Low-Frequency Response of Superionic Conductors

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It is shown that the low-frequency response of a superionic conductor yields all the relevant aspects of ionic diffusion at moderate temperatures. Hence, microwave measurements in these systems can give results concerning ionic transport that are much harder to obtain by quasielastic neutron scattering or tracer diffusion techniques. The results are used to analyze the available data on CuI. The general formalism we present is applicable to any system that displays activated transport properties.

Some time ago we proposed a microscopic transport theory in superionic conductors which, based on a liquidlike description of the ionic carriers, accounted well for the observed behavior found in these systems.[1] Central to the theory is the realization that below a temperature-dependent cutoff frequency the response of the charged system is diffusive, while above that frequency one observes the response of a stochastically driven damped harmonic oscillator. By working out expressions for the frequency and temperature dependences of the conductivity it was found that there exist three regimes which one is likely to encounter in superionic conductors: i.e., (i) a Debye-like behavior, (ii) a charged-liquid-like behavior, and (iii) a Drude regime to which the whole response crosses over as the cutoff frequency moves towards the ionic Debye frequency.

There is one result of our theory concerning the low-frequency behavior of the ionic conductivity that deserves some comment, for it turns out that by looking at the dielectric response in a certain frequency regime all the relevant aspects of ionic diffusion can be studied at moderate temperatures. As we will show, microwave measurements in superionic conductors can yield results concerning transport behavior that are much harder to obtain by quasielastic neutron scattering or tracer diffusion techniques at the same temperatures.

The ionic conductivity is given by[1]

$$\sigma(\omega) = \frac{n(Ze)^2}{M}\left[\left(\frac{\omega_0}{\omega_D}\right)^3 \frac{\gamma}{\gamma^2+\omega^2} + \frac{3\Gamma\omega^2}{\omega_D{}^3} F(\omega,\Gamma)\right], \quad (1)$$

with

$$F(\omega,\Gamma) = \int_{\omega_0{}^2}^{\omega_D{}^2} \frac{x\,dx}{(x-\omega^2)^2 + 4\Gamma^2\omega^2 x}, \quad (2)$$

where ω_D is the Debye frequency of the ionic carriers with mass M, n their concentration, Ze their charge, Γ a damping factor, and ω_0 the cutoff frequency ($\omega_0 = 6D/r_0{}^2$ with D the diffusion coefficient and r_0 the distance between potential minima), and γ is given in terms of ω_0 and D by

$$\gamma = (k_B T/MD)(\omega_0/\omega_D)^3, \quad (3)$$

with $D = D_0 e^{-\beta U}$ and U the hopping activation energy.

From Eq. (1) we can see that the very low-frequency behavior ($\omega < \omega_0$) is dominated by the first term, which gives a Lorentzian centered at $\omega = 0$ and with a half-width given by γ of Eq. (3). As $\omega \to \omega_0$ the contribution from the second term of Eq. (1) adds a term slowly rising as ω^2, and for $\omega_0 < \omega < \omega_D$ (but with $\omega_0 < \omega_D$) $F(\omega,\Gamma)$ contributes a Debye-like spectrum peaked near ω_D. It should be mentioned that even in the case of an Einstein density of states (as in the case of isolated impurities in the extremely dilute limit) one would get a peak around the Einstein frequency above ω_0, with the remaining features below ω_0 persisting. The Einstein peak can be in turn broadened either by (i) critical overdamping or by (ii) a distribution of Einstein frequencies of a general nature.

The general behavior outlined above is illustrated in Fig. 1, where we plot the ionic conductivity for typical parameter values of a superionic conductor. As can be seen, for a diffusion coefficient of 10^{-4} cm^2 sec^{-1} at around 700°K the half-width of the Lorentzian is of the order of 3.6 cm^{-1}, which can be easily seen by using microwave or rf techniques. As usual the $\omega = 0$ value of the conductivity is given by the Nernst-Einstein relation. Since $\gamma \simeq k_B T D^{-1} \omega_0{}^3$ as the temperature increases, both the half-width and the peak value of the Lorentzian will grow, and as $\omega_0 \to \omega_D$ the whole frequency spectrum becomes Drude-like. The point to be stressed is that, while a knowledge of the Debye peak yields in-

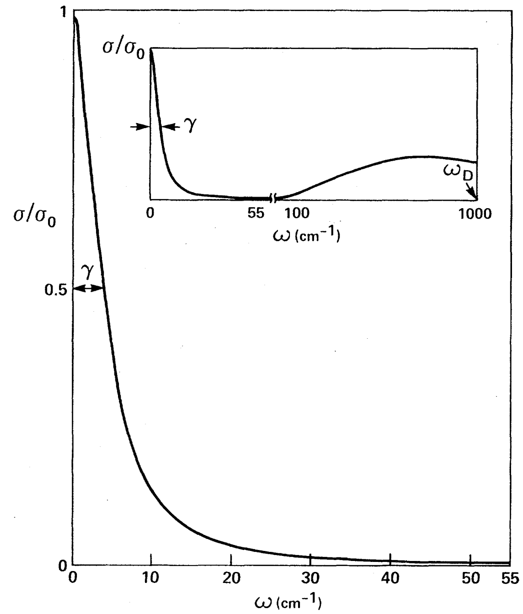

FIG. 1. The reduced ionic conductivity as a function of frequency for $\omega < \omega_0$. The parameter values are $U = 0.4$ eV, $D_0 = 0.075$ cm^2 sec^{-1}, $M = M_{\mathrm{Cu}^+}$, $n = 10^{22}$ ions cm^{-3}, $T = 723$°K, and $\omega_\mathrm{D} = 1000$ cm^{-1}. The inset shows the full frequency-dependent conductivity up to the Debye frequency.

formation on the ionic attempt frequency only,[2] a measurement of the half-width of the low-frequency conductivity gives the diffusion coefficient, so that the hopping activation energy can also be extracted from a knowledge of the full dielectric response in the regime $0 < \omega < 2\omega_\mathrm{D}$ and with $\omega_0/\omega_\mathrm{D} < 1$.

The microwave and infrared response in CuI and AgI has been measured by Funke and collaborators.[3] In the ion disordered phase the conductivity looks as shown in the inset of Fig. 1. Although the low-frequency measurements have large error bars, a least-squares fit of the microwave CuI data to a Lorentzian yields a half-width of about 0.72 cm^{-1}, which implies a diffusion coefficient $D \simeq 5.7 \times 10^{-6}$ cm^2 sec^{-1} at 723°K. From a knowledge of the Debye peak for the ionic carriers we can extract an order-of-magnitude estimate for $U \simeq 0.3$ eV. Of course more careful measurements in the microwave regime are needed before any meaningful numbers can be extracted.

It should be mentioned that since the incoherent quasielastic neutron-scattering cross section is also proportional to the velocity autocorrelation function,[4] one would expect that a measurement of its half-width in these systems would provide the same value of γ. From an experimental point of view, however, the resolution required to measure half-widths of the order of 0.1 cm^{-1} makes the conductivity techniques a much more straightforward and simpler technique.

In closing we should mention that the general formalism we have employed in calculating $\sigma(\omega)$ is universal in the sense that it applies to *any* system whose transport properties at low temperatures are of the activated type. The high diffusion coefficients found in superionic conductors allow for the manifestation of the salient features of the theory and provide a simple basis for the study of charged liquid systems.

[1]B. A. Huberman and P. N. Sen, Phys. Rev. Lett. 33, 1379 (1974).

[2]As shown by S. J. Allen, Jr., and J. P. Remeika [Phys. Rev. Lett. 33, 1478 (1974)], the hopping activation energy can be estimated if a functional form for the ionic potential is assumed.

[3]K. Funke and R. Hackenberg, Ber. Bunsenges. Phys. Chem. 76, 885 (1972); K. Funke and A. Jost, Ber. Bunsenges. Phys. Chem. 75, 435 (1971).

[4]A. Rahman, K. S. Singwi, and S. Sjölander, Phys. Rev. 126, 997 (1962).