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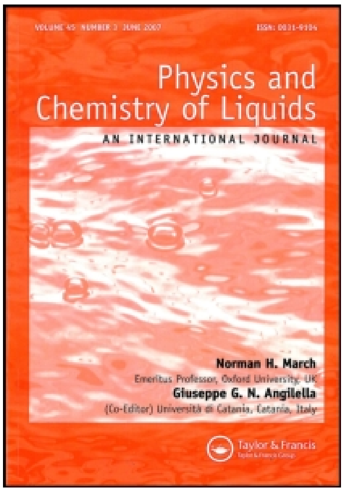

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Electrical Resistivity of Expanded Fluid Rubidium

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ELECTRICAL RESISTIVITY OF EXPANDED FLUID RUBIDIUM

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The problem of electronic transport in expanded alkali metals is explored in detail—with particular reference to rubidium. One objective is to assess the extent to which the self-consistent inclusion of a mean free path for electron–ion scattering into a formulation for electron transport, based upon the force–force correlation approach, could account for the observed resistivity of expanded liquid rubidium, at thermodynamic states near to the liquid–vapour coexistence curve. The results presented indicate that the self-consistent approach gives the same general trend with density as the traditional Bhatia–Krishnan–Ziman formula. Though the latter gives quantitatively better agreement with experiment, both theories fail as the critical point is approached as they are weak scattering treatments. At higher densities the need for an accurate description of the large wave number components of the pseudopotential emerges.

KEY WORDS: Inverse transport, mean free path.

1 INTRODUCTION

Of all the properties of liquid metals that are accessible to experiment, electrical resistivity offers probably the most direct means of assessing the changing role of the electron–ion interactions as the density is altered. Particularly for rubidium and caesium, the behaviour of the electrical resistivity has provided the most direct indication of the occurrence of a metal-insulator transition to the high density side of the liquid–vapour critical point in these metals, through the pioneering experiments of Hensel and coworkers[1,2,3]. While this paper focusses on electrical resistivity therefore, it may be noted that the marked increase in resistivity at around twice the critical density also correlates with the change in sign of the temperature coefficient of conductivity here[4], and the behaviour of the thermopower[1]. Hall effect measurements also indicate free electron character down to 1 g cm^{-3} for caesium[5].

2 FORCE-CORRELATION APPROACH TO RESISTIVITY AND ROLE OF MEAN FREE PATH

Following the early work of Bhatia and Krishnan[6–8], the nearly free electron model of the electronic transport properties of liquid metals was developed into its present, well established, form by Ziman[9,10]. The results of this theory will be presented below, and compared for rubidium with the subsequent treatments of Ferraz and March[11], and the later extension by Laevens *et al.*[12].

Briefly the starting point taken by these latter workers is the theory of Rousseau, Stoddart and March[13,14] who derived an expression for the resistivity of an arbitrary array of scattering sites, in terms of the Dirac density matrix. Their model was based on the inverse transport approach[15–18], while the derivation given in Ref. 13 owed much to the work of Greenwood[19]. The result for the resistivity, R, of a given configuration of scattering sites, is

$$R = \frac{\pi\hbar}{6V\rho^2 e^2} \iint \langle \nabla_{r_1} W(\mathbf{r}_1) \cdot \nabla_{r_2} W(\mathbf{r}_2)/\sigma(\mathbf{r}_1, \mathbf{r}_2, E_f)|^2 \rangle d\mathbf{r}_1 d\mathbf{r}_2 \tag{2.1}$$

This expression will form the basis for the approach to the calculation of resistivities of expanded fluid alkalis adopted below. In Eq. (2.1), W is the total scattering potential, V is the total volume and $\sigma(\mathbf{r}_1, \mathbf{r}_2\ E)$ is the energy derivative of the Dirac density matrix (including spin) given by

$$\sigma(\mathbf{r}_1, \mathbf{r}_2, E) = \sum_i \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\delta(E - E_i) \tag{2.2}$$

where ψ_i and E_i are the electronic wave functions and energies respectively. In order to give the resistivity of a fluid, the result (2.1) has been averaged over the ionic configurations. As the original authors[13,14] pointed out, to obtain an exact result within the one-electron framework, one would need to know the density matrix for each ionic configuration, and the many-particle correlation functions for the ions, to complete the configurational average. Approximations are evidently necessary in order to proceed further.

Clearly one consequence of scattering will be to effect some modification of the density matrix from that corresponding to plane wave electronic states. If, however, this change is neglected, then the configurationally averaged form of σ may be evaluated using the plane wave functions, as

$$\langle \sigma_0(\mathbf{r}_1, \mathbf{r}_2, E_f) \rangle = \frac{mk_f}{\pi^2\hbar^2} \frac{\sin(k_f|\mathbf{r}_1 - \mathbf{r}_2|)}{k_f|\mathbf{r}_1 - \mathbf{r}_2|} \tag{2.3}$$

Now putting Eq. (2.1) into Fourier transform gives

$$R = \frac{\pi h}{6V\rho^2 e^2} \frac{1}{8\pi^3\rho^3} \int k^2 W(k) W(-k) \Gamma(k) d\mathbf{k} \tag{2.4}$$

where

$$\Gamma(k) = \rho \int \langle \sigma_0(\mathbf{r}_1, \mathbf{r}_2, E_f) \rangle^2 e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} d(\mathbf{r}_1 - \mathbf{r}_2)$$

$$= \frac{\rho m^2}{\pi^2\hbar^4 k} \theta(2k_f - k) \tag{2.5}$$

and

$$W(k) = \rho \int W(\mathbf{r}) \mathrm{e}^{ik\cdot r} d\mathbf{r}. \tag{2.6}$$

But if W is of the form

$$W(\mathbf{r}) = \sum_i w(\mathbf{r} - \mathbf{R}_j) \tag{2.7}$$

for ionic sites i, then

$$W(k)W(-k) = NS(k)|w(k)|^2 \tag{2.8}$$

where $S(k)$ is the static structure factor of the ions. Combining these results, and using $k_f^3 = 3\pi^2\rho$, gives

$$R = \frac{3\pi m^2}{4\rho e^2\hbar^3 k_f^6}\int_0^{2k_f} k^3 S(k)|w(k)|^2\,dk \tag{2.9}$$

which is precisely the Ziman formula[9,10]. Notice that the use of Eqs. (2.7) and (2.11) constitutes a *separate* configurational averaging of the potential and density matrix terms in the basic expression (2.1).

As has been mentioned, Ferraz and March[11] suggested how the effects of a finite mean free path for electrons might be included self-consistently into the treatment of electron transport outlined here. Their attention focused on the function denoted $\Gamma(k)$ in Eq. (2.5), noting that the Heaviside function in this term at $2k_f$ is a consequence of a well-defined Fermi surface, implicit in the form of $\langle\sigma(\mathbf{r}_1, \mathbf{r}_2, E_f)\rangle$ employed—that is Eq. (2.3). More specifically, this is directly related to the undamped oscillatory off-diagonal behaviour of the derivative of the density matrix. In a first attempt to address the self-consistency question, Ferraz and March[11] used an approximate argument due to Bardeen[20] to allow for the effects of scattering, and wrote the configurationally averaged result

$$\langle\sigma(\mathbf{r}_1, \mathbf{r}_2, E_f)\rangle = \langle\sigma_0(\mathbf{r}_1, \mathbf{r}_2, E_f)\rangle\exp(-|\mathbf{r}_1 - \mathbf{r}_2|/2l) \tag{2.10}$$

Here, $\langle\sigma_0\rangle$is the free electron form (2.3), while l represents an electronic mean free path. This then leads to

$$\Gamma(k) = \frac{2\rho m^2}{\pi^3\hbar^4 k}\left[\tan^{-1}(kl) - \tfrac{1}{2}\tan^{-1}\left(\frac{2kl}{1 + 4(k_f l)^2 - (kl)_2}\right)\right.$$
$$\left. - \frac{\pi}{2}\theta(k - \sqrt{(4k_f^2 + l^{-2})})\right] \tag{2.11}$$

and the resistivity

$$R = \frac{\hbar}{12\pi e^2\rho^4}\int_0^\infty k^4 S(k)|w(k)|^2\Gamma(k)dk_0 \tag{2.12}$$

The form of $k\Gamma(k)$ is indicated in Figure 1, where the modification of the simple result $k\Gamma(k) \propto \theta(2k_f - k)$, due to finite l, is clearly seen. The main feature is the 'softening' of the discontinuity at $2k_f$, since behaviour at $k = 0$ is largely masked by the vanishing k^3 term already present in the integrand. By combining Eq. (2.12) with the simple formula $l = \hbar k_f/\rho e^2 R$, Ferraz and March[11] proposed an iterative route to a self-

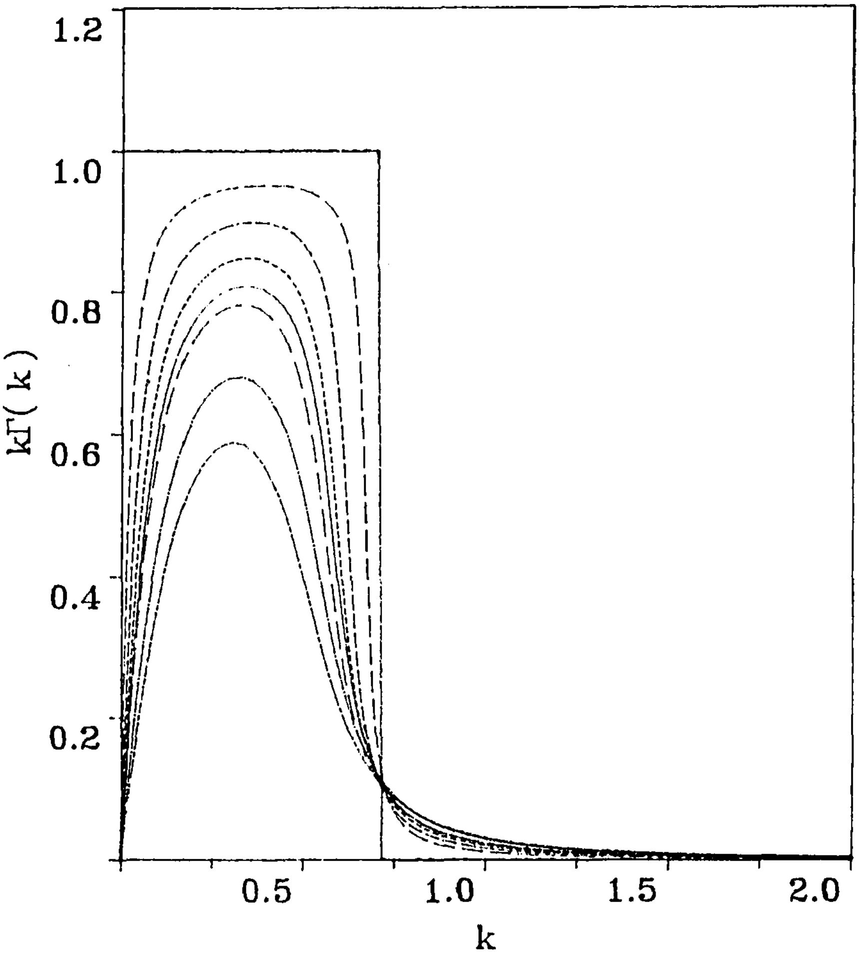

Figure 1 Plot of $k\Gamma(k)$ for different values of the mean free path l using Eq. (2.11). The rectangle indicates the limit of infinite l.

consistent resistivity, by solving these together for given input $S(k)$ and $w(k)$. They did not present numerical work on this point, but did caution that for full consistency, the influence of l on $w(k)$, by way of the dielectric function of the perturbed electron gas, must be incorporated. This point is pursued in Sections 3 and 4. Some limited implementations of the Ferraz–March scheme have since been performed for simple metals, using *model* structure factors by Khajil and Tomak[21] and by Daver, Khajil and Tomak[22].

3 SELF-CONSISTENT SCHEME FOR THE CALCULATION OF THE ELECTRICAL RESISTIVITIES OF SIMPLE LIQUID METALS

The attempts at a self-consistent approach to the resistivity problem by Ferraz and March[11] were subsequently extended by Leavenas *et al.*[12], [hereafter referred to as

LMTFM.]† Their method will be adopted in the calculations here, and it is therefore instructive to summarize the theoretical basis for the model.

The first important improvement was the the use of a non-local first-principles scattering potential. Re-writing Eq. (2.1) in the form appropriate for such a potential, $W(\mathbf{r}_1, \mathbf{r}_2)$, leads to

$$R = \frac{\pi\hbar}{6Ve^2}\iiiint \langle F(\mathbf{r}_1, \mathbf{r}'_1)F(\mathbf{r}_2, \mathbf{r}'_2)\sigma(\mathbf{r}'_1, \mathbf{r}_2)\sigma(\mathbf{r}'_2, \mathbf{r}_1)\rangle d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \tag{3.1}$$

where

$$F(\mathbf{r}, \mathbf{r}') = |\nabla_x W(\mathbf{r} + \mathbf{x}, \mathbf{r}' + \mathbf{x})|_{\mathbf{x}=0} \tag{3.2}$$

$$W(\mathbf{r}, \mathbf{r}') = \sum_i w(\mathbf{r} - \mathbf{R}_i, \mathbf{r}' - \mathbf{R}_i) \tag{3.3}$$

with $\mathbf{R}_i$ denoting the ion sites, as before. To simplify the configurational average these authors assumed that the force and density matrix terms may be averaged separately. Then, after Fourier transformation, Eq. (3.1) becomes

$$R = \frac{\hbar}{48e^2\rho^2\pi^2}\frac{1}{8\pi^3\rho^3}\iint |\mathbf{k} - \mathbf{k}'|^2 S(k)|w(\mathbf{k}, \mathbf{k}')|^2\sigma(\mathbf{k})\sigma(\mathbf{k}')d\mathbf{k}\, d\mathbf{k}' \tag{3.4}$$

with

$$\sigma(\mathbf{k}) = \rho\int \langle\sigma(\mathbf{r}_1, \mathbf{r}_2, E_f)\rangle e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)}d(\mathbf{r}_1 - \mathbf{r}_2) \tag{3.5}$$

With this basic result LMTFM used the Ferraz–March form (2.10) for $\langle\sigma(\mathbf{r}_1, \mathbf{r}_2, E_f)\rangle$, which gives

$$\sigma(k) = \frac{4ml\rho}{\pi\hbar^2 k}\left[\frac{1}{1 + 4l^2(k - k_f)^2} - \frac{1}{1 + 4l^2(k + k_f)^2}\right] \tag{3.6}$$

However, they used a more sophisticated approach to determine the mean free path l, which will now be outlined. First, note that the quantity $\sigma(\mathbf{r}_1, \mathbf{r}_2, E_f)$ is related to the advanced Green function $G^+(\mathbf{r}_1, \mathbf{r}_2, E)$ by

$$\sigma(\mathbf{r}_1, \mathbf{r}_2, E_f) = -\frac{2}{\pi}\operatorname{Im} G^+(\mathbf{r}_1, \mathbf{r}_2, E_f) \tag{3.7}$$

where the 2 allows for the inclusion of electron spin. If the configurational average of G^+ is denoted as $\mathscr{G}$, then clearly

$$\sigma(k) = -\frac{2}{\pi}\operatorname{Im}\mathscr{G}(k, E_f) \tag{3.8}$$

---

† Several typographical errors appear in this paper. These have been corrected in what follows here: see also Chapman[23].

Now $\mathscr{G}$ may be expressed in the form

$$\mathscr{G}(k, E) = \frac{\rho}{E - E_k - \Sigma(k, E)} \tag{3.9}$$

where $\Sigma(k, E)$ is the self-energy function. (The 'ρ' appears since in this description, Fourier transforms are taken to preserve dimensionality. This results in a non-standard definition of $\mathscr{G}(k, E)$, but this has little influence on subsequent analysis). To second order of perturbation theory, the self-energy may be written following Ballentine[24] as

$$\Sigma(k, E) = \frac{1}{8\pi^3\rho} \int \frac{S(|\mathbf{k} - \mathbf{k}'|)|w(\mathbf{k}, \mathbf{k}')|^2}{E - E_{k'} - \Sigma(k', E)} d\mathbf{k}' \tag{3.10}$$

From Eqs (3.8) and (3.9) it follows that

$$\sigma(k) = \frac{2b(k, E_f)\rho/\pi}{[E_f - E_k - a(k, E_f)]^2 + [b(k, E_f)]^2} \tag{3.11}$$

where $\Sigma(k, E_f) = a(k, E_f) - ib(k, E_f)$. Taking the imaginary part of Eq. (3.10) for $E = E_f$, substituting Eq. (3.11), then multiplying by $\sigma(k)$ and integrating gives

$$\int b(k, E_f)\sigma(k)d\mathbf{k} = \frac{1}{16\pi^2\rho^2} \iint S(q)|w(\mathbf{k}, \mathbf{k}')|^2\sigma(k)\sigma(k')d\mathbf{k}\, d\mathbf{k}' \tag{3.12}$$

where q-$\mathbf{k}' - \mathbf{k}$. Defining the functions

$$\theta_1(q) = \frac{\hbar^4 q}{8\pi m^2\rho^2} \int \sigma(k)\sigma(|\mathbf{k} + \mathbf{q}|)d\mathbf{k} \tag{3.13}$$

and

$$|w_{\text{eff}}^1(q)|^2 = \frac{\int |w(\mathbf{k}, \mathbf{k}')|^2\sigma(k)\sigma(k')d\mathbf{k}}{\int \sigma(k)\sigma(k')d\mathbf{k}} \tag{3.14}$$

then Eq. (3.12) becomes

$$\int b(k, E_f)\sigma(k)d\mathbf{k} = \frac{2m^2}{\hbar^4} \int_0^\infty qS(q)|w_{\text{eff}}^1(q)|^2\theta_1(q)dq \tag{3.15}$$

Now recall that $\langle\sigma(\mathbf{r}_1, \mathbf{r}_2, E_f)\rangle$ differs from $\langle\sigma_0(\mathbf{r}_1, \mathbf{r}_2, E_f)\rangle$ only in the off-diagonal elements, so that the density of states is unaltered from the free electron value. This is, of course, $mk_f/\pi^2\hbar^2$, and must be given by $(1/8\pi^3\rho) \int \sigma(k)d\mathbf{k}$. Furthermore, if it is assumed that the self-energy, $\Sigma(k, E_f)$, is not too strongly dependent on k near to E_f, then Eq. (3.15) may be simplified to

$$b = \frac{3\pi m}{4\hbar^2 k_f^4} \int_0^\infty qS(q)|w_{\text{eff}}^1(q)|^2\theta_1(q)dq \tag{3.16}$$

using $k_f^3 = 3\pi^2\rho$. Returning to Eq. (3.11) one may expand the energy term in the denominator to linear terms in k, to give

$$\sigma(k) = \frac{2b\rho/\pi}{[-\hbar^2 k_f(k - k_f)/m]^2 + b^2} \tag{3.17}$$

Denoting the length $\hbar^2 k_f/2mb$ as l, then from Eqs. (3.16) and (3.17)

$$l^{-1} = \frac{3\pi m^2}{2\hbar^4 k_f^5}\int_0^\infty qS(q)|w_{\text{eff}}^1(q)|^2\theta_1(q)dq \tag{3.18}$$

and

$$\sigma(k) = \frac{4ml\rho}{\pi\hbar^2 k_f}\left[\frac{1}{1 + [2l(k - k_f)]^2}\right] \tag{3.19}$$

Finally, Eq. (3.4) may be written as

$$R = \frac{3\pi m^2}{4e^2\hbar^3\rho k_f^6}\int_0^\infty q^3 S(q)|w_{\text{eff}}^{l_0}(q)|^2\theta_{l_0}(q)dq \tag{3.20}$$

where l_0 is the value determined self-consistently from Eq. (3.18). This result is very similar to the Ferraz–March formula (2.12), with a more general form for the matrix elements. It is readily confirmed that in the limit as $l \to \infty$, $\theta_1(q) \to \theta(2k_f - q)$ and $w_{\text{eff}}^l(q) \to w_{k_f}(q)$, so that the Ziman result (2.9) is regained.

Comparing Eqs. (3.6) and (3.19), one can see that for k near to k_f, and large l, the two expressions for $\sigma(k)$ are very similar. In fact, as one result of the approximations in this derivation, the integral over k of $\sigma(k)$ from Eq. (3.19) is unbounded, while Eq. (3.6) gives the density of states at the Fermi level, as required. In the calculations described here, Eqs. (3.6), (3.13), (3.14) and (3.18) were used together to determine a consistent mean free path l_0, before determining the resistivity from Eq. (3.20). (Note that, if Eq. (3.6) is used for $\sigma(k)$, then θ_{l_0} is exactly the function Γ of Section 2, evaluated for $l = l_0$).

4 INPUT TO THE RESISTIVITY CALCULATIONS

In order to apply the scheme given in the previous section, three basic quantities are required as input: i) a liquid structure factor at a given density and temperature, ii) a bare ion pseudopotential and iii) a form for the dielectric function of the electron gas. For the first of these, the experimental results of Winter, Hensel, Bodensteiner and Gläser[25] for states along the liquid-vapour coexistence curve were used. For the bare pseudopotential, the method of LMTFM has been followed, by using the energy-independent first-principles form due to Rasolt and Taylor[26]. With regard to the screening, the influence of the mean free path l on the dielectric function must be allowed for, and so one may write

$$\varepsilon(q, l) = 1 + \frac{e^2}{\varepsilon_0 q^2}\Pi(q, l) \tag{4.1}$$

with

$$\Pi(q, l) = \frac{\Pi_0(q, l)}{1 + \frac{e^2}{\varepsilon_0 q^2} G(q)\Pi_0(q, l)} \tag{4.2}$$

Here, $\Pi_0(q, l)$ is the Lindhard function modified to include a finite mean free path, l, and as derived by LMTFM (in a form consistent with Eq. (3.6)) it may be expressed as

$$\Pi_0(q, l) = \frac{mk_f}{\pi^2\hbar^2}\left[\frac{1}{2} - \frac{1}{2y}\left[\tan^{-1}\left(\frac{2y}{1 + y^2(x^2 - 1)}\right) + \pi\theta(1 - x^2 - y^2)\right] + \frac{1 - x^2 + y^{-2}}{8x}\ln\left(\frac{((xy)^2 + 1 + xy^2)^2 + y^2}{((xy)^2 + 1 - xy^2)^2 + y^2}\right)\right] \tag{4.3}$$

where $x = q/2k_f$ and $y = 2k_f l$. The local-field term $G(q)$ is assumed independent of l, and the form of this function used was that due to Ichimaru and Utsumi[27]. Finally, following LMTFM, a vertex correction due to Rasolt[28] was used, in order to describe the non-locality of electron–electron interactions. In the present notation this is

$$H(q) = Z_f\Pi_0(q)\left[\frac{1}{\Pi(q)} - \frac{1}{\Pi(0)} + \frac{\hbar^2\pi^2}{mk_f Z_f}\right] \tag{4.4}$$

where Π and Π_0 are evaluated in the $l \to \infty$ limit, and Z_f is the discontinuity in the single-particle occupation probability at the Fermi surface of an electron gas. The neglect of l in this correction term is consistent with the use of the unmodified local-field term, both being, in essence, higher order corrections to the simple Hartree self-consistent screening. Data for Z_f were taken from the Fermi hypernetted chain calculations on the electron gas by Lantto[29] and it was found that over a range of interelectronic spacings (r_s) spanning the region of interest here, the linear fitting $Z_f = 0.91–0.05\ r_s$ gave a good representation of her results (with r_s in atomic units). The total screened pseudopotential term is thus given by Eq. (19) of Rasolt and Taylor[26] evaluated with the l-dependent screening functions described, and multiplied by the vertex correction $H(q)$.

5 RESULTS OF THE SELF-CONSISTENT RESISTIVITY CALCULATIONS

Following the scheme outlined, the effect of mean free path corrections to Ziman theory resistivities was examined for expanded liquid Rb focusing on the thermodynamic states along the liquid–vapour coexistence curve for which structure factor data are available. For each state, a self-consistent mean free path was determined iteratively, according to Eq. (3.18), and when satisfactory convergence was obtained ($\approx 10^{-2}$ au) the corresponding resistivity was calculated. Using the same input information, Ziman theory resistivities were also evaluated, precisely as was done by Chapman[23] for fluid Cs. The resistivities thus obtained for fluid Rb are plotted in Figure 2 as a function of density, scaled with its critical value. The self-consistent

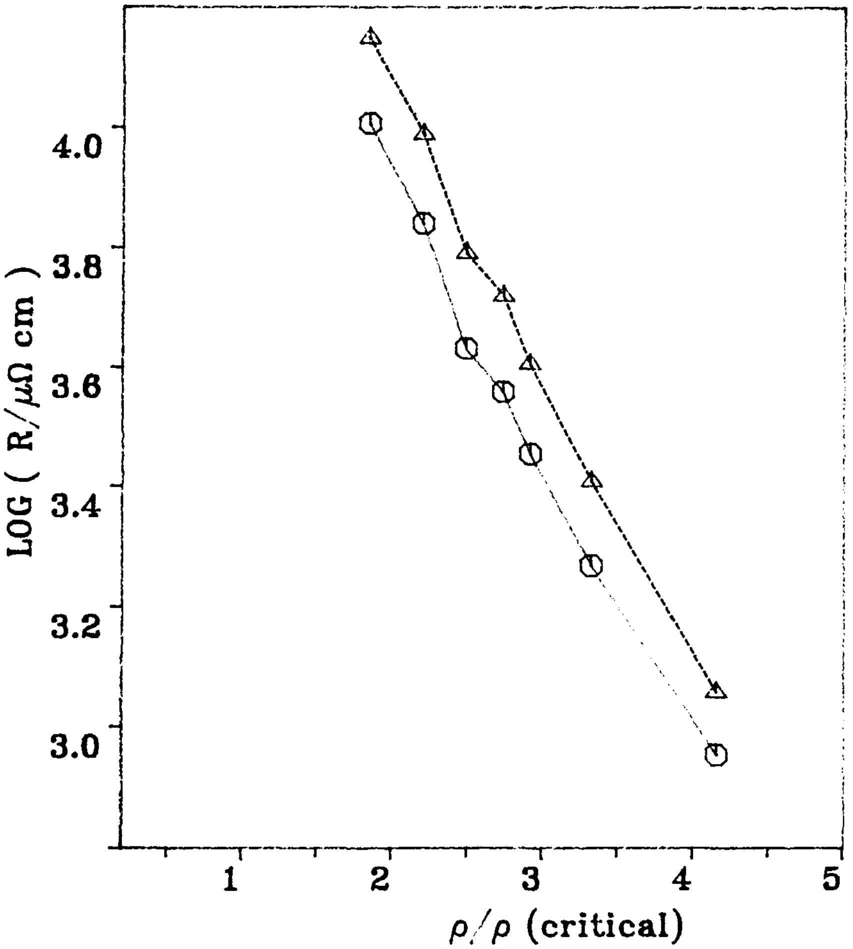

Figure 2 Shows resistivity trends as a function of density ρ measured in units of the critical density. Upper curve: self-consistent method. Lower curve: Ziman theory as implemented in present study.

method, over the range plotted, gives results which are higher than the Ziman results over the whole range of the plot. This contrasts with the results of Chapman[23] for Cs, where there is across-over of the two curves at a particular density. As Chapman notes, there is sensitivity of the self-consistent results to large wave number components of the pseudopotential. More work on this aspect is clearly required in future studies. Figure 3 shows resistivity versus temperature, again scaled with the critical temperature. Experimental results are denoted by the crosses. Up to $T/T_{\text{critical}} \sim 0.8$, the self-consistent results reflect the experimental trend but are quantitatively less satisfactory than the Ziman values. Both theories, however, being based on weak scattering assumptions, will eventually break down as the critical point is approached. Chapman[23] has given a full discussion of the difficulties of the pseudopotential calculations for Cs; we shall not go into further details here.

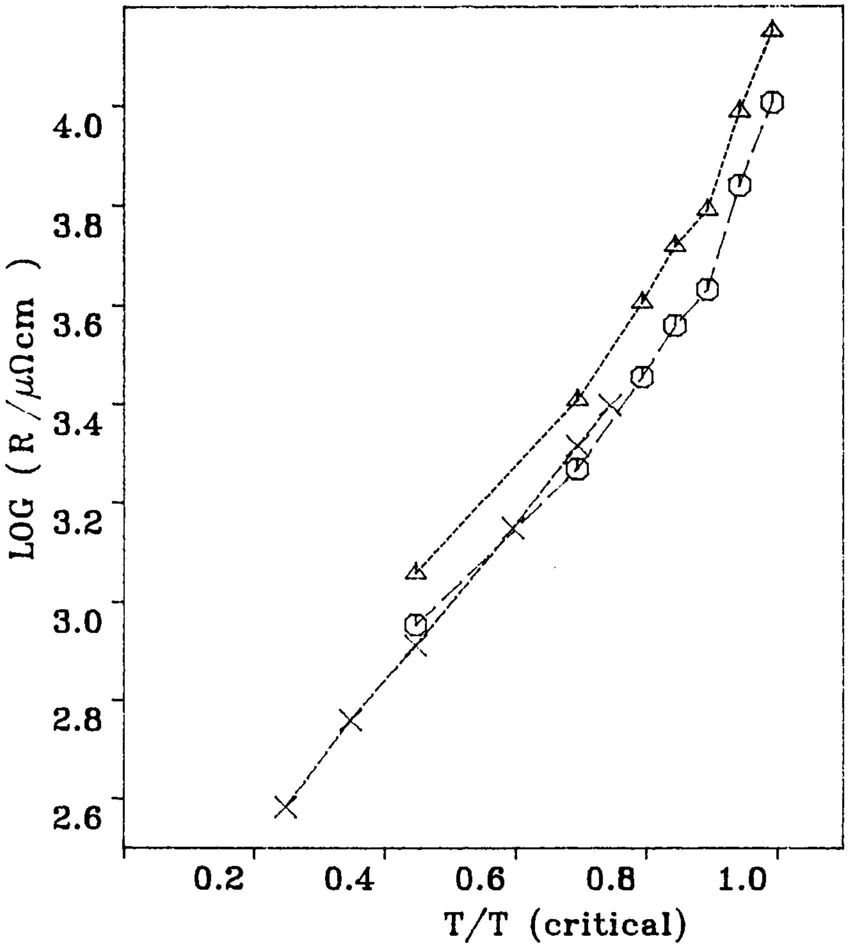

Figure 3 Trends of resistivity with temperature. Upper curve: self-consistent method. Lower circles: Ziman results. Crosses show some experimental values for comparison.

It should though be noted that the present treatment has some common elements with the approach of Oosten and Geerstma[30] who also aimed at a self-consistent treatment of the nearly free electron model.

The decrease in mean free path on expansion which is indicated by the calculations reported above on Rb and also by Chapman's results on Cs is entirely as expected. Clearly, as the free path approaches the mean ionic separation the methods used here become inappropriate. As the metal-insulator transition in an expanded alkali fluid is approached, both electron-ion and electron-electron interactions become strong.

7 SUMMARY

This paper has been concerned with electron transport in the liquid alkali metal Rb, developing further the investigation of the manner in which the increasingly important electron-ion and electron-electron interactions manifest themselves in physical properties as these materials are expanded along the liquid–vapour coexistence curve.

The influence of finite mean free paths for electron–ion scattering in calculations of resistivity has been examined using a self-consistent scheme based on the force–force correlation approach to electron transport. When applied to liquid alkalis near to melting, resistivities are uniformly increased relative to those calculated using the traditional Ziman theory which agrees quantitatively with the experimental value near the melting point. For liquid rubidium it has been shown that there is sensitivity of the calculated resistivities to the description of the high momentum transfer region in the self-consistent method.

Finally, it is clear that a different theory is needed near to the critical point, since as mentioned above there one has both strong electron–ion and electron–electron interactions. These aspects have been discussed by one of us elsewhere[31].

Acknowledgments

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