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**Etude de la diffusion multiple des électrons dans  
les métaux désordonnés**

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Raymond Frésard

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# IMPRIMATUR POUR LA THÈSE

Etude de la diffusion multiple des électrons  
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de Monsieur Raymond Frésard

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La Faculté des sciences de l'Université de Neuchâtel  
sur le rapport des membres du jury,

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autorise l'impression de la présente thèse.

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Multiple Scattering Effects in Liquid and Amorphous Metals: Cluster Calculations.

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Multiple Scattering Effects in Electronic Transport in Liquid and Amorphous Metals.

R. Frésard, H. Beck  
Zeit. für Phys. Chemie Neue Folge 157, 617 (1988)

Electrons in Non-Crystalline Metals - Still a Challenging Problem.

H. Beck, R. Frésard, Y. Cuhe  
Z. Phys. B Cond. Matter 68, 237 (1987)

Scattering From Two Non-Overlapping Centers.

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Study of the temperature coefficient of the resistivity of liquid and amorphous metals: Cluster calculations.

R. Frésard, H. Beck  
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En outre l' article:

Multiple Scattering Theory of Electron Transport in Disordered Metals in the Muffin-tin Model: I - EMA Formulation and the Separation of Off-shell Corrections, par M. Itoh, H. Beck et R. Frésard, a été accepté pour publication par Journal of Physics: Condensed Matter,

ainsi que l'article:

Muffin-tin Ema Calculations of Electrical Resistivity for Liquid and Amorphous Metals, par R. Frésard, H. Beck et M. Itoh, qui apparaîtra dans les Proceedings of the LAM-7 Conference, Kyoto, Japan, 1989, Ed: H. Endo, en tant que numéro spécial du Journal of Non-Crystalline Solids.

Un exemplaire complet de ce travail de thèse est déposé à la bibliothèque de l'université de Neuchâtel, 26 avenue du 1<sup>er</sup> Mars 2000 Neuchâtel

## MULTIPLE SCATTERING EFFECTS IN LIQUID AND AMORPHOUS METALS: CLUSTER CALCULATIONS

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We have calculated the density of states, the resistivity  $\rho$  and the thermopower of small clusters of  $s$ -scatterers using the full, multiple scattering amplitude for the conduction electrons. The density of states shows a structure induced minimum. The multiple scattering contributions to  $\rho$  can be positive or negative depending on the position of the Fermi energy. The influence of disorder (temperature) on  $\rho$  can be quite different from the Ziman rule, pointing to predominantly negative temperature coefficients of  $\rho$  in strong scattering systems (Mooji rule).

### 1. Introduction

The calculation of transport coefficients for disordered (in particular liquid and amorphous) metals is an outstanding problem, which, in spite of much theoretical effort, has not yet found a satisfactory solution. Whereas in crystalline metals very reliable band structure calculations are available, and the “only” problem consists in finding the appropriate form of electron–phonon interaction, the absence of long range order still represents a serious theoretical difficulty.

Most of the calculations of electrical resistivity, for example, have been done in the framework of Ziman’s theory, using either a pseudopotential or an atomic  $t$ -matrix in order to describe the electron–ion scattering [1]. This approach has the merit of leading to concrete results without too much computational effort, but it neglects all multiple scattering effects. Moreover, one is often forced to make assumptions about the values of the Fermi energy  $E_F$  and the Fermi wave vector  $k_F$ , which may not be “consistent” with each other [2].

Better approximations can be based on exact formulae for electrical transport coefficients, which are of two different types. The Kubo–Greenwood formula on one hand expresses the conductivity in terms of a (configurationally averaged) two-electron Green function [3]. Suitable

approximations for the one-electron self-energy and the vertex function yield corrections to the Ziman expression, which are of higher order in the atomic  $t$ -matrix [4, 12]. In the same Kubo–Greenwood approach the effective medium approximation of Roth [5] has been applied to transport properties by Itoh et al. [6, 7].

This paper is based on an alternative approach, offered by an expression for the resistivity  $\rho$  in terms of the total scattering matrix  $T(k, k')$  of the metal giving the scattering amplitude for an elastic electron–ion collision from momentum  $\hbar k$  to  $\hbar k'$ . At zero temperature it has the form

$$\rho = \frac{3\hbar}{2^7\pi\Omega e^2 k_F^4} \int d\Omega_k \times \int d\Omega_{k'} (k - k')^2 |T(k, k', E_F)|^2. \quad (1.1)$$

$\Omega$  being the volume of the system and the integrations running over the directions of  $k$  and  $k'$ , the absolute value of which is given by  $k^2 = k'^2 = k_F^2 = 2mE_F/\hbar^2$ . As stated by Dunleavy and Jones [8] this result can be obtained by a Boltzmann equation approach [9] where the transition probability in the collision integral is given by  $|T(k, k')|^2$ . Expression (1.1) can also be found starting from a force–force correlation

function expression for  $\rho$  [10]. However, the exact form of  $\rho$  in such an approach also involves a denominator. Rather than entering into the controversy about the correct form of  $\rho$  in this context [11, 8] we motivate our choice of studying (1.1) by two arguments. First, the Boltzmann equation approach appeals to our physical intuition. Its usual limitation to the regime of long mean free path is not valid here, since the quantity  $|T(\mathbf{k}, \mathbf{k}')|^2$  entering (1.1) rigorously describes the scattering effect of all the ions on an incoming free electron and thus (1.1) yields the resistivity of a piece of metal which is connected to a perfect conductor (i.e. free electron boundary conditions). Secondly, eq. (1.1) – even if it is not rigorously the exact expression for the resistivity – allows for an interesting discussion of multiple scattering contributions to the scattering properties of a given arrangement of ions, which is the main goal of this work.

An expansion of the scattering amplitude  $T$  of a given system in terms of the  $t$ -matrix of the individual atom is particularly useful for an ensemble of non-overlapping muffin-tin scatterers. In this situation only the energy-shell part of  $T$  is needed, which can be calculated, in principle at least, by a simple matrix inversion. The main results of such a multiple scattering expansion for  $T$ , namely the density of states  $D(E)$  and the resistivity, are summarized in section 2. For a concrete system one would first evaluate the Fermi energy  $E_F$ , using the rigorous form of  $D(E)$ . This fixes the length  $\hbar k_F = (2mE_F)^{1/2}$  of the momenta  $\hbar k$  and  $\hbar k'$  of the incoming and outgoing electrons, respectively. The integral (1.1) then yields the resistivity. It is important to notice that the free electron relation  $(\hbar k)^2 = (\hbar k')^2 = 2mE_F$  is only a consequence of the boundary conditions used in the scattering ring calculation (a piece of metal immersed in a free electron gas) and does *not* mean that “band structure effects” induced by the electron-ion interaction are neglected. The latter are, of course, included in the exact form of  $T$ .

Previous calculations of  $\rho$  which included some multiple scattering effects [8, 4, 12] have shown that multiple scattering contributions can lead to positive or negative corrections to the lowest

order (single site) Ziman result. However, evaluating multiple scattering in  $|T|^2$  invariably necessitates some approximation for higher order ionic correlation functions, which are not easy to control.

The goal of our calculations, presented here, is to obtain more insight into the qualitative behaviour and the quantitative contribution of multiple scattering in electronic transport in disordered metals, without making any approximation for ionic structure factors. In order to be able to implement the results of section 2 we have concentrated on small systems, i.e. clusters of a small number of muffin-tin scattering centers, for which we evaluate  $\delta D(E)$ , the correction to the free electron state density due to the ions, the resistivity  $\rho(E_F)$  and the thermopower  $Q(E_F)$ . The relevance of these results is twofold: on one hand they can be taken as cluster results in their own right and can in principle be compared with experimental data, if one succeeds in implanting small clusters of a given element into a free electron like matrix (like Cu or an alkali metal). If these clusters are sufficiently distant from each other in the matrix the measured  $\Delta D$  and  $\rho$  would simply be the (incoherent) sum of the contributions of each cluster, or – stated differently – they would be equal to the average  $\delta D_c$  and  $\rho_c$  (for a cluster) multiplied by the number  $N_c$  of clusters:

$$\delta D = N_c \delta D_c, \quad \rho = N_c \rho_c. \quad (1.2)$$

On the other hand, these equations can also be used as an approximation for  $\delta D$  and  $\rho$  of a macroscopic (concentrated) system the local structure of which is given by clusters of the type used to compute  $\delta D_c$  and  $\rho_c$ . Eqs. (1.2) then amount to neglecting all coherence effects between the multiple scattering of an electron from different clusters (i.e. by neglecting all terms in (2.2) which involve  $t$ -matrices in different clusters): the solid is modelled by a dense packing of small clusters, whereby the multiple scattering inside a cluster is treated exactly, but the coherence effects between clusters is neglected.

This is certainly an incomplete approach for calculating the resistivity of a given metal, and

thus we have not done our calculations with the intention to compare our numbers with experimental data. Rather, we wish to exploit such cluster calculations in two ways:

(i) The importance of multiple scattering in the results for  $\delta D_c$  and  $\rho_c$  is investigated as a function of cluster structure, cluster size and Fermi energy. Some general features concerning for example the difference between the full result for  $\rho$  and the single-site approximation, as a function of  $E_F$  and similar aspects are extracted and explained in simple physical terms.

(ii) The cluster data shall be used as a guideline and as a "judge" for developing analytic approximations in the calculation of  $\rho$  for a macroscopic system which go beyond the Ziman approximation. This is the scope of future work.

The rest of the paper is organized as follows: section 2 summarizes the (muffin-tin) multiple scattering formalism, section 3 gives more details about our cluster calculations (types of clusters treated etc.). The numerical results are presented in section 4 and a summary is given in the last section.

## 2. Summary of multiple scattering results

We consider the scattering properties of the one-electron Hamiltonian

$$H = \frac{p^2}{2m} + \sum_{n=1}^N V_n(r - R_n), \quad (2.1)$$

where  $V_n$  is a muffin-tin potential attached to site  $R_n$ . According to the general multiple scattering formalism, summarized, for example, by Ehrenreich and Schwartz [13] the total scattering operator  $T$  is expressed by the single-site scattering operators  $t_n$  and the free electron propagator  $G_0$ :

$$T = \sum_n t_n + \sum_{\substack{n,m \\ (n \neq m)}} t_n G_0 t_m + \dots \quad (2.2)$$

Alternatively,  $T$  can be decomposed in a sum over "path operators"  $\tau_{nm}$  such that the matrix element of  $T$  in plane wave states is given by

$$T(k, k') = \sum_{n,m} e^{ik \cdot R_n - ik' \cdot R_m} \tau_{nm}(k, k'). \quad (2.3)$$

Each  $\tau_{nm}$  has an angular momentum decomposition ( $L \equiv l, m$ )

$$\tau_{nm}(k, k') = (4\pi)^2 \sum_{LL'} Y_L(k) \tau_{nm}^{LL'} Y_L(k'). \quad (2.4)$$

In principle  $T$  and each  $\tau$  depend on an energy variable  $E$ . However, owing to our free electron boundary conditions for scattering, we only need "energy-shell matrix elements", for which  $E = (\hbar k)^2/2m = (\hbar k')^2/2m \equiv (\hbar \kappa)^2/2m$  then,  $\tau_{nm}^{LL'}(k, k')$  - which we denote by  $\tau_{nm}^{LL'}(\kappa)$  - is given by [13]

$$\tau_{nm}^{LL'}(\kappa) = ([\tau^{-1}(\kappa) - B(\kappa)]^{-1})_{nm}^{LL'}. \quad (2.5)$$

Here

$$B_{nm}^{LL'} = 4\pi i \kappa \sum_{L_1} i^{(l-l'-l_1)} C_{LL'L_1} \times Y_{L_1}(R_n - R_m) h_{l_1}^+(\kappa | R_n - R_m) (\delta_{nm} - 1) \quad (2.6)$$

with

$$C_{LL'L'} = \int d\Omega Y_L(r) Y_{L'}(r) Y_{L'}(r) \quad (2.7)$$

and  $h_l^+$  being the outgoing spherical Hankel function. The matrix  $\tau$  involving the single-site phase-shifts  $\delta_n^L$  is diagonal

$$\tau_{nm}^{LL'}(\kappa) = -\delta^{LL'} \delta_{nm} \kappa^{-1} e^{i\delta_n^L(\kappa)} \sin \delta_n^L(\kappa). \quad (2.8)$$

Inserting the solution of (2.5) and (2.3) into (1.1) we can in principle evaluate the resistivity  $\rho$  of a metal composed of  $N$  such muffin-tin ions. A more explicit form for  $\rho$  will be written down below for the case of s-scattering only.

The change in the electronic density of states can also be expressed by the matrices  $\tau$  and  $B$  [13]. An interesting alternative is offered by the generalized cluster phase-shifts [14, 15]. They are defined in such a way that the matrix  $\tau$  (eq. (2.5)) is diagonalized.

Using  $h_l^+ = j_l + i n_l$  we can decompose  $B$  into its real and imaginary parts:

$$B = \kappa[N - i(J - 1)] \quad (2.9)$$

with

$$N_{nm}^{LL'} = (1 - \delta_{nm} \delta^{LL'}) 4\pi \sum_{L_1} C_{LL'L_1} i^{(l-l_1)} \times Y_{L_1}(\mathbf{R}_n - \mathbf{R}_m) n_{l_1}(\kappa |\mathbf{R}_n - \mathbf{R}_m|), \quad (2.10)$$

$$J_{nm}^{LL'} = 4\pi \sum_{L_1} C_{LL'L_1} i^{(l-l_1)} \times Y_{L_1}(\mathbf{R}_n - \mathbf{R}_m) j_{l_1}(\kappa |\mathbf{R}_n - \mathbf{R}_m|). \quad (2.11)$$

Thus, from (2.5),

$$\tau^{-1} = -\kappa[N + C - iJ] \quad (2.12)$$

with

$$C_{nm}^{LL'} = \delta_{nm} \delta^{LL'} \text{ctg } \delta_n^L. \quad (2.13)$$

We now diagonalize the matrix

$$M \equiv I^{-1}(N + C)I^{-1}. \quad (2.14)$$

$I = J^{1/2}$  being the square root of the non-negative matrix  $J$ , and we relate the eigenvalues of  $M$  to the cluster phase-shifts  $n_\lambda$

$$M_{nm}^{LL'}(\kappa) = \sum_\lambda \varphi_n^{L'}(\lambda) \text{ctg } \eta_\lambda(\kappa) \varphi_m^L(\lambda), \quad (2.15)$$

$\varphi(\lambda)$  being the eigenvector number  $\lambda$ . With the help of  $\mathcal{M} \equiv M - i1$  the matrix  $\tau$  can be written as

$$\tau = -\frac{1}{\kappa} (IM I)^{-1} \quad (2.16)$$

or

$$\tau_{nm}^{LL'} = -\frac{1}{\kappa} \sum_{\substack{n_1, n_2 \\ L_1, L_2, \lambda}} I^{-1}{}_{nn_1}{}^{LL_1} \varphi_{n_1}^{L_1*}(\lambda) \times e^{in_\lambda} \sin \eta_\lambda \varphi_{n_2}^{L_2}(\lambda) I^{-1}{}_{n_2m}{}^{L_2L'}. \quad (2.17)$$

In this result the generalized phase-shifts  $\eta_\lambda$  appear in a similar way as the single-ion phase-shifts in (2.8). The number  $N_p$  of non-zero phase-shifts equals the sum  $\sum_{n=1}^N D_n$ , where  $D_n$  is

the number of non-vanishing phase-shifts of the  $n$ th scatterer. Using the formula [16]

$$\delta N(\kappa) = \frac{2}{N\pi} \text{Im Tr ln } T(\kappa) \quad (2.18)$$

for the change in the *integrated* density of states per site (spin included) we find the exact, Friedel-like relation

$$\delta N(\kappa) = \frac{2}{N\pi} \sum_\lambda \eta_\lambda(\kappa). \quad (2.19)$$

For the sake of exhibiting multiple scattering effects it will be useful to compare the exact results (1.1) and (2.19) for  $\rho$  and  $\delta N$ , respectively, with corresponding single-site approximations. For the resistivity truncating the series (2.2) after the first term yields the usual Ziman  $T$ -matrix formula [17]:

$$\rho_{ss} = \frac{3\hbar\pi^3}{e^2 k_F^6 \Omega_0} \int_0^{2k_F} dq q^3 S(q) |\tau(q, \kappa_F)|^2 \quad (2.20)$$

with

$$\tau(q, \kappa) = -\frac{1}{\kappa} \sum_l (2l+1) e^{i\delta_l(\kappa)} \sin \delta_l(\kappa) P_l(\cos \theta), \quad (2.21)$$

$$q^2 = 2\kappa^2(1 - \cos \theta), \quad (2.22)$$

$\theta$  being the scattering angle between  $\mathbf{k}$  and  $\mathbf{k}'$ .

The single-site approximation for the density of states is given by the Friedel sum

$$\delta N_{ss} = \frac{2}{N\pi} \sum_{nL} \delta_n^L(\kappa) = \frac{2}{N\pi} \sum_{nL} (2l+1) \delta_n^L(\kappa). \quad (2.23)$$

This limit can be obtained by considering very distant scattering centers in eqs. (2.10) and (2.11). Then  $n_l$  and  $j_l$  go to zero and therefore  $N=0$  and  $J_{nm}^{LL'} = \delta_{nm} \delta^{LL'}$ . Thus, in (2.14),  $M \approx C$  is diagonal and has eigenvalues  $\text{ctg } \delta_n^L$ .

It will be interesting to consider an intermediate approximation for the cluster phase-shifts, obtained by expanding (2.14) for weak

scatterers, where the phase-shifts are small and  $\text{ctg } \delta_n^L$  is large. Neglecting  $N$  with respect to  $C$  we then have to diagonalize

$$\hat{M} = I^{-1}CI^{-1} \quad (2.24)$$

and the corresponding approximate phase-shifts  $\hat{\eta}_\lambda$  can be inserted into (2.19). In contrast to the Friedel sum (2.33), the density of states so calculated contains structural information through the matrix  $I$  in (2.24).

### 3. Some details concerning our calculations

We have applied the results of section 2 to various clusters of identical s-scatterers. The neglect of all single-site phase  $\delta_l$  for  $l \geq 1$  considerably simplifies the computational scheme and should be adequate in order to discuss electronic properties of simple metals. The muffin-tin potential was modelled by a square well of depth  $-V_0$  and radius  $a$ . Where we use  $V_0$  values for which the phase-shifts  $\delta_l$ ,  $l \geq 1$ , would be non-negligible, our restriction to s-phase shifts has of course only model character, independent of the real behavior of the square well potential. The number  $N_p$  of cluster phase-shifts ( $\lambda = 1 \cdots N_p$ ) is now equal to the number  $N$  of sites in the cluster.

We have studied the following types of clusters:

(i) Ordered clusters of fcc symmetry comprising the first and the second shell of neighbors, i.e.  $N = 13$  and  $N = 19$ . The distance  $d$  between nearest neighbors was chosen to be  $2.2a$ , yielding an atomic volume  $\Omega_0 = (2.2a)^3/\sqrt{2}$ . The fcc structure has the advantage of yielding simple expressions for the  $R_n$ . At the same time it represents a close packed neighbor structure typical of an amorphous or a liquid metal with a high coordination number. Even though it has the point symmetry of a perfect crystal the electronic properties of such a cluster are typical of a disordered metal, since by summing the contribution of many clusters incoherently, as in (1.2), we discard any long range order. Moreover, expression (1.1) for the resistivity involves au-

tomatically an angular average over the directions of the incoming and outgoing electrons. The two clusters will be denoted as (13.O) and (19.O).

(ii) In order to study the influence of the cluster structure, more particularly of its degree of order or disorder, on its electronic properties, we have deformed the two ordered fcc-like clusters by random displacements of the ionic sites. For the details of this deformation procedure we have followed Cubiotti et al. [18]. The position of the  $n$ th scattering center is shifted by a vector  $S_n$ . The  $3N$  components  $s_i$  ( $i = 1 \cdots 3N$ ) of these displacements are random variables, calculated by the formula:

$$s_i = 2[i\sqrt{2} - \text{int}(i\sqrt{2}) - \frac{1}{2}]\eta a. \quad (3.1)$$

Here  $\text{int}(x)$  is the integer part of  $x$  and the factor  $\eta$  allows to go from "weak" to "strong" disorder. It is always chosen sufficiently small so that the muffin-tin spheres do not overlap. (Since for the fcc structures  $d > 2a$ , there is some "free room" between the muffin-tin spheres.)

These deformed clusters will be denoted as (13.D) and (19.D), respectively. Two clusters with the same number of particles but with different degrees of disorder can be used to simulate the effect of thermal vibrations of the ions on the electronic properties. In the regime of sufficiently high temperatures an electron moving through the cluster sees the instantaneous ionic configuration. Thus the disordered clusters will represent a high temperature system (large amplitudes of thermal vibrations leading to strongly asymmetric instantaneous configurations) and the ordered (fcc) clusters model the same system at low  $T$ . This can be justified by going to the limit of  $T$  larger than the Debye temperature in the formula [19]

$$\rho = \frac{3\pi^3 \hbar}{e^2 k_F^6 \Omega_0} \int_0^{2k_F} dq q^3 |\tau(q)|^2 \times \int d\omega \frac{\hbar \beta \omega}{e^{\hbar \beta \omega} - 1} S(q, \omega) \quad (3.2)$$

for the resistivity that replaces (2.20) at low  $T$ , where inelastic scattering has to be taken into account. At high  $T$  the frequency integral over the dynamic structure factor  $S(q, \omega)$  reproduces the static structure factor  $S(q)$ . In this limit a description in terms of elastic scattering from a rigid arrangement of ions (described by  $S(q)$ ) and one in terms of the sum of all inelastic scattering (given by  $\int d\omega S(q, \omega)$ ) are equivalent, and the  $T$  dependence of  $\rho$  is essentially given by that of the ionic structure.

In order to characterize the structure of our clusters we have plotted in fig. 1 the angular average of the structure factor

$$S(q) \equiv \frac{1}{4\pi N} \int d\Omega_q \sum_{nm} e^{iq(R_n - R_m)} \\ = \frac{1}{N} \sum_{nm} j_0(q|R_n - R_m|). \quad (3.3)$$

For  $qa \geq 2$ ,  $S(q)$  has a similar behaviour as found in a liquid or amorphous metal. The first peak is located at  $k_p \approx 7.3/(2a)$ , which is consistent with experimental structure factors, where  $7 \leq k_p d \leq 8$  [30]. The small size of our clusters is, however, reflected in the following features:

- (i) The height of the first peak ( $\approx 1.8$  for the ordered and 1.5 for the disordered case) is lower than that in an amorphous or liquid metal.
- (ii) The secondary oscillations are more pronounced, and show shoulders, which are, how-

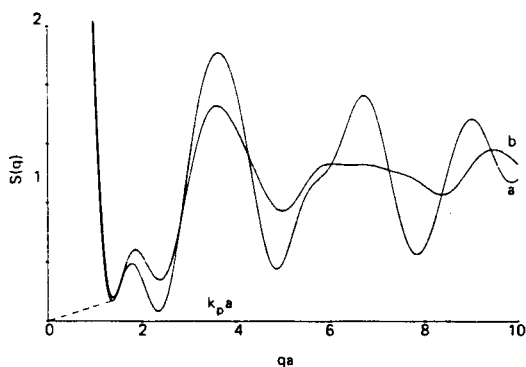


Fig. 1. A comparison of the structure factor (3.2) of the ordered (a) and a disordered (b) 19-particle cluster. The dashed line represents the truncated structure factor used for calculating  $\rho_{ss}$  (see fig. 5).

ever, of a different shape than the one usually seen on the second peak for a metallic glass. Moreover, there is a small "prepeak" near  $qa = 2$ .

(iii) There is a central peak of height  $N$  and of width  $\sim 1/D$ ,  $D$  being the diameter of the cluster. In an infinite system this yields the usual  $\delta(q)$  contribution which is subtracted from (3.3), and which does not contribute to the Ziman integral (2.20). In order to judge for which domain of Fermi energies the central peak will lead to a behaviour of  $\rho$  for our clusters which is qualitatively different from the one of a large system we have calculated the Ziman resistivity by using a truncated  $S(q)$  as shown in fig. 1. The results will be discussed in section 4.

On the other hand the two curves in fig. 1, for the ordered and the deformed 19-particle clusters, show very directly the influence of increasing disorder on the structure factor of the cluster. The effect is indeed the same as that of an increasing temperature, seen in diffraction experiments on amorphous and liquid metals.

For each cluster we have computed the following quantities:

(a) The cluster phase shifts  $\eta_\lambda$ . For the ordered clusters the eigenfunctions of  $M$  (2.14, 15) transform according to irreducible representations of the cubic point group, and we find degeneracies in  $\eta_\lambda$  of order 1, 2 and 3.

(b) The density of states  $D(E)$ . Following the procedure outlined in the Introduction (eq. (1.2)), we multiply the contribution of one cluster by the number of clusters needed to build a macroscopic system out of such cluster units of the same mean atomic volume. This yields for the integrated density of states per unit volume (including the free electron contribution)

$$N(\kappa) = \frac{\kappa^3}{3\pi^2} + \frac{2}{N\Omega_0\pi} \sum_\lambda (\eta_\lambda(\kappa) - \eta_\lambda(0)). \quad (3.4)$$

(We use Rydberg units.) Subtracting out  $\eta_\lambda(0)$  removes the contribution of bound states. The (differential) density of states  $D(E)$  is then obtained by numerical differentiation.

(c) The resistivity  $\rho$ , according to eqs (1.1) and (2.20), respectively.

(d) The thermopower  $Q$ . Without going into details we remark that the latter can be calculated in the same multiple scattering framework [1]:

$$Q = \frac{\pi^2 k_B^2 T}{3e} \left. \frac{\partial \ln \rho(E)}{\partial E} \right|_{E=E_F}, \quad (3.5)$$

where  $\rho(E)$  is the energy-dependent resistivity given by (1.1) with  $E_F = \hbar^2 k_F^2 / (2m)$ . The multiple scattering resistivity (1.1) is differentiated numerically, whereas in the single-site approximation one obtains from (2.20) the well-known result [1]:

$$Q_{ss} = -\frac{\pi^2 k_B^2 T}{3e E_F} \left( 3 - 2p - \frac{r}{2} \right) \quad (3.6)$$

with

$$p = \frac{|\tau(2k_F, \kappa_F)|^2 S(2k_F)}{I(2k_F)}, \quad (3.7)$$

$$r = \frac{1}{4k_F^3 I(2k_F)} \int_0^{2k_F} dq q^3 S(q) \frac{\partial}{\partial \kappa_F} |\tau(q, \kappa_F)|^2, \quad (3.8)$$

$$I(2k_F) = \frac{1}{4k_F^4} \int_0^{2k_F} dq q^3 S(q) |\tau(q, \kappa_F)|^2. \quad (3.9)$$

## 4. Results

### (a) Cluster phase-shifts

Fig. 2 shows the results for the potential strength  $V_0 a^2 = 2.4$ . As the curve for the single-well phase shift shows, this is a relatively "strong" potential, which almost has a bound state (the critical value above which there is at least one bound state is  $V_0 a^2 = 0.25 \pi^2$ ). The cluster (13.O) has 6 distinct phase shifts. The corresponding eigenvectors (2.15) transform according to the irreducible representations  $A_{1g}(2)$ ,  $E_g(1)$ ,  $T_{1g}(1)$ ,  $T_{2u}(2)$  of the point group

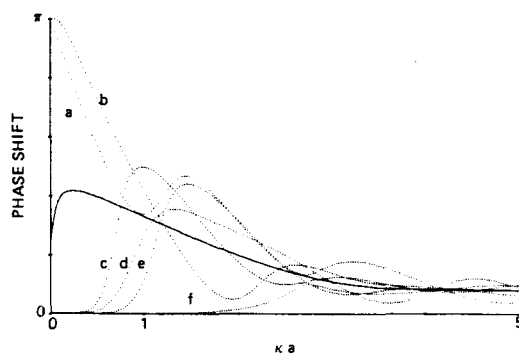


Fig. 2. Phase shifts for  $V_0 a^2 = 2.4$ . Full curve: phase-shift of the potential well. Dotted lines: cluster phase-shifts for the (13.O) cluster, belonging to the following irreducible representations of the group  $O_h$ :  $A_{1g}$ (a, f),  $T_{2u}$ (b, e),  $T_{1g}$ (c),  $E_g$ (d).

$O_h$ , the multiplicities being given in parentheses. The cluster has 4 bound states: 4 phase-shift curves ( $A_{1g}$  and  $T_{2u}$ ) start out at  $\pi$ . The results for the disordered counterpart (13.D) would be qualitatively similar. However, the degeneracies are removed, and there are only three bound states.

### (b) Density of states

$D(E)$ , computed by differentiating (3.4), is shown for different (13.D) clusters in fig. 3, together with the free electron curve. At low energies there is structure in these curves which depends on the particular behavior of the phase-shifts for a given potential and a given arrangement of the scatterers. These structures are smoothed out when the average is taken over several clusters of the same degree of disorder. At high energies ( $E \geq 6.5$ ) all curves follow the free electron behavior, albeit with a possible overall shift.

The most interesting feature, however, is the minimum between those two-energy regimes, at  $E = E_m$ . It is fully developed for the strong potentials, whereas for  $V_0 a^2 = 0.9$  only an indication of a minimum is visible. Such minima have been found by approximate calculations of the averaged self-energy of an electron moving in a random potential, using self-consistent perturb-

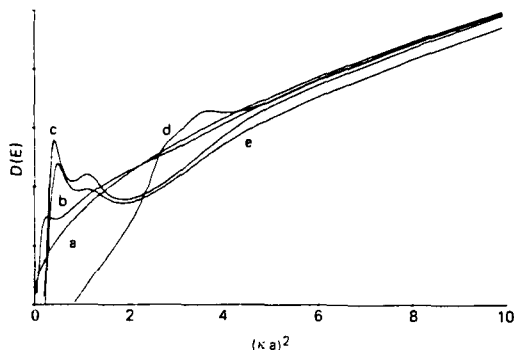


Fig. 3. Densities of states for the cluster (13.D) with different well-depths:  $V_0 a^2 = 0$ (a), 0.9(b), 2.4(c), 15(d), 22(e). The arrows indicate the position of the structure induced minima at  $E = E_m$ .

ation theory [20] or an effective medium approach [21]. Photoelectron spectroscopy has revealed the existence of such a minimum in amorphous AuSn alloys [22]. It also plays an important part in a simple stability argument for metallic glasses involving simple metals put forward by Nagel and Tauc [23].

It is interesting to note that the value of  $E_m$  varies considerably with potential strength. On the other hand, we have calculated the number  $Z_m$  of electrons per ion for which the Fermi energy would lie at  $E_m$ . We find  $1.3 \leq Z_m \leq 1.8$ , with little dependence on  $V_0 a^2$ . Our  $Z_m$  is consistent with  $Z_m = 1.6$  given by Nicholson and Schwartz [21], who have 11.6 for Cu alloys including the filled d-band.

These facts, i.e. strong variation of  $E_m$  at almost constant  $Z_m$  and the existence of a minimum itself, may be understood by the help of a fictitious mean dispersion curve  $\varepsilon(k)$  of the electron moving in the ionic potential. We take  $\varepsilon(k)$  to be that dispersion curve which would yield the true density of states through the formula

$$D(E) = \frac{2}{N\Omega_0} \sum_k \delta(E - \varepsilon(k)). \quad (4.1)$$

It is the inverse of the function  $k(\varepsilon)$ , given by

$$k(\bar{\varepsilon}) = (3\pi^2 N(\bar{\varepsilon}))^{1/3}. \quad (4.2)$$

Here  $\bar{\varepsilon} = E - E_0$  is the energy variable counted from the value  $E_0$  at which  $N(E)$ , the integrated density of states (3.4) begins to deviate from zero. The resulting  $\bar{\varepsilon}(k)$  are shown in fig. 4. The flat position of the curves A and B, followed by a steeper rise and even an "overshooting" of the free electron line in A, can be understood in the usual "quasi crystalline" picture [20], [23] which would yield a gap (or at least a pseudogap) at some wave vector  $k_g$ , representing the spherically averaged zone boundary. We stress that  $\varepsilon(k)$  has been determined "a posteriori" and that our calculation of  $D(E)$  is not based on the existence of such a hypothetical dispersion function, but fig. 4 shows in a simple way the effect of ionic structure on the electronic properties in a disordered metal. In particular, it is interesting to note that  $k_{gA}$  and  $k_{gB}$  are in fact different from each other and from  $k_p/2$  (see fig. 1), where the "average zone boundary" would be expected to lie. These differences can be interpreted by noticing that the effective average wave number  $k \equiv \sqrt{E - V}$  "inside" the system can be larger or smaller than the free electron value  $k_0 = \sqrt{E}$  depending on whether the average potential  $V$  is attractive or repulsive. In the case  $V_0 a^2 = 2.4$  the single-site potential is truly attractive ( $\delta_0$  is positive and smaller than  $\pi/2$ ), therefore  $k > k_0$ , and thus the value  $k_{gA}$  for the wave number of the incoming electron which will correspond to the

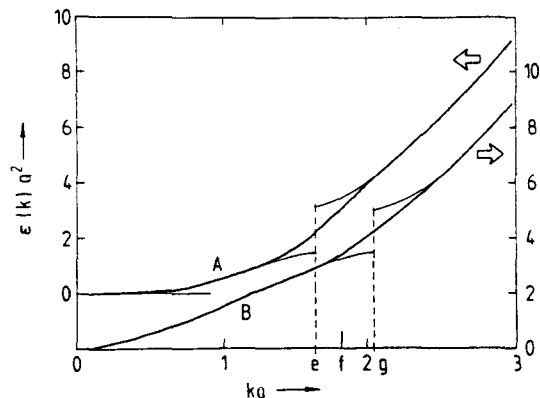


Fig. 4. "Dispersion curves", calculated according to eq. (4.2) for the (19.O) cluster with  $V_0 a^2 = 15$  (repulsive pseudopotential). The letters e, f, g mark the position of  $k_{gA}$ ,  $k_p/2$ ,  $k_{gB}$ , respectively (see text).

zone boundary  $k_p/2$  inside the system is effectively smaller than  $k_p/2$ . The opposite is true for  $V_0 a^2 = 15$ , where  $\delta$  starts at  $\pi$  and decreases towards  $\pi/2$  in the relevant energy domain ( $E \leq 5$ ). Disregarding the bound state we can therefore speak of a repulsive pseudopotential the phase-shift of which is negative (modulo  $\pi$ ), and  $k < k_0$ .  $V_0 a^2 = 22$  has a similar phase-shift as  $V_0 a^2 = 2.4$  (modulo  $\pi$ ), and the two potentials indeed yield similar densities of states. The repulsive nature of  $V_0 a^2 = 15$  is also reflected in the fact that  $D(E)$  takes off at  $E_0 = 1.6$  only: there are no states between  $E = 0$  and  $E = E_0$  (in reality our superposition of cluster densities of states according to (1.2) yields a slightly negative  $D(E)$  between zero and  $E_0$ , which has to be discarded).

The minimum of  $D(E)$  at  $E_m$  is a direct structure effect, seen in the electronic state density. Indeed, the Friedel approximation (2.23), which includes no structural information, yields a smooth density of states without any minimum. On the other hand, the phase-shifts  $\tilde{\eta}_\lambda$  diagonalizing (2.24) also yield a minimum qualitatively similar as the exact formula (3.4). For identical s-scatterers, eq. (2.24) is particularly suggestive:

$$\tilde{M}_{nm} = \text{ctg } \delta \cdot (J^{-1})_{nm} \quad (4.3)$$

and, according to (2.15), applied to  $\tilde{M}$ , the values of  $\text{ctg } \tilde{\eta}_\lambda$  are given by  $\text{ctg } \delta$  divided by the eigenvalues of the "structure matrix"  $J$ , related to the structure factor by

$$S(q) = \frac{1}{4\pi N} \sum_{n,m} J_{nm}(q), \quad (4.4)$$

see eqs. (2.11) and (3.2)

(c) Resistivity

Fig. 5 shows the resistivities as a function of the Fermi wave number (denoted by  $k_F$  or  $\kappa$  in the following) of the clusters (19.O) and (19.D) for two potential strengths, calculated exactly ( $\rho_{MS}$ ) according to (1.1) and in the single-site approximation ( $\rho_{SS}$ ) according to (2.21), with

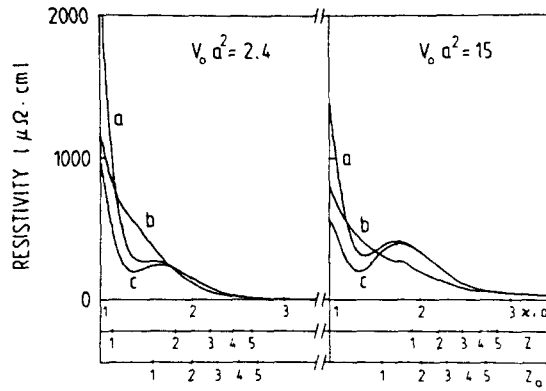


Fig. 5. Left: (a) Resistivity of the cluster (19.O) for  $V_0 a^2 = 2.4$ . The three curves denote  $\rho_{SS}(a)$ ,  $\rho_{MS}(b)$  and  $\rho_{SS}(c)$  using a truncated structure factor. Below, the position of the Fermi wave vector for various valences, calculated by the use of the true density of states ( $Z$ ) and for free electrons ( $Z_0$ ). Right: (b) Idem. for  $V_0 a^2 = 15$ .

$l = 0$  only. The well-known structure of  $\rho_{SS}$  with a maximum at  $2k_F = \kappa_p$ , due to the "Ziman integral" in (2.21) is less pronounced than usual, due to the influence of the large central peak in  $S(q)$  (it is also washed out by the energy dependence of the single-site phase-shift). For comparison we have calculated  $\bar{\rho}_{SS}$  using a truncated structure factor, the low  $q$  behavior of which is sketched in fig. 1. The resistivity  $\bar{\rho}_{SS}$  indeed deviates from  $\rho_{SS}$  for  $k_F a \leq 1.6$ . Therefore we should not use our results for comparison with experimental data from macroscopic samples (in particular at low Fermi energies), but the various conclusions concerning the effect of multiple scattering, to be drawn below, should still be valid, at least semi-quantitatively.

The energy dependence of  $\rho_{MS}$  is much more monotonic than for  $\rho_{SS}$ : the maximum at  $k \approx k_p/2$  has practically disappeared. Even considering the above mentioned effect of  $S(q)$  at low  $q$ , the curves for  $\rho_{MS}$  and  $\rho_{SS}$  show that multiple scattering effects tend to decrease the strong structural (Bragg-type) scattering near  $\kappa = k_p/2$ , although the latter is still active (or even enhanced by multiple scattering) in the density of states, producing the minimum discussed above. We do not show curves for weak potentials, since there  $\rho_{MS}$  differs little from  $\rho_{SS}$ .

In order to follow in more detail the different behaviors of  $\rho_{MS}$  and  $\rho_{SS}$  we have plotted in fig. 6 the ratio  $\alpha \equiv \rho_{MS}/\rho_{SS}$ . It is interesting to note that we find  $\alpha < 1$  and  $\alpha > 1$ , i.e. multiple scattering does not necessarily enhance the resistivity as one might naively assume. We have made the following observations:

(i) Cluster size influences the details of  $\alpha(\kappa)$ , but not the positions of its maxima and minima.

(ii) Disorder damps the oscillations in  $\alpha$ , but does not shift the maxima and minima.

(iii) For "attractive" pseudopotentials (see above)  $\alpha$  oscillates between  $\alpha > 1$  and  $\alpha < 1$ , whereas for "repulsive" ones it is most often smaller than 1.

(iv) For weak potentials  $\alpha > 1$  around the first peak of  $S(q)$ , whereas for stronger potentials  $\alpha$  is typically larger than 1 for  $\kappa < k_p/2$  and  $\alpha < 1$  for  $\kappa = k_p/2$ .

(v) The maxima of  $\alpha$  are typically shifted to somewhat lower values of  $k$  with increasing  $V_0 a^2$ , but they do not depend strongly on the latter quantity. The wavelengths  $\lambda_i \equiv 2\pi/k_i$ , corresponding to the wave numbers  $k_i$  of the  $i$ th maximum are roughly the following:  $\lambda_1 \approx 2d$ ,  $\lambda_2 \approx d$ ,  $d = 2.2 a$  being the mean neighbor distance in the cluster (19.D). These simple relations suggest that enhancement or suppression of  $\rho$  through multiple scattering processes is a "matching effect" between the de Broglie wavelength of the scattered particle and the

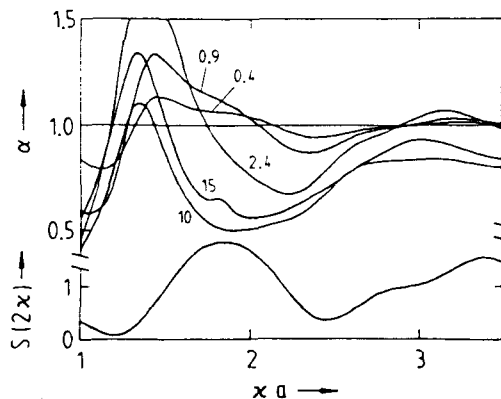


Fig. 6.  $\alpha = \rho_{MS}/\rho_{SS}$  for the cluster (19.O). The curves are labelled by the values of  $V_0 a^2$ . Below the structure factor is shown for comparison.

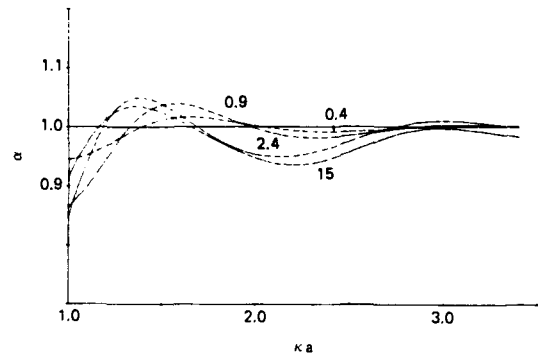


Fig. 7.  $\alpha$  for a dumbbell with different potential strengths.

(mean) distance between two neighboring scatterers. This is corroborated by fig. 7, showing  $\alpha$  for a dumbbell ( $N = 2$ ). Indeed,  $\alpha$  has its first maximum at about the same value as in the 19-particle cluster. The amplitude of its oscillations, however, is much smaller (between about 0.9 and 1.1), even for strong potentials. Thus the curves in fig. 6 can be viewed as the superposition of a certain number of "dumbbell curves", with the additional effect of a shift of the  $\alpha$ -values towards  $\alpha < 1$  for the repulsive potentials.

Multiple scattering has yet another effect on the theoretical value of  $\rho$  for a metal with a given atomic potential: through the modification of the density of states the Fermi energy  $E_F$  is shifted with respect to the nearly free electron value for a given valence  $Z$  and atomic volume  $\Omega_0$ . In fig. 5 we show  $E_F(Z)$ , calculated both in the NFE approximation and using the true density of states. As the figures show, this shift of  $E_F$  may, depending on  $V_0 a^2$  and  $Z$ , enhance or counterbalance the effect of multiple scattering on  $\rho$ , as represented by the ratio  $\alpha$  at fixed  $k$ . For example, the values of  $\rho_{MS}$  for  $Z = 1$  and  $\rho_{SS}$  for the corresponding  $Z_0 = 1$  in fig. 5b are about equal, although  $\alpha(k) < 1$  in that energy domain, showing that the single-site approximation would be quantitatively correct.

We have also investigated the convergence of the multiple scattering series (2.2). As expected, for wave numbers higher than some threshold  $\kappa_1$ , the triple or even double scattering approximation to (2.5), obtained by expanding

$$(\tau^{-1} - B)^{-1} = (1 - \tau B)^{-1} \tau \approx \tau + \tau B \tau + \tau B \tau B \tau + \dots \quad (4.5)$$

reproduce  $\rho$  quite well. For  $V_0 a^2 = 0.9$ , for example,  $\kappa_1 a = 1.2$ . Below  $\kappa_1$  a given approximation to  $\rho$  deviates more and more from the true result, the lower the energy. As shown in fig. 8, for  $V_0 a^2 = 2.4$ , the series for  $\alpha$  is probably divergent for  $\kappa a \leq 1.5$ , since there all the shown approximations of  $\alpha$  tend to larger and larger values when  $\kappa$  decreases, whereas the exact  $\alpha (= \alpha_\infty)$  decreases. This is obviously related to the occurrence of 4 "cluster bound states" for this potential strength.

One of the most interesting results is the influence of disorder on the transport behavior of our systems. Following the discussion in section 3 we consider the results for ordered (disordered) clusters to be typical of low (high) temperatures and we introduce the quantity

$$\gamma = \frac{\rho_{DIS}}{\rho_{ORD}} - 1 \quad (4.6)$$

in an obvious notation.  $\gamma$  can be thought of as the "temperature coefficient of resistivity", in particular  $\gamma < 0$  when increasing disorder lowers the resistivity, which is "unusual" for a "normal" metal. From numerous applications of Ziman's formula (2.20) it is well known that  $\gamma < 0$  when  $2k_F$ , the upper limit of integration in eq. (2.20) lies near the peak of  $S(q)$ , located at  $k_p$ . (See

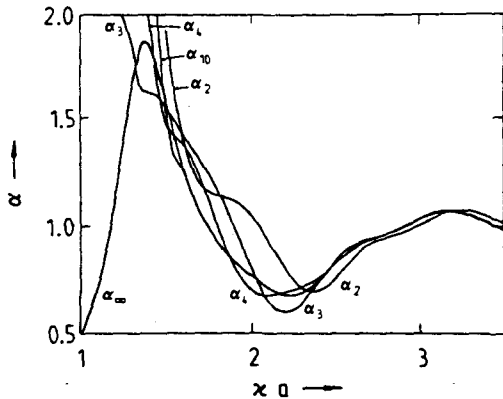


Fig. 8. Various approximations to the ratio  $\alpha = \rho_{MS}/\rho_{SS}$  for the cluster (19.O).

e.g., the textbook of Shimoji [1] or Delley et al. [24].) This behavior is indeed found in our  $\gamma$ -curves for single-site scattering, denoted as  $\gamma_{SS}$  in fig. 9. The domains of negative  $\gamma_{SS}$  are indeed centered around successive peaks of  $S(q)$ . It should be noted that our disordered cluster is quite strongly deformed, therefore the variation in  $\gamma_{SS}(\kappa)$  is rather pronounced.

The multiple scattering curves,  $\gamma_{MS}(\kappa)$ , on the other hand, show rather interesting deviations from  $\gamma_{SS}$ , when  $V_0 a^2$  is large enough. (For  $V_0 a^2 = 0.4$  and  $0.9$ ,  $\gamma_{SS}$  and  $\gamma_{MS}$  differ little.) In the case  $V_0 a^2 = 2.4$ ,  $\gamma_{MS}$  also oscillates around 1, but there is a "phase-shift": the first domain where  $\gamma_{MS} < 0$  is larger and is shifted towards lower wave numbers and lies now rather on the left of the first peak of  $S(q)$ ; at  $2k_F < k_p$ . Therefore, the usual criterion,  $2k_F = k_p$ , for  $\gamma < 0$ , no more holds. However, it is interesting to note that the Fermi wave number  $k_F$ , for valences  $Z \leq 2$ , is also shifted towards lower values. This means, for example, that if in the free electron approximation,  $k_F a = 1.9$  ( $Z = 1.8$ ) lies in the domain where  $\gamma < 0$ , the corresponding  $k_F a$  in the strong scattering system  $V_0 a^2 = 2.4$  lies near 1.6, which is again well in the region  $\gamma < 0$ . Thus the condition for  $\gamma < 0$  in terms of the mean conduction electron number  $Z$  per ion (i.e.  $Z \leq 2$ ) may still be the same in a strong scattering

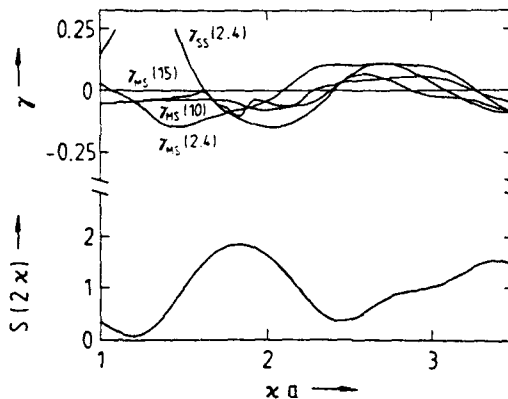


Fig. 9.  $\gamma$  (eq. (4.6)) in multiple scattering and in single-site approximation in the 19-particle clusters. The values of  $V_0 a^2$  are given in parentheses, and the structure factor  $S(2\kappa)$  is shown underneath.

system as in the NFE approximation, but the corresponding Fermi wave vector may lie well below  $k_p/2$ .

The cases  $V_0 a^2 = 10$  and 15, leading to repulsive pseudopotentials, show an interesting new behavior: whereas  $\gamma_{SS}$  (omitted from fig. 9 for reasons of clarity) has again "Ziman behavior",  $\gamma_{MS}(\kappa)$  is rather different: except for small variations, which are due to the specific form of the cluster and are smoothed out by a suitable configurational average, the curve is rather flat in the domain  $1 \leq \kappa a \leq 2.3$  and lies somewhat below zero. This seems to be a manifestation of Mooji's rule [25, 26]: when, in a disordered metal,  $\rho(\kappa)$  is larger than a critical value  $\rho_0$  on the order of  $120 \mu\Omega \text{ cm}$  (this corresponds to  $\kappa \leq 2.3$  in fig. 5b and in fig. 9 for  $V_0 a^2 = 15$ ) the temperature coefficient of  $\rho$  has a tendency of being negative. For  $\kappa a \geq 2.3$  the resistivity is below  $\rho_0$  and  $\gamma$  shows the usual Ziman-like oscillations, following the ones in  $S(q)$  (albeit in a range of  $\kappa$ -values outside the usual range of valences  $Z \leq 5$  of normal metals), like the corresponding  $\gamma_{SS}(\kappa)$ . For these strong scatterers multiple scattering effects lead to qualitative deviations from the "Ziman rule" for negative temperature coefficients. More precisely, they lead to a more general "rule", which seems to be obeyed in many disordered metals: high resistivities are typically accompanied by negative  $\gamma$ .

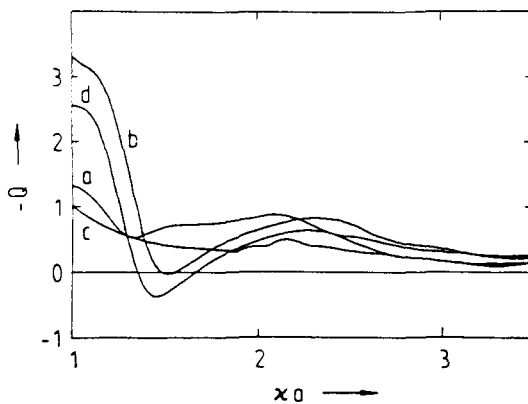


Fig. 10. Thermoelectric power of the cluster (19.0) as a function of  $\kappa_F$ :  $Q_{MS}$ (a) and  $Q_{SS}$ (b) for  $V_0 a^2 = 2.4$ ,  $Q_{MS}$ (c) and  $Q_{SS}$ (d) for  $V_0 a^2 = 10$ .

#### (d) Thermopower

The results, calculated according to (3.5) and (3.6–9), respectively, confirm the general conclusions drawn for the resistivity in the preceding paragraph. Fig. 10 shows the negative of  $Q$  as a function of  $\kappa$  for  $V_0 a^2 = 2.4$  and 10. The single site curve shows the signature of the structure-dependent term  $p$  in eq. (3.7) which varies like the structure factor and produces a minimum or even a change in sign in  $Q$  for  $\kappa \approx k_p/2$ . Like the resistivity  $\rho_{MS}$ , the multiple scattering  $Q_{MS}$  is much smoother and the structural effect near  $k_p/2$  is more or less suppressed.

### 5. Summary and conclusions

We have investigated the effect of multiple scattering of electrons in small clusters of s-wave scatterers on electronic state density and transport coefficients. Here are the main results:

(i) The electronic density of states  $D(E)$  shows a typical structure induced minimum. Its position varies considerably with the strength  $V_0$  of the single-ion potential. The Fermi energy lies in the minimum for a number  $Z$  of electrons per ion between about 1.3 and 1.8, depending on  $V_0$ . This minimum in  $D$  has also been formed by different theoretical methods [20, 21] and has been observed in amorphous noble metal-polyvalent metal films [22].

(ii) The multiple scattering contributions to the electrical resistivity  $\rho$  can be positive or negative, i.e.  $\rho_{MS}$  can be larger or smaller than the single-site approximation  $\rho_{SS}$ . This has been found by previous authors [8, 4, 12] using different methods, but it is in contrast to other recent transport theories like the ones put forward by Götze [27] or Beck and Nettel [28], where the resistivity calculated "self-consistently", is always higher than  $\rho_{SS}$ . The fact that  $\rho_{MS}$  can be considerably lower than  $\rho_{SS}$  is particularly interesting in view of the remarks by Esposito et al. [2] who find, for example,  $\rho$ -values on the order of  $1000 \mu\Omega \text{ cm}$  for late transition metals when using a "consistent" couple of values for  $k_F$  and  $E_F$  ( $(k_F \hbar)^2 = 2mE_F$ ) in a single-site calculation.

Obviously our s-scattering calculations are not valid for transition metals, but we expect the same effect in a system with predominant d-scattering. There the resonant single-ion phase-shift producing a high  $\rho_{SS}$ , the  $E_F$  is near the resonance energy, will be replaced by a family of cluster phase-shifts like in our fig. 2. Those will go through  $\pi/2$  at different energies, thereby reducing the "resonance effect" on  $\rho$ .

(iii) The energy dependence of the multiple scattering contributions, reflected in our coefficient  $\alpha(\kappa) \equiv \rho_{MS}(\kappa)/\rho_{SS}(\kappa)$ , can be understood qualitatively by interference effects in a wave picture of scattering, as it is demonstrated in fig. 7 for a dumbbell cluster.

(iv) Our most important result concerns the "temperature dependence" of  $\rho$ , which is represented by the variation of  $\rho$  with cluster disorder in our calculations. With respect to the "Ziman rule", namely  $\gamma \equiv (T/\rho)(d\rho/dT) < 0$  when  $2k_F \approx k_p$ , which is obeyed by  $\rho_{SS}$ , we find the following important modifications due to multiple scattering processes:

- For strong scatterers representing an "attractive" pseudopotential (see section 4 for this terminology) the range where  $\gamma < 0$  is enlarged and shifted to  $2k_F < k_p$ . Thus the Ziman rule is no more valid, but the domain of valences  $Z$  where  $\gamma < 0$  may still be similar as in the single-site approximation.
- For repulsive pseudopotentials we find  $\gamma < 0$  and little variation in  $\gamma$  for all relevant  $\kappa$ 's up to  $2\kappa \approx 1.4k_p$ . This is precisely the behavior expected by the "Mooji rule" [25] since the resistivity  $\rho_{MS}$  itself, which has a monotonically decreasing energy dependence, is larger than about  $120 \mu\Omega \text{ cm}$  over the same domain where  $\gamma < 0$ .

These facts may allow to understand the well-known exceptions from the Ziman behavior in the realm of liquid and glassy metals, such as  $\text{Gd}_{67}\text{Co}_{33}$  [29] which has  $\gamma < 0$  even though  $2k_F$  is not near  $k_p$ .

Although we believe that these cluster results on the influence of multiple scattering on electronic structure and transport will retain their qualitative features in a calculation for larger, and finally for macroscopic systems, we are fully

aware of the fact that this is only a first step towards an approach to calculating electronic properties of disordered metals which goes beyond the single-site approximation while, at the same time, being of sufficient simplicity so that numerical results can be found without enormous computational effort. Work in this direction, including calculations for s-, p- and d-scatterers, is in progress.

#### Acknowledgements

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## Multiple Scattering Effects in Electronic Transport in Liquid and Amorphous Metals \*

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### Abstract

We have calculated the resistivity of clusters of  $N$  ( $N < 177$ )  $s$ -scatterers arranged in a cubic symmetry in order to exhibit the contributions due to multiple scattering processes. We have then studied the influence of increasing structural disorder on the resistivity and found a transition from Ziman behaviour (weak scattering regime) to Mooij behaviour (strong scattering regime). The effects of multiple scattering on the total averaged cross-section  $\sigma$  of clusters of  $d$ -scatterers are also discussed.

### Introduction:

The calculation of transport coefficients for disordered metals is still an outstanding problem. For instance the temperature coefficient of the resistivity  $\rho$  of many amorphous and liquid metals is negative particularly when  $\rho$  is higher than a critical value of about  $150 \mu\Omega \cdot \text{cm}$ . This is Mooij's rule, which has not yet found a generally accepted explanation.

This paper is based on an expression for  $\rho$  in terms of the total scattering matrix  $T(k, k')$  of the metal giving the scattering amplitude for an elastic electron-ion collision from momentum  $\hbar k$  to  $\hbar k'$  [1]. At

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$T=0$  it has the form:

$$\rho = \frac{3 \hbar}{2^7 \pi \Omega e^2 k_F^4} \int d\Omega_k \int d\Omega_{k'} |T(\mathbf{k}, \mathbf{k}', E_F)|^2 (\mathbf{k} - \mathbf{k}')^2 \quad (1)$$

$\Omega$  being the volume of the system and the integration running over the directions of  $\mathbf{k}$  and  $\mathbf{k}'$ , with  $(\hbar \mathbf{k})^2 = (\hbar \mathbf{k}')^2 = (\hbar k_F)^2 = 2m E_F$ . We have calculated the exact T-matrix, describing rigorously the scattering effects of all ions on an incoming free electron, for some clusters.

This allows us to discuss multiple scattering contributions to  $\rho$  for a given arrangement of ions, and to study the influence of a change in this arrangement on  $\rho$ . For more details see [3].

#### Theoretical framework:

We calculate T for the one-electron Hamiltonian [4]:

$$H = \frac{p^2}{2m} + \sum_n^N V(r - R_n) \quad (2)$$

where  $V$  is a potential well of depth  $V_0$  and radius  $a$  at site  $R_n$ . In order to exhibit multiple scattering effects, it is useful to compare the results with the single site approximation  $\rho_{ss}$  (Ziman T-matrix formula [7]):

$$\rho_{ss} = \frac{3 \hbar \pi^3}{e^2 k_F^4 \Omega_0} \int_0^{2k_F} dq q^3 S(q) |\tau(q, k_F)|^2 \quad (3)$$

$$\text{where: } \tau(q, k_F) = -k_F^{-1} \sum_{l \geq 0} (2l+1) e^{i\delta_l(k_F)} \sin \delta_l(k_F) P_l(\cos \theta) \quad (4)$$

$$\text{and: } q^2 = (\mathbf{k} - \mathbf{k}')^2 = 2 k_F^2 (1 - \cos \theta) \quad (5)$$

We have done our calculations of  $\rho$  for various clusters of  $N$  identical s-scatterers and for small clusters of d-scatterers. Taking only phase-shifts considerably simplifies the computational scheme, and allows to study relatively big clusters. It should be adequate for simple metals. Where we use  $V_0$  values with non-negligible  $\delta_l$  for  $l > 1$ , the restriction to s-phase shifts has of course only model character.

We have studied the following types of clusters:

i) Ordered clusters of fcc symmetry comprising up to nine shells of

neighbors, i.e.  $13 < N < 177$ . The fcc structure has the advantage to represent a close packed neighbor structure typical of a disordered metal with a high coordination number. Even though it has the point symmetry of a perfect crystal, the electronic properties of such a cluster are typical of a disordered metal, since if one calculated the resistivity of a piece of metal by summing the contributions of many clusters incoherently one would discard any long range order.

ii) In order to study the influence of the cluster structure, more particularly of its degree of order or disorder, on its electronic properties, we have deformed the ordered fcc-like clusters by random displacements of the atomic sites, respecting the condition that two potential wells do not overlap.

Two clusters with the same number of particles but with different degree of disorder can be used to simulate the effect of thermal vibrations of the ions on the electronic properties. In the regime of sufficiently high temperatures an electron moving through the cluster sees the instantaneous ionic configuration. Thus the disordered cluster will represent a high temperature system and the ordered cluster models the same system at low T. We will use the notation (N.O) and (N.D) for ordered and disordered N-ions clusters, respectively.

#### Results:

Figure 1 shows the resistivities  $\rho_{ns}$  and  $\rho_{ss}$  as well as the quantity  $\alpha = \rho_{ns} / \rho_{ss} - 1$ , as functions of the Fermi wave number  $k_F$  for the cluster (87.0) for a strong potential, and the structure factor. It is interesting to note that  $\alpha$  can be positive or negative, i.e. multiple scattering does not necessarily enhance the resistivity as one might naively assume. We have made the following observations: For strong potentials,  $\alpha$  is most often negative ( $> -2/3$ ), whereas for weaker potentials,  $-2/3 < \alpha < 1$  for the biggest cluster. The maxima of  $\alpha$  are typically shifted to somewhat lower values of  $k_F$  with increasing  $V_0 a^2$ , but they do not depend strongly on the latter quantity. The wave-lengths  $\lambda_i \equiv 2\pi/k_i$ , corresponding to the wave numbers  $k_i$  of the i-th maximum are roughly the following:  $\lambda_1 \cong 2d$ ,  $\lambda_2 \cong d$ ,  $d = 2.2a$  being the mean neighbor distance in the clusters. These simple relations suggest that enhance-

ment or suppression of  $\rho$  through multiple scattering processes is a "matching effect" between the de Broglie wave-length of the scattered particle and the distance between two neighboring scatterers.

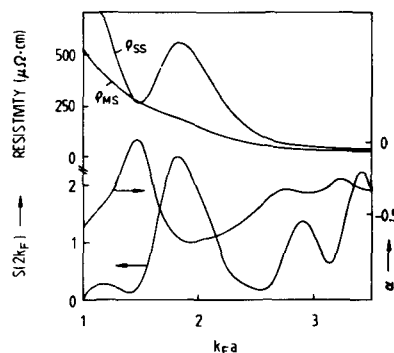


Figure 1: Multiple scattering ( $\rho_{MS}$ ) and single-site ( $\rho_{SS}$ ) resistivities, structure factor  $S$  and  $\alpha$  versus Fermi wave vector  $k_F$ .

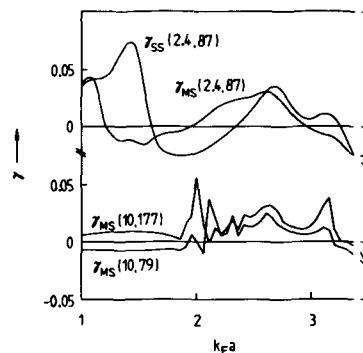


Figure 2:  $\gamma(V_0 a^2, N)$  defined in the text, for some clusters. The single-site  $\gamma_{SS}$  do not depend on  $V_0 a^2$ .

In order to discuss the influence of the degree of order of the cluster, we show in Figure 2 the quantity  $\gamma = \rho_{OIS} / \rho_{ORD} - 1$  for different potentials and clusters.  $\gamma$  can be thought of as the "temperature coefficient of the resistivity", in particular  $\gamma < 0$  when increasing disorder lowers the resistivity. The single site result,  $\gamma_{SS}$ , shows Ziman behaviour [8]:  $\gamma_{SS}$  is negative near the peaks of  $S(q)$  and positive near the minima.

The multiple scattering curves,  $\gamma_{MS}$ , on the other hand, show rather interesting deviations from  $\gamma_{SS}$ , when  $V_0 a^2$  is large enough. (For weak potentials,  $\gamma_{MS}$  and  $\gamma_{SS}$  differ little.) For  $V_0 a^2 = 2.4$ ,  $\gamma_{MS}$  also oscillates around zero, but the first domain where  $\gamma_{MS}$  is negative is shifted to lower wave numbers. For the "small" clusters, i.e.  $43 \leq N \leq 81$ , this domain is enlarged, but for the big ones, it is reduced. The case  $V_0 a^2 = 10$  shows a new behaviour. For the same "small" clusters the  $\gamma_{MS}$  curves are rather flat in the domain  $1 \leq k_F a \leq 2$  to  $2.2$ , depending on the size, and lie somewhat below zero. This is a manifestation of Mooij's rule, because the corresponding  $\rho_{MS}$  are monotonically decreasing as

functions of  $k_F$ . This cross-over between Ziman and Mooij behaviour, when the potential becomes stronger, has been interpreted elsewhere [2] in terms of generalized clusters phase-shifts defined below. For the big clusters,  $N > 100$ , the  $\gamma_{ns}$  curves look like the preceding ones, but do not lie below zero anymore. Indeed, these large clusters are more typical of fcc crystals at different temperatures, rather than amorphous and liquid metals, which is also corroborated by their structure factor showing, for example, a split first peak. Then Mooij's rule is no more applicable.

The last part of this section concerns the averaged cross-section  $\sigma$  for clusters of d-scatterers (only  $\delta_2$  is different from zero). The parameter  $V_0 a^2$  is chosen such that  $\delta_2$  shows a sharp resonance.  $\sigma$  is given by:

$$\sigma = \frac{1}{4\pi} \int d\Omega_k \int d\Omega_{k'} \left| \frac{1}{4\pi} T(k, k') \right|^2 \quad (6)$$

In Ziman's approximation, it reduces to an expression like (3) but with  $q'$  replaced by  $q$ , which leads to a sharp maximum for  $\sigma_{gs}$  at the resonance of  $\delta_2$ . The enormous reduction of  $\sigma$  through multiple scattering which we find around the resonance of the single ion phase-shift is easy to understand with the help of the generalized phase-shifts  $\eta_\lambda$  [5], [6]. The latter are the eigenvalues of the matrix  $\tau_{nm}$ , describing all scattering processes beginning at site  $n$  and ending at site  $m$ . The cross-section is given by:

$$\sigma_{gs}(k_F) = \frac{4\pi}{k_F^2} \sum_\lambda \sin^2 \eta_\lambda \quad (7)$$

Most of these phase-shifts have a resonant form, but the energies where they go through  $\pi/2$  are different for different  $\lambda$ , which is not the case for the corresponding single-site phase-shifts. This splitting of the phase-shifts due to the multiple scattering around the resonance will not only lead to a drastic reduction of  $\sigma$ , but also of  $\rho$  (calculating  $\rho$  is, however, more time consuming). This is particularly interesting in view of the remarks by Esposito et al [9] who find, for example  $\rho$  values of the order of  $1000 \mu\Omega\text{cm}$  for late transition metals

when using a "consistent" couple of values for  $k_F$  and  $E_F$  ( $(\hbar k_F)^2 = 2mE_F$ ) in a single site calculation.

#### Conclusion:

Multiple scattering processes may enhance or lower the resistivity with respect to the single site result, which has been found by previous authors [1], [10] using different methods. Around the resonance of the single site phase-shift, they lead to an important reduction of the total scattering power for d-scatterers.

Depending on the potential strength, increasing the structural disorder of the clusters leads to "Ziman" or "Mooij" behaviour in the resistivity.

We plan to do similar calculations for more realistic models of metallic glasses and for quasi-crystalline structures. Moreover the results of these numerical investigations will be used as a test and a guideline for analytic calculations going beyond Ziman approximation. This work has been supported by the Swiss National Foundation.

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## Electrons in Non-Crystalline Metals – Still a Challenging Problem

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*Dedicated to Professor Harry Thomas on the occasion of his 60th birthday*

The following aspects of the electronic properties of liquid and amorphous metals are studied: (i) density of states of polyvalent liquid metals by means of finite cluster calculations, (ii) the Hall coefficient of simple metals by the use of a generalised transport equation, (iii) the effect of multiple scattering on the electrical resistivity.

Measuring electronic densities of states (DOS) and electrical transport coefficients in liquid and amorphous metals is an everyday activity of the Basel solid state group. Therefore any condensed matter theoretician working there is exposed to the question how to calculate such quantities in a simple but well founded theoretical framework. It is the purpose of this contribution to summarize some recent calculations aiming at a better understanding and a more quantitative description of the electronic properties in non-crystalline metals – a fascinating problem of condensed matter physics on which the first author has had many stimulating discussions with H. Thomas.

### 1. Electronic Densities of States in Simple Metals

DOS measurements in these systems have revealed interesting deviations from free electron behaviour in the form of minima, observed in amorphous noble metal polyvalent metal films [1] and in polyvalent liquid metals like Pb, Sn, Bi, Tl [2, 3]. In the latter metals the minima are unexpectedly strong and almost appear as pseudogaps. Self-consistent calculations of the electronic self-energy, second order in the pseudo-potential [4], seem to produce only relatively weak deviations from the free electron curve  $D_0(E)$ . In order to include higher order effects in the electron-ion interaction (multiple scattering (MS) effects) we

have calculated the full scattering amplitude ( $T$ -matrix) for a cluster of  $N$  muffin tin ions embedded in a free electron gas.  $T$  can be calculated by inversion of a matrix of dimension  $N \cdot P$ ,  $P$  being the number of non-zero phase-shifts considered for each site [5]. The correction  $\delta D(E)$  to  $D_0(E)$ , due to the presence of one such cluster, is then given by the energy derivative of the trace of  $\log T$  [5], and the density of states of a macroscopic system can be obtained approximately by multiplying  $\delta D$  by the cluster density before adding it to  $D_0$  (corresponding to an incoherent sum of individual cluster contributions).

Calculations for various structures and sizes ( $N \leq 180$ ) of cluster of  $s$ -scatterers [6] have indeed reproduced the structure induced minima observed in [1], and explained also [7] by effective medium calculations (EMA). The minimum is due to an increased electron-ion scattering for wave numbers  $k$  close to the "effective zone boundary", i.e.  $2k \approx k_p$ , the latter being the position of the first maximum of the structure factor  $S(q)$ .

Figure 1 shows some new results for a cluster of 19 scatterers, which represents a polyvalent simple metal, the  $s$  and  $p$  phase shifts ( $\delta_0$  and  $\delta_1$ ) being the only ones that are non-zero in the relevant energy domain. The structure of the cluster has been obtained by subjecting the 18 neighbors of a given site in a  $fcc$  lattice to some random displacements [6] in order to simulate a small region of a close packed liquid metal (the angular average of the cluster struc-

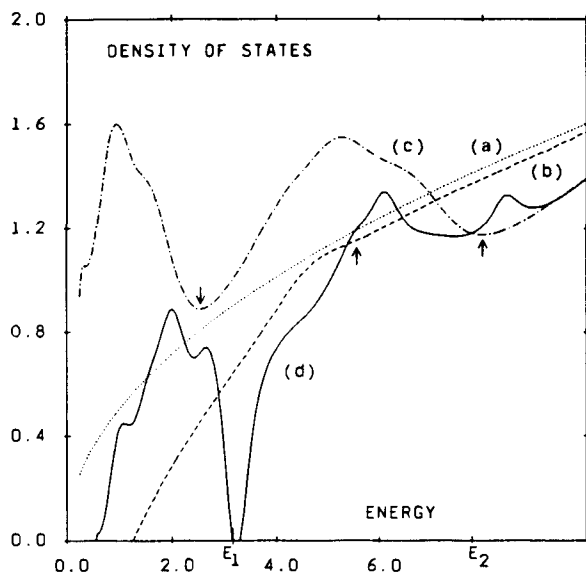


Fig. 1. Density of states  $D(E)$  for a cluster of 19  $s-p$  scatterers (non-overlapping potential wells of radius  $a$  and depth  $V_0$  with  $V_0 a^2 = 4.5$ ). The following curves are shown: free electron density of states (a),  $D(E)$  taking into account  $s$ -phase shifts only (b),  $D(E)$  for  $p$ -phase shifts only (c),  $D(E)$  for  $s$  and  $p$  phase shifts (including hybridization effects). The arrows mark the positions of structure induced minima, and the energies  $E_1$  and  $E_2$ , corresponding to the first and second peak in  $S(q)$  are also indicated. Units are chosen such that  $\hbar = 1$  and  $2m = 1$

ture factor is qualitatively the same as the one of a typical liquid metal). Curve (b) shows the density of states  $D(E)$  when only  $\delta_0$  is taken into account. The bottom of the band would then be shifted to positive energies (for the chosen potential  $\delta_0$  is negative, which represents an effective repulsion [6]). A small structure induced minimum is indicated by an arrow.  $D(E)$ , given by  $\delta_1$  only (curve c) shows two pronounced minima (arrows) which are clearly also due to structure scattering since they appear near the energies  $E_i = \hbar^2(k_i/2)^2/2m$ , related through the free electron  $E$  versus  $k$  relation to the positions  $k_1$  and  $k_2$  of the first two maxima of the structure factor. Apparently this structural effect is even stronger for  $p$ -scattering than for  $s$ -scattering, since for the latter only the influence of the main peak in  $S(q)$  is visible in all the clusters we have considered. Curve (d) includes  $\delta_0$  and  $\delta_1$  and shows therefore the important effect of " $s-p$  hybridisation", which produces a real gap in  $D(E)$ . (The slightly negative values of  $D(E)$  in the region is due to our superposition of individual cluster contributions). It is interesting to note that the shape of curve (c) is quite similar for various cluster sizes and structures and for different potential depths (showing some "universality" of the structural scattering), whereas the details of curve (d) can vary

appreciably, showing the usual geometry and wave function dependence of a hybridisation mechanism. Nevertheless, these cluster calculations seem to be in agreement with the recent DOS measurements of the Basel group [2, 3]. More work aiming at interpreting the results in Fig. 1 in terms of "cluster phase shifts" and complementing the cluster data by EMA calculations for macroscopic systems are in progress.

## 2. Hall Coefficient in Simple Amorphous Metals

Measurements on alloys of noble and polyvalent metals, such as  $\text{Au}_{1-x}\text{Sn}_x$  [8] have shown systematic deviations of the Hall constant  $R$  from the free electron value  $R_0$ : starting at pure Au, were  $R \approx R_0$ ,  $|R|$  gets smaller than  $|R_0|$  when  $x$  increases from zero to about 0.25, moving back towards  $|R_0|$  when  $x > 0.25$ . The effect is weak in the liquid state and rather pronounced in quench condensed films at low  $T$ . The generalized transport equation for electrons in electric and magnetic fields, derived by Mahan [9] by using the true equilibrium spectral function for the electronic quasiparticles which are scattered by the ions, still restricting the collision kernel in the Boltzmann equation to second order in the electron ion potential, offers an interesting framework for calculating the Hall constant  $R$ , since it is well known that in the usual calculation of  $R$ , based on a relaxation time solution of Boltzmann's equation, at  $T=0$ , the effects of electron-ion collisions drop out. When a finite spectral width of the electrons is accounted for the collision term in the transport equation becomes a true integral operator. Preliminary calculations we have performed in this framework, appropriate for simple metals, produce deviations of  $R$  from the free electron value  $R_0$  for two reasons:

- i) The renormalized band energy  $E(k)$  of such a disordered simple metal is typically flatter than  $E_0(k) \equiv \hbar^2 k^2/2m$  for  $k < k_p/2$ , but it rises more steeply than  $E_0$  for  $k > k_p/2$  (see e.g. self energy calculations for pseudopotential systems in [4]). This yields a Hall constant  $R$  which is typically smaller in absolute value than  $R_0$  for  $k_F < k_p/2$ , and becomes larger for  $k_F \approx k_p/2$  and  $k_F > k_p/2$  ( $k_F$  is the concentration dependent Fermi wave number).
- ii) The effect of the integral operator in the collision equation is smaller than the "band structure effect" (i). It generally leads to an increase of  $|R|$ , the  $k_F$ -dependence of this effect being related to the wave number dependence of  $S(q)$ .

Quantitatively the effect on  $R$  is still relatively small for reasonable pseudopotentials and yields deviations  $\delta R \equiv R - R_0$  corresponding to those reported

for the liquid state [8] as to their magnitude and concentration dependence. In order to explain the larger  $\delta R(x)$  for the low  $T$  films one may again have to invoke  $s-p$  hybridization.

In transition metal alloys such hybridisation effects may even be more important, causing significant deviations from the free electron "band structure". Incidentally one of the authors (H.B.) is in possession of a letter from H. Thomas (dated October 14, 1980), in which he points out the possibility of obtaining deviations from  $R_0$ , in particular the often observed positive values of  $R$ , by assuming an effective dispersion  $E(k)$  with portions of positive and negative slope at the Fermi energy, due to  $s-d$  hybridisation. Later on, such hybridisation effects have been studied in more detail by various authors [10], who have indeed obtained positive Hall coefficients on this basis.

### 3. Multiple Scattering Effects in the Electrical Resistivity

As is well-known, the striking feature of the electrical resistivity  $\rho$  in many amorphous metals is its negative temperature coefficient  $\alpha \equiv \frac{1}{\rho} \frac{d\rho}{dt}$  [1]. The experimental findings are often summarized by Mooji's rule (originally found for disordered crystalline alloys [12]), stating that typically  $\alpha < 0$  when  $\rho > \rho^* \approx 150 \mu\Omega \text{ cm}$ .

We have used our results for the  $T$ -matrix of muffin-tin clusters in order to investigate the influence of multiple scattering (MS), which is neglected in the usual weak-scattering approaches like the Ziman formula, on electrical transport coefficients. We postpone the general question, how the full  $T$ -matrix should finally appear in a generalized transport equation, to the end of this paragraph, and we first present some facts concerning the exact "scattering power" of a single small cluster, represented by its total cross-section  $\bar{\sigma}(E)$  and its contribution  $\rho(E)$  to the electronic resistivity, given by

$$\rho(E_F) = \frac{3h}{2^7 \pi \Omega e^2 k_F^4} \int d\mathbf{k} \int d\mathbf{k}' (\mathbf{k} - \mathbf{k}')^2 |T(\mathbf{k}, \mathbf{k}'; E_F)|^2 \quad (1)$$

which is the result of a Boltzmann equation approach with the transition probability in the collision integral being given by  $|T|^2$ , the differential cross section for a collision of the electron at the Fermi energy  $E_F$  with the full ensemble of (rigid) ions. ( $\Omega$ , the volume of the total system formed by the cluster and the surrounding electron gas, is given for later discussion and is of no relevance for the cluster calculations).

The following main results reveal some interesting insight into the physics of multiple scattering [6]:

i) MS can increase or decrease the scattering power of the cluster with respect of the single scattering result (where  $T$  is replaced by the sum of the individual atomic  $t$ -matrices), depending on the energy  $E$  of the scattered electron. The effect is easily understood by considering the condition for constructive or destructive interference of a de Broglie wave diffracted by two neighboring atoms in the cluster. In fact the case of a dumbbell (2 site cluster) which can be solved analytically for  $s$ -scattering, for example, already exhibits the main features of this interferences effect.

A very drastic reduction through MS of  $\bar{\sigma}(E)$  or  $\delta\rho(E)$  can occur for  $d$ -scatterers in the energy domain where the single site phase shift goes through resonance. This effect may then eliminate the discrepancy between calculated and measured  $\rho$ -values in transition metals or rare earths [13, 14].

ii) Comparing  $\bar{\sigma}$  or  $\delta\rho$  for a cluster of symmetric structure with one which has undergone random deformations yields insight into the structure sensitivity of MS. For weak scatterers the ratio  $\gamma(E) \equiv \delta\rho_{\text{def}}(E)/\delta\rho_{\text{sym}}(E)$  oscillates around one. In particular  $\gamma < 1$  (i.e. the deformations have reduced the total scattering power) around the energy value  $E \equiv k_F^2/2m$  with  $2k_F \approx k_p$ . This reconfirms the Ziman prediction for negative temperature coefficients  $\alpha$  of  $\rho$ , the higher "temperature" of the cluster being expressed by its less ordered structure. Strong scatterers show an entirely different behavior: here  $\gamma$  is somewhat smaller than one in a rather large energy domain, in which  $\delta\rho(E)$  is relatively large. This is consistent with Mooji's rule: negative  $\alpha$ 's are usually accompanied by large values of  $\rho$ . This result shows that in a strong scattering system the Ziman criterion  $2k_F \approx k_p$  for  $\alpha < 0$ , which requires a strong correlation between electronic and ionic structure, loses its importance and is replaced by Mooji's rule which may be viewed as a precursor effect of localisation in strongly disordered metals [15]. It also becomes clear from such cluster calculations that the Ziman approximation becomes more unreliable when the structure (in a relatively large cluster) is rather ordered, because the coherence effects in multiple scattering (which make the resistivity of a perfectly periodic lattice vanish!) are ignored. This should certainly be remembered in the calculation of  $\rho$  for quasicrystalline or nanocrystalline alloys.

Let us now, as a final point, examine how the full  $T$ -matrix of a non-crystalline metal, which contains all the multiple scattering information on the system, should appear in an improved transport theory. The most natural expression for  $\rho$  might be (1) used by various authors [16], approximating  $|T|^2$  for a macroscopic system by suitably factorizing higher order ionic structure factors. Expression (19 is, indeed, related to a rigorous expression for  $\rho$  of the

form [17, 18]:

$$\rho = N/(1 + D) \quad (2)$$

where  $N$  is a force-force and  $D$  a velocity-force correlation function for the conducting electrons.  $N$  can be shown to be equal to expression (1) [17], so, if one is willing to neglect  $D$  with respect to 1, Eq. (1) turns out to be exact and may be expected to be the best generalisation of Boltzmann result. This is, however, a fallacy!

Our cluster calculations give indeed a first, "naïve" indication that something is wrong with (1): the values of  $\rho(E)$  and  $\bar{\sigma}(E)$ , when the normalizing volume  $\Omega$  (showing up in equation (1)) is taken to be the cluster volume, get smaller and smaller for larger and larger clusters. This is related to the fact that cross-sections increase only like an area and therefore it appears that one can only obtain a finite thermodynamic limit from (1) by making approximations! In particular the single site (Ziman) approximation which neglects all the coherence due to MS (or any similar approach which would describe the macroscopic solid by superposing the results from small cluster regions) brings in sums of the form  $\sum_{n,m} \exp(i\mathbf{q}(\mathbf{R}_n - \mathbf{R}_m))$  which guarantee a finite thermodynamic limit for expression (1).

Huberman and Chester [18] have carefully analyzed the relationship between expression (2) for  $\rho$  and the Kubo formula for the conductivity  $\sigma$ . They have shown that both, numerator and denominator of (2), vanish in the limit  $\varepsilon \rightarrow 0$ ,  $\exp(\varepsilon|t|)$  being the usual convergence factor in time integrals showing up in  $N$  and  $D$ . The ratio  $N/(1 + D)$  nevertheless goes to a finite limit, coinciding with the inverse of  $\sigma$ , as expected. Unfortunately, this means that (1) cannot be used for calculating  $\rho$ . By doing partial integrations in time Milinski [19] has put the dynamic conductivity in the form of a force-force correlation function:

$$\sigma(\omega) = \frac{N(\omega) - im\omega}{\omega^2} \quad (3)$$

Here,  $N(\omega)$  is the frequency dependent force-force correlation function. Due to the denominator, we need the coefficient of  $\omega^2$  of  $N$ , even in order to evaluate the zero frequency conductivity! When  $N$  is again rewritten in terms of the total  $T$ -matrix, this means that – in contrast to what was assumed in Eq. (1) – we need the off-energy-shell  $T$ -matrix in order to calculate  $\rho$  or  $\sigma$ .

All these considerations show that it is not a simple task to incorporate multiple scattering in a "sound" way into electronic transport of strongly scattering disordered metals. A promising approach

seems to be the effective medium approximation (EMA) that has proven to be quite successful in accounting for short-range order in the calculation of the density of states and the one-electron spectral function of liquid and amorphous metals [20]. Roth and Singh [21] have used the same ideas for transport by deriving a Bethe-Salpeter equation for the two-electron vertex function. However, much more work has to be done in order to reduce the computational effort to a level, where "every day calculations" can be performed and where a simple insight into the effect of multiple scattering, as they have been revealed in our cluster calculations, becomes possible.

It is a great pleasure to thank H. Thomas for many illuminating discussions on transport phenomena. We thank Steve Nettel for drawing our interest to Milinski's work, and M. Itoh, as well as W. Götze for many valuable discussions. This work has been supported by the Swiss National Science Foundation.

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## SCATTERING FROM TWO NON-OVERLAPPING CENTERS ☆

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The scattering of a particle by two non-overlapping fixed centers is studied in the limit where the individual scatterings take place in one partial wave only. The resulting scattering amplitude and its generalized phaseshifts are obtained in closed analytical form. Numerical calculations are presented in the case of d-waves.

The problem of multiple scattering from fixed scatterers has a long history in several branches of physics: its modern quantum-mechanical solution was first found by Foldy [1] in the case of s-waves. Then Korringa [2] and Kohn and Rostoker [3] introduced it in connection with band theory. Independently it was initiated in nuclear physics by Brueckner [4] and Drell and Verlet [5] for the scattering of pi-mesons from the deuteron. Shortly after came the demonstration of the so-called Bég theorem [6]. This theorem states that if the scatterers do not overlap then the total scattering amplitude can be expressed entirely in terms of the on-shell scattering amplitudes from the individual scatterers. This has the important consequence that multiple scattering from an assembly of non-overlapping scatterers can be calculated without knowledge of the individual potentials. Extensive use of this property has been made in the analysis of nuclear reactions since.

The main purpose of this letter is to give a pedagogical summary of the results concerning the scattering from two non-overlapping centers when scattering from the individual centers is dominated by one partial wave  $l$ . This includes the important physical cases of low energy ( $l=0$ ) or resonance scattering in particle physics as well as electronic properties of simple ( $l=0$ ) or transition ( $l=2$ ) metals in solid state physics. The derivation of the formulae will not be repeated here since they can be

gathered (sometimes with painful work) from the extensive literature on the subject. The general expression of the scattering amplitude for an arbitrary number of non-overlapping potentials of spherical symmetry has been derived in great detail by Agassi et al. in a series of papers [7]. Due to the necessary expansion into partial waves their expressions involve quite a large number of angular recouplings. However in our case of two scatterers in one partial wave the scattering amplitude from incoming momentum  $k$  to outgoing momentum  $k'$  can be cast into the simple analytical form

$$F(k', k) = 4\pi \sum_m Y_m^l(k') Y_m^{*l}(k) \times \frac{2f_l \cos(\frac{1}{2}q \cdot d) + 2kf_l^2 H_{lm} \cos(K \cdot d)}{1 - (kf_l H_{lm})^2}, \quad (1)$$

where  $q = k' - k$  denotes the momentum transfer,  $K = \frac{1}{2}(k' + k)$  the average momentum,  $f_l$  the partial wave amplitude for the scattering from one center and  $|k| = |k'| = k$ . By choosing the quantization axis along the separation distance  $d$  of the two scatterers, the structure functions  $H_{lm}$  of eq. (1) are diagonal in  $m$ ,

$$H_{lm} = \sum_{\substack{l' \text{ even} \\ 0 \leq l' \leq 2l}} (-1)^{l'/2} \sqrt{4\pi(2l'+1)} \times \int d\Omega Y_m^{*l} Y_m^l Y_0^{l'} h^{(+)}(kd) \equiv N_{lm} + iJ_{lm}, \quad (2)$$

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the integration over the three spherical harmonics being known as Gaunt numbers [8] and the  $h\}^{+}$  as outgoing spherical Bessel functions (we use the definition of ref. [9]). The functions  $J_{lm}$  and  $N_{lm}$  result from the decomposition of  $h\}^{+}$  into its irregular  $n_l$  and regular  $j_l$  part. For real values of  $k$  they also coincide with the real and imaginary parts of  $H_{lm}$ . Expression (1) for the scattering amplitude was first proposed by Brueckner [4] for the special case of s- or p-wave. Its standard interpretation in terms of multiple scatterings is obvious: The first term in the numerator describes the scattering from one center only (single scattering), the second from two centers (double scattering) and the denominator leads to rescattering terms on the same center. As can be seen from the presence of the scalar products  $q \cdot d$  and  $K \cdot d$  in the trigonometric functions, eq. (1) does not correspond to a partial wave expansion of the scattering amplitude  $F(k', k)$ . As found in ref. [7] this special form is particularly hard to generalize to the presence of more than one partial wave or more than two centers. This is not the case however if generalized partial wave phase-shifts are introduced.

The method of partial waves for nonspherical scatterers was introduced by Demkov and Rudakov [10] in the case where the potential is invariant under a given symmetry group. For two centers the symmetry group corresponds to the  $D_{\infty}$  group and the characteristic scattering amplitudes

$$A_{\lambda} = C_{\lambda} Y_m^l(\hat{k}) \cos(\frac{1}{2}k \cdot d), \quad \text{if } \lambda = (l, m, \epsilon = +1),$$

$$= C_{\lambda} Y_m^l(\hat{k}) \sin(\frac{1}{2}k \cdot d), \quad \text{if } \lambda = (l, m, \epsilon = -1),$$

(3)

form a complete set of orthogonal functions on the surface of the unit sphere. They can be normalized by choosing the coefficients  $C_{\lambda}$  according to

$$C_{\lambda} = [\frac{1}{2}(1 \pm J_{lm})]^{-1/2}, \quad \lambda(l, m, \pm 1),$$

(4)

where the functions  $J_{lm}$  are defined through eqs. (2). With this particular choice we then obtain that

$$\int d\Omega_k A_{\lambda}^*(k) A_{\lambda}(k) = \delta_{\lambda\lambda'}$$

(5)

Note that the eigenfunctions  $A_{\lambda}$  do not depend on the dynamics but only on the symmetry group. As is the case for potentials of spherical symmetry, they diagonalize the scattering amplitude (1), the resulting expression being

$$F(k', k) = 4\pi \sum_{\lambda} A_{\lambda}(k') F_{\lambda} A_{\lambda}^*(k),$$

(6)

with

$$F_{\lambda} = \frac{1 \pm J_{lm}}{1/f_l \mp k H_{lm}}, \quad \text{for } \lambda = (l, m, \pm 1),$$

$$= 0, \quad \text{otherwise.}$$

(7)

Due to unitarity the partial amplitude  $F_{\lambda}$  of eq. (7) lies on a circle centered at the complex point  $i/2k$  with radius  $1/2k$  and consequently can be expressed in terms of generalized phase-shifts  $\eta_{\lambda}$

$$F_{\lambda} = \frac{1}{2ik} [\exp(2i\eta_{\lambda}) - 1]$$

(8)

Comparison between eqs. (7) and (8) yields

$$\eta_{\lambda} = -\arg(\text{ctg } \delta_l - i \mp H_{lm}), \quad \text{for } \lambda = (l, m, \pm 1)$$

$$= 0, \quad \text{otherwise,}$$

(9)

where  $\delta_l$  denotes the phase-shift of partial wave  $l$  for the scattering from one center. The function between parentheses whose argument gives the phase-shifts  $\eta_{\lambda}$  corresponds to the generalization of the Jost function [11] for non-spherical potentials. Eq. (9) represents the main result of this letter since it solves the problem of the scattering by two non-overlapping potentials. On the other hand it has been shown [12] that the  $\eta_{\lambda}$  satisfy the two-dimensional secular equation

$$\det \left| \begin{pmatrix} \text{ctg } \delta_l & -N_{lm} \\ -N_{lm} & \text{ctg } \delta_l \end{pmatrix} \right.$$

$$\left. - \text{ctg } \eta_{\lambda} \begin{pmatrix} 1 & J_{lm} \\ J_{lm} & 1 \end{pmatrix} \right| = 0,$$

(10)

whose solution coincides with eq. (9). Within this method numerical calculations have been performed for the scattering from up to 19 s-wave scatterers [13]. In fact eq. (10) (or rather its generalization to  $n$ -centers) is the easiest way of getting the generalized phase-shifts when there are many scatterers. This is especially useful if one only needs to calculate the forward scattering amplitude averaged over the orientation of  $k$  or  $d$ ,

$$\langle F(0) \rangle = \frac{1}{4\pi} \int d\Omega_k F(k, k) = \sum_{\lambda} F_{\lambda}, \quad (11)$$

which is determined by the phase-shifts  $\eta_{\lambda}$  alone in complete analogy with the spherical case. By applying the optical theorem to eq. (11) we also get the expression for the average total cross section

$$\langle \sigma \rangle = \frac{4\pi}{k^2} \sum_{\lambda} \sin^2 \eta_{\lambda}. \quad (12)$$

Note that the values of the  $\eta_{\lambda}$  depend on the choice of the direction of  $d$  (z-axis in this work) but  $\langle F(0) \rangle$  or  $\langle \sigma \rangle$  not. In principle the summation over  $\lambda$  in eqs. (6), (11) and (12) contains  $4l \pm 2$  terms but, due to the symmetry properties of the functions  $H_{lm}$ , the phase-shifts are degenerate according to

$$\eta_{(l,-m,\epsilon)} = \eta_{(l,m,\epsilon)}, \quad (13)$$

and only  $2l+2$  different phase-shifts subsist. Half of them determine the scattering amplitude at low energy [10] since

$$\lim_{k \rightarrow 0} (k^{-2l-1} \eta_{\lambda})$$

$$= \frac{2a_l}{1 - \gamma_{lm} a_l / d^{2l+1}}, \quad \text{if } \lambda = (l, m, +1),$$

$$= 0, \quad \text{otherwise,} \quad (14)$$

where  $a_l$  denotes the same limit for the phase-shift  $\delta_l$  and

$$\gamma_{lm} = (-1)^{l-m} [(2l-1)!!]^2 \frac{(2l+1)!}{(l-m)!(l+m)!}. \quad (15)$$

This can be seen clearly in fig. 1 which shows the behavior of the six non-degenerate partial total cross sections as functions of the incident momentum in the case of the d-wave. The indexes  $\lambda$  have been labeled by the irreducible representations of the  $D_{\infty h}$  group with the obvious correspondence

$$\lambda(2, 0, +1) \leftrightarrow \Sigma_g^+, \quad \lambda(2, 0, -1) \leftrightarrow \Sigma_u^+,$$

$$\lambda(2, \pm 1, \pm 1) \leftrightarrow \Pi_u, \quad \lambda(2, \pm 1, -1) \leftrightarrow \Pi_g,$$

$$\lambda(2, \pm 2, +1) \leftrightarrow \Delta_g, \quad \lambda(2, \pm 2, -1) \leftrightarrow \Delta_u, \quad (16)$$

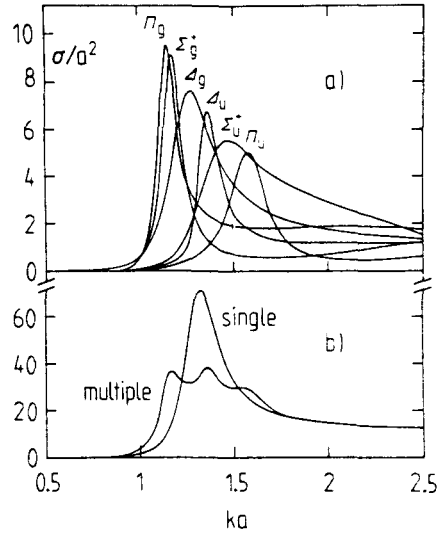


Fig. 1. Partial total cross sections (a) and their sum (b) for the scattering by two non-overlapping potential wells of range  $a$ . The curves correspond to the six non-degenerate values of  $\lambda$ . The input parameters are  $2mV_0 a^2 / \hbar^2 = -17$  and  $d/a = 2.4$ . Also represented in (b) is the single scattering result.

The  $l=2$  phase-shift  $\delta_l$  needed as input corresponds to the solution of the Schrödinger equation for a square-well potential of depth  $2mV_0 a^2 / \hbar^2 = -17$ . This special value was chosen since it gives rise to a resonance in the  $l=2$  partial wave. Fig. 1a shows that this resonance propagates to all generalized phase-shifts  $\eta_{\lambda}$  but with a certain splitting in energy. In other words each partial wave amplitude  $F_{\lambda}$  (7) has a pole in the complex  $k$ -plane close to the real axis which correspond to the complex zeros of the Jost function [14]. The trajectories of these poles when the separation distance  $d$  is varied are shown in fig. 2. Although it can be qualitatively understood in term of the structure functions  $H_{lm}(kd)$  with  $k$  equal to the zero of  $\text{ctg}(\delta_l) - i$ , the behavior of the positions and widths of these resonances are rather complicated functions of  $d$ . This genuine multiple scattering effect gives rise to a decrease and broadening of the total cross section compared to the single scattering limit. This is clearly seen in fig. 1b and well known in the field of pion scattering by nuclei [15]. The same effect has also been advocated for explaining the overestimation of the resistivity in the coherent single scattering calculations for some transition

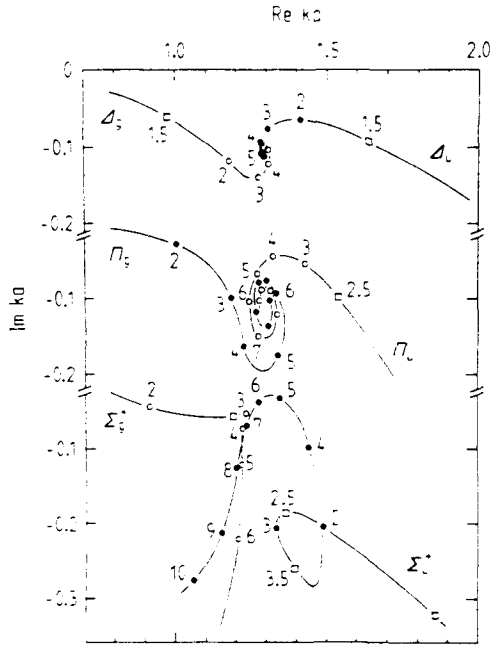


Fig. 2. Trajectories of the resonant  $l=2$  poles in the complex  $k$ -plane for the scattering by two non-overlapping potential wells of range  $a$ . The curves correspond to the six non-degenerate values of  $\lambda$ . Note the shift in the vertical scale between the  $m=0, 1$  and  $2$  cases. The numbers beside the poles give the corresponding values of the separation distance  $d/a$ . The input parameter is  $2mV_0a^2/\hbar^2 = -17$ .

metals [16,17].

In conclusion the method of the generalized phase-shifts gives rise to a very simple analytical solution to the problem of the scattering by two centers when scattering from the individual centers is dominated by one partial wave. The equations quoted in this letter have been derived under the non-overlapping hypothesis but they are also valid in the special case of separable potentials if the structure functions  $H_{lm}$  are changed accordingly [18]. The generalized phase-shifts  $\eta_\lambda$  can easily be obtained by solving the secular equation (10) and the averaged total cross section depends only on these. This is also true for more than two scatterers and Demkow and Rudakov [10] give the exact expression for a cubic arrangement of eight

s-wave centers. The extension of the method to more than one partial wave is also possible and should lead to analytical results in the case of a few numbers of scatterers. This could happen to be very efficient for calculating both pion- $^{12}\text{C}$  elastic scattering within the alpha-particle model [19] and electrical resistivity of small clusters of vacancies in irradiated metals.

We are extremely grateful to Professor H. Beck for suggesting this work and for enlightening discussions. Useful comments from Professor P. Huguenin are also acknowledged.

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# STUDY OF THE TEMPERATURE COEFFICIENT OF THE RESISTIVITY OF LIQUID

## AND AMORPHOUS METALS : CLUSTERS CALCULATIONS.

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**Abstract:** Using a multiple scattering approach, we have studied the influence of increasing structural disorder on the resistivity of small clusters of s-scatterers. We find a transition from Ziman behaviour (weak scattering regime) to Mooij behaviour (strong scattering regime).

1. **Introduction:** The temperature coefficient of the resistivity  $\rho$  of many amorphous and liquid metals is negative particularly when  $\rho$  is higher than a critical value of about  $150 \mu\Omega \cdot \text{cm}$ . This is Mooij's rule, which has not yet found a generally accepted explanation.

This paper is based on an expression for  $\rho$  in terms of the total scattering matrix  $T(\mathbf{k}, \mathbf{k}')$  of the metal giving the scattering amplitude for an elastic electron-ion collision from momentum  $\hbar \mathbf{k}$  to  $\hbar \mathbf{k}'$ . At  $T=0$  it has the form:

$$g = \frac{3 \hbar}{2^7 \pi \Omega e^2 k_F^4} \int d\Omega_{\mathbf{k}} \int d\Omega_{\mathbf{k}'} |T(\vec{\mathbf{R}}, \vec{\mathbf{R}}', E_F)|^2 (\vec{\mathbf{R}} - \vec{\mathbf{R}}')^2 \quad (1)$$

$\Omega$  being the volume of the system and the integration running over the directions of  $\mathbf{k}$  and  $\mathbf{k}'$ , with  $(\hbar \mathbf{k})^2 = (\hbar \mathbf{k}')^2 = (\hbar \mathbf{k}_F)^2 = 2mE_F$ . As stated by [1], this result can be obtained by a Boltzmann equation approach [2] where the transition probability in the collision integral is given by  $|T(\mathbf{k}, \mathbf{k}')|^2$ . We have calculated the exact T-matrix, describing rigorously the scattering effects of all ions on an incoming free electron, for some clusters. The resistivity of a piece of metal, connected to a perfect conductor, is then taken to be the incoherent sum of cluster contributions, calculated according to (1). This allows us to discuss multiple scattering contributions to  $\rho$  for a given arrangement of ions, and to study the influence of a change in this arrangement on  $\rho$ . For more details see [3].

2. **Theoretical framework:** We consider the one-electron Hamiltonian:

$$H = \frac{p^2}{2m} + \sum_{n=1}^N V_n(\vec{\mathbf{r}} - \vec{\mathbf{R}}_n) \quad (2)$$

where  $V_n$  is a muffin-tin potential at site  $\mathbf{R}_n$ . For such a Hamiltonian it is possible, [4], to calculate the T-matrix and the generalized phase-shift [5], [6]. The latter are the eigenvalues of the matrix  $\tau_{nm}$ , describing all scattering processes beginning at site  $n$  and ending at site  $m$ . In order to exhibit multiple scattering effects, it will be useful to compare the results with the single site approximation  $\rho_{ss}$  given by the usual Ziman T-matrix formula [7]:

$$g_{ss} = \frac{3 \hbar \pi^3}{e^2 k_F^6 \Omega} \int_0^{2k_F} dq q^3 S(q) |T(q, k_F)|^2 \quad (3)$$

where:

$$q^2 = 2 k_F^2 (1 - \cos \theta) \quad (4)$$

and:

$$T(q, k_F) = - \frac{1}{k_F} \sum_{\ell \geq 0} (2\ell+1) e^{i\delta_\ell(k_F)} \sin \delta_\ell(k_F) P_\ell(\cos \theta) \quad (5)$$

$\theta$  being the scattering angle between  $k$  and  $k'$ . We have done our calculations for various clusters of  $N$  identical  $s$ -scatterers. The neglect of all single-site phase-shifts  $\delta_\ell$  for  $\ell > 1$  considerably simplifies the computational scheme and should be adequate in order to discuss simple metals. The muffin-tin potential was modelled by the square well of depth  $V_0$  and radius  $a$ . Where we use  $V_0$  values for which the phase-shifts  $\delta_\ell$ ,  $\ell > 1$  would be non-negligible, our restriction to  $s$ -phase shifts has of course only model character.

We have studied the following types of clusters:

i) Ordered clusters of fcc symmetry comprising the first and second shell of neighbors, i.e.  $N=13$  and  $N=19$ . The distance  $d$  between nearest neighbors was chosen to be  $2.2 a$ . The fcc structure has the advantage to represent a close packed neighbor structure typical of a disordered metal with a high coordination number. Even though it has the point symmetry of a perfect crystal, the electronic properties of such a cluster are typical of a disordered metal, since by summing the contributions of many clusters incoherently we discard any long range order.

ii) In order to study the influence of the cluster structure, more particularly of its degree of order or disorder, on its electronic properties, we have deformed the two ordered fcc-like clusters by random displacements of the atomic sites, respecting the condition that two potential wells do not overlap.

Two clusters with the same number of particles but with different degree of disorder can be used to simulate the effect of thermal vibrations of the ions on the electronic properties. In the regime of sufficiently high temperatures an electron moving through the cluster sees the instantaneous ionic configuration. Thus the disordered cluster will represent a high temperature system and the ordered cluster models the same system at low  $T$ . We will use the notation (13.0) and (13.0) for ordered and disordered  $N=13$  clusters, respectively.

3. Results: Let us introduce the quantity

$$\mu = \frac{S_{DIS}}{S_{ORD}} - 1$$

in an obvious notation.

$\gamma$  can be thought of as the "temperature coefficient of the resistivity" in particular  $\gamma < 0$  when increasing disorder lowers the resistivity which is "unusual" for a "normal" metal. Figure 1 shows  $\gamma$ , the structure factor and the resistivity as functions of  $k_F$ . The single site result  $\gamma_{SS}$  has the same behaviour for all values of the potential: it is negative when  $2 k_F$  is located near a peak of  $S(q)$ . This is the well-known Ziman behaviour [8], [9]. The  $\gamma_{MS}$  curves for weak potentials differ little from  $\gamma_{SS}$ , and therefore follow Ziman's behaviour too. For strong potentials,  $\gamma_{MS}$  oscillate little and lies somewhat below 0 up to a value of  $k_F$  corresponding to a critical value  $\rho_c$  of  $\rho$ . Having chosen an interatomic distance typical of simple metals,  $\rho_c$  is around  $120 \mu\Omega \cdot \text{cm}$ . It is interesting to notice that  $\rho_c$  is augmented by decreasing the disorder. Here  $\gamma_{MS}$  obeys Mooij's rule: when, in a disordered metal  $\rho$  is larger than a critical value, (of the order of  $150 \mu\Omega \cdot \text{cm}$  in real systems), the temperature coefficient is negative, otherwise it is positive.

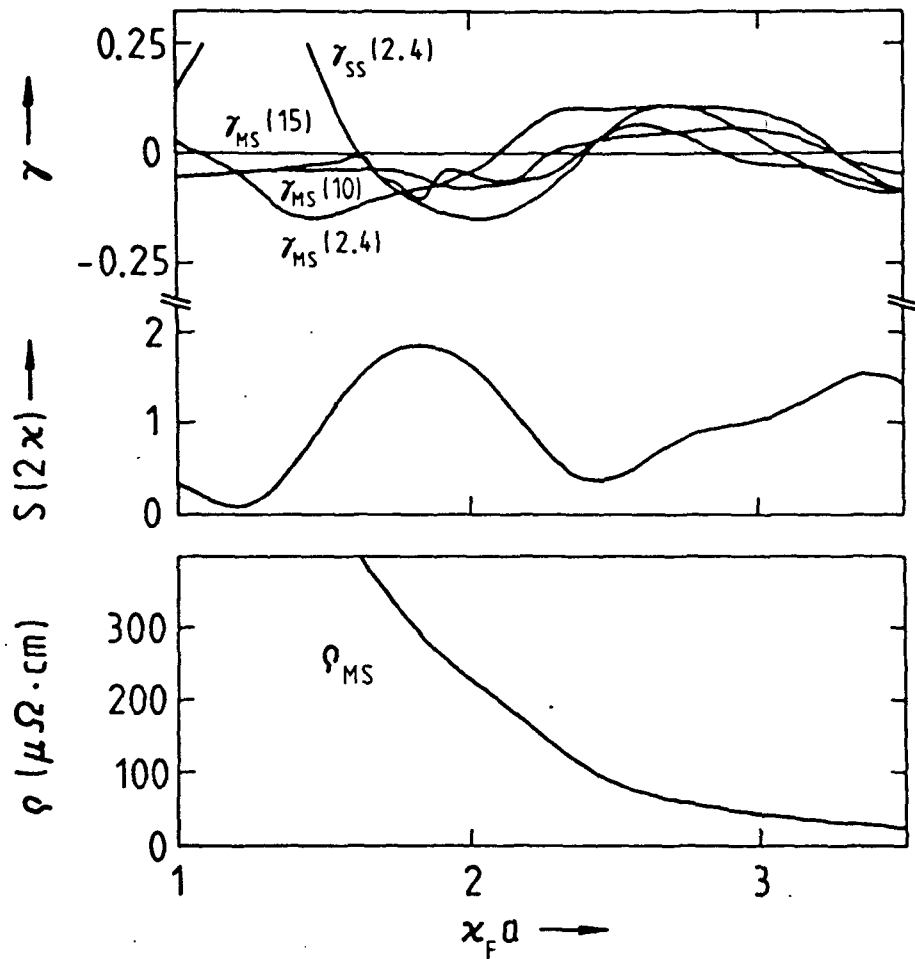


fig. 1

Figure 2 shows the cluster phase-shifts as functions of the Fermi wave number  $k_F$  for the potential strength  $V_0 a^2 = 10$ . This is a strong potential which has a bound state. Due to the symmetry, the cluster (13.0) has only 6 distinct phase-shifts, the degeneracies of which are removed by the disorder. Let us discuss the influence of increasing disorder on the scattering power of the cluster in terms of the total cross-section given by [5]:

$$\sigma = \frac{4\pi}{k_F^2} \sum_{\lambda} \sin^2 \eta_{\lambda}(k_F) \quad (6)$$

For the cluster (13.0) a three-fold degenerated phase-shift  $\eta_{\lambda}$  yields the contribution  $\sigma_{\lambda}^{(0)} = (4\pi/k^2)3 \sin^2 \eta_{\lambda}$  to  $\sigma$ . In the cluster

(13.0) the corresponding branch is split into three  $\eta_{\lambda}^1, \eta_{\lambda}^2, \eta_{\lambda}^3$ , which yields  $\sigma_{\lambda}^{(D)} = 4\pi/k^2 \sum_i \sin^2 \eta_{\lambda}^i$ . For strong scattering systems many branches  $\eta_{\lambda}$  are close to  $\pi/2$  for typical values of  $k_F$  for simple metals (this case is shown in Fig. 2). For such a branch,  $\sigma_{\lambda}$  is large ( $\sin \eta_{\lambda} = 1$ ) and a simple estimate yields  $\sigma_{\lambda}^{(D)} < \sigma_{\lambda}^{(0)}$ .

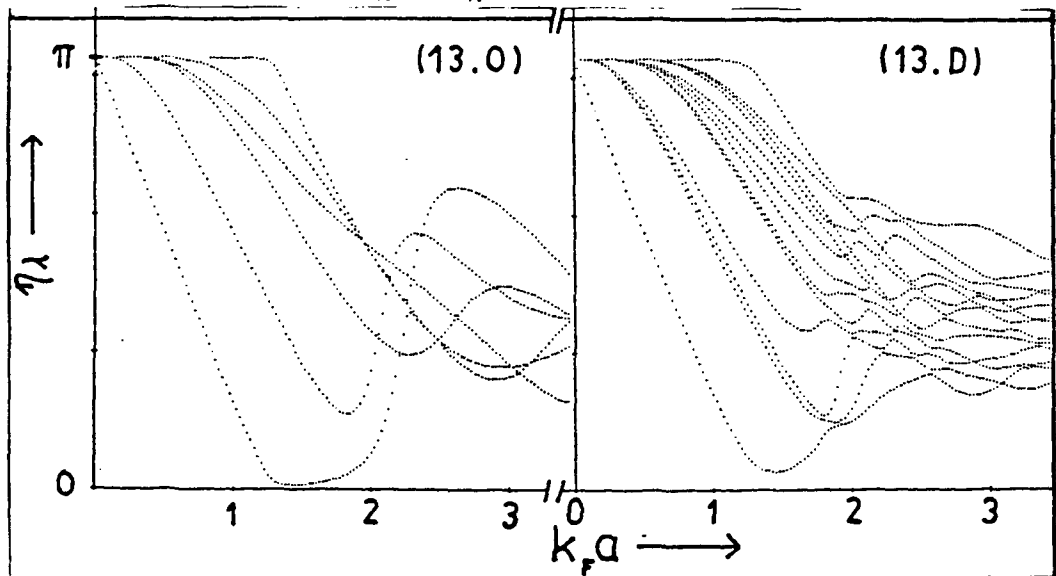


fig. 2

Contrary to this, for weak potentials, the relevant phase-shifts are small. Then  $\sigma_{\lambda}$  is small and  $\sigma^{(D)} > \sigma^{(0)}$ . Therefore Mooij's rule for the total cross-section,  $\sigma^{(D)} < \sigma^{(0)}$  if  $\sigma$  is larger than a critical value finds a simple explanation in terms of the splitting of local degeneracies of the cluster phase-shifts by an increasing disorder.

4. Conclusion: Our cluster calculations exhibit both Ziman and Mooij behaviour, depending on the potential strength which suggests that the  $T$ -dependence of the resistivity of liquid and amorphous materials can be explained in the framework of potential scattering. Obviously such cluster calculations will not yield reliable numerical values for the resistivity of real systems but they can be used as a test for an analytical calculation. Work in this direction is in progress. This work has been supported by the Swiss National Foundation.

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