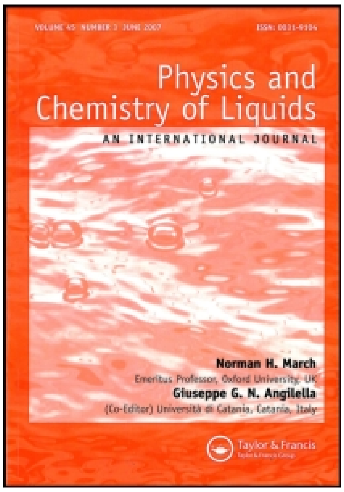

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INTERPLAY OF STRUCTURES AND FORCES IN THE ELECTRONIC CONDUCTIVITY OF LIQUID MERCURY

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Liquid mercury has long been known as a "dirty" liquid metal, i.e. one in which the typical separation of physical scales is blurred. In the present paper microscopic and macroscopic origins of this behaviour are discussed. It is shown that a two-parameter pseudopotential is sufficient to reproduce the experimental conductivity close to the melting point. With certain approximations an analytical formula for the conductivity can be derived.

KEY WORDS: Electron-ion pseudo potential, structure factor.

INTRODUCTION

The conductivity of an ideal liquid metal is given rise to by itinerant degenerate electrons which are only weakly scattered by the ions. The ions, in turn, still show a marked structure strongly reminiscent of a solid which is expressed in the ionic structure factor $S(\vec{k})$. For this physical situation the conductivity σ can be derived using an electron-ion pseudopotential $\tilde{v}_{ei}$[1]

$$\sigma = 12\pi^3 Z^2 \frac{\hbar^3 \varepsilon_0^2}{m_e^2 e^2} n_i \left[\int_0^{2k_F} dq\, q^3 S(q) \left| \frac{\tilde{v}_{ei}}{\varepsilon(q)} \right|^2 \right]^{-1} \tag{1}$$

In (1) the medium effects are modelled by the electronic dielectric function $\varepsilon(q)$ and the integration limit is given by the Fermi momentum k_F. This clearly is a zero-temperature theory which is justified because of the strong degeneration. Finite temperature correction amount to fractions of per cents and are totally meaningless within the overall accuracy of the presented theory. More elaborate theories for ε incorporate local field corrections. We have used the form given by Ichimaru and Utsumi[2] for $T = 0$. n_i is the density of the ions, Z their charge and all the physical constants have their usual meaning. The pseudopotential $\tilde{v}_{ei}$ has to take into account the cancellation of nuclear attraction and repulsion by the core electrons near the nucleus. This effect is most clearly seen in the so-called Ashcroft potential:

$$\tilde{v}_{ei}^{\mathrm{ash}} = -4\pi Z e^2 \frac{\cos kR_c}{k^2}, \tag{2}$$

where the potential inside a sphere of radius R_c (the Ashcroft radius) is set zero. It turns out that, for mercury, the Ashcroft potential is too simple to reproduce the experimental values[3]. The potential of Heine and Abarenkov (see e.g.[4]) assigns the potential inside the R_c-sphere a finite value a, yielding in $\vec{k}$-space:

$$\tilde{v}_{\mathrm{ei}}^{HA} = \frac{-4\pi e^2 \cos k R_c}{k^2}[Z - aR_c] - 4\pi a \frac{\sin k R_c}{k^3} \tag{3}$$

The structure factor S is the Fourier transform of the pair correlation function $h(r)$ in real space and is thus linked to thermodynamics. Especially,

$$S(0) = n_i k_B T \kappa \tag{4}$$

where κ is the compressibility of the system. Generally, for an ensemble of electrons and ions the structure factor would have to take any microscopic interaction into account. It is a typical feature of liquid metals that the more or less itinerant electrons play no role in the ion formation and that the Coulomb effects are roughly balanced out by the still crystal-like structure. Hence the structure factor of a system of hard spheres which has been known for a long time (see for instance[5]) is a good approximative description of the ionic structure in a liquid metal. Of course, this approximation has to fail near the critical region since the hard sphere fluid does not display critical behaviour.

In the liquid metal regime energetic and spatial scales separate clearly. This encourages attempts to reduce the integral formulation (1) to a parametric one using only characteristic quantities. In the appendix a simple evaluation of σ resulting from these considerations is given.

SELFCONSISTENT MEAN FREE PATH IN REAL LIQUID METALS

Ferraz and March[6] have noticed a theoretical inconsistency in the conductivity as following from the liquid metal concept. The assumption of ideal, completely degenerate electrons (which is inherent in the dielectric function ε) would entail an infinite mean free path (MFP) l_f. This would necessarily cause the conductivity σ to diverge. In their reasonsing Ferraz and March start from the näive formula

$$\sigma^{-1} = \frac{\hbar k_F}{ne^2 l_f} \tag{5}$$

connecting MFP and conductivity.

A finite MFP must furthermore mean a blurring of the Fermi edge in the spirit of the Heisenberg uncertainty relation $l_f \Delta k_F \sim 1$. Employing the formalism of density matrices it is then possible to expand the integral in (1) to infinity and to introduce a suitable weight resulting in a softened Fermi block:

$$\sigma = 12\pi^3 Z^2 \frac{\hbar^3 \varepsilon_0^2}{m_e^2 e^2} n_i \left[\int_0^{\infty} dq\, q^4 \Gamma(q; k_F, l_f)\, S(q) \left| \frac{\tilde{v}_{ei}}{\varepsilon(q)} \right|^2 \right]^{-1}$$

$$\Gamma(q; k_F, l_f) = \int d\vec{R}\, \exp(e\vec{q}\vec{\mathrm{R}}) |\sigma_0|^2 \exp\left(-\frac{R}{l_f}\right) \tag{6}$$

where σ_0 is the energy derivative of the free electron density matrix. We note here that it is possible to evaluate Γ analytically:

$$\Gamma = \frac{1}{\pi^3 q} \{2\arctan(l_f q) - [\arctan[l_f(q + 2k_F)] + \arctan[l_f(q - 2k_F)]]\} \tag{7}$$

Two comments have to be made. Firstly, the blurring of the Fermi block is an interaction effect and thus arises also at zero temperature. Secondly, it has to be cautioned that the presented argument works *a posteriori*. That means that the l_f thus obtained is certainly not the actual physical average distance between any two collisions. It has rather to be understood as an indicator whether the liquid metal scale separation $l_f \gg$ *struct. length* is upheld.

RESULTS FOR MERCURY

The above picture of the liquid metal as a peculiar state of matter in which structure and interaction can be split up uniquely into electronic, ionic and electron-ion parts turns out not to be valid for liquid mercury. Instead of an asymptotic region of validity in the density-temperature plane as, e.g. emerges for the alkalis, only a very narrow density range around the melting point can be described in stringent liquid metal spirit. Ongoing thermodynamical work[7] suggests that not all valence electrons are delocalized at the melting point. In the following it is, however, assumed that mercury is a clean liquid metal with Heine-Abarenkov interaction.

The conductivity discussed above contains three parameters; two of the pseudopotential and the hard sphere diameter λ. For consistency reasons it is desirable to keep the amount of fitting to a minimum. Therefore λ is taken from analysis of the Lennard-Jones phase and left untouched at $\lambda = 5.22$ in atomic units. Physically this means that the structure is regarded as fixed and theoretical accord with the dilute phase is maintained. The fitting of the potential parameters then has to be understood as the reliable formulation of the electron-ion interaction.

Taking the melting point as a reference point a set of tupels (a, R_c) is found to reproduce the correct σ as measured by Even and Jortner[3]. Among these tupels the one is regarded as optimal that gives the correct slope if the density is decreased from the melting point. Our result is

$$R_c = 3.4$$

$$a = 0.2883 \tag{8}$$

in atomic units. Figure 1 shows the σ according to (1) and (8) in comparison with the experiment. In the logarithmic plot the theory (1) gives a linear curve whereas the experimental values decrease much faster with decreasing density. This points to a fundamental limitation of the liquid metal concept for mercury which shall be discussed in the following section.

The positive value of the parameter a suggests, within the reasoning of Heine and Abarenkov, a significant Pauli effect of the core electrons resulting in a small distance repulsion. It has to be cautioned, though, that a is much more a numerical fit parameter than a sensible physical quantity.

It may be worth pointing out that in the fitting of the Ashcroft potential alone the parameter R_c is fixed between ~ 0.72 (with inclusion of local field corrections) and 0.9 atomic units (Ashcrofts original result). The value given above comes much nearer to the hard sphere radius which should signal improved consistency.

The MFP-based argument presented in the foregoing section yields for mercury near the melting point typical values $l_f \sim 40$ atomic units (see Fig. 2). This clearly leads into a domain of theory where the metallic character is challenged and for which so far no better naming than "dirty metal" has been found.

DISCUSSION

The microscopical explanation of diminishing metallic properties of liquid mercury may be contrasted by a thermodynamic argument. Let us adopt the point of view of

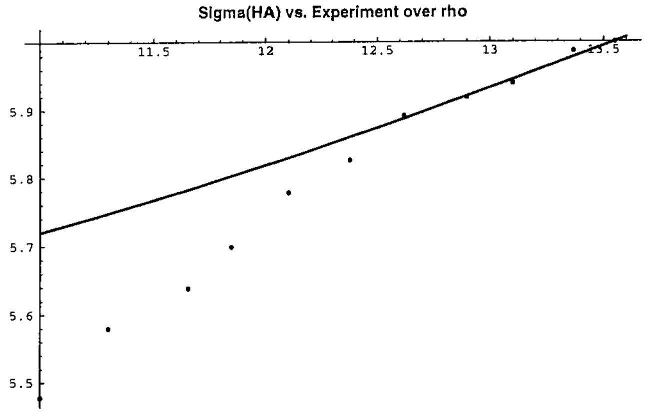
Sigma(HA) vs. Experiment over rho

Figure 1 Experimental vs. theoretical conductivity σ (in$(\Omega \text{m})^{-1}$) over density ρ in g/cm^3.

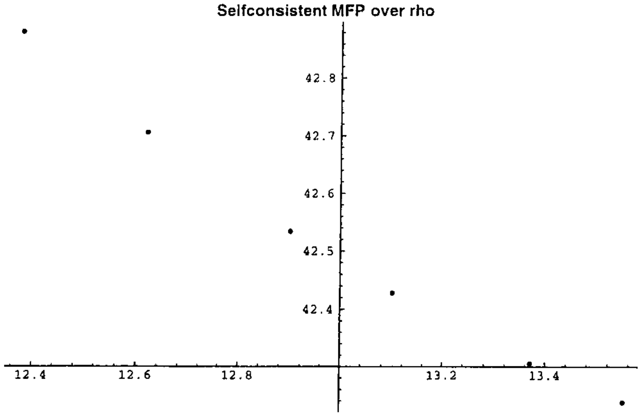

Figure 2 Selfconsistent MFP following Ferraz and March over density ρ.

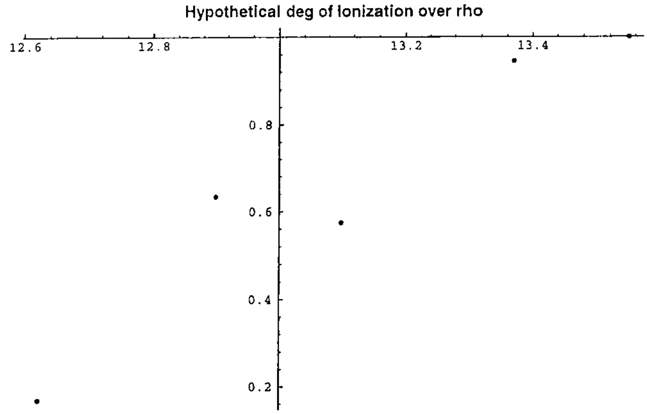

Figure 3 Hypothetical degree of ionization as following from the experimental values with assumed ideal behaviour of the electrons over density ρ.

plasma physics, i.e. describe an ensemble of nuclei and electrons on the basis of a Mass Action Law (MAL): the Helmholtz Free Energy F is, for a given temperature, minimized over the densities of electrons, ions and atoms. The result is an ionization equilibrium characterized by the degree of ionization $\alpha = \text{free e}^-/\text{all e}^-$. For a dilute system (the Lennard-Jones phase) α is almost zero. For increasingly dense packing, as in the liquid metal, more and more electrons are forced into the valence band, or, in terms of plasma, become ionized. Recent work[7] suggests, however, that the concentration of atoms at the melting point is far from zero. Starting from the experimental σ-values it is possible to extract α under the assumption that the remaining free electrons are indeed nearly free (i.e. their MFP is far larger than the one found above). The result is given in Figure 3. Over the density interval $\sim 12.5\,\text{g/cm}^3$ to

$\sim 13.6\ \mathrm{g/cm^3}$ the degree of ionization increases dramatically. In plasma physics such a behaviour is typical for the so-called density ionization.

Of course the assumption of a few zero-temperature free electrons at the melting point is unphysical; it had been employed here for argumentative reasons. The emerging picture for liquid mercury seems to combine elements from both approaches: the emergence of the atomic subfluid will destroy the ionic order and Coulomb scattering of the itinerant electrons will be replaced by more complex forms of interaction with the atomic and ionic cores.

In summary it can be stated the mercury proves to be a worthwhile study case for probing the conventional liquid metal concept. A physical situation as outlined in the last paragraph certainly opens up a variety of interesting new questions.

APPENDIX

As argued in the main text a liquid metal can be described by a number of fundamental lengths. In particular they are:

- k_F–the Fermi momentum, a statistical length
- k_{FT}–the Fermi-Thomas momentum, a quantum statistical length describing the screening of an ideal Fermi liquid entering the asymptotic form of ε, $\varepsilon \simeq 1 + k_{FT}^2/q^2$
- λ–the hard sphere diameter, a basic structural length
- R_c–the Ashcroft radius, a length describing collective effects in the effective interaction

For simplicity $R_c = 0$ is set in the following. The structure factor is expanded up to fourth order which allows the integral in (1) to be evaluated analytically. The result (in units $(\Omega\mathrm{m})^{-1}$, density in cm^{-3}) is:

$$\sigma = 3.21212\ 10^{-18} n_i I^{-1} \tag{9}$$

where

$$\begin{aligned} I = {} & \gamma_0 \frac{-4k_F^2}{4k_F^2 + k_{FT}^2} + (\gamma_0 - \gamma_1 k_{FT}^2) \log\left(1 + \frac{4k_F^2}{k_{FT}^2}\right) \\ & + 4k_F^2(\gamma_1 - \gamma_2 k_{FT}^2) + \gamma_2 [8k_F^4 + 4k_F^2 k_{FT}^2], \end{aligned} \tag{10}$$

$$\gamma_0 = s_0 - s_2 k_{FT}^2 \lambda^2 + s_4 k_{FT}^4 \lambda^4$$

$$\gamma_1 = s_2 \lambda^2 - 2 s_4 k_{FT}^2 \lambda^4$$

$$\gamma_2 = s_4 \lambda^4 \tag{11}$$

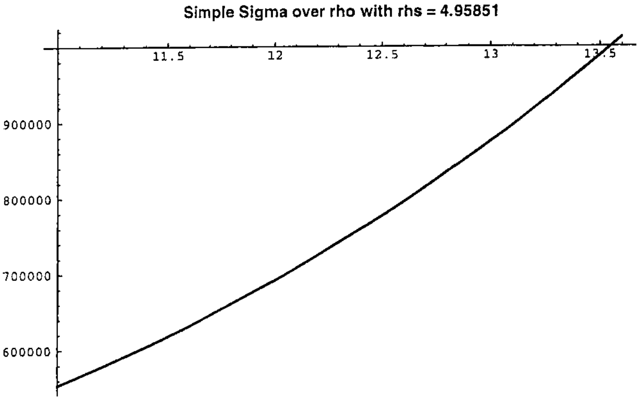

Figure 4 Conductivity σ according to simple analytical formula (9).

with

$$s_0 = \frac{1}{1-c_0}$$

$$s_2 = \frac{c_2}{(1-c_0)^2}$$

$$s_4 = \frac{c_2^2}{(1-c_0)^3} + \frac{c_4}{(1-c_0)^2}, \tag{12}$$

$$c_0 = \eta(8a + 6b + 4c)$$

$$c_2 = -\eta\left(\frac{4a}{5} + \frac{2b}{3} + \frac{c}{2}\right)$$

$$c_4 = \eta\left(\frac{a}{35} + \frac{b}{40} + \frac{c}{50}\right) \tag{13}$$

where $\eta = \pi/6\, n_i \lambda^3$ is the packing fraction and

$$a = -\frac{(1+2\eta)^2}{(1-\eta)^4}$$

$$b = 6\eta \frac{\left(1 + \frac{1}{2}\eta\right)^2}{(1-\eta)^4}$$

$$c = -\frac{\eta}{2} \frac{(1+2\eta)^2}{(1-\eta)^4} \tag{14}$$

Figure 4 shows the relative good results obtained with (9) in the liquid metal regime.

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