

Monte Carlo Calculation of the Order-Disorder Transformation in the Body-Centered Cubic Lattice

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The order-disorder transformation in the body-centered cubic structure was investigated by a Monte Carlo method. A critical temperature was observed at the point $(v/kT) = -0.315$. The results of the calculation are in close agreement with the best analytical approximations. The calculated variation of order with temperature is in good agreement with experimental data on β brass and β -AgZn. Some information on the kinetics of the transformation was obtained. It appears likely that the rate-limiting process for diffusion in the ordered structure is jumping of vacancies to second neighbor positions.

INTRODUCTION

THE order-disorder transformation problem has been solved exactly only for the one-dimensional case, and for certain two-dimensional cases. No complete analytic solution for any three-dimensional lattice has been obtained, although a variety of approximate results exist. Since there are several recent reviews of this field,¹ no extensive discussion of analytic methods will be given here.

The Monte Carlo method² is useful for studying this problem for several reasons. In addition to providing quite accurate numerical results for the equilibrium state of the system, this method permits a study of the kinetics of the transformation and of the detailed structure of intermediate states. Also, the introduction of complicating factors such as off-stoichiometric composition, or interactions with other than nearest neighbors can be dealt with relatively easily.

The use of the Monte Carlo method for order-disorder problems was suggested by Murray in 1952,³ and apparently first used by Fosdick for a two-dimensional lattice.⁴ We attempted a calculation for the body-centered lattice of 250 atoms, using a Datatron computer,⁵ but it soon became evident that crystal and computer were both too small for satisfactory results. The present calculation was carried out on an IBM 704 for a 2000-atom crystal. This structure has also been studied by Fosdick⁶ and Guttman⁷ using smaller crystals and different jump procedures.

GENERAL THERMODYNAMIC CONSIDERATIONS

Before discussing the details of the calculation, it will be well to consider briefly the thermodynamics of

¹ T. Muto and Y. Takagi, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 194; L. Guttman, *ibid.* **3**, 146 (1956); C. Domb, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London), Vol. 9, p. 150.

² See N. Metropolis *et al.*, J. Chem. Phys. **21**, 1087 (1953).

³ F. J. Murray, J. Operations Research Soc. Am. **1**, 75 (1952).

⁴ L. D. Fosdick, Bull. Am. Phys. Soc. **2**, 239 (1957). Also Phys. Rev. **116**, 565 (1959).

⁵ P. A. Flinn, G. M. McManus and J. Bardeen, Bull. Am. Phys. Soc. **3**, 59 (1958).

⁶ J. R. Ehrman, L. D. Fosdick, and D. C. Handscomb, J. Math. Phys. **1**, 547 (1960).

⁷ L. Guttman, J. Chem. Phys. **34**, 1024 (1961).

the problem. The parameters which describe the state of order of the system are unusual in that they are observable, but not directly subject to external manipulation, as are the usual variables: temperature, pressure, etc. They are, however, well defined functions of the ordinary variables under equilibrium conditions. Two types of parameters are useful: the α 's of Cowley⁸ which describe the local structure of the lattice, and the Bragg-Williams long-range order parameter, which we shall denote by w , to avoid confusion with entropy. These parameters are defined as follows:

$$\alpha_i = 1 - (p_{ABi}/m_A), \quad (1)$$

where p_{ABi} = probability of finding an A atom as the i th neighbor of a B atom, m_A = mole fraction of A atoms, and

$$w = (r_A - m_A)/m_B, \quad (2)$$

where r_A is the fraction of A sites occupied by A atoms. It may readily be shown that these parameters are not independent; for example:

$$|\alpha_n| \geq w^2 \text{ for all } n;$$

also

$$\alpha_1 = 1, \alpha_2 = 0 \text{ is impossible.}$$

A complete description of the interrelations has not been obtained, however, and the problem of obtaining one appears to be of the same order of difficulty as the Ising problem itself.

Since we wish to consider only nearest neighbor interactions, the energy of our system will depend only on α_1 ; in fact,

$$E = -Nm_{Am_B}c\alpha_1, \quad (3)$$

where N = number of atoms in system, m_A, m_B = mole fraction of components, c = coordination number, and v = interaction energy, the change of energy when one additional unlike bond is formed.

The entropy of the system will not, in general, be simply a function of α_1 , since α_1 does not completely determine the configuration. If, however, we specify that the higher α 's be such as to maximize the entropy for a given α_1 ; that is, that the structure be as random as possible, then the entropy will be well defined. When

⁸ J. M. Cowley, Phys. Rev. **77**, 669 (1950).

we speak of the entropy as a function of α_1 , this condition is implied. This condition will, of course, be satisfied when the system is at equilibrium.

The equilibrium value of α_1 is a function of temperature and interaction energy; this dependence can be expressed in terms of the single parameter v/kT , which we will denote by λ . Once the dependence of α_1 on λ is determined, the energy as a function of temperature can be obtained from Eq. (3) and then any desired thermodynamic quantity can be calculated by using the appropriate classical thermodynamic identity.

METHOD OF CALCULATION

In our system, the energy of any given configuration is equal to the number of unlike bonds present in that state multiplied by v , the energy per unlike bond. The corresponding probability for that state is proportional to the Boltzmann factor:

$$q_i = C e^{-n_i \lambda}, \quad (4)$$

where q_i = probability of the i th configuration and n_i = number of unlike bonds present in the i th configuration. If the Monte Carlo process is to generate a Markov chain which will converge to the small canonical ensemble (the states of the system will occur with frequencies proportional to q_i), three conditions must be satisfied by the transition probabilities.⁹ The first is that they be normalized:

$$\sum_j p_{ij} = 1 \text{ for all } i, \quad (5)$$

where p_{ij} is the transition probability that carries the state i into the state j . This is simply the requirement that all states terminate by a transition to *some* other state of the system. The second condition is the ergodic requirement: all states of the system must be accessible by some route. Finally, the p_{ij} must satisfy the condition of microscopic reversibility

$$q_i p_{ij} = q_j p_{ji} \text{ all } i, j. \quad (6)$$

Using (5), this is seen to be equivalent to the condition

$$\sum_i q_i p_{ij} = q_j \text{ for all } j. \quad (7)$$

A variety of jump procedures can be devised which satisfy the above requirements. If, however, one wishes to study the kinetics of the transformation as well as the equilibrium states, it is necessary to approximate the physical process by which the transformation occurs, presumably vacancy motion. We use the following procedure: consider a vacancy at a given lattice site, and the possibility of a jump to one of the neighboring sites (considering only nearest neighbors at the moment). We pick one of the eight possible jumps at random and consider the change in the number of unlike bonds which will result if that jump occurs. The probability of the jump is taken to be:

$$e^{-\Delta n_{ij} \lambda} / (1 + e^{-\Delta n_{ij} \lambda}). \quad (8)$$

The transition probability is one-eighth of this, since the probability of picking this particular direction is one-eighth. Hence we have:

$$p_{ij} = \frac{1}{8} e^{-\Delta n_{ij} \lambda} / (1 + e^{-\Delta n_{ij} \lambda}),$$

and the probability of no jump occurring on this particular try is:

$$p_{ii} = 1 - \sum_{j \neq i} p_{ij},$$

which satisfies condition (5). We now test to see if condition (7) is satisfied:

$$\begin{aligned} \sum_i q_i p_{ij} &= \frac{1}{8} \sum_{i \neq j} \frac{C e^{-n_i \lambda} e^{-\Delta n_{ij} \lambda}}{1 + e^{-\Delta n_{ij} \lambda}} + q_j p_{jj} \\ &= \frac{1}{8} \sum_{i \neq j} \frac{C e^{-n_j \lambda}}{1 + e^{-\Delta n_{ij} \lambda}} + C e^{-n_j \lambda} - \frac{1}{8} \sum_{i \neq j} \frac{C e^{-n_i \lambda}}{1 + e^{-\Delta n_{ij} \lambda}} \\ &= C e^{-n_j \lambda} = q_j \end{aligned}$$

as required. The condition of accessibility is satisfied as long as nearest neighbor jumps are permitted. Second neighbor jumps alone, however, would not be adequate, since the vacancy would be confined to a simple cubic sub-lattice.

In a reasonable time it is possible to traverse only a small fraction of all possible configurations, even for a small number of atoms. What we do is to proceed far enough to destroy the influence of the starting configuration; that is, to approximate equilibrium, and then to average over a sufficient number of steps to reduce the statistical fluctuations to an acceptably small value. The test for approximate equilibrium is the usual one: we approach the final state from both sides; from a completely random structure, and from a perfectly ordered structure.

It became apparent in the course of the calculation that equilibrium could not be reached in any reasonable time with only nearest neighbor jumps when the equilibrium state was one with long range order. The difficulty lies in the fact that after the vacancy jumps so as to put an atom in a wrong site, the probability is overwhelming that on the next move it will go right back. As a result of this effect, a vacancy is almost completely immobile in the presence of long range order in this structure. To enable the calculation to proceed, the program was changed so that in addition to the eight nearest neighbor jumps, the six neighbor jumps were also considered for each step, to make a total of fourteen choices. Since second neighbor (cube edge) positions lie on a sublattice of atoms of the same kind in the ordered structure, the vacancy can move freely, without putting atoms into wrong sites. Quite aside from considerations of physical plausibility, this change was necessary to get equilibrium results, which, as discussed above, are independent of mechanism. The model, however, is not completely unreasonable for a

⁹ W. W. Wood and F. R. Parker, J. Chem. Phys. **27**, 720 (1957).

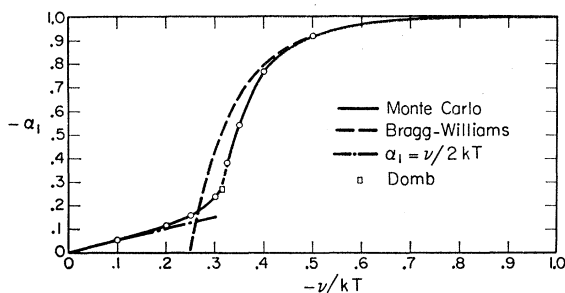
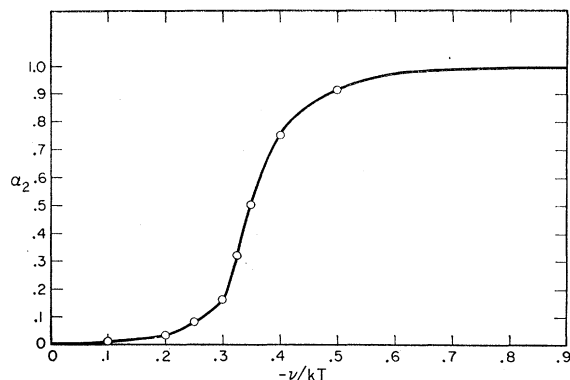
TABLE I. The calculated short- and long-range order parameters. N is the number of jumps to equilibrium.

$-\lambda$	$-\alpha_1$	α_2	w	$10^{-3}N$
0.10	0.054 ± 0.002	0.012 ± 0.002	...	53
0.20	0.115 ± 0.002	0.034 ± 0.002	...	49
0.25	0.155 ± 0.002	0.078 ± 0.002	...	118
0.30	0.237 ± 0.002	0.160 ± 0.002	...	303
0.325	0.379 ± 0.003	0.317 ± 0.003	0.470 ± 0.005	446
0.35	0.540 ± 0.003	0.500 ± 0.003	0.673 ± 0.004	180
0.40	0.766 ± 0.002	0.751 ± 0.002	0.864 ± 0.002	178
0.50	0.918 ± 0.002	0.915 ± 0.002	0.957 ± 0.002	69

real crystal. This will be discussed further in the section on kinetics.

The calculation was carried out for a crystal of ten unit cells on an edge, a total of 2000 atoms. A sort of cyclic boundary condition was used: the atom at the end of each row was joined to the first atom of the next row; the last row of each plane joined to the first row of the next plane of the same sublattice; and the last atom of the top plane of each sublattice to the first atom of the bottom plane of the same sublattice. This was used in preference to conventional cyclic boundary conditions primarily for computational convenience. At the start of each calculation the lattice was filled with equal numbers of A and B atoms (1's and 0's), at random, perfectly ordered, or according to the results of a previous calculation. The number of A atoms as first and second neighbors of each point was computed and stored. A vacancy was then introduced into a location selected at random, and allowed to jump. A random integer from 1 to 8 (or 14) was generated and used to specify the neighboring site to be considered. The probability given by (8) was computed, and compared with a random number between zero and one. Whenever the random number was less than the probability for the jump, it was made; otherwise not. α_1 , α_2 , and w were cumulatively averaged for 1000 jumps, then printed, and a new average started. Each 1000 jumps required approximately 20 seconds of machine time. About 1.5×10^6 jumps were required for the entire calculation.

The pseudo-random numbers required were generated

FIG. 1. The short-range order parameter α_1 versus v/kT , together with the various analytical approximations.FIG. 2. The short-range order parameter α_2 versus v/kT .

by Lehmer's method,¹⁰ i.e., by multiplying the preceding number by 3125 and taking the remainder modulo 2^{15} .

EQUILIBRIUM RESULTS

The numerical results for α_1 , α_2 , and w are given in Table I, and α_1 is shown as a function of (v/kT) in Fig. 1.

Also shown in Fig. 1 are the curves for the approximate analytic solutions valid in the limiting cases of almost perfectly ordered, and almost random structures. The Bragg-Williams (B-W) approximation is equivalent to assuming that $\alpha_1 = w^2$, so that above the critical temperature the structure is completely random, and below it the structure is as random as possible consistent with the long range order present. Thus the B-W curve lies below the true curve, approaching it asymptotically in the limit of perfect order, as α_1 approaches w^2 . For $(-\lambda)$ greater than 0.4, the difference between the two curves is quite small, and the B-W approximation was used in the calculation of thermodynamic functions.

In the limit of almost random structure, the one-dimensional result becomes a valid approximation. The well-known result may be expressed as

$$\alpha_1 = \tanh(v/2kT), \quad (9)$$

which may be approximated by

$$\alpha_1 = v/2kT. \quad (10)$$

The approximation (10) is actually closer to the Monte Carlo curve than is (9) because (10) curves downward, while the Monte Carlo function curves upward. Also shown in Fig. 1 is the short range order at the critical point, as determined analytically by Domb.¹¹ His results give $\lambda_c = -0.315$ and $\alpha_{1c} = -0.268$, in excellent agreement with the Monte Carlo values. Domb's high-

¹⁰ See O. Taussky and J. Todd in *Symposium on Monte Carlo Methods*, edited by H. Meyer (John Wiley & Sons, Inc., New York, 1956), p. 15.

¹¹ See Domb, reference 1, p. 288.

and low-temperature expansions¹² give results in close agreement with the present results in the range $-\lambda < 0.3$ and $0.4 < -\lambda$.

The results for α_2 are plotted in Fig. 2. It is apparent that α_2 varies parabolically with λ near the origin. This is to be expected from the one-dimensional case, for which

$$|\alpha_n| = |\alpha_1|^n.$$

The calculated values for long-range order as a function of the reduced temperature, along with experimental results for β brass¹³ and β -AgZn,¹⁴ are shown in Fig. 3. The agreement with the experimental results is satisfactory.

From the experimentally observed critical temperatures for β brass and β -AgZn, we can compute the interaction energy for these alloys on the basis of the result $v = -0.315 kT_c$, and find for β brass $v/k = 232^\circ\text{K}$, for β -AgZn $v/k = 172^\circ\text{K}$. Using the observed heats of solution for these alloys, calculations on the basis of the quasi-chemical theory¹⁵ give 484° and 365°K , respectively, for β brass and β -AgZn.

It appears that only about one-half of the heat of mixing of these alloys is associated with nearest neighbor interaction, a result which is not surprising, considering the failure of the simple quasi-chemical approach in other systems.¹⁶

THERMODYNAMIC RESULTS

We may rewrite Eq. (3) in the form:

$$(E/Nv) = -2\alpha_1, \quad (11)$$

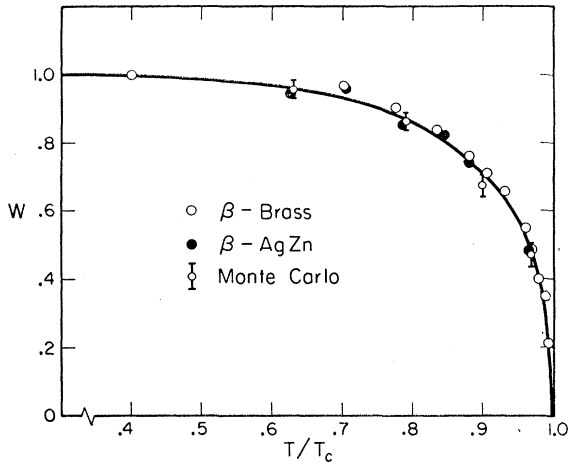


FIG. 3. The calculated and experimental long range order versus the reduced temperature.

¹² C. Domb and M. F. Sykes, *Phil. Mag.* **2**, 733 (1957); *Proc. Roy. Soc. (London)* **A235**, 247 (1956).

¹³ D. Chipman and B. E. Warren, *J. Appl. Phys.* **21**, 696 (1950).

¹⁴ L. Muldower, *J. Appl. Phys.* **22**, 663 (1951).

¹⁵ L. Kaufmann (to be published).

¹⁶ R. A. Oriani, *Acta Met.* **1**, 144 (1953).

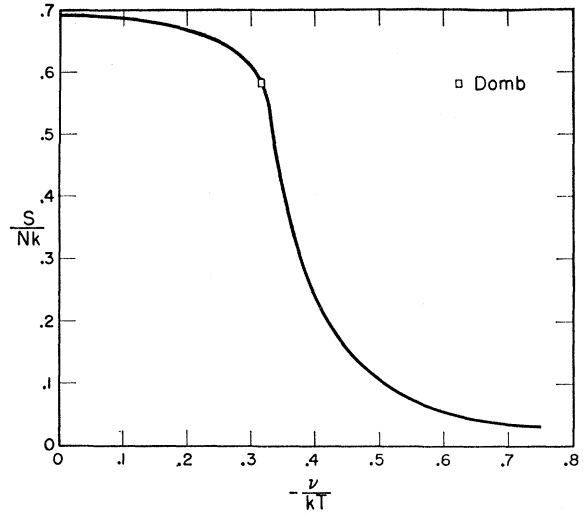


FIG. 4. The entropy of mixing versus v/kT .

so that the plot of α_1 against λ is essentially also a plot of energy against λ . To obtain the entropy as a function of λ we use the thermodynamic relation:

$$dS = (1/T)dE \quad (dV=0). \quad (12)$$

After differentiating 11, substituting in 12, dividing by k and integrating, we find

$$(1/k) \int_{\lambda=0}^{\lambda} dS = -2N \int_{\lambda=0}^{\lambda} \lambda d\alpha_1. \quad (13)$$

At the lower limit the structure is random, so that

$$S/Nk = \ln 2,$$

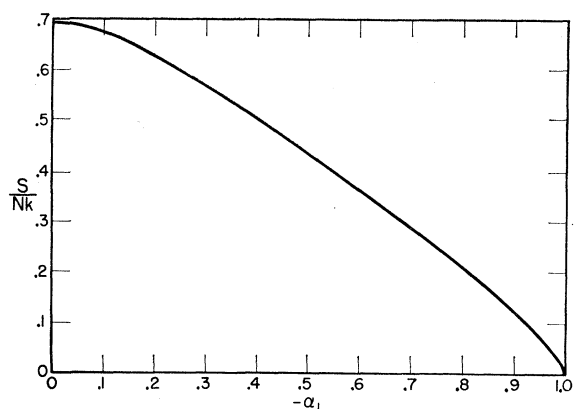
and thus

$$S(\lambda)/Nk = \ln 2 - \int_{\lambda=0}^{\lambda} \lambda d\alpha_1. \quad (14)$$

The integral was evaluated by graphical integration of the curve of Fig. 1 and the result is shown in Fig. 4. The entropy at the critical point is in agreement with the value obtained by Domb, $S_c = 0.586 Nk$, and with the experimental value of $0.54 Nk$.^{7,17} The limiting value of the integral in Eq. (14) provides an additional check, since S must vanish in the limit of infinite λ (zero temperature).

Since we now know S as a function of λ , and α_1 as a function of λ , we can determine S as a function of α_1 . This relation is shown in Fig. 5. The important feature of the curve is the extended region which is almost linear. Since the energy is a linear function of α_1 , we may expect that in some temperature range the free energy will be almost constant over a wide range of α_1 . This occurs, as it must, in the region of the critical tempera-

¹⁷ H. Moser, *Physik. Z.* **37**, 737 (1936).

FIG. 5. The entropy of mixing versus α_1 .

ture, as shown in Fig. 6, in which the quantity,

$$F/NkT = -2\lambda\alpha_1 - (S/Nk),$$

is plotted as a function of α_1 for various values of λ . This insensitivity of the free energy to the degree of order near the critical temperature leads to large fluctuations in order and slow attainment of equilibrium in this temperature range.

The specific heat (both pressure and volume are constant in our system) can be obtained by using the relation:

$$C = dE/dT,$$

which is readily transformed into the result,

$$C/Nk = 2\lambda^2(d\alpha/d\lambda).$$

The derivative was evaluated graphically from the curve of Fig. 1, and the result is shown in Fig. 7. This curve is not in very good agreement with the experimental results of Moser,¹⁷ however, since the lattice

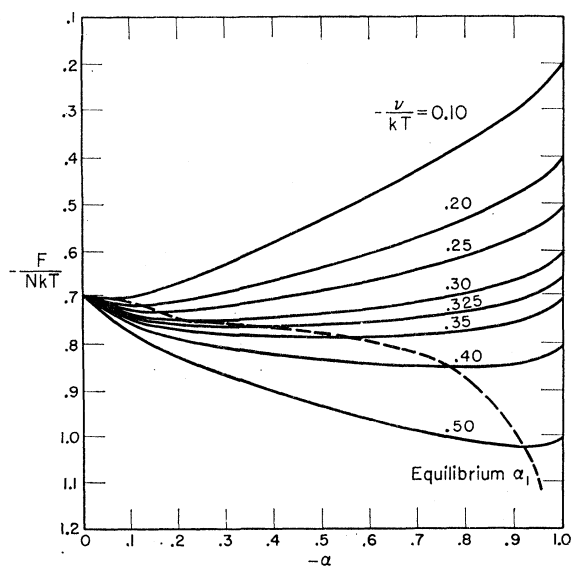
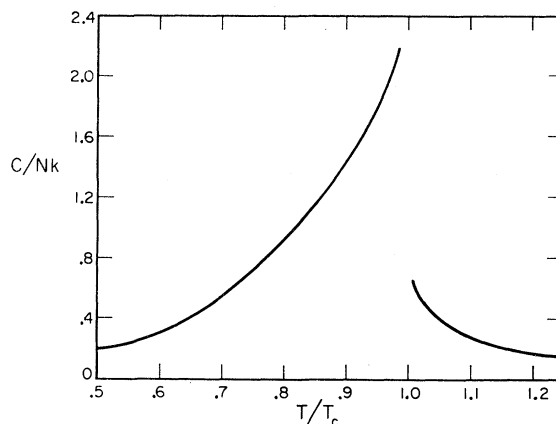
FIG. 6. The free energy versus α_1 for various values of v/kT .

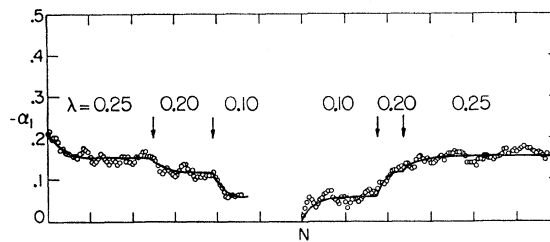
FIG. 7. The excess specific heat versus the reduced temperature.

contribution to the specific heat is not known, and an adequate comparison with experiment is not possible.

KINETICS OF ORDERING

The approach to equilibrium for various values of (v/kT) not too close to the critical value is shown in Figs. 8 and 9. No simple rate law is obeyed, but it is clear that about 20 000 jumps, or ten jumps per atom, are sufficient to reach approximately the equilibrium degree of order. The kinetic behavior for a value of (v/kT) close to the critical is shown in Figs. 10 and 11. Again ten jumps per atom bring the system fairly close to equilibrium, but the final change in the degree of order close to the critical value is very sluggish. Particularly interesting is the long persistence of a metastable state with α_1 about -0.35 during the approach to equilibrium from a state of long-range order, as seen in Fig. 11. This behavior is, of course, to be expected, since the flatness of the free energy curve in this region means that there is very little driving force for a change in order. The curves for values of $(-\lambda)$ above 0.3 were obtained allowing second neighbor, as well as nearest neighbor, jumps, since, as mentioned earlier, in the presence of long-range order, nearest neighbor jumps alone were singularly ineffective in attaining equilibrium.

It is difficult to construct an alternative mechanism in this structure. Divacancy motion as a unit is not possible, since two atoms which are nearest neighbors of a given atom are not nearest neighbors of each other.

FIG. 8. The approach to equilibrium for $T > T_c$. Each point represents 1000 moves.

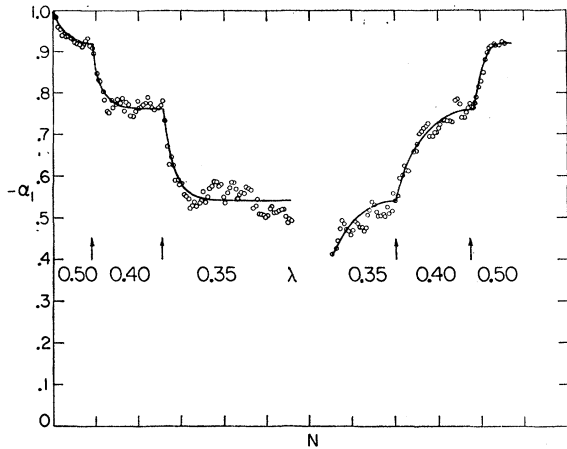


FIG. 9. The approach to equilibrium for $T < T_c$. Each point represents 2000 moves.

Second neighbor jumps, however, although certainly requiring a larger activation energy than nearest neighbor jumps, and occurring much less frequently, may very well occur to some extent. The second neighbor distance is not much greater than the nearest neighbor distance, and the lattice distortion required is not enormously greater. If second neighbor jumps do occur, they will be the rate-limiting process in diffusion, since nearest neighbor jumps contribute almost nothing to vacancy travel. This effect may well explain the large increase in activation energy observed in beta brass on

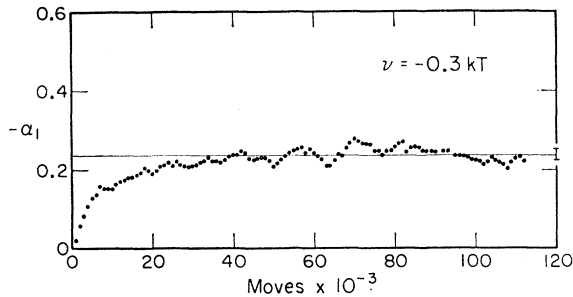


FIG. 10. The approach to equilibrium from disorder for $\nu = -0.3 kT$.

ordering¹⁸; above the critical temperature the activation energy is that for nearest neighbor jumps, and below it, that for second neighbor jumps.

CONCLUSIONS

The results of this Monte Carlo calculation are in quite good agreement with the results obtained by Domb by analytic methods. Unfortunately, no sufficiently accurate experimental data seem to be available to provide a critical test of the adequacy of the nearest neighbor approximation. Higher neighbor interactions can readily be introduced, but there seems no great need to do so until better data are available. Other generalizations which may be of considerable interest

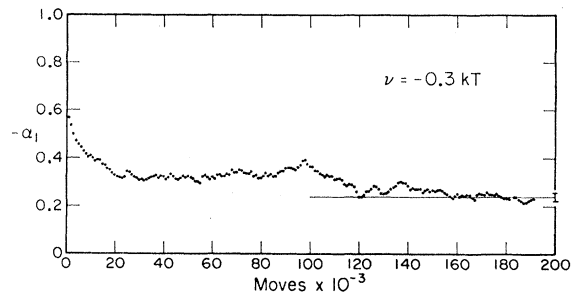


FIG. 11. The approach to equilibrium from order for $\nu = -0.3 kT$.

are the case of off-stoichiometric composition, and the case of clustering ($\lambda > 0$), which has received relatively little attention.

ACKNOWLEDGMENTS

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¹⁸ A. B. Kuper *et al.*, Phys. Rev. **104**, 1536 (1956).