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Lattice gas theory of ionic conductivity*

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The ionic conductivity is calculated for a solid in which the ions are undergoing an order-disorder phase transition. The interacting ion system is described by a lattice gas with a weak hopping term. Exact results are obtained in one and two dimensions by using the exact results known for the Ising model. The calculated theoretical conductivity agrees very well with the temperature dependence found experimentally.

I. INTRODUCTION

Ionic conductivity in crystalline salts is usually described by a diffusion process whereby the ion hops from site to site. The dc ionic conductivity is usually very well described by an Arrhenius relation[1]

$$\sigma = (C/T)e^{-\Delta/kT}, \qquad (1.1)$$

where C is a constant and Δ is the activation energy. The traditional interpretation of Δ is that it represents the height of a potential barrier over which the ion must hop in changing sites. Several years ago Flynn suggested that another contribution to Δ arose from dynamic polarization effects.[2] The ion is a small polaron, and when hopping must carry its polarization cloud with it. The theory of this predicts a polaron contribution to the activation energy, and estimates show that this is a significant contribution to observed experimental values.[2,3]

Superionic conductors are ionic crystals which have unusually high values of ionic conductivity, typically because a significant fraction [e.g., (40–50)%] of the ions are disordering.[4] There is usually an order-disorder phase transition, which may be first order, second order, or gradual as the temperature is increased. If the ion disordering proceeds gradually with increasing temperature, either through a second-order phase transition, or a diffuse (i.e., no sharp transition temperature) disordering, then the disordering process itself also contributes to Δ.[5,6] This occurs because the disordering ions interact with each other, which inhibits their movements. The increasing disorder with increasing temperature apparently generates more ion arrangements wherein an ion finds hopping agreeable.

The first extensive treatment of this was by Sato and Kikuchi.[6] The model we adopt is similar to theirs. This is a lattice gas with nearest-neighbor interactions between diffusing ions: they called this parameter ϵ, while we call it U. But there are some basic differences between Sato and Kikuchi and us in the mathematical method of solution. They introduce thermal fluctuations classically, while we introduce them quantum mechanically through the explicit use of phonon coordinates. This permits us to introduce another parameter λ, which is the coupling of the ion hop to the surrounding lattice vibrations. The size of this parameter determines the rate of energy transfer between hopping ion, and the thermal bath of phonons.

Another difference in mathematical technique is the treatment of the electric field. They introduce it directly into the equations to be solved, and calculate the degree of nonequilibrium it causes, and hence obtain the ionic conductivity. We adopt the simpler but equivalent procedure of using the Kubo formula.[7] This assumes the conductivity is proportional to the electric field, and calculates the constant of proportionality using equilibrium statistical mechanics.

The model we use is the same as that of Pardee and Mahan.[5] Here we wish to show that this model can, in several special circumstances, be solved exactly. Because of the analogy between the Ising model and the lattice gas, the exact solution of the Ising model in two dimensions can be used to solve the lattice gas also. One can exactly evaluate the current correlation function in the approximation of taking only single ion hops.

Pardee and Mahan considered a solid where disordering is a second-order phase transition. The ionic conductivity, calculated including the effects of lattice gas and phonons, had the following two features: the conductivity appeared to be thermally activated below the transition temperature, it was continuous at the phase transition, and the activation energy changed value at the phase transition. That is, a plot of $\ln(\sigma T)$ vs $1/T$ appeared to change slope at the phase transition. These features are observed in experimental measurements on solid electrolytes which have second-order phase transitions: $RbAg_4I_5$ at 209 K,[8] CaF_2,[9] and $C_5H_6NAg_5I_6$.[10] The theoretical results of Pardee and Mahan were obtained using mean-field theory.

Some of these results were previously obtained by Sato and Kikuchi,[6] whose path probability method is also a form of mean-field theory.[11] Their factor VWf, which is similar to our S in (5.3), had the following features: in β-alumina it decreased with $1/T$, and appeared to be thermally activated. However, the bend over at small $1/T$ was not due to a second-order phase transition, which is absent in this material; in β''-alumina, a kink was observed in VWf at the temperature of a second-order phase transition, whenever one occurred in the theory. However, the low-temperature conductivity did not appear thermally activated at low temperatures—indeed, VWf increased with increasing $1/T$. Thus they did not directly explain the experimental results mentioned above.

There have also been several recent theories of first-order phase transitions in solid electrolytes.[12,13] These also include discussions of the conductivity changes which occur, which are discontinuous.

The mathematical model we solve is called the lattice gas.[14,15] The solid is represented as a network of sites where the ion can sit. There are usually more sites than ions, and no more than one ion on each site. The mathematical problem is isomorphic to the Ising model, with spin up or down equivalent to the ion on or off a site. Interactions are permitted between ions on neighboring sites, and we restrict our model to a repulsive interaction U between nearest neighbors. Conductivity can only occur if we let the ions move, so we introduce the hopping terms with a matrix element t_0. This gives the Hamiltonian

$$H=\frac{U}{2}\sum_{j\delta} n_j n_{j+\delta} + t_0 \sum_{j\delta} C^\dagger_{j+\delta} C_j ,$$
$$n_j = C^\dagger_j C_j , \tag{1.2}$$

where the summation δ is over the nearest-neighbor sites. The phase diagram of this system has recently been investigated, mostly by mean-field theory.[14,15] However, our interest is in calculating the ionic conductivity.

The hopping matrix element t_0 is taken to be proportional to an attempt frequency ω_a and an exponential factor with an activation energy

$$t_0 = \hbar\omega_a \exp(-\tfrac{1}{2}\Delta_a/KT). \tag{1.3}$$

The activation energy Δ_a is interpreted as the static barrier over which the atom must hop in going from site to site. In our simple model we are assuming that all sites have equivalent lattice symmetry, except for disorder. This interpretation of t_0 arises from the result obtained for the conductivity from single hops in an uncorrelated system

$$s=\frac{n}{d}\left(\frac{et_0}{\hbar}\right)^2 \frac{\delta^2}{KT}\,\frac{1}{\omega_0}, \tag{1.4}$$

where δ is the jump distance, n is the density of hopping ions, $\omega_0 \approx \omega_a$ is a relaxation frequency, and d is the dimensionality. This reduces to the standard expression[1] when (1.3) is used for t_0. Thus this form of t_0 permits the static barrier to be introduced in a phenomenological way.

The current operator for the Hamiltonian (1.2) is

$$\vec{\mathrm{j}} = \frac{iet_0}{\hbar} \sum_{j\delta} \vec{\delta} C^\dagger_{j+\delta} C_j , \tag{1.5}$$

where $\vec{\delta}$ is the hop distance and e is the charge of the ion. The conductivity is found from the Kubo formula. First evaluate the correlation function in the Matsubara notation

$$\Pi_{\alpha\beta}(\tau) = \langle T_\tau j_\alpha(\tau) j_\beta(0)\rangle .$$

We are interested in the isotropic systems, so replace this by the scaler

$$\Pi(\tau) = (1/d)\langle T_\tau \vec{\mathrm{j}}(\tau)\cdot\vec{\mathrm{j}}(0)\rangle, \tag{1.6}$$
$$\Pi(i\omega) = \int_0^\beta dt\, e^{i\omega t}\, \Pi(\tau),$$

where d is the dimensionality of the system. The retarded function $\Pi_r(\omega)$ is obtained by letting $i\omega \to \omega + i\delta$. The conductivity, which is used here to signify the real part of the conductivity, is

$$\sigma(\omega) = -\operatorname{Im}\Pi_r(\omega)/\omega V, \tag{1.7}$$

where V is the volume of the system. By combining (1.5) and (1.6) we obtain

$$\Pi(\tau) = -\frac{1}{d}\frac{(et_0)^2}{\hbar^2}\sum_{j\delta,\, i\delta'} \vec{\delta}\cdot\vec{\delta}' \times \langle T_\tau C^\dagger_{j+\delta}(\tau) C_j(\tau) C^\dagger_{i+\delta'} C_i\rangle. \tag{1.8}$$

The ionic conductivity (1.7) is obviously proportional to t_0^2. But it has a further dependence upon t_0 because the hopping term is still in the Hamiltonian (1.2) which affects the time development of the correlation function. We make the approximation that t_0 may be ignored in the time development of the correlation function, so that we evaluate

$$\Pi(\tau) = -\frac{1}{d}\frac{(et_0)^2}{\hbar^2}\sum \vec{\delta}\cdot\vec{\delta}' \times \langle T_\tau C^\dagger_{j+\delta}(\tau) C_j(\tau) C^\dagger_{i+\delta'} C_i\rangle_{t_0=0} . \tag{1.8$'$}$$

Another way to state this approximation is to say that we evaluate this correlation function for the lattice gas alone, without the hopping term. This approximation assumes that t_0 is small. The physical basis of this assumption is very clear. We are assuming that each hop is an independent event, which is uncorrelated with any previous hop. This approximation automatically excludes a description of such interesting processes as the caterpillar mechanism,[16] or the free-ion model,[4] since they do correlate successive hops. We are in the process of testing this approximation by calculating the correlation function with t_0 retained, and these results will be reported elsewhere. However, the ultimate justification is whether the theory explains experiments. The ionic-conductivity curves we derive agree very well with the experimental results.[8-10] This is particularly true in the striking feature that the conductivity is thermally activated (1.1) below the transition temperature, but not above. It is also striking that these features are evident in every solid which shows a second-order ionic order-disorder transition.

We show that the correlation function may be solved exactly in one and two dimensions for a lattice gas which has 50% of the sites occupied. This relies on the exact solution to the Ising model.[17,18] These results are given in Secs. III and IV. Some general results for all dimensions are presented in Sec. II.

II. GENERAL PROPERTIES

We wish to evaluate the time-dependent correlation function

$$\Pi(\tau) = -\frac{1}{d}\left(\frac{et_0}{\hbar}\right)^2 \sum_{ij\delta\delta'} \vec{\delta}\cdot\vec{\delta}' \times \langle T_\tau C^\dagger_{i+\delta'}(\tau) C_i(\tau) C^\dagger_{j+\delta} C_j\rangle, \tag{2.1}$$

$$H = \frac{U}{2}\sum_{\delta j} n_j n_{j+\delta}.$$

The terms in the summation vanish unless $\vec{\delta} = -\vec{\delta}'$ and $i+\delta' = j$. We shall restrict our attention to lattices in which all sites are translationally equivalent. In this case the sum over i and δ may be replaced by NZ, where N is the number of lattice sites and Z is the coordination number of the lattice. Thus we have

$$\Pi(\tau) = \frac{NZ}{d}\left(\frac{et_0\delta}{\hbar}\right)^2 \langle T_\tau C^\dagger_j(\tau) C_{j+\delta}(\tau) C^\dagger_{j+\delta} C_j\rangle. \tag{2.2}$$

Since the ions are large, we insist that only one or none can occupy each lattice site. Thus two C_j operators should anticommute on the same lattice site, but commute at different lattice sites. They are neither fermion nor bosons operators, but are really $S=\frac{1}{2}$ spin operators. Evaluating the commutators gives

$$e^{\tau H} C^\dagger_j e^{-\tau H} = \exp\left(\tau U \sum_{\delta'} n_{j+\delta'}\right) C^\dagger_j, \tag{2.3a}$$

$$e^{\tau H} C_{j+\delta} e^{-\tau H} = \exp\left(-\tau U \sum_{\delta'} n_{j+\delta+\delta'}\right) C_{j+\delta}, \tag{2.3b}$$

so that

$$\Pi(\tau) = \frac{NZ}{d}\left(\frac{et_0\delta}{\hbar}\right)^2 e^{\tau U} \times \left\langle T_\tau \exp\left(\tau U \sum_{\delta'} (n_{j+\delta'} - n_{j+\delta+\delta'})\right) \times C^\dagger_j C_{j+\delta} C^\dagger_{j+\delta} C_j \right\rangle. \tag{2.4}$$

The extra factor of $\exp(\tau U)$ in front comes from commuting the exponential factor in (2.3b) through $C^\dagger_j$. Define the correlation function $M(\tau)$,

$$M(\tau) = 4e^{\tau U}\left[\exp\left(\tau U \sum_{\delta'} (n_{j+\delta'} - n_{j+\delta+\delta'})\right) \times (1 - n_{j+\delta}) n_j\right], \tag{2.5}$$

$$\Pi(\tau) = (1/4d) NZ (et_0\delta/\hbar)^2 M(\tau). \tag{2.6}$$

The correlation function $M(\tau)$ describes an ion which hops from site j to $j+\delta$. The factor n_j indicates that the initial site j must be occupied, and $(1-n_{j+\delta})$ indicates that this final site must be initially empty. The exponential factors are also easy to understand. They are simply $\exp[\tau(E_i - E_f)]$, where the energies in the initial and final state are

$$E_i = U\sum_{\delta'} n_{j+\delta'},$$

$$E_f = U\sum_{\delta'} n_{j+\delta+\delta'} - U.$$

It is convenient to eliminate the factor $\exp(\tau U)$ by restricting the summation δ' to the $Z-1$ neighbors of the initial and final state site which are not involved in the hop—so the summation $\sum_{\delta'} n_{j+\delta'}$ does not include the site $j+\delta$, etc.

The energy difference between the initial and final site is an integral multiple of U,

$$E_f - E_i = lU.$$

In fact, the integer l is restricted to have values between

$$-(Z-1) \leq l \leq Z-1,$$

since this represents the maximum and minimum change in configurational energy of a single hop

$$M(\tau)=\sum_{l=-(Z-1)}^{Z-1} P_l e^{-\tau l U}. \tag{2.7}$$

The exponent lU is the amount of energy change during an ion hop, while P_l is the probability of having a configuration of ions which permits this energy change. Equation (2.7) is an exact consequence of (2.5). From it, the conductivity is easily derived[5]

$$\sigma(\omega)=\frac{N\pi Z}{V4d\omega}(1-e^{-\beta\omega})\left(\frac{et_0\delta}{\hbar}\right)^2 \sum_{l=1-Z}^{Z-1} P_l\delta(\omega-lU). \tag{2.8}$$

The evaluation of the conductivity is thus reduced to the problem of finding the $2Z-1$ coefficients P_l. For a given lattice, these coefficients are just a function of the dimensionless parameter βU and also the concentration of ions. Usually one has the problem of a given lattice with a known concentration, in which case the conductivtiy calculation reduces to finding $P_l(\beta U)$ as single parameter functions.

One theorem which simplifies this procedure is that

$$\sigma(-\omega)=\sigma(\omega), \tag{2.9}$$

from which it is easy to show that

$$P_{-l}=e^{-\beta l U}P_l. \tag{2.10}$$

This reduces to Z the number of independent P_l which need to be determined. The result (2.9) is quite general, and is proved in many references.[19] If one uses states $|n\rangle$ and $|m\rangle$ which are exact eigenstates of the Hamiltonian $K=H-\mu N$ then

$$\Pi(\tau)=\sum_{n,m} e^{-\beta E_n} e^{\tau(E_n-E_m)}\langle n|j|m\rangle\langle m|j|n\rangle$$

and

$$\sigma(\omega)=\frac{\pi}{\omega}(1-e^{-\beta\omega}) \times\sum_{n,m}\delta(\omega+E_n-E_m)e^{-\beta E_n}|\langle n|j|m\rangle|^2. \tag{2.11}$$

Now taking $\omega\rightarrow-\omega$ gives

$$\sigma(-\omega)=-\frac{\pi}{\omega}(1-e^{\beta\omega}) \times\sum_{n,m}\delta(\omega+E_m-E_n)e^{-\beta E_n}|\langle n|j|m\rangle|^2,$$

which can be shown to be the same as (2.11) except for interchanging the dummy summation variables n and m.

The Z probabilities P_l may be determined from the moments of the distribution. Define these moments as

$$M^{(j)}=(-1)^j U^{-j}\left(\frac{\partial^j}{\partial\tau^j}M(\tau)\right)_{\tau=0}, \tag{2.12}$$

$$M^{(j)}=4\left\langle\left(\sum_{\delta'}{}' n_{j+\delta'+\delta}-\sum_{\delta'}{}' n_{j+\delta'}\right)^j \times(1-n_{j+\delta})n_j\right\rangle. \tag{2.13}$$

Multiple differentiation of (2.7) gives our basic equation

$$\sum_{l=1-Z}^{Z-1} l^j P_l=M^{(j)}. \tag{2.14}$$

One needs Z of these equations, in order to provide enough equations to determine the Z variables P_l for $l\geqslant 0$. The moments $M^{(j)}$ are evaluated by a series of static correlation functions (2.13). Using (2.10), then (2.14) may be rewritten

$$0^j P_0+\sum_{l=1}^{Z-1}P_l l^j[1+(-1)^j e^{-l\beta U}]=M^{(j)}, \tag{2.15}$$

where 0^j equals one if $j=0$, and zero otherwise.

The static correlation functions (2.13) are sometimes most easily evaluated in terms of the analogous spin functions. In terms of the Pauli spin operators $n_j=\frac{1}{2}(1+\sigma_j^Z)$,

$$M^{(j)}=(\tfrac{1}{2})^j\left\langle\left(\sum_{\delta'}{}'\sigma^Z_{j+\delta+\delta'}-\sum_{\delta'}{}'\sigma^Z_{j+\delta'}\right)^j \times(1-\sigma^Z_{j+\delta})(1+\sigma^Z_j)\right\rangle, \tag{2.16}$$

$$K=H-\mu N=\frac{U}{8}\sum_{j\delta}\delta^Z_j\sigma^Z_{j+\delta} +\frac{1}{2}\left(\frac{ZU}{2}-\mu\right)\sum_j\sigma^Z_j+\frac{N}{2}\left(\frac{UZ}{4}-\mu\right). \tag{2.17}$$

In evaluating the partition function, the summations over possible values $n_j=(0,1)$ are replaced by $\sigma^Z_j=(-1,1)$. The linear term in σ^Z_j in K makes the spins act as if they were in an effective magnetic field. The prime on the summation over δ' means to exclude the term for which the neighbor is either the initial or final hopping site. Henceforth the Z superscript will be omitted from the σ^Z_j.

The above formulas are quite general. They apply for any concentration of ions, on any kind of lattice structure. However, the solutions we discuss here are restricted to a special case. This is where the lattice sites are 50% occupied. In this case the chemical potential is a constant, independent of temperature, and equals $\mu=\frac{1}{2}ZU$.

Then the term linear in σ vanishes from (2.17), and the statistical mechanics are identical to those for an Ising model in zero magnetic field. For any value of concentration other than 50%, the chemical potential varies with temperature, and the term linear in σ must be retained. This is equivalent to adding a magnetic field to the Ising model, which makes the statistical mechanics much more difficult.

Our results also only apply to certain kinds of lattice structures, namely, those which can be 50% occupied in an orderly way, with every other lattice site empty or occupied. Not every lattice structure has this property—the hcp in two dimensions and the fcc in three dimensions are examples of structures which do not have this property.

We assume that the interaction U is repulsive, since the ions are charged. This is equivalent to antiferromagnetic ordering of the equivalent Ising problem.

For the case which we are considering, static spin correlation functions (2.16) vanish if they contain an odd number of spins.[17,18] This eliminates half of the terms in (2.16)

$$M^{(0)}=1-\langle\sigma_0\sigma_\delta\rangle, \tag{2.18a}$$

$$M^{(1)}=-\frac{1}{2}\left\langle(\sigma_0-\sigma_\delta)\sum_{\delta'}{}'(\sigma_{\delta'}-\sigma_{\delta+\delta'})\right\rangle, \tag{2.18b}$$

$$M^{(2)}=\frac{1}{4}\left\langle(1-\sigma_0\sigma_\delta)\left(\sum_{\delta'}{}'(\sigma_{\delta'}-\sigma_{\delta+\delta'})\right)^2\right\rangle, \quad \text{etc.} \tag{2.18c}$$

In the limit of zero temperature, the lattice gas is completely ordered, as is the equivalent Ising system. All correlation functions in (2.18) are either plus or minus one, in such a way that all terms add. At zero temperature, $M^{(j)}$ is just the number of terms divided by 2^j,

$$\lim_{T\to 0} M^{(j)}=2(Z-1)^j. \tag{2.19}$$

When this result is inserted into (2.15), the following solution is obtained for P_l:

$$\lim_{T\to 0} P_l=\begin{cases}2, & l=Z-1,\\ 0, & l\leqslant Z-2.\end{cases}$$

This result is quite easy to understand. An example is provided in Fig. 1(a) for the two-dimensional square lattice. If all the ions are ordered at zero temperature, then any ion jump must go from a configuration of zero neighbors to one with $Z-1$ which is 3 in this example. This is the only possible transition, so that all of the oscillator strength is in this one peak

$$\lim_{T\to 0}\sigma(\omega)=\left(\frac{N}{2V}\right)\frac{\pi}{dU}\left(\frac{Z}{Z-1}\right)\left(\frac{et_0\delta}{\hbar}\right)^2\delta(\omega-(Z-1)U). \tag{2.20}$$

The first correction terms to these asymptotic expansions do not depend upon the particular crystal structure, and may also be worked out in general. Denote D as any two-spin correlation function, S as any four-spin correlation function, then (2.18) becomes

$$M^{(0)}=1+D, \tag{2.21a}$$

$$M^{(1)}=2(Z-1)D, \tag{2.21b}$$

$$M^{(2)}=\tfrac{1}{2}(Z-1)+(Z-1)^2D+\tfrac{1}{2}(Z-1)(2Z-3)S, \quad \text{etc.} \tag{2.21c}$$

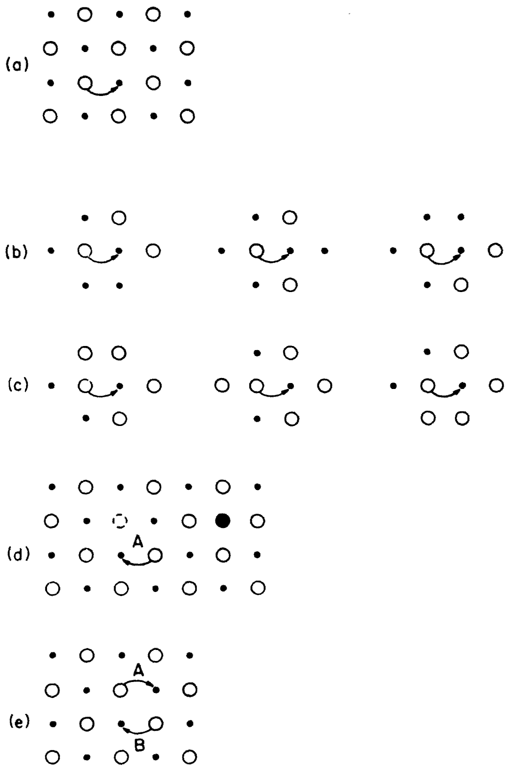

FIG. 1. Some possible hops, and ion arrangements, for the two-dimensional square lattice. (a) At zero temperature, with perfect ordering, the only permitted hops go from zero neighbors to three. (b) The only three neighbor configurations where an ion hops from zero initial neighbors to two final ones. (c) The three configurations where the ion hops from one neighbor configuration to three final ones. (d) A possible defect where an ion leaves its ordered site (dashed circle) and goes to a site with four neighbors (solid circle). Any hop A contributes to P_2. (e) After hop A has occurred, a hop B contributes to P_1.

The sign convention on each spin correlation function is chosen so that it goes to plus one at $T \to 0$. At low temperature, it is easy to show that in two and three dimensions,

$$D = 1 - 4e^{-\beta ZU/2}, \tag{2.22a}$$

$$S = 1 - 8e^{-Z\beta U/2}. \tag{2.22b}$$

This may be derived by assuming a perfectly ordered system, which gives the 1 term, and then possible single spin flips in the evaluation of the trace. Thus we get

$$M^{(0)} = 2 - 4e^{-\beta ZU/2},$$

$$M^{(1)} = 2(Z-1) - 8(Z-1)e^{-\beta ZU/2},$$

$$M^{(2)} = 2(Z-1)^2 - 4(Z-1)(3Z-4)e^{-\beta ZU/2}.$$

When these are inserted into (2.15), there is the solution

$$\lim_{T\to 0}\begin{cases} P_{Z-1} = 2 - 4Ze^{-Z\beta U/2}, \\ P_{Z-2} = 4(Z-1)e^{-Z\beta U/2}. \end{cases} \tag{2.23}$$

All correction terms, and other probabilities, fall off with higher multiples of U in the exponent. However, the next term in the expansion seems more dependent upon the details of the structure, beyond the simple dependence upon the coordination number Z. The one dimensional result is different, and is given in Sec. III.

Next we consider the limit of high temperature, where $T \to \infty$. Here all spin correlations vanish. Thus we obtain from (2.21),

$$\lim_{T\to\infty} M^{(0)} = 1,$$

$$\lim_{T\to\infty} M^{(1)} = 0,$$

$$\lim_{T\to\infty} M^{(2)} = \tfrac{1}{2}(Z-1),$$

$$\lim_{T\to\infty} M^{(3)} = 0,$$

$$\lim_{T\to\infty} M^{(4)} = \tfrac{1}{4}(Z-1)(3Z-4).$$

Inserting this into (2.15) gives the solution

$$\lim_{T\to\infty} P_l = (\tfrac{1}{2})^{2Z-2}\binom{2Z-2}{Z-1+l}.$$

This result is also easy to understand. At very high temperatures there is no order of any kind, and all ion arrangements are equally probable. Thus the determination of how many ion arrangements leads to an energy change of lU is simply a combinatorial problem of how many different arrangements are permitted. For example, consider the probability of an energy change by $2U$ in the two dimensional Ising model for the square lattice $Z=4$. An energy change of $2U$ happens because either an ion hops from having zero neighbors to two, or from one neighbor to three. There are only three combinations of neighbors which permit this in each case, and these six are shown in Figs. 1(b) and 1(c). This is exactly what is given by the combinatorial factor for $Z=4$ and $l=2$,

$$\binom{2Z-2}{Z-1+l} = \binom{6}{5} = 6.$$

The additional factor of $(\frac{1}{2})^6$ enters P_2 because $\frac{1}{2}$ is the probability that an ion does or does not occupy any site, and there are six neighboring ions involved as neighbors. Further aspects of these combinatorial methods applied to lattice gas conductivity are presented in Ref. 5.

III. ONE DIMENSION

The one-dimensional Ising model can be solved exactly, even with a magnetic field. So the lattice gas conductivity may be calculated for any concentration of ions. This general result is a bit complicated, and here we shall only present the simple result for 50% concentration.

Here $Z=2$, so that only two probabilities P_0 and P_1 need to be found from (2.15),

$$P_0 + P_1(1+\eta) = M^{(0)}, \tag{3.1a}$$

$$P_1(1-\eta) = M^{(1)}, \tag{3.1b}$$

where we have introduced the symbol

$$\eta = e^{-\beta U}. \tag{3.2}$$

The moments are determined from (2.18)

$$M^{(0)} = 1 - \langle\sigma_0\sigma_1\rangle, \quad M^{(1)} = \langle\sigma_0\sigma_2\rangle - \langle\sigma_0\sigma_1\rangle.$$

These two spin correlations are well known, and in any case are easily determined from standard transfer matrix methods

$$\langle\sigma_0\sigma_1\rangle = -\tanh(\tfrac{1}{4}\beta U), \quad \langle\sigma_0\sigma_2\rangle = \tanh^2(\tfrac{1}{4}\beta U).$$

Equations (3.1) may be solved to obtain the probabilities P_l. The results are conveniently written by first defining

$$n = 1/(1+e^{+\beta U/2}) = \sqrt{\eta}/(1+\sqrt{\eta}),$$

where n is the probability that the B sites are occupied. At zero temperature every other site is occupied by an ion, and these sites we call the A sites. The empty sites are B. As the temperature is increased, the ions gradually disorder, thereby partially occupying the B sites, and n is this probability.

$$P_1 = 2(1-n)^3,$$

$$P_0 = 4n(1-n)^2,$$

$$P_{-1} = 2n^2(1-n).$$

The conductivity is given by

$$\sigma(\omega)=\frac{N\pi}{2\,\omega}(1-e^{-\beta\omega})\left(\frac{et_0\delta}{\hbar}\right)^2(1-n)$$
$$\times[n^2\delta(\omega+U)+2n(1-n)\delta(\omega)+(1-n)^2\delta(\omega-U)],$$

where $\frac{1}{2}N$ is the number of ions, and the other factors are the conductivity per ion. This one-dimensional model is characterized by the absence of a phase transition, and the absence of long-range correlations.

Pardee and Mahan derived an approximate result using a model which neglected correlations. Their result had the form

$$\sigma(\omega)=\frac{N\pi}{2\,\omega}\left(\frac{et_0\delta}{\hbar}\right)^2(1-e^{-\beta\omega})[n^2+(1-n)^2]$$
$$\times\sum_l P_l(\omega-lU), \tag{3.3a}$$

$$P_l=\binom{2Z-2}{Z-1+l}n^{Z-1-l}(1-n)^{Z-1+l}. \tag{3.3b}$$

This is very similar to the exact one dimensional result, where $Z=2$. The difference is only in the prefactor, where the exact result is $(1-n)$ instead of $n^2+(1-n)^2$.

IV TWO DIMENSIONS

The static spin correlation functions for the two-dimensional Ising model may be solved exactly.[17,18] The Ising model has a phase transition, which corresponds to the order-disorder transition of the lattice gas. This two-dimensional example is the most interesting case for which an exact solution may be obtained for the ionic conductivity. These spin-correlation functions may only be obtained exactly in the case that there is no magnetic field, which corresponds to the lattice gas with half of the sites occupied. We have solved the particular case of the square lattice.

We need to solve four equations from (2.15) [$\eta=\exp(-\beta U)$],

$$\begin{aligned}
&P_0+P_1(1+\eta)+P_2(1+\eta^2)+P_3(1+\eta^3)=M^{(0)},\\
&P_1(1-\eta)+2P_2(1-\eta^2)+3P_3(1-\eta^3)=M^{(1)},\\
&P_1(1+\eta)+4P_2(1+\eta^2)+9P_3(1+\eta^3)=M^{(2)},\\
&P_1(1-\eta)+8P_2(1-\eta^2)+27P_3(1-\eta^3)=M^{(3)}.
\end{aligned} \tag{4.1}$$

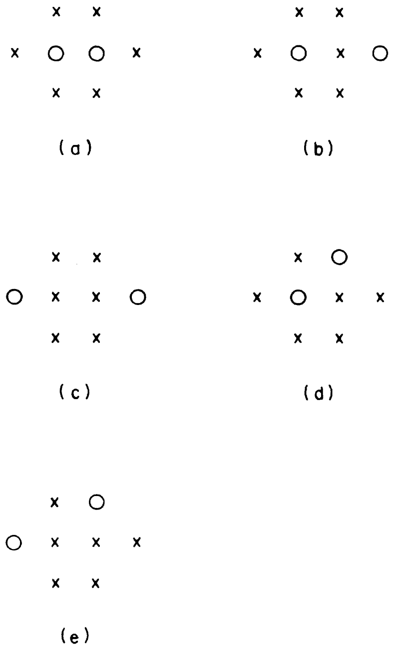

FIG. 2. Two spin-correlation functions which were numerically evaluated. Each circle represents a spin site.

It is straightforward to solve these equations, to obtain the P_l as linear combinations of the $M^{(j)}$. These lengthy results are presented in the Appendix. The $M^{(j)}$ are combinations of two and four spin correlation functions. The five correlations involving two spins are shown in Fig. 2, and the 13 correlations involving four spins are shown in Fig. 3. The two spin functions are denoted D_α, where the subscript $\alpha=a,b,c,d,$ or e corresponds to the spin arrangements of Fig. 2(a). So

$$D_a=-\langle\sigma_{00}\sigma_{01}\rangle,\quad D_b=+\langle\sigma_{00}\sigma_{02}\rangle,$$
$$D_d=\langle\sigma_{00}\sigma_{11}\rangle,\ \text{etc.}$$

Similarly, the four spin functions are denoted S_α, with α corresponding to the arrangements in Fig. 3(a).

$$\begin{aligned}
M^{(0)}&=1+D_a,\\
M^{(1)}&=3D_a+D_b+2D_d,\\
M^{(2)}&=\tfrac{3}{2}+\tfrac{5}{2}D_a+D_b+\tfrac{1}{2}D_c+2D_d+3D_e\\
&\quad+\tfrac{1}{2}S_a+S_b+S_c+3S_d+2S_e,\\
M^{(3)}&=4M^{(1)}+3S_c+\tfrac{3}{2}S_d+3S_e+\tfrac{3}{2}S_f+6S_g\\
&\quad+3S_h+\tfrac{3}{2}S_i+3S_j+3S_k+3S_l+\tfrac{3}{2}S_m.
\end{aligned} \tag{4.2}$$

There remains just the problem of calculating these spin correlation functions for each value of temperature. For this we used the method of Montroll, Potts, and Ward.[17] They give explicit formulas for the two spin functions, and their method is easily extended to four spin functions. These numerical methods are described further in the Appendix.

Figure 4 shows plots of two spin-correlation functions as a function of the dimensionless variable βU. Not all five correlations are presented,

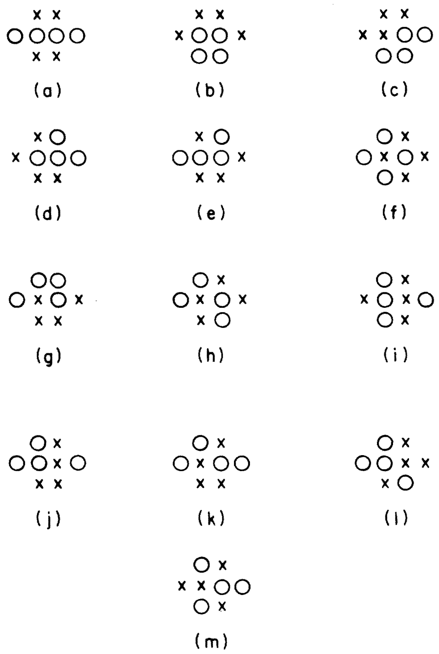

FIG. 3. Four spin-correlation functions which were evaluated. Each circle represents a spin site.

in order to avoid cluttering Fig. 4. The correlations have nearly the same value in the ordered state. The long-range order is sufficiently strong that the separation of the spins is only of secondary importance. This feature has already been noted in (2.22a). In fact, this asymptotic expansion may be carried one step further, with the result

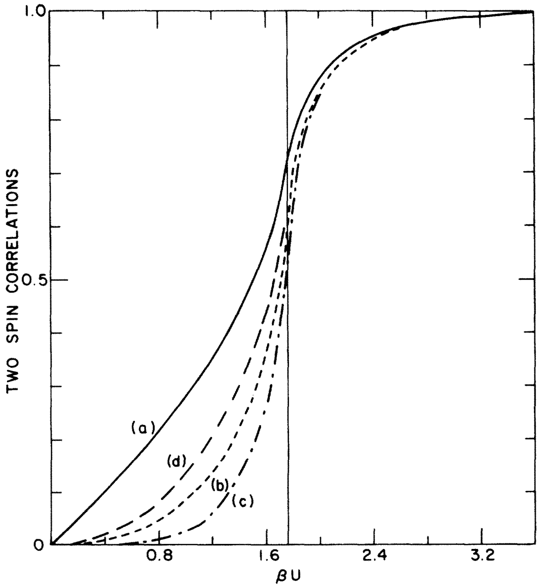

FIG. 4. Temperature dependence of the two spin correlation functions. A curve labeled (a), (b), or (c) corresponds to the spin arrangement in Figs. 2(a), 2(b), or 2(c). The phase transition is at $\beta_c U \simeq 1.76$, with the ordered state to the right.

$$\begin{aligned} &D_\alpha = 1 - 4\eta^2 - 4k\eta^3 + O(\eta^4), \\ &k = 4 - (\text{number of bonds}). \end{aligned} \tag{4.3}$$

A bond is defined as a line joining two spins which are immediate neighbors. Thus D_a has one bond so $k=3$, while the other D_α have no bonds and $k=4$. This asymptotic behavior is also discernible from Fig. 4, where D_a approaches unity at large βU slightly faster than the other lines, which merge into one line as their asymptotic expansions are identical to order $O(\eta^4)$. The vertical line is the transition temperature at

$$\beta_c U = 2\ln(\sqrt{2}+1) \simeq 1.76$$

Above this temperature, each correlation behaves differently.

Several of the four spin-correlation functions are shown in Fig. 5. They also have similar asymptotic values at low temperature. They obey the rule

$$\begin{aligned} &S_\alpha = 1 - 8\eta^2 - 4k'\eta^3 + O(\eta^4), \\ &k' = 8 - (\text{number of bonds}). \end{aligned} \tag{4.4}$$

By counting bonds one can come up with the following values (Table I)

The probabilities P_l are shown in Fig. 6. The values for $l<0$ are not shown, but are easily obtained from (2.10). The curves do have the asymptotic behavior, at both low and high temperature, which was described above.

The asymptotic expansion at low temperature has been carried one step further than the general case in Sec. II. Putting (4.3) and (4.4) into (4.2) gives

$$\begin{aligned} &M^{(0)} = 2 - 4\eta^2 - 12\eta^3 + O(\eta^4), \\ &M^{(1)} = 6 - 24\eta^2 - 84\eta^3 + O(\eta^4), \\ &M^{(2)} = 18 - 96\eta^2 - 280\eta^3 + O(\eta^4), \\ &M^{(3)} = 54 - 336\eta^2 - 1068\eta^3 + O(\eta^4); \end{aligned}$$

and putting these into (4.1) gives

$$\begin{aligned} &P_3 = 2 - 16\eta^2 - 46\eta^3 + O(\eta^4), \\ &P_2 = 12\eta^2 + 28\eta^3 + O(\eta^4), \\ &P_1 = 4\eta^3 + O(\eta^4), \\ &P_0 = O(\eta^4). \end{aligned} \tag{4.5}$$

Thus at low temperature, all of the probabilities have the form

$$P_l = A_l e^{-\beta U \gamma_l}. \tag{4.6}$$

The values of A_l and γ_l are listed in Table II. The prefactor A_0 is not known. Unfortunately it cannot

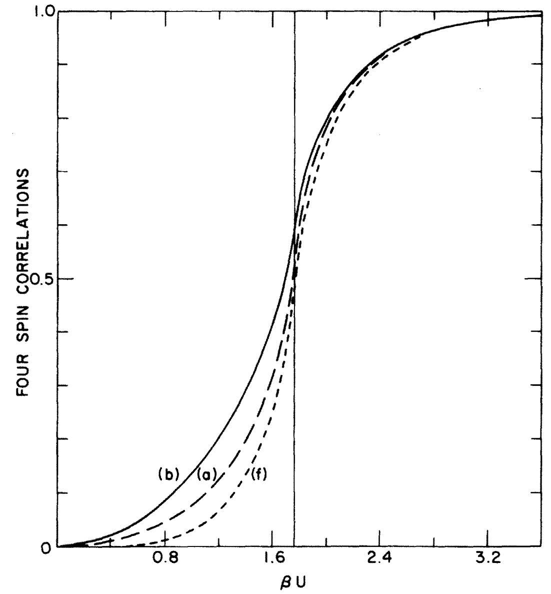

FIG. 5. Temperature dependence of some four spin-correlation functions. A curve labeled (a), (b), or (f) corresponds to the spin arrangement in Figs. 3(a), 3(b), or 3(f). The phase transition is at $\beta_c U \simeq 1.76$, with the ordered state to the right.

even be determined from the numerical results. Observe in (4.1) that the last three equations are solved for P_1, P_2, and P_3, and then P_0 is obtained from

$$P_0 = M^{(0)} - P_1(1+\eta) - P_2(1+\eta^2) - P_3(1+\eta^3). \tag{4.7}$$

At low temperature $\eta \rightarrow 0$, one has that P_3 and $M^{(0)}$ both go to 2, so that P_0, which is exponentially small, is obtained by subtracting two numbers of order 2. Our numerical accuracy was about eight significant figures, which is more than adequate to assure the correctness of Fig. 6. But in the asymptotic region, which we estimate to be $\beta U > 4$, P_0 is already 10^{-7} and dropping fast, so that we do not accurately determine P_0 in the asymptotic region.

These low temperature probabilities may be understood as arising from simple defect structures. We have previously explained P_3 as being due to hops such as shown in Fig. 1(a). The probability P_2 caused by a Frenkel-type defect as shown in Fig. 1(d). An ion has left its ordered site (dotted circle) and sits elsewhere (solid circle). This process requires an energy of $4U$, since the new site (solid circle) has four neighbors. It is well known in defect theory that the equilibrium distribution of these defects is determined by an activation energy which is half of this, or $2U$.[20] This explains why $\gamma_2 = 2$. Any ion hop in the vicinity of the vacancy, such as A in Fig. 1(d), causes an energy change of $2U$, so that this hop contributes to P_2.

Figure 1(e) shows an ion A hopping. Then a subsequent hop B goes from one neighbor to two, and

TABLE I. Values resulting from counting bonds.

k'	
8	S_f
7	S_h, S_k, S_m
6	S_g, S_i, S_j, S_l
5	S_a, S_c, S_d, S_e
4	S_b

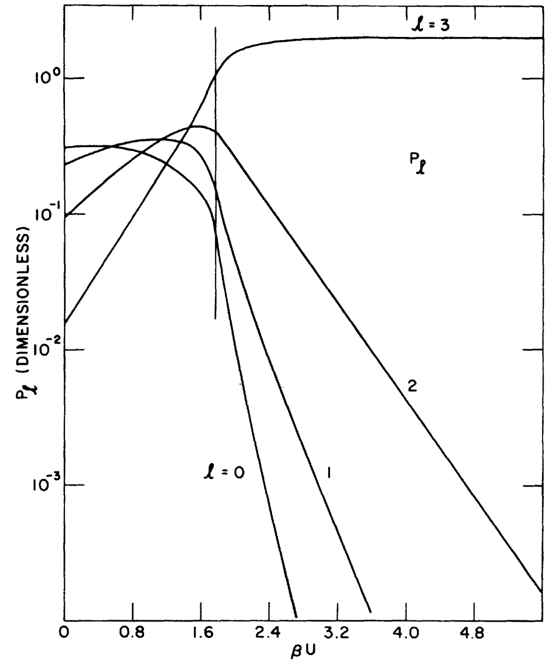

FIG. 6. Temperature dependence of probabilities P_l for the two-dimensional lattice gas.

TABLE II. For the two-dimensional lattice gas, the probabilities P_l at $T \ll T_c$ asymptotically behave as $A_l \exp(-\beta U \gamma_l)$. The values A_l and γ_l are listed. The values γ_l^- are the new values obtained when thermal fluctuations are included.

l	A_l	γ_l	γ_l^-
3	2	0	3
2	12	2	4
1	4	3	4
0	?	4	4
−1	4	4	4
−2	12	4	4
−3	2	3	3

contributes to P_1. The probability of this is the probability that A happened, which gives $\gamma_1 = 3$. Another possible event, in Fig. 1(e), is for A to hop back rather than B to hop. This reversing of A contributes to P_{-3}. The probability of this happening is still the probability that A hopped originally, which gives $\gamma_{-3} = 3$.

Our objective is to calculate the dc conductivity $\sigma(0)$. Our theory gives $\sigma(\omega)$ as a sum of δ functions, and it is not obvious how to deduce the dc limit, i.e., how to take the limit $\omega \to 0$. Our view is that this is proportional to the $l = 0$ probability.

$$\sigma_{\mathrm{dc}} \propto \beta P_0, \tag{4.8}$$

where β is the $\omega \to 0$ limit of the prefactor $(1 - e^{-\beta U})/\omega$. This conclusion is based upon the simple argument that P_0 describes the probability that the ion can hop without changing its configuration energy. This is necessary since the dc electric field provides negligible energy to the hopping ion. In Sec. V we show that the inclusion of polaron coupling makes the conductivity calculation more complicated.[5] The fluctuations in the phonon system provide a source or sink of energy to the hopping ion. The inclusion of this effect yields the result that the dc conductivity now involves a sum over all of the P_l.

V. THERMAL FLUCTUATIONS

The operators n_j and C_j describe whether an ion sits or moves from a site $\vec{R}_j$. While in this site, the ion may oscillate about its equilibrium position. It also may interact with the ions in its vicinity, which may also oscillate. These vibrations are called phonons. They provide a sink or source of energy, which is coupled to the configurational energy of the ions. In fact the ion can undergo a hop which changes its configurational energy by mU, with $m \neq 0$, as long as this energy is either provided or absorbed by the phonon system.

We will assume an Einstein model for the phonon spectrum, with constant frequency ω_0. This is a standard model for optical phonons. Infrared and Raman experiments in solid electrolytes show that the optical phonons have increasing width as the degree of disorder increases.[21-24] This is true in AgI and also the fluorites where a substantial fraction of the ions in the solid are disordering. It is not true in β-alumina, which has only a small fraction (5%) of the ions involved in the disorder.[23-25] We shall try to account for this width by introducing a phenomenological damping.

The model we use to include these phonons is standard. It evolved originally in the theory of conduction by hopping electrons—small polarons. Flynn pointed out the applicability of this model to ionic hopping conduction,[2] and we described it in Ref. 5. For single hop processes of the type being considered here, one just adds to $\Pi(\tau)$ in (2.6) and (2.7) a factor $e^{-\Phi(\tau)}$,

$$\Pi(\tau) = \frac{1}{4d} NZ \left(\frac{e t_0}{\hbar}\right)^2 e^{-\Phi(\tau)} \sum_{l=1-Z}^{Z-1} P_l e^{-l\tau U},$$
$$\Phi(\tau) = \lambda[(N_0+1)(1-e^{-\tau\omega_0}) + N_0(1-e^{\tau\omega_0})], \tag{5.1}$$

where λ is an ion-phonon coupling constant which is derived previously, and $N_0 = [\exp(\beta\omega_0\hbar) - 1]^{-1}$. Using the standard expansion

$$e^{-\Phi(\tau)} = \exp[-\lambda(2N_0+1)] \times \sum_{m=-\infty}^{\infty} I_m(X_0) e^{+\beta(\hbar/2)\omega_0 m} e^{-\tau\omega_0 m},$$
$$X_0 = 2\lambda[N_0(N_0+1)]^{1/2}, \tag{5.2}$$

gives the conductivity

$$\sigma(\omega) = \frac{\pi}{4d} \frac{NZ}{V} \left(\frac{e t_0 \delta}{\hbar}\right)^2 \frac{(1-e^{-\beta\omega})}{\omega} \times \sum_{l=1-Z}^{Z-1} \sum_{m=-\infty}^{\infty} P_l I_m(X_0) \times e^{m\beta\omega_0/2} \delta(\omega - lU - m\omega_0),$$

where I_m are Bessel functions of complex argument.

We will now use the fact that the phonons have a finite width. The summation over the discrete numbers of phonons m, which is really a summation over the discrete phonon energy $m\omega_0$, is replaced by a continuous integration variable $y = m\omega_0$. If f is the argument of the summation

$$\sum_m f(m\omega_0)\delta(\omega - m\omega_0 - lU) \to \frac{1}{\omega_0}\int_{-\infty}^{\infty} dy\, f(y)\delta(\omega - lU - y) = \frac{1}{\omega_0} f(\omega - lU).$$

Thus a discrete envelope of values is replaced by a continuous envelope of the same shape. This smoothing process could also be attributed to the acoustical phonons. For the dc conductivity at $\omega = 0$ we obtain

$$\sigma_{\mathrm{dc}} = \frac{\pi\beta}{4d\omega_0} \frac{NZ}{V} \left(\frac{e t_0 \delta}{\hbar}\right)^2 S,$$
$$S = \exp[-\lambda(2N_0+1)] \sum_{l=1-Z}^{Z=1} P_l I_{|l|U/\omega_0}(X_0) e^{-l\beta U/2}. \tag{5.3}$$

This is similar to the result obtained in Ref. 5.

Figure 7 shows plots S vs βU for $\lambda = 10$. This is not quite proportional to $\sigma_{\mathrm{dc}} T$ since there is addi-

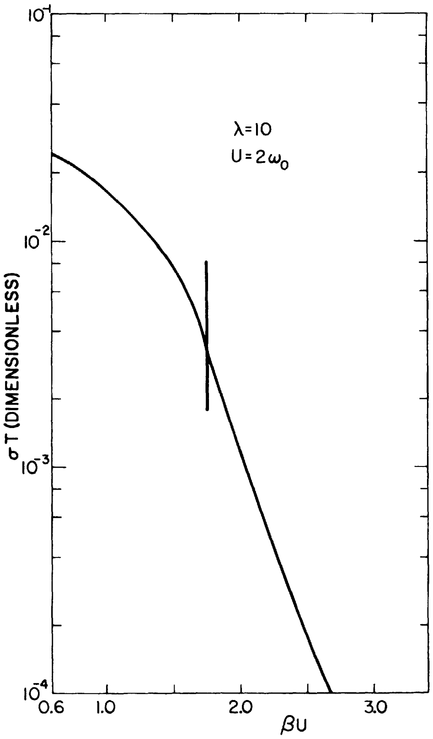

FIG. 7. Plot of the function S in (5.3), which is proportional to $T\sigma_{dc}$. $\lambda = 10$ is the ion-phonon coupling parameter, and $U = 2\omega_0$, where ω_0 is the attempt frequency. The theoretical curve gives a dc conductivity which is thermally activated below the second order phase transition, and not above.

tional temperature dependence in t_0, as mentioned earlier. This latter contribution would just add another linear term to the semilog plot. For this example we have arbitrarily chosen $U = 2\omega_0$.

The quantity S in (5.3) is the lattice gas and phonon contribution to the experimental quantity $\sigma_{dc}T$. Below the order-disorder transition temperature of $\beta_c U = 1.76$ the conductivity appears to be thermally activated. At smaller values of βU the conductivity bends over, and appears to change its activation energy. This is exactly the experimental behavior observed in solid electrolytes such as CdF_2, $RbAg_4I_5$, and $C_5HgNAg_5I_6$ which are believed to have disorder phase transitions of the second type. This behavior was shown in Ref. 5 using mean-field theory, and is now verified by the present calculations, which contain a more rigorous treatment of disordering than Ref. 5.

It is interesting to examine the function S at low temperature. Here N_0 goes to zero, as does X_0. Evaluating the Bessel function for small argument yields

$$S = e^{-\lambda} \sum_{l=1-Z}^{Z-1} P_l \frac{\lambda^l e^{-U(l+|l|)/2}}{\Gamma(1+|l|U/\omega_0)} . \qquad (5.4)$$

Recall from (4.6) that each P appears thermally activated at low temperature. Thus each term in the summation is

$$S = e^{-\lambda} \sum_{l} \frac{A_l \lambda^l}{\Gamma(1+|l|U/\omega_0)} \exp(-\beta U \gamma_l^-) , \qquad (5.5)$$

where the exponential factor is

$$\gamma_l^- = \gamma_l + \tfrac{1}{2}(l + |l|) . \qquad (5.6)$$

They are also shown in Table II.

The factor γ_l^- is quite sensible. For example, consider P_3. It describes the probability of hops whereby the ion changes its configurational energy by $3U$. It requires a phonon energy of $3U$ to do this, and the probability of having such a contribution is $\exp(-3\beta U)$. This is just the additional factor which arises in (5.4) from the phonon contribution. Now P_{-3} describes events whereby the hopping ion gives up $3U$ of energy to the phonon system. This it can do anytime—it does not need a thermal fluctuation for this. This intuitively explains the factor in γ_l^- of

$$\tfrac{1}{2}(l + |l|) = \theta(l) .$$

For $l > 0$ it is necessary to acquire energy from the phonons, which has a probability of $e^{-l\beta U}$, but the hopping ion can always give up energy to the phonons.

The dc ionic conductivity is now given by a summation over all values of l. This is a result of introducing phonons into the theory—or thermal fluctuations. At the very lowest temperatures the conductivity is dominated by the term in (5.4) with the smallest value of γ_l^-. These have $l = \pm 3$. The case $l = 3$ is the event in Fig. 1(a), which is just a simple disordering hop. Thus the ionic conductivity is not dominated by special defects, but by the simplest of disordering jumps. This may be a general feature of all lattices, in two or three dimensions. Combining (2.23) and (5.6),

$$\gamma_{Z-1}^- = (Z-1) , \quad \gamma_{Z-2}^- = \tfrac{3}{2}Z - 2 ,$$

so that $\gamma_{Z-2}^- > \gamma_{Z-1}^-$ for all Z above 2—i.e., for all but one dimension. Another feature of γ_l^- in Table II is that a large number of l values have the same value of γ^-, and therefore contribute nearly equally at low temperature. We guess this to be a peculiar feature of the simple quadratic lattice.

VI. DISCUSSION

Our objective has been to calculate the dc ionic conductivity. This has been done for a lattice gas which has a order-disorder transition at some temperature. Thermal fluctuations were included in the calculation. The results, shown in Fig. 6, predict that the conductivity is continuous through an order-disorder transition. However, the conductivity appears to change its activation energy at the phase transition. These two features are observed in solid electrolytes which do have a second order phase transition of the order-disorder type.

The present calculation only evaluated the conductivity from events where the ion made a single hop. That is, each hop is statistically independent from any other. The next logical step is to consider double hop events, wherein two subsequent hops are correlated. We have spent very much time doing this, and so far have extracted very little physics. There are two difficulties. First, there are many different kinds of ion arrangements and combinations for two jumps, so many terms are involved. Second, the thermal fluctuations are far more complicated. For example, because the phonons can cause two ions to interact at a distance, two ion hops may be correlated even when they are spatially far apart. It is even hard to evaluate two successive jumps of the same ion. This is still being investigated.

Our final result is the conductivity as a function of frequency. Although our interest was to apply this to dc conductivity, one might consider its application to ac measurements. Many recent results have been reported on the infrared and Raman response of superionic conductors.[21-24] To calculate the frequency-dependent conductivity for infrared, two contributions are needed. The one we evaluated was the contribution from hopping from site to site. There is also the term where an ion just oscillates at one site. For a simple damped oscillator this is

$$\sigma = \frac{1}{2}\frac{N}{V}e^2\frac{\omega\Gamma}{(\omega^2-\omega_0^2)^2+\omega^2\Gamma^2}\,. \tag{6.1}$$

A comparison of (6.1) with the hopping result (5.2) shows that (6.1) is much larger in magnitude in the infrared. Thus the hopping contribution may be neglected in this region. Thus our theory is really only of interest for dc. We also note that several more sophisticated theories of infrared conductivity have been recently published.[24-26] Our reason for presenting the simple result (6.1) was to establish the magnitude of the onsite contribution.

The exact results presented here show up several errors in the mean-field theory of Ref. 5. Mean-field theory predicts that the conductivity is continuous at the phase transition, but that the slope is discontinuous—there is a kink in the curve. This does not happen in the present case. This is probably because short-range order was neglected in the mean-field theory, while it is retained in the exact theory. Short-range order is important for determining the actual configuration in the vicinity of a hopping ion, and hence the real values of P_l. Short-range order does not abruptly vanish at the phase transition, but dies out slowly with increasing temperature. Experimental curves do not display any kinks.

Mean-field theory also did not give the correct value for the activation energy in the low-temperature regime. Pardee and Mahan found for $T \ll T_c$,

$$\gamma_l = \tfrac{1}{2}Z(Z-1-l)\,, \quad A_l = \begin{pmatrix} 2Z-Z \\ Z-1+l \end{pmatrix}.$$

If we set $Z=4$ and compare this with the exact results of Table II, it predicts some of the exponents correctly and some incorrectly. Again, the error appears to be in the neglect of short-range order. Attempts are underway to see whether mean-field theory can be improved to produce the correct results.

APPENDIX

The spin-correlation functions for the two-dimensional Ising model were obtained using the results of Montroll, Potts, and Ward,[17] which are similar to those obtained by Green and Hurst.[18] A two-spin-correlation function

$$\langle \sigma_{0,0}\sigma_{m,l}\rangle = (1-Z^2)^{m+l}P_{m+l}(\overleftrightarrow{\mathrm{y}}^{-1}+\overleftrightarrow{\mathrm{Q}})\,,$$
$$Z=\tanh(\tfrac{1}{4}\beta U)$$

is evaluated as a Pfaffian $P_{l+m}(\overleftrightarrow{\mathrm{y}}^{-1}+\overleftrightarrow{\mathrm{Q}})$. If a matrix is antisymmetric, with zero elements on the diagonal, its determinant is a perfect square. For example,

$$\det\begin{vmatrix} 0 & a_{12} & a_{13} & a_{14} \\ -a_{12} & 0 & a_{23} & a_{24} \\ -a_{13} & -a_{23} & 0 & a_{34} \\ -a_{14} & -a_{24} & -a_{34} & 0 \end{vmatrix} = (a_{12}a_{34}-a_{13}a_{24}+a_{14}a_{23})^2.$$

The Pfaffian is the square root of the determinant. The second-order Pfaffian for the above is

$$P_2(\overleftrightarrow{\mathrm{a}}) = a_{12}a_{34}-a_{13}a_{24}+a_{14}a_{23}\,.$$

We define the order $n=m+l$ of the Pfaffian as one-half the dimensionality of the equivalent determinent.

The elements $\overleftrightarrow{\mathrm{y}}^{-1}$ and $\overleftrightarrow{\mathrm{Q}}$ are both antisymmetric matrices, which are determined as follows. The two spins are connected by a continuous series of bonds. An example is shown in Fig. 8(a) for the correlation function $\langle\sigma_{00}\sigma_{12}\rangle$. The circles represent the spins which are to be correlated, and the x's are the intervening spins. Each circle can only be connected by one or three bonds, while each × by two or four bonds. Each bond can leave a spin in one of four directions: right, left, up, or down, denoted R, L, U, D. The degree of the Pfaffian equals the number of bonds. Each bond has two ends, and these are each labeled with the spin location (α, β) and the direction it leaves that spin: R, L, U, D. These $2n$ bond ends label the rows and columns of the matrix $\overleftrightarrow{Q}$. They may be arranged in any order, with the proviso that the sign of the correlation function be chosen such that at zero temperature the up spins give +1 and the down spins −1. Our example in Fig. 8(a) gives

$$\overleftrightarrow{Q}=\left|\begin{array}{cccccc|c} R(0,0) & L(0,1) & U(0,1) & D(1,1) & R(1,1) & L(1,2) & \\ 0 & [0,1]_{RL} & [0,1]_{RU} & [1,1]_{RD} & [1,1]_{RR} & [1,2]_{RL} & R(0,0) \\ & 0 & [0,0]_{LU} & [1,0]_{DL} & [1,0]_{LR} & [1,1]_{LL} & L(0,1) \\ & & 0 & [1,0]_{UD} & [1,0]_{UR} & [1,1]_{UL} & U(0,1) \\ & & & 0 & [0,0]_{DR} & [0,1]_{DL} & D(1,1) \\ & & & & 0 & [0,1]_{RL} & R(1,1) \\ & & & & & 0 & L(1,2) \end{array}\right. ,$$

where only the upper diagonal values are shown. The elements of Q are obtained by subtracting the columns coordinates from those of the rows. Thus the element $[\alpha-\alpha', \beta-\beta']_{XY}$ comes from row $X[\alpha', \beta']$ and column $Y[\alpha, \beta]$. The evaluation of the quantities $[\alpha-\alpha', \beta-\beta']_{XY}$ is described in Ref. 17. They are given as explicit linear combinations of quantities called $F_{n,m}$, which in turn are explicit combinations of elliptic integrals.

The matrix $\overleftrightarrow{y}^{-1}$ has mostly zeros for elements. Its nonzero elements are obtained by inspecting the matrix $\overleftrightarrow{Q}$ and locating all its elements which are either $\pm[0,1]_{RL}$ or else $\pm[1,0]_{UD}$. In each of these elements $\overleftrightarrow{y}^{-1}$ has the value $\mp(Z^{-1}-Z)^{-1}$.

There is often more than one way to connect up the intervening bonds. For example, Fig. 8(b) shows an alternative to Fig. 8(a). Both give the same numerical result although the elements in the two Pfaffians are mostly different. We checked for numerical mistakes by evaluating many of these correlations by two different bond arrangements.

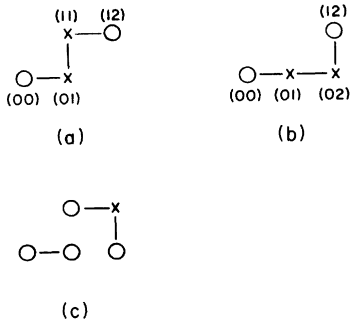

FIG. 8. Some bond arrangements in evaluating spin-correlation functions.

The four spin-correlation functions are evaluated according to the same rules. One draws in as few bonds as possible, such that each correlated spin is connected with one or three bonds, and each intervening spin by two or four bonds. In Figs. 3(a)–3(c) this can be accomplished with only two bonds. In Fig. 3(d) it takes three bonds, as shown in Fig. 8(c). The correlation function is given by

$$\langle\sigma\sigma\sigma\sigma\rangle=(1-Z^2)^n P_n(\overleftrightarrow{y}^{-1}+\overleftrightarrow{Q}),$$

where n is the number of bonds. The antisymmetric matrices $\overleftrightarrow{y}^{-1}$ and $\overleftrightarrow{Q}$ are constructed as before.

The other result we present in this Appendix is the solution to (4.1),

$$P_1=\tfrac{1}{2}(1-\eta)^{-5}[6M^{(1)}(1+\eta+6\eta^2+\eta^3+\eta^4) - 5M^{(2)}(1-\eta^3)(1+\eta) + M^{(3)}(1-\eta)^2(1+3\eta+\eta^2)],$$

$$P_2=\tfrac{1}{2}(1-\eta)^{-5}[-3M^{(1)}(1+\eta)^3+4M^{(2)}(1-\eta^3) - M^{(3)}(1+\eta)(1-\eta)^2],$$

$$P_3=\tfrac{1}{2}(1-\eta)^{-5}[2M^{(1)}(1+4\eta+\eta^2)-3M^{(2)}(1-\eta^2) + M^{(3)}(1-\eta)^2].$$

These results may be used to obtain P_0 from (4.7).

*Research Supported by the NSF.

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