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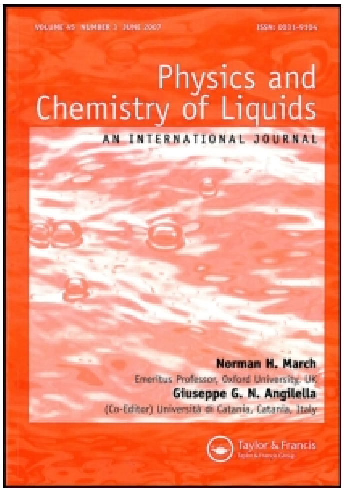

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Finite Mean-Free-Paths and the Electrical Resistivity of Liquid Simple Metals

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Finite Mean-Free-Paths and the Electrical Resistivity of Liquid Simple Metals

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Using a resistivity theory based on force-force correlation functions, we estimate for several liquid metals the finite-mean-free-path effects arising from the off-diagonal behaviour of the Dirac density matrix. The investigation is limited to systems for which an experimental structure factor is available and for which a nearly-free-electron treatment of the electron-ion interaction is appropriate. In all cases considered, the inclusion of finite mean-free-path effects increases the calculated resistivity; the enhancement varies from ~4% in Mg to ~27% in Li. Discrepancies between experiment and theory remain and some possible reasons for these are discussed.

1 INTRODUCTION

The widely used Ziman formula[1] for the electrical resistivity (ρ) of a nearly-free-electron (nfe) liquid metal is

$$\rho_Z = \frac{3\pi m^2}{4Ze^2\hbar^3 n k_F^6}\int_0^\infty \mathrm{d}q\, q^3 S(q)|V(q, k_F)|^2\theta(2k_F - q). \tag{1.1}$$

The two essential ingredients are the liquid structure factor $S(q)$ accessible from neutron or X-ray scattering experiments, and the screened electron-ion pseudopotential form factor $V(q, k_F)$ for elastic scattering on the Fermi surface. The conduction electron density n is related to the Fermi wavenumber k_F by $k_F = (3\pi^2 n)^{1/3}$. θ is the unit step function. m and e are the electron mass and charge respectively, and Z is the number of conduction electrons per ion.

The assumption of a sharp Fermi surface is implicit in (1.1) because the integral over the magnitude of the wavevector transfer $\mathbf{q}$ is restricted to the range $0 \leq q \leq 2k_F$. However, Eq. (1.1) leads to a finite resistivity and hence to a finite transport mean-free-path

$$l_{\mathrm{tr}} \equiv \frac{\hbar k_F}{ne^2\rho}. \tag{1.2}$$

It is therefore of interest to study whether the consequent blurring of the Fermi surface implied by the Heisenberg uncertainty principle can be built into the theory. This naturally implies transcending the first order time-dependent perturbation theory on which Eq. (1.1) rests.

As a start on such a programme, Ferraz and March (FM)[2] showed that the approach of inverse transport coefficients, based on the force-force correlations experienced by electrons in a metal,[3] can lead to a natural generalization of the nfe formula (1.1). In this generalization the mean-free-path l is built into the right-hand side via an approximation to the Dirac density matrix in which the off-diagonal elements reflect directly the kinetic theory result[4] for the probability of a given value of l. The difference between l and l_{tr} is then ignored so that the resistivity is calculated by solving the resulting integral equation for l_{tr} and then using Eq. (1.2).

In this paper we refine the FM approach in two ways: (1) it is extended to allow for non-locality in the electron-ion pseudopotential, and (2) the mean-free-path to be used in their generalization of (1.1) is determined from more fundamental considerations. We then use the modified FM resistivity formula to assess the importance of finite mean-free-path effects on the electrical resistivity of several liquid metals.

In Section II we summarize the derivation of the expression used for ρ and discuss our choice of input for the calculations. In Section III we outline the method used to treat the l dependence of the dielectric function which enters the expression for the electron-ion interaction form factor. Finally, in Section IV we present and discuss our results for ρ in Li, Na, K, Rb, Cs, Mg and Al.

II FM APPROXIMATION FOR ρ

The FM method[2] for including finite mean-free-path effects is based on the force-force correlation function formula for the electrical resistivity.[5,6] If we adopt the pseudopotential approach and replace the electron-ion interaction by a non-local but weaker pseudo-interaction, $V(\mathbf{r}, \mathbf{r}')$, this expression becomes

$$\rho = \frac{2\pi}{3\,\Omega n^2 e^2} \int d\mathbf{r}_1 \int d\mathbf{r}_1' \int d\mathbf{r}_2 \int d\mathbf{r}_2' \langle F(\mathbf{r}_1, \mathbf{r}_1')\sigma(\mathbf{r}_1', \mathbf{r}_2)F(\mathbf{r}_2, \mathbf{r}_2')\sigma(\mathbf{r}_2', \mathbf{r}_1)\rangle \tag{2.1a}$$

where

$$\sigma(\mathbf{r}, \mathbf{r}') = \sum_n \psi_n^*(\mathbf{r})\psi_n(\mathbf{r}')\delta(E_F - E_n) \tag{2.1b}$$

$$F(\mathbf{r}, \mathbf{r}') \equiv \nabla_{\mathbf{X}}\Phi(\mathbf{r} + \mathbf{X}, \mathbf{r}' + \mathbf{X})|_{\mathbf{X}=0}, \tag{2.1c}$$

$$\Phi(\mathbf{r}, \mathbf{r}') = \sum_{\boldsymbol{\alpha}} V(\mathbf{r} - \boldsymbol{\alpha}, \mathbf{r}' - \boldsymbol{\alpha}), \tag{2.1d}$$

$\boldsymbol{\alpha}$ labels the ionic sites, $V(\mathbf{r}, \mathbf{r}')$ is the non-local screened electron-ion interaction and $\langle 0 \rangle$ denotes the configurational average of 0. In Eq. (2.1b) $\{\psi_n(\mathbf{r})\}$ is the set of eigenfunctions of the Hamiltonian for a given ionic configuration. In the weak-scattering limit these eigenfunctions are replaced by plane-waves, $\sigma(\mathbf{r}, \mathbf{r}')$ becomes $\sigma_0(|\mathbf{r} - \mathbf{r}'|)$, and Eq. (1.1) is recovered. To proceed further in the general case we will assume that the F and σ factors in Eq. (2.1) may be configurationally averaged separately. Upon Fourier transforming this yields

$$\rho = \frac{2\pi}{3ne^2} \sum_{\mathbf{k},\mathbf{k}'} |V(\mathbf{k}, \mathbf{k}')|^2 |\mathbf{k} - \mathbf{k}'|^2 S(|\mathbf{k} - \mathbf{k}'|)\sigma(\mathbf{k})\sigma(\mathbf{k}') \tag{2.2}$$

where

$$\sigma(\mathbf{k}) = \int d\mathbf{r} \exp(i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}'))\langle \sigma(\mathbf{r}, \mathbf{r}')\rangle. \tag{2.3}$$

In their treatment FM follow Bardeen[4] in writing

$$\langle \sigma(\mathbf{r}, \mathbf{r}')\rangle_{\mathrm{FM}} \simeq \sigma_0(|\mathbf{r} - \mathbf{r}'|) \exp\left(-\frac{|\mathbf{r} - \mathbf{r}'|}{2l}\right) \tag{2.4}$$

and then identify l with l_{tr}. In this work we also adopt Eq. (2.4) but attempt to be more quantitative in choosing l by examining the perturbation expansion for $\langle \sigma(\mathbf{r}, \mathbf{r}')\rangle$. We first note that

$$\sigma(\mathbf{r}, \mathbf{r}') = -\frac{1}{\pi} \operatorname{Im}(G(E_F + i\eta)) \tag{2.5}$$

where the Green function G is defined by

$$G(\mathbf{r}, \mathbf{r}'; E) \equiv \sum_n \frac{\psi_n^*(\mathbf{r})\psi_n(\mathbf{r}')}{E - E_n}. \tag{2.6}$$

Then, following standard perturbative treatments[7] of $\langle G\rangle \equiv \boldsymbol{G}$ we obtain

$$\boldsymbol{G}(k, E) \equiv \int d\mathbf{r} \exp(i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}'))\langle G(\mathbf{r}, \mathbf{r}'; E)\rangle = (E - \varepsilon_k - \Sigma(k, E))^{-1} \tag{2.7}$$

where

$$\Sigma(k, E) = V(0) + \frac{1}{N}\sum_{k'}\frac{S(|\mathbf{k}'-\mathbf{k}|)|V(\mathbf{k}, \mathbf{k}')|^2}{E - \varepsilon_{k'} - \Sigma(k', E)}. \tag{2.8}$$

To obtain an approximate expression for $\sigma(k)$ from Eqs. (2.7) and (2.8) we let $E = E_F$, average Eq. (2.8) over k according to the spectral weight of $\boldsymbol{G}(k, E)$ at $E = E_F$ and then neglect the k-dependence of $\Sigma(k, E_F)$ for k very near the Fermi surface. This leads to

$$\sigma(k) = \frac{4l}{k\pi}\left[\frac{1}{1 + (2l(k - k_F))^2}\right], \tag{2.9}$$

where

$$l^{-1} = \frac{3m^2\pi}{2\hbar^4 k_F^5}\int_0^\infty dq\, qS(q)|V_l^{\text{eff}}(q)|^2\theta_l(q), \tag{2.10}$$

$$\theta_l(q) = \frac{\pi^2 q}{k_F^2}\int\frac{d\mathbf{k}}{(2\pi)^3}\sigma(k)\sigma(|\mathbf{k}+\mathbf{q}|), \tag{2.11}$$

and

$$|V_l^{\text{eff}}(q)|^2 = \frac{\int d\mathbf{k}\sigma(k)\sigma(|\mathbf{k}+\mathbf{q}|)|V(\mathbf{k}, \mathbf{k}+\mathbf{q})|^2}{\int d\mathbf{k}\sigma(k)\sigma(|\mathbf{k}+\mathbf{q}|} \tag{2.12}$$

We note that $\lim_{l\to\infty}\theta_l(q) = \theta(2k_F - q)$ and $\lim_{l\to\infty}|V_l^{\text{eff}}(q)|^2 = |V(q, k_F)|^2$. Equation (2.9) may be compared with the expression obtained by Fourier transforming Eq. (2.4)

$$\sigma_{\text{FM}}(k) = \frac{4l}{k\pi}\left[\frac{1}{1 + (2l(k - k_F))^2} - \frac{1}{1 + (2l(k + k_F))^2}\right] \tag{2.13}$$

For $k_F l \gg 1$ and $k \cong k_F$ the second term in Eq. (2.13) is negligible compared to the first and hence the mean-free-path appearing in this equation should be determined by solving Eq. (2.10). This must be done self-consistently since $|V_l^{\text{eff}}(q)|^2$ and $\theta_l(q)$ depend on l; we denote the solution by l_0.

In terms of Eqs. (2.11) and (2.12), Eq. (2.2) may be rewritten as

$$\rho_{\text{FM}} = \frac{3\pi m^2}{4Ze^2\hbar^3 k_F^6}\int_0^\infty dq\, q^3 S(q)|V_{l_0}^{\text{eff}}(q)|^2\theta_{l_0}(q) \tag{2.14}$$

This expression differs from that originally suggested by FM[2] only in that (1) the local pseudopotential form-factor has been replaced by the appropriate average of non-local form-factors (Eq. (2.12)) and (2) Eq. (2.14) is to be evaluated using the mean-free-path l_0 obtained from Eq. (2.10) rather than by replacing l_0 on the right-hand side of Eq. (2.14) by l_{tr} and then solving (1.2) and (2.14) self-consistently. The first difference allows us to consider the many systems for which a local pseudopotential treatment is inappropriate while the second can produce important quantative changes.

It should be noted that in using Eq. (2.14) to evaluate the resistivity we are not including all the higher-order effects which occur in Eqs. (2.1). In particular we have neglected the k and E dependence of $\sum (k, E)$ near the Fermi surface which corresponds to an unmodified diagonal element of the Dirac density matrix. This may be serious in metals such as Be and Hg in which the dip in the density of states near E_F which occurs in the solid seems to persist in the liquid and in metals, such as Pb, with particularly short mean-free-paths. We will return to this point in discussing our results.

An obvious necessary condition for a significant finite mean-free-path correction to ρ_Z is that l_0 be sufficiently small, i.e. that the scattering of electrons be sufficiently strong. However, this is not the entire story–the size, and even the sign, of the correction also depends on a subtle competition between contributions of opposite sign. This point is most clearly demonstrated by assuming that the l dependence of $V_l^{\mathrm{eff}}(q)$ is unimportant. (For the metals considered here this turns out to be a good approximation.) In this case, $\rho_{\mathrm{FM}} - \rho_Z$ is proportional to an integral over all q of

$$q^3 S(q) |V^{\mathrm{eff}}(q)|^2 [\theta_{l_0}(q) - \theta(2k_F - q)].$$

When Eq. (2.13) is substituted for $\sigma(k)$ in (2.11) we obtain

$$\theta_{l_0}(q) = \frac{2}{\pi}\left[\tan^{-1}(q l_0) - \tfrac{1}{2}\tan^{-1}\left(\frac{2 q l_0}{1 + (4k_F^2 - q^2) l_0^2}\right)\right] - \theta\left(q - \sqrt{4k_F^2 + l_0^{-2}}\right). \tag{2.15}$$

Now $q^3 S(q) |V^{\mathrm{eff}}(q)|^2 \geq 0$ for all q, and it is not difficult to prove that $[\theta_{l_0}(q) - \theta(2k_F - q)] \leq 0$ for $q < 2k_F$ and ≥ 0 for $q > 2k_F$. Hence, for finite l_0, scattering processes with $q < 2k_F$ give a negative contribution to $\rho_{\mathrm{FM}} - \rho_Z$ while those with $q > 2k_F$ give a positive contribution. Figure 1 shows $[\theta_{l_0}(q) - \theta(2k_F - q)]$ for $k_F l_0 = 30$. The (negative) peak at $q = 0$ is not particularly important because both q^3 and $S(q)$ are very small in this region. For the range of values of $k_F l_0$ of interest here, $[\theta_{l_0}(q) - \theta(2k_F - q)]$ is otherwise large in magnitude only in the immediate vicinity of $2k_F$. However, the range of important q can extend considerably beyond this region because of the large amount of cancellation that can occur there. It is clear that in order to obtain a reliable estimate of $\rho_{\mathrm{FM}} - \rho_Z$ we must use a structure factor and pseudopotential form factor that are accurate, particularly for $q \sim 2k_F$. For this reason we limit the investigation to simple liquid metals for which experimental structure factors are available. We must further limit these to those for which reliable pseudopotential form factors $V(\mathbf{k}, \mathbf{k}')$ are also available.

Dagens, Rasolt and Taylor (DRT)[8] constructed non-local, energy-independent pseudopotentials for a number of simple metals by fitting first-order perturbation theory calculations of the electronic charge density induced around an isolated ion in an electron gas to the results of full non-linear calculations. (This effectively folds in all multiple scatterings from a single ion.) Using the bare electron-ion interaction determined in this way, in combination with the dielectric function of Geldart and Taylor[9] and Rasolt's form for the vertex function describing non-locality in the electron-electron interaction,[10] has proven a very successful prescription for calculations of the properties of simple metals in the solid state.[5,8–11] Accurate electron-ion pseudopotential form factors $V_{\mathrm{DRT}}(\mathbf{k}, \mathbf{k})$, can easily be constructed following this prescription, for Na and K[8], Rb and Cs[14], and Li, Mg, and Al[8].

The experimental liquid structure factors used in our calculations are taken from the extensive compilation of Waseda.[15] Since the atomic weights of some of the metals, particularly Li, are small we include a correction for the inelasticity of the electron-ion scattering processes by replacing $S(q)$ in the relevant formulae of this and the previous section by[16]

$$S(q) - \frac{\hbar^2 q^2}{6Mk_B T} \tag{2.16}$$

where M is the ionic mass.

III DIELECTRIC FUNCTION FOR A FINITE MEAN-FREE-PATH

The non-local pseudopotentials $V(\mathbf{k}, \mathbf{k}')$ considered in this paper depend on l only through the l-dependence of the dielectric function. In considering this l-dependence we begin by generalizing the Lindhard dielectric function to include the effect of a finite mean-free-path l. To proceed consistently with Ref. 2, we employ the form of Dirac density matrix used there. In terms of the free electron density matrix,

$$\sigma_0(\mathbf{r}, \mathbf{r}', E_F) = \frac{mk_F}{\pi^2\hbar^2} \frac{\sin(k_F|\mathbf{r} - \mathbf{r}'|)}{k_F|\mathbf{r} - \mathbf{r}'|}, \tag{3.1}$$

the modified off-diagonal elements are incorporated using the form given in Eq. (2.4).

The dielectric function is then obtained as follows. Consider a test charge interacting with the conduction electrons of the liquid metal. The displaced charge round the test probe is

$$\delta\rho(\mathbf{r}, E) = \int \mathrm{d}\mathbf{r}' F(\mathbf{r}, \mathbf{r}', E) V(\mathbf{r}') \tag{3.2}$$

where $V(\mathbf{r})$ is the screened test charge potential, while F is the one-body linear response function given by[17]

$$\frac{\partial F(\mathbf{r}, \mathbf{r}', E)}{\partial E} = 2\,\mathrm{Re}\{G^{>}(\mathbf{r}, \mathbf{r}', E)\sigma(\mathbf{r}', \mathbf{r}, E)\}. \tag{3.3}$$

The Green function G is related to the Dirac density matrix by Eq. (2.5). However, if we know the imaginary part of G, we can calculate the real part from the Kramers–Krönig relation

$$\mathrm{Re}\, G^{>}(\mathbf{r}, \mathbf{r}', E) = -\!\!\!\!\!\!\int \frac{\mathrm{d}E'}{\pi} \frac{\mathrm{Im}\, G^{>}(\mathbf{r}, \mathbf{r}', E')}{E' - E}. \tag{3.4}$$

Hence it follows that

$$G^{>}(\mathbf{r}, \mathbf{r}', E) = -\frac{\exp(i\hbar^{-1}\sqrt{2mE}\,|\mathbf{r} - \mathbf{r}'|)\exp(-|\mathbf{r} - \mathbf{r}'|/2l)}{\pi|\mathbf{r} - \mathbf{r}'|} \tag{3.5}$$

and thus, in this approximation, the linear response function is simply

$$F(\mathbf{r}, \mathbf{r}', k_F, l) = F_0(\mathbf{r}, \mathbf{r}', k_F)\exp\left(-\frac{|\mathbf{r} - \mathbf{r}'|}{l}\right) \tag{3.6}$$

where F_0 is the free electron response function

$$F_0(\mathbf{r}, \mathbf{r}', k_F) = -\frac{4k_F}{\pi^3}\frac{j_1(2k_F|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|^2} \tag{3.7}$$

with $j_1(x) = \sin x - x\cos x)/x^2$. The static dielectric function $\varepsilon(q)$ can be defined by

$$V_{\mathrm{el}}(q) = \frac{V_{\mathrm{ext}}(q)}{\varepsilon(q)}, \tag{3.8}$$

where $V_{\mathrm{ext}}(q)$ is the external potential due to the test charge, and

$$V_{\mathrm{el}}(q) = V_{\mathrm{ext}}(q) + \frac{4\pi e^2}{q^2}\rho(q) \tag{3.9}$$

is the electrostatic potential of the system. Here $\rho(q)$ is the Fourier transform (FT) of the displaced charge $\delta\rho(r)$ of Eq. (3.2). In the Hartree self-consistent field approximation, the FT of the total one-body potential $V(q)$ is simply $V_{el}(q)$. Hence the generalized Lindhard dielectric function, with account taken of a finite mean-free-path l, is given by

$$\varepsilon_0(q, l) = 1 + \frac{4k_F}{\pi a_0 q^2} f_0(q, l) \tag{3.10}$$

where a_0 is the Bohr radius and $f_0(q, l)$ is (to within a constant factor) the FT of the one-electron response function of Eq. (3.6). Using our results it follows that

$$\begin{aligned} f_0(q, l) = \tfrac{1}{2}\Bigg\{1 - \frac{1}{2k_F l}\Bigg(&\tan^{-1}\left[\frac{4k_F l}{1 + (ql)^2 - (2k_F l)^2}\right] \\ &+ \pi\theta(4k_F^2 - q^2 - l^{-2})\Bigg)\Bigg\} \\ &+ \frac{[1 - (q/2k_F)^2 + (2k_F l)^{-2}]}{8(q/2k_F)} \ln\left\{\frac{[(ql)^2 + 1 + 2k_F q l^2]^2 + (2k_F l)^2}{[(ql)^2 + 1 - 2k_F q l^2]^2 + (2k_F l)^2}\right\} \end{aligned} \tag{3.11}$$

from which one recovers the Lindhard dielectric function in the limit as l tends to infinity.

Going beyond the Lindhard function we have included the effects of exchange and correlation in an approximate manner by replacing $f_0(q, l)$ in Eq. (3.10) by the function

$$f(q, l) = \frac{f_0(q, l)}{1 - \lambda(1 + 0.1534\lambda) f_0(q, l)} \tag{3.12}$$

where $\lambda = (\pi a_0 k_F)^{-1}$. In the large l limit Taylor[18] has pointed out that this dielectric function is a good approximation to that of Geldart and Taylor.[9] If we make the reasonable assumption that the l-dependence of the local field effects is small then Eq. (3.12) becomes an obvious generalization of the full dielectric function to finite l.

For the vertex correction $H(q)$ which takes account of non-local electron-electron scattering events we use the form of $H(q)$ suggested by Rasolt,[10] i.e.

$$H(q) = Z(E_F) f_0(q, 0)[Z(E_F)^{-1} + f(q, 0)^{-1} - f(0, 0)^{-1}],$$

where $Z(E_F)$ is the quasi-particle renormalization factor. Consistent with the local field corrections we take $H(q)$ to be independent of l. We note that

$$V_{l_0}^{\text{eff}}(q = 0) = -\left(1 + \frac{\pi}{4k_F l_0}\right)\frac{2}{3} Z E_F \quad (k_F l_0 \gg 1).$$

The relationship of the argument producing Eq. (3.11) to other attempts to incorporate scattering effects into the response function deserves some attention. Much of the work of which we are aware is based on a relaxation-time-approximation for the single-particle density matrix.[19–21] As emphasized by Mermin[21] the static limit of any such approach cannot include the effects of Fermi surface blurring, the focus of the present investigation, since the assumption of collisions between well-defined quasiparticles is implicit. Our approach is similar in spirit to that proposed by de Gennes[22] and has in common with his results a softening of the singularity in the response function at $q = 2k_F$. Mermin's emphasis is on the requirements posed by the equation of continuity on the frequency-dependent response functions which would have to be taken into account in generalizing Eq. (3.11) to the finite-frequency case. (Equation (3.11) is trivially number conserving in the $\omega = 0$ case.) This, however, is outside the scope of the present investigation since aside from the small correction for inelasticity given by (2.16) we are only concerned with transport calculations in a frozen-liquid-approximation.

IV RESULTS AND DISCUSSION

The results of our resistivity calculations are summarized in Table I. For each of the liquid metals considered we find that $\rho_{FM} > \rho_Z$, the enhancement varying from ~4% in Mg (953 K) to ~27% in Li (463 K). This is contrary to the suggestion made in Ref. 2 that ρ_{FM} must be less than ρ_Z. The reasoning behind this suggestion is not correct. The difference between ρ_{FM} and ρ_Z can

TABLE I

The electrical resistivities calculated with the Ziman formula (1.1) and the modified Ferraz–March formula (2.14) are compared for several liquid metals. The mean-free-path l_0 appearing in the FM resistivity integral is compared with the corresponding transport mean-free-path l_{tr}

Material	ρ^{exp} ($\mu\Omega$ cm)	ρ_Z ($\mu\Omega$ cm)	ρ_{FM} ($\mu\Omega$ cm)	$(\rho_{FM} - \rho_Z)/\rho_Z$ (%)	$k_F l_0$	$k_F l_{tr}$
Li(463 K)	25.1[a]	13.9	17.7	27	66	62
Na(378 K)	9.7[a]	10.2	10.9	7	81	125
K(343 K)	14.3[a]	15.9	16.9	6	72	99
Rb(313 K)	22.6[a]	28.2	29.9	6	59	57
Cs(303 K)	37.1[a]	29.2	33.3	14	61	54
Mg(953 K)	25.5[b]	21.5	22.4	4	33	41
Al(943 K)	24.4[c]	19.5	20.5	5	27	35

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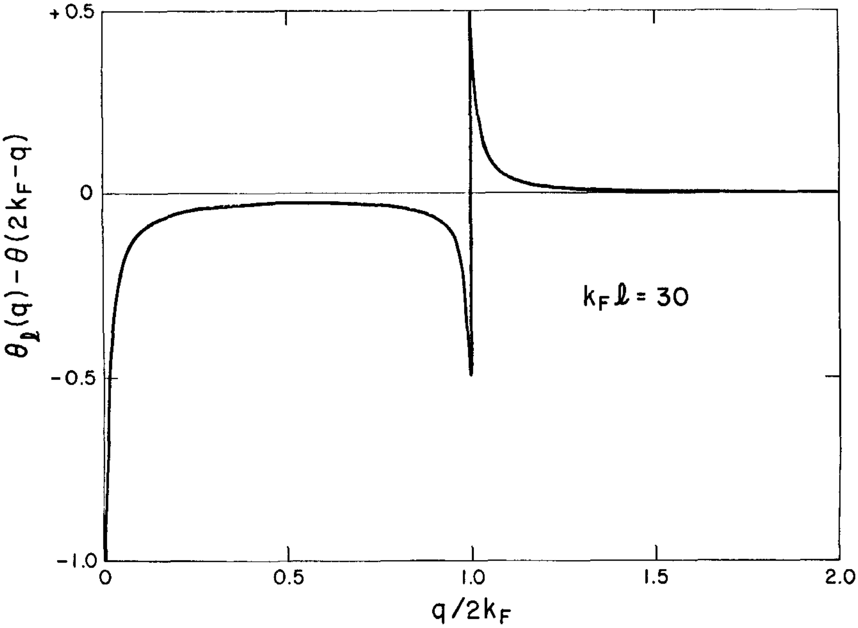

FIGURE 1 The q dependence of $\theta_l(q) - \theta(2k_F - q)$ for $k_F l = 30$. The discontinuity of $+1$ and the change of sign at $q = 2k_F$ occurs for any finite value of $k_F l$.

be of either sign depending on the q dependence of $S(q)$ and of $V_{l_0}^{\text{eff}}(q)$, particularly for $q \sim 2k_F$. Since $S(q)$ and $V_{l_0}^{\text{eff}}(q)$ are not completely independent quantities (e.g. they are both strongly influenced by the electronic screening) it is an interesting question whether or not, for any *actual* system, they can be such that $\rho_Z > \rho_{\text{FM}}$.

With Figure 1 and the related discussion in Section II in mind it is not difficult to account for the fact that the mean-free-path effect is much larger in Li than in Mg. For Li, with $Z = 1$, the structure factor $S(q)$ is large and very rapidly increasing at $q = 2k_F$ thus favouring a positive contribution to $\rho_{\text{FM}} - \rho_Z$; for Mg, with $Z = 2$, $S(q)$ is large and very rapidly decreasing at $q = 2k_F$ thus favouring a negative contribution. For Mg the factor $q^3|V_{l_0}^{\text{eff}}(q)|^2$ which gives stronger weight to the positive contribution evidently wins, but the net effect is much smaller than in Li where $S(q)$ and $q^3|V_{l_0}^{\text{eff}}(q)|^2$ act in concert near $q = 2k_F$.

The effect of switching off the l dependence of the dielectric function $\varepsilon_0(q, l)$ is, in all cases, to reduce ρ_{FM} by only a small fraction of the total mean-free-path enhancement. The effect is so small because the resistivity integrand is very small near $q = 0$ where the difference between $\varepsilon_0(q, l)$ and $\varepsilon_0(q, l = \infty)$ is most pronounced. Moreover, the l-dependence of $V_{l_0}^{\text{eff}}(q)$

induced by averaging $V(\mathbf{k}, \mathbf{k}')$ with an l-dependent weight factor is unimportant relative to the l-dependence of $\theta_l(q)$. This justifies the simplifying assumption made to facilitate the discussion of Section II and the preceding paragraph.

Figures 2 and 3 show $V_{l_0}^{\text{eff}}(q)$, the correct effective local pseudopotential form factor to be used in the FM resistivity formula, for Li and Cs respectively. They were calculated from $V_{\text{DRT}}(\mathbf{k}, \mathbf{k}')$ using Eq. (2.12). Also shown are two earlier guesses:

$$V_{l_0}^{(1)}(q) = \theta(2k_F - q)V_{\text{DRT}}(\mathbf{k}, \mathbf{k}')_{k=k'=k_F} + \theta(q - 2k_F)V_{\text{DRT}}(\mathbf{k}, \mathbf{k}')_{k=k'=q/2}, \tag{4.1}$$

$$V_{l_0}^{(2)}(q) = \theta(2k_F - q)V_{\text{DRT}}(\mathbf{k}, \mathbf{k}')_{k=k'=k_F} + \theta(q - 2k_F)V_{\text{DRT}}(\mathbf{k}, \mathbf{k}')_{k=k_F, k'=q-k_F}, \tag{4.2}$$

with $\mathbf{k}' \equiv \mathbf{k} + \mathbf{q}$. Both of these guesses give a good representation of $V_{l_0}^{\text{eff}}(q)$ for $q < 2k_F$ but fail badly for $q > 2k_F$. We have been unable to devise any simple prescription for generating a good approximation to $V_{l_0}^{\text{eff}}(q > 2k_F)$. From the behaviour of $\theta_{l_0}(q)$ for $q > 2k_F$ (see Figure 1) it might erroneously

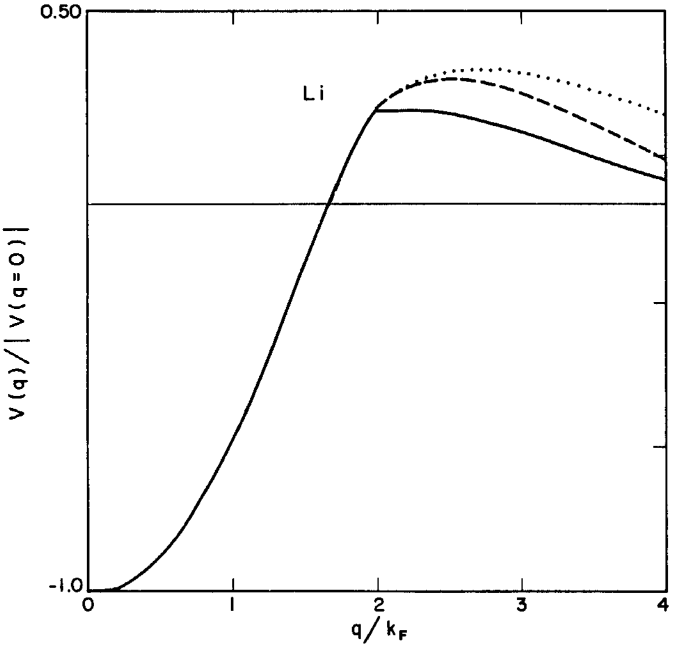

FIGURE 2 The solid curve represents $V_{l_0}^{\text{eff}}(q)$, the effective local electron-ion pseudopotential form factor to be used in the modified Ferraz–March resistivity formula, for Li at 463 K. The dotted and dashed curves show two guesses, $V_{l_0}^{(1)}(q)$ and $V_{l_0}^{(2)}(q)$ respectively, for $V_{l_0}^{\text{eff}}(q)$.

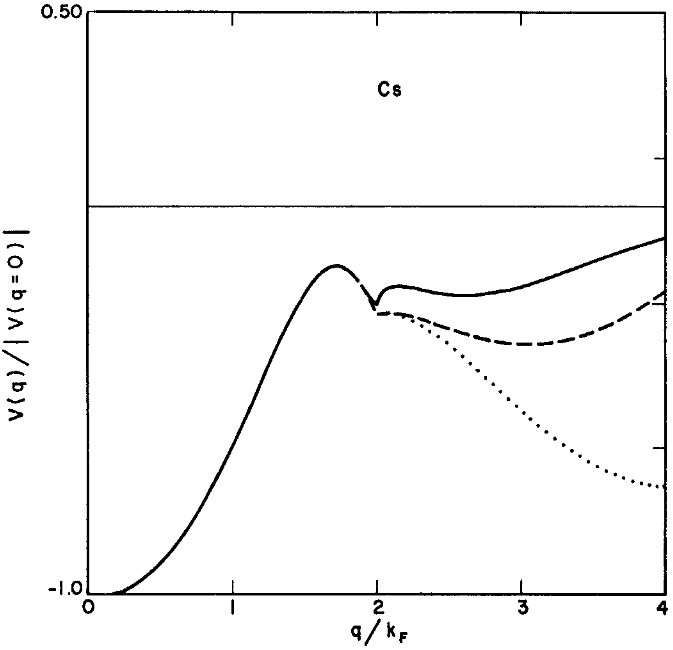

FIGURE 3 The solid, dotted, and dashed curves represent $V_{l_0}^{\rm eff}(q)$, $V_{l_0}^{(1)}(q)$, and $V_{l_0}^{(2)}(q)$ respectively for Cs at 303 K.

be concluded that the q-dependence of $V_{l_0}^{\rm eff}(q)$ for $q \gg 2k_F$ is of negligible importance. However, the leading order term in an expansion of $\theta_{l_0}(q)$ in powers of $(k_F l_0)^{-1}$ and $(q/2k_F)^{-1}$ is $\pi^{-1}(k_F l_0)^{-1}(q/2k_F)^{-3}$. This means that for $k_F l_0 \gg 1$ and $q \gg 2k_F$ the integrand of Eq. (2.14) for $\rho_{\rm FM}$ is proportional to $(k_F l_0)^{-1}|V_{l_0}^{\rm eff}(q)|^2$. Thus the convergence of the resistivity integral depends on the large q behaviour of $|V_{l_0}^{\rm eff}(q)|^2$ which is represented so poorly by (4.1) and (4.2). Calculation of $\rho_{\rm FM}$ for Li with $V_{l_0}^{(1)}(q)$ in place of the correct $V_{l_0}^{\rm eff}(q)$ leads to a correction to ρ_Z which is too large by a factor of 2. If, in addition, l_0 is replaced by $l_{\rm tr}$ (with $l_{\rm tr}$ determined self-consistently as originally suggested by FM) the correction is too large by a further factor of 2. These comments emphasize the necessity of using a first principles pseudopotential, which may be highly non-local, in estimating the finite-mean-free-path effects.

It is of interest to ask whether the present approach can meaningfully be applied to liquid metals with particularly short mean-free-paths, such as liquid Pb and Hg. In such a case, the approximate form (3.2) of the Dirac density matrix has to be transcended to include the distortion of the diagonal density of states due to the strong scattering potentials. The Bardeen form

(3.2) only modifies the density matrix relatively far from the diagonal, and does not change the density of states from its free electron form. Since such a modified density of states may well play an important role in determining the transport properties of liquid Pb and Hg, it seems clear that the umost caution should be used before applying (2.14) to such a metal. This is borne out by our calculation for Pb (613 K):[23] despite a finite mean-free-path enhancement of 20%, ρ_{FM} is smaller than ρ_{exp} by over 50%. (In this case, a significant part of the discrepancy may arise from our use of the DRT form factor which is much less reliable for Pb than for the metals considered in Table I.)

The comparison with experimental resistivities in Table I makes it clear that some, but not dramatic, improvement in agreement results from our inclusion of finite-mean-free-path effects. At the present time the extent to which uncertainties in the experimental structure factors are obscuring this comparison is somewhat uncertain; certainly both ρ_Z and ρ_{FM} are very sensitive to the form assumed for $S(q)$.[24] Among the possible sources of error in the formula we have used, the omission of density-of-state modifications due to the electron-ion interaction, mentioned earlier, seems easiest to remove. However, for the metals listed in Table I, sizable effects would be expected only in Li and Cs in which cases the calculated values of ρ would be expected to increase.[25] This would leave us in a situation in which all the calculated resistivities in the liquid alkali metals would be above experimental values by ~20%. This situation is particularly puzzling for Na and K since the corresponding solid state calculations,[11] which appear to be based on similar physical approximations, yield agreement on the ~4% level. In fact the inclusion of the effect of multiphonon processes and the Debye–Waller factor improves the agreement to the 1% level,[26] thus demonstrating that the DRT form factors are entirely appropriate for the calculation of transport properties. Therefore, if one can be confident in the accuracy of the experimental structure factors, it seems that the discrepancies noted in Table I are a reflection of errors introduced by the assumption (implicit in the derivations of both ρ_Z and ρ_{FM}) that the scattering function for the electrons only depends on the ionic configuration in an average sense (see the discussion of Ref. 5). In any case, our results establish that finite-mean-free-path effects alter significantly the calculated electrical resistivity of several liquid simple metals from that given by the Ziman formula.

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