

Brownian motion in a polarizable lattice: Application to superionic conductors

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We discuss the Brownian motion of a set of interacting particles. The general problem is formulated in terms of generalized Langevin equations and the frequency-dependent conductivity $\sigma(\omega)$ is computed from the velocity-velocity correlation function. In particular we consider a case pertaining to superionic conductors. We apply the formalism to a system consisting of a polarizable periodic sublattice built up of one ion species and oppositely charged mobile ions. Approximate solutions for $\sigma(\omega)$ are derived by choosing the simplest analytical memory functions which fulfill all asymptotic conditions. We show that lattice polarizability leads to structure at the transition frequency from diffusion-controlled to oscillation-controlled properties. The formalism is applied to α -AgI. The different interactions in superionic conductors, i.e., effective potential seen by mobile ion, lattice polarizability, and correlation of jumps of mobile ions, can be split and studied separately in their respective characteristic frequency regimes.

I. INTRODUCTION

Superionic conductors are solids characterized by an ionic conductivity comparable to liquid electrolytes.^{1,2} Despite their technological importance in modern electrochemistry, not much is known about the factors which determine the ionic mobility.¹⁻⁷

The remarkably high conductivity of this class of solid compounds is a consequence of two facts: First the barrier height for diffusion is rather small, since barrier heights of the order of kT are not uncommon, and second essentially all ions of one species are mobile. From a theoretical point of view, this is a situation of formidable complexity; before any progress can be achieved, it is necessary to introduce rather dramatic simplifications.

In previous papers we have investigated a rather simple model which neglects polarizability of the lattice and correlated jumps of the ions.⁵⁻⁷ In this model we considered the Brownian motion of a particle in a rigid periodic potential. The particle is described by a Langevin equation. Coupling to the thermal bath is provided by a friction term and a stochastic driving force.

A continued-fraction expansion technique similar to the well-known Mori technique⁸ for Hamiltonian systems can be applied to such problems.⁹ It was found that the exact solution can be approximated by a simple exponentially decaying memory function.⁶

With regard to application to superionic conductors, the model has two major drawbacks. It neglects the polarizability of the lattice and correlated jumps among the mobile ions. Lattice polarizability leads to structure in the frequency-dependent conductivity $\sigma(\omega)$ at the transition frequency

from diffusion-controlled to oscillation-controlled behavior. Correlated jumps on the other hand affect $\sigma(\omega)$ at $\omega \lesssim \tau_R^{-1}$, where τ_R is a characteristic residence time.⁷

In general, τ_R^{-1} is much smaller than all relevant lattice frequencies. Hence the effect of correlation on $\sigma(\omega)$ can be split off and treated as a separate problem independent of the dynamics of the lattice.⁷ This, however, is not true for the lattice polarizability.

It is the purpose of this paper to introduce a model which describes Brownian motion of a particle in a polarizable periodic potential. As opposed to the rigid-potential model⁶ we no longer are able to give exact solutions. Instead we will use an approximation which contains all essential physical features and which has been successfully tested in the rigid-potential case.

We proceed as follows: In Sec. II we investigate a set of N -coupled Langevin equations describing N -coupled particles. Following Kubo's matrix notation¹⁰ we introduce the memory-function formalism and, by making use of the fluctuation-dissipation theorem, express the current-current correlation functions and $\sigma(\omega)$ in terms of memory functions.

Based on this formalism we discuss in Sec. III the case of a lattice buildup of two oppositely charged ions per unit cell of which one species is mobile, whereas the other provides a fixed sublattice. From general physical arguments a number of asymptotic conditions for the memory functions can be found. We introduce a set of simple analytical memory functions which fulfill the asymptotic conditions. From this set, $\sigma(\omega)$ is computed. At this point the model only includes the ionic (displacive) part of the polarizability. In Sec. IV we generalize the model to also include

the electronic part and apply it to experimental results on α -AgI.

To sum up (Sec. V) we have introduced a model which allows us to take into account lattice polarizability. This is particularly important in the case of AgI-type superionic conductors.

II. GENERAL FORMALISM

In this section we discuss the general problem of the motion of N -interacting charged particles described by N -coupled Langevin equations.^{11,12} We are mainly interested in the frequency-dependent conductivity which we calculate by using techniques pioneered by Kubo.¹⁰ Before we start discussing examples of physical interest we briefly reformulate Kubo's matrix formalism for correlation functions and introduce a memory function ansatz for the coupled Langevin equations. The frequency-dependent conductivity $\sigma(\omega)$ is then obtained from the current-current correlation function.

We consider a system of N particles described by their masses m_i ($i=1, \dots, N$), charges q_i , and coordinates x_i . The current of the i th particle at the time t is

$$j_i(t) = q_i \dot{x}_i(t). \quad (2.1)$$

The total wave-vector-dependent current is then given by

$$J(k, t) = \sum_{i=1}^N j_i(t) e^{ikx_i}, \quad (2.2)$$

k being the wave vector. The current-current correlation function for the whole system is

$$\begin{aligned} S(k, t) &= \langle J(k, t) J(k, 0) \rangle \\ &= \sum_{i,j=1}^N q_i q_j \langle \dot{x}_i(t) \dot{x}_j(0) e^{ik(x_i - x_j)} \rangle, \end{aligned} \quad (2.3)$$

where the average $\langle \dots \rangle$ is taken over an ensemble in thermal equilibrium. According to the fluctuation-dissipation theorem, we can write the total conductivity of the system in terms of the correlation function (2.3) as

$$\sigma(k, \omega) = \frac{1}{K_B T} \int_0^\infty e^{i\omega t} S(k, t) dt = \frac{S[k, \omega]}{K_B T}, \quad (2.4)$$

where K_B and T are Boltzmann constant and temperature, respectively. $S[k, \omega]$ is the Laplace transform of $S(k, t)$:

$$S[k, \omega] = \int_0^\infty e^{i\omega t} S(k, t) dt. \quad (2.5)$$

It is convenient to introduce a matrix notation: Let Q be the matrix of charge with matrix elements given by

$$Q_{ij} = q_i q_j. \quad (2.6)$$

The correlation matrix C is defined as

$$C_{ij}(t) = \langle \dot{x}_i(t) \dot{x}_j(0) e^{ik(x_i - x_j)} \rangle. \quad (2.7)$$

Equation (2.3) can be now rewritten

$$S(k, t) = \sum_{i,j=1}^N Q_{ij} C_{ji} = \text{Tr} Q C, \quad (2.8)$$

where Tr indicates the trace operation. The problem is then reduced to the calculation of the correlation functions (2.7).

We now consider a system of N interacting particles described by a set of equations of the form

$$m_i \ddot{x}_i + \sum_{j=1}^N F_{ij}(x_i - x_j) = 0, \quad (2.9)$$

where F_{ij} represents the interaction between particles.

Equations of this form using realistic interaction potentials and up to several hundred particles have been numerically solved in the case of liquids.¹³⁻¹⁸ However, we want to avoid the use of large computers and hence proceed in a different way. We replace the set of nonlinear equations (2.9) by the following set of linear equations:

$$m_i \ddot{x}_i(t) + \Gamma_i \dot{x}_i(t) + \sum_{j=1}^N \hat{M}_{ij}(\dot{x}_i - \dot{x}_j) = f_i(t). \quad (2.10)$$

In the above set of coupled linearized Langevin equations, Γ_i represents a damping and f_i represents a stochastic driving force.¹² The nonlinearities in Eq. (2.9) are represented by the stochastic driving forces f_i .¹⁰ The memory-function operators \hat{M}_{ij} are defined by

$$\hat{M}x(t) = \int_0^t M(t-t') \dot{x}(t') dt', \quad (2.11)$$

where $M(t)$ is the so-called memory function. Equation (2.10) is linear and the current-current correlation function, or $\sigma(\omega)$, can be readily calculated in terms of the \hat{M}_{ij} . In simple cases the asymptotic form of the \hat{M}_{ij} for large and small t follows from physical arguments. There is hope that simple analytical expressions for the $M_{ij}(t)$, which fulfill all asymptotic conditions, will produce approximate solutions for the correlation functions and for $\sigma(\omega)$. We note then that causality poses additional constraints on the choice of the memory function. The $M_{ij}(t)$ have to be such that the poles of a response function are located in the lower complex half-plane.

We now introduce the matrices M^* (mass) and E (interaction) and the vectors F (force) and V (velocity) by defining their elements as follows:

$$M_{ij}^* = m_i \delta_{ij}, \quad V_i = \dot{x}_i, \quad F_i = f_i, \quad (2.12)$$

$$E_{ij} = \left(\Gamma_i + \sum_{\substack{j=1 \\ (j \neq i)}}^N \hat{M}_{ij} \right) \delta_{ij} - \hat{M}_{ij}.$$

The systems of equations (2.10) can be now written in a compact form as

$$M^* \cdot \dot{V} + E \cdot V = F. \quad (2.13)$$

Multiplying Eq. (2.13) from right with the matrix of the $\dot{x}_j(0)e^{ik(x_i - x_j)}$, and taking the thermal average, we have

$$M^* \cdot \dot{C} + E \cdot C = 0. \quad (2.14)$$

(Causality requires, in fact, that $\langle f_i(t)\dot{x}_j(0) \rangle = 0$.) A Laplace transform of Eq. (2.14) results in

$$B[\omega] \cdot \dot{C}[\omega] = M^* \cdot C(0). \quad (2.15)$$

The matrix $B[\omega]$ is defined by

$$B[\omega] = -i\omega M^* + E[\omega]. \quad (2.16)$$

$C(0)$ is formed by the elements (2.7) at the time $t=0$:

$$C_{ij}(0) = \langle \dot{x}_j^2(0) \rangle \delta_{ij} = (K_B T / m_i) \delta_{ij}, \quad (2.17)$$

having made use of the equipartition principle. From Eq. (2.15) we obtain

$$C[\omega] = B^{-1}[\omega] \cdot M^* \cdot C(0). \quad (2.18)$$

Inserting now (2.18) into (2.8) the frequency-dependent conductivity becomes

$$\begin{aligned} \sigma(k, \omega) &= \frac{1}{K_B T} \text{Tr} Q \cdot C[\omega] \\ &= \frac{1}{K_B T} \text{Tr} Q \cdot B^{-1}[\omega] \cdot M^* \cdot C(0) \\ &= \text{Tr} Q \cdot B^{-1}[\omega]. \end{aligned} \quad (2.19)$$

The problem is therefore reduced to the calculation of the matrix elements of $B^{-1}[\omega]$. In the general case this is an $N \times N$ matrix and the explicit calculation is possible only for a very small number of particles. In some cases, however, symmetry can simplify the problem. For example, if translational invariance is present the problem becomes equivalent to that of the normal mode of a periodic system and the size of the matrix is reduced to the number of atoms in the unit cell.¹⁹

III. BROWNIAN MOTION IN A LATTICE

In this section we discuss the Brownian motion of a particle in a solid in terms of simple phenomenological models. The basic assumption is that the solid is built up of at least two species of ions of which one species is allowed to diffuse whereas the others provide a stable framework. This is

the situation which applies to superionic conductors such as α -AgI.²

We discuss the problem in two steps. First we describe the sublattice of immobile ions by a rigid potential, derive $\sigma(\omega)$ using a simple memory-function approach, and compare the thus-obtained approximate $\sigma(\omega)$ with exact solutions. Having gained confidence in the memory-function technique we apply it to a more complex and more realistic situation for which no exact solutions exist. In this second model the lattice potential is no longer rigid and interaction between the different ion species is included. This is particularly important for experimental systems with large polarizabilities such as α -AgI.

The first model was discussed in previous papers⁵⁻⁷ and will be treated only briefly. In terms of a memory function the generalized Langevin equation for a particle in a rigid potential is^{6,20}

$$m\ddot{x} + \Gamma\dot{x} + \int_0^t M(t-t')\dot{x}(t') dt' = f(t), \quad (3.1)$$

which results in a frequency-dependent conductivity

$$\sigma(\omega) = q^2 (-i\omega m + \Gamma + M[\omega])^{-1}, \quad (3.2)$$

where $M[\omega]$ denotes the Laplace transform of $M(t)$. For a harmonic potential (3.1) has to describe a damped oscillator which requires $M(t) = c > 0$. In the limit of exclusively frictional forces which is the classical Brownian-motion picture,¹¹ (3.1) has to represent a diffusion equation which results in $M(t) = a\delta(t)$.

We are interested in the Brownian motion of a particle in a periodic potential in which the potential barrier for diffusion is comparable to kT . Equation (3.1) thus has to include both oscillatory and diffusive aspects. In particular, we require (3.1) to describe an oscillating particle at $t \rightarrow 0$ and a diffusing particle at $t \rightarrow \infty$. The simplest choice of $M(t)$ which fulfills the above asymptotic conditions is^{5,7}

$$M(t) = m\bar{\omega}_0^2 e^{-\gamma t}, \quad (3.3)$$

where $\bar{\omega}_0$ is an effective resonance frequency. This form of the memory function also reproduces the first terms of a continued fraction expansion for the nonlinear problem.⁶ The corresponding conductivity is

$$\sigma(\omega) = q^2 [-i\omega m + \Gamma + m\bar{\omega}_0^2 / (-i\omega + \gamma)]^{-1}. \quad (3.4)$$

$\tau = 1/\gamma$ characterizes the transition time between oscillatory and diffusive motion. (Note that this is not identical to the average residence time.⁵)

It can be shown that (3.4) represents a good approximation of the exact solution obtained from a generalized continued fraction expansion. A more

detailed discussion can be found in Ref. 6. We have presented this model mainly to demonstrate how a simple analytical memory function which fulfills the appropriate asymptotic boundary conditions can lead to a good approximation of the correct $\sigma(\omega)$. Our aim is now to apply the same procedure to a more complex situation for which no exact solutions exists.

In the following we construct a model which specifically pertains to superionic conductors and includes lattice polarizability. We consider a system with two oppositely charged ions per unit cell. One of the two ion species can diffuse while the other provides the fixed lattice. As in the previous example the response of this system is characterized by two asymptotic regimes. At high frequencies we are dealing with a standard $k=0$ optical phonon in which oppositely charged ions are oscillating against each other. For symmetry reasons the problem reduces to a two-particle problem.¹⁹ In the low-frequency limit the mobile ion species fulfills a diffusion equation and the symmetry argument no longer holds. However, as long as the jump rate of the particle is small compared to all characteristic lattice frequencies, we may, in the low-frequency limit, describe the lattice by an effective potential. This approximation is justified for virtually all experimental systems except for hydrogen in some transition metals.²¹ Our phenomenological model thus

includes three entities: the mobile (x_1, m_1) and immobile ions (x_2, m_2) , and in the low-frequency limit, the effective lattice denoted by index 3. As indicated above in this regime the diffusing particle is moving in an effective rigid potential and the generalized Langevin equations for x_1 and x_2 become

$$m_1 \ddot{x}_1 + \Gamma_1 \dot{x}_1 + \hat{M}_{13} \dot{x}_1 + \hat{M}_{12} (\dot{x}_1 - \dot{x}_2) = f_1, \quad (3.5a)$$

$$m_2 \ddot{x}_2 + \Gamma_2 \dot{x}_2 + \hat{M}_{23} \dot{x}_2 + \hat{M}_{12} (\dot{x}_2 - \dot{x}_1) = f_2, \quad (3.5b)$$

where M_{12} describes the coupling between the two oscillating sublattices, M_{13} is the coupling to the rigid potential, and M_{23} ensures stability of x_2 at $t \rightarrow \infty$. The formalism of Sec. II can be now directly applied to this problem also if the system (3.5) has the extra memory functions \hat{M}_{13} and \hat{M}_{23} compared to the system (2.1). The matrix $B[\omega]$ defined by the Eq. (2.16) has, for the system (3.5), the following matrix elements:

$$B_{11}[\omega] = -i\omega m_1 + \Gamma_1 + M_{13}[\omega] + M_{12}[\omega],$$

$$B_{22}[\omega] = -i\omega m_2 + \Gamma_2 + M_{23}[\omega] + M_{12}[\omega], \quad (3.6)$$

$$B_{12}[\omega] = B_{21}[\omega] = -M_{12}[\omega].$$

With $q_1 = 1$ and $q_2 = -1$, Eq. (2.19) gives

$$\sigma(\omega) = \frac{-i\omega(m_1 + m_2) + \Gamma_1 + \Gamma_2 + M_{13}[\omega] + M_{23}[\omega]}{\det B}. \quad (3.7)$$

The dc conductivity $\sigma(0)$ is then explicitly given by

$$\sigma(0) = \frac{\Gamma_1 + \Gamma_2 + M_{13}[0] + M_{23}[0]}{(\Gamma_1 + M_{13}[0] + M_{12}[0])(\Gamma_2 + M_{23}[0] + M_{12}[0]) + M_{12}^2[0]}. \quad (3.8)$$

We have now to choose appropriate memory functions in Eqs. (3.5) to fulfill the following asymptotic conditions:

(a) At high frequencies ($t \rightarrow 0$) (3.5) has to describe a damped harmonic oscillation of the two particles x_1 and x_2 . This requires

$$M_{13}(0) = M_{23}(0) = 0 \quad \text{and} \quad M_{12}(0) = c > 0.$$

(b) In the low-frequency diffusive limit ($t \rightarrow \infty$), we require diffusion for x_1 , complete decoupling for x_1 and x_2 , and no diffusion for x_2 . This is fulfilled if $M_{12}(\infty) = 0$, $\int_0^\infty M_{12}(t) dt = 0$, $M_{13}(\infty) = 0$, and $M_{23}(\infty) = c > 0$. We also require that, in the limit $\dot{x}_2 = 0$, Eq. (3.5a) has to be identical to Eq. (3.1). This implies $M_{12}(t) + M_{13}(t) = M(t)$.

The simplest choice of the M_i , which fulfills all the above conditions and also deviates as little as possible from the exponential form of $M(t)$, which was found to yield a very good approximation in the single-particle case, is

$$\begin{aligned} M_{12}(t) &= m_1 \omega_{12}^2 (1 - \gamma t) e^{-\gamma t}, \\ M_{13}(t) &= m_1 \omega_{12}^2 \gamma t e^{-\gamma t}, \\ M_{23}(t) &= m_2 \omega_{12}^2 (1 - e^{-\gamma t}). \end{aligned} \quad (3.9)$$

The Laplace transforms are

$$\begin{aligned} M_{12}[\omega] &= m_1 \omega_{12}^2 \gamma / (-i\omega + \gamma)^2, \\ M_{13}[\omega] &= m_1 \omega_{12}^2 [-i\omega / (-i\omega + \gamma)^2], \\ M_{23}[\omega] &= m_2 \omega_{12}^2 \gamma / -i\omega(-i\omega + \gamma). \end{aligned} \quad (3.10)$$

IV. APPLICATION TO EXPERIMENTAL SYSTEMS

In this section we compare the model discussed in Secs. II and III to experimental results on superionic conductors. Before we can do this it is necessary to study in somewhat more detail the physical significance of the formalism developed in Sec. III and introduce a generalization.

The situation discussed in Sec. III roughly corresponds to α -AgI. α -AgI possesses a disordered

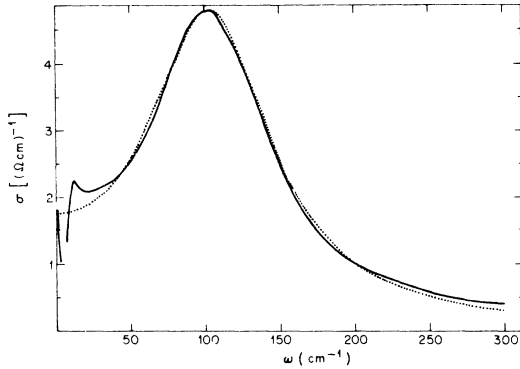


FIG. 1. Frequency-dependent conductivity of α -AgI ($T = 453$ K) (solid line) derived from a Kramers-Kronig analysis of reflectivity data. The dotted line shows a fit based on a rigid-potential model [Eq. (3.4)] with the parameters (expressed in frequency units of cm^{-1}) $\omega_0 = 105$ cm^{-1} , $\Gamma/m_{\text{Ag}} = 45$ cm^{-1} , and $\gamma = 53$ cm^{-1} . Note the good fit at $\omega \geq 20$ cm^{-1} and the strong deviations at $\omega \leq 20$ cm^{-1} .

sublattice of mobile Ag^+ ions and an ordered (cubic) sublattice of immobile I^- ions. The two asymptotic features of the model, an optical mode in the infrared caused by the coupled oscillation of Ag^+ and I^- ions, and a dc conductivity due to diffusive motion of Ag^+ , are clearly observed.^{2,5}

In an earlier paper⁶ we have applied the rigid-potential model to α -AgI and shown that it leads to a very good fit of the observed $\sigma(\omega)$ except at low frequencies where structure is observed which is impossible to reconcile with the model⁷ (see Fig. 1). A main shortcoming of the rigid-potential single-particle model is that it neglects lattice polarizability which is known to be important in α -AgI. This was exactly the starting point for the construction of the model of Sec. III which is the simplest model able to include lattice polarizability.

However, as it stands, the model includes only part of the total lattice polarizability. By construction we have included the relative nuclear motion of the Ag^+ and I^- ions in the oscillatory regime but not the polarizability of the ion shells. We now show that within the spirit of the phenomenological model also effects of shell polarizability can be included by a rather trivial generalization.

Lattice polarizability, in general, affects oscillator strength and frequency of optical modes and the barrier height for diffusion.²² Dynamic polaron effects²³⁻²⁶ which may lead to correlated jumps, have been excluded in the derivations of the model and are unimportant in superionic conductors.²⁷ Within the model-oscillation frequency and barrier height for diffusion (dc conductivity) are adjustable

parameters and need not be discussed.

The oscillator strength, however, can be calculated in terms of the model parameters. Hence polaron effects on the oscillator strength have to be discussed.

First we restrict ourselves to the discussion of the oscillatory part of the motion. For a silver ion moving in a rigid potential the oscillator strength S is given by

$$S = \int_0^\infty \sigma(\omega) d\omega = \frac{\pi}{2} \frac{q^2}{m}. \quad (4.1)$$

In the model discussed in Sec. III also anions take part in the motion and

$$S = \frac{1}{2} \pi q^2 / \bar{m}, \quad (4.2)$$

where the reduced mass \bar{m} is given by

$$\bar{m}^{-1} = m_{\text{Ag}}^{-1} + m_{\text{I}}^{-1}. \quad (4.3)$$

However, shell polarizability of the ions further complicates the situation.^{19,28} It leads to a dynamic charge (Szigeti charge) q^* different from the true charge and a local field E^* different from the external field E . For instance, for the transverse mode of a diatomic cubic crystal it is found

$$E^*/E = \frac{1}{3}(\epsilon_\infty + 2), \quad (4.4)$$

where ϵ_∞ denotes the high-frequency dielectric constant. The oscillator strength is thus enhanced by a factor

$$K = (m_{\text{Ag}} \sqrt{\bar{m}}) (q^*/q)^2 \left[\frac{1}{3}(\epsilon_\infty + 2) \right]^2, \quad (4.5)$$

with respect to oscillation of silver ions in a rigid potential. Experimentally, K is about 4 for a α -AgI which together with $\epsilon_\infty \sim 5$ results in $q^*/q \sim 0.6$.

So far we have been talking about oscillation. All above corrections do not apply to diffusion. The quantities which determine the dc conductivity of a classical particle are the true charge q , the external field E , and the mass of transport is the bare mass of the mobile particle.

Obviously there is a transition from dressed oscillation to bare diffusion of the mobile particle. The crucial assumption now is that we can treat this transition exactly parallel to the transition from oscillatory to diffusive motion discussed in Sec. III. If this is correct we can include polarization effects trivially by replacing \bar{m} by

$$\bar{m}^* = \bar{m} (q/q^*)^2 \left[3/(\epsilon_\infty + 2) \right]^2, \quad (4.6)$$

or what is equivalent to treat m_2 as a freely adjustable parameter which takes care of local fields and Szigeti charges in the oscillatory regime. For instance, in the case of AgI the effects of reduced mass, local field, and Szigeti charge result in an enhancement of the oscillator strength by a factor

of 4 which can be accounted for by taking $m_1 = m_{Ag}$ and $m_2 = \frac{1}{3}m_{Ag}$.

Figure 2 shows the result of a fit of Eq. (3.9) to the experimentally observed conductivity of α -AgI. Except for the parameters of the oscillatory regime m_2 , ω_0 , and Γ , the fit contains only one additional parameter γ which is fixed by the dc conductivity. Keeping in mind that the experimental accuracy in determining $\sigma(\omega)$ below ~ 20 cm^{-1} is rather poor, the fit is well within experimental error.

The key difference between the single-particle rigid-potential model and the model discussed above is the shoulder at $\omega \sim 15$ cm^{-1} which is a direct consequence of the transition from oscillation of the effective particle to diffusion of the bare particle. If one looks how the shoulder evolves as a function of temperature² then at first sight one is tempted to assign it to anharmonicity. As the temperature is raised from $T=0$ in the β -phase of AgI, side bands start to develop on the low-frequency side of the TO optical mode. The side bands gradually increase in number and intensity with increasing temperature until they wash out in the α -phase and form the shoulder at $\omega \sim 15$ cm^{-1} . One thus is tempted to argue that the structure at $\omega \sim 15$ cm^{-1} is due to a combination band as a consequence of anharmonicity. This statement is true to the extent that in superionic conductors anharmonicity is of crucial importance. In fact an elementary particle jump requires the superposition of a large number of phonons and in this respect a particle jump is the ultimate anharmonic event. Hence it makes no sense to talk about anharmonicity in superionic conductors in terms of low-order multiphonon processes as given by perturbation theory. A microscopic model of the transition from dressed oscillation to bare diffusion has to involve strong anharmonicity. In our model strong anharmonicity is phenomenologically included by construction (requirement of bare diffusion at $t \rightarrow \infty$).

The model discussed above and in Sec. III is essentially a single-particle model in the sense that interaction among the mobile ions is only incompletely included. Since the barrier height for diffusion is a freely adjustable parameter, the part of the interaction which contributes to the average barrier height is trivially included. However, we have neglected correlated jumps of particles.

Correlated jumps²⁹ affect $\sigma(\omega)$ at $\omega \lesssim \omega_R$ where $\tau_R = \omega_R^{-1}$ is a characteristic residence time of a particle. For α -AgI, ω_R is estimated to be ~ 1 cm^{-1} assuming random jumps. On the other hand, if backward correlation would be dominant, ω_R could easily be ~ 15 cm^{-1} and a shoulder would be observed at $\omega \sim \omega_R$. Nevertheless we do not believe

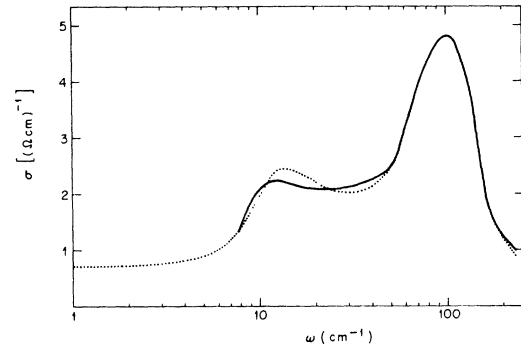


FIG. 2. Frequency-dependent conductivity of α -AgI ($T=453$ °K, solid line) is reported in a logarithmic scale to illustrate the structure at $\omega \sim 15$ cm^{-1} . The dotted curve is the fit calculated from Eqs. (3.5) and (3.9). The fit parameters are $\Gamma_1/m_1 = \Gamma_2/m_2 = 62$ cm^{-1} , $\omega_{12} = 50$ cm^{-1} , and $\gamma = 24$ cm^{-1} . As described in Sec. IV, $m_1 = m_{Ag}$ and $m_2 = \frac{1}{3}m_{Ag}$. The fit is within the numerical accuracy of the Kramers-Kronig transform. The structure at ~ 15 cm^{-1} is due to the transition from oscillation of the dressed particle to diffusion of the bare particle.

the structure at $\omega \sim 15$ cm^{-1} in α -AgI is caused by correlated jumps. First, model calculations of backward correlated jumps (double-well potential) lead to rather poor fits.³⁰ Second, we know based on absolutely general grounds that a transition from dressed oscillation to bare diffusion exists, e.g., there necessarily exists a structure due to such effects and the only question is whether correlation effects are superimposed. To further clarify this question, experimental studies are in progress.

V. SUMMARY AND CONCLUSIONS

The phenomenological model introduced in this paper allows for the first time a comprehensive discussion of $\sigma(\omega)$ in the full frequency range. In the optical-phonon regime the mobile particle oscillates as an effective particle with effective charge in a local field. At low frequencies the particle is diffusing with its bare properties. We are thus dealing with a transition from an excitation localized in k space (optical phonon) to an excitation localized in real space (diffusion jump). The structure observed in $\sigma(\omega)$ at this transition is a direct measure of the importance of effects of lattice polarizability (local fields, effective charge, effective mass). This of course is strongly related to the polaron problem in that the same interactions which affect the polaron contribution to the activation energy for diffusion also determine local fields and effective charges.

The prime achievement of the model is that we have essentially reduced the exceedingly complex

problem of the motion of strongly interacting particles in a polarizable lattice into three subproblems governed by different interactions. The optical-phonon regime can be discussed in terms of a single effective particle in a rigid effective potential. Polarizability effects show up and can be studied at lower frequencies at the transition to diffusive behavior. Effects of correlated jumps finally become important at $\omega \lesssim \tau_R^{-1}$ which is usually at much smaller frequencies. For instance, in α -AgI the restrahl frequency is at $\sim 100 \text{ cm}^{-1}$; the shoulder due to lattice polarizability is at $\sim 15 \text{ cm}^{-1}$, and $\tau_R^{-1} \sim 1 \text{ cm}^{-1}$. We can thus define fre-

quency regimes in which $\sigma(\omega)$ is primarily controlled by an effective single-particle potential, lattice polarizability, and correlated jumps of mobile ions, respectively. This represents a tremendous conceptual simplification and sets the stage for further progress in understanding the factors controlling ionic mobility in solid electrolytes.

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