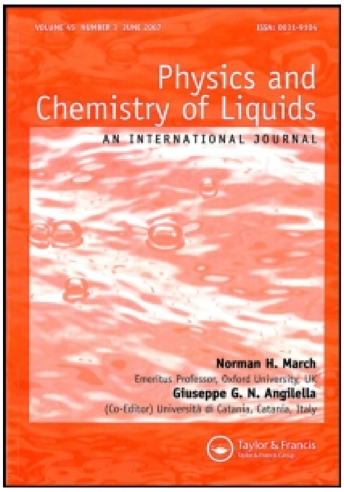

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Mean Free Path Effects in the Dielectric Function of a Liquid Metal

N. H. March[a b]; B. V. Paranjape[c]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, England [b] Department of Physics, University of Alberta, Edmonton [c] Department of Physics, University of Alberta, Edmonton, Alberta, Canada

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Mean Free Path Effects in the Dielectric Function of a Liquid Metal

N. H. MARCH*

Theoretical Chemistry Department, University of Oxford,
1 South Parks Road, Oxford, OX1 3TG, England.

and

B. V. PARANJAPE

Department of Physics, University of Alberta,
Edmonton, Alberta, Canada, T6G 2J1.

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Mean free path effects are introduced into the frequency and wavenumber dependent dielectric function $\epsilon(q, \omega)$ of a simple liquid metal such as Na. It is pointed out that, at least in principle, $\epsilon(q, 0)$ can be brought into contact with experiment through (a) electrical resistivity and (b) effective ion–ion interactions.

The frequency dependence of $\epsilon(q, \omega)$ is then considered, using the Lindhard expression as a starting point. This is shown to link the real parts of the dielectric function $\epsilon(q, \omega)$ and the conductivity $\sigma(q, \omega)$ via a function dependent on Fermi surface blurring. The frequency dependence of this function is determined in the long wavelength limit, and contact with the Drude–Zener theory is established.

Finally, the long wavelength form of $\epsilon(q, \omega)$ is related to plasmon properties of liquid metals and to the ion–ion dynamical structure factor.

Key words: Mean free path effects, liquid metal, dielectric function.

1 INTRODUCTION

In liquid metals the electronic mean free path l is finite and this implies, via the Uncertainty Principle, that there is a blurring of the Fermi surface, Δk_f say, according to

$$l \Delta k_f \sim 1. \tag{1.1}$$

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* Much of this work was completed while on leave at the University of Alberta, Department of Physics, Edmonton.

This fact has been utilized by Ferraz and March[1] in their generalization of the nearly free electron theory of the electrical resistivity of liquid metals.

The aim of the present work is to study in some detail the effect of such Fermi surface blurring on the frequency and wavenumber dependent dielectric function $\epsilon(q, \omega)$ of a simple liquid metal. To introduce the discussion, we summarize in Section 2 below the main results of Leavens *et al.*[2] for $\epsilon(q, 0)$ and point out that, in addition to electrical resistivity already referred to, the effective pair interaction between ions is to be expected to reflect more directly mean free path effects in the static dielectric function of the liquid metal.

In Section 3 we set out the present approach to the frequency dependence of $\epsilon(q, \omega)$; the Lindhard formula being taken as starting point, as in the earlier work of Mermin[3] and of Götze[4]. However, the major departure from their methods is that we introduce Fermi surface blurring directly through the Lindhard expression. The resulting theory is then worked out in some detail for small q in Section 4, while Section 5 makes contact with the dynamical structure factor of the ions. Section 6 discusses the relation to experiment further.

2 STATIC DIELECTRIC FUNCTION

Following Leavens *et al.*[2], the real part of the generalized Lindhard dielectric function, with introduction of a finite mean free path l, is given by

$$\epsilon_1(q, l) = 1 + \frac{4k_f}{\pi a_0 q^2} f(q, l) \tag{2.1}$$

where $f(q, l)$ is given by

$$\begin{aligned} f(q, l) \\ = \frac{1}{2}\left\{1 - \frac{1}{2k_f l}\left(\tan^{-1}\left[\frac{4k_f l}{1 + (ql)^2 - (2k_f l)^2}\right] + \pi(4k_f^2 - q^2 - l^{-2})\right)\right\} \\ + \frac{[1 - (q/2k_f)^2 + (2k_f l)^{-2}]}{8(q/2k_f)} \ln\left\{\frac{[(ql)^2 + 1 + 2k_f q l^2]^2 + (2k_f l)^2}{[(ql)^2 + 1 - 2k_f q l^2]^2 + (2k_f l)^2}\right\} \end{aligned} \tag{2.2}$$

from which one recovers the Lindhard dielectric function in the limit $l \rightarrow \infty$.

2.1 Approximate inclusion of exchange and correlation

Leavens *et al.*[2] include the effects of exchange and correlation in an approximate manner by replacing $f(q, l)$ in Eq. (2.1) by the function

$$F(q, l) = \frac{f(q, l)}{1 - \lambda(1 + 0.1534\lambda)f(q, l)}, \tag{2.3}$$

where $\lambda = (\pi a_0 k_f)^{-1}$. In the large l limit, Taylor[5] has shown that this dielectric function is a good approximation to that of Geldart and Taylor[6]. With the seemingly reasonable assumption that the mean free path changes local field effects in a minor fashion, Eq. (2.3) represents an obvious generalization of Eq. (2.2).

Figures 1 and 2 show how finite free path effects influence the static dielectric function $\epsilon_1(q)$, without and with exchange and correlation.

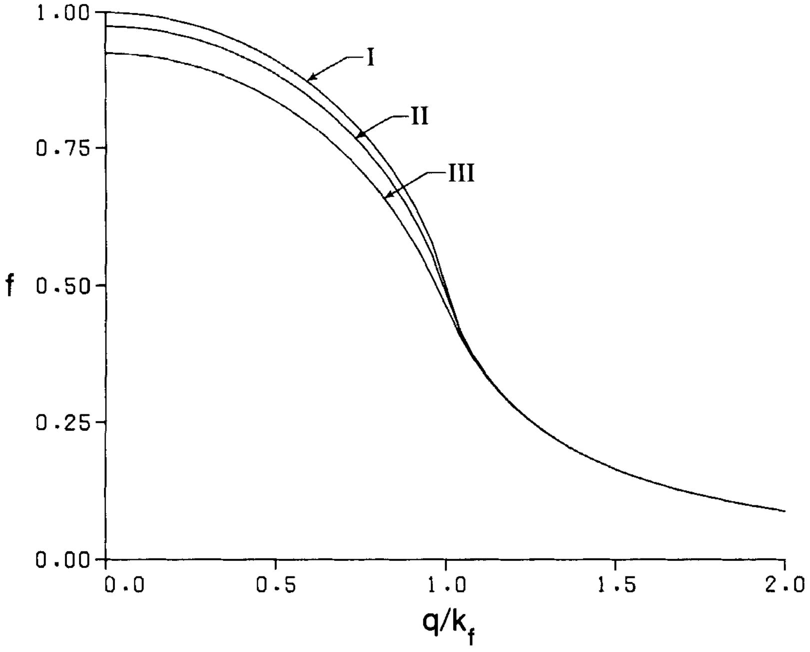

Figure 1 Shows influence of finite mean free path on the static dielectric function $\epsilon_1(q)$ according to Eqs (2.1) and (2.2).

Quantity actually plotted is f in Eq. (2.2), as a function of the variable q/k_f, for the values of the mean free path l, corresponding to:

Curve I: $k_f l = 1000$
Curve II: $k_f l = 30$
Curve III: $k_f l = 10$

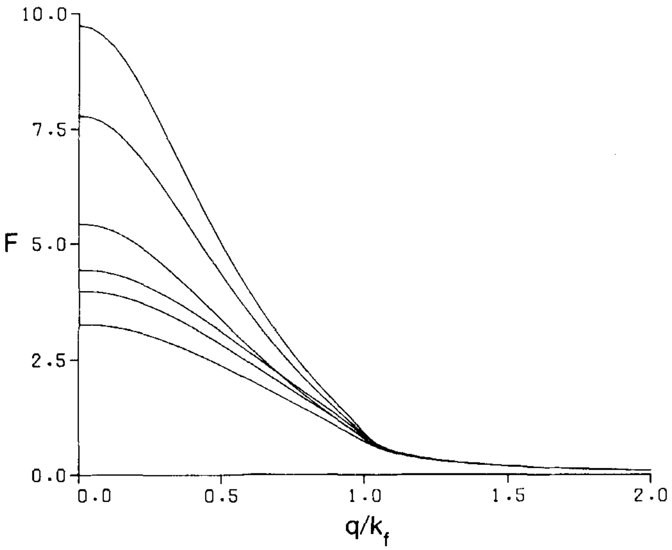

Figure 2 Shows influence of exchange and correlation on the static dielectric function $\epsilon_1(q)$.

Quantity actually plotted is F in Eq. (2.3) as a function of the variable q/k_f, two values of λ, namely 0.7 and 0.8, and for three values of l for each λ, the l values being as in Figure 1. Top three curves correspond to $\lambda = 0.08$.

It should be noted that the choices of λ correspond to strong exchange and correlation interactions: in normal applications of the formula (2.3), the effect of these interactions will be substantially less.

2.2 Application to ion–ion pair potentials

One test of the static form (2.1) of $\epsilon_1(q, l)$ could be made through the fact that in nearly free electron metals the ion–ion pair potential $\phi_{ii}(r)$ involves[7]

$$\int \frac{|U_b(q)|^2}{\epsilon_1(q, l)} \exp(i\mathbf{q}\cdot\mathbf{r})\, d\mathbf{q} \tag{2.4}$$

where $U_b(q)$ is the bare ion pseudopotential. Since l is expected to vary with temperature, and this integral is known to be sensitive to $\epsilon_1(q, l)$ it may be that there will be significant variation of $\phi_{ii}(r)$ with temperature. This application is currently of interest because of the successful inversion of the static structure factor $S(q)$ near the melting point of Na to extract $\phi_{ii}(r)$ for this liquid metal[8]; so far, however, only at the melting temperature.

Other tests of $\epsilon_1(q, l)$ may be feasible: for instance divalent impurity excess resistivity in liquid Na, but to date the measurements needed for comparison do not seem to be available.

We turn next therefore to consider the frequency-dependent dielectric function $\epsilon(q, \omega)$.

3 CONSEQUENCES OF LINDHARD FORM, WITH FERMI SURFACE BLURRING, OF $\epsilon(q, \omega)$

We now assume that Fermi surface blurring can be introduced into $\epsilon(q, \omega)$ of a liquid metal by exploiting the structure of the Lindhard form of the dielectric function[7], namely

$$\epsilon(q, \omega) = 1 + \frac{4\pi e^2}{q^2} H(q, \omega) \tag{3.1}$$

where

$$H(q, \omega) = \sum \frac{f_k - f_{k+q}}{\epsilon_{k+q} - \epsilon_k - \hbar\left(\omega + \frac{i}{\tau}\right)}. \tag{3.2}$$

We note that if Fermi surface blurring is introduced via the occupation probabilities f_q, then one ought, to be consistent, to have a finite relaxation time τ in the denominator, Boltzmann's transport equation yielding the appropriate modification as in Eq. (3.2); i.e. replacing ω by $(\omega + i/\tau)$.

Forming the real and imaginary parts of $H(q, \omega)$ in Eq. (3.2) we find

$$\operatorname{Re} H = \sum \frac{(f_k - f_{k+q})(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_k - \hbar\omega)}{(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_k - \hbar\omega)^2 + \frac{\hbar^2}{\tau^2}} \tag{3.3}$$

and

$$\operatorname{Im} H = \sum \frac{(f_k - f_{k+q})\left(\frac{\hbar}{\tau}\right)}{(\epsilon_{k+q} - \epsilon_k - \hbar\omega)^2 + \frac{\hbar^2}{\tau^2}} \tag{3.4}$$

An immediate consequence of Eqs (3.3) and (3.4) is that the summation involving $\hbar\omega$ in the numerator of Eq. (3.3) can be expressed in terms of Im H to yield

$$\operatorname{Re} H = F(q, \omega) - \omega\tau \operatorname{Im} H \tag{3.5}$$

where $F(q, \omega)$ is given by

$$F(q, \omega) = \sum \frac{(f_{\mathbf{k}} - f_{\mathbf{k}+\mathbf{q}})(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}})}{(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \hbar\omega)^2 + \dfrac{\hbar^2}{\tau^2}} \tag{3.6}$$

Combining Eqs (3.1) and (3.5) with the general relation between $\epsilon(q, \omega)$ and the conductivity $\sigma(q, \omega)$:

$$\epsilon(q, \omega) = 1 + \frac{4\pi i \sigma(q, \omega)}{\omega} \tag{3.7}$$

we have

$$\epsilon_1(q, \omega) = 1 - \frac{4\pi\sigma_2(q, \omega)}{\omega} \tag{3.8}$$

and

$$\epsilon_2(q, \omega) = \frac{4\pi\sigma_1(q, \omega)}{\omega}. \tag{3.9}$$

From Eq. (3.1) we find

$$\epsilon_1(q, \omega) = 1 + \frac{4\pi e^2}{q^2} \operatorname{Re} H(q, \omega) \tag{3.10}$$

and

$$\epsilon_2(q, \omega) = \frac{4\pi e^2}{q^2} \operatorname{Im} H = \frac{4\pi\sigma_1(q, \omega)}{\omega}. \tag{3.11}$$

Substituting in Eq. (3.5) after multiplying that equation by $4\pi e^2/q^2$ yields

$$\epsilon_1(q, \omega) - 1 = \frac{4\pi e^2}{q^2} F(q, \omega) - 4\pi\tau\sigma_1(q, \omega). \tag{3.12}$$

Of course, to put further physical content into Eq. (3.12) one must input energy levels and Fermi surface blurring into Eq. (3.6). However we shall see in Section 4 below in the small q or long wavelength regime that $F(q, \omega)$ must reflect the dynamical structure factor of the ions in the liquid metal. To introduce this limit $q \to 0$, let us note from Eq. (3.12) that

$$\epsilon_1(0, \omega) - 1 = \lim_{q \to 0} \frac{4\pi e^2}{q^2} F(q, \omega) + 4\pi\tau\sigma_1(0, \omega) \tag{3.13}$$

$$\equiv f_1(\omega) \qquad + 4\pi\tau\sigma_1(0, \omega) \tag{3.14}$$

where the latter equation evidently defines $f_1(\omega)$. It is a straightforward matter to show that the Drude-Zener model:

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}, \tag{3.15}$$

with σ_0 the D.C. conductivity, corresponds to $f_1(\omega) = 0$. Of course, one must not assume that consistently with the Drude-Zener model, $F(q, \omega)$ in Eq. (3.12) is zero; only that the limit $q \to 0$ in Eq. (3.13) yields zero in this model. By direct evaluation of the small q limit in Eq. (3.6), we shall obtain in Section 4 an expression for $f(\omega)$ in terms of a form of $f_{\mathbf{k}}$ consistent with Fermi surface blurring.

One final comment worth making here is that one could introduce $\tau \to \tau(\omega)$ into Eq. (3.2) and Eq. (3.12) would still follow as a consequence, with τ in that equation and in Eq. (3.6) now being ω-dependent. But, of course, the justification for such a substitution into Eq. (3.2) would require transcending the Boltzmann transport equation argument given above. We shall return to this point in Section 5, when we consider the consequence of a two-component theory (electrons and ions) following the work of Tosi *et al.*[9]

4 LONG WAVELENGTH EVALUATION OF $\epsilon(q, \omega)$

This is the point at which we must consider in detail the evaluation of $F(q, \omega)$ in Eq. (3.6) in the long wavelength or small q limit. Then plainly in this limit $q \to 0$, we can put $\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_k$ in the denominator equal to zero, to obtain first of all

$$\lim_{q \to 0} F(q, \omega) \to \frac{\sum_{\mathbf{k}} (f_{\mathbf{k}} - f_{\mathbf{k}+\mathbf{q}})(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}})}{\frac{\hbar^2}{\tau^2}[1 + \omega^2\tau^2]}. \tag{4.1}$$

To find the small q limit, we Taylor expand both factors in the numerator to lowest order in q. Then, with $\mu \equiv \cos\theta$, θ being the angle between $\mathbf{k}$ and $\mathbf{q}$, we find to lowest order

$$\lim_{q \to 0} F(q, \omega) = \frac{q^2}{\frac{\hbar^2}{\tau^2}[1 + \omega^2\tau^2]} \iint_{-1}^{1} \frac{\partial f}{\partial \epsilon} \left(\frac{\hbar^2}{2m}\right)^2 (2kq\mu)^2 \, d\mu 2\pi \frac{k^2 \, dk}{4\pi^3} \tag{4.2}$$

where the isotropy of the liquid metal has been employed in the form $\epsilon_k = \epsilon(|\mathbf{k}|)$. Hence, the function $f_1(\omega)$ in Eq. (3.14) is given by

$$f_1(\omega) = \frac{4\pi e^2}{(1 + \omega^2\tau^2)} \int \frac{\partial f}{\partial \epsilon} \left(\frac{\hbar\tau}{2m}\right)^2 \frac{4}{3\pi^2} \frac{k^4 \, d\epsilon}{(\partial\epsilon/\partial k)}. \tag{4.3}$$

This shows clearly that while the frequency dependence of $f(\omega)$ is quite explicit, the magnitude depends on the detailed nature of the Fermi surface blurring through the function $\partial f/\partial \epsilon$, as well as on any departures of the $\epsilon(k)$ relation from the free-electron form $\epsilon(k) = \hbar^2 k^2/2m$.

In fact, the above integral now has an explicit limiting value as the Fermi surface blurring tends to zero, when it can be expressed in terms of the density of states at the Fermi surface. However, in real liquid metals, following the work of Refs 1 and 2, we must expect the blurring defined by $\partial f/\partial \epsilon$ to be a function of the relaxation time τ. In turn, in a liquid metal, the mean free path l, and hence τ must be expected to be temperature dependent. The conclusion of the above argument is that, with n the electron density,

$$f_1(\omega) = \frac{\tau^2}{(1 + \omega^2\tau^2)} h(\tau, n, T), \tag{4.4}$$

where the function h can plainly be calculated from Eq. (4.3) given models of $\partial f/\partial \epsilon$ and $\epsilon(k)$. We stress, however, that the frequency-dependence of $f_1(\omega)$ in the present model is explicit and of Drude-Zener form.

In Section 6, we test Eq. (3.14), with $f(\omega)$ given by Eq. (4.4), using experimental data on $\epsilon_1(0, \omega)$ and $\sigma_1(0, \omega)$ for liquid Na.

5 REAL PART OF A.C. CONDUCTIVITY IN TERMS OF DYNAMICAL STRUCTURE OF IONS

Tosi *et al.*[9] (see also Hinkelmann[10]) show that for a liquid metal:

$$\mathrm{Re}\, \sigma_e(0, \omega) = \frac{\pi e^2 m^2 \omega}{m_e^2} [1 - e^{-\beta\omega}] \lim_{q \to 0} \frac{1}{q^2} S_{ii}(q, \omega) - \frac{\pi n_i m_e^2}{m_e^2} \delta(\omega) \tag{5.1}$$

where

$$\sigma_e(0, \omega) \equiv \sigma(0, \omega)/\epsilon(0, \omega). \tag{5.2}$$

$S_{ii}(q, \omega)$ is the dynamical structure factor of the ions, of number density n_i. Using Eq. (3.7) one finds

$$\operatorname{Re} \sigma_e(\omega) = \frac{\sigma_1(\omega)}{\epsilon_1^2(\omega) + \left(\dfrac{4\pi\sigma_1}{\omega}\right)^2}. \tag{5.3}$$

Writing

$$\frac{\pi e^2 m^2 \omega}{m_e^2}[1 - e^{-\beta\omega}] \equiv [g(\omega)]^{-1} \tag{5.4}$$

and

$$\lim_{q \to 0} \frac{1}{q^2} S_{ii}(q, \omega) \equiv [T(\omega)]^{-1} \tag{5.5}$$

one obtains from Eqs (5.1) and (5.3)

$$\frac{16\pi^2}{\omega^2}\sigma_1^2 - gT\sigma_1 + \epsilon_1^2 = 0, \tag{5.6}$$

with solution near the plasma frequency, where $\epsilon_1 \to 0$:

$$\sigma_1(\omega \sim \omega_p) = \frac{\omega_p^2}{16\pi^2} gT|_{\omega \sim \omega_p}. \tag{5.7}$$

Generally the solution of the quadratic (5.6) can be written

$$\sigma_1(\omega) = \frac{\omega^2}{32\pi^2}\left[gT + \sqrt{g^2T^2 - \frac{64\pi^2}{\omega^2}\epsilon_1^2}\right] \tag{5.8}$$

which reduces to Eq. (5.7) as $\epsilon_1 \to 0$.

Equation (5.6) can, alternatively, be used to gain information on the dynamical structure factor as reflected by $T(\omega)$ in Eq. (5.5), in frequency regimes away from $\omega = 0$ where $\sigma_1(\omega)$ and $\epsilon_1(\omega)$ are known from experiment. This route is considered by using experimental data for liquid Na in Section 6 below.

6 SOME POINTS OF CONTACT WITH EXPERIMENT

In this section, we shall attempt to bring the theory outlined above into contact with experiment. We shall begin by considering the prediction made in Eqs (3.14) and (4.4).

6.1 Relation between $\sigma_1(\omega)$ and $\epsilon_1(\omega)$ in liquid Na

The data on the optical constants n and k of liquid Na obtained by Inagaki *et al.*[11] has been utilized to test the form of Eq. (3.14), with $f_1(\omega)$ taking the form of Eq. (4.4). Thus, in Figure 3 we have plotted $nk\omega$ versus $1 - n^2 + k^2$, the former quantity being proportional to $\sigma_1(\omega)$ and the latter to $\epsilon_1(\omega)$.

The most striking thing to note is at the high frequency end of this plot, which is near the origin, one can draw a straight line through the origin passing through the observed points in this limit. Taking the relaxation time τ from Inagaki *et al.* as $\tau = 1.6 \times 10^{-14}$ sec, it is easily verified that this slope of the $\sigma_1 - \epsilon_1$ plot is near to $4\pi\tau$ as predicted by

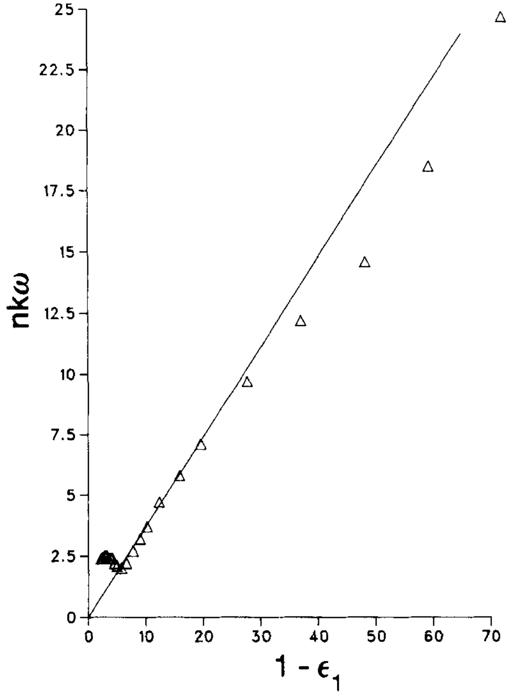

Figure 3 Experimental data on the optical constants n and k for liquid metal Na as measured by Inagaki *et al.*

Actual plot is of $nk\omega$ versus $1 - n^2 + k^2$, the former quantity being essentially the real part $\sigma_1(\omega)$ of the conductivity and the latter being $1 - \epsilon_1(\omega)$, with ϵ_1 the real part of the dielectric constant.

This plot is motivated by Eqs (3.14) and (4.4).

The straight line drawn is a Drude-Zener-like prediction at frequencies such that $f_1(\omega)$ is Eq. (3.14) is negligible. However, points shown near the origin of the Figure reflect remnants of 'interband' transitions in the liquid metal, and the theory does not incorporate these.

Eqs (3.14) and (4.4) for $\omega^2\tau^2 \gg 1$. Since, in the high frequency limit, $f_1(\omega) \to 0$, one is recovering the Drude-Zener relation between σ_1 and ϵ_1. However, since according to Eq. (4.4), $f_1(\omega) \to$ constant for $\omega^2\tau^2 \ll 1$, at the low frequency end the prediction is another parallel straight line, having the same slope, but when extrapolated back to $\varepsilon_1 = 0$ cuts the σ_1 axis at the value $-h(\tau, n, T)$. The 'deviation' from the 'Drude-Zener' line drawn in Figure 3 is compatible with this prediction. However, we have no doubt that the calculation of h from first principles is a task well beyond the theoretical framework used in this paper.

To see the basic reason for this, let us return to Eq. (3.14), substitute $f_1(\omega)$ from Eq. (4.4), and let $\omega \to 0$. Then we find

$$h = \epsilon_1(0,0) - 1 - 4\pi\tau\sigma_1(0,0). \tag{6.1}$$

It is, of course, well known that the D.C. conductivity $\sigma_1(0,0)$ of a liquid metal is connected intimately with the short-range ionic order as reflected in the liquid structure factor $S(q)$. Furthermore, while, as Inagaki *et al.* demonstrate, the experimental data for $\epsilon_1(0,\omega)$ is well reproduced by the plasma formula

$$\epsilon_1(0,\omega) = 1 - \frac{\omega_p^2}{\omega^2} \tag{6.2}$$

over a wide range of frequencies, this formula must become mean free path limited for sufficiently low frequencies. Thus, h turns out in Na to be a small difference between large quantities, each of which must, in turn, be sensitive to the details of the liquid structure and also the nature of the Fermi surface blurring.

6.2 Dispersion of plasmon

The success of the simple plasma formula (6.2) in liquid Na in representing the experimentally determined $\epsilon_1(0,\omega)$ over a substantial frequency range has prompted us to conclude this section by presenting the results of a simple calculation of the way the plasmon dispersion relation $\omega_p(q)$ and more importantly the plasmon damping was affected by mean free path, or equivalently finite relaxation time, effects.

However, although the main structure of the present paper has hinged on introducing Fermi surface blurring into the Lindhard formula, available evidence, including the success of the formula (6.2), points to the fact that the main effect in determining the dispersion relation

$$\epsilon_1(q, \omega_p(q)) = 0 \tag{6.3}$$

from Eqs (3.1) and (3.2) is the presence of τ in the denominator. Thus, we can, in determining $\omega_p(q)$, simplify the present approach, neglect the blurring of the Fermi surface in the numerator of Eq. (3.2), when we are led back to the treatment of Mermin[3]. In the Appendix, we have set out the detailed way in which this can be used to find $\omega_p(q)$ from Eq. (6.3). Then equations (A.1) and (A.2) have been solved numerically and the damping of $\omega_p(q)$ vs τ^{-1} is displayed in Figure A3.

7 SUMMARY AND DIRECTIONS FOR FUTURE WORK

The experimental results on the optical constants n and k for liquid Na are in general accord with Eq. (3.14) with $f_1(\omega)$ having the frequency dependence shown in Eq. (4.4). We have emphasized, however, that the function $h(\tau, n, T)$ in Eq. (4.4) depends crucially on the liquid structure, as well as on the detailed nature of the Fermi surface blurring. Equation (4.3) seems not to reflect this structure in a sufficiently profound manner, even though both $f(\epsilon)$ and $\partial\epsilon/\partial k$ will be structure dependent.

Therefore, it may well prove important eventually to transcend the Lindhard expression (3.1), and to work directly with the more basic relation (5.8) in relating $\sigma_1(\omega)$ and $\epsilon_1(\omega)$. In this context, it is clear from Eqs (5.1) and (5.3) that experimental measurement of the frequency dependence of both $\sigma_1(\omega)$ and $\epsilon_1(\omega)$ over a common range of frequency will allow the quantity $\lim_{q\to 0} 1/q^2 S_{ii}(q, \omega) = s(\omega) = [T(\omega)]^{-1}$ to be extracted. Since one of the aims of the theory of liquid metals is to predict electronic properties from observed structure, both the static structure factor $S(q)$ and the dynamic structure factor $S_{ii}(q, \omega)$ of the ions, it is clearly of interest to establish some of the features of $S_{ii}(q, \omega)$ beyond those presently known from neutron inelastic scattering. For liquid Rb, for example, such neutron studies by Copley and Rowe[12] reveal collective modes, which were subsequently found in the computer experiments of Rahman[13]. It needs no emphasis that it would be valuable to connect such information with studies of $\sigma_1(\omega)$ and $\epsilon_1(\omega)$ over the widest possible frequency range on this particular liquid metal. As discussed by Tosi *et al.* the D.C. conductivity is, in fact, related to $s(\omega)$ defined above in the limit $\omega \to 0$.

Related to the above discussion, we note also that use of Eq. (6.2) in the form $\omega^2 \equiv \omega^2(\epsilon_1)$ in Eqs (3.14) and (4.4) would yield $\sigma_1 \equiv \sigma_1(\epsilon_1)$ and the utility of such a relationship is exemplified by Figure 3. Comparison with Eq. (5.8) would then imply that gT must be a function of ϵ_1 and it would be of obvious interest to confront this prediction of the present work with experiment when independent measurements of $\epsilon_1(\omega)$ and $\lim_{q\to 0} q^{-2}S_{ii}(q, \omega) \equiv s(\omega)$ become available for the same liquid metal in overlapping ranges of frequency.

The functional relation between $\sigma_1(\omega)$ and $\epsilon_1(\omega)$ proposed above is quite different, of course, from the exact connection between nk and $n^2 - k^2$ given by the Kramers–Krönig relation. It would, in the future when the optical constants n and k become available for a particular liquid metal over a fuller frequency range, be of interest to insert $[\epsilon_1(0, \omega) - f_1(\omega)]$ appearing in Eq. (3.14), with $f_1(\omega)$ given by Eq. (4.4), into such a Kramers–Krönig integral and hence to explore the dependence of $\sigma_1(\omega)$ thereby obtained on the choice of $h(\tau, n, T)$. As already exemplified in Eq. (6.1), we strongly suspect that h must turn out to be much smaller than implied by a formula such as Eq. (4.3).

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Appendix Method of calculation of plasmon properties as function of phenomenological relaxation time

For reasons outlined in the text, we shall make direct use of Mermin's formula for $\epsilon(q, \omega)$, in which a relaxation time τ is introduced. Because we are concerned with high-frequency (plasmon) properties, the limitation of the Mermin formula, referred to in the text, that it does not reflect the blurring of the Fermi surface in the static limit $\omega = 0$ is evidently not serious for the present application.

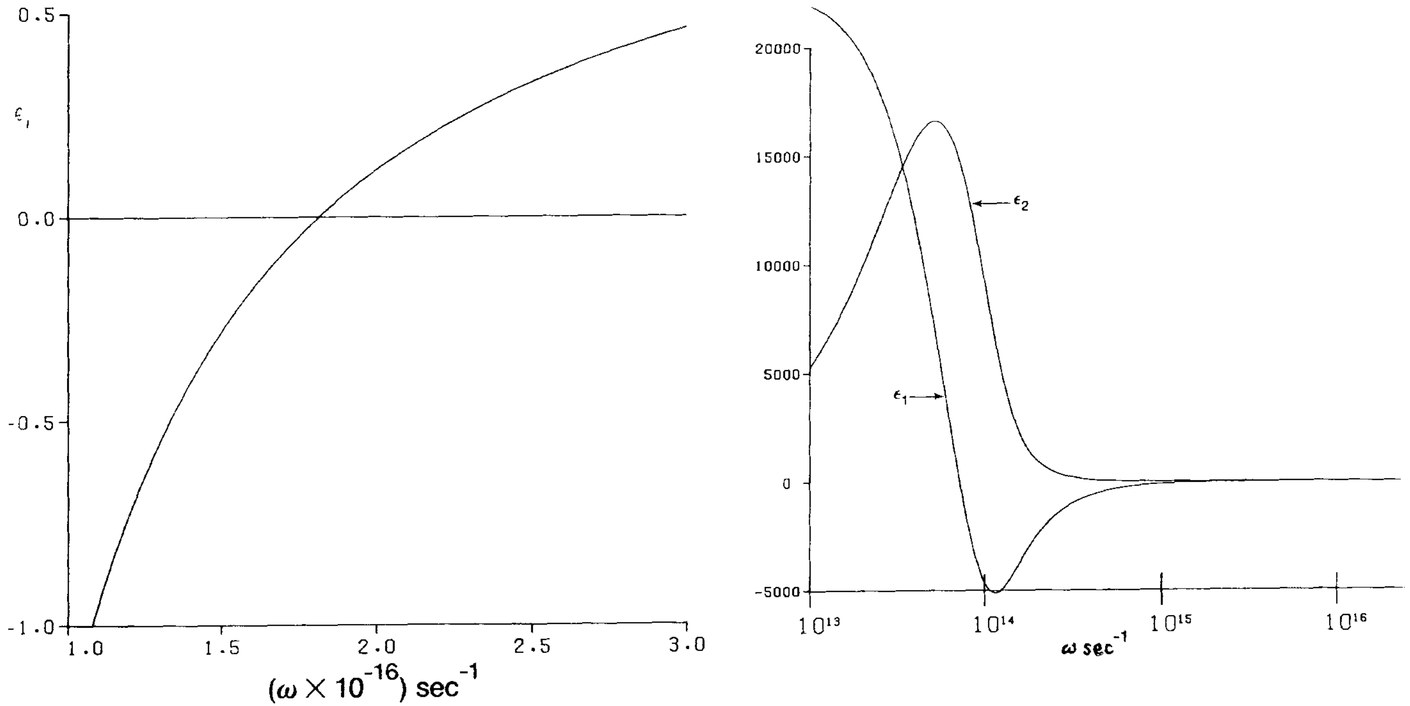

Figure A1 Real and imaginary parts of the dielectric function $\epsilon(q, \omega)$ defined in Eq. (A1) plotted for fixed $q(10^7\ \mathrm{m}^{-1})$ as a function of ω. These are shown for τ appropriate to liquid metal Na (1.6×16^{-14} sec). Note tail on imaginary part due to finite relaxation time τ. For $\tau \to \infty$, ϵ_2 is zero for $\omega > v_f q$, where v_f is the Fermi velocity.

Denoting now the free-electron Lindhard dielectric function without Fermi surface blurring by $\epsilon^0(q, \omega)$, Mermin's result takes the form

$$\epsilon(q, \omega) = 1 + \frac{\left(1 + \dfrac{i}{\omega\tau}\right)\left[\epsilon^0\left(q, \omega + \dfrac{i}{\tau}\right) - 1\right]}{1 + \left\{\left(\dfrac{i}{\omega\tau}\right)\left[\epsilon^0\left(q, \omega + \dfrac{i}{\tau}\right) - 1\right]\Big/[\epsilon^0(q, 0) - 1]\right\}}. \tag{A1}$$

Because the plasmon is essentially a long wavelength electronic excitation, we shall specify $\epsilon_1(q, \omega)$ for small q only.

To do so, we return to Eqs (3.1) and (3.2), substitute $\epsilon_k = \hbar^2k^2/2m$ and f_k by the usual Fermi step function (i.e. $T = 0$ and no blurring due to disorder scattering). In the small q limit, exploiting the fact that the

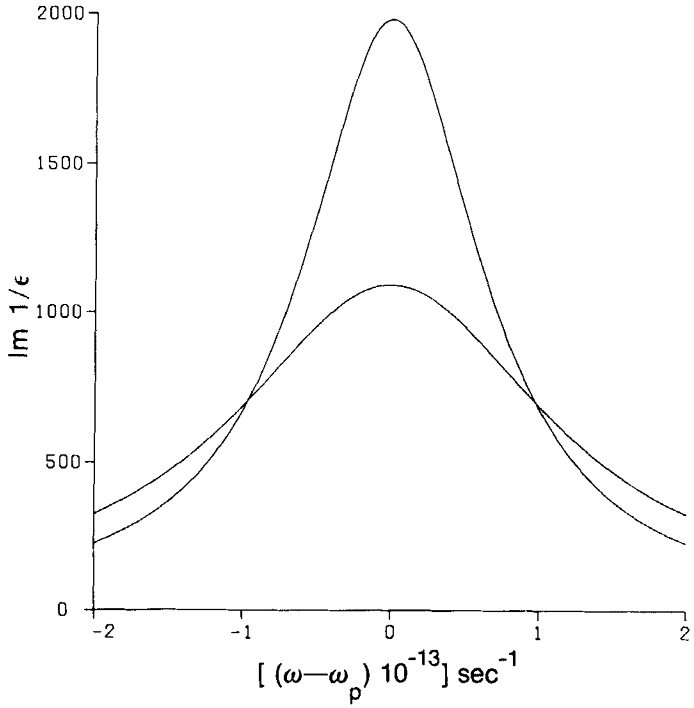

Figure A2 Energy loss function Im $1/\epsilon(q, \omega)$ plotted as a function of ω for fixed q ($q = 10^8$, and $10^9\,\mathrm{m}^{-1}$). Note the peaks at the plasmon frequency ω_p have non-zero width because of the finite relaxation time τ. As $\tau \to \infty$, one recovers a delta function peak at ω_p.

derivative of the Fermi function is a delta function at the Fermi surface, we obtain, with $\mu = \mathbf{q}\cdot\mathbf{k}/qk$,

$$H^0(q,\omega) = \frac{1}{2\pi^2}\int_{-1}^{1} \mathrm{d}\mu \frac{k_f \frac{m}{\hbar^2}[2k_f q\mu + q^2]}{2k_f q\mu + q^2 - \frac{2m}{\hbar}\omega}. \tag{A2}$$

Clearly $\epsilon^0(q,\omega + i/\tau)$ required in Eq. (A1) is to be obtained from Eq. (3.1) by putting $H = H^0(q,\omega + i/\tau)$.

With this form for $\epsilon^0(q,\omega + i/\tau)$, Eq. (A1) has been used to plot the real and imaginary parts of $\epsilon(q,\omega)$ as a function of ω for fixed q in Eq. (A1) and these are shown in Figure A1 for a value of τ appropriate to liquid Na.

From the real part of this plot, it turns out that the plasmon dispersion, corresponding to $\epsilon_1(q,\omega) = 0$, is negligibly affected by τ, and indeed by a shorter relaxation time by an order of magnitude. Thus, Eq. (A1) shows no changes of significance from the usual Lindhard result for the plasmon dispersion.

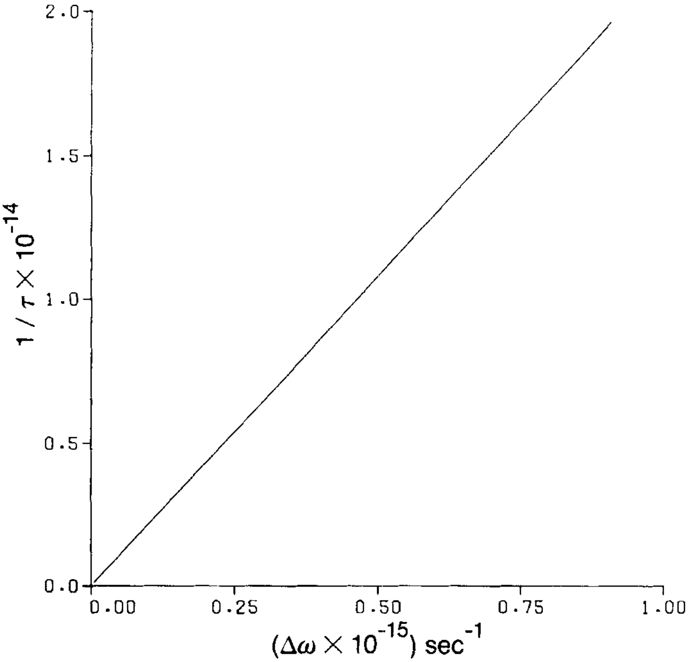

Figure A3 Total width at half maximum peak height from Figure A2, plotted as a function of relaxation time τ.

However, as Figure A1 shows, the effect on ϵ_2 of τ is qualitative. Whereas with $\tau \rightarrow \infty$, ϵ_2 vanishes for $\omega > v_f q$, v_f being the Fermi velocity, there is now a 'tail' on ϵ_2 for ω greater than this value.

Therefore, we have also studied the energy loss function Im $1/\epsilon(q, \omega)$ from the result (A1). This function is plotted in Figure A2 for $\tau = 10^{-14}$ sec. It will be seen that while, as already mentioned, the plasma frequency is not affected by finite τ of physical magnitudes, the delta function peak in the loss function at $\omega_p(q)$ is broadened because of the collisions built in through finite τ. The total width of the peak at half maximum height is plotted against $1/\tau$ in Figure A3. To date, for pure liquid metals we know of no data directly comparable with the damping of the plasmon shown in this Figure.