STATISTICAL THERMODYNAMICS
OF
ONE DIMENSIONAL TWO COMPONENT
HARMONIC LATTICES

by

Michael Brewer McNeil

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF ARTS

Houston, Texas
June, 1962
**CONTENTS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>The Exact One-Dimensional Solution</td>
<td></td>
</tr>
<tr>
<td>The Monte Carlo Solution</td>
<td></td>
</tr>
<tr>
<td>Results of Computations</td>
<td></td>
</tr>
<tr>
<td>Conclusion</td>
<td></td>
</tr>
<tr>
<td>Appendices</td>
<td></td>
</tr>
</tbody>
</table>

**APPENDICES**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Approximate Theoretical Treatments of the Ising Problem</td>
<td></td>
</tr>
<tr>
<td>B The Theory of the Monte Carlo Method</td>
<td></td>
</tr>
<tr>
<td>C Exact Solution for the Ising Problem in One Dimension</td>
<td></td>
</tr>
<tr>
<td>D Expression of $C_v$ in Terms of Energy Averages</td>
<td></td>
</tr>
<tr>
<td>E The Choice of a Potential Function</td>
<td></td>
</tr>
</tbody>
</table>
INTRODUCTION

Since Ising proposed in 1925 a simple model for the investigation of ferromagnetism, there has been considerable interest in calculating theoretically the thermodynamic properties of disordered binary lattices. Most of this work has been done on the Ising model: the energy of interaction of two atoms is assumed to be zero if they are not nearest neighbors. If they are nearest neighbors, it has some value determined by the types of the two atoms. All effects depending on displacements of the atoms from their equilibrium sites are disregarded; thus no allowance can be made for vibrational effects.

This model leads to a very simple solution in one dimension.\(^1\) In two dimensions, the thermodynamic properties can in principle be derived exactly for a 50-50 mole percent mixture, but only through extremely involved computations.\(^2\) Not even a formal solution has so far been written for a three-dimensional system, though several approximate techniques are available.\(^3\) The two principal approximate methods are the "Bragg-Williams" approach, in which the energy of a configuration of the system is considered to be a function only of the long-range order, and the "Quasi-chemical" approach, in which one writes the correct expression for the energy of each possible configuration of the lattice, but then uses the wrong combinatorial factor for summing over them. These two techniques are discussed in detail in Appendix B.
Efforts have been made in recent years to include the effects of vibrational interactions in these treatments, or to produce the vibrational spectrum of disordered lattices, from which the vibrational partition function could be calculated. Independent of these considerations, Kikuchi, Prigogine, and Longuet-Higgins have presented exact solutions for the thermodynamic properties of one-dimensional binary systems with fairly general nearest-neighbor interactions. The method of Prigogine and Longuet-Higgins has been adapted in this paper for treatment of the vibrational behavior of an alloy. It is unfortunate that these methods all depend on properties of the one-dimensional system that have no analogues in two or three dimensions.

Booth and Rowlinson have corrected the Quasi-chemical approach to allow for inclusion of vibrational effects, by assuming that the vibrational behavior of an atom in a lattice is determined solely by its nearest neighbors and, furthermore, is dependent only upon the numbers of atoms of the two species present among the first nearest neighbors, and not upon their positions relative to it. Having made this assumption, one applies the "regular solution" approximation that the vibrational partition function of each atom is a linear function of the fraction of unlike nearest neighbors among its nearest neighbors. With these assumptions, it is possible to include the vibrational effects in the Quasi-chemical treatment. Fitting an energy parameter so as to get the correct temperature of the transformation, one can, in the case of $\beta$-brass, get a better
prediction of the value of the discontinuity in the heat capacity than in available from an uncorrected Quasi-chemical procedure.

The scope of the present work is this: the Booth-Rowlinson approach to the vibrational problem might be a very valuable aid in investigating the thermodynamic behavior of alloys, especially as the assumption that the vibrational behavior of each atom is determined primarily by its nearest neighbors and hence that the vibrational behavior of the whole lattice can be approximated by a study of the vibrational behavior of single atoms in their environments, need not be coupled with the Quasi-chemical approach. However, there is some question as to whether the Booth-Rowlinson method is really good per se, or whether it merely shuffles all the error into the curve-fitting parameter which is used to get the correct transition temperature.

Accordingly, a one-dimensional binary alloy has been investigated using both the Booth-Rowlinson vibrational procedure combined with a Monte Carlo sampling procedure, and an exact procedure after Longuet-Higgins. In the present adaptation of the Booth-Rowlinson procedure, however, there is no adjustable constant. A definite set of interatomic potentials is selected, approximating a mixture of Cu and Ag atoms, and the frequencies of vibration of atoms in the various possible environments are calculated, on the assumption that each atom vibrates under the influence of its first nearest neighbors only, which interact as if they were fixed.
2: Appendix C
EXACT ONE-DIMENSIONAL ANALYSIS

In the following section, a Laplace transform procedure is used to obtain a fundamental thermodynamic equation of state for a binary alloy with fairly general nearest-neighbor interactions. In Appendix E, the results are specialized to the particular potential function used in the present problem. All results in the present section are implied in the work of Prigogine and Longuet-Higgins, except for the application of the method to the specialized potential.

Consider \((N+2)\) point-mass atoms located on the \(X\)-axis, and constrained to move in the \(X\)-direction only. These will be numbered serially in the \(X\)-direction \(0, 1, 2\ldots N+1\). The zeroth atom is considered to be fixed at the point \(x = 0\), and the \((N+1)\)th at \(x = L\); the coordinate of the \(i\)th atom will be designated by \(x_i\). The atoms are of two types; there is a mole fraction \(\xi\) of type 1 atoms, and a mole fraction \(1 - \xi\) of type 2 atoms. It is assumed that the potential energy of interaction of atoms numbered \(i\) and \(j\) is zero unless \(|i-j| = 1\), in which case it is given by \(kTf_k(x_i-x_j)\), where atom \(i\) is of type \(k\) and atom \(j\) is of type 1. It is not felt necessary to distinguish between the subscript \(k\) indicating the type of atom and Boltzmann's constant.
The total potential energy of the system can evidently be written:

\[ E = kT \sum_{j=1}^{N+1} f_{kl} (X_j - X_{j-1}) \]  

(1.1)

Furthermore, if \( D_k \) is the internal partition function of an atom of type \( k \) and \( m_k \) its mass, and if \( L_k = h^{-1/2} (2\pi m_k T)^{1/2} \), the partition function of the system is given by:

\[ Q = \left( \frac{D_1}{L_1} \right)^{\xi N} \left( \frac{D_2}{L_2} \right)^{(1-\xi)N} \frac{1}{[\xi (N+1)!] [\xi (N-1)! (N+1)!]} \mathcal{Z} \]  

(1.2)

where:

\[ \mathcal{Z} = \sum_{\sigma} \int_{0}^{L} \int_{0}^{L} \cdots \int_{0}^{L} e^{-\frac{E}{kT}} dx_1 \cdots dx_N d^N \]  

(1.3)

The sum over \( S \) denotes a sum over all possible configurational states of the system; that is, over all orderings of the atoms on the lattice sites.

In each term in the sum over \( S \), the position of each atom in the chain, say that numbered \( j \), is restricted by the requirement \( x_{j+1} > x_j > x_{j-1} \); for, were this not so, the state in question would correspond to another ordering of the atoms and hence
different state in the sum. Hence (I.3) can be rewritten:

\[ \mathcal{Z} = \sum_{s} \int_{0}^{1} \int_{0}^{1} \cdots \int_{0}^{1} e^{-\frac{E}{kT}} d\chi_{1} \cdots d\chi_{N-1} d\chi_{N} \]

Furthermore, it can be seen that all states in the sum over S differing only by the interchange of identical atoms will make equal contributions, so the sum over S can be replaced by a sum over S', the distinguishable states of the system, if every term in S' is counted \((\frac{1}{(n+2)}!) \cdot \left((1-\frac{1}{3})(n+2)\right)!\) times. Hence (I.2) can be written:

\[ Q = \left( \frac{D_1}{L_1^3} \right)^{\frac{S}{2}} \left( \frac{D_2}{L_1^3} \right)^{(n-1)N} \sum_{s'} \int_{0}^{1} \int_{0}^{1} \cdots \int_{0}^{1} e^{-\frac{E}{kT}} d\chi_{1} \cdots d\chi_{N} \]

Using the expression (I.1) for the energy of the system, this leads to:

\[ Q = \left( \frac{D_1}{L_1^3} \right)^{\frac{S}{2}} \left( \frac{D_2}{L_1^3} \right)^{(n-1)N} \sum_{s'} \int_{0}^{1} e^{-\frac{E}{kT}} \cdots \int_{0}^{1} e^{-\frac{E}{kT}} d\chi_{1} \cdots d\chi_{N} \]

In (I.6), the indices \(k\) and \(l\) on each \(f\) function are determined by the value of \(S'\); i.e., the ordering of the atoms on the line.

Equation (I.6) is in the form of a sum over multiple Stieltjes convolutions. The convolution of two functions, \(g\) and \(h\), is
defined as: \( g * h = \int_0^\infty g(x) h(y-x) \, dx \)

It is readily shown that \( g * h = h * g \) and that, if \( L(\ell) \) is defined by

\[
L(\ell) = \int_0^\infty e^{-\frac{\ell L^2}{4}} f(L) \, dL
\]

then \( L(\ell_{23}) = L(\ell_1) \cdot L(\ell_2) \). These properties hold also for multiple convolutions.

In a constant pressure ensemble it can be shown that:

\[
(1.7) \quad e^{-\frac{G}{kT}} = \int_0^\infty e^{-\frac{\ell L^2}{4}} Q(L) \, dL
\]

Before applying this formula to (1.6), it seems desirable to establish some notation. Let the total number of nearest-neighbor pairs of like atoms of type one be \( N_{11} \), that of like atoms of type 2 be \( N_{22} \), and that of unlike atoms be \( N_{12} \). It can be easily seen that, neglecting end effects,

\[
(1.8) \quad N_{11} + \frac{N_{12}}{2} = \xi N \quad \quad \quad N_{22} + \frac{N_{12}}{2} = (1-\xi) N
\]

It is also desirable to use the notation:

\[
L(e^{-\frac{f_{12}}{L^2}}) = F_{12}
\]

Using this notation and equation (1.7), an expression for the Gibbs free energy of the system can be had from (1.6):

\[
(1.9) \quad e^{-\frac{G}{kT}} = \left( \frac{d_1}{L_1^3} \right)^{\xi N} \left( \frac{d_2}{L_2^3} \right)^{(1-\xi) N} \sum_{S'} F_{11}^{N_{11}(S')} F_{12}^{N_{12}(S')} F_{22}^{N_{22}(S')}
\]
For sufficiently long chains, (1.8) will hold and (1.9) can be rewritten:

\[ E = -\frac{G}{kT} = \left( \frac{D_i}{L_i} \right)^{\xi} \left( \frac{D_z}{L_z} \right)^{(1-\xi)} \sum_{s'} \frac{F_{s'}^2}{F_{s'} F_{s2}} \]

Or:

\[ E = -\frac{G}{kT} = \left( \frac{D_i F_{sI}}{L_i^3} \right)^{\xi} \left( \frac{D_z F_{s2}}{L_z^3} \right)^{(1-\xi)} \sum_{N_{s2}} e^{N_{s2} \beta} \]

where \( \beta = \ln \frac{F_{s2}}{\sqrt{F_{sI} F_{s2}}} \)

In the limit of an infinitely long chain, this sum can be approximated by its largest term. This process is discussed in detail in Appendix C. This analysis shows that, in the present case, the maximum term corresponds to:

\[ \tau = \frac{N_{s2}}{N} = (1 - e^{-2\beta})^{-1} \left[ 1 - \left( 1 - 4 \xi (1-\xi)(1-e^{-7\beta}) \right)^{\frac{1}{2}} \right] \]

It has now been shown that, in the limit of large \( N \),

\[ E = -\frac{G}{kT} = \left( \frac{D_i F_{sI}}{L_i^3} \right)^{\xi} \left( \frac{D_z F_{s2}}{L_z^3} \right)^{(1-\xi)} \sum_{N_{s2}} e^{\tau N \beta} \]

\( g(\tau N) \) being the multiplicity of the maximum-term state.

Inserting the value of \( g(\tau N) \) from the exact Ising treatment, one obtains the formal solution of the problem:
From this, it is readily seen that

\[
\frac{G}{NkT} = -\xi \ln \left( \frac{D_1 F_{11}}{L_1^3} \right) - (1-\xi) \ln \left( \frac{D_2 F_{22}}{L_2^3} \right) - B t + \frac{t}{2} \ln \left( \frac{t}{2(1-\xi)} \right) + \frac{t}{2} \ln \left[ \frac{t}{2(1-\xi)} \right] \]  

From this, it is readily seen that

\[
\frac{V}{N} = -\xi \frac{\partial F_{11}}{\partial S} - (1-\xi) \frac{\partial F_{22}}{\partial S} - B \frac{\partial t}{\partial S} - t \frac{\partial G}{\partial S} + \frac{\partial t}{\partial S} \left[ \ln t - \frac{1}{2} \ln \left( \frac{2(1-\xi) - t}{2(1-\xi)} \right) \right] \]  

These are the basic expressions used in the solution of the problem. As noted above, the generation of the transform functions $F_{k1}$ is carried out in Appendix E; the final numerical expressions used are contained in Appendix E.

1: I. Prigogine: op.cit.
4: A.A. Sack: Molecular Physics, 2, 8 (1950).
The model of an alloy under consideration will now be investigated by means of statistical mechanics, using a Canonical ensemble approach.

The energy is considered to be the sum of two terms: $E_o$, the interaction energy of the atoms at rest on their lattice sites, which is a function of $S'$, the vector specifying the ordering of the atoms on the X-axis, and $E_1$, the energy due to their displacements from the minimum-energy positions. This is a function of a vector $R$, which is taken as specifying the displacements of all the atoms from their equilibrium sites. It is assumed that the probability of finding the system in one of the states in $S'$ is given by a Boltzmann distribution, which is justifiable since they are distinguishable configurations of particles of such a size as to be macroscopic as far as most quantum effects are concerned.

The average energy, $\overline{E}$, can be written:

$$ (\text{II.1}) \quad \overline{E} = \sum_{S'} \int \left[ E_o(s) + E_1(R) \right] P dR $$

Where $S'$, being a set of discrete vectors, must be summed over, but $R$, a continuously variable vector, may be integrated over. In this expression,

$$ (\text{II.2}) \quad P = C^{-1} e^{-\frac{1}{kT} \left[ E_o + E_1 \right]} \quad \text{where} \quad C = \sum_{S'} \int e^{-\frac{1}{kT} \left[ E_o + E_1 \right]} dR $$
In this expression, values of \( R \) in a term corresponding to some value of \( S' \) are restricted to those consistent with the ordering specified by \( S' \).

But, since \( E_0 \) is not a function of \( R \),

\[
(II.3) \quad \bar{E} = \sum_{s'} E_0(s') \frac{e^{-\frac{E_0}{kT}}}{C} \int e^{-\frac{E_i}{kT}} dR + \sum_{s'} e^{-\frac{E_i}{kT}} C^{-1} \int E_i(g) e^{-\frac{E_i}{kT}} dR
\]

\[
(II.4) \quad \bar{E} = C^{-1} \sum_{s'} E_0(s') Q(s') e^{-\frac{E_0}{kT}} + C^{-1} \sum_{s'} e^{-\frac{E_i}{kT}} \int E_i(g) e^{-\frac{E_i}{kT}} dR
\]

where \( Q(s') = \int e^{-\frac{E_i}{kT}} dR \)

Note that \( \bar{E}_{vb}(s) = \frac{\int E_i e^{-\frac{E_i}{kT}} dR}{Q} \) assuming a Boltzmann distribution for the displacements.

Let \( U(s) = \frac{E_0(s)}{kT} - \ln Q(s) \)

\[
(II.5) \quad \bar{E} = C^{-1} \sum_{s'} E_0(s') e^{-U(s')} + C^{-1} \sum_{s'} e^{-\frac{E_0}{kT}} Q(s') \bar{E}_{vb}(s)
\]

\[
(II.5a) \quad \bar{E} = C^{-1} \sum_{s'} \left[ E_0(s') + \bar{E}_{vb}(s') \right] e^{-U(s')}
\]

But:

\[
(II.6) \quad C = \sum_{s'} e^{-\frac{E_0}{kT}} \int e^{-\frac{E_i}{kT}} dR = \sum_{s'} Q(s) e^{-\frac{E_0}{kT}} = \sum_{s'} e^{-\frac{U(s)}{kT}}
\]
In essence, the above argument has established $U$ as the weighting factor for averaging the total energy over possible configurational states.

By an argument similar to that above, it can be seen that

$$\langle \frac{E}{kT} \rangle^2 = \sum_{i'} e^{-U^{(i')}} \left[ E_i^2 + \langle E_{v_i^b} \rangle^2 + 2E_i \bar{E}_{v_i^b} \right] C^{-1}$$

A Monte Carlo procedure was designed to sample the possible states of the system in such a fashion that, as the number of samplings became indefinitely large, the average of the energy over the states sampled would approach the correct ensemble average. It can be seen that a suitable transition-probability matrix can be formulated as follows: Given the state $i$, let a state be selected differing from $i$ by the interchange of two randomly chosen atoms. If the new state has an energy less than or equal to that of state $i$, let the transition probability be one; if it has an energy greater than that of the $i$th state, let the transition probability be $\exp (-U_{\text{new}} + U_i)$.

The transition probabilities were handled in this fashion: $\exp (-U_{\text{new}} + U_i)$ was formed and compared with a random fraction generated by a pseudo-random-number generator of very large cycle. The transition was made if the fraction was larger; if the fraction were smaller, the new state was taken to be identical to the old, and the process was repeated. The ergodicity of this game has
already been investigated.\(^3\) It will obviously satisfy the restrictions of the transition probability matrix\(^4\) if the states of the system indeed obey a Boltzmann probability distribution. The energy, and the number of nearest neighbor bonds, are calculated for each state sampled and averaged directly. The square of the energy is also averaged.

It is shown in Appendix D that
\[
(II.8) \quad \frac{C_v}{k_c} = \left( \frac{E}{k_c \tau} \right)^2 - \left( \frac{\bar{E}}{k_c \tau} \right)^2
\]

It was intended to calculate this from the averages formed. However, by mistake a related fluctuation quantity \(K_v\) was calculated. This is discussed in detail in the section on the results.

1: Appendix B
RESULTS

The exact one-dimensional analysis produced the volume per atom of the one-dimensional chain as a function of the reduced pressure. It was difficult to select a precise reduced pressure to correspond to the volume used in the Monte Carlo calculations, as $V$ is a rather slowly varying function of pressure. It is felt that the values of the pressure selected as corresponding to the preselected volume are correct at least in order of magnitude, and probably have one significant figure. Corresponding to the reduced pressure selected at each temperature, the Gibbs free energy relative to the separated atoms by infinite distances was calculated.

The Monte Carlo scheme computes $N_{12}$ properly, using the proper weighting factor. However, this is the only average from the Monte Carlo procedure which permits of a simple interpretation. The energy given by the Monte Carlo procedure is a hybrid energy, given by the relation:

$$\frac{E}{kT} = \frac{N_{11}E_{11}}{kT} + \frac{N_{12}E_{12}}{kT} + \frac{N_{22}E_{22}}{kT} - \frac{N_1E_u}{kT} - \frac{N_2E_{12}}{kT} - \ln Q$$

For each state in the chain, this is the zero-displacement energy of configurational interaction, plus the average of the excess energy due to vibrational motion. Unfortunately, the excess energy due to vibrational motion is represented by $\ln Q$, which is the excess Helmholtz energy due to vibration. This is
purely the result of a mistake on the part of the calculator, and was quite unnecessary.

As a result of this error, the fluctuations in U which we denote by

$$\frac{K_v}{k} = \frac{E_2 - E_1}{(kT)^2}$$

do not represent a common thermodynamic variable and are used solely to give an estimate of the convergence of the Monte Carlo chain.

The following procedure was followed to reconcile the results of the two procedures: The expression for the total entropy of the system was gotten from the exact solution by taking the derivative of G with respect to T. This expression, which is too involved to be reproduced here but which is readily obtained by application of the chain rule to (1.13), remembering that g is a function of T at fixed pressure, divides rather conveniently into a term of the form $k_s \xi \ln \xi + k(1-\xi) \ln(1-\xi)$, which obviously corresponds to the ideal entropy of mixing, plus a term of more involved form in the interactions. The latter term, in turn, can be separated into a term dependent only upon zero-point interactions, plus another correction which vanishes if the springs are all made infinitely stiff so as to preclude vibrational motion. The term in zero-point interactions might be identified as a "configurational entropy correction" and the term dependent on spring constants as a "vibrational entropy correction." Fortunately, both corrections were negligible in the two higher-temperature cases; it was felt necessary to include the configurational term in the 10° case.
Thus the Gibbs energy from the exact solution was reduced to a form comparable to the Monte Carlo energy by the subtraction of $N_1E_{11} + N_2E_{22} - T^2E_{mixing}$. This reduction was chosen instead of running Monte Carlo procedures on the two pure components and getting the actual energy of mixing as it would be experimentally observed for a reason: the purpose of this calculation is to determine the value of the Booth-Roullinon approximation. It was felt that an effort should be made to apply this approximation in only one place; if it were applied to the pure metals as well, errors due to the application of this approximation to the alloy might be "washed out" by similar errors made in the same calculation in the pure metal, leading to false agreement of results. There is no evidence that this would occur; but, in the process as used, it cannot occur.

No numbers were derived from the Monte Carlo calculation which could be compared to the heat capacity obtained from the Ising and exact solutions.
RESULTS OF EXACT ONE DIMENSIONAL SOLUTION

\[ T = 30 \text{ Degrees } K. \]

\[ a = \frac{p}{12T}, \text{ cm}^{-1} \]

<table>
<thead>
<tr>
<th>( \frac{V}{N} ) cm x 10^8</th>
<th>( \frac{N_{12}}{N} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -1 \times 10^{-8} )</td>
<td>3.02107</td>
</tr>
<tr>
<td>( -1 \times 10^{-6} )</td>
<td>3.00010</td>
</tr>
<tr>
<td>( -1 \times 10^{-4} )</td>
<td>2.99989</td>
</tr>
<tr>
<td>( -1 \times 10^{-2} )</td>
<td>2.99989</td>
</tr>
<tr>
<td>( -1 \times 10^{-1} )</td>
<td>2.99987</td>
</tr>
<tr>
<td>( 1 \times 10^{-1} )</td>
<td>2.99987</td>
</tr>
<tr>
<td>( 1 \times 10^{-2} )</td>
<td>2.99989</td>
</tr>
<tr>
<td>( 1 \times 10^{-3} )</td>
<td>2.99989</td>
</tr>
<tr>
<td>( 1 \times 10^{-4} )</td>
<td>2.99989</td>
</tr>
<tr>
<td>( 1 \times 10^{-5} )</td>
<td>2.99989</td>
</tr>
<tr>
<td>( 1 \times 10^{-6} )</td>
<td>2.99968</td>
</tr>
<tr>
<td>( 1 \times 10^{-7} )</td>
<td>2.99777</td>
</tr>
<tr>
<td>( 1 \times 10^{-8} )</td>
<td>2.97871</td>
</tr>
<tr>
<td>( 1 \times 10^{-9} )</td>
<td>2.78808</td>
</tr>
</tbody>
</table>

The approximate \( a \) corresponding to \( \frac{V}{N} = 3.0000 \times 10^{-8} \) cm. is \( -5 \times 10^{-1} \) cm.
RESULTS OF EXACT ONE-DIMENSIONAL CALCULATION

\[ T = 300 \text{ Degrees K.} \]

\[
\begin{array}{cccc}
\text{s = } p \frac{\text{cm}}{\text{K}} & \text{V, cm x 10}^8 & \frac{N}{N}^2 \\
-1 \times 10^8 & 3.21168 & .49421 \\
-1 \times 10^6 & 3.00201 & .49415 \\
-1 \times 10^4 & 2.99991 & .49415 \\
-1 \times 10^2 & 2.99989 & .49415 \\
-1 & 2.99989 & .49415 \\
-1 \times 10^{-2} & 2.99989 & .49415 \\
-1 \times 10^{-4} & 2.99989 & .49415 \\
1 \times 10^{-4} & 2.99989 & .49415 \\
1 \times 10^{-2} & 2.99989 & .49415 \\
1 & 2.99989 & .49415 \\
1 \times 10^2 & 2.99989 & .49415 \\
1 \times 10^4 & 2.99987 & .49415 \\
1 \times 10^5 & 2.99968 & .49415 \\
1 \times 10^6 & 2.99777 & .49415 \\
1 \times 10^7 & 2.94787 & .49415 \\
1 \times 10^8 & 2.78810 & .49421 \\
\end{array}
\]

The approximate s corresponding to \( \frac{V}{N} = 3.0000 \times 10^8 \) cm. is \(-5 \times 10^{-4} \) cm.
RESULTS OF EXACT ONE DIMENSIONAL CALCULATION

\[ T = 900 \text{ Degrees K.} \]

\[ s = \frac{p}{RT}, \text{ cm}^{-1} \]

\[
\begin{array}{ccc}
\text{E} & \text{V, cm} \times 10^8 \frac{N}{N} & N_{12} \\
-1 \times 10^8 & 3.63526 & .49339 \\
-1 \times 10^6 & 3.00650 & .49322 \\
-1 \times 10^4 & 3.00022 & .49322 \\
-1 \times 10^2 & 3.00016 & .49322 \\
1 & 3.00016 & .49322 \\
-1 \times 10^{-2} & 3.00016 & .49322 \\
-1 \times 10^{-4} & 3.00016 & .49322 \\
1 \times 10^{-4} & 3.00016 & .49322 \\
1 \times 10^{-2} & 3.00016 & .49322 \\
1 & 3.00016 & .49322 \\
1 \times 10^2 & 3.00016 & .49322 \\
1 \times 10^4 & 3.00009 & .49322 \\
1 \times 10^5 & 2.99952 & .49322 \\
1 \times 10^6 & 2.99381 & .49322 \\
1 \times 10^7 & 2.93671 & .49322 \\
1 \times 10^8 & 2.36944 & .49339 \\
\end{array}
\]

The approximate \( s \) corresponding to \( \frac{V}{N} = 3 \times 10^{-8} \text{ cm.} \) is \( 5 \times 10^{-6} \text{ cm.} \).
MONTE CARLO RESULTS $T = 30^\circ$ KELVIN

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>$N_{12}$ Averaged over last 10,000 trials</th>
<th>Mean deviation of 1,000 trial averages from 10,000 trial average</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>20.382</td>
<td>.383</td>
</tr>
<tr>
<td>20,000</td>
<td>20.132</td>
<td>.542</td>
</tr>
<tr>
<td>30,000</td>
<td>20.214</td>
<td>.223</td>
</tr>
<tr>
<td>40,000</td>
<td>20.539</td>
<td>.430</td>
</tr>
<tr>
<td>50,000</td>
<td>20.448</td>
<td>.157</td>
</tr>
<tr>
<td>60,000</td>
<td>20.220</td>
<td>.630</td>
</tr>
<tr>
<td>70,000</td>
<td>20.564</td>
<td>.290</td>
</tr>
<tr>
<td>100,000</td>
<td>20.314</td>
<td>.388</td>
</tr>
<tr>
<td>110,000</td>
<td>20.420</td>
<td>.256</td>
</tr>
<tr>
<td>120,000</td>
<td>20.621</td>
<td>.557</td>
</tr>
<tr>
<td>130,000</td>
<td>20.238</td>
<td>.361</td>
</tr>
</tbody>
</table>

Average over 130,000 trials = 20.374.

Mean deviation of 10,000 trial averages from 130,000 trial average = .136.
### MONTE CARLO RESULTS $T = 30°$ KELVIN

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>$\langle E \rangle_{KT}$ Averaged over last 10,000 trials</th>
<th>Mean deviation of 1,000 trial averages from 10,000 trial average</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>-12.757</td>
<td>.234</td>
</tr>
<tr>
<td>20,000</td>
<td>-12.606</td>
<td>.323</td>
</tr>
<tr>
<td>30,000</td>
<td>-12.656</td>
<td>.133</td>
</tr>
<tr>
<td>40,000</td>
<td>-12.849</td>
<td>.255</td>
</tr>
<tr>
<td>50,000</td>
<td>-12.794</td>
<td>.205</td>
</tr>
<tr>
<td>60,000</td>
<td>-12.659</td>
<td>.375</td>
</tr>
<tr>
<td>70,000</td>
<td>-12.876</td>
<td>.250</td>
</tr>
<tr>
<td>100,000</td>
<td>-12.714</td>
<td>.232</td>
</tr>
<tr>
<td>110,000</td>
<td>-12.780</td>
<td>.150</td>
</tr>
<tr>
<td>120,000</td>
<td>-12.897</td>
<td>.333</td>
</tr>
<tr>
<td>130,000</td>
<td>-12.669</td>
<td>.189</td>
</tr>
</tbody>
</table>

Average over 130,000 trials = $-12.751$.

Mean deviation of 10,000 trial averages from 130,000 trial average = .111.
### MONTE CARLO RESULTS $T = 30^\circ$ KELVIN

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>$K_N/N_k$ Averaged over last 10,000 trials</th>
<th>Mean deviation of 1,000 trial averages from 10,000 trial average</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>3.082</td>
<td>.704</td>
</tr>
<tr>
<td>20,000</td>
<td>3.304</td>
<td>.353</td>
</tr>
<tr>
<td>30,000</td>
<td>2.890</td>
<td>.311</td>
</tr>
<tr>
<td>40,000</td>
<td>2.687</td>
<td>.389</td>
</tr>
<tr>
<td>50,000</td>
<td>3.016</td>
<td>.228</td>
</tr>
<tr>
<td>60,000</td>
<td>3.072</td>
<td>.384</td>
</tr>
<tr>
<td>70,000</td>
<td>3.258</td>
<td>.400</td>
</tr>
<tr>
<td>100,000</td>
<td>3.489</td>
<td>.888</td>
</tr>
<tr>
<td>110,000</td>
<td>3.174</td>
<td>.227</td>
</tr>
<tr>
<td>120,000</td>
<td>2.438</td>
<td>.414</td>
</tr>
<tr>
<td>130,000</td>
<td>3.161</td>
<td>.470</td>
</tr>
</tbody>
</table>

Average over 130,000 trials = 3.052.

Mean deviation of 10,000 trial averages from 130,000 trial average = .214.
Monte Carlo Results for 300° Kelvin

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>( \bar{N}_{12} ) Averaged over ( N ) last 10,000 trials</th>
<th>Mean deviation of 10,000 trial averages from 100,000 trial average</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>20.280</td>
<td>.448</td>
</tr>
<tr>
<td>20,000</td>
<td>20.328</td>
<td>.515</td>
</tr>
<tr>
<td>30,000</td>
<td>20.066</td>
<td>.240</td>
</tr>
<tr>
<td>40,000</td>
<td>20.237</td>
<td>.252</td>
</tr>
<tr>
<td>50,000</td>
<td>20.350</td>
<td>.477</td>
</tr>
<tr>
<td>60,000</td>
<td>20.527</td>
<td>.379</td>
</tr>
<tr>
<td>70,000</td>
<td>20.181</td>
<td>.397</td>
</tr>
<tr>
<td>100,000</td>
<td>20.446</td>
<td>.436</td>
</tr>
<tr>
<td>110,000</td>
<td>20.098</td>
<td>.279</td>
</tr>
</tbody>
</table>

Average over 100,000 trials = 20.279.

Mean deviation of 10,000 trial averages from 100,000 trial average = .134.
MONTE CARLO RESULTS FOR 300° KELVIN

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>E Averaged over kT last 10,000 trials</th>
<th>Mean deviation of 1,000 trial averages from 100,000 trial average</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>-1.2696</td>
<td>.0270</td>
</tr>
<tr>
<td>20,000</td>
<td>-1.2723</td>
<td>.0251</td>
</tr>
<tr>
<td>30,000</td>
<td>-1.2567</td>
<td>.0143</td>
</tr>
<tr>
<td>40,000</td>
<td>-1.2668</td>
<td>.0126</td>
</tr>
<tr>
<td>50,000</td>
<td>-1.2736</td>
<td>.0284</td>
</tr>
<tr>
<td>60,000</td>
<td>-1.2842</td>
<td>.0226</td>
</tr>
<tr>
<td>70,000</td>
<td>-1.2635</td>
<td>.0226</td>
</tr>
<tr>
<td>100,000</td>
<td>-1.2794</td>
<td>.0260</td>
</tr>
<tr>
<td>110,000</td>
<td>-1.2585</td>
<td>.0167</td>
</tr>
</tbody>
</table>

Average over 100,000 trials = -1.2694.

Mean deviation of 10,000 trial averages from 100,000 trial average = .0043.
## Monte Carlo Results for 300° Kelvin

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>$\frac{K_v}{N} \text{ Averaged over 10,000 trials}$</th>
<th>Mean deviation of 1,000 trial averages from 10,000 trial average</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>.03217</td>
<td>.00702</td>
</tr>
<tr>
<td>20,000</td>
<td>.03345</td>
<td>.00577</td>
</tr>
<tr>
<td>30,000</td>
<td>.03308</td>
<td>.01386</td>
</tr>
<tr>
<td>40,000</td>
<td>.03328</td>
<td>.00419</td>
</tr>
<tr>
<td>50,000</td>
<td>.02274</td>
<td>.00363</td>
</tr>
<tr>
<td>60,000</td>
<td>.03439</td>
<td>.00756</td>
</tr>
<tr>
<td>70,000</td>
<td>.03566</td>
<td>.00460</td>
</tr>
<tr>
<td>100,000</td>
<td>.02990</td>
<td>.00492</td>
</tr>
<tr>
<td>110,000</td>
<td>.02815</td>
<td>.00419</td>
</tr>
</tbody>
</table>

Average over 100,000 trials = .031425

Mean deviation of 10,000 trial averages from 100,000 trial average = .00245.
MONTE CARLO RESULTS FOR 900° KELVIN

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>E Averaged over 10,000 trials</th>
<th>Mean deviation of 1,000 trial averages from 10,000 trial average</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>-.42320</td>
<td>.00887</td>
</tr>
<tr>
<td>20,000</td>
<td>-.42409</td>
<td>.01250</td>
</tr>
<tr>
<td>30,000</td>
<td>-.41888</td>
<td>.00477</td>
</tr>
<tr>
<td>40,000</td>
<td>-.42228</td>
<td>.00502</td>
</tr>
<tr>
<td>50,000</td>
<td>-.42462</td>
<td>.00907</td>
</tr>
<tr>
<td>60,000</td>
<td>-.42483</td>
<td>.00664</td>
</tr>
<tr>
<td>70,000</td>
<td>-.42255</td>
<td>.01050</td>
</tr>
<tr>
<td>100,000</td>
<td>-.42301</td>
<td>.00705</td>
</tr>
</tbody>
</table>

Average over 100,000 trials = .42293.

Mean deviation of 10,000 trial averages from 100,000 trial average = .00128.
### MONTE CARLO RESULTS FOR 900° KELVIN

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>$N_{12}$ Averaged over 10,000 trials</th>
<th>Mean deviation of averages over 1,000 trials from average over 10,000 trials</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>20.283</td>
<td>.446</td>
</tr>
<tr>
<td>20,000</td>
<td>20.327</td>
<td>.516</td>
</tr>
<tr>
<td>30,000</td>
<td>20.065</td>
<td>.240</td>
</tr>
<tr>
<td>40,000</td>
<td>20.237</td>
<td>.252</td>
</tr>
<tr>
<td>50,000</td>
<td>20.354</td>
<td>.433</td>
</tr>
<tr>
<td>60,000</td>
<td>20.365</td>
<td>.333</td>
</tr>
<tr>
<td>70,000</td>
<td>20.250</td>
<td>.530</td>
</tr>
<tr>
<td>100,000</td>
<td>20.241</td>
<td>.427</td>
</tr>
</tbody>
</table>

Average over 100,000 trials = 20.265.

Mean deviation of 10,000 trial averages from 100,000 trial average = .0518.
**MONTE CARLO RESULTS FOR 900° KELVIN**

<table>
<thead>
<tr>
<th>Number of Trials (octal)</th>
<th>$\frac{K_V}{N_t}$ Averaged over 10,000 trials</th>
<th>Mean deviation of 1,000 trial averages from 10,000 trial average</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>0.003574</td>
<td>0.000780</td>
</tr>
<tr>
<td>20,000</td>
<td>0.003716</td>
<td>0.000641</td>
</tr>
<tr>
<td>30,000</td>
<td>0.003424</td>
<td>0.000325</td>
</tr>
<tr>
<td>40,000</td>
<td>0.003587</td>
<td>0.000465</td>
</tr>
<tr>
<td>50,000</td>
<td>0.003250</td>
<td>0.000657</td>
</tr>
<tr>
<td>60,000</td>
<td>0.003694</td>
<td>0.000905</td>
</tr>
<tr>
<td>70,000</td>
<td>0.003704</td>
<td>0.000369</td>
</tr>
<tr>
<td>100,000</td>
<td>0.003656</td>
<td>0.000524</td>
</tr>
</tbody>
</table>

Average over 100,000 trials = 0.003576.

Mean deviation of 10,000 trial averages from 100,000 trial average = 0.000120.
COMPARISON OF RESULTS: \( \frac{N_{12}}{N} \)

This is the average ratio of nearest neighbor bonds to the total number of atoms.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>30°</th>
<th>300°</th>
<th>900°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Ising Solution</td>
<td>0.6449</td>
<td>0.5213</td>
<td>0.5000</td>
</tr>
<tr>
<td>Monte Carlo Solution</td>
<td>0.5094</td>
<td>0.5070</td>
<td>0.5066</td>
</tr>
<tr>
<td>Exact Solution due to Longuet-Higgins</td>
<td>0.5110</td>
<td>0.4942</td>
<td>0.4932</td>
</tr>
</tbody>
</table>
## Comparison of Results

### Energies

<table>
<thead>
<tr>
<th>Temperature, Degrees K.</th>
<th>Ising</th>
<th>Monte Carlo</th>
<th>Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>-.3948</td>
<td>-.3188</td>
<td>-.04007</td>
</tr>
<tr>
<td>300</td>
<td>-.03111</td>
<td>-.03173</td>
<td>-.0257</td>
</tr>
<tr>
<td>900</td>
<td>-.009945</td>
<td>-.01057</td>
<td>-.00538</td>
</tr>
</tbody>
</table>

### Heat Capacities

<table>
<thead>
<tr>
<th>Temperature, Degrees K.</th>
<th>Ising</th>
<th>Monte Carlo</th>
<th>Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>.12762</td>
<td>3.052</td>
<td>.08832</td>
</tr>
<tr>
<td>300</td>
<td>.01332</td>
<td>.0314</td>
<td>.003357</td>
</tr>
<tr>
<td>900</td>
<td>.00878</td>
<td>.003576</td>
<td>.003140</td>
</tr>
</tbody>
</table>
**AUXILIARY DATA**

Temperature, Degrees K. | Probability of making transition to another distinguishable state on each of the first 100 trials
--- | ---
30 | .38
900 | .49

The following averages were obtained from Monte Carlo scheme altered so as to take no account of vibrational effects. The averages are taken over the first 10,000 (octal) trials and the quantities in parentheses are the mean deviations of 1,000 trial averages from the 10,000 trial average.

| Quantity | $30^\circ$ | $300^\circ$ | $900^\circ$
| --- | --- | --- | ---
| $\frac{\mu_{12}}{N}$ | .5628 (.012) | .5180 (.0096) | .5017 (.0110)
| $\frac{E}{NkT}$ | -.3350 (.008) | -.0310 (.0006) | -.0102 (.0002)
| $\frac{K_N}{Nk}$ | 2.78 (.70) | .025 (.007) | .006 (.001)
CONCLUSIONS

It is unfortunate that an incorrect fluctuation variable was chosen; however, it appears that some conjectures can be made from the results.

First of all, the Booth-Rowlinson approximation is basically a high-temperature approximation, and it should not be surprising that the results should be markedly better for the high-temperature cases than for the low-temperature case. As has been remarked, this method essentially approximates the vibration spectrum by its optical branch, and would be expected to lead to incorrect results at low temperatures, where the vibrational behavior of the system would be determined by the acoustical branch.

One may still enquire whether the errors in the results are due to failings in the Booth-Rowlinson approximation, or in the potential function used, or in the Monte Carlo scheme itself. First of all, the potential function is not to blame: the results may not reproduce the physical system Cu-Ag, but that is a separate question: the same potential function has been used throughout this work, and the question is whether the Monte Carlo scheme reproduces the properties of the pseudo-Cu-Ag alloy in question, which are represented exactly (for the purposes of this argument) by the exact one-dimensional analysis.

Examination of the auxiliary data tables suggests that the Monte Carlo scheme is satisfactory in the two high-temperature cases.
One should be hesitant about drawing conclusions from runs of only 10,000 trials, but it is noteworthy that the runs without vibrational analysis are in all cases much closer to the exact Ising results than the Monte Carlo results. It appears that in the two high-temperature cases the cause of the errors lies in the Booth-Rowlinson approximation itself, and it seems reasonable to conclude that this approximation does not satisfactorily reproduce the correct results at the temperatures at which most ordering processes take place, at least in situations comparable to the one investigated. Without further studies, it is not felt that one can conclude that this is true for all alloy systems.

In the low-temperature case the Monte Carlo results without vibrational interaction fail to agree significantly with the exact Ising results, although they do appear to tend toward this value. It is not easy to attribute the difficulties at the low temperature to a single cause. It was thought at one time that the trouble lay in nonconvergence of the Monte Carlo scheme due to the system's reaching one state of quite low energy and having, owing to the size of $kT$, essentially no probability of getting out of it. This would slow convergence radically, but without seriously increasing the statistical spread of the data. This has not been verified, but the results in the auxiliary data table lend some support to this conjecture; it must be noted that many of the transitions made during the first hundred trials represent substantial decreases of configurational energy, and the difference in transition probability
of about .1 must represent considerable difficulty in the system's making a transition to a state with even slightly higher energy. The "transition probability" referred to in this section is not a Markov-chain transition probability but represents the probability that the Monte Carlo games would, on one trial, make a transition to a distinguishable state. A strong argument against this conjecture is this: that in the case where the vibrational analysis is blanked off, if this were indeed the situation, one would expect the system to rapidly approach the state of minimum energy (with a large number of unlike-neighbor bonds) and then remain there, with essentially zero scatter in the data from there on. This is not observed.

From the information available, it appears that the best conclusion can be made is this: that there seems reason to expect trouble from the Monte Carlo scheme at low temperatures but that, in light of the apparently satisfactory behavior of the Monte Carlo scheme at high temperatures, the low-temperature error will be provisionally attributed to the Booth-Rowlinson approximation.

One word in passing seems appropriate concerning the Ising results. The energy from the Ising calculations is not strictly comparable to the other energies, due to the presence in them of a vibrational-entropy term. However, this appears to be negligible in all cases.

In conclusion, it is felt that the results presented here strongly suggest that the Booth-Rowlinson approximation is unsatisfactory throughout the temperature range considered.
Two theoretical treatments of the statistical mechanics of disordered lattices, neglecting the dependence of the vibrational partition function on the arrangement of the atoms on the sites, have had some success in two- and three-dimensional problems. Of course, since the one-dimensional Ising problem can be solved exactly, they have no immediate relevance to this work; it is, however, felt that they are necessary to get a better insight into the Booth-Rowlinson treatment.

Before proceeding further with a discussion of the Bragg-Williams and Quasi-Chemical methods, a discussion of order parameters seems desirable. Consider a binary alloy. In a state of perfect order the atoms of one kind (type 1) will occupy one subset of the lattice sites, called Sublattice A; those of the other type will occupy the remaining lattice sites, which will be designated as belonging to Sublattice B. Then the "Long-range Order Parameter" $S$ can be defined as the excess of type 1 atoms on A sites over that expected for a completely random crystal; this is readily shown to be equal to the same ratio for type 2 atoms on B sites. Generally, for mathematical convenience, this is expressed in slightly different form, by dividing the number of type 1 atoms on A sites in excess of the number for a purely random arrangement by the number for a purely random arrangement. Then the two quantities derived no longer are equal, but have a more obvious physical interpretation.
(it might, for instance, not be obvious whether $S = 3.78 \times 10^{22} \text{ cm}^{-3}$ were a high or low degree of ordering).

This is clearly not a complete specification of the degree of ordering; a crystal could have a very considerable tendency for type 1 atoms to clump around type 2 atoms and still have very little order in this sense. Accordingly, one could ask what a complete set of order parameters are, in the sense that specifying them completely specifies the macroscopically observable properties of the crystal. Consider the set $P(j, j', k, r, s)$ where $P(j, j', k, r, s)$ is the probability that if a given site of the $r$th sublattice is occupied by a type $j$ atom, its $k$th nearest neighbors on the $s$th sublattice are of type $j'$. This set of parameters has the advantage that it is readily extended to more complex alloys. An extended discussion of such parameters would constitute too lengthy a digression; it is worthwhile noting that they describe both short and long range order.

In the Bragg-Williams approximation to the Ising treatment, the configurational partition function for the lattice (from which the vibrational partition function can, in this approximation, be factored) is separated into a sum over values of the long-range order parameter $S$; the term corresponding to each value of $S$ is the sum of partition-function terms corresponding to this $S$:

$$Q = \sum_{S} \sum_{S^{th} + s} e^{-\frac{\omega}{kT}}$$
Bragg and Williams used, for each \( S \), an averaged interaction energy:

\[
\omega(S) = \overline{N}_{11}(S) E_{11} + \overline{N}_{12}(S) E_{12} + \overline{N}_{22}(S) E_{22}
\]

The \( \overline{N}_{ij} \) are simple unweighted averages over all configurations of given \( S \). It can be shown that, for a lattice consisting of the two sublattices \( A \) and \( B \), where each site on lattice \( A \) has \( Z \) nearest neighbors on lattice \( B \),

\[
\overline{N}_{11} = \frac{1}{Z} Z N (1-S^1) x_1
\]

\[
\overline{N}_{12} = \frac{1}{Z} Z N (2 x_1 x_2 + 2 x_1^2 s^2)
\]

\[
\overline{N}_{22} = \frac{1}{Z} Z N (x_2^2 - x_1^2 s^2)
\]

In the above expressions, \( x_1 \) is used for the mole fraction of atoms of type \( i \), and \( N \) for the total number of sites.

Then

\[
\omega(S) = \frac{N \overline{N}}{2} (x_1^2 E_{11} + x_2^2 E_{22} + 2 x_1 x_2 E_{12}) + N Z x_1^2 s^2 J
\]

where

\[
J = \frac{1}{2} (2 E_{12} - E_{11} - E_{22})
\]

and

\[
\omega(S) = \omega_0 + Z N x_1^2 s^2 J
\]

\[
\therefore \quad Q(S) = q(S) \cdot e^{-\frac{1}{F} (\omega_0 + Z N x_1^2 s^2 J)}
\]

The degeneracy factor \( g(S) \) can readily be evaluated from combinatorial analysis; it has the form:

\[
q(S) = \frac{[\frac{1}{2} N]!}{[\frac{1}{2} x_1 N (1+S)]! [\frac{1}{2} x_2 (x_2-x_1 s)]! [\frac{1}{2} N (x_2+x_1 s)]! [\frac{1}{2} N x_1 (1-s)]! [\frac{1}{2} N (x_2+y_1 s)]!}
\]

With this formulation, one is in a position to apply the maximum term procedure in a fashion parallel to the exact one-
dimensional Ising treatment. Application of this procedure to real three-dimensional alloys predicts a sharp drop in the long range order at one temperature, accompanied by an anomaly in the specific heat curve; but it predicts a discontinuity less than that observed experimentally, in the cases where it has been applied.

In the Quasi-Chemical approximation, one improves on this by using a better approach to the dependence on order of the energy. The above treatment essentially assumed that \( P(j,j',k,r,s) \) was not a function of \( k \).

Let \( P(1,1,1,1,2) = P \); let a fraction \( f_a \) of the sites on sublattice A be occupied by type 1 atoms, and a fraction \( f_b \) of the sites on sublattice B. Then, using \( x_i \) for mole fractions again,

\[
\begin{align*}
N_{11} &= \frac{1}{2} Z N f_a P \\
N_{12} &= \frac{1}{2} Z N \left( f_a + f_b - 2 f_a P \right) \\
N_{22} &= \frac{1}{2} Z N \left( f_a P + 1 - 2 x_1 \right)
\end{align*}
\]

Hence one can write

\[
\omega(p) = \frac{1}{2} Z N E_{22} + Z N x_1 E_{12} + \frac{1}{2} Z N f_a J P - Z N x_1 E_{22}
\]

where \( J = E_{11} + E_{22} - 2 E_{12} \).

Thus one can write for the partition function:

\[
Q = \sum_{f_a} \sum_{P} Z(f_a, P) = \sum_{f_a} \sum_{P} G(f_a, P) e^{-\frac{1}{kT} E(f_a, P)}
\]
However, there is now no simple expression for the degeneracy factor $G(f_a,P)$.

The approximation in this procedure is introduced at this point: there are four possible sorts of nearest neighbor pairs between a type $j$ atom on sublattice $r$ and a type $j'$ atom on sublattice $s$. It is assumed that $G(f_a,P)$ is proportional to the number of ways the $1/2NZ$ total pairs in the lattice can be divided into these four groups; i.e., $G(f_a,P) = \frac{\eta(f_a)}{\left[\frac{1}{2}NZf_a(1-P)\right]!\left[\frac{1}{2}NZ(1-f_aP)\right]!\left[\frac{1}{2}N(1-f_a-f_aP)\right]!\left[\frac{1}{2}N(1-f_aP)\right]!}\left[\frac{1}{2}NZ\right]!\left[\frac{1}{2}N\right]!$

This is inexact; it is, in fact, equivalent to assuming that all the pairs in the lattice are independent entities. It allows, for instance, the same site to be part both of a $1-1$ pair and a $2-2$ pair. This is corrected for, to some extent, by the use of a proportional fudge factor $h(f_a)$, which is determined by the requirement that each sublattice contains only the given number of atoms of each type:

$$\sum_p G(f_a,P) = \eta(f_a) = \frac{\left[\frac{1}{2}N\right]!\left[\frac{1}{2}N\right]!}{\left[\frac{1}{2}NF_a\right]!\left[\frac{1}{2}N(1-f_a)\right]!\left[\frac{1}{2}NF_{a'}\right]!\left[\frac{1}{2}N(1-f_{a'})\right]!}$$

$G(f_a,P)$ is now replaced by $G(f_a,P^*)$, where $P^*$ is the most probable value for given $f_a$. Then $G(f_a,P^*) = G(f_a)$ in the limit of a large system (by the maximum-term technique), which is given by the above expression. Evaluating $h(f_a)$, one gets an involved expression.
Application of the maximum-term method to the sum over $f_a$ now leads to the expression from which the method gets its name:

$$\frac{\left[ f_a (1-p) \right] \left[ f_b - f_a p \right]}{\left[ f_a p \right] \left[ 1-2X_1 + f_a p \right]} = e^{-\frac{2J}{kT}}$$

The numerator of the left hand side is the product of the number of type 1 atoms on sublattice A minus the number of type 2 atoms on sublattice B times the number of type 2 atoms on A minus the number of type 1 atoms on B. The denominator is the product of the number of type 1 atoms on A minus the number of type 1 atoms on B times the number of type 2 atoms on A minus the number of type 2 atoms on B. Hence, it has the general form of an equilibrium constant.

The quasi-chemical method gives no qualitatively different results from the Bragg-Williams, but does seem to give a somewhat better fit to experiment. It is not obvious that it is a better approximation, since the improvement derived from the use of a formulation giving the correct answer were the distribution function correct might be cancelled out by the use of an inexact distribution function. One can see the improvement a little more clearly, perhaps, if one realizes that both methods involve regarding independent entities as being in the smoothed-out field of the other sites, occupied in a random manner. The difference is, that whereas Bragg and Williams regarded single sites as the entities, in the quasi-chemical method the independent entities are pairs of sites.
Booth and Rowlinson have attempted to include the effects of vibrations in the quasi-chemical method. They treated specifically \( \theta \)-brass, a 50 mole percent alloy of Zn and Cu, in whose ordered state all type 1 atoms occupy sites on sublattice A and all type 2 atoms sites on sublattice B. Consider a state in which \( N_{fA} \) type 1 atoms are on sites of sublattice A, and there are \( ZN_{s} \) nearest neighbor pairs of type 1 atoms altogether. In the nearest-neighbor approximation, one can write

\[
E = N \frac{Z}{2} E_{12} - N \frac{S}{2} J + E(R)
\]

where \( J = 2E_{12} - E_{11} - E_{22} \), and \( E(R) \) is the energy due to displacements of the atoms. To the approximation in which the energy can be written as a sum of two-body potentials, \( E(R) \) for any given atom can be written as the sum of interactions with type 1 atoms on lattice A, type 2 atoms on A, type 1 atoms on B, and type 2 atoms on B:

\[
E(R) = \sum_{i=1}^{N_{fA}} E_1^a(R_i, R) + \sum_{j=1}^{N_{fB}} E_2^B(R_j, R) + \sum_{k=1}^{N(1-f_\theta)} E_1^B(R_k, R) + \sum_{l=1}^{N(1-f_\theta)} E_2^a(R_l, R)
\]

The approximation will be the treatment of the motion of each atom as isolated in the smoothed-out field of the other atoms. The coupling of vibrations is neglected entirely.

In the following, \( R \) will be the displacement vector from the equilibrium lattice site of an atom of type 1 to its actual position. Suppose the atom under consideration, the \( i \)th in the lattice,
has \(Z_{\text{w}_i}\) nearest neighbors of opposite type. The classical partition function for its motion near its site is:

\[
j(\omega_i^a)_1 = \int e^{-\frac{1}{kT} E_i^a(R_i; \omega_i^a)} d\omega_i^a
\]

The integration is carried out only over the Wigner-Seitz cell surrounding the atom, since it will in all probability be confined to this, but there is no reason not to extend it at will. The partition function is, accordingly:

\[
Q = \sum_{\eta} \sum_{\omega} g(\eta, \omega) e^{-\frac{1}{kT} \left[ N\omega E_\eta - N\omega^2 J^s \right]} \prod_i j(\omega_i^a) \cdot \prod_i j(\omega_i^b) \cdot \prod_{\omega^a} j(\omega^a) \cdot \prod_{\omega^b} j(\omega^b) \cdot j(\omega^d) \cdot j(\omega^e)
\]

\(G\) is a combinatory factor. \(E_{ij}\) are functions of volume and the \(j(\omega_i)\) are functions of volume and temperature.

Now, paralleling the theory of regular solutions, it is assumed that

\[
|n_j(\omega_i^a) = \omega_i^a \cdot J^a_1 + (1 - \omega_i^a) \cdot J_0^a
\]

etc.

The \(J_0^a, J_1^a, J_0^b, J_1^b\) are yet to be specified. It is apparent, since \(j\) is independent of long range order, that they are independent of the choice of sublattice, and hence \(J_0^a = J_0^b, J_1^a = J_1^b\).

From the definition of \(w_i\),

\[
\sum_{i=1}^{N^a} \omega_i = \sum_{i=1}^{N^a} \omega_j = N(f-s) \quad \sum_{\omega^a_{\kappa}} \omega_{\kappa} = \sum_{\omega^b_{\ell}} \omega_{\ell} = N(1-f-s)
\]
Hence one can write:

\[ Q = \sum_{s} \sum_{f} g(N,s,f) e^{-\frac{1}{kT} \left[ N\Sigma E_{12} - N\Sigma J'_{1s} \right]} \]

where

\[ E_{12}' = E_{12} - \frac{kT}{2} \ln \frac{J_{1}^{a} J_{1}'^{b}}{J_{0}^{a} J_{0}'^{b}} \]

Thus, the effect of including lattice vibrations in this fashion is to replace \( E_{12} \) and \( J \) by the primed quantities. The further evaluation of \( Q \) depends on the selection of a weighting factor. In fact, Booth and Rowlinson use a quasi-chemical treatment and, adjusting their parameters to reproduce the experimental transition temperature, get a somewhat better value for the discontinuity in the heat capacity than the uncorrected quasi-chemical treatment does.

It is worth noting that this method can readily be applied to alloys where it is desirable to consider the atoms other than in pairs; e.g., \( \text{AuCu}_{3} \) can be treated by considering a tetrahedral group of four sites, one from each sublattice.

3: W.L. Bragg and E.C. Williams, op.cit.
4: Appendix C
6: Booth and Rowlinson, op.cit.
APPENDIX B

THE MONTE CARLO METHOD

Consider a system specified by a set of parameters which will be denoted by a vector \( \mathbf{s} \). Assume that there are \( \mathcal{U} \) possible values for \( \mathbf{s} \). If it is desired to form the average value of some property \( g(\mathbf{s}) \) for the system, one needs the probability of finding the system in a state \( \mathbf{s} \), which may be designated by \( \mathcal{U}(\mathbf{s}) \). Having this, one can form

\[
\bar{g} = \frac{1}{\mathcal{U}} \sum_{i=1}^{\mathcal{U}} g(\mathbf{s}_i) \mathcal{U}(\mathbf{s}_i) = \sum_{i=1}^{\mathcal{U}} g_i \mathcal{U}_i
\]

A Markov Chain will be considered to consist of \( \mathcal{N} \) possible configurations of the system, ordered in some fashion and indexed by \( \mathbf{s} \). The \( j \)th configuration in the chain will be the state corresponding to the \( j \)th value of \( \mathbf{s} \), since it is clearly possible to order the possible values of \( \mathbf{s} \) and index them with \( j \).

If \( \mathcal{U}_j \) denotes the number of states in the chain corresponding to the \( j \)th value of \( \mathbf{s} \), one can define:

\[
G(N) = \frac{1}{N} \sum_{i=1}^{N} g(\mathbf{s}_i) = \frac{1}{N} \sum_{j=1}^{\mathcal{U}} \mathcal{U}_j g_j = \sum_{j=1}^{\mathcal{U}} \frac{\mathcal{U}_j}{N} g_j
\]

The question now arises: is it possible to add more and more states to the chain in such a fashion that, as the number of states in the chain increases indefinitely, \( G(N) \) approaches \( \bar{g} \)?
If one considers a large assembly of chains, each of N states, one can define for each state:

\[ G(N) = \sum_{j=1}^{W} f_j(N) g_j \]

\[ f_j(N) = \frac{w_j(N)}{N} \]

If the \( f_j \) are considered as the components of a \( W \)-dimensional vector \( F \), the projections of \( F \) on the coordinate axes of this space will be the \( f_j \), if the axes are taken as the \( g_j \), which are obviously a basis for the space in question. Let the metric in this space be defined such that:

\[ \| F - F' \| = \sum_{j=1}^{W} (f_j - f'_j)^2 \]

One can now give a definition: By \( F \to A \), where \( A = \sum_{j=1}^{W} a_j g_j \), is meant that:

\[ \| i_{\alpha \to b} F - A \| = 0 \]

Attention will now be restricted to a particular sort of Markov chain: The first state in the chain will be one of the permissible states of the system, and the probability of observing a particular state of the system at the \( k+1 \)th step will depend solely on the configuration at the \( k \)th step. A process will be developed for choosing the state at the \( k+1 \)th step from the state at the \( k \)th step such that as more and more steps are added to the chain, \( F(N) \) will converge to a vector whose projections on the axes will be the same as the weighting factors in the original averaging.
Consider for the present a large assembly of chains of fixed length, and try to calculate the average value of some \( f_3 \) for all states in this assembly, for fixed \( N \). The probability of getting the chain \( i_1 i_2 i_3 \cdots i_N \), starting with a given \( i_1 \), is \( P_{i_1 i_2} P_{i_2 i_3} \cdots P_{i_{N-1} i_N} \), where \( P_{ik} \) is the probability that the configuration corresponding to state \( i \) will be followed in the chain by the configuration corresponding to state \( k \); this is assumed to have a given constant value.

Then one can write, for the ensemble average,

\[
\overline{f}_i = \sum_{j_2=1}^{N} \sum_{j_3=1}^{N} \cdots \sum_{j_N=1}^{N} p(j_1, j_2 \cdots j_N) \cdot f_i
\]

where \( p(j_1, j_2 \cdots j_N) = P_{j_1 j_2} \cdot P_{j_2 j_3} \cdots P_{j_{N-1} j_N} \)

Further,

\[
f_i = \frac{1}{N} \sum_{\tau = 2}^{N} \delta(i, j_{\tau})
\]

Hence one can write:

\[
\overline{f}_i = \sum_{j_2=1}^{N} \sum_{j_3=1}^{N} \frac{1}{N} \sum_{\tau = 2}^{N} \delta(i, j_{\tau}) p(j_1 \cdots j_N) = \sum_{\tau = 2}^{N} \left\{ \sum_{j_2=1}^{N} \sum_{j_3=1}^{N} \sum_{\tau = 2}^{N} \frac{\delta(i, j_{\tau}) p(j_1 \cdots j_N)}{N} \right\}
\]

Now consider the \( P_{ik} \) as the elements of a \( N \times N \) matrix \( P \), and let \( P^\tau = (P)^\tau \), where multiplication is defined by the ordinary matrix-multiplication rules. It is apparent that, since after any
number of steps the system must be in some state, one can write:

\[
\sum_{j_{t+1}=1}^{\omega} \ldots \sum_{j_N=1}^{\omega} P_{j_t \ldots j_N} = \sum_{j_N=1}^{\omega} P_{j_t j_N} = 1
\]

One can also use the matrices to rewrite the expression for the average of \( \bar{f}_t \):

\[
\bar{f}_t = \sum_{t=2}^{N} \sum_{j_{t+1}=1}^{\omega} P_{j_t j_{t+1}} \left( \frac{\delta_{j_t j_{t+1}}}{N} \right) = \frac{1}{N} \sum_{t=2}^{N} P^{(t-1)}
\]

Now consider the limiting process in which the chain length approaches infinity. Since there is a unique ensemble average, all dependence of the initial state must be lost; i.e., the expression above must hold for all \( j_1 \).

In the \( \mathcal{W} \)-dimensional space there is a vector \( U \), and operators corresponding to the various powers of \( P \). Consider the set \( \lambda_j \), the eigenvalues of \( P \), and \( v_j \) the left eigenvectors. The left eigenvectors are a basis for the space \( \mathcal{W} \) and any vector in \( \mathcal{W} \) can be represented by a linear combination of them.

In particular this holds for the vector \( R_{j_1} = \begin{bmatrix} p_{j_1,1} \\ p_{j_1,2} \\ \vdots \\ p_{j_1,N} \end{bmatrix} \)

It will be assumed that \( R_{j_1} = \sum_{\kappa=1}^{\omega} c_{\kappa} v_{\kappa} \begin{bmatrix} p_{j_1,1} \\ p_{j_1,2} \\ \vdots \\ p_{j_1,N} \end{bmatrix} \)
Consider the expression for $\bar{e}_1$ derived above:

$$\bar{e}_i = \frac{1}{N} \sum_{s=2}^{N} (P_{i,s})^{-1}$$

This is equivalent to:

$$F = \frac{1}{N} \sum_{s=2}^{N} R_{i1} \cdot P^{-1}$$

Consider also the vector $R_{i1} \cdot P = \sum_{k=1}^{\omega} c_k \lambda_k V_k \cdot P = \sum_{k=1}^{\omega} c_k \lambda_k V_k$.

It is apparent that $R_{i1} \cdot P = \sum_{k=1}^{\omega} c_k \lambda_k V_k$.

Now one may inquire what happens as $N \to \infty$. Clearly, for $\lambda_k < 1$, $F$ will tend to the null vector. Further, it can be shown\(^2\) that, for properly normalized probabilities, $\lambda \lesssim 1$. For $\lambda = 1$, $F \to c_1 v_1$, from which it appears that the result will depend on the choice of initial state.

To see that this is not so, consider $\sum_{i=1}^{\omega} P_{j1} = \sum_{i=1}^{\omega} c_k v_k = 1$. Since this is a finite sum, it may be rearranged at will. Rearrange it to $\sum_{k=1}^{\omega} c_k \sum_{i=1}^{\omega} v_k i$. It can be readily established that $\sum_{k=1}^{\omega} v_k i = 0$ for all $\nu$ except that corresponding to $\lambda_k = 1$.

$$V_k \cdot P = \lambda_k V_k \quad \therefore \lambda_k V_k; = \sum_{j=1}^{\omega} V_k; P_{j1}$$

$$\lambda_k \sum_{i=1}^{\omega} V_k i = \sum_{i=1}^{\omega} \sum_{j=1}^{\omega} V_k j P_{j1} = \sum_{j=1}^{\omega} V_k j \sum_{i=1}^{\omega} P_{j1} = \sum_{j=1}^{\omega} V_k j$$

Therefore either $\lambda_k = 1$ or $\sum_{j=1}^{\omega} v_k j = 0$. If the vector for $k = 1$ is chosen such that $\sum_{j=1}^{\omega} v_1 j = 1$, one can conclude that $\sum_{k=1}^{\omega} c_k \sum_{j=1}^{\omega} v_k j = c_1 = 1$, so the initial configuration really does not determine the final result.
Thus one may conclude that it is necessary to select a matrix of transition probabilities such that it has one eigenvalue of 1, all the other eigenvalues being less, and such that all the eigenvectors are independent.

It can be shown that a sufficient condition to ensure the satisfaction of the above conditions is that \( U_i P_{ij} = U_j P_{ji} \) for all \( i, j \). It is, of course, necessary to select a method of extending the chains so that all the states in the ensemble can be sampled; that is equivalent to saying the Monte Carlo game must be ergodic.

APPENDIX C

EXACT ISING SOLUTION OF A ONE-DIMENSIONAL LATTICE

Consider a one-dimensional crystal containing two kinds of atoms, type 1 and type 2. Let the energy of interaction of a pair of atoms be identically zero unless they are nearest neighbors. Let a nearest-neighbor pair of atoms, both of type i, have interaction energy \( E_{ii} \), and let a mixed pair have the interaction energy \( E_{12} \).

If the lattice has \( N_{11} \) pairs of type 1 atoms nearest neighbor to one another, \( N_{22} \) pairs of type 2 atoms, and \( N_{12} \) mixed pairs, the total interaction energy of the system can be written:

\[
E = N_{11}E_{11} + N_{22}E_{22} + N_{12}E_{12}.
\]

Since \( 2N_{11} + N_{12} = 2N_1 \) and \( 2N_{22} + N_{12} = 2N_2 \), where \( N_1 \) is the number of atoms of type 1, the energy can be written:

\[
E = N_1E_{11} + N_2E_{22} + JN_{12}, \text{ where } J = E_{12} - \frac{1}{2}(E_{11} + E_{22}).
\]

The Canonical ensemble partition function \( Q \) is given by:

\[
Q = \sum_{\text{confs.}} e^{-\frac{E}{kT}}
\]

This can be rewritten as a sum over \( N_{12} \), letting \( q(N_{12}) \) be the number of configurations of the system corresponding to a given \( N_{12} \), since all these will make equal contributions to the sum:

\[
Q = \sum_{N_{12}} q(N_{12}) e^{-\frac{N_{12}E_{12}}{kT} - \frac{N_1E_{11}}{kT} - \frac{N_2E_{22}}{kT}}
\]
It is now desired to evaluate \( g(N_{12}) \). Suppose first of all that \( N \) is so large that one need not worry about the evenness or oddness of it. Consider the possible arrangements of the atoms beginning with a type 1. If the arrangement is thought of as a series of bunches of atoms of the same type, separated by unlike-neighbor bonds, \( 1/2(N_{12} + 1) \) of these will contain atoms of type 1. If \( K = 1/2(N_{12} + 1) \), the number of ways of arranging the type 1 atoms in these groupings is

\[
\frac{(N_1 - 1)!}{(N_i - K)! (K - 1)!}
\]

The number of ways of arranging the type 2 atoms in the other groupings is

\[
\frac{(N_2 - 1)!}{(N_2 - K)! (K - 1)!}
\]

Accordingly, using the binomial notation, one can write:

\[
g(N_1, N_2, N_{12}) = 2 \left( \frac{N_1 - 1}{K - 1} \right) \left( \frac{N_2 - 1}{K - 1} \right)
\]

Where the factor 2 enters because of the possibility of starting the chain with either a type 1 or a type 2 atom. Accordingly,

\[
Q = 2 e^{\frac{-N_i E_i + M_i E_{1i}}{kT}} \sum_{N_{12}} \left( \frac{N_1 - 1}{K - 1} \right) \left( \frac{N_2 - 1}{K - 1} \right) e^{-\frac{N_{12} J}{kT}}
\]

As \( N \) becomes large, the partition function should become asymptotically equal to its largest term.\(^1\) If \( N_{12} \) is regarded as a continuous variable, the derivative of the largest term with respect to it should equal zero; alternatively, since the largest term will clearly be nonvanishing, the derivative of the logarithm of the largest term should vanish.
Thus, for the value of $N_{12}$ giving the largest term,

$$\frac{J}{kT} - \frac{\partial}{\partial N_{12}} \left( \frac{N_{1} - 1}{N_{12}} \right) - \frac{\partial}{\partial N_{12}} \left( \frac{N_{2} - 1}{N_{12}} \right) = 0$$

Using Sterling's approximation, one can reduce this to

$$\frac{\sqrt{N_{1} - 1} \sqrt{N_{2} - 1}}{N_{12}} = \frac{J}{kT}$$

Neglecting unity in comparison to the large numbers, one gets for the numbers of different types of bonds corresponding to the largest term,

$$\sqrt{\frac{N_{11}^{*} N_{22}^{*}}{N_{12}^{*}}} = \frac{1}{2} e^{\frac{J}{kT}}$$

Here the asterisk denotes properties of the maximum-term state.

It is now possible to write an asymptotic form for the partition function for a large system:

$$Q = e^{-\frac{1}{kT} \left[ N_{1} E_{1} + N_{2} E_{2} \right]} e^{\left( N_{12}^{*} \frac{J}{kT} \right)}$$

This leads to:

$$E = kT \frac{\partial}{\partial T} \ln Q = N_{1} E_{1} + N_{2} E_{2} + N_{12}^{*} \frac{J}{kT}$$

$N_{12}^{*}$ can be written:

$$\frac{N_{12}^{*}}{N} = \frac{1 - \gamma}{1 - B}$$

where

$$\gamma = \sqrt{1 - 4 \frac{N_{1} N_{2}}{N^{2}} (1 - B)}$$

and

$$B = e^{\frac{2J}{kT}}$$
Likewise $C_v$ can be obtained by taking a derivative:

$$
\frac{C_v}{N} = J \left\{ \frac{1-Y}{(1-\theta)^2} \frac{d\bar{r}}{dT} - \frac{1}{1-\theta} \frac{dY}{dT} \right\}
$$

Where

$$
\frac{d\bar{r}}{dT} = -\frac{2J}{\kappa T^2} \bar{r} \\
\frac{dY}{dT} = \frac{2}{N} \frac{N_s}{N^2} \bar{r} \frac{d\bar{B}}{dT}
$$

THE EXPRESSION OF $C_v$ IN TERMS OF ENERGY AVERAGES

Let $i$ index the possible states of the system, and let $U_i$ be the energy of the $i$th state

$$
E = \left( \sum_i U_i e^{-\frac{U_i}{kT}} \right) \left( \sum_i e^{-\frac{U_i}{kT}} \right)^{-1}
$$

$$
\left( \frac{\partial E}{\partial T} \right)_v = \frac{-1}{kT^2} \frac{\partial E}{\partial \left( \frac{1}{kT} \right)} = \frac{\sum_i U_i^2 e^{-\frac{U_i}{kT}}}{\sum_i e^{-\frac{U_i}{kT}}} - \frac{\left( \sum_i \frac{U_i}{kT} \right)^2}{\left( \sum_i e^{-\frac{U_i}{kT}} \right)^2}
$$

$$
\left( \frac{\partial E}{\partial T} \right)_v = \frac{1}{kT^2} \left\{ \bar{E}^2 - \bar{E} \right\}
$$

$$
\frac{C_v}{k} = \left\{ \left( \frac{\bar{E}}{kT} \right)^2 - \left( \frac{\bar{E}}{kT} \right)^2 \right\}
$$
APPENDIX E

Although these investigations have been carried out primarily to investigate the question of whether the approximate treatment following Booth and Rowlinson would yield results consistent with an exact calculation in the one-dimensional case, an effort was made to select a potential corresponding to the physical parameters of a system of interest.

If a potential function is to represent a real substance, there are certain restrictions on it: the force must be repulsive at small distances and attractive at large distances, leading to a minimum and a finite equilibrium separation; the potential must decrease more rapidly with the separation \( r \) than \( r^3 \), since the cohesive energy must be finite; and all elastic constants must be positive. In addition, it can be shown \(^{1}\) that \( C_{11} - C_{12} > 0 \) is required for mechanical stability, where \( C_{11} \) and \( C_{12} \) are the elastic constants. Although, owing to the presence of Brillouin zone effects and the existence of many low-lying excited electronic states, the use of any two-body potential for the investigation of metallic systems is questionable, Girifalco and Weizer \(^{2}\) have investigated the elastic properties of pure metals using a Morse potential, of the form:

\[
V_{ij} = D_{ij} \left[ e^{-2a(r_{ij}-a_s)} - 2 e^{-a(r_{ij}-a_s)} \right]
\]
The use of this potential function, with the parameters chosen to give the experimental elastic constants, seems to reproduce the mechanical behavior of a number of monovalent metals over a fairly wide range of pressure.\(^3\) It can be shown that this function satisfies all the conditions stated for an acceptable function. It is apparent that \( -D \) is the binding energy and \( a_0 \) the equilibrium separation.

In the present problem the masses of the particles were taken equal to the masses of Cu (type 1) and Ag (type 2) atoms; the potential functions for like neighbors were chosen to be those found by Girifalco and Weizer altered so \( a_0 = 3 \times 10^{-8} \) cm. for all potentials; those for unlike pairs were chosen to be reasonable intermediate values, with the binding energy so selected that there was a tendency to ordering. The reason for the selection of this particular system instead of a more familiar one (e.g., CuAu) was the nearness of the ratio of the masses to 2.0, as this seems to be a mass-ratio that has been studied more than others.\(^4\)

In any event, the Morse potentials for the system can be expressed for small displacements in a Taylor series about \( r = a_0 \):

\[
\sqrt[r]{V(r)} = V(a_0) + (r-a_0) \frac{dV}{dr} a_0 + \frac{(r-a_0)^2}{2} \frac{d^2V}{dr^2} a_0 + \ldots
\]

For the purposes of this problem it is necessary to have this in the form

\[
\sqrt[r]{V(r)} = V_o + \sum_{j=1}^{\infty} \frac{A_j}{r^j}
\]
To do this, one must write

$$(r-a) = (-1)(a)(1 - \frac{r}{a})$$

$$(r-a)^k = (-1)^k a^k \sum_{t=1}^{\infty} \frac{k!}{t!(k-t)!} (-1)^t \left(\frac{r}{a}\right)^t$$

Hence

$$V(r) = \sum_{k=0}^{\infty} \frac{a^k (-1)^k}{k!} \left(\frac{d}{dr^k}\right) \sum_{t=0}^{\infty} \frac{k!}{t!(k-t)!} (-1)^t \left(\frac{r}{a}\right)^t$$

Or:

$$V(r) = \sum_{k=0}^{\infty} \frac{d}{dr^k} \left(\frac{V(r)}{a}ight)^k \sum_{t=1}^{\infty} \frac{(-1)^t \left(\frac{r}{a}\right)^t}{t!(k-t)!}$$

In this particular problem the Taylor series about $r = a_0$ is truncated after the second term, and the expansion in $r$ can be written

$$V(r) = V_0 + A_1 \frac{r}{a} + A_2 \left(\frac{r}{a}\right)^2$$

Thus, if for each of the three potentials in the problem for (11), (12), and (22) pairs, one lets

$$V_{k\ell}(r) = \hbar \tau f_{k\ell}(r)$$

one has the problem reduced to the form in which it is treated in the section on the exact one-dimensional solution. Since $f_{k\ell}(r)$ is of the form $A_1 k_1 + A_2 k_2 + A_3 k_2^2$, its Laplace transform is readily evaluated:
\[ I_{\kappa\ell} = \int_0^\infty e^{-sr} A_1^\kappa_\ell - A_2^\kappa_\ell r - A_3^\kappa_\ell r^2 \, dr \]

\[ I_{\kappa\ell} = e^{-A_1^\kappa_\ell} \int_0^\infty e^{-A_3^\kappa_\ell} \left[ \int r + r \left( \frac{A_2^\kappa_\ell + s}{A_3^\kappa_\ell} \right) \right] \, dr \]

\[ I_{\kappa\ell} = e^{-A_1^\kappa_\ell + \frac{(A_2^\kappa_\ell + s)^2}{4A_3^\kappa_\ell}} \int_0^\infty e^{-A_3^\kappa_\ell} \left[ r + \frac{(A_2^\kappa_\ell + s)^2}{2A_3^\kappa_\ell} \right] \, dr \]

\[ I_{\kappa\ell} = e^{-A_1^\kappa_\ell + \frac{(A_2^\kappa_\ell + s)^2}{4A_3^\kappa_\ell}} \int_0^\infty e^{-A_3^\kappa_\ell} \left[ s + \frac{A_2^\kappa_\ell}{2A_3^\kappa_\ell} \right] \, ds \]

\[ I_{\kappa\ell} = \frac{e^{-A_1^\kappa_\ell + \frac{(A_2^\kappa_\ell + s)^2}{4A_3^\kappa_\ell}}}{\sqrt{A_3^\kappa_\ell}} \int_0^\infty e^{-\eta} \eta^\ell \, d\eta \]

\[ s + \frac{A_2^\kappa_\ell}{2\sqrt{A_3^\kappa_\ell}} \]
In the particular case under consideration, the lower limit in
the last integral is negative for all reasonable pressures; hence
this expression can be rewritten $I_{k1} = K_{k1} \cdot (1 + \text{erf} |I_{k1}|)$,
where
$$K_{k1} = \frac{\sqrt{\pi}}{4 \pi} e^{\frac{1}{\pi} \left( A_{k1} + 5 \right)^2 - A_{k1}}$$

$$J_{k1} = \frac{S + A_{k1}}{2 \sqrt{A_{k1}}}$$

The parameters found by Girifalco and Weizer are:

<table>
<thead>
<tr>
<th></th>
<th>(Å⁻¹)</th>
<th>r₀(Å)</th>
<th>Mol.Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>.3429</td>
<td>1.3588</td>
<td>2.866</td>
</tr>
<tr>
<td>Ag</td>
<td>.3323</td>
<td>1.3690</td>
<td>3.115</td>
</tr>
</tbody>
</table>

This then allows the definition of the following

$$\frac{D}{D_{\text{Cu}}} = \lambda = 1.000 \quad 0.980 \quad 0.969$$

$$\frac{\overline{Z}}{\overline{Z}_{\text{Cu}}} = \lambda = 1.000 \quad 1.005 \quad 1.010$$

Pair type: Cu-Cu, Cu-Ag, Ag-Ag

The intermediate numbers are, of course, estimates which were
chosen in an effort to synthesize the actual behavior of the system.
As a first-order guess, it seemed reasonable that the curvature of
the Cu-Ag potential should be roughly halfway between those of the pure metals. The choice of the configurational interaction was governed by the determination to put in a slight configurational ordering tendency.

The equations used to actually calculate the exact results were

\[ J_{ij} = J'_{ij} + J''_{ij} s \quad \kappa_{ij} = \kappa'_{ij} \cdot 10^{K'}_{ij} \cdot 10^{K''_{ij} s^2} \]

The values of the parameters found at thirty degrees are:

\[ J_{11} = -14.6500 \quad J_{12} = -14.5668 \quad J_{22} = -14.5293 \]
\[ J_{11} = 1.0238 \times 10^{-9} \quad J_{12} = 1.0288 \times 10^{-9} \quad J_{22} = 1.0322 \times 10^{-9} \]
\[ K_{11} = 7.0915 \times 10^{-4} \quad K_{12} = 5.6604 \times 10^{-4} \quad K_{22} = 3.9647 \times 10^{-4} \]
\[ K_{11} = K_{12} = K_{22} = -1.3026 \times 10^{-8} \]
\[ K_{11} = 4.5515 \times 10^{-19} \quad K_{12} = 4.5997 \times 10^{-19} \quad K_{22} = 4.6270 \times 10^{-19} \]

At three hundred degrees:

\[ J_{11} = -4.6341 \quad J_{12} = -4.6090 \quad J_{22} = -4.5939 \]
\[ J_{11} = 3.238 \times 10^{-9} \quad J_{12} = 3.255 \times 10^{-9} \quad J_{22} = 3.265 \times 10^{-9} \]
\[ K_{11} = 2.0808 \times 10^{-8} \quad K_{12} = 2.0443 \times 10^{-8} \quad K_{22} = 2.0224 \times 10^{-8} \]
\[ K_{11} = K_{12} = K_{22} = 1.3026 \times 10^{-8} \]
\[ K_{11} = 4.5515 \times 10^{-18} \quad K_{12} = 4.5997 \times 10^{-18} \quad K_{22} = 4.6270 \times 10^{-18} \]
At nine hundred degrees:

\[
J_{11} = -2.6752 \quad J_{12} = -2.6607 \quad J_{22} = -2.6530 \\
J_{11} = 5.607 \times 10^{-9} \quad J_{12} = 5.638 \times 10^{-9} \quad J_{22} = 5.654 \times 10^{-9} \\
K_{11} = 1.5206 \times 10^{-8} \quad K_{12} = 1.5239 \times 10^{-8} \quad K_{22} = 1.5213 \times 10^{-8} \\
K_{11} = K_{12} = K_{22} = -1.3026 \times 10^{-8} \\
K_{11} = 1.3652 \times 10^{-17} \quad K_{12} = 1.3799 \times 10^{-17} \quad K_{22} = 1.3862 \times 10^{-17}
\]

3: ibid.
4: G. Weiss and A. Maradudin, op. cit.
BIBLIOGRAPHY


Prigogine, I.: The Molecular Theory of Solutions, North Holland Publishing Co., 1957, Chap. VI.


