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Two-Component Ising Chain with Nearest-Neighbor Interaction

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The one-dimensional, two-component linear Ising chain with nearest-neighbor interaction is formulated by using the transfer matrix method, with emphasis placed on the case in which the two components are randomly distributed along the chain. Certain recurrence formulas appear such that the mth-order partition function of one of the components is dependent on the lower-order ones. The algorithm provides a working basis for discussing the thermodynamic and magnetic functions with various concentrations of one of the components. An exact expression for the partition function is derived for a linear chain which is composed of a periodic distribution of the two components. The construction of a periodic sequence which would approximate a random distribution of the two components is briefly discussed.

KEY WORDS: Ising model; disordered system; one-dimensional chain.

1. INTRODUCTION

It is well known that the linear Ising chain with short-range interaction between neighboring sites does not exhibit phase transition.[1] The intrinsic interest remains, however, in that the model is relatively simple to investigate

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in comparison to the two- and three-dimensional systems. In addition, a chain of spins may serve in a certain approximation as a model of long molecules, which has found important applications in polymer physics as well as in biological systems.[2,3] Experimentally, a number of crystalline organic free radicals[4,5] and rare earth chlorides[6,7] are known to exhibit properties characteristic of a one-dimensional system; in both cases, the molecules or magnetic ions are arranged to form parallel chains such that the exchange interaction between ions of different chains is much weaker than that between ions within the same chain. Theoretical study using a generalized Ising model has been able to achieve reasonable comparison with the observed thermodynamic and magnetic functions of these substances.

In this paper, we investigate the properties of a two-component linear Ising model, with emphasis placed on the case in which the two components are randomly distributed along the chain.[8,9] The formulation utilizes the transfer matrix method[10] which enables the partition functions of the system with few defects to be computed in a straightforward manner. We will see that certain recurrence formulas appear so that the mth-order defect partition function is dependent on the lower-order ones.[2] The algorithm provides a working basis for discussing the thermodynamic and magnetic functions with various concentrations of one of the components.

Exact expressions for the partition functions can be derived for a linear chain which is composed of periodic distributions of the two components. While such distributions do not occur naturally in a real system, one expects that the qualitative similarities and differences resulting from various compositions within a periodic chain, which is equivalent to an alteration of the concentration of one of the components, whould show up in these cases. The partition functions of the periodic systems are evaluated in Section 5 and in Section 8, we discuss briefly the construction of a periodic sequence of the two components which would approximate a random distribution of the two components. Our calculation is made for systems in which the sequence of the two components remains forever frozen in.

2. FORMULATION OF THE PROBLEM

Let us consider a ring of N localized spins equally spaced on lattice sites which are labeled consecutively 1, 2,..., N. A spin at site i is identified by a variable σ_i with $\sigma_i = 1$ corresponding to a spin-"up" configuration and $\sigma_i = -1$ to a spin-"down" configuration. The ring configuration implies periodic boundary conditions $\sigma_{i+N} \equiv \sigma_i$. Since we shall be concerned with two-component systems (species A and B), there will be three kinds of nearest-neighbor interaction. We let E_{AA}, $E_{AB} = E_{BA}$, and E_{BB} represent

the energies of interaction between the various types of pairs AA, AB, and BB and define three coupling parameters ($\beta = 1/kT$)

$$K_1 = \beta E_{AA}, \qquad K_2 = \beta E_{AB}, \qquad K_3 = \beta E_{BB} \tag{1}$$

If μ_j is the magnetic moment of spins of species j ($j = 1 \equiv A, j = 2 \equiv B$), we define

$$J_j = \beta \mu_j H, \qquad j = 1, 2 \tag{2}$$

where $\mu_j H$ is the interaction energy of the spin with an external field of magnitude H in the "up" direction.

The Hamiltonian of our system of spins can be written as

$$-\beta \mathscr{H} = \sum_{i=1}^{N} (K^i \sigma_i \sigma_{i+1} + J^i \sigma_i) \tag{3}$$

where K^i has one of the values K_1, K_2, K_3 depending on the species located at points i and $i + 1$, and J^i is J_1 if i is of species A and J_2 if it is of species B. The properties of a perfect lattice of species A depend on the largest characteristic values λ_1 of the matrix P whose matrix elements are

$$P(\sigma, \sigma') = \exp[K_1 \sigma\sigma' + \tfrac{1}{2} J_1(\sigma + \sigma')] = \sum_{j=1}^{2} \lambda_j \psi_j(\sigma)\, \psi_j(\sigma') \tag{4a}$$

with

$$\lambda_j = e^{K_1} \cosh J_1 \pm [e^{-2K_1} + e^{2K_1} \sinh^2 J_1]^{1/2} \tag{4b}$$

and the ψ_j are the eigenvectors of P corresponding to the eigenvalues λ_j, which satisfy the orthogonality relationship

$$\sum_{\sigma = \pm 1} \psi_j(\sigma)\, \psi_k(\sigma) = \delta_{jk} \tag{5}$$

We now define two other matrices Q and R whose matrix elements are

$$R(\sigma, \sigma') = \exp[K_3 \sigma\sigma' + \tfrac{1}{2} J_2(\sigma + \sigma')] = \sum_{j=1}^{2} \rho_j \theta_j(\sigma)\, \theta_j(\sigma') \tag{6}$$

$$Q(\sigma, \sigma') = \exp[K_2 \sigma\sigma' + \tfrac{1}{2} J_2(\sigma + \sigma')] = \sum_{j=1}^{2} \gamma_j \phi_j(\sigma)\, \phi_j(\sigma') \tag{7}$$

The θ's and ϕ's also satisfy the orthogonality relations

$$\sum_{\sigma} \theta_j(\sigma)\, \theta_k(\sigma) = \delta_{jk}, \qquad \sum_{\sigma} \phi_j(\sigma)\, \phi_k(\sigma) = \delta_{jk} \tag{8}$$

with the characteristic values ρ_j and γ_j, respectively, given by formulas like Eq. (4b) but with the new appropriate subscripts on J and K.

3. PARTITION FUNCTION OF A RING WITH ONE DEFECT

We place our defect at lattice point 1 on our ring. Then the partition function of the system is given by

$$\begin{aligned} Z_1 &= \sum_{\sigma} \exp\left[K_2\sigma_1\sigma_2 + \sum_{i=2}^{N-1} K_1\sigma_i\sigma_{i+1} + K_2\sigma_N\sigma_1 + J_2\sigma_1 + \sum_{i=2}^{N} J_1\sigma_i\right] \\ &= \sum_{\sigma} \exp[\tfrac{1}{2}\epsilon(\sigma_N + \sigma_2)] \exp[K_2\sigma_1\sigma_2 + \tfrac{1}{2}J_2(\sigma_1 + \sigma_2)] \\ &\quad \times \prod_{i=2}^{N-1} \exp[K_1\sigma_i\sigma_{i+1} + \tfrac{1}{2}J_1(\sigma_i + \sigma_{i+1})] \exp[K_2\sigma_N\sigma_1 + \tfrac{1}{2}J_2(\sigma_N + \sigma_1)] \\ &= \sum_{\sigma} \exp[\tfrac{1}{2}\epsilon(\sigma_N + \sigma_2)]\, Q(\sigma_1, \sigma_2) \prod_{i=2}^{N-1} P(\sigma_i, \sigma_{i+1})\, Q(\sigma_N, \sigma_1) \\ &= \sum_{\sigma=\pm 1} P(\sigma, \sigma; N) \end{aligned} \tag{9}$$

where we have defined $\epsilon = J_1 - J_2$,

$$\begin{aligned} P(\sigma, \sigma'; t) &= \sum_{\sigma_2 \cdots \sigma_t} \sum \exp[\tfrac{1}{2}\epsilon(\sigma_2 + \sigma_t)]\, Q(\sigma, \sigma_2) \\ &\quad \times \prod_{i=2}^{t-1} P(\sigma_i, \sigma_{i+1})\, Q(\sigma_t, \sigma'), \qquad t > 2 \end{aligned} \tag{10}$$

If we use the notation

$$(j, k) = \sum_{\sigma} \psi_j(\sigma)[\exp(\tfrac{1}{2}\epsilon\sigma)]\, \phi_k(\sigma) \tag{11}$$

then substitution of Eq. (4a) and (7) into (10) and application of the orthogonality relations (5) and (8) yields for $t > 3$

$$P(\sigma, \sigma'; t) = \sum_{j_1 j_2 j_3 = 1}^{2} \gamma_{j_1} \lambda_{j_2}^{t-2} \gamma_{j_3} \phi_{j_1}(\sigma)(j_2, j_1)(j_2, j_3)\, \phi_{j_3}(\sigma')$$

By introducing a few more definitions,

$$\begin{aligned} &\omega_j = \gamma_j/\gamma_1, \qquad \omega = \lambda_2/\lambda_1, \qquad y_{ij} = (i, j)/(1, 1) \\ &f_i(\sigma) = \sum_j \omega_j y_{ij} \phi_j(\sigma), \qquad P_i(\sigma, \sigma') = f_i(\sigma) f_i(\sigma) f_i(\sigma') \\ &F_1(\sigma, \sigma'; t) = P_1(\sigma, \sigma') + \omega^{t-2} P_2(\sigma, \sigma') \end{aligned} \tag{12}$$

we see that

$$P(\sigma, \sigma'; t) = \lambda_1^{t-2} \gamma_1^2 (1, 1)^2 F_1(\sigma, \sigma'; t) \tag{13}$$

Returning to Eq. (9), we find that

$$Z_1 = \lambda_1^{N-2}\gamma_1^2(1,1)^2 \sum_{\sigma=\pm 1} [f_1(\sigma)f_1(\sigma) + \omega^{N-2} f_2(\sigma) f_2(\sigma)]$$

$$= \lambda_1^{N-2}\gamma_1^2(1,1)^2[(1 + \omega_2^2 y_{12}^2) + \omega^{N-2}(y_{21}^2 + \omega_2^2 y_{22}^2)]$$

We choose λ_1 to be the larger of the two characteristic values of the matrix P so that $(\lambda_2/\lambda_1)^N = \omega^N \to 0$ as $N \to \infty$. Then

$$Z_1 \cong \lambda_1^{N-2}\gamma_1^2(1,1)^2(1 + \omega_2^2 y_{12}^2) \qquad \text{as} \qquad N \to \infty \tag{14}$$

To be consistent with a pattern we shall use later, we write

$$Z_1 = \lambda_1^{N-2}\gamma_1^2(1,1)^2 h_1 \qquad \text{with} \quad h_1 = 1 + \omega_2^2 y_{12}^2 \tag{15}$$

4. PARTITION FUNCTION WITH TWO DEFECTS AND THERMODYNAMIC FORMULAS FOR LOW DEFECT CONCENTRATIONS

Let us place one defect at lattice point 1 and another at n. Then are three possibilities to consider (a) $3 < n < N - 1$, (b) $n = 3$, (c) $n = 2$. If we let t be the number of lattice sites between defects, these cases are $t > 2$, $t = 2$, and $t = 1$.

Consider case (a) with $t \geqslant 3$. By using Eq. (10), it can be easily shown that the partition function of the system is

$$Z_2(t) = \sum_{\sigma_1,\sigma_{t+1}} \sum P(\sigma_1, \sigma_{t+1}; t)\, P(\sigma_{t+1}, \sigma_1; N - t)$$

$$= \lambda_1^{N-4}\gamma_1^4(1,1)^4 \sum_{\sigma,\sigma'} \sum [P_1(\sigma,\sigma') + \omega^{t-2} P_2(\sigma,\sigma')]$$

$$\times [P_1(\sigma',\sigma) + \omega^{N-t-2} P_2(\sigma',\sigma)] \tag{16}$$

where $\sigma_1 \equiv \sigma$, $\sigma_{t+1} \equiv \sigma'$. As $N \to \infty$ for fixed t, $\omega^{N-t-2} \to 0$ since $0 < \omega < 1$. Hence

$$Z_2(t) = \lambda_1^{N-4}\gamma_1^4(1,1)^4 h_2(t) \tag{17}$$

with

$$h_2(t) = \sum_{\sigma,\sigma'} \sum [P_1(\sigma,\sigma') + \omega^{t-2} P_2(\sigma,\sigma')]\, P_1(\sigma',\sigma)$$

$$= \sum_{\sigma,\sigma'} \sum f_1(\sigma)\, F_1(\sigma,\sigma';t) f_1(\sigma') \tag{18a}$$

$$= A_{11}^2 + \omega^{t-2} A_{12}^2 \qquad \text{if} \quad t > 2 \tag{18b}$$

with

$$A_{ij} = \sum_{\sigma} f_i(\sigma) f_j(\sigma) = y_{i1} y_{j1} + \omega_2^2 y_{i2} y_{j2} = A_{ji} \tag{19}$$

A_{ij} can be treated as the elements of a 2×2 symmetric matrix A so that

$$| A | = \det A = \omega_2^2 (y_{22} - y_{12} y_{21})^2 \tag{20}$$

An alternative form of Eq. (18) is

$$h_2(t) = (1 + \omega_2^2 y_{12}^2)^2 + \omega^{t-2} (y_{21} + \omega_2^2 y_{12} y_{22})^2, \qquad t \geqslant 3 \tag{18c}$$

In case (b) in which $t = 2$ and only one host particle appears between the two defects, the partition function can be written as ($\sigma_1 \equiv \sigma$, $\sigma_3 \equiv \sigma'$)

$$Z_2(2) = \sum_{\sigma,\sigma'} \sum P(\sigma, \sigma'; 2)\, P(\sigma', \sigma; N - 2) \tag{21}$$

where

$$\begin{aligned} P(\sigma, \sigma'; 2) &= \sum_{\sigma''} Q(\sigma, \sigma'')[\exp(\epsilon\sigma'')]\, Q(\sigma'', \sigma') \\ &= \sum_{ij} \gamma_i \phi_i(\sigma)[i, j]\, \phi_j(\sigma')\, \gamma_j \end{aligned} \tag{22}$$

with

$$[j, k] = \sum_{\sigma} \phi_j(\sigma)[\exp(\epsilon\sigma)]\, \phi_k(\sigma) = [k, j] \tag{23}$$

If we let $N \to \infty$ and note that $P(\sigma, \sigma'; N - 2) \to P_1(\sigma, \sigma')$, we see from combining (22) with (12) that

$$Z_2(2) = \lambda_1^{N-4} \gamma_1^4 (1, 1)^4\, h_2(2) \tag{24}$$

which

$$h_2(2) = [(1 + \omega_2^2 x_{12} y_{12}) + \omega_2^2 y_{12}(x_{21} + \omega_2^2 x_{22} y_{12})][1, 1]/(1, 1)^2 \tag{25}$$

$$x_{jk} = [j, k]/[1, 1] \tag{26}$$

It will be useful to express $P(\sigma, \sigma'; 2)$ in terms of $f_i(\sigma)$. Equation (12) can be inverted to give $\phi(\sigma)$ as a function of $f_i(\sigma)$ as follows:

$$\phi_1(\sigma) = \omega_2 [y_{22} f_1(\sigma) - y_{12} f_2(\sigma)]/| A |^{1/2} \tag{27a}$$

$$\phi_2(\sigma) = [f_2(\sigma) - y_{21} f_1(\sigma)]/| A |^{1/2} \tag{27b}$$

With these relations, we can also introduce an $F_1(\sigma, \sigma'; 2)$ which is consistent with (13) so that

$$P(\sigma, \sigma'; 2) = \gamma_1^2 (1, 1)^2\, F_1(\sigma, \sigma'; 2) \tag{28}$$

If we substitute (27a, b) into (22), we find that

$$F_1(\sigma, \sigma'; 2) = \sum_{jk} f_j(\sigma')\, B_{jk}(2) f_k(\sigma) \tag{29a}$$

where

$$\begin{aligned} B_{11}(2) &= B_0(2)[y_{22}(y_{22} - x_{12}y_{21}) - y_{21}(x_{21}y_{22} - x_{22}y_{21})] \\ B_{12}(2) &= B_0(2)[-y_{12}(y_{22} - x_{12}y_{21}) + (x_{21}y_{22} - x_{22}y_{21})] \\ &= B_{21}(2) \\ B_{22}(2) &= B_0(2)[y_{12}(y_{12} - x_{12}) - (x_{21}y_{12} - x_{22})] \\ B_0(2) &= [1, 1]\, \omega_2{}^2/[(1, 1)^2 \mid A \mid] \end{aligned} \tag{29b}$$

One can again treat $B_{ij}(2)$ as the elements of the 2×2 symmetric matrix $B(2)$, so that

$$\mid B(2)\mid = \det B(2) = [1, 1]^2\, \omega_2{}^2(x_{22} - x_{12}x_{21})/[(1, 1)^4 \mid A \mid] \tag{30}$$

For all $t > 2$, we can also define the corresponding $B_{jk}(t)$ analogous to (29b):

$$F_1(\sigma, \sigma'; t) = \sum_{jk} f_j(\sigma')\, B_{jk}(t) f_k(\sigma) \tag{31}$$

with

$$B_{jk}(t) = \delta_{jk}(\lambda_j/\lambda_1)^{t-2}, \qquad t > 2 \tag{32a}$$

$$\mid B(t)\mid = \det B(t) = \omega^{t-2}, \qquad t > 2 \tag{32b}$$

One can then obtain $Z_2(2)$ from (21) and (28). On that basis,

$$\begin{aligned} h_2(2) &= \sum_{ij} \sum_{\sigma\sigma'} f_1(\sigma') f_j(\sigma') f_j(\sigma')\, B_{ji}(2) f_i(\sigma)\, f_1(\sigma) \\ &= \sum_{ij} A_{1j} B_{ji}(2)\, A_{i1} \end{aligned}$$

which can be verified to be exactly (25) as it should be.

The pattern is now clear so that in case (c) with $t = 1$, the partition function can be written as

$$Z_2(1) = \sum_{\sigma\sigma'} P(\sigma, \sigma'; 1)\, P(\sigma', \sigma; N - 1) \tag{33}$$

where

$$P(\sigma, \sigma'; 1) = (\gamma_1{}^2/\lambda_1)\, F_1(\sigma, \sigma'; 1) \tag{34}$$

$$F_1(\sigma, \sigma'; 1) = \sum_{jk} f_j(\sigma')\, B_{jk}(1) f_k(\sigma) \tag{35}$$

If we use the notation

$$\langle j, k\rangle = \sum_{\sigma} \theta_j(\sigma)\, \phi_k(\sigma), \qquad z_{jk} = \langle j, k\rangle/\langle 1, 1\rangle \tag{36}$$

then we have

$$\begin{aligned} B_{11}(1) &= B_0(1) \sum_{i=1}^{2} \rho_i(\omega_2 y_{22} z_{i1} - y_{21} z_{i2})^2 \\ B_{21}(1) &= -B_0(1) \sum_{i} \rho_i(\omega_2 y_{22} z_{i1} - y_{21} z_{i2})(\omega_2 y_{12} z_{i1} - z_{i2}) \\ &= B_{12}(1) \\ B_{22}(1) &= B_0(1) \sum_{i} \rho_i(\omega_2 y_{12} z_{i1} - z_{i2})^2 \\ B_0(1) &= \lambda_1\langle 1, 1\rangle^2/(\gamma_1^2 \mid A \mid) \end{aligned} \tag{37a}$$

and

$$\mid B(1) = \det B(1) = [\lambda_1^2\langle 1, 1\rangle^4/(\gamma_1^4 \mid A \mid)]\rho_1\rho_2(z_{22} - z_{12}z_{21})^2 \tag{37b}$$

Equation (33) can be simplified to give

$$Z_2(1) = \lambda_1^{N-4}\gamma_1^4(1, 1)^4\, h_2(1) \tag{38a}$$

$$h_2(1) = [\lambda_1\rho_1\langle 1, 1\rangle^2/\{\gamma_1^2(1, 1)^2\}][(1 + \omega_2 y_{12} z_{12})^2 + \zeta_2(z_{21} + \omega_2 y_{12} z_{22})^2] \tag{38b}$$

with $\zeta_j = \rho_j/\rho_1$.

We can now consider $F_1(\sigma, \sigma'; t)$ to be defined for all positive integer values of t by (29a), where the $B_{ij}(t)$ are defined by (29b), (32), and (37a).

The explicit representations of the quantities λ_j, γ_j, and ρ_j are

$$\begin{aligned} \left.\begin{matrix}\lambda_1\\ \lambda_2\end{matrix}\right\} &= c_1 e^{K_1} \pm (e^{-2K_1} + s_1^2 e^{2K_1})^{1/2} \\ \left.\begin{matrix}\gamma_1\\ \gamma_2\end{matrix}\right\} &= c_2 e^{K_2} \pm (e^{-2K_2} + s_2^2 e^{2K_2})^{1/2} \\ \left.\begin{matrix}\rho_1\\ \rho_2\end{matrix}\right\} &= c_2 e^{K_3} \pm (e^{-2K_3} + s_2^2 e^{2K_3})^{1/2} \end{aligned}$$

where $c_i = \cosh J_i$, $s_i = \sinh J_i$. The quantities (i, j), $\langle i, j\rangle$, and $[i, j]$ are explicit functions of the J's and K's. One finds

$$\begin{aligned} (1, 1) &= (A_1A_2)^{-1/2} \cosh[\tfrac{1}{2}(\epsilon + \theta_{12})]\, e^{-K_1-K_2} \\ (1, 2) &= (A_1A_2)^{-1/2}\{s_2 \cosh[\tfrac{1}{2}(\epsilon + \theta_{12})] - A_2 \sinh[\tfrac{1}{2}(\epsilon + \theta_{12})]\, e^{K_2-K_1}\} \\ (2, 1) &= (A_1A_2)^{-1/2}\{s_1 \cosh[\tfrac{1}{2}(\epsilon + \theta_{12}] - A_1 \sinh[\tfrac{1}{2}(\epsilon + \theta_{12})]\, e^{K_1-K_2}\} \\ (2, 2) &= (A_1A_2)^{-1/2} \cosh[\tfrac{1}{2}(\epsilon - \theta_{12})]\, e^{-K_1-K_2} \end{aligned}$$

where

$$A_i = s_i^2 + e^{-4K_i}, \qquad i = 1, 2$$
$$\theta_{12} = 2(K_1 + K_2) + \log[(s_1 + A_1)(S_2 + A_2)]$$

Similarly, one finds that

$$\langle 1, 1\rangle = (A_2A_3)^{-1/2}(\cosh \tfrac{1}{2}\theta_{23})\, e^{-K_2-K_3} = \langle 2, 2\rangle$$
$$\langle 1, 2\rangle = (A_2A_3)^{-1/2}[A_3(\sinh \tfrac{1}{2}\theta_{23}) - s_2(\cosh \tfrac{1}{2}\theta_{23})]\, e^{K_3-K_2}$$
$$= -\langle 2, 1\rangle$$

where

$$A_3 = s_2^2 + e^{-4K_3}, \qquad \theta_{23} = 2(K_2 + K_3) + \log[(s_2 + A_2)(s_2 + A_3)]$$

Finally,

$$[1, 1] = \cosh \epsilon + s_2(\sinh \epsilon)/A_2$$
$$[1, 2] = -e^{-2K_2}(\sinh \epsilon)/A_2 = -[2, 1]$$
$$[2, 2] = \cosh \epsilon - s_2(\sinh \epsilon)/A_2$$

The thermodynamic properties of a chain with a low concentration of defects can be expressed in terms of the formulas derived so far. For a system with n defects located at $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$, a thermodynamic function $\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ can be written as[3]

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \equiv \Phi(n) = \Phi_0 + \sum_{j=1}^{n} [\Phi(\mathbf{r}_j) - \Phi_0] + \sum_{j=1;k=j+1}^{n-1} \sum^{n} [\Phi(\mathbf{r}_j, \mathbf{r}_k) - \Phi(\mathbf{r}_j) - \Phi(\mathbf{r}_k) + \Phi_0] + \cdots \tag{39}$$

where Φ_0 is the thermodynamic function for a perfect system, $\Phi(\mathbf{r}_j)$ is that for a system with one defect at $\mathbf{r}_j$, etc. In particular, if $\Phi(n) = \log Z_n(n)$, where $Z_n(n) \equiv Z_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, r_n)$ is the partition function for a system with n defects, (39) becomes

$$\log Z_n(n) = \log Z_0 + \sum_{j=1}^{n} \log[Z_1(\mathbf{r}_j)/Z_0] + \sum_{j=1,k=j+1}^{n-1} \sum^{n} \log\{Z_2(\mathbf{r}_j, \mathbf{r}_k)\, Z_0/[Z_1(\mathbf{r}_j)\, Z_1(\mathbf{r}_k)]\} + \cdots \tag{40}$$

For our linear system, $Z_1(\mathbf{r}_j)$ is independent of $\mathbf{r}_j$[Eq. (15)], and $Z_2[\mathbf{r}_j, \mathbf{r}_k)$ depends only on the relative separation $|\mathbf{r}_j - \mathbf{r}_k| = t$ of the two defects

located at $\mathbf{r}_j$ and $\mathbf{r}_k$. Let $n(s)$ be the number of successive pairs whose members are separated by s lattice sites. Then the double sum in (40) can be written as

$$\sum_{s=1} n(s) \log[Z_2(s)\, Z_0/Z_1^2]$$

If the defect concentration is c, given a defect site, the probability that another one is s lattice spacings away is c. Since the total number of defects is Nc, the expected number $n(s)$ of defect pairs separated by s intervening lattice sites in a very large ring is $Nc \cdot c = Nc^2$ independent of s. Hence, to order c^2,

$$\log Z(c)/N = \log \lambda_1 + 2c \log[(1, 1)\, \gamma_1/\lambda_1] + c \log h_1 + c^2 \sum_{s=1}^{\infty} \log[h_2(s)\, h_0/h_1^2] + \cdots \tag{41}$$

with $h_0 = 1$. Thermodynamic properties of the system can be calculated from this expression in the usual manner.[5]

5. PROPERTIES OF SYSTEMS WITH SIMPLE PERIODIC ARRANGEMENT OF DEFECTS

The partition function of an arbitrary sequence of A's and B's is

$$Z = \sum_{\sigma=\pm 1} \prod_{j=1}^{N} \exp[K^{j,j+1}\sigma_j\sigma_{j+1} + \tfrac{1}{2}J^j\sigma_j + \tfrac{1}{2}J^{j+1}\sigma_{j+1}] \tag{42}$$

where $K^{j,j+1}$ has values K_1, K_2, or K_3, depending on whether the pair $j, j+1$ is an AA pair, an AB (BA) pair, or a BB pair. Also, J^j is J_1 if j is an A and J_2 if j is a B. Now let

$$W^{j,j+1}(\sigma, \sigma') = \exp[K^{j,j+1}\sigma\sigma' + \tfrac{1}{2}J^j\sigma + \tfrac{1}{2}J^{j+1}\sigma'] \tag{43}$$

There are four possible W's. In terms of (4a, b), (6), (7), and (10), these are

$$W_1 = P, \qquad W_3 = R$$
$$W_2(J_1, J_2) = \begin{pmatrix} e^{\epsilon/2} & 0 \\ 0 & e^{-\epsilon/2} \end{pmatrix} Q, \qquad W_2(J_2, J_1) = Q \begin{pmatrix} e^{\epsilon/2} & 0 \\ 0 & e^{-\epsilon/2} \end{pmatrix} \tag{44}$$

The partition function is then

$$Z = \mathrm{tr}(W^{1,2}W^{2,3} \cdots W^{N,1}) \tag{45}$$

This section will be concerned with periodic arrangements of defects and, therefore, periodic arrangements of W's in Z. The simplest periodic

sequence is the alternating one $ABABAB\cdots$. In that case, all $W^{j,j+1}$ equal $W_2(J_1, J_2)$ or $W_2(J_2, J_1)$ and

$$Z = \mathrm{tr}[W_2(J_1, J_2)\, W_2(J_2, J_1)]^{N/2} \sim [\Lambda_1(1, 1)]^{N/2} \tag{46}$$

where $\Lambda_1(1, 1)$ is the largest root of the characteristic equation

$$[\Lambda(1, 1)]^2 - 2\Lambda(1, 1)\,\Lambda_{1,1} + \Delta_{1,1} = 0 \tag{47a}$$

defining

$$\begin{aligned} 2\Lambda_{1,1} &= \mathrm{tr}[W_2(J_1, J_2)\, W_2(J_2, J_1)] \\ &= 2[e^{2K_2}\cosh(J_1 + J_2) + e^{-2K_2}\cosh(J_1 - J_2)] \end{aligned} \tag{47b}$$

and

$$\Delta_{1,1} = \det[W_2(J_1, J_2)\, W_2(J_2, J_1)] = (2\sinh 2K_2)^2 \tag{47c}$$

Generally, suppose that the defect sequence is periodic with period n. Then the $(n+1)$th particle of the chain is the same as the first, and if $Mn = N$,

$$Z = \mathrm{tr}(W^{1,2}W^{2,3}\cdots W^{n,1})^M \sim \Lambda_1{}^M \tag{48}$$

where Λ_1 is the largest characteristic value of the quadratic equation (since the product of the W's is still a 2×2 matrix)

$$\Lambda^2 - \mathrm{tr}(W^{1,2}W^{2,3}\cdots W^{n,1}) + \det(W^{1,2}W^{2,3}\cdots W^{n,1}) = 0 \tag{49}$$

Since the determinant of a product of matrices is the product of their determinants, we have

$$\det(W^{1,2}W^{2,3}\cdots W^{n,1}) = \prod_{j=1}^{n} \det(W^{j,j+1}) = \prod_{j=1}^{n} [2\sinh(2K^{j,j+1})] \tag{50}$$

The trace of the product of the W's is more sensitive to the sequence and, rather than writing a general formula, we calculate it for several special cases.

In order to see the effect of changing the defect concentration, let us suppose that there is one defect for each n atoms, so that each defect is followed by $n-1$ host atoms. The concentration is $c = 1/n$. We identify the appropriate Λ by $\Lambda(n-1, n)$. The W sequence follows from $W^{1,2} = W_2(J_2, J_1)$, $W^{n,1} = W_2(J_1, J_2)$, all other $W^{j,j+1} = W_1$. Then

$$\begin{aligned} W^{j,j+1} &= W_2(J_2, J_1)\, W_1^{n-2} W_2(J_1, J_2) \\ &= Q \begin{pmatrix} e^{\epsilon/2} & 0 \\ 0 & e^{-\epsilon/2} \end{pmatrix} P^{n-2} \begin{pmatrix} e^{\epsilon/2} & 0 \\ 0 & e^{-\epsilon/2} \end{pmatrix} Q \end{aligned} \tag{51}$$

Then, from (10) and (8),

$$\operatorname{tr}(W^{1,2} \cdots W^{n,1}) = \sum_{\sigma} P(\sigma, \sigma; n), \qquad n > 1$$

$$= \lambda_1^{n-1}[\gamma_1^2(1,1)^2 + \gamma_2^2(1,2)^2] + \lambda_2^{n-2}[\gamma_1^2(2,1)^2 + \gamma_2^2(2,2)^2] \tag{52}$$

Hence, our characteristic equation (47a)) becomes

$$\Lambda^2(n-1,1) - 2\Lambda(n-1,n)\,\Lambda_{n-1,1} + \Delta_{n-1,1} = 0 \tag{53a}$$

where

$$2\Lambda_{n-1,1} = \lambda_1^{n-2}\gamma t^2(1,1)^2[(1+\omega_2^2 y_{12}^2) + \omega^{n-2}(y_{21}^2 + \omega_2^2 y_{22}^2)] \tag{53b}$$

$$\Delta_{n-1,1} = (2\sinh 2K_2)^2(2\sinh 2K_1)^{n-2} \tag{53c}$$

Another example which can be dealt with in a similar manner is that of periodic blocks, say n_2 B's followed by n_1 A's, etc., with $n_1 + n_2 = n$. Then, if $Mn = N$,

$$Z = \operatorname{tr}[W_3^{n_2-1}W_2(J_2, J_1)\, W_1^{n_1-1}W_2(J_1, J_2)]^M \tag{54}$$

Now, if $n_1 > 1$ and $n_2 > 1$,

$$\Delta_{n_1,n_2} = \det[W_3^{n_2-1}W_2(J_2, J_1)\, W_1^{n_1-1}W_2(J_1, J_2)]$$

$$= (2\sinh 2K_1)^{n_1-1}(2\sinh 2K_3)^{n_2-1}(2\sinh 2K_2)^2 \tag{55a}$$

$$2\Lambda_{n_1,n_2} = \operatorname{tr}[W_3^{n_2-1}W_2(J_2, J_1)\, W_1^{n_1-1}W_2(J_1, J_2)]$$

$$= \sum_{j_1 \cdots j_4=1}^{2} \lambda_{j_1}^{n_1-1}\gamma_{j_2}\rho_{j_3}^{n_2-1}\gamma_{j_4}(j_1, j_4)(j_1, j_2)\langle j_3, j_2\rangle\langle j_3, j_4\rangle \tag{55b}$$

Then

$$Z \sim [\Lambda(n_1, n_2)]^M \tag{56a}$$

with $\Lambda(n_1, n_2)$ the larger root of the equation

$$[\Lambda(n_1, n_2)]^2 - 2\Lambda_{n_1,n_2}\Lambda(n_1, n_2) + \Delta_{n_1,n_2} = 0 \tag{56b}$$

Since λ satisfies the equations

$$\lambda^2 - 2\lambda e^{K_1}\cosh J_1 + 2\sinh 2K_1 = 0 \tag{57a}$$

$$\lambda^n - 2\lambda^{n-1}e^{K_1}\cosh J_1 + 2\lambda^{n-2}\sinh 2K_1 = 0 \tag{57b}$$

it can be easily shown that

$$\Lambda_{n_1+2,n_2} = 2\Lambda_{n_1+1,n_2}e^{K_1}\cosh J_1 - 2\Lambda_{n_1,n_2}\sinh 2K_1 \tag{58a}$$

$$\Lambda_{n_1,n_2+2} = 2\Lambda_{n_1,n_2+1}e^{K_3}\cosh J_2 - 2\Lambda_{n_1,n_2}\sinh 2K_3 \tag{58b}$$

6. PARTITION FUNCTION OF A RING WITH AN ARBITRARY CONCENTRATION AND LOCATION OF DEFECTS

When the defects are not periodically arranged, we can no longer find a closed formula for the partition function or for the thermodynamic properties of our ring. However, a series expansion in the concentration can be found.

In the three-defect case with t_1 lattice points separating the second defect from the first and t_2 separating the third from the second, it can be easily shown that as $N \to \infty$ for fixed t_1 and t_2,

$$\begin{aligned} Z_3(t_1, t_2) &= \sum_{\sigma} P(\sigma, \sigma'; t_1)\, P(\sigma', \sigma''; t_2)\, P(\sigma'', \sigma; N - t_1 - t_2) \\ &\sim \lambda_1^{N-6}\gamma_1^6(1, 1)^6 \sum_{\sigma} F_1(\sigma, \sigma'; t_1)\, F_1(\sigma', \sigma''; t_2)\, P_1(\sigma'', \sigma) \end{aligned} \tag{59}$$

It is convenient to define

$$F_2(\sigma, \sigma''; t_1, t_2) = \sum_{\sigma'} F_1(\sigma, \sigma'; t_1)\, F_1(\sigma', \sigma''; t_2) \tag{60a}$$

$$F_n(\sigma, \sigma''; t_1, t_2, \ldots, t_n) = \sum_{\sigma'} F_{n-1}(\sigma, \sigma'; t_1, t_2, \ldots, t_{n-1})\, F_1(\sigma', \sigma''; t_n) \tag{60b}$$

$$= \sum_{\sigma'} F_1(\sigma, \sigma'; t_1)\, F_{n-1}(\sigma', \sigma; t_2, t_3, \ldots, t_n) \tag{60c}$$

$$G_{ij}^{(n)}(t_1, t_2, \ldots, t_n) = \sum_{\sigma,\sigma'} f_j(\sigma)\, F_n(\sigma, \sigma'; t_1, \ldots, t_n)\, f_i(\sigma') \tag{61}$$

Then, as $N \to \infty$,

$$Z_3(t_1, t_2) = \lambda_1^{N-6}\gamma_1^6(1, 1)^6\, h_3(t_1, t_2) \tag{62a}$$

with

$$h_3(t_1, t_2) = G_{11}^{(2)}(t_1, t_2) \tag{62b}$$

Incidentally, by referring back to (18), we see that

$$h_2(t) = G_{11}^{(1)}(t) \tag{63}$$

For a linear chain with n defects, it can be easily shown that as $N \to \infty$ for $t_1, t_2, \ldots, t_{n-1}$ fixed,

$$Z_n(t_1, \ldots, t_{n-1}) = \lambda_1^{N-2n} \gamma_1^{2n}(1, 1)^{2n} h_n(t_1, \ldots, t_{n-1}) \tag{64a}$$

with

$$h_n(t_1, \ldots, t_{n-1}) = G_{11}^{(n)}(t_1, \ldots, t_{n-1}) \tag{64b}$$

In the appendix, we show that $h_n(t_1, \ldots, t_{n-1})$ satisfies a simple recurrence relationship [Eq. (A.10)]:

$$h_{n+1}(t_1, \ldots, t_n)\, h_{n-1}(t_2, \ldots, t_{n-1}) = h_n(t_1, \ldots, t_{n-1})\, h_n(t_2, \ldots, t_n) + D_{21}(t_1)\, C_{12}(t_n) |A|^{n-1} \prod_{j=2}^{n-1} |B(t_j)|, \quad n > 1 \tag{65a}$$

where

$$C_{ij}(t) = \sum_m A_{im} B_{mj}(t) \tag{65b}$$

$$D_{ij}(t) = \sum_m B_{im}(t)\, A_{mj} \tag{65c}$$

The elements A_{ij} and $B_{ij}(t)$ for $t = 1, 2,, \geqslant 3$ are defined in Section 4.

With these results, we can find a simple expression for $\log Z_n$ in terms of the h_n. To see how this goes, we note that $\omega = \lambda_2/\lambda_1$, and it was postulated that $\lambda_2 = \min(\lambda_1, \lambda_2)$. If the defect concentration is small, then $(t_1 + t_2 \cdots + t_n)$ is large since it is the number of lattice spacings between the first and the nth defects. In fact, if the concentration is practically zero, we can neglect the right-hand side of (65a) when $n > 1$. Then

$$h_2(t_1)\, h_0 = h_1 h_1 \tag{66a}$$

This implies that

$$h_n(t_1, t_2, \ldots, t_{n-1}) = h_1{}^n \tag{66b}$$

We may call this the zeroth approximation to h_n and therefore to Z_n.

The first approximation, which is a slight improvement, can be obtained by supposing that the right-hand side of (65a) can be neglected when $n > 2$. Then

$$h_3(t_1, t_2) = [h_2(t_1)/h_1{}^2][h_2(t_2)/h_1{}^2]\, h_1{}^3 \tag{67a}$$

On the basis of the hypothesis,

$$\begin{aligned} h_4(t_1, t_2, t_3) &= h_3(t_1, t_2)\, h_3(t_2, t_3)/h_2(t_2) \\ &= [h_2(t_1)/h_1{}^2][h_2(t_2)/h_1{}^2][h_2(t_3)/h_1{}^2]\, h_1{}^4 \end{aligned} \tag{67b}$$

For the first approximation,

$$h_n(t_1, t_2, \ldots, t_{n-1}) = {h_1}^n \prod_{j=1}^{n-1} [h_2(t_j)\, h_0/{h_1}^2] \tag{67c}$$

Clearly, if all t_j are large so that $h_2(t_j) = {h_1}^2$, we recover the zeroth approximation.

If we proceed to a second approximation, the pattern will become clear so that we can generalize to the complete solution of the problem. Let us suppose that the right-hand side of (65a) can be neglected when $n > 3$. Then

$$h_4(t_1, t_2, t_3)\, h_2(t_2) = h_3(t_1, t_2)\, h_3(t_2, t_3) \tag{68a}$$

which leads to

$$h_4(t_1, t_2, t_3) = \frac{h_1 h_3(t_1, t_2)}{h_2(t_1)\, h_2(t_2)} \frac{h_1 h_3(t_2, t_3)}{h_2(t_2)\, h_2(t_3)} \prod_{j=1}^{3} \frac{h_0 h_2(t_j)}{{h_1}^2}\, {h_1}^4 \tag{68b}$$

For our second approximation, we obtain

$$h_n(t_1, t_2, \ldots, t_{n-1}) = {U_1}^n \prod_{j=1}^{n-1} U_2(t_j) \prod_{j=1}^{n-2} U_3(t_j, t_{j+1}) \tag{68c}$$

where we define

$$U_1 = h_1, \qquad U_n(t_1, \ldots, t_{n-1}) = \frac{h_n(t_1, \ldots, t_{n-1})\, h_{n-2}(t_2, \ldots, t_{n-2})}{h_{n-1}(t_1, \ldots, t_{n-2})\, h_{n-1}(t_2, \ldots, t_{n-1})}, \qquad n > 1 \tag{69}$$

The zeroth approximation is ${U_1}^n$, the first is ${U_1}^n$ multiplied by the product of the U_2's, the second is the product of the U_1's, U_2's, and the U_3's. It is not difficult to guess that the general formula for h_n is

$$h_n(t_1, \ldots, t_{n-1}) = U_1 \prod_{j=1}^{n-1} U_2(t_j) \prod_{j=1}^{n-2} U_3(t_j, t_{j+1}) \prod_{j=1}^{n-3} U_4(t_j, t_{j+1}, t_{j+2}) \times \cdots \tag{70}$$

so that

$$\begin{aligned} \log Z_n(t_1, \ldots, t_{n-1}) = {} & N \log \lambda_1 + 2n \log[(\gamma_1/\gamma_1)(1, 1)] \\ & + n \log U_1 + \sum_{j=1}^{n-1} \log U_2(t_j) + \sum_{j=1}^{n-2} \log U_3(t_j, t_{j+1}) \\ & + \sum_{j=1}^{n-3} \log U_4(t_j, t_{j+1}, t_{j+2}) + \cdots \end{aligned} \tag{71}$$

Rather than giving a formal proof of (70), we examine one special case to observe the basic pattern behind the equation. Let us suppose that we

wish to calculate the contribution of the U_5's to h_{22} when it is postulated that $h_{n+1}h_{n-1} = h_n h_n$ when $n > 15$. Then if (70) is valid for h_{21},

$$h_{22}(t_1,\ldots,t_{21}) = h_{21}(t_1,\ldots,t_{20})\, h_{21}(t_2,\ldots,t_{21})/h_{20}(t_2,\ldots,t_{20})$$
$$= \cdots \frac{U_5(t_1,\ldots,t_4)[U_5(t_2,\ldots,t_5)\cdots U_5(t_{17},\ldots,t_{20})]^2\, U_5(t_{18},\ldots,t_{21})}{U_5(t_2,\ldots,t_5)\, U_5(t_3,\ldots,t_6)\cdots U_5(t_{17},\ldots,t_{20})} \cdots$$
$$= \cdots U_5(t_1,\ldots,t_4)\, U_5(t_2,\ldots,t_5)\cdots U_5(t_{17},\ldots,t_{20})\, U_5(t_{18},\ldots,t_{21})\cdots$$

The crucial feature is that the numerator contains the square of the U functions which appear in both h_{21}'s. These are exactly the U's which appear once in $h_{20}(t_2,\ldots,t_{20})$, so that one of the two factors of the square cancels the denominator. This observation can be made on the basis of an induction proof of (70) in that the value of n for which one sets $h_{n+1}h_{n-1} = h_n h_n$ can be made as large as one wishes in the case $N \to \infty$.

It must be emphasized that any specific U which we wish to use in (71) must be calculated from the exact recurrence formula (65a) and the definition (69).

7. ALGORITHM FOR log Z_n WHEN DEFECTS ARE RANDOMLY LOCATED

The numerical value of any $U_j(t_1,\ldots,t_{j-1})$ depends explicitly on the number of lattice spacings between successive defects. Consider first $\sum_j \log U_2(t_j)$. There are a certain number of successive defects separated by one lattice spacing, a certain number by two, etc., so that if $n(s_1)$ is the number of successive pairs whose numbers are separated by s_1 lattice spacings, the sum over the U_2 becomes

$$\sum_{s_1=1}^{\infty} n(s_1) \log U_2(s_1) \tag{72}$$

Now let $n(s_1, s_2)$ be the number of successive defect triples such that s_1 is the number of lattice spacings between the first two members of the triple and s_2 that between the second two. Then the U_3 term of (71) becomes

$$\sum_{s_1=1}\sum_{s_2=1} n(s_1, s_2) \log U_3(s_1, s_2) \tag{73}$$

Successive triples are overlapping: If the first triple is characterized by (s_1, s_2), the next is characterized by (s_2, s_3), and so on. We can similarly define $n(s_1, s_2, s_3)$ for U_4, so that (71) becomes, as $N \to \infty$,

$$N^{-1} \log Z_n(n) = \log \lambda_1 + 2(n/N) \log[(1, 1)\, \gamma/\lambda_1] + (n/N) \log U_1$$
$$+ N^{-1} \sum_{s_1=1} n(s_1) \log U_2(s_1)$$
$$+ N^{-1} \sum_{s_1, s_2=1}\sum n(s_1, s_2) \log U_3(s_1, s_2) + \cdots \tag{73}$$

When our defects are distributed randomly with concentration c, we can find explicit formulas for $n(s_1)$, $n(s_1, s_2)$, $n(s_1, s_2, s_3)$, etc. The number of successive pairs whose elements are separated by s_1 lattice spacings are $nc(1-c)^{s_1-1}$, since such a configuration corresponds to a defect (of which there are n) followed by $s_1 - 1$ host atoms. Similarly, the number of triples with spacings s_1 and s_2 is $nc(1-c)^{s_1-1}\, c(1-c)^{s_2-1}$, the number of quadruples $nc(1-c)^{s_1-1}\, c(1-c)^{s_2-1}\, c(1-c)^{s_3-1}$, etc. Since $c = n/N$, we obtain, as $N \to \infty$,

$$N^{-1} \log Z(c) = \log \lambda_1 + 2c \log[(1, 1)\, \gamma_1/\lambda_1] + c \log U_1 + \sum_{j=1}^{\infty} c^{j+1} \sum_{s_1 \cdots s_j = 1} \sum (1-c)^{s_1+s_2+\cdots+s_j-j} \log U_{j+1}(s_1 \cdots s_j) \quad (75)$$

8. APPROXIMATION OF ARBITRARY DISTRIBUTIONS BY PERIODIC ONES

In Section 4, we found that in a chain with random distribution of defects (hereafter denoted by B) at concentration c, the expected number of B pairs separated by s intervening lattice sites in a very large ring is Nc^2 independent of s. One can approximate a random chain by a periodic one by constructing a sequence of A (host sites) and B's such that the number of B pairs occur in the correction proportion Nc^2. If the period is small, only the nearest- and perhaps the next-nearest neighbors occurs in Nc^2 times, but as the period becomes larger, one can expect more distant neighbor pairs to appear in the correct number.

As an example, we consider a random chain of equal numbers of A and B of length N. Then the number of pairs of B's separated by an integral number of lattice spacings is $N/4$. In a chain of period four,

$$AABB \mid AABB \mid AABB \mid AABB$$

the number of pairs of B which agree with $N/4$ comes from the first, third, fifth, seventh, ninth, etc., neighbor pairs, but wrong in the second, fourth, sixth, eighth, etc., neighbor pairs. The chain of period eight,

$$AAABABBB \mid AAABABBB|AAAABABBB$$

has the required number $N/4$ of pairs of B separated by $8j-7$, $8j-6$, $8j-4$, $8j-2$, $8j-1$ with $j = 1, 2, \ldots$. A chain with period 12 which agrees with a random chain in the number of first, second, third, and fourth neighbors is

$$BBBBABAAABAA \mid BBBBABAAABAA$$

Table I

c	Period	Sequence	Correct to n neighbors
1/2	4	*AABB|AABB*	First
	8	*AAABABBB|AAABABBB*	Second
	12	*BBBBABAAABAA|BBBBABAAABAA*	Fourth
	16	*BBBAAAABAABABBBA|BBBAAAABAABABBBA*	Sixth
	20	*BABABBAABBBBABBAAAAA|BABABBAABBBBABBAAAAA*	Sixth
	24	*BBABAABBBABBBABABBAAAAAA|BBABAABBBABBBABABBAAAAAA*	Eighth
	28	*BBABABBAABBBBBAABBABABAAAAAA|BBABABBAABBBBBAABBABABAAAAAA*	Eighth
	32	*BBBABABBABBBAABBBABAABBABAAAAAAA|BBBABABBABBBAABBBABAABBABAAAAAAA*	Tenth
1/3	9	*ABAAAAABB|ABAAAAABB*	Third
	18	*ABAABAAAAAABAAABBB|ABAABAAAAAABAAABBB*	Seventh
	27	*AABAAABAAAAAAABAABABAAABBBB|AABAAABAAAAAAABAABABAAABBBB*	Tenth
	36	*AABABAAAABAABAAAAABAAABAAABAAAABBBBB|AABABAAAABAABAAAAABAAABAAABAAAABBBBB*	Tenth
1/4	16	*AAAAAAAAABABAABB|AAAAAAAAABABAABB*	Sixth
	32	*AABAABABAAABAAAAABAAAAAAAAAABBB|AABAABABAAABAAAAABAAAAAAAAABBB*	Ninth
1/5	25	*ABAAAAABAAAAAAAAAABAAABB|ABAAAAABAAAAAAAAAABAAABB*	Ninth

An example of a case of period 16 which agrees with a random chain up to the sixth neighbors is

$$BBBAAAABAABABBBA \mid BBBAAAABAABABBBA$$

In Table I, we have compiled the periodic sequence for various concentrations c which would approximate a random two-component chain correct to n neighbors.

9. THERMODYNAMIC PROPERTIES OF A TWO-COMPONENT LINEAR ISING CHAIN: GRAPHICAL AND DISCUSSIONS

The thermodynamic properties of the various two component Ising chains obtained in Sections 6 and 7 are investigated graphically (Figs. 1–3).

The zero-field specific heats for ferromagnetic components are computed for the two-component chain with random distribution (Section 7) and periodic distribution (Section 6) for the concentration range $0 < c < 1$. The theoretical curves have rather similar structures. For small concentration c, the specific heat rises toward a maximum and then tails off gently at high temperatures. The behavior is typically that of a perfect chain with type A atoms. For large c, the specific heat tends to peak at a temperature typical

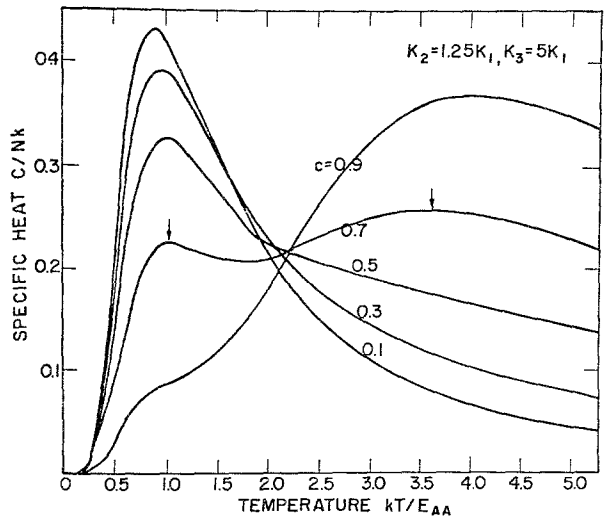

Fig. 1. Zero-field specific heat for two-component random Ising chain, both components ferromagnetic $K_2 = 1.25K_1$, $K_3 = 5K_1$, versus reduced temperature kT/E_{AA}. Note the presence of two maxima for $c = 0.7$.

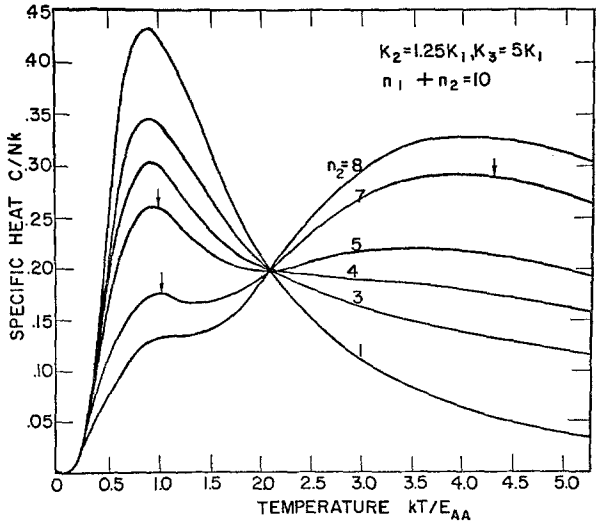

Fig. 2. Zero-field specific heat for two-component periodic Ising chain, with $n_1 + n_2 = 10$, both components ferromagnetic (same parameters as in Fig. 1). Note again the presence of double maxima.

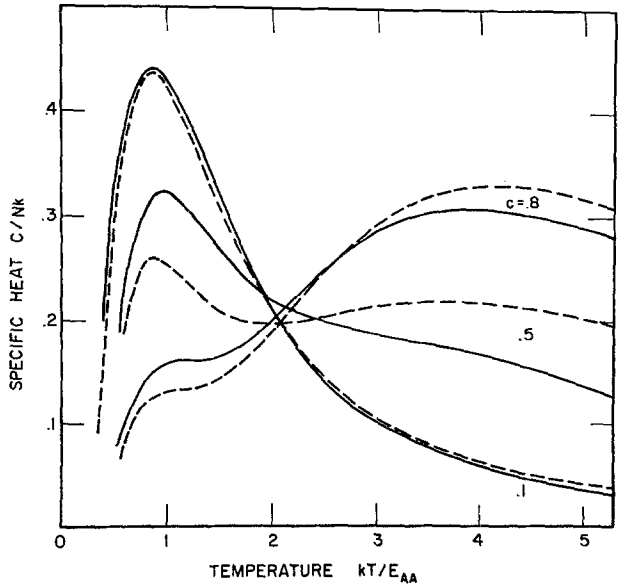

Fig. 3. Zero-field specific heats. The approximation of a random chain by a periodic one is more evidently displayed here for various concentrations c. (——) The random chain; (– – –) the periodic chain.

of the type B atoms. In the intermediate range of concentrations, there is a competition between these two specific heat maxima, which ultimately settles at, for certain concentrations, a double peak structure in the specific heat curve. The positions of the two maxima depend on the exchange interaction constants K_2 and K_3 (normalized against K_1), and is apparantly a characteristic of a multicomponent spin system described by more than one exchange interaction constant. It should, however, be emphasized here that the basic idea we have used to compute the thermodynamic quantities of the systems differ from that of the equilibrium Ising lattice.[11] This can be seen from the following arguments. Consider a large sample divided into a statistically large number of subunits, each of which contains a statistically large number of atoms (and defects). If we neglect surface interactions among the subunits, each subunit behaves independently of the others and would contribute to the sum total of the free energy of the sample. The crucial idea is that the free energy to be calculated is averaged over random distribution of the defects. In the equilibrium model, the free energy per particle of each subunit must be the same since a state of equilibrium is that in which

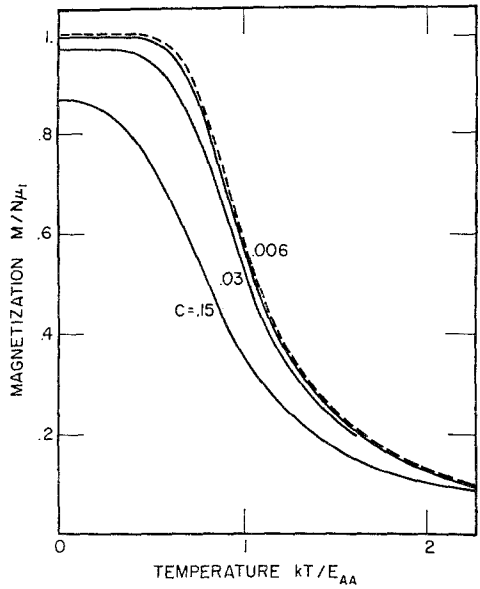

Fig. 4. Reduced magnetization $M/N\mu_1$ versus temperature at constant external field $\mu_1 H/E_{AA} = 0.1$ for paramagnetic defects antiferromagnetically coupled to host atoms, $K_2 = -0.05K_1$, $K_3 = 0$, $J_1 = J_2$, (——) series expansion to $O(c^3)$ term, (– – –) perfect chain.

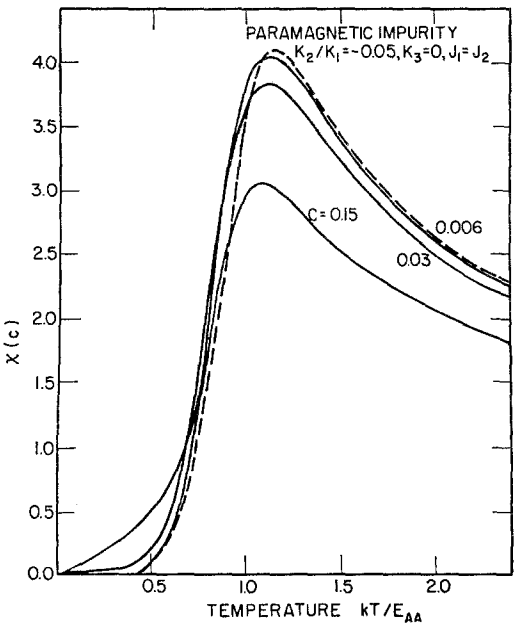

Fig. 5. Reduced susceptibility $\chi(c) = kTX/N\mu_1^2$, where $X = dM/dH$ is the susceptibility of the system. Parameters same as for Fig. 4.

both mechanical and thermal equilibrium have been achieved. This implies that the thermodynamic free energy has to be averaged over all possible spatial configuration of the defects.[13]

In the presence of magnetic field, the thermodynamic function of the random system is given by an infinite series in powers of c. If c is small, the series converge rapidly, since the correlation effects between any defect pair is presumably small. On this basis, we have plotted in Figs. 4 and 5 the magnetization and reduced susceptibility at constant field for the case where one component is paramagnetic. In each case, we have terminated the series at $O(c^4)$ term, and a separation of 20 lattice sites between any pair has been chosen for numerical computation. Inclusion of the $O(c^4)$ term and reduction of lattice separation to ten sites contributes insignificantly to third decimal places.

APPENDIX

We have, from (64b),

$$h_n(t_1, \ldots, t_{n-1}) = G_{11}^{(n-1)}(t_1, \ldots, t_{n-1}) \tag{A.1}$$

From the definition of $G_{ij}^{(n)}$, (61), we have

$$\begin{aligned} G_{ij}^{(n)}(t_1,\ldots,t_n) &= \sum_{\sigma,\sigma',\sigma''} f_j(\sigma)\, F_{n-1}(\sigma,\sigma'';t_1,\ldots,t_{n-1})\, F_1(\sigma'',\sigma';t_n) f_i(\sigma') \\ &= \sum_{\sigma,l,m}\sum f_j(\sigma)\, F_{n-1}(\sigma,\sigma'';t_1,\ldots,t_{n-1})\, B_{lm}(t_n) f_m(\sigma'') f_i(\sigma') f_i(\sigma') \\ &= \sum_{l,m} A_{il} B_{lm}(t_n)\, G_{mj}^{(n-1)}(t_1,\ldots,t_{n-1}) \\ &= C_{i1}(t_n)\, G_{1j}^{(n-1)}(t_1,\ldots,t_{n-1}) + C_{i2} G_{2j}^{(n-1)}(t_1,\ldots,t_{n-1}) \end{aligned} \tag{A.2}$$

where

$$C_{ij}(t) = \sum_m A_{im} B_{mj}(t) \tag{A.3a}$$

so that the matrix $C(t)$ is defined by

$$C(t) = AB(t) \tag{A.3b}$$

Similarly,

$$G_{ij}^{(n)}(t_1,\ldots,t_n) = G_{i1}^{(n-1)}(t_2,\ldots,t_n)\, D_{1j}(t_1) + G_{i2}^{(n-1)}(t_2,\ldots,t_n)\, D_{2j}(t_1) \tag{A.4}$$

where

$$D_{mj}(t) = \sum_l B_{ml}(t)\, A_{lj}\,, \qquad D(t) = B(t)\, A \tag{A.5}$$

The determinant of $G^{(n)}$ satisfies a simple recurrence formula, as can be observed by calculating

$$\begin{aligned} |\, G^{(n)}(t_1,\ldots,t_n)| &= |\, C(t_n)|\, |\, G^{(n-1)}(t_1,\ldots,t_{n-1})| \\ &= |\, G^{(1)}(t_1)|\, |\, C(t_2)|\, |\, C(t_3)| \cdots |\, C(t_n)| \end{aligned} \tag{A.6a}$$

with

$$|\, G^{(1)}(t)| = |\, C(t)|\, |\, A\,| \tag{A.6b}$$

Furthermore, from (A.3),

$$|\, C(t)| = |\, A\,|\, |\, B(t)|$$

Hence

$$|\, G^{(n)}(t_1,\ldots,t_n)| = |\, A\,|^{n+1} \prod_{j=1}^{n} |\, B(t_j)| \tag{A.7}$$

We shall now use these results to establish a recurrence formula for $h_n(t_1,\ldots,t_{n-1})$. Let

$$\begin{aligned}\Delta_n &= h_{n+1}(t_1,\ldots,t_n)\,h_{n-1}(t_2,\ldots,t_{n-1}) - h_n(t_1,\ldots,t_{n-1})\,h_n(t_2,\ldots,t_n)\\ &= G_{11}^{(n)}(t_1,\ldots,t_n)\,G_{11}^{(n-2)}(t_2,\ldots,t_{n-1}) - G_{11}^{(n-1)}(t_1,\ldots,t_{n-1})\,G_{11}^{(n-1)}(t_2,\ldots,t_n)\end{aligned} \tag{A.8}$$

If the recurrence formula (A.2) is applied twice to $G_{11}^{(n)}$ to reduce it to $G_{11}^{(n-2)}$ by removing t_1 and t_n, the first product in Δ_n is

$$\begin{aligned}&G_{11}^{(n-2)}(t_2,\ldots,t_{n-1})[C_{11}(t_n)\,G_{11}^{(n-1)}(t_1,\ldots,t_{n-1}) + C_{12}(t_n)\,G_{21}^{(n-1)}(t_1,\ldots,t_{n-1})]\\ &\quad= G_{11}^{(n-2)}(t_2,\ldots,t_{n-1})\\ &\qquad\times\{C_{11}(t_n)[G_{11}^{(n-2)}(t_2,\ldots,t_{n-1})\,D_{11}(t_1) + G_{12}^{(n-2)}(t_2,\ldots,t_{n-1})\,D_{21}(t_1)]\\ &\qquad+ C_{12}(t_n)[G_{21}^{(n-2)}(t_2,\ldots,t_{n-1})\,D_{11}(t_1) + G_{22}^{(n-2)}(t_2,\ldots,t_{n-1})\,D_{21}(t_1)]\}\end{aligned}$$

A similar expression exists for the second product in (A.8). The difference between the two is

$$\begin{aligned}\Delta_n &= C_{12}(t_n)\,D_{21}(t_1)|\,G^{(n-2)}(t_2,\ldots,t_{n-1})|\\ &= D_{21}(t_1)\,C_{12}(t_n)|\,A\,|^{n-1}\prod_{j=1}^{n-1}|\,B(t_j)|\end{aligned} \tag{A.9}$$

with

$$\Delta_2 = D_{21}(t_1)\,C_{12}(t_2)|\,A\,|$$

By combining (A.8) and (A.9), we find a recurrence relation for h_n:

$$\begin{aligned}h_{n+1}(t_1,\ldots,t_n)\,h_{n-1}(t_2,\ldots,t_{n-1}) &= h_n(t_1,\ldots,t_{n-1})\,h_n(t_2,\ldots,t_n)\\ &\quad+ D_{21}(t_1)\,C_{12}(t_n)|\,A\,|^{n-1}\prod_{j=1}^{n-1}|\,B(t_j)|,\quad n>1\end{aligned} \tag{A.10}$$

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