} \quad (5)$$

where  $T$  is the absolute temperature;  $V$  is the volume as expressed by the lattice spacing which is implicitly contained in the energy parameters  $\varepsilon_{AA}$ ,  $\varepsilon_{BB}$  and  $\varepsilon_{AB}$ ;  $\mu_A$  and  $\mu_B$  are the chemical potentials of the  $A$  and  $B$  particles respectively; and  $\beta = 1/k_B T$ , with  $k_B$  being Boltzmann's constant. The inner summation in equation (5) is over all configurations  $s$  while the outer summation is over the number of  $A$  particles, this summation being taken into account also in the chemical potential sum. Using the form (3) for the potential energy  $V(s)$ , we may write the partition function in the form

$$\Xi = \sum_{N_A=0}^N \sum_s \exp\left\{ \beta \left( -J \sum_{\langle s \rangle} s_i s_j + \xi \sum_i s_i + \eta \right) \right\}, \quad (6)$$

with  $\xi = \frac{1}{2}(\mu_A - \mu_B) - \gamma$  and  $\eta = -E_0 + \frac{1}{2}N(\mu_A + \mu_B)$ . Clearly, we may regard  $\xi$  as a normalized relative chemical potential for the two particle-species. In the simulation process, when the alloy system has reached the equilibrium state for the given temperature, the running averages over the equilibrium sequence of configurations will yield estimates for the various mean values associated with the grand canonical distribution function as expressed in equation (6). Thus, for example, we may estimate the average number of  $A$  particles and the average occupancies of the  $L_\alpha$  and  $L_\beta$  lattices, that is, the long-range order parameters for these lattices.

To implement the simulation process, we shall assume the transitions by which the alloy passes from one configuration to another to be those of particle interchange between nearest-neighbour sites of the lattice  $L$ . These transitions are similar to the spin-exchange transitions first introduced by Kawasaki (1966) and used by Binder (1974) and others in alloy simulation problems. It must be emphasized that this exchange process is not intended to be the actual physical mechanism for the transition process which determines the behaviour of the alloy, where presumably the 'real' mechanism is controlled by the movement of vacancies. However, it should be sufficient to enable the computation of quantities such as equilibrium-critical exponents, which, if universality is to have any meaning at all, must not depend too strongly on the detailed nature of the transition process. The simulation process will be set up by regarding the transitions as defining a stochastic process taken over the set of configurations of the alloy and which we shall assume to be a Markov process with the transition probabilities depending only on the particle configuration immediately before the transition. In point of fact, it will turn out that the dependence is less than this, with the transition probabilities depending only on the energy of the transition and not on the current configuration itself. That is, there are no 'memory' effects at all, and this will mean that the rate of convergence to equilibrium will be the 'slowest possible'.

We first define long-range order statistics based on the particle occupancy of the sites of the lattices  $L_\alpha$  and  $L_\beta$ . If  $n$  be a positive even integer, consider an  $n \times n$  subsystem from the lattice  $L$  having the same coordination and lattice spacing. We define  $n_{A\alpha}$  as the number of  $\alpha$ -sites occupied by  $A$  particles and  $n_{B\beta}$  as the number of  $\beta$ -sites occupied by  $B$  particles. Then, if in the  $n \times n$  subsystem there be  $n_\alpha$   $\alpha$ -sites and  $n_\beta$   $\beta$ -sites, with  $n_\alpha + n_\beta = n \times n$ , we define

$$L_\alpha \text{ order parameter:} \quad \sigma_\alpha = 2n_{A\alpha}/n_\alpha - 1, \quad (7a)$$

$$L_\beta \text{ order parameter:} \quad \sigma_\beta = 2n_{B\beta}/n_\beta - 1, \quad (7b)$$

with the  $L$  order parameter  $\sigma$  defined by

$$\sigma = (n_\alpha \sigma_\alpha + n_\beta \sigma_\beta) / (n_\alpha + n_\beta). \quad (8)$$

These order parameters are defined so that, for a 50:50 *AB* alloy at zero temperature with each species having the same chemical potential, all the  $\alpha$ -sites are occupied by *A* particles and all the  $\beta$ -sites are occupied by *B* particles, with the result that

$$\sigma_\alpha = \sigma_\beta = \sigma = 1.$$

At very high temperatures each site is just as likely to be occupied by an *A* particle as by a *B* particle, so that

$$\sigma_\alpha = \sigma_\beta = \sigma = 0.$$

In the computer simulation of the behaviour of the present *AB* alloy, we simulate the behaviour of a finite  $n \times n$  subsystem or sample from the infinite system and then use the sample statistics to estimate the behaviour of the infinite system. Now, the sample particles interact with each other and with the particles outside in exactly the same way, according to equation (2). The state of each external lattice site (i.e. its occupancy) is unknown and must be estimated in some way, preferably using the sample statistics, before the sample-particle-external-particle interaction can be computed. Since we allow only nearest-neighbour interaction, it will be sufficient to estimate only the states of the sites immediately outside the  $n \times n$  sample. As discussed in the Introduction, the conventional method of estimating these states by introducing periodic boundary conditions is unsatisfactory for our purposes and we now consider application of the alternative method proposed earlier (Johnson 1978).

Since every site of the lattice  $L$  is always occupied, either by an *A* or *B* particle, the most satisfactory way of estimating the occupancies of the external sites is to assign them in probability using distribution functions whose moments are equal to those of the sample particles. The occupancy of each external site is then not fixed but can vary in a manner determined by the statistical behaviour of the sample particles, which, by the very notion of a sample, must behave in the same way as any other sample from the infinite system. That is, the external particles must behave in the same way as the internal particles. On assigning the occupancies in this way, it follows that after particle interchange between an internal and an external site the relative numbers of *A* and *B* particles in the sample will change, but in such a way that the total number of particles in the sample remains constant. This change in the relative numbers of *A* and *B* particles will reflect the difference in chemical potential for the two particles-species, so that, if the correct variation of chemical potential difference with temperature is given, the relative numbers of *A* and *B* particles will, apart from fluctuations, be the same for all equilibrium states of the alloy.

The simplest probability function that can be used to assign the states of the external sites is the one-particle site probability function defined by

$$p_\alpha(s_i = \pm 1) = \frac{1}{2}[1 \pm \sigma_\alpha] \quad (9a)$$

for a site on the  $L_\alpha$  lattice and

$$p_\beta(s_i = \pm 1) = \frac{1}{2}[1 \mp \sigma_\beta] \quad (9b)$$

for a site on the  $L_\beta$  lattice. The forms (9) follow immediately from the definitions of  $\sigma_\alpha$  and  $\sigma_\beta$  as site means for a one-particle sample in a simple Ising system (see Johnson 1978). The values to be given to these parameters as they appear in equations (9) are the running values obtained from the simulation. That is, the probability functions (9) have the same first moments as the sample particles, so that use of these probability functions in the boundary conditions provides a self-consistent scheme for estimating the values of the order parameters for the infinite system.

In the course of the simulation, to assign the state of an external site we proceed as follows. Taking  $\mathcal{R}$  as the value of a random variable uniformly distributed over the interval (0, 1), we assume:

$$\text{for } i \in L_\alpha, \quad \text{if } p_\alpha(s_i = +1) > \mathcal{R} \quad \text{then } s_i = +1 \quad \text{else } s_i = -1; \quad (10a)$$

otherwise

$$\text{for } i \in L_\beta, \quad \text{if } p_\beta(s_i = -1) > \mathcal{R} \quad \text{then } s_i = -1 \quad \text{else } s_i = +1. \quad (10b)$$

We shall refer to the application of these conditions as applying 'probability boundary conditions' to the  $n \times n$  sample from the infinite system.

We must now compute the energy change involved in a single transition and then use this to define the transition probabilities. Consider first a transition involving particles on two internal nearest-neighbour sites of the sample and let all the nearest neighbours of these two sites be internal sites as well. It follows that the occupancies of both transition sites and their nearest-neighbour sites are known. Denote the state variables for the two transition sites by  $s_1$  and  $s_2$  and use the notation  $s_k^e, s_k^n, s_k^w, s_k^s$  for the respective states of the nearest-neighbour sites, with  $k = 1, 2$ . Let us suppose for the moment that before the transition we have  $s_2 = s_1^n$  and  $s_1 = s_2^s$ . In the initial configuration with  $s_1$  and  $s_2$  as given, the initial energy  $E_I$  of the  $n \times n$  sample may be written

$$E_I = Js_1(s_1^e + s_1^w + s_1^s) + Js_2(s_2^e + s_2^n + s_2^w) \\ + Js_1 s_2 + E_{\text{rem}} - N_A \mu_A - N_B \mu_B,$$

where  $E_{\text{rem}}$  is the energy from the remaining sites. On interchanging the two particles, we have the final energy  $E_F$  given by

$$E_F = Js_1(s_2^e + s_2^n + s_2^w) + Js_2(s_1^e + s_1^w + s_1^s) \\ + Js_1 s_2 + E_{\text{rem}} - N_A \mu_A - N_B \mu_B.$$

The energy change  $\Delta E = E_F - E_I$  resulting from the transition is then simply

$$\Delta E = J(s_1 - s_2)\{(s_2^e + s_2^n + s_2^w) - (s_1^e + s_1^w + s_1^s)\},$$

since the numbers of  $A$  and  $B$  particles in the sample are unchanged in this transition. Using the fact that the transition particles are on nearest-neighbour sites, we may write the energy change in the form

$$\Delta E = J(s_1 - s_2)\{(s_2^e + s_2^n + s_2^w + s_2^s) - (s_1^e + s_1^n + s_1^w + s_1^s) - (s_1 - s_2)\}. \quad (11)$$

This expression for  $\Delta E$  is symmetric in each of  $s_k^e, s_k^n, s_k^w$  and  $s_k^s$  for  $k = 1, 2$  and therefore holds for all transitions where the transition particles and their nearest neighbours are all on internal sites. It is important to note that all the state variables

appearing in equation (11) are to be given their values just prior to the transition, that is, they are all initial values.

If now the particle interchange sites are both inside the sample region but some of their nearest neighbours are outside, we assign the states of these external sites using the conditions (10) and proceed as before. Again, the numbers of *A* and *B* particles do not change as a result of the transition, so that there is no change in the chemical potential contribution to the energy change and equation (11) still holds.

Now suppose one of the interchange sites to lie within the sample and the other to lie without. Since we have only interchange between nearest neighbours, the inner site must lie at the edge of the sample. The states of the external site and its nearest neighbours, apart from the other transition particle, are first assigned using the rules (10). On particle interchange, the numbers of *A* and *B* particles in the sample will each change by unity, since all the lattice sites must remain occupied. (It goes without saying that if both transition particles are the same—both *A*'s or both *B*'s—there is no transition.) Consequently, there will be a change in chemical potential in the sample leading to an energy change of  $\Delta E + (\mu_A - \mu_B)$  if the external particle is an *A* particle and  $\Delta E + (\mu_B - \mu_A)$  if the external particle is a *B* particle. In the present work the chemical potentials of each particle species were assumed site-independent, but any such dependence could easily be taken into account.

As we are concerned essentially with the equilibrium properties of the *AB* alloy, we construct the probability  $W(s_1 \leftrightarrow s_2)$  for the transition involving interchange on nearest-neighbour sites 1 and 2 simply by requiring that  $W(s_1 \leftrightarrow s_2)$  and its inverse satisfy the condition of detailed balance in the equilibrium state, with the probability of occurrence of the equilibrium configurations coming from the grand canonical probability distribution function as defined by equation (5). This leads to  $W(s_1 \leftrightarrow s_2)$  being a function of  $\Delta E/k_B T$  only and also requires that it satisfy a certain functional equation (Johnson 1978). This functional equation has a variety of solutions and, in the present computations, we have used the particular form

$$W(s_1 \leftrightarrow s_2) = \{1 + \exp(\Delta E/k_B T)\}^{-1}. \quad (12)$$

Note that  $\Delta E$  contains both the change in exchange energy in the transition as well as any possible changes in chemical potential of the sample.

### 3. Numerical Results

The simulation of the behaviour of a  $32 \times 32$ -particle sample has been computed for the *AB* alloy set on a simple square lattice and estimates have been made of the equilibrium values for the energy, long-range lattice order and particle concentrations for a range of temperatures and values of the relative chemical potential. The simulation was based on a Markov process using the transition probabilities (12), and the states of the nearest-neighbour external particles were estimated using probability boundary conditions with the one-particle probability distribution functions (9), which depend only on the one-particle correlation functions  $\sigma_\alpha$  and  $\sigma_\beta$ . The simulation used an ensemble of five  $32 \times 32$ -particle samples, each sample being given the same weight when computing ensemble averages. The members of the ensemble were allowed to relax simultaneously rather than consecutively, as this was found to reduce the fluctuation level inherent in the simulation, particularly as probability boundary conditions were being used. The simulation was operated as follows. Initially, each

member of the ensemble was set in the well-ordered low-temperature configuration with  $A$  particles occupying all the  $L_\alpha$  sites and  $B$  particles all the  $L_\beta$  sites. The temperature was then set equal to 1.5 (in units of  $J/k_B$ ) and each member of the ensemble was allowed to relax over one cycle, that is,  $32 \times 32 = 1024$  simulation steps, the initial values of  $\sigma_\alpha$  and  $\sigma_\beta$  being used in the estimation of the states of the external lattice sites. At the end of the first cycle, the ensemble averages of both long-range order parameters were computed. Each member of the ensemble was then allowed to relax over a second cycle, using the ensemble averages for  $\sigma_\alpha$  and  $\sigma_\beta$  computed at the end of the previous cycle in the estimates of the occupancies of the external sites. At the end of this cycle, new ensemble averages for  $\sigma_\alpha$  and  $\sigma_\beta$  were computed and the relaxation process continued over third and subsequent cycles. After 100 cycles each ensemble member appeared to be in a stationary state, as evidenced by the stationary nature of the sample statistics, and thermodynamic equilibrium was deemed to have been attained. The ensemble was then allowed to run over a further 20 cycles, with ensemble-averaged data being collected every cycle. At the end of this sequence, the sequence averages, that is, the averages of the 20 values of energy, long-range order and particle numbers, together with their standard deviations were computed. The temperature was then increased and, taking the final configurations of the ensemble members as the initial states, the ensemble was allowed to relax as before. This process extended over a number of temperatures and different values of the relative chemical potential. The ensemble could have been used to compute the variation in free energy with temperature and chemical potential but this was not done, as the level of the fluctuations appeared to be too high.

The simulation results for the  $32 \times 32$  sample are given in Table 1*a* for the case of zero chemical potential difference between the two particle-species. On examining the variation with temperature of energy and long-range order on the  $L_\alpha$  lattice, we see that the order has gone to zero by  $T = 2.45$ , although the fluctuations (i.e. the standard deviations of the ensemble mean values, as shown in parentheses) in both the energy and the order indicate that the 'critical region' has begun at a very much lower temperature (around  $T = 2.20$ ). It is interesting to note that the average concentration of  $A$  particles (and hence of  $B$  particles, since there are equal numbers of  $\alpha$ - and  $\beta$ -sites and every site is occupied) remains at 0.5, to within the level of fluctuations.

Table 1*b* contains the results for the case where the relative chemical potential is again constant but is nonzero and equal to 2.0. We see that the behaviour of the energy and the order is much the same as before, but the concentration of the  $A$  particles does not remain constant but increases slowly with temperature, this increase being significantly above the level of the fluctuations.

The results listed in Table 1*c* are for the case where the relative chemical potential is chosen to be that function of temperature which yields the constant value of 0.7 for the particle concentration. The variation of chemical potential with temperature is approximately correct, the variations in mean concentration all lying within the level of the fluctuations. It is to be noted that the fluctuations here at temperatures away from the critical region are greater than the corresponding values in Tables 1*a* and 1*b*. This is because the simulations for the first two cases were done with an ensemble while the third was done with a single sample. We note also that in all three sets of results there is no change in the level of fluctuations in the  $A$  particle concentration as we pass through the critical region.

**Table 1. Simulation estimates of equilibrium values**

Estimates from a  $32 \times 32$ -particle sample are presented for the equilibrium values of lattice energy, long-range order on the  $L_x$  lattice and the fraction  $F_A$  of sites of the  $L$  lattice occupied by  $A$  particles. Three cases are considered: (a) zero chemical potential difference between the particle species, (b) a constant potential difference of 2.0 and (c) a potential difference varying with temperature in such a way to keep  $F_A$  approximately constant at 0.7. Standard deviations of the estimates are shown in parentheses

Temperature $T$	Potential $\mu_B - \mu_A$	Lattice energy	Lattice order $\sigma_x$	Fraction $F_A$ of $A$ particles
<i>(a) Zero potential difference</i>				
1.50	0.0	-2069(04)	0.982(0.001)	0.499(0.015)
1.60		-2036(04)	0.974(0.001)	0.499(0.009)
1.70		-2014(04)	0.974(0.003)	0.499(0.015)
1.80		-1923(06)	0.923(0.003)	0.498(0.015)
1.90		-1852(05)	0.908(0.006)	0.495(0.014)
2.00		-1669(09)	0.929(0.009)	0.492(0.015)
2.10		-1664(14)	0.821(0.009)	0.500(0.014)
2.20		-1493(15)	0.678(0.018)	0.496(0.013)
2.25		-1388(11)	0.685(0.009)	0.494(0.005)
2.30		-1324(10)	0.536(0.025)	0.488(0.015)
2.35		-1170(08)	0.266(0.061)	0.491(0.010)
2.40		-1084(16)	0.110(0.099)	0.484(0.015)
2.45		-1044(10)	-0.056(0.080)	0.500(0.005)
2.50		-1013(14)	-0.070(0.038)	0.506(0.009)
2.55		-995(08)	0.088(0.087)	0.498(0.008)
2.60		-956(16)	0.068(0.041)	0.498(0.014)
2.70		-878(11)	-0.031(0.033)	0.498(0.015)
3.00		-784(10)	-0.013(0.019)	0.501(0.013)
<i>(b) Constant nonzero potential difference</i>				
1.50	2.0	-2059(33)	0.997(0.000)	0.502(0.016)
1.60		-1987(05)	0.986(0.000)	0.508(0.016)
1.70		-1918(46)	0.971(0.000)	0.512(0.015)
1.80		-1768(11)	0.959(0.007)	0.527(0.015)
1.90		-1580(09)	0.916(0.004)	0.541(0.012)
2.00		-1390(06)	0.833(0.011)	0.554(0.006)
2.10		-1192(14)	0.647(0.016)	0.561(0.014)
2.20		-1002(10)	0.286(0.046)	0.566(0.010)
2.25		-905(13)	0.016(0.076)	0.585(0.016)
2.30		-788(16)	0.207(0.071)	0.598(0.017)
2.35		-697(09)	0.161(0.027)	0.614(0.014)
2.40		-677(09)	0.228(0.018)	0.613(0.014)
2.45		-600(07)	0.317(0.027)	0.630(0.011)
2.50		-512(08)	0.282(0.021)	0.638(0.006)
2.55		-427(14)	0.319(0.017)	0.652(0.018)
2.60		-416(10)	0.312(0.023)	0.649(0.018)
2.70		-338(08)	0.318(0.016)	0.665(0.026)
3.00		-237(08)	0.347(0.015)	0.671(0.018)
<i>(c) Variable potential difference (<math>F_A</math> const.)</i>				
1.50	10.0	-453(54)	0.774(0.029)	0.691(0.010)
2.00	5.0	-110(34)	0.558(0.041)	0.717(0.016)
2.10	2.5	-74(28)	0.362(0.047)	0.720(0.025)
2.20	2.0	-62(46)	0.364(0.037)	0.720(0.029)
2.30	2.0	39(27)	0.454(0.038)	0.730(0.030)
2.40	2.0	6(27)	0.462(0.033)	0.726(0.025)
2.50	1.5	-59(33)	0.404(0.040)	0.711(0.031)

It is clear from the numerical results shown in Table 1 that no satisfactory estimates of either critical temperatures or critical exponents could be obtained from the data. A larger sample would probably achieve this, although a more satisfactory method would be to include higher moments in the probability boundary conditions (Johnson 1978). Further, it is not possible to determine the nature of the transition (i.e. its order) although, by analogy with the Ising model for antiferromagnetism in a zero magnetic field, a second-order phase transition would be expected for the  $AB$  alloy with zero chemical potential difference between the particle species. It is possible that a first-order transition is hidden in the data of Tables 1*b* and 1*c* but more detailed numerical work would be needed to show this. It was thought at first that the difference in the order of the transition might show up in a simple Bragg-Williams (1934) treatment of the problem but, as might be expected, the usual mean-field results are recovered for the zero chemical potential difference and the nonzero case yields the same result. This is discussed in the Appendix. It may be possible to extend the Bragg-Williams analysis in the manner of Kirkwood (1938), possibly incorporating the probability boundary conditions (9).

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## Appendix. $AB$ Alloy in Bragg-Williams Approximation

Let there be  $N$  sites on the lattice  $L$  and let  $N_A$  be the number of  $A$  particles and  $N_B$  the number of  $B$  particles. The grand canonical partition function may be written (cf. equation (5) in the text)

$$\Xi(V, T, \mu_A, \mu_B) = \sum_{N_A, N_B} Z(V, T; N_A, N_B) \exp\{(N_A \mu_A + N_B \mu_B)/k_B T\}, \quad (\text{A1})$$

where the canonical partition functions  $Z(V, T; N_A, N_B)$  are defined by

$$Z \equiv Z(V, T; N_A, N_B) = \sum_s \exp\{-V(s)/k_B T\}. \quad (\text{A2})$$

Proceeding in the manner of the usual Bragg-Williams (1934) approximation, we classify all the configurations  $s$  of the alloy particles into equivalence classes defined by the ordered pairs  $(s_\alpha, s_\beta)$ , where  $s_\alpha = \sigma_\alpha$  and  $s_\beta = \sigma_\beta$ , so that for a given  $(s_\alpha, s_\beta)$

equivalence class we can write  $Z$  in the form

$$Z \equiv Z(V, T; s_\alpha, s_\beta) = \zeta(s_\alpha, s_\beta) \exp\{-W(s_\alpha, s_\beta)/k_B T\}, \quad (\text{A3})$$

where  $\zeta(s_\alpha, s_\beta)$  is the weight of the equivalence class, and is in fact the number of ways of distributing  $N_A$   $A$  particles and  $N_B$   $B$  particles over the sites of  $L$ , and  $W(s_\alpha, s_\beta)$  is the potential energy of the class. It follows then that

$$\zeta(s_\alpha, s_\beta) = \frac{n_\alpha!}{n_{A\alpha}! n_{B\alpha}!} \frac{n_\beta!}{n_{B\beta}! n_{A\beta}!},$$

which, on using Stirling's approximation  $\log N! \sim N \log N$ , may be written

$$\log \zeta(s_\alpha, s_\beta) \sim -\{n_\alpha h(s_\alpha) + n_\beta h(s_\beta)\}, \quad (\text{A4})$$

where

$$h(s) = \frac{1}{2}(1+s) \log\{\frac{1}{2}(1+s)\} + \frac{1}{2}(1-s) \log\{\frac{1}{2}(1-s)\}. \quad (\text{A5})$$

The potential energy  $W(s_\alpha, s_\beta)$  is the sum of nearest-neighbour pairwise interactions and in the present context may be written

$$W(s_\alpha, s_\beta) = v_{AA} \varepsilon_{AA} + (v_{AB} + v_{BA}) \varepsilon_{AB} + v_{BB} \varepsilon_{BB},$$

where  $v_{AA}$  is the average number of  $AA$  interactions,  $(v_{AB} + v_{BA})$  is the average number of  $AB$  interactions and  $v_{BB}$  is the average number of  $BB$  interactions. Using the definitions of  $n_{A\alpha}$  etc. given in Section 2, we find

$$W(s_\alpha, s_\beta) = -2NJs_\alpha s_\beta + N\gamma(s_\alpha - s_\beta) + 2E_0, \quad (\text{A6})$$

where  $J$ ,  $\gamma$  and  $E_0$  are as defined by equations (4).

Expressing the chemical potential terms in equation (A1) in terms of  $s_\alpha$  and  $s_\beta$ , we have

$$\Xi(V, T, \mu_A, \mu_B) = \exp(-Na) \sum_{s_\alpha, s_\beta} \zeta(s_\alpha, s_\beta) \exp\left(\frac{1}{2}NK \{s_\alpha s_\beta + \mu(s_\alpha - s_\beta)\}\right), \quad (\text{A7})$$

where

$$a = \{2E_0 N^{-1} - \frac{1}{2}(\mu_A + \mu_B)\}/k_B T, \quad \mu = \frac{1}{8}J^{-1}(\mu_A - \mu_B - 4\gamma), \quad K = 4J/k_B T;$$

$K$  thus has the role of a reciprocal temperature. Introduction of the functional form (A4) for  $\zeta$  into equation (A7) then gives

$$\Xi = \exp(-Na) \sum_{s_\alpha, s_\beta} (\exp\{-q(s_\alpha, s_\beta)\})^N, \quad (\text{A8})$$

where

$$q(s_\alpha, s_\beta) = \frac{1}{2}(h(s_\alpha) + h(s_\beta)) - K \{s_\alpha s_\beta + \mu(s_\alpha - s_\beta)\}. \quad (\text{A9})$$

To evaluate the partition function, we assume the maximum term in equation (A8) to dominate, with its value determined by the values of  $s_\alpha$  and  $s_\beta$  which satisfy

$$\partial q / \partial s_\alpha = 0, \quad \partial q / \partial s_\beta = 0.$$

These two conditions lead to the two equations

$$s_\alpha = \tanh\{K(s_\beta + \mu)\}, \quad s_\beta = \tanh\{K(s_\alpha - \mu)\}. \quad (\text{A10})$$

Consider first the case  $\mu = 0$ . There are three solutions to equations (A10) for  $\mu = 0$ , namely the null solution  $s_\alpha = s_\beta = 0$  and the two solutions  $s_\alpha = s_\beta = \pm s$ , where  $s$  satisfies

$$s = \tanh(Ks). \quad (\text{A11})$$

The solution for  $-s$  is obtained from that for  $+s$  simply by interchanging the two sublattices  $L_\alpha$  and  $L_\beta$ . Equation (A11) is the usual Bragg-Williams (1934) solution for the  $AB$  alloy, and it is readily shown (graphically) that there is a transition temperature  $T_c$  corresponding in the present notation to  $K = 1$ . Expanding  $\tanh(Ks)$  around  $s = 0$  we find

$$s \sim (T - T_c)^{\frac{1}{2}} \quad \text{as} \quad T \rightarrow T_c^-, \quad (\text{A12})$$

which is the mean-field result. Moreover, the second derivative of the free energy is discontinuous at  $T_c$  so that the transition is second order.

Consider now the case  $\mu \neq 0$ . Here there is a solution  $s_\alpha = s$ ,  $s_\beta = -s$ , with  $s$  satisfying

$$s = -\tanh\{K(s - \mu)\}. \quad (\text{A13})$$

However, this solution yields no critical point, as  $s$  is a continuously differentiable function of  $K$  for all  $K$ ; it reduces to the null solution as  $\mu \rightarrow 0$ . From equations (A10) with  $\mu \neq 0$  it is again readily shown (graphically) that there is a transition temperature, which depends on  $\mu$ . To determine the nature of the transition we expand equations (A10) for small  $s_\alpha$  and  $s_\beta$  and find

$$s_\gamma \sim (T - T_c(\mu))^{\frac{1}{2}} \quad \text{as} \quad T \rightarrow T_c(\mu)^- \quad (\gamma = \alpha, \beta), \quad (\text{A14})$$

from which it is clear that the transition is again second order. The result (A14) reduces to (A12) as  $\mu \rightarrow 0$ .