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Hopping conduction and superionic conductors

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The frequency dependence of the conductivity of superionic conductors is investigated from a classical-hopping-model point of view. It is shown both formally and through an example that any hopping model must yield a conductivity which increases monotonically with frequency up to frequencies comparable with phonon frequencies. This result is generally consistent with experimental data on β-alumina, but is inconsistent with data on AgI.

I. INTRODUCTION

The anomalously large dc conductivity observed in superionic conductors[1,2] is often interpreted in terms of a random hopping of mobile ions from site to site. Although this hopping model is reasonable for ordinary diffusion in solids, the conductivity in some superionic conductors is so great that its applicability can reasonably be questioned.[3,4] In particular, it is not clear that a hopping model can explain the frequency-dependent conductivity of superionic conductors, and some alternatives to hopping have been proposed to explain the observed microwave conductivity of AgI and β-alumina.[5-11]

A hopping model characterizes the mobile ions as moving quickly from one metastable equilibrium position in the lattice to another. In order to make good sense, the average time between hops τ should be considerably larger than the actual hopping time τ_0. An argument by Rickert[3] suggests that in some superionic conductors the hopping model may be inappropriate because estimates of τ and τ_0 yield similar numbers. In silver iodide at 150 °C, for example, a mobile silver ion with an average thermal velocity will take $\tau_0 \approx 7\times10^{-13}$ sec to travel half a lattice constant. However, the random-hopping model requires that τ be only 5×10^{-12} to 6×10^{-12} sec to explain the observed conductivity of AgI [$\sim 1.3\,(\Omega\,\mathrm{cm})^{-1}$ at 150 °C]. If one considers AgI at a higher temperature, or postulates a shorter-hopping distance, the difference between τ and τ_0 becomes even smaller. A similar calculation for β-alumina at 150 °C yields a somewhat larger ratio for τ/τ_0. These time scale estimates emphasize the point that the hopping model is an idealization. Whether or not it is an appropriate model of a superionic conductor may depend on the material and temperature range being considered.

When $\tau \gg \tau_0$, the ionic motion can be considered to consist of vibrations about local equilibria with occasional hopping from one equilibrium configuration to another. If one probes such a solid with electromagnetic radiation with frequency ω, the response seen when $\omega\tau_0 \approx 1$ should reflect primarily the vibration spectrum of the ionic motion. However, when $\omega\tau \approx 1$ and $\omega\tau_0 \ll 1$, the radiation probes the correlations among the hops. In this low-frequency range which might typically correspond to microwave frequencies, the vibrational motion of the ions contributes only a positive frequency-independent term to the dielectric constant of the material.

A familiar simple example of hopping is single-ion hopping in which a mobile ion in the superionic conductor moves from one site to another, but the rest of the crystal remains essentially unchanged. For an ideal lattice, with independent mobile ions, the dc conductivity can be written in terms of the residence time τ as

$$\sigma = \beta\rho(Ze)^2 a^2/6\tau\,, \tag{1}$$

where β is the inverse of the temperature times Boltzmann's constant, ρ and Ze are the mobile ion density and charge, a is a hopping distance, and the system is assumed to be cubic. For $\omega\tau_0 \ll 1$, the conductivity is essentially frequency independent for this simple model.

In real solids, the single-ion hopping picture may be too simplified. Interactions between the ions, imperfections in the lattice, hopping involving the motion of larger numbers of mobile ions, and the response of the immobile lattice to the mobile-ion hopping can all significantly change the dc conductivity from the simple expression given in Eq. (1). Furthermore, because these effects can introduce correlations between subsequent hops, it is no longer true that the hopping model predicts a frequency-independent conductivity. Intuitively, one can argue that if an ion hops from A to B, one might expect the ion to be "bounced back" to site A fairly often when interactions and imperfections are present. This "bounce-back" effect would tend to reduce the dc conductivity relative to the ac conductivity. Alternatively, one can argue that when one ion hops it will tend to push other ions in the same direction in subsequent hops. This "caterpillar mechanism"[12] would enhance the dc conductivity relative to the ac conductivity. The primary result presented in this paper is a proof that under quite general conditions, the "bounce-back" mechanism is dominant so that the conductivity is an increasing function of frequency. The proof of this result, which is presented in Secs. II and III, is essentially a generalization of work by Kawasaki[13] on the time-dependent Ising model. The general formalism is applied to a simple soluble hopping model in Sec. IV. Some of these results are similar to conclusions obtained by Dieterich, Peschel, and Schneider[14] and by Richards.[15] Discussion and a comparison of the results with experiments will be presented in Sec. III.

II. CLASSICAL HOPPING

It is assumed that a superionic conductor possesses metastable equilibrium configurations, and that ionic motion consists of oscillations about these local-energy minima with occasional hopping from one configuration to another. The hopping can be a generalized motion of many particles of the type described by Vineyard.[16]

The configurations, labeled $|\alpha\rangle$, can be taken to be the orthonormal basis of a real vector space, so

$$\langle\alpha|\beta\rangle=\delta_{\alpha,\beta}\,. \tag{2}$$

A state of the system is defined to be an ensemble of configurations with non-negative probabilities P_α such that

$$\sum_\alpha P_\alpha=1\,. \tag{3}$$

The state, which lies in the vector space defined by the configurations, can be denoted as

$$|P\rangle=\sum_\alpha P_\alpha|\alpha\rangle\,. \tag{4}$$

It is assumed that essentially all initial states of the system naturally evolve in time to an equilibrium state denoted by

$$|\phi^2\rangle=\sum_\alpha\phi_\alpha^2|\alpha\rangle\,, \tag{5}$$

where $\phi_\alpha^2=P_\alpha^{(0)}$ is probability of finding the configuration $|\alpha\rangle$ in equilibrium.

States evolve in time by the hopping of ions or groups of ions. The hopping rate $\Gamma_{\gamma\alpha}$ from a configuration $|\alpha\rangle$ to $|\gamma\rangle$ is assumed to depend only on the configurations and temperature. The actual time it takes to make a hop, τ_0, must be small compared to $\Gamma_{\gamma\alpha}^{-1}\approx\tau$ if the hopping model is to be valid. When the hopping has these properties, the time dependence of the P's is determined by the following master equation:

$$\frac{dP_\alpha}{dt}=\sum_\gamma(\Gamma_{\alpha\gamma}P_\gamma-\Gamma_{\gamma\alpha}P_\alpha)\,, \tag{6}$$

where the first term on the right corresponds to hopping into the configuration $|\alpha\rangle$ and the second term corresponds to hops out of the $|\alpha\rangle$ configuration.

A formal simplification can be achieved by defining the real symmetric matrix $T_{\alpha\gamma}$ to be

$$T_{\alpha\gamma}=-(\Gamma_{\alpha\gamma}\Gamma_{\gamma\alpha})^{1/2}\quad(\alpha\neq\gamma)\,,$$

and

$$T_{\alpha\alpha}=\sum_{\gamma\neq\alpha}\Gamma_{\gamma\alpha}\,. \tag{7}$$

Then the master equation can be written

$$\frac{dP_\alpha}{dt}=-\sum_\gamma T_{\alpha\gamma}\left(\frac{\Gamma_{\alpha\gamma}}{\Gamma_{\gamma\alpha}}\right)^{1/2}P_\gamma\,. \tag{8}$$

Physically, the net rate of hopping from the configuration $|\gamma\rangle$ to the configuration $|\alpha\rangle$ must be zero in the equilibrium state. Hence

$$\Gamma_{\alpha\gamma}\phi_\gamma^2-\Gamma_{\gamma\alpha}\phi_\alpha^2=0\,, \tag{9}$$

and

$$\left(\frac{\Gamma_{\alpha\gamma}}{\Gamma_{\gamma\alpha}}\right)^{1/2}=\frac{\phi_\alpha}{\phi_\gamma}\,, \tag{10}$$

with the ϕ's picked to be positive. This means the master equation can be written

$$\frac{dP_\alpha}{dt}=\sum_\gamma\phi_\alpha T_{\alpha\gamma}\phi_\gamma^{-1}P_\gamma\,. \tag{11}$$

Defining the operators T and ϕ by

$$\langle\alpha|T|\gamma\rangle=T_{\alpha\gamma}\,, \tag{12}$$

$$\langle\alpha|\phi|\gamma\rangle=\delta_{\alpha,\gamma}\phi_\alpha\,, \tag{13}$$

allows one to rewrite the master equation as

$$\frac{d|P\rangle}{dt}=-\phi T\phi^{-1}|P\rangle\,. \tag{14}$$

Left multiplication of Eq. (14) by $\langle\alpha|$ yields Eq. (11). Integration of Eq. (14) gives a time evolution operator

$$U(t)=\phi e^{-tT}\phi^{-1}\,. \tag{15}$$

Note that since $|\phi^2\rangle$ is independent of time

$$T\phi^{-1}|\phi^2\rangle=T|\phi\rangle=0\,, \tag{16}$$

where

$$|\phi\rangle=\sum_\alpha\phi_\alpha|\alpha\rangle\,. \tag{17}$$

Since states decay in time to the equilibrium state, T cannot have negative eigenvalues, and $|\phi\rangle$ is a normalized "ground state" of T with eigenvalue zero. The ground state $|\phi\rangle$ is unique if there is only one equilibrium state of the system. It is convenient to think of $|\phi\rangle$ as a pseudoquantum state. For example, the probability of finding a configuration $|\alpha\rangle$ in equilibrium is

$$P_\alpha^{(0)} = |\langle\phi|\alpha\rangle|^2 . \tag{18}$$

III. CONDUCTIVITY

The longitudinal conductivity $\sigma(q,\omega)$ is the ratio of the electric current to a small applied electric field. For simplicity the conductivity tensor is taken to be a scalar. The externally applied infinitesimal field is taken to be in the $\hat{x}$ direction and

$$\vec{E} = E_0 \hat{x} \cos(\vec{q}\cdot\vec{x}) e^{-i\omega t} . \tag{19}$$

All of the resulting current will not, in general, be proportional to $\cos(\vec{q}\cdot\vec{x})$ because the superionic conductor may not be perfectly homogeneous. If the amplitude of the Fourier component of the current proportional to $\cos(\vec{q}\cdot\vec{x})e^{-i\omega t}$ along $\hat{x}$ is $J_q(\omega)$, the conductivity is defined to be

$$\sigma(q,\omega) \equiv J_q(\omega)/E_0 . \tag{20}$$

This conductivity is defined even for imperfect crystals and amorphous systems.

The hopping model is classical, so the conductivity is given by the classical Kubo formula[17]

$$\sigma(q,\omega) = \frac{\beta}{\Omega T_0}\int_0^{T_0} dt_0 \int_{t_0}^{\infty} dt e^{i\omega(t-t_0)} \times J_q(t) J_q(t_0) , \tag{21}$$

where Ω is the volume, and the integral over the "initial time" t_0 is a simple way to obtain a thermodynamic average. The averaging time T_0 can be made arbitrarily large. Because the applied field is proportional to $\cos(\vec{q}\cdot\vec{x})$, the quantity $J_q(t)$ is the cosine transform of the current density at time t. The current $J_q(t)$ is related to the sine transform of the charge density $\rho_q(t)$ by

$$J_q(t) = \frac{1}{q}\frac{d}{dt}\rho_q(t) , \tag{22}$$

and

$$\rho_q(t) = \sum_i \sqrt{2}\, Z_i e \sin[qX_i(t)] . \tag{23}$$

Here $Z_i e$ and $X_i(t)$ are the charge and position (along $\hat{x}$) of the ith ion and the sum over i includes both mobile and immobile ions.

The charge density $\rho_q(t)$ varies with time only during the short periods during which the system hops from one configuration to another. When the system is in a configuration $|\alpha\rangle$, the charge density is denoted $\rho_{q\alpha}$. The operator ρ_q, defined by

$$\langle\alpha|\rho_q|\gamma\rangle = \rho_{q\alpha}\delta_{\alpha\gamma} , \tag{24}$$

will be used later.

Because the currents $J_q(t)$ in an idealized hopping model are nonzero only during the short hopping intervals, the conductivity can be written as a sum of simpler integrals in which t and t_0 are confined to the periods of a single hop. These terms are conveniently classified as "single-hop" terms if the time intervals for t and t_0 are the same, and "double-hop" terms if t and t_0 are integrated over the periods of two distinct hops. The conductivity can then be written as the sum of single-hop and double-hop terms

$$\sigma(q,\omega) = \sigma_1 + \sigma_2 . \tag{25}$$

Let the short time interval $t_j \le t \le t_j + \tau_0$ encompass the period of the jth hop. Then

$$\sigma_1 = \frac{\beta}{\Omega T_0}\sum_j \int_{t_j}^{t_j+\tau_0} dt_0 \int_{t_0}^{t_j+\tau_0} dt\, J_q(t) J_q(t_0) , \tag{26}$$

and

$$\sigma_2 = \frac{\beta}{\Omega T_0}\sum_j \sum_{k>j} e^{i\omega(t_k-t_j)} \times \int_{t_j}^{t_j+\tau_0} dt_0 \int_{t_k}^{t_k+\tau_0} dt\, J_q(t) J_q(t_0) , \tag{27}$$

where we have approximated terms like $e^{i\omega\tau_0}$ by 1. The single-hop conductivity σ_1 would be an exact expression for the conductivity if there were no correlations between hops. The double-hop conductivity describes the correlation corrections to the conductivity which might be produced by the "bounce-back" or "caterpillar" mechanisms mentioned in Sec. I. It is important to recognize that correlations discussed here differ from the Bardeen-Herring correlations which are important in isotope diffusion.[18,19]

In a formal sense, Eqs. (26) and (27) are exact only in the limit that the hopping time τ_0 is infinitesimal. When $\tau_0 \ne 0$ there is the possibility that hop number $j+1$ may start before hop number j has finished. Since the total hopping rate is proportional to the volume, one can find an Ω large enough so that the system is essentially always hopping. Physically, we know that the large-volume limit should not cause trouble because hops which take place at widely separated regions in the sample will not significantly affect each other.

If one wishes to formally show that no problems occur in the $\tau_0 \neq 0$ and large Ω limit, one can proceed as follows: (i) hops are still labeled by a sequential index j but hop j may not be finished before hop $j+1$ is initiated; (ii) the conductivity $J_q(t)$ is replaced by $J_{qj}(t)$, where $J_{qj}(t)$ is the total current produced only by the jth hop; (iii) the expression for the single-hop conductivity remains valid provided that in the integration over the jth time interval in Eq. (26), $J_q(t) \rightarrow J_{qj}(t)$ and $J_q(t_0) \rightarrow J_{qj}(t_0)$. This modified expression for the single-hop conductivity is unchanged if one lets $\tau_0 \rightarrow 0$, and this justifies assuming that τ_0 is infinitesimal for the single-hop conductivity; (iv) the double-hop conductivity is similarly modified in that $J_q(t) \rightarrow J_{qk}(t)$ and $J_q(t_0) \rightarrow J_{qj}(t_0)$. Furthermore one must add the restriction to the integrals in Eq. (27) that $t \geq t_0$. This last restriction is not independent of τ_0. However, if the hopping rate for individual ions is small compared to $1/\tau_0$, then the nearly simultaneous hops are likely to be separated by such large distances that they will have negligible contributions to the double-hop conductivity. Thus the assumption made earlier that the residence time τ is much greater than the hopping time τ_0 is sufficient to justify treating τ_0 as an infinitesimal.

The expressions for the single-hop and double-hop conductivities can be simplified and written compactly in the pseudoquantum formalism. The simplification is somewhat tedious. Anyone interested only in the final result can skip to Eq. (45).

The symmetry associated with the interchange of t and t_0 means that

$$\int_{t_j}^{t_j+\tau_0} dt_0 \int_{t_0}^{t_j+\tau_0} dt\, J_q(t) J_q(t_0) = \frac{1}{2}\left(\int_{t_j}^{t_j+\tau_0} dt\, J_q(t)\right)^2 . \tag{28}$$

Because $qJ_q(t)$ is the derivative of $\rho_q(t)$ [Eq. (22)],

$$\sigma_1 = \frac{\beta}{2\Omega T_0 q^2} \sum_j [\rho_q(t_j+\tau_0) - \rho_q(t_j)]^2 . \tag{29}$$

Similarly,

$$\sigma_2 = \frac{\beta}{\Omega T_0 q^2} \sum_j \sum_{k>j} e^{i\omega(t_k - t_j)} [\rho_q(t_k+\tau_0) - \rho_q(t_k)] \times [\rho_q(t_j+\tau_0) - \rho_q(t_j)] . \tag{30}$$

If the averaging time T_0 is made sufficiently large, the sum over individual hops can be replaced by a sum over the initial and final configurations of the hops multiplied by the average number of times each type of hop occurs. For example, the average number of hops from configuration $|\alpha\rangle$ to configuration $|\gamma\rangle$ which occur in T_0 is

$$n_{\gamma\alpha} = T_0 \Gamma_{\gamma\alpha} P_\alpha^{(0)} . \tag{31}$$

This means

$$\sigma_1 = \frac{\beta}{2\Omega q^2} \sum_{\alpha\gamma} (\rho_{q\gamma} - \rho_{q\alpha})^2 \Gamma_{\gamma\alpha} P_\alpha^{(0)} . \tag{32}$$

The double-hop conductivity can be similarly calculated. After the first hop from $|\alpha\rangle$ to $|\gamma\rangle$, the probability that the system evolves to configuration $|\delta\rangle$ after a time t is $\langle\delta|U(t)|\gamma\rangle$. The time evolution operator $U(t)$ was defined in Eq. (15). Finally the hopping rate from $|\delta\rangle$ to $|\epsilon\rangle$ is $\Gamma_{\epsilon\delta}$. Thus

$$\sigma_2 = \frac{\beta}{\Omega q^2} \sum_{\substack{\alpha\gamma \\ \delta\epsilon}} (\rho_{q\epsilon} - \rho_{q\delta}) \Gamma_{\epsilon\delta} \int_0^\infty \langle\delta|U(t)|\gamma\rangle e^{i\omega t} dt \times (\rho_{q\gamma} - \rho_{q\alpha}) \Gamma_{\gamma\alpha} P_\alpha^{(0)} . \tag{33}$$

In equilibrium, $dP_\alpha^{(0)}/dt = 0$, so the master equation [Eq. (6)] becomes

$$\sum_\alpha \Gamma_{\gamma\alpha} P_\alpha^{(0)} = \sum_\alpha \Gamma_{\alpha\gamma} P_\alpha^{(0)} . \tag{34}$$

Using this relation,

$$\sum_{\alpha\gamma} \rho_{q\gamma}^2 \Gamma_{\gamma\alpha} P_\alpha^{(0)} = \sum_{\alpha\gamma} \rho_{q\gamma}^2 \Gamma_{\alpha\gamma} P_\gamma^{(0)} = \sum_{\alpha\gamma} \rho_{q\alpha}^2 \Gamma_{\gamma\alpha} P_\alpha^{(0)} , \tag{35}$$

and the single-hop conductivity can be written as

$$\sigma_1 = \frac{\beta}{\Omega q^2} \sum_{\gamma\alpha} (\rho_{q\alpha}^2 - \rho_{q\alpha}\rho_{q\gamma}) \Gamma_{\gamma\alpha} P_\alpha^{(0)} . \tag{36}$$

This can be written in the pseudoquantum formalism as

$$\sigma_1 = (\beta/\Omega q^2) \langle\phi|\rho_q T \rho_q|\phi\rangle . \tag{37}$$

The equivalence of Eqs. (36) and (37) can be shown by expanding the latter expression in terms of the complete set of configurations $|\alpha\rangle$. Because ρ_q is a diagonal operator [Eq. (24)], Eq. (37) becomes

$$\sigma_1 = \frac{\beta}{\Omega q^2} \sum_{\alpha\gamma} \langle\phi|\alpha\rangle \rho_\alpha T_{\alpha\gamma} \rho_\gamma \langle\gamma|\phi\rangle . \tag{38}$$

The validity of the pseudoquantum expression can then be shown from Eq. (18), the definition of $T_{\alpha\gamma}$ [Eq. (7)], and the relation

$$(\Gamma_{\alpha\gamma}\Gamma_{\gamma\alpha})^{1/2} \langle\gamma|\phi\rangle = \langle\alpha|\phi\rangle \Gamma_{\gamma\alpha} ,$$

which follows from Eq. (10).

The double-hop conductivity can be simplified. If [,] denotes a commutator, the relations

$$P_\alpha^{(0)} = |\langle\phi|\alpha\rangle|^2 , \tag{39}$$

$$\Gamma_{\gamma\alpha}(\rho_{q\gamma} - \rho_{q\alpha}) = \frac{1}{\langle\phi|\gamma\rangle} \langle\gamma|[\rho_q, T]|\alpha\rangle\langle\alpha|\phi\rangle , \tag{40}$$

$$\langle \delta | U(t) | \gamma \rangle = \frac{1}{\langle \phi | \delta \rangle} \langle \delta | e^{-tT} | \gamma \rangle \langle \phi | \gamma \rangle \ , \tag{41}$$

$$\Gamma_{\epsilon\gamma}(\rho_{q\epsilon} - \rho_{q\delta}) = \frac{1}{\langle \phi | \epsilon \rangle} \langle \epsilon | [\rho_q, T] | \delta \rangle \langle \phi | \delta \rangle \ , \tag{42}$$

follow from Eqs. (18), (7), (24), (10), and (15). Taking the product of Eqs. (39)–(42) and comparing with Eq. (33) yields

$$\sigma_2 = \frac{\beta}{\Omega q^2} \int_0^\infty e^{i\omega t} \langle \phi | [\rho_q, T] e^{-tT} [\rho_q, T] | \phi \rangle \, dt. \tag{43}$$

Finally, σ_2 is obtained by performing the time integrations and using Eq. (16) to simplify the commutators.

$$\sigma_2 = (-\beta/\Omega q^2) \langle \phi | \rho_q [T^2/(T - i\omega)] \rho_q | \phi \rangle \ . \tag{44}$$

The basic formal result is obtained by adding σ_1 and σ_2 to get the total conductivity.

$$\sigma(q, \omega) = (\beta/\Omega q^2) \langle \phi | \rho_q [T - T^2/(T - i\omega)] \rho_q | \phi \rangle \ . \tag{45}$$

Note that this implies that the real part of the conductivity is an increasing function of frequency for $\omega > 0$ because T is a positive operator and

$$\frac{d}{d(\omega^2)} \mathrm{Re}[\sigma(q, \omega)] = \langle \phi | \rho_q [T^3/(T^2 + \omega^2)^2] \rho_q | \phi \rangle \ , \tag{46}$$

which is clearly non-negative.

Practically speaking, the $q \to 0$ limit of the conductivity $[=\sigma(\omega)]$ is particularly important because in the microwave frequency range q is essentially zero. In this limit, and for systems with reflection symmetry across the $x = 0$ plane, an alternative to Eq. (44) is often easier to use. The reflection symmetry means that if $\rho_{q\alpha}$ is redefined as

$$\rho_{q\alpha} = \sum_i \exp(iqX_{i\alpha}) eZ_i \ , \tag{47}$$

the resulting conductivity is an average of conductivities for electric fields which are even and odd with respect to the reflection symmetry. Define the operator J by

$$J = \lim_{q \to 0} \frac{[\rho_q, T]}{q} \ . \tag{48}$$

Then

$$\langle \gamma | J | \alpha \rangle = i(\Gamma_{\gamma\alpha} \Gamma_{\alpha\gamma})^{1/2} \sum_i eZ_i (\Delta X_i)_{\gamma\alpha} \ , \tag{49}$$

where $(\Delta X_i)_{\gamma\alpha}$ is the distance moved by the ith ion in the hop from $|\alpha\rangle$ to $|\gamma\rangle$. When this definition of J is inserted into the $q \to 0$ limit of Eq. (43), we obtain the alternative expression for $\sigma_2(\omega)$

$$\sigma_2(\omega) = \frac{-\beta}{\Omega} \langle \phi | J [1/(T - i\omega)] J | \phi \rangle \ . \tag{50}$$

In the same $q \to 0$ limit it is often simplest not to use the pseudoquantum formalism to calculate $\sigma_1(\omega)$. Instead, taking the limit $q \to 0$ in Eq. (32) yields a standard result

$$\sigma_1(\omega) = \frac{\beta}{2\Omega} \sum_{\gamma\alpha} \Gamma_{\gamma\alpha} P_\alpha^{(0)} D_{\gamma\alpha}^2 \ , \tag{51}$$

and

$$D_{\gamma\alpha} = \sum_i eZ_i (\Delta X_i)_{\gamma\alpha} \ . \tag{52}$$

IV. APPLICATIONS

The fundamental result of this paper is the expression for the general structure of the conductivity [Eq. (45)], which shows that the conductivity is always a nondecreasing function of frequency for any hopping model. The general significance of this result to experiments will be discussed in Sec. V. In this section the general result will be applied to a simple example of interacting ions hopping on rings. This example shows how ion-ion interaction can produce a significant frequency dependence in the conductivity.

One of the simplest hopping models which gives an interesting result for the frequency-dependent conductivity is a ring of six sites occupied by three identical mobile ions. The sites are separated by a distance a and the ions have charge Ze. The ions in this model hop, one at a time, only to nearest-neighbor unoccupied sites, and the hopping rates are chosen to reflect the effect of an effective short-range ion-ion potential. Any allowed nearest-neighbor hop which does not change the number of nearest-neighbor mobile-ion pairs is assumed to proceed at a rate Γ. Hops which decrease the number of nearest-neighbor pairs by one occur at a rate $\gamma\Gamma$ and hops which increase the number of nearest-neighbor pairs by one occur at a rate $\gamma^{-1}\Gamma$. This choice of hopping rates means that the equilibrium probability of a configuration $|\alpha\rangle$ is

$$P_\alpha^{(0)} = K\gamma^{-2N} \ , \tag{53}$$

where K is a constant and N is the number of nearest-neighbor ion pairs in configuration $|\alpha\rangle$. The same values of $P_\alpha^{(0)}$ would be obtained in a simple lattice-gas model for the ions in which the nearest-neighbor ion-ion potential V is given by

$$\beta V = 2 \ln\gamma \ . \tag{54}$$

For simplicity, only the $q = 0$ conductivity of this model will be presented here. To obtain σ_1 using Eq. (51), the 20 possible configurations of the ions $|\alpha\rangle$ are multiplied by the appropriate probabilities $P_\alpha^{(0)}$ and hopping rates $\Gamma_{\delta\alpha}$. When these products are summed over α and δ, we obtain

$$\sigma_1 = \sigma_0\, 2\gamma(\gamma^2+\gamma+1)/(\gamma^4+6\gamma^2+3)\ , \tag{55}$$

where

$$\sigma_0 = 3\beta(Ze)^2 a^2/\Omega \tag{56}$$

is 3 times the conductivity of a single ion on the ring. Note that when $\gamma = 1$, $\sigma_0 = \frac{3}{5}$, which is the probability that a site adjacent to a mobile ion will be vacant if the ions are noninteracting.

The expression for the double-hop conductivity of this model [Eq. (50)] can be written

$$\sigma_2(\omega) = \frac{-\beta}{\Omega} \sum_n |\langle\psi_n|J|\phi\rangle|^2 \frac{1}{\epsilon_n - i\omega}\ , \tag{57}$$

where $|\psi_n\rangle$ and ϵ_n are the eigenfunctions and eigenvalues of the operator T.

The task of finding the relevant $|\psi_n\rangle$ and ϵ_n, can be simplified by a consideration of the symmetries of this problem. The ring has rotation and reflection symmetry, and $|\phi\rangle$ is unchanged when the ring is rotated or reflected. This means the states $|\psi_n\rangle$ which contribute to the conductivity in Eq. (54) must also be rotationally invariant. Also, since J is reflection antisymmetric only antisymmetric $|\psi_n\rangle$ need be considered. One cannot construct such states with only two ions, so the simplest ring which exhibits a frequency-dependent conductivity is the half-filled ring with six sites. The necessity of considering three mobile ions is related to the fact that interaction effects appear in T in the form of many-body terms rather than more familiar two-body terms.

The following notation is used in the construction of rotation-invariant states. The ionic sites on the ring are labeled 1 through 6. The configuration with ions at sites 1, 2, and 4 is denoted as $|1,2,4\rangle_0$. The subscript "0" is deleted for rotationally invariant states constructed from these configurations. For example,

$$\begin{aligned}|1,2,4\rangle = (1/\sqrt{6})(&|1,2,4\rangle_0+|2,3,5\rangle_0+|3,4,6\rangle_0\\ &+|4,5,1\rangle_0+|5,6,2\rangle_0+|6,1,3\rangle_0)\,,\end{aligned} \tag{58}$$

and

$$|1,3,5\rangle = \frac{1}{\sqrt{2}}(|1,3,5\rangle_0+|2,4,6\rangle_0)\,.$$

The ground state $|\phi\rangle$ can be obtained from the relation $P_\alpha^{(0)} = |\langle\alpha|\phi\rangle|^2$ [Eq. (18)], so

$$\begin{aligned}|\phi\rangle = [&|1,2,3\rangle+\gamma|1,2,4\rangle+\gamma|1,2,5\rangle\\ &+(\gamma^2/\sqrt{3})|1,3,5\rangle]/(1+2\gamma^2+\gamma^4/3)^{-1/2}\ .\end{aligned} \tag{59}$$

The only rotation invariant, inversion-antisymmetric state which can be constructed for this six-site ring is

$$|\psi\rangle = (1/\sqrt{2})(|1,2,4\rangle - |1,2,5\rangle)\,. \tag{60}$$

The eigenvalue ϵ associated with $|\psi\rangle$ is

$$\langle\psi|T|\psi\rangle = \Gamma(\gamma+\gamma^{-1}+4)\ . \tag{61}$$

The matrix element of the current operator is

$$\langle\phi|J|\psi\rangle = i\Gamma(\gamma-1)^2[2/(1+2\gamma^2+\gamma^4/3)]^{1/2}\,. \tag{62}$$

Substitution of Eqs. (61) and (62) into Eq. (57) gives $\sigma_2(\omega)$. This is added to σ_1 from Eq. (55) to yield the conductivity for the six-site ring.

$$\frac{\sigma}{\sigma_0} = \frac{2}{\gamma^4+6\gamma^2+3}\left(\gamma(\gamma^2+\gamma+1) - \frac{(\gamma-1)^4}{(\gamma+\gamma^{-1}+4)-i\omega/\Gamma}\right). \tag{63}$$

The real part of $\sigma(\omega)/\sigma_0$ for $\gamma = 20$ is plotted as a function of ω/Γ in Fig. 1. We also show $\ln[\sigma(0)/\sigma_0]$ and $\ln[\sigma(\infty)/\sigma_0]$ as functions of $\ln(\gamma)$ in Fig. 2. If $2\ln(\gamma)$ is associated with βV as is described in Eq. (54), then Fig. 2 clearly shows that the low-frequency and high-frequency conductivities are thermally activated. Note that the effective activation associated with the dc conductivity is about twice the high-frequency activation energy.

It is our contention that the results for the six-site ring are a good approximation to the conductivity of an infinite one-dimensional hopping model. One bit of evidence in favor of this contention can be obtained from a comparison of the conductivity for the six- and eight-site rings. A calculation of the conductivity of the eight-site ring involves only a little extra effort because there are two nonzero matrix elements which determine σ_2. The result is

$$\begin{aligned}&\sigma(\omega)/\sigma_0 = 2(A+B+C)/(4+18\gamma^2+12\gamma^4+\gamma^6)\,,\\ &A = 1+2\gamma+4\gamma^2+2\gamma^3+\gamma^4\,,\\ &B = -(\gamma-1)^4/(\gamma+\gamma^{-1}+2-i\omega)\,,\\ &C = -\gamma^2(\gamma-1)^4/(\gamma+3\gamma^{-1}+2-i\omega)\,.\end{aligned} \tag{64}$$

A numerical comparison of the high- and low-frequency conductivities of the two chains for $-1 \leqslant \ln\gamma \leqslant 7$ indicates a better than 10% agreement. For large negative values of $\ln\gamma$ the agreement is worse because the effective ion-ion attraction tends to place the ions in lumps and the conductivity is no longer proportional to the number of ions.

In two and three dimensions, interaction effects appear to inhibit the conductivity even more strongly. To get at least a qualitative idea of the effects of dimensionality, the conductivity of two coupled chains of four sites was also calculated. This model is essentially a two-dimensional lattice only two-sites wide and four-sites long with periodic boundary conditions applied in the long direction. Ions are allowed to hop only along the long direc-

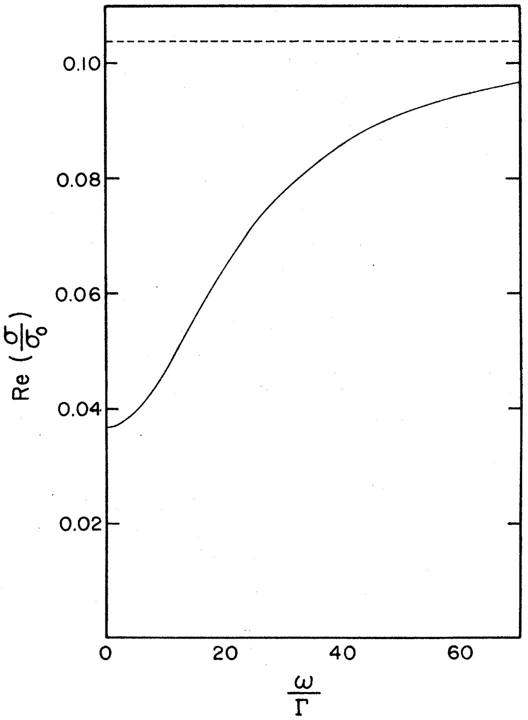

FIG. 1. Frequency dependence of the conductivity for three ions hopping on a six-site ring. The parameter γ which characterizes the relative hopping rates is 20. The high-frequency limit of σ/σ_0 is shown by the dotted line.

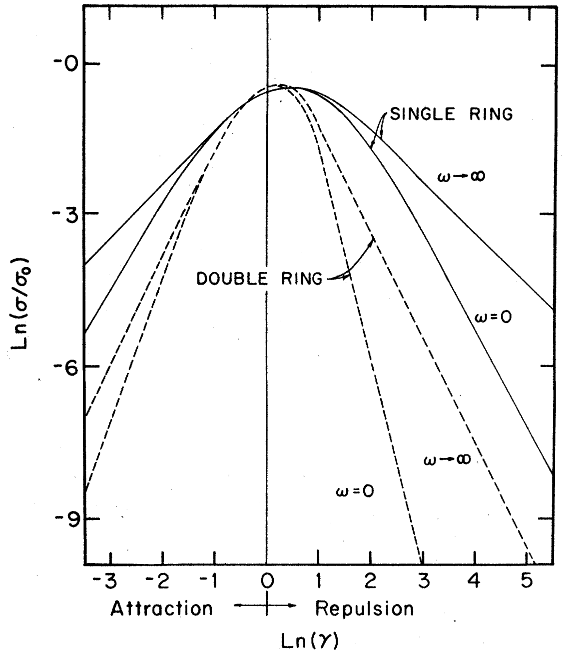

FIG. 2. High-frequency and low-frequency conductivities of the six-site ring and the double four-site ring. Since $2\ln\gamma$ can be related to βV, where V is an ion-ion interaction, this figure indicates thermally activated hopping for both the high-frequency and low-frequency conductivities.

tion, hopping rates are determined by

$$\Gamma_{\delta\alpha} = \Gamma\gamma^{N_\alpha - N_\delta} , \tag{65}$$

where N_α is the total number of nearest neighbor sites on or between the two chains, in configuration α.

Two ions are placed in each chain. Again symmetry considerations make the conductivity calculation relatively simple ($|\phi\rangle$ is symmetric with respect to interchange of the two chains). The result is

$$\begin{aligned} &\sigma(\omega)/\sigma_0 = 2(A+B)/(2+4\gamma^2+11\gamma^4+\gamma^8) , \\ &A = \gamma^2(1+2\gamma+2\gamma^2+\gamma^4) , \\ &B = (1-2\gamma+\gamma^4)^2/(\gamma^2+2+2\gamma^{-1}+\gamma^{-2}-i\omega) . \end{aligned} \tag{66}$$

The high- and low-frequency conductivities are compared with the single-chain results in Fig. 2. As one expects, the localization effect is more important for this crude approximation of a two-dimensional system than for the one-dimensional rings.

V. DISCUSSION

The basic result obtained here is that the conductivity of any hopping model must be a nondecreasing function of frequency. This result is expressed formally and generally in Eq. (45) and it was illustrated in the examples sited in Sec. IV. Only at high frequencies can one expect the conductivity to be simply proportional to the hopping rate. The time correlations between subsequent hops can only decrease the dc conductivity relative to the high-frequency conductivity. Another characteristic of hopping models is that the imaginary part of the conductivity is always negative, which means these systems are capacitive rather than inductive.

A phenomenological form for the real part of the conductivity which satisfies the exact conditions of a hopping model is

$$\mathrm{Re}[\sigma(\omega)] = \sigma_0\{1 - R/[1+(\omega\bar{\tau})^2]\} . \tag{67}$$

An example of such a curve is shown in Fig. 1.

Physically, σ_0 can be associated with the simple hopping conductivity of the form given in Eq. (1), R represents the fraction of the time that an ion is forced to return to its original site after making a hop and $\bar{\tau}$ is the average time it takes to return. If the frequency dependence of the conductivity arises primarily from impurity effects, then one would expect the factor R to be relatively independent of temperature. However, if ion-ion interactions are important in limiting the current, the factor R

should approach 1 as the temperature is lowered. The high-frequency and low-frequency conductivities should exhibit differing activation energies as is illustrated in Fig. 2.

Other models of ionic motion in superionic conductors have been proposed.[8-11] In general, these models yield predictions for the frequency dependence of the conductivity which differ significantly from the prediction of the hopping model. Hence an examination of the frequency-dependent conductivity can yield a clear indication of which model is most accurate even when the models may be nearly indistinguishable when only dc experiments are performed.[20]

Consider, for example, a comparison of the conductivities one would expect from a hopping model and a free-ion-like model. The free-ion model conductivity has been calculated by Rice and Roth.[10] They obtained a Drude-like result

$$\sigma(\omega)\approx\sigma(0)/[1+(\omega\tau_f)^2]\,, \qquad (68)$$

where τ_f is the mean lifetime of the free ion. Of course, the free-ion model can make sense only if τ_f is greater than τ_0, the time necessary to travel from one interstitial site to another. This result clearly differs from the hopping model result because $\sigma(\omega)$ decreases with frequency.

The imaginary parts of the conductivities for the free-ion and hopping models differ in sign because the free-ion model is inductive and the hopping model is capacitive.

Experimental microwave data have been obtained for β-alumina by Strom *et al.*[5] and Barker *et al.*[6] and for AgI by Funke and Jost.[7] Although these data are imprecise, it appears that the data on β-alumina are generally consistent with the theoretical results presented here, since $\sigma(\omega)$ increases with ω, approaching a high-frequency plateau. For example, a reasonable fit to the data of Strom *et al.* at 180 K can be obtained using the phenomenological Eq. (37) with $\sigma_0 \simeq 10^{-2}$ $(\Omega\ \mathrm{cm})^{-1}$, $R\simeq \frac{29}{30}$, and $\tau \approx 10^{-8}$ sec. Note that τ is much greater than the transmit time τ_0. Strom *et al.* offer another explanation of these data involving tunneling which cannot be treated in a classical hopping model.

The microwave data on AgI are clearly inconsistent with the hopping results presented here because $\sigma(\omega)$ is a decreasing function of ω which appears to show some structure. A phenomenological Drude conductivity of the type given in Eq. (68) with

$$\tau_f \approx 2\times 10^{-11}\ \mathrm{sec}$$

could be used to approximately fit the observed low-frequency data on AgI. The peak seen in the AgI microwave data cannot be explained by a free-ion or a hopping model.

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[1] *Fast Ion Transport in Solids*, edited by W. van Gool (North-Holland, Amsterdam, 1973).

[2] *Superionic Conductors*, edited by G. D. Mahan and W. L. Roth (Plenum, New York, 1976).

[3] H. Rickert, in Ref. 1, p. 4.

[4] C. P. Flynn, Phys. Rev. Lett. 35, 1721 (1975).

[5] U. Strom, P. C. Taylor, S. G. Bishop, T. L. Reinecke, and K. L. Ngai, Phys. Rev. B 13, 3329 (1976).

[6] A. S. Barker, Jr., J. A. Ditzenberger, and J. P. Remeika, Phys. Rev. B 14, 4254 (1976).

[7] K. Funke and A. Jost, Ber. Bunsenges. Phys. Chem. 75, 436 (1971).

[8] B. A. Huberman and P. N. Sen, Phys. Rev. Lett. 33, 1379 (1974); 34, 1059 (1975).

[9] G. D. Mahan, Phys. Rev. B 14, 780 (1976).

[10] M. J. Rice and W. L. Roth, J. Chem. Phys. 55, 677 (1971).

[11] H. R. Zeller, P. Brüesch, L. Pietronero, and S. Strässler, Ref. 2, p. 201.

[12] I. Yokoto, J. Phys. Soc. Jpn. 21, 420 (1966).

[13] K. Kawasaki, Phys. Rev. 148, 375 (1966); *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2, Chap. 11.

[14] W. Dieterich, I. Peschel, and W. R. Schneider, Comments Phys. 2, 175 (1977).

[15] P. M. Richards, Phys. Rev. B 16, 1393 (1977).

[16] G. H. Vineyard, J. Phys. Chem. Solids 3, 121 (1957).

[17] R. Kubo, J. Phys. Soc. Jpn. 12, 570 (1957).

[18] A. D. LeClaire and A. B. Lidiard, Philos. Mag. 1, 518 (1956).

[19] N. L. Peterson, in *Diffusion in Solids; Recent Developments*, edited by A. S. Norwick and J. J. Burton (Academic, New York, 1975), Chap. 3.

[20] C. W. Haas, J. Solid State Chem. 7, 155 (1973).