

Incoherent Scattering and Electron Transport in Metal-Ammonia Solutions. I*

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Electron transport is considered in the metallic range of metal-ammonia solutions; the scattering centers are (i) ions and ammonia dipoles weakly bound in solvated ion complexes, and (ii) free ammonia dipoles. They form a binary liquid mixture, but only one of the three possible partial structure factors is required. From the orientational degrees of freedom of the dipoles, it can be shown that much of the scattering is incoherent. This, combined with the observation that solvated ions are relatively weak scatterers, accounts in large measure for the high conductivities measured in metal-ammonia solutions.

I. INTRODUCTION

Above a certain concentration of the metallic component (about 8 mole % metal¹), metal-ammonia solutions are, by all the usual definitions, good metals. One feature they exhibit is, however, quite unusual: We refer to the extraordinary dependence of their conductivities on the concentration of metallic ions. They increase sharply as a function of the concentration of metal, a behavior which at the very least is difficult to reconcile with elementary Drude theory incorporating a single relaxation time τ . For if, at a given concentration, n_e is the assumed density of free electrons, then the conductivity σ is given as usual by

$$\sigma = n_e e^2 \tau / m ; \quad (1)$$

and while it is, of course, clear that an increase in n_e (in proportion to metal concentration) should be followed by an increase in σ , we cannot escape the accompanying consequence that an increase in the number of ions regarded as scatterers should shorten τ . An elementary interpretation of (1) leads to a very weak dependence of σ on n_e , something like $n_e^{1/3}$.

The experiments, on the other hand, suggest a dependence more like n_e^3 (depending on the system); and to account for this curious behavior we propose that the over-all scattering of electrons proceeds by two basically independent scattering mechanisms to be described in detail in the following sections. The basic point concerns the presence of orientable dipoles as electron scatterers, both "free" and bound up in so-called solvated ions. Calculations of the conductivity for the metallic solutions clearly involve the execution of configuration averages of both density fluctuations and dipolar moment fluctuations. The latter, being to a good approximation independent of the former, reduces much of the total cross section to that expected from a set of independent or inco-

herent scatterers.

The formalism is set up in a pseudopotential approximation.² As a consequence, the usual one-electron potentials seen by conduction electrons are canceled and much reduced in the core-state regions of ions. This is also true in molecules, and we assume it to be true in the NH_3 molecules, whether bound or free. As it happens, the practical ramifications of this assumption are minimal, since for these metals the maximum momentum transfer $2k_F$ is quite small and only the screened long-range parts of the various potentials are pertinent. Further, there is experimental evidence³ that electron scattering from ammonia is well reproduced by a point-dipole potential using (as we shall here) the Born approximation.

In the present paper, we shall outline the calculation of σ : While the bulk of the numerical work for a variety of systems will be given in a later work, we will illustrate the physical points as they arise with the system $\text{Li}(\text{NH}_3)_x$.

II. ELECTRON SCATTERING MECHANISMS

Even in the most concentrated metallic range, it appears that the metallic ions are solvated: The field of an ion polarizes the NH_3 molecules, a few of which (say, λ) subsequently bind themselves weakly to the ion. (Freely moving conduction electrons are largely excluded by orthogonalization from the interior of these complexes and therefore cannot entirely screen out the ion-ammonia bond.) The following physical picture of the solution now seems to be established: As the metal is dissolved into solution, the valence electrons dissociate, each resulting ion combining with λ ammonia molecules⁴ and concomitantly decreasing the number of unbound (which we call "free") molecules.

Metal-ammonia solutions (for general metal-metallic concentrations) may be viewed as binary mixtures, the components being solvated ions and

free-ammonia molecules. Schroeder and Thompson⁵ have already exploited this model in a calculation of the thermodynamic functions of metal-ammonia solutions.

We take the solvated ion and the dipolar ammonia molecule to be the two basic scatterers, whose cross sections will be evaluated (in accordance with our assumptions pertaining to a pseudo Hamiltonian) in first Born approximation. For a binary system of *spherically symmetric* scatterers, the resistivity is proportional to⁶

$$\int_0^1 dy y^3 [(1-x)V_1^2(y)S_{11}(y) + 2[x(1-x)]^{1/2}V_1(y) \times V_2(y)S_{12}(y) + xV_2^2(y)S_{22}(y)] , \quad (2)$$

where $V_1(y)$, $V_2(y)$ are the Fourier transforms⁷ of the spherically symmetric electron-ion interactions for the two species, $(1-x)$ and (x) are their concentrations, and the $S_{ij}(y)$ are the partial-structure factors. We now outline the necessary modifications to (2) which result from the obvious anisotropy inherent in electron scattering from metal-ammonia systems.

To elucidate the important physical differences, let us initially consider the first term in (2). It arises in the Born approximation⁸ from configuration averages over Fermi-surface scattering matrix elements of the kind

$$|\langle \vec{k}' | \sum_{\vec{r}_1} V_1(\vec{r} - \vec{r}_1) | \vec{k} \rangle|^2 , \quad (3)$$

where \vec{r}_1 are the instantaneous positions of the centers of the potential $V_1(\vec{r})$. Equation (3) gives

$$\langle \rho_{\vec{k}-\vec{k}'}^{(1)} \rho_{\vec{k}'-\vec{k}}^{(1)} \rangle |V_1(\vec{k}' - \vec{k})|^2 ,$$

$$\text{where } \rho_{\vec{k}-\vec{k}'}^{(1)} = \sum_{\vec{r}_1} e^{-i(\vec{k}-\vec{k}') \cdot \vec{r}_1} \quad (4)$$

is a Fourier component of the density fluctuation of ions of species (1), and the quantity $\langle \rho_{\vec{k}-\vec{k}'}^{(1)} \rho_{\vec{k}'-\vec{k}}^{(1)} \rangle$ leads to the partial-structure factor S_{11} .

We repeat the argument for a potential $V_1(\vec{r})$ that is no longer spherically symmetric. In fact, let us associate $V_1(\vec{r})$ with the potential of a point dipole⁹ of moment $\vec{\mu}$. For a collection of these at points \vec{r}_1 , the interaction energy with an electron at point \vec{r} is

$$(-e) \sum_{\vec{r}_1} \vec{\mu}_1 \cdot (\vec{r} - \vec{r}_1) / |\vec{r} - \vec{r}_1|^3 ;$$

its matrix elements in plane wave states are¹⁰

$$(-e) \langle \vec{k}' | \sum_{\vec{r}_1} \vec{\mu}_1 \cdot (\vec{r} - \vec{r}_1) / |\vec{r} - \vec{r}_1|^3 | \vec{k} \rangle$$

$$= \sum_{\vec{r}_1} e^{-i\vec{r}_1 \cdot (\vec{k}' - \vec{k})} \frac{i4\pi e}{(\vec{k}' - \vec{k})^2} \vec{\mu}_1 \cdot (\vec{k}' - \vec{k}) ,$$

and its square with $\vec{K} = \vec{k}' - \vec{k}$ is

$$\left(\frac{4\pi e}{K^2} \right)^2 \sum_{\vec{r}_1, \vec{r}_1'} e^{i(\vec{r}_1' - \vec{r}_1) \cdot \vec{K}} (\vec{\mu}_1 \cdot \vec{K}) (\vec{\mu}_1' \cdot \vec{K}) . \quad (5)$$

It is (5) which must now be averaged over all spatial configurations (S), in any particular one of which *all* angular orientations (A) of the dipoles are assumed equally likely.¹¹ It follows that in

$$\left(\frac{4\pi e}{K^2} \right)^2 \left\langle \sum_{\vec{r}_1, \vec{r}_1'} e^{i(\vec{r}_1' - \vec{r}_1) \cdot \vec{K}} \times (\vec{\mu}_1 \cdot \vec{K}) (\vec{\mu}_1' \cdot \vec{K}) \right\rangle_{S,A} , \quad (6)$$

the terms with $\vec{r}_1' \neq \vec{r}_1$ may be written

$$\begin{aligned} & \left(\frac{4\pi e}{K^2} \right)^2 \left\langle \sum_{\vec{r}_1 \neq \vec{r}_1'} e^{i(\vec{r}_1' - \vec{r}_1) \cdot \vec{K}} \right. \\ & \quad \left. \times (\vec{\mu}_1 \cdot \vec{K}) (\vec{\mu}_1' \cdot \vec{K}) \right\rangle_{S,A} \\ & = \left(\frac{4\pi e}{K^2} \right)^2 \left\langle \sum_{\vec{r}_1 \neq \vec{r}_1'} e^{i(\vec{r}_1' - \vec{r}_1) \cdot \vec{K}} \right. \\ & \quad \left. \times \langle \vec{\mu}_1 \cdot \vec{K} \rangle_A \langle \vec{\mu}_1' \cdot \vec{K} \rangle_A \right\rangle_S \\ & = 0, \end{aligned}$$

since $\langle \vec{\mu} \cdot \vec{K} \rangle_A$ vanishes. With N_d the number of free dipoles, the left-hand side of (6) becomes

$$N_d \left(\frac{4\pi e}{K^2} \right)^2 \langle (\vec{\mu}_1 \cdot \vec{k})^2 \rangle_A , \quad (7)$$

and therefore represents independent scattering.

We turn now to the equivalent of the third term in Eq. (2). In the present case, the scattering is given by

$$\langle |\langle \vec{k}' | \sum_{\vec{r}_2} V_2(\vec{r} - \vec{r}_2) | \vec{k} \rangle|^2 \rangle_{S,A} , \quad (8)$$

where, in accordance with the model of the solvated atom,

$$V_2(\vec{r}) = V_i(\vec{r}) + \sum_{l=1}^{\lambda} V'_{1,l}(\vec{r} - \vec{r}_l) .$$

Basis vectors of the ammonia molecules linked to the metal ion are denoted by \vec{r}_l , and the electron-

ion interaction is described by a local pseudopotential $V_i(\vec{r})$. The prime on $V_{1,l}$ indicates that because of molecular bonding and polarization the dipolar potential differs slightly from $V_1(\vec{r})$. Writing $\vec{K} = \vec{K}' - \vec{k}$ again, Eq. (8) becomes

$$\left\langle \sum_{\vec{r}_2, \vec{r}'_2} e^{-i\vec{K} \cdot (\vec{r}_2 - \vec{r}'_2)} \left[V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right] \right. \\ \left. \times \left[V_i^*(\vec{K}) + \sum_{m=1}^{\lambda} e^{i\vec{K} \cdot \vec{r}_m} V'_{1,m}^*(\vec{K}) \right] \right\rangle_{S,A}, \quad (9)$$

where $V'_{1,m}(\vec{K})$ is the \vec{K} th Fourier component of the electron interaction with the dipole at site m on the ion at position \vec{r}'_2 .

First consider terms with $\vec{r}_2 = \vec{r}'_2$. These give a contribution

$$N_i \left\langle \left| V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right|^2 \right\rangle_A. \quad (10)$$

The remaining terms of (9) always involve ions at different positions ($\vec{r}_2 \neq \vec{r}'_2$), and now the angular averages (A) of any such two solvated ions are independent for rotations about each central ion:

$$\left\langle \sum_{\vec{r}_2 \neq \vec{r}'_2} e^{-i\vec{K} \cdot (\vec{r}_2 - \vec{r}'_2)} \left[V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right] \left[V_i^*(\vec{K}) + \sum_{m=1}^{\lambda} e^{i\vec{K} \cdot \vec{r}_m} V'_{1,m}^*(\vec{K}) \right] \right\rangle_{S,A} \\ = \left\langle \sum_{\vec{r}_2 \neq \vec{r}'_2} e^{-i\vec{K} \cdot (\vec{r}_2 - \vec{r}'_2)} V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right\rangle_A \left\langle V_i^*(\vec{K}) + \sum_{m=1}^{\lambda} e^{i\vec{K} \cdot \vec{r}_m} V'_{1,m}^*(\vec{K}) \right\rangle_A \\ = \left\langle \sum_{\vec{r}_2, \vec{r}'_2} e^{-i\vec{K} \cdot (\vec{r}_2 - \vec{r}'_2)} \left| \left\langle V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right\rangle_A \right|^2 \right\rangle_S - \left\langle \sum_{\vec{r}_2 = \vec{r}'_2} \left| \left\langle V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right\rangle_A \right|^2 \right\rangle_S \\ = N_i S_{ii}(\vec{K}) \left| \left\langle V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right\rangle_A \right|^2 - N_i \left| \left\langle V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right\rangle_A \right|^2, \quad (11)$$

where N_i is the number of ions (and therefore of solvated atoms) and S_{ii} is the partial-structure factor for the solvated ions. Hence, combining (10) and (11), (9) becomes

$$N_i S_{ii}(\vec{K}) \left| \left\langle V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right\rangle_A \right|^2 \\ + N_i \left[\left\langle \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right\rangle_A^2 - \left\langle \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right\rangle_A^2 \right]. \quad (12)$$

[We have used the fact that $V_i(\vec{K})$ has no angular dependence.]

Finally, we consider the two cross terms (dipole, solvated-ion) corresponding to the second term of Eq. (2), one of which is

$$\left\langle \sum_{\vec{r}_1, \vec{r}_2} e^{i\vec{K} \cdot (\vec{r}_1 - \vec{r}_2)} \left[V_i(\vec{K}) + \sum_{l=1}^{\lambda} e^{-i\vec{K} \cdot \vec{r}_l} V'_{1,l}(\vec{K}) \right] \left[V_{1,\mu_1}^*(\vec{K}) \right] \right\rangle_{S,A},$$

$$\text{or} \quad \left\langle \sum_{\vec{r}_1, \vec{r}_2} e^{i\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)} \langle V_i(\vec{k}) + \sum_{l=1}^{\lambda} e^{-i\vec{k} \cdot \vec{r}_l} V'_{1,l}(\vec{k}) \rangle_A \cdot \langle V_{1, \vec{\mu}_1}^*(\vec{k}) \rangle_{A/S} \right\rangle = 0,$$

since $\langle V_{1, \vec{\mu}_1}(\vec{k}) \rangle_A$ vanishes. We are thus left with (12) and (7) as the total scattering which corroborates our assertion of two independent classes of scatterers,¹² at least in the Born approximation.

We remark that the physical significance of performing independent angular averages (as we have done here) is familiar in another context: We refer to the incoherent terms in neutron scattering from liquids. These are independent of liquid structure and bear at least a formal similarity to (7). Contributions of this nature to electron scattering may also be referred to as incoherent. In the case of electron scattering from free dipoles, we have (for low-momentum transfers) completely incoherent scattering, in contrast to electron-solvated atom scattering where no simple division between coherent and incoherent is evident.

III. FORM OF RESISTIVITY FOR INDEPENDENT SCATTERERS

The dipoles and solvated atoms act as independent scattering groups; the scattering from the solvated ions still involves a knowledge of their correlations. In the Born approximation, the resistivity for this system may be written

$$\rho = (m/n_e e^2) (\tau_i^{-1} + \tau_d^{-1}),$$

where n_e is the electron density

$$3\pi^2 n_e = (mv_F/\hbar)^3 = k_F^3,$$

and

$$\frac{1}{\tau_i} = 2\pi v_F n_e \int_0^\pi \left(\frac{d\sigma_i}{d\Omega} \right) (1 - \cos\theta) \sin\theta d\theta, \quad (13)$$

$$\frac{1}{\tau_d} = 2\pi v_F (n_d - \lambda n_e) \int_0^\pi \left(\frac{d\sigma_d}{d\Omega} \right) (1 - \cos\theta) \sin\theta d\theta. \quad (14)$$

By n_d and $n_d - \lambda n_e$ we mean, respectively, the total density of NH_3 molecules (whether bound or free) and the density of free NH_3 molecules. The quantities $(d\sigma_i/d\Omega)$ and $(d\sigma_d/d\Omega)$ denote the differential scattering cross sections per scatterer of solvated ions and of free NH_3 molecules.¹³ These are easily calculated using the configuration averaged matrix element expressions of Sec. II:

$$\begin{aligned} \left(\frac{2\pi\hbar^2}{m} \right)^2 \left(\frac{d\sigma_i}{d\Omega} \right) &= S_{ii}(K) \left| \langle V_i(\vec{k}) + \sum_{l=1}^{\lambda} e^{-i\vec{k} \cdot \vec{r}_l} \right. \\ &\times V'_{1,l}(\vec{k}) \rangle_A \left. \right|^2 + \left| \langle \sum_{l=1}^{\lambda} e^{-i\vec{k} \cdot \vec{r}_l} V'_{1,l}(\vec{k}) \rangle_A \right|^2 \\ &- \left| \langle \sum_{l=1}^{\lambda} e^{-i\vec{k} \cdot \vec{r}_l} V'_{1,l}(\vec{k}) \rangle_A \right|^2 \end{aligned} \quad (15)$$

and

$$\left(\frac{2\pi\hbar^2}{m} \right)^2 \left(\frac{d\sigma_d}{d\Omega} \right) = \langle | \langle \vec{k}' | V_{1,l}(\vec{r}) | \vec{k} \rangle |^2 \rangle_A. \quad (16)$$

The (solvated-ion)-(solvated-ion) structure factor $S_{ii}(K)$ is calculated from the theory of Ashcroft and Langreth.¹⁴ Expressed in units of mole % metal, its behavior at 9.8, at 17.4, and at saturation, 20, for the $\text{Li}(\text{NH}_3)_x$ system is shown in Fig. 1.

IV. DISCUSSION

We are now in a position to see why the resistivity drops so rapidly with increasing metallic con-

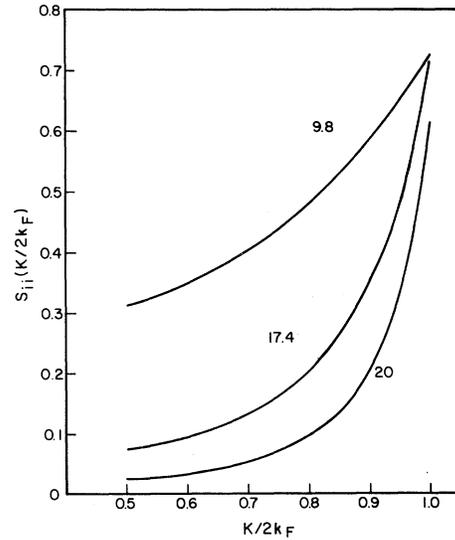


FIG. 1. Behavior of $S_{ii}(K)$ for the solvated ions in the $\text{Li}(\text{NH}_3)_x$ system (taken from Ref. 14). Expressed in units of mole % metal, the curves refer to concentrations of 9.8, 17.4, and 20 (the latter corresponding to saturation where the system is a single-component liquid). We draw attention to the substantial change which occurs in lowering the concentration from saturation to 17.4. The region of K that is plotted dominates the integrands in the formulas for ρ .

centration. As the concentration of the metallic component increases (n_e increases), the number of unbound NH_3 is speedily depleted ($n_d - \lambda n_e$ rapidly decreases). At the same time, the scattering from the solvated ions, measured by $d\sigma_i/d\Omega$, decreases rapidly and is, in fact, rather small in the first place. The reason for this can be seen by examining (15): The two terms involving only the dipoles are both numerically large, have approximately the same magnitude but clearly differ in sign. The subsequent cancellation is a reflection mainly of the characteristic size and geometry of solvated atoms, and although we demonstrate it here explicitly for the case of $\text{Li}(\text{NH}_3)_x$, it persists in other systems. The first term in (15) involves the angular average of the potential of the central ion plus the potentials of the bound dipoles. At large K , where the most important scattering takes place, the ion potential is canceled by the dipole potentials. In other words, because of the internal structure of the solvated ion, the scattering (relative to that of a single ion) is greatly diminished. We also note that all of the bare potentials are divided (and hence reduced) by the Lindhard screening function¹⁵ $\epsilon(K)$ which accounts for the response of the conduction electrons to the fields of dipoles and ions.

The combined rapid variations of τ_i^{-1} and τ_d^{-1} dominate the rather slow variation of n_e itself. In the case of lithium amine, the calculation results in the curve shown in Fig. 2. Following Sienko,¹⁶ $\lambda = 4$ and the four NH_3 molecules are taken to have a tetrahedral arrangement about the central ion with dipole moments pointing radially outwards. Dipoles and ions are separated by a distance of 2.2 Å: The over-all size or hard-sphere diameters which are required in S_{ii} are taken from Ref. 5. For unbound NH_3 molecules, the dipole moment has a value of 1.47×10^{-18} esu.¹⁷ Bound dipoles have a moment of value 1.86×10^{-18} esu.¹⁸ The angular averages can all be calculated in closed form.¹⁹

In addition to the efficient cancellation of the second and third terms in (15), we draw attention to the behavior of the first term²⁰ as a function of n_e . As well as being important in the temperature dependence of ρ ,¹⁹ the presence of $S_{ii}(K)$ causes a sharp variation in its contribution. It can be seen in Fig. 1 that at concentrations near saturation almost the entire weight of the integral comes from around $2k_F$. With a decrease in metal concentration, contributions from other K values enter with

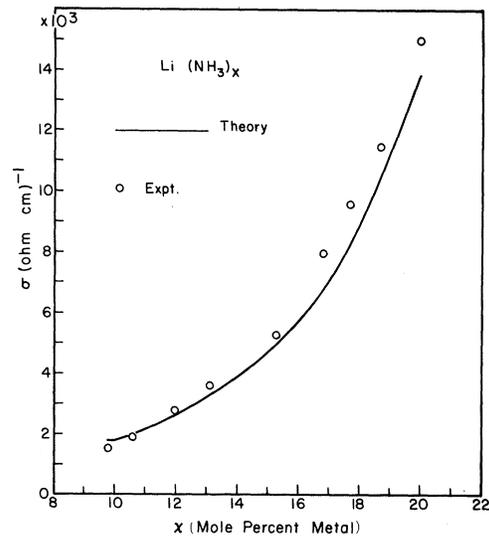


FIG. 2. Comparison of measured and calculated conductivities for the system $\text{Li}(\text{NH}_3)_x$ at 210°K. The experimental data is taken from J. A. Morgan, R. L. Schroeder, and J. C. Thompson, *J. Chem. Phys.* **43**, 4494 (1965); and D. S. Kyser and J. C. Thompson, *ibid.*, **42**, 3910 (1965).

rapidly increasing weight.

Finally we emphasize that although the trend of the theoretical curve given in Fig. 2 can now be understood, the rather exceptional numerical agreement must be regarded as partly fortuitous. In the first place, some of the parameters required in Eqs. (15) and (16) are not known with the best precision. In the second place, the calculation of ρ is performed only to lowest order. While it is true that because of the additional rotational degrees of freedom (and the associated phase averaging) some of the higher-order terms in ρ are bound to vanish, others – particularly those in the coherent scattering – will remain and the usual difficulties with this kind of calculation will prevail.

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¹We will use the concentration notation adopted in the review article of M. H. Cohen and J. C. Thompson, *Advan.*

Phys. **17**, 857 (1968).

²See, for example, W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

³L. G. Christophorou and A. A. Christodoulides, *J.*

Phys. B2, 71 (1969).

⁴In some systems λ may be a function of concentration.

⁵R. L. Schroeder and J. C. Thompson, Phys. Rev. 179, 124 (1969); and (to be published).

⁶T. Faber and J. M. Ziman, Phil. Mag. 11, 153 (1965); N. W. Ashcroft and D. C. Langreth, Phys. Rev. 159, 500 (1967).

⁷The basic-wave number variable y is expressed in units of $2k_F$.

⁸As is common, we approximate the pseudowave function by a plane wave.

⁹We have already remarked that there will be finite size corrections to the dipole field. These are included in the definition of the molecular pseudopotential and they are important only for large $\vec{k} - \vec{k}'$.

¹⁰The orientation of $\vec{\mu}$ differs from molecule to molecule. As a notational simplification, we write $\vec{\mu}_1$ when, in fact, we mean $\vec{\mu}_1(\vec{r}_1)$.

¹¹It is not *a priori* obvious that the orientational degrees of freedom of a dipole are independent of the spatial degrees. The fields tending to align the dipoles certainly relate to the configurations of the dipoles. While this argument cannot be disputed for a collection of pure dipoles, its efficiency is reduced substantially when electrons are present. Electron screening limits the dipole-dipole interactions to an exceedingly short range; the long-range spatial coupling of the dipoles is virtually eliminated and hence the angular orientations should become independent of the spatial configurations. It is precisely the long-range behavior which is of interest here.

¹²By independent we mean that the scattering from dipoles and solvated atoms suffers no interference. The

solvated atoms, though independent of the free dipoles in the transport problem, give a contribution dependent on their own correlations.

¹³The momentum transfer $\vec{k}' - \vec{k}$ is related to θ by $|\vec{k}' - \vec{k}| = 2k_F \sin(\frac{1}{2}\theta)$.

¹⁴N. W. Ashcroft and D. C. Langreth, Phys. Rev. 156, 685 (1967).

¹⁵See, for example, D. Pines and P. Nozieres, The Theory of Quantum Liquids (W. A. Benjamin, Inc., New York, 1966), Vol. I. On physical grounds, we expect the density of the electron gas around the free dipoles to be slightly lower than average, while around the solvated ions it is slightly higher. By using Lindhard screening for both, there will be a slight overscreening of the dipoles and underscreening of the solvated ion. Correcting for this will lead to a somewhat sharper rise in the calculated σ .

¹⁶Metal Ammonia Solutions, edited by G. Lepoutre and M. J. Sienko (W. A. Benjamin, Inc., New York, 1964), p. 25.

¹⁷A. L. McClellan, Tables of Experimental Dipole Moments (W. H. Freeman and Co., San Francisco, 1963).

¹⁸Small changes either side of this value are found to cause minor increases in ρ . For example, increasing μ to 2.3×10^{-18} changes ρ by about 10%. The increase in μ is a reasonable estimate of the additional moment produced by the (slightly screened) field of the ion.

¹⁹G. Russakoff (to be published).

²⁰The potential $V_i(K)$ for lithium is taken as an empty core pseudopotential [N. W. Ashcroft, J. Phys. C1, 232 (1968)]. Note, however, that the density of carriers is sufficiently low that core corrections to point ion scattering are small.