Electrical Resistivity of Liquid Metals in Regime of Short Mean Free Path

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Electrical Resistivity of Liquid Metals in Regime of Short Mean Free Path

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Using the force–force correlation function formula for electrical resistivity, plus an approximate result of Bardeen for the effect of scattering on the off-diagonal elements of the density matrix, a self-consistent method of calculating the electronic mean free path in liquid metals is proposed.

1 INTRODUCTION

The weak scattering theory of the electrical resistivity ρ of simple liquid metals[1,2] has been successful in dealing with long mean free path situations. One of its limitations is that the finite electronic mean free path corresponds to a blurring of the Fermi surface, and this is obviously not included when one writes[3]

$$\rho_{nfe} = \frac{3\pi}{\hbar e^2 v_f^2 \rho_i} \frac{1}{(2k_f)^4} \int_0^{2k_f} S(k) |v(k)|^2 \, 4k^3 \, dk, \tag{1}$$

since the sharp Fermi surface assumption is clear from the limits of the momentum transfer integration. Here, as usual, v_f is the Fermi velocity, ρ_i is the mean ionic density, k_f the Fermi wave number, $S(k)$ the liquid structure factor and $v(k)$ the pseudopotential for a single screened ion.

Though modifications of Eq. (1) have been proposed, no relaxation of the sharp Fermi surface condition appears to have been contemplated in the presence of a finite electronic mean free path l. Therefore, there is a need for an internally consistent generalization of Eq. (1) in which the Fermi surface blurring is incorporated consistently with the finite mean free path which emerges from the calculation.

2 FORCE-FORCE CORRELATION FUNCTION AND FERMI SURFACE BLURRING

To effect an approximate generalization of Eq. (1), we start from the force–force correlation function formula for electrical resistivity.[4,5] This reads, with F denoting the force–force correlation,

$$\rho \propto F = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \frac{\partial V(\mathbf{r}_1)}{\partial \mathbf{r}_1} \cdot \frac{\partial V(\mathbf{r}_2)}{\partial \mathbf{r}_2} \, |\sigma(\mathbf{r}_1 \mathbf{r}_2 E_f)|^2 \tag{2}$$

where V is the total scattering potential while σ is the energy derivative of the Dirac density matrix evaluated at the Fermi energy E_f. If we write

$$V(\mathbf{r}) = \sum_i v(\mathbf{r} - \mathbf{R}_i) \tag{3}$$

for the ionic configuration $\mathbf{R}_i$, then inserting the free-electron approximation σ_0 for σ in Eq. (2), namely

$$\sigma_0(\mathbf{r}_1 \mathbf{r}_2 E_f) = \frac{k_f}{\pi^2} \frac{\sin(k_f|\mathbf{r}_1 - \mathbf{r}_2|)}{k_f|\mathbf{r}_1 - \mathbf{r}_2|} \tag{4}$$

the result (Eq. 1) follows after performing a liquid average. The essential step involved is to consider the convolution

$$\int \frac{\partial V(\mathbf{r}_2)}{\partial \mathbf{r}_2} \, |\sigma_0(\mathbf{r}_1 - \mathbf{r}_2)|^2 \, d\mathbf{r}_2$$

in Fourier transform (FT) which yields

$$FT \int \frac{\partial V(\mathbf{r}_2)}{\partial \mathbf{r}_2} \, |\sigma_0(\mathbf{r}_1 - \mathbf{r}_2)|^2 \, d\mathbf{r}_2 = i\mathbf{k} V(\mathbf{k}) FT \, |\sigma_0(\mathbf{r}_1 \mathbf{r}_2)|^2$$

$$= i\mathbf{k} V(\mathbf{k}) \Gamma_0(k, k_f) \tag{5}$$

Using Eq. (4), apart from unimportant factors, one finds

$$\Gamma_0(k, k_f) = \frac{1}{k} \quad \text{for } k < 2k_f$$

$$= 0 \quad \text{for } k > 2k_f \tag{6}$$

Evidently $V(\mathbf{k})$ is the Fourier transform of the total scattering potential $V(\mathbf{r})$.

Now we have the hint we need to insert approximately the Fermi surface blurring. For it is clear that the cut-off in the Fourier transform of $|\sigma_0|^2$ at $2k_f$ is directly related to part of the undamped oscillatory off-diagonal form $(\sin k_f R/k_f R)^2$ with $R = |\mathbf{r}_1 - \mathbf{r}_2|$, at large distances R from the

diagonal. Since this can be rewritten as, apart from factors

$$\frac{1}{R^2} - \frac{\cos 2k_f R}{R^2} \tag{7}$$

it is clear that $1/R^2$ at large R comes directly from the $1/k$ singularity of Γ_0 at small k while $\cos 2k_f R/R^2$ comes from the discontinuity at $2k_f$ in Γ_0 given by Eq. (6). Though it would seem, at first sight, that only the latter term in (7) is altered by Fermi surface blurring due to disorder scattering, in fact we shall see below that modifications can also occur at fairly small k.

3 BARDEEN'S APPROXIMATION FOR OFF-DIAGONAL DENSITY MATRIX IN PRESENCE OF SCATTERING

It is clear that to calculate σ in Eq. (2) exactly for an arbitrary ionic array of potentials at $\mathbf{R}_i$ given by Eq. (3) is an impossible task. But Bardeen[6] has given an approximate argument which we shall utilize in order that the effect of scattering, plus configurational averaging, is subsumed into the off-diagonal density matrix $\sigma(\mathbf{r}_1\mathbf{r}_2)$ by writing

$$\sigma(\mathbf{r}_1\mathbf{r}_2 E_f) = \sigma_0(\mathbf{r}_1\mathbf{r}_2 E_f) \exp\left(\frac{-R}{2l}\right): \quad R = |\mathbf{r}_1 - \mathbf{r}_2| \tag{8}$$

where l is the electronic mean free path. Since this is at the heart of our proposal to generalize Eq. (1) to deal with short mean free paths, we give what is essentially Bardeen's argument to motivate the choice of the approximate form (Eq. 8) in the Appendix. It is now quite clear that the evaluation of the force–force correlation function F can be carried through precisely as in Section 2, except that $\Gamma_0(k, k_f)$ must be replaced by $\Gamma(k, k_f, l)$ given by

$$\Gamma(k, k_f, l) = \int e^{i\mathbf{k}\cdot\mathbf{R}} |\sigma_0(R)|^2 e^{-R/l} \, d\mathbf{R} \tag{9}$$

$$= \frac{4k_f^2}{\pi^3} \int_0^\infty e^{-R/l} \frac{\sin kR}{kR} \frac{\sin^2 k_f R}{(k_f R)^2} R^2 \, dR \tag{10}$$

Clearly, because of the Bardeen damping factor $e^{-R/l}$, the quantity $\Gamma(k, k_f, l)$ will no longer have a discontinuity at $k = 2k_f$ as depicted in Figure 1. Due to the linear term in R at small R in the Bardeen damping factor, it is easy to show that $\Gamma(k, k_f, l)$ falls of as k^{-4} at large k, with amplitude proportional to $1/l$, and therefore decaying to zero in the sharp Fermi surface limit $l \to \infty$. The detailed form of $\Gamma(k, k_f, l)$ is obtained from the

one-dimensional integral

$$\Gamma(k, k_f, l) = \frac{2}{\pi^3} \int_0^\infty e^{-R/l} \frac{\sin kR}{kR} \frac{(1 - \cos 2k_f R)}{R^2} R^2 \, dR$$

$$= \frac{2}{\pi^3 k} \left[\text{arctg } kl - \tfrac{1}{2}\text{arctg } \frac{2kl}{1 + 4(k_f l)^2 - (kl)^2} \right.$$

$$\left. - \frac{\pi}{2} \theta\left(k - \sqrt{\frac{1}{l^2} + 4k_f^2}\right) \right] \tag{11}$$

where θ is the step function. This reduces to the explicit form $\Gamma_0(k, k_f)$ of Eq. (6) in the limit $l \to \infty$.

Carrying the argument further, as in the nearly free electron theory, we reach the desired result, with p_f the Fermi momentum,

$$\rho = \frac{m}{ne^2 \tau} = \frac{p_f}{ne^2 l} = \int_0^\infty k^4 S(k) |v(k)|^2 \Gamma(k, k_f, l) \, dk \tag{12}$$

with the appropriate constants included now in Γ. Equation (12) is the basic result of the present proposal for dealing with Fermi surface blurring. It must be solved iteratively to get a self-consistent value for the electrical resistivity ρ.

Of course, if we insert Γ_0 for Γ, then we regain ρ_{nfe} of Eq. (1). Suppose the corresponding mean free path is l_0. Then one can insert this in Eq. (10) and hence the right-hand side of Eq. (12) to obtain a new estimate of the resistivity, say ρ_1. Provided in the iteration the same input data is used for $S(k)$ and $v(k)$ at each stage, then it is readily shown that $\rho_1 < \rho_{nfe}$. From ρ_1, a new free path, l_1 say, results which can be used in Eq. (10), and subsequently in the right-hand side of Eq. (12). Since l_1 is greater than l_0, the new approximation for the resistivity, ρ_2 say, is greater than ρ_1, though less than ρ_0. Thus a convergent scheme results.

Naturally, it would never make sense physically if the mean free path l became less than the average interionic spacing.

We must caution that the above argument assumed that the same input information, i.e. the same $S(k)$ and $v(k)$, was used at every stage of the iteration. As far as the structure factor $S(k)$ is concerned, one would use the measured values, and no problem would then arise. But for a given bare-ion pseudopotential, the screening would be done with a dielectric function $\varepsilon(k)$. This is usually taken to have a kink at $2k_f$; for example from the Lindhard dielectric function and its refinements.[7] In fact, this function will depend on the mean free path, and this problem is currently being considered.

4   STATUS OF THE FORCE–FORCE CORRELATION FUNCTION

Since there has been some discussion of the status of formula for ρ in terms of F in Eq. (2), as in the review by March[8] we conclude by clarifying this point. It is clear from the work of Edwards[9] that for weak scatterers distributed randomly, the usual Boltzmann formula comes back from the form of the Kubo-Greenwood formula involving the momentum matrix elements. Thus the formula F in Eq. (2) of Rousseau, Stoddart and March[4] is the form directly comparable to the above form of the Kubo-Greenwood formula, which is known to be valid for the extended states appropriate to the liquid metal problem.

However, there is an alternative form of the Kubo-Greenwood formula, in terms of position rather than momentum matrix elements, which is appropriate to localized states. Here, the form of Eq. (2) is inappropriate. One must return to the discussion of Edwards[10] and include his denominator to yield a form

$$\rho = \frac{N}{1 + D} \tag{13}$$

where the numerator is essentially Eq. (2) as before, but where, in the denominator, D is proportional to

$$\int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \frac{\partial V(\mathbf{r}_2)}{\partial \mathbf{r}_2} \cdot \frac{\partial}{\partial \mathbf{r}_1} \, \sigma(\mathbf{r}_1 \mathbf{r}_2 F_f) \sigma(\mathbf{r}_1 \mathbf{r}_2 F_f). \tag{14}$$

For extended states $D = 0$.[4] However, in the localized states case, the answer is insensitive to boundary conditions, and it can be shown that both N and $1 + D$ in Eq. (13) are zero for "box" boundary conditions. Though this result appears strange, it is clear that if one resolves the indeterminacy by, say, using L'Hopital's rule, one must find that the denominator goes more strongly to zero than the numerator, yielding correctly ρ tends to infinity for localized states.

5   SUMMARY

The basic result of the paper is Eq. (12) which must be solved self-consistently for the electronic mean free path. This equation reduces to the nearly free electron formula for the electrical resistivity of liquid metals when the mean free path tends to infinity on the right-hand side of this equation. Provided the same input, i.e. the same $S(k)$ and $v(k)$ is used as in the nearly free electron case, the resistivity is lowered relative to the nearly free electron result.
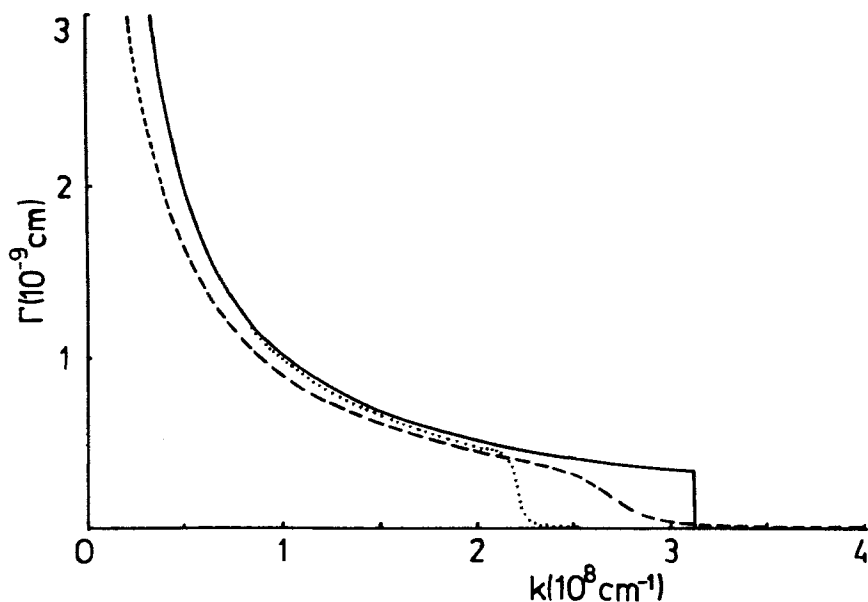
FIGURE 1 Shows effect of finite mean free path, i.e. Fermi surface blurring, on the function Γ_0 defined by Eq. (6) and plotted in continuous curve, with k_f appropriate to Pb.

The Fermi surface blurring is small for the k_f and the measured mean free path of Li, which corresponds to the dotted curve.

Substantial blurring occurs for Hg, as shown by the dashed curve.

However, the dielectric function is in fact altered by the finite mean free path, and hence $v(k)$ becomes also dependent on the free path. This problem is under consideration, and it is intended to present numerical results of the effect of Fermi surface blurring at a later stage. However, the results in Figure 1 of this paper show the nature of the corrections that are thereby incorporated into the resistivity theory.

Appendix

Since it is not possible to calculate exactly the Dirac density matrix for electrons scattered by a distribution of ionic potentials in a liquid metal compatible with the observed short-range order, the argument of Bardeen[6] is very useful in motivating the basic assumption (Eq. 8). He supposes that all the scattering centres in his model are distributed randomly in a slab of width Δ, as shown in Figure A1. Thus, outside the slab, the electron wave
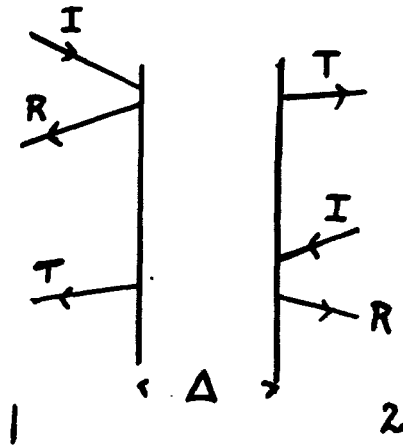
FIGURE A1 Shows Bardeen's model for electron scattering by a random distribution of ions enclosed within a slab of width Δ. I, R and T denote incident, reflected and transmitted beams respectively. Regions marked 1 and 2 are referred to in the text.

functions are plane waves since there are no scattering centres in this region in the Bardeen model. Hence, using simple scattering theory and assuming that the scattering is incoherent, the first-order Dirac density matrix $\rho(\mathbf{r}_1, \mathbf{r}_2)$ with $\mathbf{r}_1$ and $\mathbf{r}_2$ outside the slab, can be determined exactly.

The wave function of one electron hitting the slab from the left, in region 1, is given by

$$\psi_{\mathbf{k}}(\mathbf{r}_1) = e^{i\mathbf{k}.\mathbf{r}_1} + \sum_{k'} R_{\mathbf{kk'}}\, e^{-i\mathbf{k'}.\mathbf{r}_1} \sqrt{\frac{\cos \theta_k}{\cos \theta_{k'}}} \tag{A1}$$

where the cosine is a normalization factor. The transmitted electron wave function, in region 2, is

$$\psi_{\mathbf{k}}(\mathbf{r}_1) = \sum_{k'} T_{\mathbf{kk'}}\, e^{i\mathbf{k'}.\mathbf{r}_1} \sqrt{\frac{\cos \theta_k}{\cos \theta_{k'}}} \tag{A2}$$

Similarly, for one electron entering the slab from the right, the wave function in region 2 is

$$\psi_{\mathbf{k}}(\mathbf{r}_1) = e^{-i\mathbf{k}.\mathbf{r}_1} + \sum_{k'} R_{\mathbf{kk'}}\, e^{i\mathbf{k}.\mathbf{r}_1} \sqrt{\frac{\cos \theta_{\mathbf{k}}}{\cos \theta_{\mathbf{k'}}}} \tag{A3}$$

and the scattered wave to the left of the slab is

$$\psi_{\mathbf{k}}(\mathbf{r}_1) = \sum_{k'} T_{\mathbf{kk'}}\, e^{-i\mathbf{k'}.\mathbf{r}_1} \sqrt{\frac{\cos \theta_k}{\cos \theta_{k'}}} \tag{A4}$$

Assuming that the phases of the scattered waves add randomly, the Dirac density matrix $\rho(\mathbf{r}_1, \mathbf{r}_2)$ with, say, $\mathbf{r}_1$ on the left and $\mathbf{r}_2$ on the right of the slab is

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{|k| < k_f} \psi_k^*(\mathbf{r}_2)\psi_k(\mathbf{r}_1) = \sum_{|k| < k_f} T_{kk} e^{i\mathbf{k}.(\mathbf{r}_1 - \mathbf{r}_2)} \tag{A5}$$

where T_{kk}^2 is the probability that the electron passes through the slab without being scattered by any of the ions. However, if the distance that the electron moves is R this probability is simply $e^{-R/l}$ where l is the electronic mean free path. Therefore the off-diagonal terms of the Dirac density matrix are reduced by a factor $e^{-R/2l}$, where $R = |\mathbf{r}_1 - \mathbf{r}_2|$, due to disorder scattering. Hence the energy derivative of $\rho(\mathbf{r}_1, \mathbf{r}_2)$ has also the approximate form given by Eq. (8).

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