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WORKING PARTY

ON

"PHYSICS OF CONDENSED MATTER AT PLANETARY PRESSURES"

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TRANSPORT IN LIQUID METALS

by

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Thermal conductivity of liquid metals

Electronic term in thermal conductivity, χ_e say, requires solution of Boltzmann eqn (standard texts): I'll merely give the answer:

$$\frac{\chi_e \rho}{T} = \frac{\pi^2 k_B^2}{3e^2} \equiv \text{LORENZ NUMBER}$$

(2·45 in units used in Table below)

Result does not depend on specific assumption about Fermi surface, density of electron states, nature of scattering potential etc, but it DOES involve general assumption that the scattering is elastic.

Table

$(\chi \rho / T)$ at melting point from experiment.

Li	2·6	Al	2·4
Na	2·2	Ga	2·07
K	2·1	Tl	3·2
Cs	2·4	Sn	2·9
Zn	3·2	Pb	2·4
Cd	2·5	Sb	2·6
Hg	2·75	Bi	2·5

Extreme strong scattering limit

(≡ 'impurity' resistivity)

['incoherent' scattering in which liquid structure does not appear — contrast with weak scattering theory where $S(k)$ is CRUCIAL].

At least under normal conditions, theory is not good enough for 3d transition metals (eg liquid Fe): scattering of conduction electrons of one Fe centre is not sufficiently strong.

Almost good enough for rare earth metals, it turns out.

I'll start from this limit. Then we'll see how one can construct, essentially from the same starting point, a nearly free electron theory appropriate to s, p metals (alkalis etc)

Huang (1948) derived exact expression in terms of phase shifts $\eta_\ell \equiv \eta_\ell(k_F)$ for the excess resistivity of a metal in which independent free electrons are scattered by a spherical potential $V(r)$. NUB of Huang formula (see, e.g. Ziman's book: Electrons & Phonons) is the sum

$$S = \sum_{\ell=0}^{\infty} \ell \sin^2(\eta_{\ell-1}-\eta_\ell).$$

Gerjuoy, and independently, and much later Gaspari & Gyorffy showed that radial wave functions R_ℓ satisfy

$$\int_0^\infty dr\, r^2 R_{\ell-1}(r) \frac{\partial V}{\partial r} R_\ell(r) = \sin(\eta_\ell-\eta_{\ell-1})$$

where, outside the range of $V(r)$

$$R_\ell(r) = j_\ell \cos\eta_\ell - n_\ell \sin\eta_\ell$$

spherical Bessel : spherical Neumann fn

Can be manipulated by writing 'OFF-DIAGONAL DENSITY of STATES

$$\sigma(r_1 r_2) = \sum_\ell (2\ell+1)\, \sigma_\ell(r_1, r_2)\, P_\ell(\cos\gamma)$$

$R_\ell(r_1)\, R_\ell(r_2)$ essentially

into FORCE-FORCE CORRELATION FUNCTION

Incoherent scattering limit applied to liquid rare earth metals

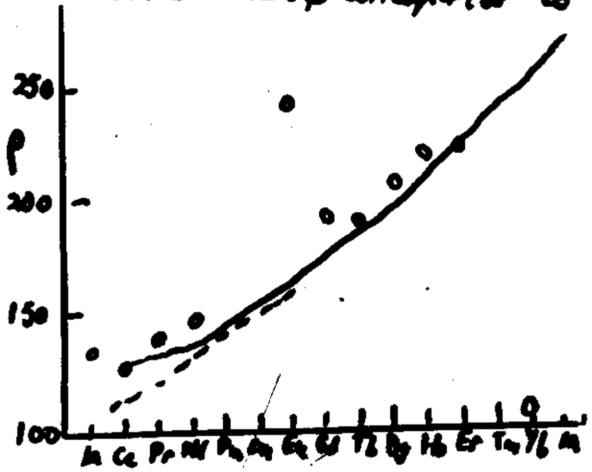
(Parrinello, March & Tosi, 1977)

Band structure calcs (Hill & Kmetko, 1975) indicate that a substantial amount of valence charge density in rare earths arises from states of d character.

Zeroth order: Neglect η_ℓ except for $\ell = 2$.

$$\rho_0 = \frac{20\pi\hbar}{Ze^2k_F}\sin^2(\pi Z/10) \quad : \text{Valence } Z \text{ of } 3$$

yields $\rho_0 \sim 400\,\mu\Omega\,cm$. Including f and s yields curves (broken curve corresponds to $\eta_0 = 0$).



• Exptl results of Guntherodt et al (1975)

Eu & Yb are exceptional.

[Absolute mag ...]

Replacement of σ by a simple average off-diagonal density of states

$$\sigma(r_1 r_2) = \sigma_0(|r_1 - r_2|) \exp\left(-\frac{|r_1 - r_2|}{2\ell}\right)$$

(ℓ: electronic mean free path)

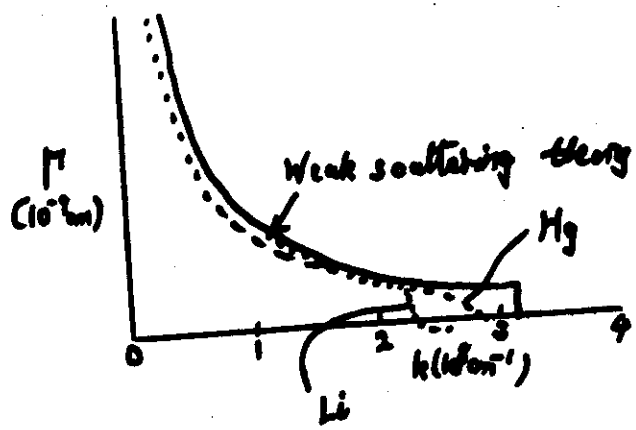
Note that the DIAGONAL DENSITY of STATES is not changed from free-electron form. In that sense, we still have a weak scattering assumption built in.
BUT FERMI SURFACE BLURRING by DISORDER SCATTERING is now taken into account SELF-CONSISTENTLY.

(N.B. $\varepsilon(k)$ also depends on free path: this has been incorporated, but is of smaller consequence in simple sp liquid metals).

Solution of a self-consistent transport theory

$$\rho = \frac{k k_F}{n e^2 \ell} = \int_0^\infty q^4 S(q) |U(q)|^2 \Pi(q, k_F, \ell) dq$$

$$\Pi(q, k_F, \ell) = \int e^{i \underset{\sim}{q} \cdot \underset{\sim}{R}} |\sigma_0(R)|^2 e^{-R/\ell} d\underset{\sim}{R}$$



Solid curve leads back to WEAK SCATTERING THEORY RESULT with sharp Fermi surface:

$$\rho_{\text{Weak Sc}} = \frac{3\pi}{\hbar e^2 v_F^2 \rho_i} \frac{1}{(2k_F)^4} \int_0^{2k_F} S(q) |U(q)|^2 4 q^3 dq$$

Götze (for random systems) developed a related approach independently. The detailed form of Π is a little different, but essential features are the same.

Numerical results of self-consistent approach to MF Path for liquid Transition metals [Brown, J.S. J. Phys F. Metal Phys 11 (1981) 2099].

(no modification of density of states due to scattering: method to 'incorporate' modified density of states proposed by van Oosten and W. Geertsma (private communication): namely $\rho_{\text{Prime}} \times g^2$: $g = N(E_f)/N_0(E_f)$ — free electron.

[g estimated to range from 1·13 in Li to 0·72 in Ba in metals they have studied so far]

Brown's results

(int. c with calcs of Esposito, Ehrenreich & Gelatt, 1978).

Liquid metal	$\rho_{(\text{exp})}$ (Brown)	ρ_{EEG}	$\rho_{(\text{self-cons})}$ Brown
Fe	136	1180	476
Co	115	329	178
Ni	83	74	52
Cu	21.	41	30

Elementary derivation of Kubo-Green formula for self-diffusion constant D

In large r, long time limit, $G_s(r,t)$ satisfies diffusion eqn

$$D\nabla^2 G_s = \frac{\partial G_s}{\partial t}$$

Soln satisfying $G_s(r,0) = \delta(r)$ is

$$G_s(r,t) = \frac{1}{\{4\pi D|t|\}^{\frac{3}{2}}} \exp\left(\frac{-r^2}{4D|t|}\right)$$

Hence

$$S_s(q,\omega) = \frac{D q^2}{\pi[\omega^2 + (Dq^2)^2]}$$

Evidently then

$$\frac{D}{\pi} = \lim_{\omega\to 0} \omega^2 \lim_{q\to 0} \frac{S_s(q,\omega)}{q^2}$$

Theory ONLY if S_s calcd from a pair potential $\phi(r)$

Define a frequency function

N.B. $\int_{-\infty}^{\infty} \omega^2 S_s(q,\omega) = z(\omega)\, q^2 k_B T/M$.

Ernst et al (1970) ATOMIC TRANSPORT

Discuss the asymptotic time behaviour of the velocity autocorrelation function. Their results are expressed in terms of the transport coefficients and are valid for all densities.

Their work followed MD calculation of Alder and Wainwright (1970) of the velocity correlation function for a 2 and 3 dimensional system of hard 'spheres'. They observed a 'long-time tail' of the form $t^{-d/2}$.

Alder and Wainwright proposed a hydrodynamical explanation of their observations on the basis of a numerical solution of the Navier–Stokes eqn. discussed in the lectures of Prof. Cole.

$$z(\omega) = \omega^2 \lim_{k\to 0} S_s(k\omega)/k^2.$$

Gaskell and March (1970) establish that $z(\omega)$, which is an even function of ω in classical liquids has an expansion

$$z(\omega) = \frac{D}{\pi} + d_1\omega^{1/2} + d_2\omega + d_3\omega^{3/2} + d_4\omega^2 + \cdots$$

around $\omega = 0$.

Use result of Ernst et al [1970] that at long times, velocity correlation fn given by

$$\frac{\langle V(0).V(t)\rangle}{\langle V(0)^2\rangle} \sim \frac{2}{3\rho}\left[4\pi\left(D + \frac{\eta}{\rho M}\right)t\right]^{-3/2}$$

(ρ = number density)

where η is shear viscosity and M the atomic mass

Get

$$d_1 = -(2\pi)^{\frac{1}{2}}\frac{2}{3\rho}\left[4\pi\left(D + \frac{\eta}{\rho M}\right)\right]^{-\frac{3}{2}}\frac{k_B T}{M\pi}$$

$z(\omega)$ decreases initially from value $z(0) = D/\pi$: this was observed explicitly by Egelstaff (1967) and also by Randolph (1964) for Na

At T_m, Brun–March results for Dun in $d_1 \propto \frac{T_m^{\frac{1}{4}}}{1}$

Comparison of shear viscosity η at melting point with expt

$$\eta = \text{constant}\ T^{\frac{1}{2}} M^{\frac{1}{2}} / \Omega^{2/3}$$

(Ω: atomic volume)

Constant taken from Andrade empirical result.

Liquid metal	Expt (poise)	Theory
Li	0·0060	0·0056
Na	0·0069	0·0062
K	0·0054	0·0050
Rb	0·0067	0·0062
Cs	0·0069	0·0066
Cu	0·041	0·042
Ag	0·039	0·041
Au	0·054	0·058
In	0·019	0·020
Sn	0·021	0·021

Zwanzig's generalization of Stokes-Einstein relation

Connection most often written

$$D\eta\sigma/k_B T = C$$

(σ: mol. diameter; C: constant ($\frac{1}{2\pi}$ or $\frac{1}{3\pi}$ according to Einstein who uses hydrodynamics: Stokes law.)

Zwanzig writes

$$D = (1/3N)\int_0^\infty dt \sum_j \langle \underset{\sim}{v}_j(t) \cdot \underset{\sim}{v}_j(0)\rangle .$$

In 'oscillator-like' theory, $\sum_j$ becomes sum over normal modes, term dep at one vib. Introducing a damping factor $\exp(-t/\tau)$ he gets

$$D = \frac{k_B T}{3MN} \sum_{\omega} \tau/(1+\omega^2\tau^2)$$

Use Debye spectrum: and liken long. and transverse (both η shear moduli respectively) to longitudinal and shear viscosity η_c and η.

He gets

$$D = (k_B T/5\pi)(3N/4\pi V)^{1/3}\left(\frac{1}{\eta_c} + \frac{2}{\eta}\right).$$

Hence ($v = V/N$)

$$(D\eta/k_B T)\, v^{\frac{1}{3}} = 0{\cdot}066\left(2 + \frac{\eta}{\eta_c}\right) = C'$$

$\eta_c = \frac{4}{3}\eta + 5 \cdot \frac{\eta}{\eta_c}$ lies between 0 and $\frac{5}{4}$

$\therefore$ C' between 0·13 and 0·18 ($1/2\pi \sim 0{\cdot}16$)

Summary

1. Problems in fundamental electronic transport noted are:

(a) Explanation of deviation of K_0/T from Lorenz number (inelastic corrections estimated by M.J. Rice are much too small to explain experimental numbers.)

(b) Treatment of intermediate strength scatterers: e.g. liquid Fe. How does one incorporate (i) higher order correlation functions and (ii) realistic liquid density of states at Fermi level?

2. Success of Andrade's formula for shear viscosity raises questions as to whether frequency function $s(\omega)$ (for $\frac{4}{3}\eta + \zeta$) and correspondingly $\kappa(\omega)$ for diffusion have basic insensitivity to potentials (e.g. can they be related, say, to Onsager-Zernike direct correlation function) at MELTING POINT. Also Li isotope effect?

3. What of links: Wiedmann-Franz; Stokes-Einstein generalization: Lindemann $\Theta_D - T_m$: remain useful over extensive pressure range? (Prof. Schirmacher's lectures)