

## Hopping conductivity in a quasi-one-dimensional lattice gas with three-dimensional ordering

Peter M. Richards

Sandia Laboratories, Albuquerque, New Mexico 87115

(Received 25 August 1977)

The dc ionic conductivity is calculated for one-dimensional (1-D) classical hopping with effects of nearest-neighbor repulsion included. Repulsion between ions in different channels which leads to three-dimensional ordering of the ions is accounted for in a mean-field manner. The intrachannel repulsion  $U$  is treated exactly by using results for the equivalent Ising antiferromagnet in a staggered field. It is shown that several choices can exist for the dependence of transition probabilities on nearest-neighbor occupation numbers and still satisfy detailed balance. In almost any case, however, the activation energy increases by  $U/2$  as the temperature  $T$  goes through the ordering temperature  $T_c$  from above. An appreciable change in activation energy should then be observed in a 1-D superionic conductor which undergoes an order-disorder transition, provided this transition is triggered by interactions between the mobile ions. The dependence of activation energy upon  $U$  above  $T_c$  depends on the range of the forces and whether the hopping is purely classical or involves tunneling. We find that Kikuchi's result of a decrease in activation energy by  $U/2$  from the noninteracting value is reproduced if very-short-range forces and classical activation over a barrier are assumed. On the other hand, we get Mahan's result of an increase by  $U/2$  if the transition rate is governed by tunneling through a barrier.

### I. INTRODUCTION

The lattice-gas model has been used as a convenient starting point for describing the hopping dynamics in superionic conductors.<sup>1-4</sup> It consists of  $\rho N$  particles constrained to reside on  $N$  lattice sites such that no two particles occupy the same site. Interactions are between nearest neighbors only, whereby thermodynamics of the system can be related to those of a nearest-neighbor Ising model. Specific calculations have been performed for pure one- and two-dimensional (1-D and 2-D) systems. These are of more than academic interest since a number of the real compounds have layer or channel structures which suggest that the conductivity should be confined to one or two dimensions. An example of note is 1-D  $\beta$ -eucryptite ( $\text{LiAlSiO}_4$ ) where a highly anisotropic conductivity has been confirmed.<sup>5</sup>

The ideal 1-D lattice gas, in common with all 1-D systems with short-range interactions, does not have a phase transition. Interactions between ions in neighboring channels are present in real systems and can trigger a 3-D order-disorder transition at a finite temperature  $T_c$ . This paper addresses the question of how the conductivity in a quasi-1-D system is affected by weak inter-channel interactions, particularly in the vicinity of  $T_c$ . A partial motivation for the work is the observation<sup>6</sup> that the mobile  $\text{Li}^+$  ions in  $\beta$ -eucryptite are 3-D ordered only below about 450°C, although precise details of the apparent order-disorder transition are unknown.

Although thermodynamics of the lattice gas are straightforwardly related to those of the Ising

model, dynamics which lead to ionic transport require additional consideration. The high temperatures and heavy (compared with electrons) particles of interest should lead to incoherent hopping processes with negligible quantum tunneling and coherence effects. In this case a classical hopping formalism via rate equations seems appropriate, as used for Kikuchi's pure 1-D calculation<sup>3</sup> and in the path-probability method.<sup>2</sup>

An alternate approach was taken by Mahan<sup>1</sup> who added a transfer term  $t_0 c_i^\dagger c_j$  to the lattice-gas Hamiltonian  $\mathcal{H}_0$  which moves an ion from site  $j$  to  $i$ . (The unperturbed  $\mathcal{H}_0$  is of the form  $\sum_{ij} U_{ij} P_i P_j$ , where  $P_i = c_i^\dagger c_i$  is the occupation-number operator and  $c_i^\dagger$  and  $c_i$  are fermion creation and annihilation operators for an ion at site  $i$ .) He then calculated the conductivity to lowest non-vanishing order in  $t_0$  using the Kubo formalism.<sup>7</sup> It is not at all clear that this represents an improvement over the rate equations used here to describe ionic hopping at elevated temperatures. For example, a first-principles  $t_0$  would have no explicit temperature dependence, and lead to coherent processes in the absence of further interaction terms in the Hamiltonian; but it was necessary for Mahan to make the somewhat *ad hoc* assumption  $t_0^2 \propto \exp(-V/k_B T)$  in order for his results to produce activated hopping over a barrier  $V$  at temperature  $T$ .

Even within the framework of classical hopping<sup>8</sup> the lattice-gas model can only be regarded as a crude approximation to the realities of superionic conductors. Effects such as lattice relaxation are ignored by the assumption that the probability for

a particular ion to hop depends only on the initial configuration of its neighboring ions. As the ion and its neighbors move the saddle-point energy and phase-space volume<sup>8</sup> can be modified so as to complicate the simple rate equations beyond tractability. Nonetheless, the lattice-gas model provides useful physical insight into the hopping and ordering of interacting models even though it may be risky to attempt detailed comparison of its results with experiments on complex structures.

The calculations of Kikuchi and Mahan which show the effect of an interaction  $U$  on activation energy are inadequate for the present purpose since they do not allow for ordering in quasi-1-D systems. Here we account for the possibility of ordering by including interchannel interactions which are approximated by mean-field theory while the intrachannel ones are treated exactly with well-known results of the 1-D Ising model in an external field. Conductivity is calculated in the same manner as presented in a previous publication,<sup>9</sup> referred to as I, for the noninteracting system. An expression is obtained for the steady-state current in a weak electric field by considering the hopping-rate equations. This current depends on static correlation functions which are evaluated from known properties of the 1-D Ising model in a mean field.

The dependence of the hopping transition probability  $W$  upon  $U$  is only partially fixed by requirements of detailed balance for the dynamics of the lattice-gas or equivalent Ising model.<sup>10</sup> We show that above  $T_c$  the activation energy can either increase or decrease with  $U$  depending on the particular form taken for  $W$ . In any event, however, there is an abrupt increase in activation energy by an amount of the order of  $\frac{1}{2}U$  as  $T$  goes through  $T_c$  from above. In fact the choice of  $W$  which reproduces Kikuchi's result that the activation energy is decreased by  $\frac{1}{2}U$  for  $T > T_c$  leads to an activation energy independent of  $U$  for  $T < T_c$ . We further demonstrate that the activation energy for  $T \ll T_c$  is greater than that for  $T$  just below  $T_c$  by an amount proportional to the interaction  $U'$  between ions in different channels. This latter effect is a result of correlations for inequivalent sites as discussed in I.

## II. HOPPING EQUATIONS

If  $W_{i,j}$  is the probability per unit time of an ion jumping from site  $i$  to  $j$  in the absence of an electric field, then as in I the rate equation is

$$\frac{\delta P_i}{\delta t} = \sum_j -W_{ij}P_i(1-P_j)(1+\epsilon_{ij}\Delta) + W_{ji}P_j(1-P_i)(1+\epsilon_{ji}\Delta), \quad (1)$$

where  $P_i$  is 1 or 0 according to whether site  $i$  is occupied or unoccupied, respectively,  $\Delta = \frac{1}{2}\beta e E a_0$  ( $\beta = 1/k_B T$ ) describes the effect of a weak electric field  $E$  in altering the rate at which a particle of charge  $e$  hops a distance  $a_0$ , and  $\epsilon_{ij} = +1$  if site  $j$  is to the right of  $i$  and  $\epsilon_{ij} = -1$  if  $j$  is to the left of  $i$ . Only nearest-neighbor hops on a 1-D lattice are considered so that  $j = i \pm 1$ . The quantity  $\delta P_i$  represents the average change in  $P_i$  during a small time interval  $\delta t$ . The reader is referred to I for a discussion of how Eq. (1) is related to stochastic processes and a more-detailed description of the meaning of  $\delta P_i$ . The steady current is proportional to the net flow of probability between  $i$  and  $i+1$  given by

$$\mathcal{J} = (1+\Delta)\{W_{i,i+1}P_i(1-P_{i+1})\} - (1-\Delta)\{W_{i+1,i}P_{i+1}(1-P_i)\}, \quad (2)$$

where the curly brackets indicate a steady-state average taken in the presence of the electric field. The probability flow  $\mathcal{J}$  is of course independent of position in the steady state.

Equation (2) is used as in I to calculate the conductivity, proportional to  $\mathcal{J}/\Delta$ , in terms of static correlations which are in turn determined partly from the steady-state values of Eq. (1) and similar equations for  $\delta(P_i P_{i+1})$ , the correlated average change in the product  $P_i P_{i+1}$ . The difference between here and I is that we now let  $W_{i,i+1}$  include the effect of nearest-neighbor repulsion by having it depend on the occupation of sites  $i-1$  and  $i+2$ . Since  $P_j^2 = P_j$  the most general form this can take is

$$W_{i,i+1} = \bar{W}_{i,i+1} \exp[\beta U(aP_{i-1} - bP_{i+2} + cP_{i-1}P_{i+2})], \quad (3)$$

where  $\bar{W}_{i,i+1} = \bar{W}_{i,i-1}$  is the transition rate used in I, which for two inequivalent sites  $A$  and  $B$  per unit cell, is either  $\bar{W}_{AB}$  or  $\bar{W}_{BA}$  depending on whether  $i$  is an  $A$  or a  $B$  site.

Note that  $W_{i,i+1}$  is always multiplied by  $P_i(1-P_{i+1})$  in the rate equations, i.e., we demand that site  $i$  is occupied and, within the spirit of the lattice-gas approximation that only the initial configuration determines the rate, site  $i+1$  is unoccupied for the transition to occur. This eliminates the need for including  $P_i$  or  $P_{i+1}$  in Eq. (3) since they must have the values 1 and 0, respectively. Interchannel repulsions are treated by a mean-field approximation and may thus be lumped into an effective  $\bar{W}_{i,i+1}$ . The parameters  $a$ ,  $b$ ,  $c$  depend on the particular dependence assumed for transition rates on the intermediate barrier and on the range of the repulsive force. Detailed balance<sup>4,10</sup> requires only that  $a+b=1$ . These points are discussed more fully later. Since

$$\exp(\lambda P_j) = 1 - P_j + P_j e^\lambda \quad (4)$$

for any constant  $\lambda$ , we can rewrite Eq. (3) as

$$W_{i,i+1} = \bar{W}_{i,i+1} (1 + K_a P_{i-1} + K_b P_{i+2} + \bar{K}_c P_{i-1} P_{i+2}), \quad (5a)$$

and similarly

$$W_{i+1,i} = \bar{W}_{i+1,i} (1 + K_a P_{i+2} + K_b P_{i-1} + \bar{K}_c P_{i-1} P_{i+2}), \quad (5b)$$

where

$$K_a = e^{\beta U_a} - 1, \quad (6a)$$

$$K_b = e^{-\beta U_b} - 1, \quad (6b)$$

$$K_c = e^{\beta U_c} - 1, \quad (6c)$$

$$\bar{K}_c = K_c (1 + K_a + K_b) + K_a K_b. \quad (6d)$$

The result of using Eqs. (5) in (2) is

$$\begin{aligned} g = & \bar{W}_{AB} \Delta [n_A - f_{AB} + K_a (f_{AB} - f_{BAB}) + K_b (f_{AA} - f_{ABA}) \\ & + \bar{K}_c (f_{BAA} - f_{BABA})] \\ & + \frac{1}{2} (\bar{W}_{BA} - \bar{W}_{AB}) [(1 + K_a) y + \bar{K}_c z], \end{aligned} \quad (7)$$

where  $n_A = \langle P_{iA} \rangle$  is the average number of particles on an  $A$  site,  $f_{AB} = \langle P_A P_B \rangle$  and  $f_{AA} = \langle P_A P_{A+1} \rangle$  are two-particle correlations, and the higher correlations are  $f_{BAB} = \langle P_{B-1} P_A P_B \rangle$ ,  $f_{ABA} = \langle P_A P_B P_{A+1} \rangle$ ,  $f_{BAA} = \langle P_{B-1} P_A P_{A+1} \rangle$ ,  $f_{BABA} = \langle P_{B-1} P_A P_B P_{A+1} \rangle$ . In the above and following relations, sites are labeled such that if  $i=A$ , then  $i+1=B$ ,  $i-1=B-1$ ,  $i+2=A+1$ , etc. The triangular brackets indicate a thermodynamic average in zero field and we have noted that for a calculation of  $g$  to first order in  $\Delta$ , sufficient for the small-signal conductivity, the averages contained as coefficients of  $\Delta$  in (7) may be calculated for  $\Delta=0$ . The quantity  $y$  is the same as in I

$$y = \{P_A P_B - P_{B-1} P_A\}, \quad (8)$$

and, as shown in I, has an important effect on the conductivity when the sites are inequivalent ( $\bar{W}_{AB} \neq \bar{W}_{BA}$ ). The curly brackets stand for a steady-state average in the presence of a field ( $\Delta \neq 0$ ). The additional correlation in Eq. (7) is

$$z = \{P_A P_B P_{A+1} P_{B+1}\} - \{P_{B-1} P_A P_B P_{A+1}\}. \quad (9)$$

The coefficient of  $\Delta$  in Eq. (7) is explicitly for  $i$  an  $A$  site in Eq. (2). However, the steady-state condition  $\delta P_i = 0$  in Eq. (1) shows that the term with  $A$  and  $B$  interchanged is identical. Use of (1) has also been made in expressing the terms not explicitly containing  $\Delta$  in the manner shown.

An equation for  $y$  and  $z$  valid to first order in  $\Delta$  is obtained, as in I, by considering  $\delta(P_i P_{i+1}) = 0$ , which yields

$$\begin{aligned} y(1 + K_a)(\bar{W}_{AB} + \bar{W}_{BA})(1 - g) \\ = 4\Delta \bar{W}_{AB} [f_{AB} - f_{BAB} - f_{AA} + f_{ABA} \\ + K_a (f_{AB} - f_{BAB} - f_{BAA} + f_{BABA}) \\ + K_b (-f_{AA} + f_{ABA} + f_{BAA} - f_{BABA})], \end{aligned} \quad (10)$$

where the correction  $g$  is defined as

$$g = \frac{1}{y} \frac{K_a - K_b}{1 + K_a} \frac{\bar{W}_{AB}(v_A - z) + \bar{W}_{BA}(v_B - z)}{\bar{W}_{AB} + \bar{W}_{BA}} \quad (11)$$

with

$$v_A = \{P_A P_{A+1} P_{B+1} - P_{B-1} P_A P_{A+1}\}, \quad (12a)$$

$$v_B = \{P_A P_B P_{B+1} - P_B P_{B+1} P_{A+2}\}. \quad (12b)$$

The presence of  $z$  in Eq. (7) and  $g$  in Eq. (10) prevent an exact solution for  $g$  to first order in  $\Delta$ . This is no problem above  $T_c$ , where the sites are equivalent, since  $y$  and  $z$  must be zero anyway. Not too far below  $T_c$ ,  $y$  and  $z$  are small and do not affect the results much. But for very low temperatures they can have a big effect and, in certain cases, the activation energy can be influenced by the decoupling approximation employed later.

A remark is in order regarding the difference between Eq. (7) for  $\bar{W}_{BA} = \bar{W}_{AB} = W_0$  and that derived by Kikuchi<sup>3</sup> for equivalent sites and the case he considered, which corresponds to  $a=1$ ,  $b=c=0$  =  $K_b = \bar{K}_c$ . In effect he made the substitution

$$\begin{aligned} W_{i,i+1} P_i (1 - P_{i+1}) = W_{i,i+1} P_i P_i (1 - P_{i+1}) \\ \equiv W P_i (1 - P_{i+1}), \end{aligned} \quad (13)$$

and then replaced  $W$  by its average value

$$\begin{aligned} W - \langle W \rangle = W_0 \{ [1 + P_{i-1} (e^{\beta U} - 1)] P_i \} \\ = W_0 [e^{\beta U} f_{AB} + (\rho - f_{AB})], \end{aligned} \quad (14)$$

where  $\langle P_i \rangle = \rho$  for a density  $\rho$  of particles distributed on equivalent sites. The first equality in (13) is legitimate since  $P_i^2 = P_i$ . Replacement of  $W$  by  $\langle W \rangle$  neglects certain correlations which are included in Eq. (7). We show in Sec. III that, nonetheless, Kikuchi's conductivity calculated from Eq. (14) agrees with ours from Eq. (7) for the case of  $\rho = \frac{1}{2}$  and  $a=1$ ,  $b=c=0$  above  $T_c$ .

The conductivity is completely determined by using the appropriate static correlations in (7) and (10), at least if  $z$  and  $g$  can be neglected, together with a choice for the parameters  $a$ ,  $b$ ,  $c$ . The correlations are treated in Sec. III in terms of an equivalent Ising model, and the physical basis for various values of  $a$ ,  $b$ ,  $c$  is discussed.

### III. HAMILTONIAN AND CORRELATIONS

We consider a regular (nondimerized) chain with two different types of sites,  $A$  and  $B$ . There is

a nearest-neighbor repulsion  $U$  between sites  $i$  and  $i \pm 1$ . If the site  $i$  is an  $A$  ( $B$ ) type it is labeled  $i_A$  ( $i_B$ ) and has a well depth  $V_A^0$  ( $V_B^0$ ). If no distinction need be made as to the type of site, it is simply labeled  $i$ . The lattice-gas Hamiltonian which describes interaction within the chain and coupling with other chains is

$$\mathcal{H}C = U \sum_i P_i P_{i+1} - V_A^0 \sum_{i_A} P_{i_A} - V_B^0 \sum_{i_B} P_{i_B} + \sum_{i_A, i'} U_{i_A, i'} P_{i_A} P_{i'} + \sum_{i_B, i'} U_{i_B, i'} P_{i_B} P_{i'} \quad (15)$$

The last two terms in Eq. (15) express 3-D coupling to ions in other channels whose sites are denoted by  $i'$ . They are replaced in a mean-field approximation by

$$\sum_{i'} U_{i_A, i'} P_{i'} \rightarrow U'_{AA} n_A + U'_{AB} n_B, \quad (16a)$$

$$\sum_{i'} U_{i_B, i'} P_{i'} \rightarrow U'_{BA} n_A + U'_{BB} n_B, \quad (16b)$$

where  $U'_{AA} = \sum_{i_A'} U_{i_A, i_A'}$ , etc., and  $n_A$  ( $n_B$ ) is the probability that an  $A$  ( $B$ ) site is occupied. Henceforth  $A$  is taken as the preferred site ( $n_A \geq n_B$ ).

Equation (15) can then be rewritten as purely 1-D:

$$\mathcal{H}C = U \sum_i P_i P_{i+1} - V_A \sum_{i_A} P_{i_A} - V_B \sum_{i_B} P_{i_B}, \quad (17)$$

where

$$V_A = V_A^0 - U'_{AA} n_A - U'_{AB} n_B, \quad (18a)$$

$$V_B = V_B^0 - U'_{BA} n_A - U'_{BB} n_B. \quad (18b)$$

Relationships between the transition rates  $W_{i, i+1}$  and  $W_{i+1, i}$  and parameters of the Hamiltonian are established in analogy with studies of the time-dependent Ising model.<sup>4,10</sup> Consider hopping of a particle between  $i$  and  $i+1$  with all other particles fixed. Detailed balance requires

$$W_{i, i+1}/W_{i+1, i} = \exp(\beta\Phi_i)/\exp(\beta\Phi_{i+1}), \quad (19)$$

where

$$\Phi_i = -V_i + UP_{i-1} + \Phi' \quad (20a)$$

and

$$\Phi_{i+1} = -V_{i+1} + UP_{i+2} + \Phi' \quad (20b)$$

are energies of the system with the interchannel mean-field Hamiltonian (17) when the particle is at site  $i$  or at site  $i+1$ , respectively. Here  $V_i = V_A$  ( $V_B$ ),  $V_{i+1} = V_B$  ( $V_A$ ) if  $i$  is an  $A$  ( $B$ ) site and  $\Phi'$  does not depend on whether the particle is at  $i$  or  $i+1$ . We have noted that since  $i+1$  must be vacant if the particle is at  $i$ , nearest-neighbor repulsion in (20a) can occur only with site  $i-1$

occupied. Similar reasoning applies in Eq. (20b). Use of Eqs. (20) in (19) together with considerations of the symmetry of the situation— $P_{i-1}$  must appear in  $W_{i, i+1}$  in the same manner that  $P_{i+2}$  appears in  $W_{i+1, i}$ —leads to Eq. (3) with  $a+b=1$ ,  $c$  arbitrary, and  $\bar{W}_{i, i+1}$  independent of  $U$ . The activation energy of  $\bar{W}_{i, i+1}$  is  $V_A$  for  $i$ , in an  $A$  site, and  $V_B$  for  $i$ , a  $B$  site, if classical hopping over a barrier is assumed. Note from Eqs. (18) that this means that  $\bar{W}_{i, i+1}$  contains interchannel interactions and depends on the average occupations  $n_A$  and  $n_B$ .

The physical nature of the hopping process sheds further light on  $a$ ,  $b$ ,  $c$ . Referring to Fig. 1, let the positions of sites  $i$  and  $i+1$  be 0 and  $a_0$ , respectively, where the potential has local minima. The potential maximum is assumed to be at  $\frac{1}{2}a_0$ . Classical activated hopping assumes a temperature dependence

$$W_{i, i+1}^{(C)} \propto \exp\{-\beta[\phi(\frac{1}{2}a_0) - \phi(0)]\}, \quad (21)$$

where  $\phi(x)$  is the energy of a particle at position  $x$ . The sense of Eq. (21) is that enough energy must be supplied to move the particle over the barrier, leading to an activated process, and that the particle readily loses energy in getting from  $\frac{1}{2}a_0$  to  $a_0$  so that the final-state energy  $\phi(a_0)$  does not appear in the expression. A second alternative is that, assuming  $\phi(a_0) > \phi(0)$ , as sketched in Fig. 1, the ion can tunnel once it is supplied with sufficient energy to reach a level corresponding to  $\phi(a_0)$ . In this mixed quantum-classical picture we would have a temperature dependence

$$W_{i, i+1}^{(T)} \propto \begin{cases} \exp\{-\beta[\phi(a_0) - \phi(0)]\} & \text{for } \phi(a_0) > \phi(0) \\ \text{independent of temperature} & \text{for } \phi(a_0) < \phi(0) \end{cases} \quad (22)$$

Although it is unlikely for ionic mobility at the temperatures of interest, we include the process implicit in Eq. (22) for completeness. In the expressions (21) and (22) for the classical ( $C$ ) and tunneling ( $T$ ) rates we assume that the dominant temperature dependence comes from the activated

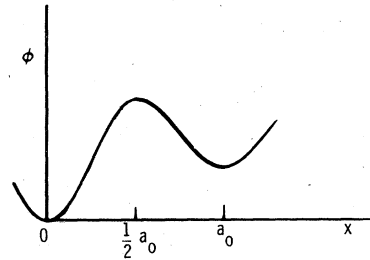


FIG. 1. Potential  $\phi$ , which includes ion-ion repulsion, vs position  $x$  for a typical configuration.

terms; any weaker variations such as  $T^2$  are taken to be "independent of temperature."

We treat first the classical rate (21) and show how it depends on the range of the force. Let the interaction part of the energy have a spatial variation  $U(x)$ , where  $U(a_0) = U$  to be consistent with the Hamiltonian of Eq. (17). We then have from (21) and Fig. 1

$$W_{i,i+1}^{(c)} \propto \exp(-\beta V_i) \exp\{-\beta P_{i-1} [U(\frac{3}{2}a_0) - U(a_0)] - \beta P_{i+2} [U(\frac{3}{2}a_0) - U(2a_0)]\}. \quad (23)$$

The term  $U(2a_0)$  must be neglected since its presence would contradict the use of a nearest-neighbor Hamiltonian. However,  $U(\frac{3}{2}a_0)$  can in principle be retained. Comparison of (23) with (3) shows that, for  $U(2a_0) = 0$

$$a = 1 - U(\frac{3}{2}a_0)/U(a_0), \quad (24a)$$

$$b = U(\frac{3}{2}a_0)/U(a_0), \quad (24b)$$

$$c = 0. \quad (24c)$$

In the limit of very-short-range forces, which is the most likely case in which the Hamiltonian (17) is justified,  $U(\frac{3}{2}a_0) \ll U(a_0)$ , and we get  $a = 1$ ,  $b = 0$ , corresponding to Kikuchi's model. In fact, he presented an argument very similar to the above in his detailed exposition of the path-probability method.<sup>11</sup> One can at least imagine other situations, such as sketched in Fig. 2, where the interaction falls off slowly between  $a_0$  and  $\frac{3}{2}a_0$  and then is abruptly cut off by screening. For example, if  $U(x)$  decays as  $1/x$  (unscreened Coulomb) before being cut off, Eqs. (24a) and (24b) would give  $a = \frac{1}{3}$ ,  $b = \frac{2}{3}$ . The case  $a = b = \frac{1}{2}$  is realizable with an interaction which decays to  $\frac{1}{2}U$  at  $\frac{3}{2}a_0$  before being cut off. Thus it is possible to have any  $a$ : $b$

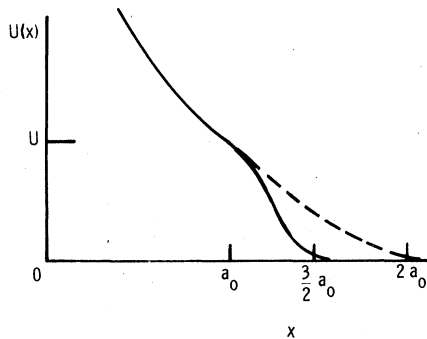


FIG. 2. Distance dependence of repulsion  $U(x)$ . Solid curve:  $U(\frac{3}{2}a_0) \ll U$  and barrier height  $\phi(\frac{1}{2}a_0)$  is unaffected by  $U(x)$ . Dashed curve:  $U(\frac{3}{2}a_0)$  is not negligible so that  $\phi(\frac{1}{2}a_0)$  is affected. Restriction to nearest-neighbor interactions demands that  $U(2a_0)$  be negligible in any case.

ratio between  $\infty$  and  $\frac{1}{2}$  in the classical hopping rate (21) for Coulomb repulsions with various forms of screening and still preserve the nearest-neighbor Hamiltonian (17). Note, however, that  $c = 0$  always in this model.

The tunneling rate (22) does not depend on  $U(\frac{3}{2}a_0)$ . If we take equivalent sites  $V_A = V_B$ , then Eq. (22) reduces to

$$W_{i,i+1}^{(T)} = \begin{cases} \nu_0 e^{-\beta U}, & P_{i-1} = 0, \quad P_{i+2} = 1 \\ \nu_0 & \text{otherwise,} \end{cases}$$

where  $\nu_0$  is an appropriate attempt frequency which is only weakly dependent on temperature. The above is equivalent to

$$W_{i,i+1}^{(T)} = \nu_0 \exp[-\beta U P_{i+2}(1 - P_{i-1})], \quad (25)$$

which means  $a = 0$ ,  $b = c = 1$ . A wide variety of choices thus exist for the parameters  $a$ ,  $b$ ,  $c$  in  $W_{i,i+1}$  depending on the nature of the hopping and details of the interaction range.

We next express the Hamiltonian (17) as an equivalent Ising model by the substitution  $P_i = \frac{1}{2}(1 + \sigma_i)$ , where  $\sigma_i = \pm 1$ ,

$$\mathcal{H} = J \sum_i \sigma_i \sigma_{i+1} - h \sum_i (\sigma_{2i+1} - \sigma_{2i}) - H \sum_i \sigma_i + \text{const}, \quad (26)$$

where  $J = \frac{1}{4}U$ ,  $h = \frac{1}{4}(V_A - V_B)$ ,  $H = \frac{1}{4}(V_A + V_B) - \frac{1}{2}U$ , and where we have taken  $A$  sites to be odd numbered ( $2i+1$ ) and  $B$  sites to be even numbered ( $2i$ ). With  $J > 0$  the above is the Hamiltonian for a 1-D Ising antiferromagnet in both a uniform field  $H$  and a staggered field  $h$ . For a fixed number of sites  $N$  and particles  $\rho N$  (canonical ensemble), we have

$$\sum_i \sigma_i = \sum_i (2P_i - 1) = (2\rho - 1)N. \quad (27)$$

In the special case of  $\rho = \frac{1}{2}$  this is zero so that the term in  $H$  is not present.

The study is henceforth restricted to the half-filled lattice  $\rho = \frac{1}{2}$ , where correlations are those appropriate to an Ising antiferromagnet in a staggered field  $h$ . Further, such correlations are identical to those of an Ising ferromagnet in a uniform field apart from a change of sign where necessary to account for the antiferromagnetic ordering, e.g.,  $\langle \sigma_i \sigma_{i+1} \rangle = -\tau_1$ , where  $\tau_1$  is the positive nearest-neighbor correlation for the ferromagnet. We then make the following identifications:

$$n_A = \frac{1}{2}(1 + \langle \sigma \rangle), \quad (28a)$$

$$f_{AB} = \frac{1}{4}(1 - \tau_1), \quad (28b)$$

$$f_{AA} = \frac{1}{4}(1 + 2\langle \sigma \rangle + \tau_2), \quad (28c)$$

$$f_{BAB} = \frac{1}{8}(1 - \langle \sigma \rangle - 2\tau_1 + \tau_2 + \langle \sigma_1 \sigma_2 \sigma_3 \rangle), \quad (28d)$$

$$f_{ABA} = \frac{1}{8}(1 + \langle \sigma \rangle - 2\tau_1 + \tau_2 - \langle \sigma_1 \sigma_2 \sigma_3 \rangle), \quad (28e)$$

$$f_{AAB} = \frac{1}{8}(1 + \langle \sigma \rangle - \tau_1 + \tau_2 - \tau_3 - \langle \sigma_1 \sigma_3 \sigma_4 \rangle), \quad (28f)$$

$$f_{BAB} = \frac{1}{16}(1 - 3\tau_1 + 2\tau_2 - \tau_3 + \langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle), \quad (28g)$$

where all correlations are positive for a ferromagnet in a uniform field  $h$ —the sign differences as well as the assumption of preferred  $A$ -site ordering ( $\langle \sigma \rangle \geq 0$ ) have been explicitly accounted for. The quantity  $\tau_j$  is defined as  $\tau_j = \langle \sigma_i \sigma_{i+j} \rangle$ . Use of Eqs. (28) in (7) and (10) gives after some algebra

$$\begin{aligned} \mathcal{J} = & \frac{1}{8} \bar{W}_{AB} \Delta \{ [1 + \exp[\beta U(a - b + c)]] C_1 \\ & + \exp[\beta U a] [1 + (1 + \epsilon) \tanh 2\beta h] C_2 \\ & + \exp[-\beta U b] [1 - (1 + \epsilon) \tanh 2\beta h] C_3 \}, \end{aligned} \quad (29)$$

where

$$C_1 = 1 + 2\langle \sigma \rangle + \tau_1 - \tau_3 - 2\langle \sigma_1 \sigma_3 \sigma_4 \rangle - \langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle, \quad (30a)$$

$$C_2 = 1 - \tau_1 - 2\tau_2 + \tau_3 - 2\langle \sigma_1 \sigma_2 \sigma_3 \rangle + 2\langle \sigma_1 \sigma_3 \sigma_4 \rangle + \langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle, \quad (30b)$$

$$C_3 = 1 + 4\langle \sigma \rangle + 3\tau_1 + 2\tau_2 + \tau_3 + 2\langle \sigma_1 \sigma_2 \sigma_3 \rangle + 2\langle \sigma_1 \sigma_3 \sigma_4 \rangle + \langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle, \quad (30c)$$

and we have used the relation

$$(\bar{W}_{BA} - \bar{W}_{AB}) / (\bar{W}_{BA} + \bar{W}_{AB}) = \tanh 2\beta h, \quad (31)$$

which follows from (19), (20), and the definition of  $h$  given under Eq. (26). The  $\tanh 2\beta h$  terms in Eq. (29) arise from the term on the right-hand side of (7) proportional to  $\bar{W}_{BA} - \bar{W}_{AB}$  which does not explicitly contain  $\Delta$ . The quantity  $\epsilon$  is a correction resulting from  $z$  in Eq. (7) and  $g$  in Eq. (10). It is evaluated by making the decoupling approximation

$$\begin{aligned} \{ & P_A P_{A+1} P_{B+1} - P_{B-1} P_A P_{A+1} \} \\ & \approx n_A \{ P_A P_B - P_{B-1} P_A \} + n_A \{ P_A P_{B+1} - P_{B-1} P_{A+1} \} \\ & \quad + n_B \{ P_A P_{A+1} - P_A P_{A+1} \} \\ & \approx 2n_A y. \end{aligned} \quad (32)$$

The second approximate equality on the right-hand side of (32) comes from assuming that the system is strongly correlated below  $T_c$  so that  $\{ P_A P_{B+1} \} \approx \{ P_A P_B \}$ , etc., and noting that the coefficient of  $n_B$  is identically zero. Similarly we take

$$z \approx 2n_A n_B y. \quad (33)$$

These approximations lead to

$$1 + \epsilon = \frac{1 + \frac{1}{2}(1 - \langle \sigma \rangle^2) e^{-\beta U a} \bar{K}_c}{1 - \frac{1}{2}(1 + \langle \sigma \rangle^2 - 2\langle \sigma \rangle^2 \tanh 2\beta h)(1 - e^{-\beta U})}. \quad (34)$$

The necessary correlations in Eqs. (30) may be calculated by transfer-matrix methods as outlined in the Appendix. Since they are rather cumbersome except for  $h = 0$ , we do not give general results for the conductivity but rather focus on specific regions of interest.

Comparison of Eqs. (18) with the definition of  $h$  under (26) shows that

$$\begin{aligned} h = & \frac{1}{4}(V_A^0 - V_B^0) - \frac{1}{8}(U'_{AA} - U'_{BB} + U'_{AB} - U'_{BA}) \\ & + \frac{1}{8}(U'_{AB} + U'_{BA} - U'_{AA} - U'_{BB}) \langle \sigma \rangle \equiv h_0 + J' \langle \sigma \rangle, \end{aligned} \quad (35)$$

since  $n_A = \frac{1}{2}(1 + \langle \sigma \rangle)$ ,  $n_B = \frac{1}{2}(1 - \langle \sigma \rangle)$ . If the potentials  $V_A^0$  and  $V_B^0$  are identical and the symmetry is such that  $U'_{AA} = U'_{BB}$ ,  $U'_{AB} = U'_{BA}$ , then  $h_0 = 0$  and  $h$  behaves like a pure mean field proportional to  $\langle \sigma \rangle$  with no "external" component. In this case there is a sharp transition to 3-D ordering at a temperature  $T_c = 1/k_B \beta_c$  such that<sup>12</sup>

$$\beta_c J' = e^{-2\beta_c J}. \quad (36)$$

The expression (36) is exact<sup>13</sup> to lowest order in  $\beta_c J'$  for the complete quasi-1-D Ising Hamiltonian, which shows the validity of using a mean-field approximation to treat the interchain couplings. Another way of stating this is that any neglected interchain short-range order is of the order of  $\beta_c J' \ll 1$  at  $T_c$  and thus negligible. If  $h_0$  is nonzero, there will be rounding of the transition but the basic features should remain the same as long as  $h_0 < J'$ . For the specific discussion which follows we take  $h_0 = 0$ , although some results are also presented for finite  $h_0$ .

#### IV. EXPRESSIONS FOR CONDUCTIVITY

We calculate the conductivity in three regions of interest.

##### A. $T > T_c$

Above  $T_c$ ,  $\langle \sigma \rangle = \langle \sigma_1 \sigma_2 \sigma_3 \rangle = \langle \sigma_1 \sigma_3 \sigma_4 \rangle = 0$ , the two-spin correlations are given by the well-known results<sup>14</sup> for  $h = 0$

$$\tau_n = (\tanh \beta J)^n, \quad (37)$$

and  $\langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle = \tau_1^2$ . Equations (30) reduce to

$$C_1 = (1 + \tau_1)^2 (1 - \tau_1), \quad (38a)$$

$$C_2 = (1 - \tau_1)^2 (1 + \tau_1), \quad (38b)$$

$$C_3 = (1 + \tau_1)^3, \quad (38c)$$

with  $\tau_1 = \tanh\beta J = \tanh\frac{1}{2}\beta U$ . In the activated region we expect  $\beta J \gg 1$  so that  $\tau_1 \approx 1 - 2e^{-\beta U/2}$ , whereby Eq. (29) becomes

$$\mathcal{J} \approx \bar{W}_{AB} \Delta \left\{ \exp(-\frac{1}{2}\beta U) + \exp[\beta U(a - b + c - \frac{1}{2})] + 2 \exp(-\beta U b) \right\} \quad (T > T_c), \quad (39)$$

where we have noted that since  $b = 1 - a$ ,  $\exp(\beta U a) C_2 \approx \exp(-\beta U b) C_3$  for  $\beta J \gg 1$ . The observed activation energy will be  $V_A + kU$ , where  $k$  is the smallest of  $\frac{1}{2}$ ,  $-a + b - c + \frac{1}{2}$ ,  $b$ , assuming that one of the exponentials in (39) dominates. For the models considered above,  $k = -\frac{1}{2}$  for classical hopping with  $U(\frac{3}{2}a_0) \ll U(a_0)$  ( $a = 1$ ,  $b = c = 0$ ), while  $k = +\frac{1}{2}$  for the others. The complete expression for  $a = 1$ ,  $b = c = 0$  may be shown to agree exactly with Kikuchi's,<sup>3</sup> even though he neglected certain correlations. The reason is that where our expression contains  $\tau_2$  or  $\langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle$ , his has  $\tau_1^2$ ; but  $\tau_2 = \langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle = \tau_1^2$  for the 1-D Ising model anyway.

#### B. $T \lesssim T_c$

This region is characterized by a nonzero  $\langle \sigma \rangle$ , but we assume that the temperature is sufficiently high that  $\beta J \langle \sigma \rangle \ll 1$ . This should be valid not too far below  $T_c$  since Eq. (36) shows that  $\beta_c J' \ll 1$  if  $J'/J \ll 1$  for a quasi-1-D system. For  $\beta h \ll 1$  the "magnetization" is given by

$$\langle \sigma \rangle = (1 - e^{-4\beta J / \beta^2 J'^2})^{1/2}, \quad (40)$$

and the quantity  $X = (\sinh^2 \beta h + e^{-4\beta J})^{1/2}$  is given by  $X = \beta J' \ll 1$ . With  $X \ll 1$  and  $\cosh \beta h \approx 1$  the results of the Appendix may be used to show that

$$\tau_n = 1 - 2nX(1 - \langle \sigma \rangle^2) + O(X^2) \approx \tau_1^n, \quad (41a)$$

$$\langle \sigma_1 \sigma_2 \sigma_3 \rangle = \langle \sigma_1 \sigma_3 \sigma_4 \rangle = \langle \sigma \rangle + O(X^2), \quad (41b)$$

$$\langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle = 1 - 4nX(1 - \langle \sigma \rangle^2) + O(X^2) \approx \tau_1^2. \quad (41c)$$

As a consequence Eqs. (38) still hold but with  $\tau_1 \approx 1 - 2\beta J'(1 - \langle \sigma \rangle^2) \approx 1 - 2e^{-\beta U} / \beta J'$  so that Eq. (39) is replaced by

$$\mathcal{J} \approx \bar{W}_{AB} \Delta \left\{ (\beta J')^{-1} \exp(-\beta U) + \exp[-\beta U(2b - c)] + (\beta J')^{-2} \exp[\beta U(a - 2)] + \exp(-\beta U b) \right\} \quad (T < T_c, \beta J' \ll 1). \quad (42)$$

The activation energy is now  $V_A + k'U$ , where  $k' = 0$  for the very-short-range case ( $a = 1$ ,  $b = c = 0$ ), and  $k' = 1$  for the tunneling model ( $a = 0$ ,  $b = c = 1$ ). For the classical hopping with  $a = \frac{1}{3}$ ,  $b = \frac{2}{3}$ ,  $c = 0$  corresponding to an initial  $1/x$  decay of the interaction out to  $x = \frac{3}{2}a_0$  followed by a rapid cutoff, some care must be used in examining Eq. (42) because of the different powers of  $\beta J' \ll 1$ . Since  $\exp(-\frac{1}{2}\beta U) / \beta J' = 1$  at  $T_c$ , the terms in  $(\beta J')^{-1}$ ,  $(\beta J')^{-2}$ , and  $(\beta J')^0$  in (42) are  $\exp(-\frac{1}{2}\beta U)$ ,  $\exp(-\frac{2}{3}\beta U)$ , and  $\exp(-\frac{2}{3}\beta U)$ , respectively. Hence

the term in  $(\beta J')^{-1}$  is initially dominant and  $k' = 1$  for  $T$  just below  $T_c$ ; but once  $T$  decreases to the point where  $(\beta J')^{-1} \exp(-\beta U) \ll \exp(-\frac{2}{3}\beta U)$ ,  $k'$  changes to  $\frac{2}{3}$ .

For all three of the models  $k' - k = \frac{1}{2}$  if  $k'$  is taken as the value immediately below  $T_c$  so that there is an increase in activation energy by an amount  $U/2$  as  $T$  goes through  $T_c$  from above. A special case of note, however, is  $a = b = \frac{1}{2}$ ,  $c = 0$  [classical hopping with  $U(\frac{3}{2}a_0) = \frac{1}{2}U(a_0)$  followed by rapid cutoff beyond  $\frac{3}{2}a_0$ ] for which  $k = k' = \frac{1}{2}$  and there is no change in activation energy at  $T_c$ .

#### C. $T \rightarrow 0$

In the very-low-temperature limit,  $\beta h > 1$  and the  $\tanh 2\beta h$  terms in Eq. (29) become important. The quantity  $\epsilon$  also has a significant effect so that quoted results depend on the validity of the decoupling approximation (32). To lowest order in  $e^{-4\beta J}$  the expressions given in the Appendix reduce to

$$\langle \sigma \rangle = 1 - \delta, \quad (43)$$

where

$$\delta = \frac{1}{2} e^{-4\beta J} / \sinh^2 \beta h, \quad (44)$$

and

$$\tau_n = 1 - 2\delta(1 - e^{-2n\beta h}), \quad (45a)$$

$$\langle \sigma_1 \sigma_2 \sigma_3 \rangle = 1 - \delta(3 - 4e^{-2\beta h} + 2e^{-4\beta h}), \quad (45b)$$

$$\langle \sigma_1 \sigma_3 \sigma_4 \rangle = 1 - \delta(3 - 2e^{-2\beta h} - 2e^{-4\beta h} + 2e^{-6\beta h}), \quad (45c)$$

$$\langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle = 1 - \delta(4 - 6e^{-2\beta h} + 4e^{-4\beta h} - 2e^{-6\beta h}). \quad (45d)$$

These lead to

$$C_1 = 8\delta(1 - e^{-2\beta h}), \quad (46a)$$

$$C_2 = O(\delta^2), \quad (46b)$$

$$C_3 = 16 + O(\delta), \quad (46c)$$

and, from Eq. (34)

$$1 + \epsilon = 1 / \tanh 2\beta h + O(e^{-4\beta J}), \quad (46d)$$

so that Eq. (29) becomes

$$\mathcal{J} = \bar{W}_{AB} \Delta \left[ e^{-2\beta h} \left\{ \exp(-\beta U) + \exp[\beta U(-2b + c)] \right\} + O(\exp[\beta U(a - 2)] e^{-4\beta h}) + O(\exp[-\beta U(b + 1)] e^{-2\beta h}) \right]. \quad (47)$$

For the three models considered [ $a = 1$ ,  $b = c = 0$ ;  $a = \frac{1}{3}$ ,  $b = \frac{2}{3}$ ,  $c = 0$ ;  $a = 0$ ,  $b = c = 1$ ] the activation energy is

$$V_A + k'U + 2h = V_A^0 - \frac{3}{2}U'_{AA} + \frac{1}{2}U'_{AB} + k'U, \quad (48)$$

where we have used Eqs. (18a) and (35) together

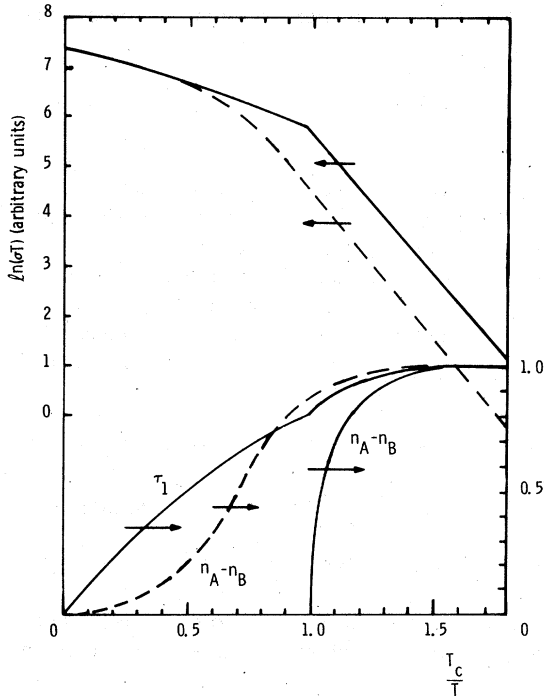


FIG. 3. Conductivity  $\sigma$ , relative site occupancy  $n_A - n_B$ , and nearest-neighbor correlation  $\tau_1$  (for  $h_0 = 0$  only). Solid curves:  $J'/J = 0.1$ ,  $h_0 = 0$ ; dashed curves:  $J'/J = 0.1$ ,  $h_0 = J'$ . Both conductivity curves are for  $a = 1$ ,  $b = c = 0$  [classical hopping with  $U(\frac{3}{2}a_0) \ll U$ ].

with  $n_A = \langle \sigma \rangle = 1$  in the low-temperature regime, and where  $k' = 0, 1, 1$  for the respective conditions on  $a, b, c$  given in square brackets. The value for  $1 + \epsilon$  (46d) which results from the decoupling approximation has an important effect, particularly for small nonzero values of  $b$  with  $c = 0$ . If we were to take  $\epsilon = 0$ , the  $C_3$  term in Eq. (29) would give

$$\mathcal{J}(C_3) = 4W_{AB} \Delta \exp(-\beta Ub) e^{-4\beta h}.$$

For  $b + 4h < 2b + 2h < b + 1 + 2h$ ,  $\mathcal{J}(C_3)$  is the dominant term and the  $U$  part of the activation energy would be reduced from  $2bU$  in Eq. (47) to  $bU$ .

Some curves for the complete conductivity are presented in Fig. 3 for values of the parameters as given.

## V. SUMMARY AND CONCLUSIONS

The dc conductivity has been calculated for a 1-D hopping model in which nearest-neighbor repulsions within a conducting channel were treated exactly with known results for the 1-D lattice gas (equivalent to a 1-D Ising model). Interchannel repulsions which allow for 3-D ordering were included by a mean-field approximation. The same hopping equations and methods were used as

in I (Ref. 9) except that here the transition rate depends on nearest-neighbor occupancy. The precise relation between transition rate and occupancy depends on such considerations as range of the interaction and whether the hopping is purely classical or tunneling.

A noteworthy feature is that the activation energy for conductivity increases by an amount of the order of  $\frac{1}{2}U$  as  $T$  goes through  $T_c$  from above. This is in spite of the fact that the model contains a good deal of short-range order above  $T_c$ ; so it is not simply a matter of the mean field suddenly switching on correlations below  $T_c$ . If the nearest-neighbor correlation  $\tau_1$  is written  $\tau_1 = 1 - \alpha$ , then a major part of the conductivity near and above  $T_c$  is proportional to  $\alpha$ . Since  $\alpha$  changes from  $2e^{-\beta U/2}$  for  $T - T_c = 0^+$  to  $2e^{-\beta U}/\beta J'$  for  $T - T_c = 0^-$ , where  $e^{-\beta_c U/2} = \beta_c J'$  at  $T_c = 1/k_B \beta_c$ , the activation energy shows the  $\frac{1}{2}U$  increase. Although this result for a discontinuous activation energy is strictly valid only within the context of the present model which treats the weak 3-D interchannel interactions by mean-field theory, it may have more-general validity. One might argue that as long as the conductivity  $\mathcal{J}/\Delta$  is proportional to the short-range correlation  $\tau$ , the activation energy  $d \ln \mathcal{J}/d\beta$  will have an anomaly if the specific heat, proportional to  $d\tau/d\beta$ , has an anomaly. Indeed such a relation has been derived and verified by others.<sup>15</sup>

Above  $T_c$  the activation energy can either increase or decrease with  $U$ , depending on details of the transition rates. The assumption of nearest-neighbor interactions restricts us to taking  $U(2a_0) = 0$ , where the repulsion varies with the distance  $x$  as  $U(x)$  and  $U(a_0) = U$ . But we are at liberty to have  $U(\frac{3}{2}a_0) \neq 0$  which affects the barrier height. For  $U(\frac{3}{2}a_0) = 0$  Kikuchi's result of a decrease in activation energy by an amount  $\frac{1}{2}U$  below its non-interacting value is reproduced. On the other hand, if  $U(\frac{3}{2}a_0) = \frac{2}{3}U$  corresponding to an unscreened Coulomb decay of the interaction, the activation energy is increased by  $\frac{1}{2}U$ . A similar increase of  $\frac{1}{2}U$  is obtained if the transition takes place by tunneling through the barrier so that only the energy difference between equilibrium sites  $i+1$  and  $i$  need be supplied by phonons. Mahan also found an increase of  $\frac{1}{2}U$ . The fact that the dependence of interaction upon distance appears to have a major effect makes it desirable to have a calculation employing other than a nearest-neighbor lattice gas.

A motivation for this work was  $\beta$ -eucryptite which is ordered below about 450 °C and apparently disordered above that temperature. The dc conductivity<sup>5</sup> does not show any obvious change in activation energy between the ordered and dis-



ordered states, although data in the high-temperature phase are rather sparse. This is consistent with the present calculation only if the nearest-neighbor repulsion is too small to make a noticeable effect, which would rule out a  $U$  comparable in value to the observed activation energy<sup>5</sup> of 0.74 eV. Since the order-disorder transition has a characteristic energy  $k_B T_c \approx 0.06$  eV, it is quite possible that the differences between site energies  $V_B^0 - V_A^0$  could account for a gradual change from  $n_A \approx n_B$  above  $T_c$  to  $n_A \gg n_B$  below  $T_c$  with less than a 10% change in activation energy.

One problem with this interpretation concerns the theory of Follstaedt and Richards<sup>16</sup> for the NMR relaxation. There it was required to have  $V_A - 2V_B$  to be of the order of +0.7 eV in order to explain the frequency-independent low-temperature relaxation, whereas here we seem to require  $V_A - 2V_B \sim -0.7$  eV to have no marked change in the conductivity at  $T_c$ . Careful conductivity and x-ray structure determinations in the vicinity of  $T_c$  would clearly be helpful toward resolving these difficulties. Ability of the lattice-gas model to describe qualitative features of real quasi-1-D superionics must be regarded at the moment as uncertain.

#### ACKNOWLEDGMENT

This work was supported in part by the U.S. Department of Energy under Contract No. AT(29-1)789.

#### APPENDIX: CORRELATIONS FOR 1-D ISING MODEL IN A FIELD

Although zero-field correlations and the finite-field partition function of the 1-D Ising model may be found in several sources,<sup>14</sup> calculations of many-spin correlations in a field  $h$  are less readily available and thus are presented here.

The Hamiltonian is taken as

$$\mathcal{H} = -J \sum_i \sigma_i \sigma_{i+1} - h \sum_i \sigma_i, \quad (\text{A1})$$

for a ferromagnetic ( $J > 0$ ) model. It gives the same correlations apart from obvious sign changes as the antiferromagnet in a staggered field only ( $H=0$ ) of Eq. (26). The transfer-matrix technique<sup>13</sup> may be generalized for arbitrary correlations to

$$\langle \sigma_i \sigma_{i+j} \cdots \sigma_{i+n} \rangle = \mathfrak{z}^{-1} \text{Tr} T^N T^{-n} \sigma T^j \sigma \cdots T \sigma, \quad (\text{A2})$$

where  $T$  is the transfer matrix, written

$$T = \begin{pmatrix} e^{\beta J} e^{\beta h} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} e^{-\beta h} \end{pmatrix}, \quad (\text{A3})$$

in the representation where the spin operator  $\sigma$  is diagonal:

$$\sigma = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (\text{A4})$$

In the above  $\mathfrak{z} = \text{Tr} T^N$  is the  $N$ -spin partition function,  $T$  appears sandwiched between the  $\sigma$ 's a total of  $n$  times, and the total number of  $\sigma$ 's may be anywhere between 1 and  $1+n$ . Equation (A2) is evaluated in a new representation where  $T$  is diagonal with eigenvalues  $\lambda_{\pm}$ . In the thermodynamic limit  $N \rightarrow \infty$  and for finite  $n$  the correlation reduces to

$$\langle \sigma_i \sigma_{i+j} \cdots \sigma_{i+n} \rangle = \langle + | \sigma T^j \sigma \cdots T \sigma | + \rangle / \lambda_+^n, \quad (\text{A5})$$

where  $\lambda_+$  is the larger of the two eigenvalues of  $T$

$$\lambda_{\pm} = e^{\beta J} [\cosh \beta h \pm (\sinh^2 \beta h + e^{-4\beta J})^{1/2}], \quad (\text{A6})$$

and the eigenstates of  $T$  are denoted by  $|\pm\rangle$ . The transformation  $S$  which diagonalizes  $T$  is given by

$$S = \begin{pmatrix} \cos \theta_+ & \cos \theta_- \\ \sin \theta_+ & \sin \theta_- \end{pmatrix}, \quad (\text{A7})$$

where

$$\cot \theta_{\pm} = -e^{-\beta J} / (e^{\beta J} e^{\beta h} - \lambda_{\pm}), \quad (\text{A8})$$

so that in the new representation we have

$$\langle + | \sigma | + \rangle = -\langle - | \sigma | - \rangle = \sinh \beta h / X \equiv r, \quad (\text{A9})$$

$$\langle + | \sigma | - \rangle = \langle - | \sigma | + \rangle = e^{-2\beta J} / X \equiv s, \quad (\text{A10})$$

where

$$X = (\sinh^2 \beta h + e^{-4\beta J})^{1/2}. \quad (\text{A11})$$

The particular correlations required for Eqs. (20) and (21) are

$$\langle \sigma \rangle = r, \quad (\text{A12})$$

$$\tau_n = \langle + | \sigma T^n \sigma | + \rangle / \lambda_+^n = r^2 + s^2 R^n, \quad (\text{A13})$$

$$\langle \sigma_1 \sigma_2 \sigma_3 \rangle = \langle + | \sigma T \sigma T \sigma | + \rangle / \lambda_+^3 = r^3 + r s^2 (2R - R^2), \quad (\text{A14})$$

$$\langle \sigma_1 \sigma_3 \sigma_4 \rangle = \langle + | \sigma T^2 \sigma T \sigma | + \rangle / \lambda_+^3 = r^3 + r s^2 (R + R^2 - R^3), \quad (\text{A15})$$

$$\begin{aligned} \langle \sigma_1 \sigma_2 \sigma_3 \sigma_4 \rangle &= \langle + | \sigma T \sigma T \sigma T \sigma | + \rangle / \lambda_+^4, \\ &= (\lambda_+ \langle + | \sigma T \sigma | + \rangle^2 + \lambda_- \langle - | \sigma T \sigma | - \rangle^2) / \lambda_+^3 \\ &= r_1^2 + r^2 s^2 R (1 - R)^2, \end{aligned} \quad (\text{A16})$$

where  $R = \lambda_- / \lambda_+$ .

Use of (A6) and (A9)–(A14) in (A12)–(A16) gives the correlations in the text for the approximations

described ( $X \ll 1$  for  $T \lesssim T_c$ ,  $X \approx \sinh \beta h$  for  $T \rightarrow 0$ ). The "magnetization"  $\langle \sigma \rangle$  is determined from the self-consistency condition

$$\langle \sigma \rangle = \sinh \beta (h_0 + J' \langle \sigma \rangle) / X, \quad (\text{A17})$$

which for  $h_0 = 0$  and  $\beta J' \ll 1$  reduces to  $\langle \sigma \rangle = 0$  for  $T > T_c$ , where  $T_c$  is the temperature at which  $\beta J' = e^{-2\beta J}$ ; and  $X = \beta J'$  converts to  $\beta^2 J'^2 \langle \sigma \rangle^2 + e^{-4\beta J} = \beta^2 J'^2$  as the equation for  $\langle \sigma \rangle$  below  $T_c$  as long as  $\beta J' \ll 1$ .

<sup>1</sup>G. D. Mahan, Phys. Rev. B 14, 780 (1976).

<sup>2</sup>H. Sato and R. Kikuchi, J. Chem. Phys. 55, 677 (1971).

<sup>3</sup>R. Kikuchi, in *Fast Ion Transport in Solids*, edited by W. van Gool (North-Holland, Amsterdam, 1973), p. 555.

<sup>4</sup>W. Dieterich, I. Peschel, and W. R. Schneider (unpublished).

<sup>5</sup>U. V. Alpen, H. Schulz, G. H. Talat, and H. Bohm, Solid State Commun. 23, 911 (1977).

<sup>6</sup>H. Schulz and V. Tscherry, Acta. Crystallogr. B 28, 2174 (1972); W. W. Pillars and D. R. Peacor, Am. Mineral. 58, 681 (1973).

<sup>7</sup>R. Kubo, J. Phys. Soc. Jpn. 12, 570 (1957).

<sup>8</sup>See, for example, C. P. Flynn, *Point Defects and Diffusion* (Oxford U.P., New York, 1972).

<sup>9</sup>P. M. Richards, Phys. Rev. B 16, 1393 (1977).

<sup>10</sup>R. J. Glauber, J. Math. Phys. 4, 294 (1963).

<sup>11</sup>R. Kikuchi, Progr. Theor. Phys. Suppl. 35, 1 (1966), see in particular Fig. 8, p. 18.

<sup>12</sup>J. W. Stout and R. C. Chisholm, J. Chem. Phys. 36, 979 (1962).

<sup>13</sup>C-Y Weng, R. B. Griffiths, and M. E. Fisher, Phys. Rev. 162, 475 (1967).

<sup>14</sup>See, for example, H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford U.P., New York, 1971).

<sup>15</sup>R. Vargas, M. B. Salamon, and C. P. Flynn, Phys. Rev. Lett. 37, 1550 (1976).

<sup>16</sup>D. M. Follstaedt and P. M. Richards, Phys. Rev. Lett. 37, 1571 (1976).