Solid State. Additional Notes.

1. Dielectrics

Non-Polar Gases
Static ε for Polar Gases
Dispersion in Non-Polar Media
Static ε for Liquids
RF Dispersion in Liquids
Methods of Determining ε.

Notes on Dielectric Theory.

No atom has permanent dipole moment ∵ charge distribn. is always symmetric; molecules may have permanent moments tho! Homonuclear molecules (H_2, N_2, O_2 etc) are non-polar, but asymmetric molecules such as HCl are polar. Unit is Debye unit ~ 10^{-18} e.s.u = 3.336×10^{-30} coulomb-metres. Cannot picture, say, HCl dipole as two ions ∵ most of charge is in fact between nuclei. Transition HCl → HI gives transition to covalent binding. Presence or absence of dipole mt. guide to molecular shape for more cplx. molecules.

Non-Polar Gases.

No permanent mts — induced mt. due to sepn. of charge centres in applied field. Forces ||l to field & for all practical field strengths proportional to it, ∴ mts. similarly. Electron displacements greater ∵ they are lighter (c. of m. unmoved). Thence $\underline{p} = \alpha \underline{E}$, α const. of substance. $\underline{E}$ = local field. Can usually be rep. by $\underline{E}_{appl}$ + const. $\underline{E}_{appl}$. Lorentz correction; do not allow for distortion ∵ cavity is mathematical, not physical.

For perf. cond. sphere, $\alpha = 4\pi\varepsilon_0 a^3$, where a is radius. Suggests that α in Clausius - Mosotti Law $\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{n_0\alpha}{3\varepsilon_0}$ should be ~ 3 × molecular vol, $n_0\alpha$ = vol. of all molecules in unit volume of bulk material.

For gases at low pressures, $\varepsilon - 1 \sim 10^{-3}$. $\therefore$ $\varepsilon + 2 = 3$ as near as makes no diffce. a $\varepsilon - 1 . \left(M/\rho\right) = N\alpha$. For high pressures, this ceases to hold, but Clausius - Mosotti good right up to ~ 1000 atm.

Static Dielectric Constant of Polar Gases.

The above is always valid for induced contribn. to ε. Applied field will always induce a contribn. For permanent dipoles, applicn. of $\underset{\sim}{E}$ defines a preferred dirn. – Boltzmann distribn. Classical stat. mech $\rightarrow$ $\underset{\sim}{P} = \frac{n_0}{3kT} p^2 \underset{\sim}{E}_{loc}$. Whence, using Lorentz still (valid for a gas) $\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho} = \frac{N}{3\varepsilon_0}\left(\alpha + \frac{1}{3} p^2/kT\right)$. This takes $pE/kT \ll 1$, well fulfilled at ordinary field strengths. At room temp $kT \sim 4 \times 10^{-21}$ joules, so even with 4 Debyes, 3×10^7 v/metre for $pE/kT \sim 0.1$. Cannot get saturation at low temps. as with mag. dipoles $\because$ polar gases tend to have high BP & MP owing to large intermolecular dipole forces. Derivn. is purely classical. How does wave mech. fit in? Answer exactly same but reasons v. diffr. Rotnl states of mol. characterised by $\angle^r$ mtm quantisation thru J. For $J \neq 0$ mol. rotates & cpt. of dipole mt. in any dirn $= 0$. For $J = 0$, no rotn. & a resultant permanent mt. No. in $J = 0$ state goes as $1/T$, const. in fact same as class. ①?

Dispersion in non-polar dielectrics

Permeability = 1 a good approxn. usually. Low-ν ε vals & optical refractive indices $\tilde{n}$ usually in v. poor agreement, except for non-polar gases. To treat phenomenon, assume incident $\lambda \gg$ at. dimensions, so that electrons experience ~ const. field everywhere in atom. True right into hard X-ray region. Natural oscilln. terms (complementary fn.) average to zero over large no. of ats. Correct for internal field via Lorentz for dense materials.

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{\tilde{n}^2-1}{\tilde{n}^2+2} = \frac{n_0e^2}{3m\varepsilon_0}\,\frac{1}{(\omega_0^2-\omega^2)+\underset{\uparrow\text{ damping.}}{i\gamma\omega}}$$

Each at. or mol. has a number of ω_0's & so a more general expression is

$$\frac{\tilde{n}^2-1}{\tilde{n}^2+2} = \frac{n_0e^2}{3m\varepsilon_0}\sum_j \frac{f_j}{(\omega_j^2-\omega^2)+i\gamma\omega}$$

f_j is oscillator strength. Classically = no. of electrons/mol. with resonant frequency ω_j. In quant. mech*, total osc. strength divided between various modes of osc & f_j not unity. Have $\sum_j f_j = 1$ for any electron tho'. In the Xray region, $\tilde{n}$ becomes -ve, calculated via $m\ddot{\underset{\sim}{x}} = -e\underset{\sim}{E}e^{i\omega t}$, $\omega \gg$ any ω_j. For mol. with permanent dipole mt., static ε has term involving dipole mt. Expect this term to be related to some absorption lines; it is - lines are the "pure rot^n." lines in the i/red.

*Mott "Elements of Wave Mechanics" P.74

Static dielectric constants of non-polar liquids & solids

For non-polar solids, Clausius-Mosotti works quite well. It can also be applied to v. dilute solns. of polar liquids in non-polar solvents, when mutual interactions of dipoles are small enough for Lorentz to hold.

Static dielectric constants of polar liquids

Clausius-Mosotti here nonsensical → water ferroelectric.

$$P/E_{loc} = \frac{P}{\underset{\sim}{E} - P/3\varepsilon_0} = \frac{n_0 p^2}{3kT(1 - n_0 p^2/9kT\varepsilon_0)} = \frac{n_0 p^2}{3k(T - T_0)}$$

Lorentz assumes all dipoles $\parallel^{l}$ to $\underset{\sim}{E}$. True for induced dipoles, but fields of ordinary magnitudes hardly affect orientations of permanent ones. Lorentz field ∴ too large.

RF dispersion in polar liquids

For polar gases, saw that $\varepsilon > n^2$, difference being mainly due to i/r dispersion assoc. with molecular rot^n. For liquids this is even more so. In a high-frequency field, dipoles unable to follow if $\omega \gg 1/\tau$, where τ is dipole relax^n time (time $\sim$ to reorientate a dipole). What is the mechanism inhibiting reorient^n? Bombardment of mol. by other mols. For spherical mol. of radius a in medium of viscosity η

Debye, "Polar Molecules", Dover

$$\overline{\theta^2} = kTt \Big/ 4\pi\eta a^3 = t/\tau \qquad \theta = \text{rot}^{n'} \measuredangle .$$

For water $\sim 3{\cdot}7 \times 10^{-11}$ sec for τ.

Now put $d\underset{\sim}{P}/dt = (\underset{\sim}{P_0} - \underset{\sim}{P})/\tau$. $\quad \underset{\sim}{P} + \tau\, d\underset{\sim}{P}/dt = \frac{n_0 p^2}{3kT} E e^{i\omega t}$

$$\underset{\sim}{P} = \frac{n_0 p^2}{3kT} \, \frac{\underset{\sim}{E} e^{i\omega t}}{1 + i\omega\tau}$$

$\underset{\sim}{E}$ here is amplitude of local osc. field, and $\underset{\sim}{P}$ is that part of pol^n due to permanent dipoles. Put $\hat{\varepsilon} = \varepsilon' - i\varepsilon''$

$$\varepsilon' = \frac{\varepsilon_{\text{static}} - \varepsilon_{\text{induced}}}{1 + \omega^2\tau^2} + \varepsilon_{\text{induced}}$$

$$\varepsilon'' = \frac{(\varepsilon_{\text{stat}} - \varepsilon_{\text{induced}})\,\omega\tau}{1 + \omega^2\tau^2}$$

Theory developed by Debye. Cannot investigate by resonant cavity method ∵ absorption too great (this for water). Use instead a waveguide filled with water, & determine propagⁿ constant of e/m waves in guide. Field in guide determined by propagⁿ constant K

$$iK = 2\pi\left\{\frac{1}{\lambda_{cutoff}^2} - \frac{\nu^2}{V^2}\right\}^{1/2}$$

Do with guides of different sizes, determine real & imag. parts sep. Easier measurable quantity is the attenuation produced by system. If find this for 2 guide dimensions, can deduce ε' and ε''. Measure attenuation with 2 piston attenuators in series, one full of water & one not. Move these in and out to keep power in receiver constant. Then get attenuation of water rel. to that of air (known).

Results fit ②^{y} well for $\tau = 1.01 \times 10^{-11}$ sec. Absorption v. strong, at $\lambda = 1.24$ cm, one wavelength attenuates by e^{-36} or $10^{-15.5}$. Find that $\varepsilon_{induced}$ is 4.9. As this is appreciably higher than $\hat{n}^2_{optical}$, deduce that water has absorption band in i/r as well.

Find that these properties vary strongly with T. This is ∵ of $\tau(T)$ variation.

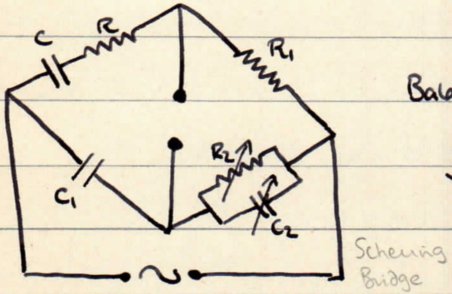
In solids the permanent dipoles are very restricted. τ very long. Dispersion in ice near 1 Mc/s, ε falls from ~80 to ~5.

Methods of determining dielectric constants

i) Solids and liquids

ε defined by ratio of capacities of condenser with & without material.

Capacitance bridges ∴ the best approach. Non-polar solvents, C_6H_6, CCl_4 for liquids, if liqs. are polar.



$Z_1/Z_2 = Z_3/Z_4$ general balance condn.

Balance here is

$$j\omega C_1\left(R + \frac{1}{j\omega C}\right) = R_1\left(\frac{1}{R_2} + j\omega C_2\right)$$

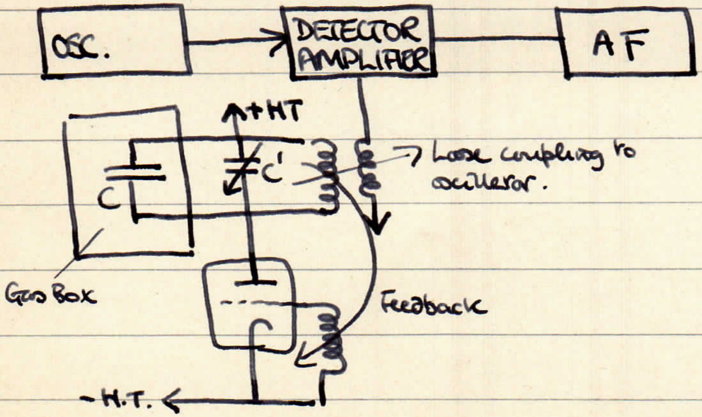
$$C = C_1(R_2/R_1)$$

$$R = R_1(C_2/C_1)$$

Measure C with and without medium inserted. R → conductivity if present.

ii) Gases

$\varepsilon - 1 \sim 10^{-3}$, ∴ special methods N. Frequency msts. are most accurate in physics, so use one such. Condenser in resonant circuit of tuned anode osc.



Frequency of oscillator compared with standard quartz xstal oscillator with C evac. & C full of gas. May either find $\Delta\nu$ directly or restore to its original value by adjusting C'. Latter less acc. ∴ C' inaccurate. Can find elect. dipole mt. by measuring ε as fn. of T. Apply corrections for thermal expansion.

Essen & Froome (1951), cavity resonator. Determine ν_{res} with resonator evac. & then full of gas. $(f'/f'')^2 = \mu\varepsilon$. Correct for μ.

Scattering of E/m radiation

Passage of e/m radn. through matter determined by 2 effects – i) collision damping, ii) scattering. Losses due to i) are due to inelastic collisions between molecules while electrons in them are re-radiating incident energy. Scattering is due to $\measuredangle^r$ distribn. of reradiated energy in absence of damping.

$\measuredangle^r$ distrib^n. of scattered radn. is fn. of distrib^n in space of scatterers. ∴ phase constant across a wavefront, oscillating dipoles are all in phase across a wavefront of incident wave. In order to find the scattering at an angle to the incident wave, need info. about distrib^n. of dipoles. If this is regular, as in xstal, diffraction phenomena result for wavelengths ~ spacing (X-rays). For ~ optical λ's only strong diffn. is forward. Scattering is by imperfections.

For a gas, due to random spacings, there is random phase diffce. everywhere except in forward direction. ∴ Add intensities

$$\sum_i \left(a\cos(\omega t-\delta_i)\right)^2 \to \tfrac{1}{2}a^2N\cos^2\omega t+\tfrac{1}{2}a^2N\sin^2\omega t=\tfrac{1}{2}Na^2$$

Energy lost by scattering dipole / unit time is $\overline{W}=\dfrac{Z_0\omega^4p^2}{12\pi c^2}$. Thus the mean incident power being $\frac{1}{2}E_0^2/Z_0$ and $p=\alpha E$,

$$\sigma=\left(Z_0^2\omega^4\alpha^2\right)/6\pi c^2$$

For X-rays, $\omega >> \omega_0$, and then $\alpha = e^2/(m\omega^2)$, giving Thomson scattering σ_T

For visible wavelengths and such molecules as air $\omega << \omega_0$, and thus

$$\alpha = \left(e^2/(m\omega_0^2)\right)$$ if we assume only one resonant ν

per molecule, giving $\sigma_R = \sigma_0(\omega/\omega_0)^4$ (Rayleigh).

∴ Molecules scatter blue more than red → blue of sky

transmit red . — — blue → red of setting sun

Raindrops, being large cf. λ scatter all =ly → white clouds.

If ν_{incident} coincides with one of ν^0, resonant scattering v. intense.

In all this, induced dipoles do not radiate ∥ to dirn. of oscilln. If incident radn. not polarised, scattered is partly polarised. If incident is polarised, no scatt. radn in poln. dirn, hence can get poln. of X-ray or γ.

Anisotropy of Diamagnetism

Xstals with layer-like lattices show anisotropy of their diamagnetic properties, the susceptibility being anomalously large in a direction perpendicular to the layers. The effect is particularly large in aromatic molecules containing a benzene ring. Pauling suggests that there are six electrons more or less free to move round the benzene ring, arising from the three unsaturated linkages in it. The contribution of the orbital motion of these will only be observed perpendicular to the plane of the ring, and so the molar anisotropy will be given by $\frac{e}{2mc} \cdot \frac{e}{2mc} \cdot m\overline{a^2}\, N^0$, the factor of $2/3$ here being inapplicable. If we use for $\overline{a^2}$ the value R^2, where R is the distance from the axis to the carbon nuclei, the value for the anisotropy is in good agreement with experiment.

Paramagnetism

χ is found to be small and positive for materials in which

i) there are an odd no. of electrons in atom (i.e. there is one unpaired spin.

ii) there is a partly filled inner shell, i.e. transition elements, ions isoelectronic with those, rare earths and actinides.

Also in iii) metallic materials (contribution of conduction electrons)

iv) a few compounds with even nos. of electrons, O_2 being an e.g.

Magnetisation of a paramagnetic material results from the alignment of the permanent dipoles in the applied field. Calcn. as for orientational polaris^n on classical Ⓣ^{y} of dielectric constant.

On quantum Ⓣ^{y} there are only two orientations of spin $\frac{1}{2}$, and the calc^n done for this gives the classical result, $\chi = N\mu^2/3KT$, $\mu = \sqrt{3}\,\mu_B$. For the angular momentum due to orbital motion, there are $2J+1$ possible orientations, and a classical type calculation is done with sums instead of integrals. This yields the same result but with $\mu = g\sqrt{J(J+1)}\,\mu_B$.

The discussion in these terms is applicable to atoms with a $(2J+1)$-fold degenerate ground state, the influence of all higher states in the atom being neglected. The values of g are to be found using the empirical Hund rules for the order of spectral terms, viz. for equivalent electrons the ground state has the maximum multiplicity 2S+1 allowed by Pauli Princ, and the maximum L consistent with this multiplicity. Then $J = |L-S|$ when shell less than $\frac{1}{2}$ full, $L+S$ when it is more.

Anomaly of Eu^{3+} & Sm^{3+}. The Brillouin function approach does not give very satisfactory results for these elements. In these ions the energy intervals between states of different J but the same L and S are of the order of kT, and higher terms must be included.

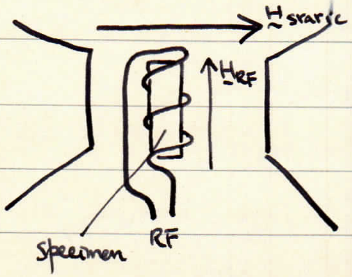
"Quenching" of orbital momentum

For salts of the iron group, the experimental magneton numbers agree better with theory if S alone is used instead of J. This phenomenon is called "quenching" of the orbital momentum. The reason is in the proximity of the paramagnetic electron to the outside of the atom. In the rare earths it is in an incomplete inner shell & is not particularly affected by local fields in the lattice. In the iron transition group, the paramagnetic electron is however very close to the outside of the ion for most of the time. The interaction of the electron with the e/s xstal field uncouples L and S. In an inhomogeneous field superposed on the nuclear field, an electron orbit may wobble about. The angular momentum components are no longer constant, and may average to zero. If the orbital momentum is affected in this way, it will not contribute to the paramagnetism and only S appears. Quenching can be alleviated by spin-orbit coupling, if the sign of this favours parallel orientation of L and S. Agreement~~s~~ is found with this idea and the experimental results.

Nuclear Paramagnetism is a small effect ∵ nuclear magneton v. small. Observed at low temp. with solid hydrogen.

NMR and ESR

Basic process: induction of transitions between magnetic substates split by a static $\underset{\sim}{H}$ (Zeeman Effect). Transition occurs between the Zeeman components of a single spectral level.



RF supply thru circuit for measuring losses. Resonance when $\hbar\omega = g\mu_0 H = \hbar\omega_L$

$\underset{\sim}{H}_{RF} \ll \underset{\sim}{H}_{static}$

To see why fields must be $\perp^r$, consider RF cpt. resolved into $\pm\bigcirc^{ly}$ polarised cpts. If $\omega = \omega_L$, one of these precesses round $\overset{static}{\underset{\sim}{H}}$ with the dipole and eventually tips it over. Other rotating component doesn't do anything.

NMR and ESR essentially v. similar. An important application of NMR is $\underset{\sim}{H}$ standardisation and mst. Once a resonance condition accurately established by someone using a well-surveyed $\underset{\sim}{H}$, can use to study other $\underset{\sim}{H}$'s when other methods of doing so not available.

Bloch, PR $\underline{70}$, 460

Macroscopic Approach

Deal with properties of whole specimen. $\underset{\sim}{M}$ = magnetic moment.

$\underset{\sim}{A}$ = angular mtm. density, then $\dot{\underset{\sim}{A}} = \underset{\sim}{M} \wedge \underset{\sim}{H}$ (unit volume eqn.)

If spin system free, $\underset{\sim}{M} = \gamma \underset{\sim}{A}$, $\gamma = ge/2mc$ (electrons)

$$\therefore \quad \dot{\underset{\sim}{M}} = \gamma \dot{\underset{\sim}{A}} = \gamma \underset{\sim}{M} \wedge \underset{\sim}{H}$$

Take static field as H_z, RF as H_x, time-dependence $e^{i\omega t}$

$$i\omega M_x = \gamma M_y H_z$$

$$i\omega M_y = \gamma(M_z H_x - M_x H_z)$$

$$i\omega M_z = -\gamma M_y H_x$$

Whence
$$-\omega^2 M_x = \gamma^2 (M_z H_z H_x - M_x H_z^2)$$

$$\chi_x = \frac{M_x}{H_x} = \frac{\gamma^2 M_z H_z}{(\gamma H_z)^2 - \omega^2}$$

Putting $\omega_L = \gamma H_z$ and writing $\chi_0 = M_z / H_z$ for the static susceptibility,

$$\chi_x = \frac{\chi_0}{(1 - [\omega/\omega_L]^2)}$$

This is evidently an oversimplification, and relaxation (damping) factors, which have been neglected, must be considered.

Magnetic Relaxation

If a constant field H_c is applied to a specimen, a magnetic moment M_c will be present in thermal equilibrium. When the field is removed, M_c decays with characteristic time τ. Similarly, when a field is switched on, a time is necessary for M to rise to its equilibrium value. As this means essentially some transitions from a state antiparallel to the field to a state parallel to it, with corresponding loss of energy, the rate at which this can be done is dependent on the coupling between the spin system and the lattice. This is described by the spin-lattice relaxation time τ_{SL},

$$(\partial M/\partial t)_{SL} = -(M - M_0)/\tau_{SL}$$

If the field is applied $\parallel^{l}$ to z, M_x and M_y average to zero. We $\therefore$ consider the lifetime of a certain $M_{x,y}$ value in the absence of the osc. field. Considering 2 adjacent dipoles i and j, each exerts a field on other which oscillates at ω_L (as both precess about $\underline{H}$ at ω_L). Thus the two may take part in a transition in which their spins flip together. As the interaction energy $\Delta E \sim \mu^2/r^3$, $\Delta t \sim \tau \sim \hbar/\Delta E = \hbar r^3/\mu^2$. This is called the spin-spin relaxation time τ_{SS}. We then have

$$(\partial M_z/\partial t)_{SL} = -(M_z - M_0)/\tau_{SL}$$

$$(\partial M_x/\partial t)_{SS} = -M_x/\tau_{SS}$$

$$(\partial M_y/\partial t)_{SS} = -M_y/\tau_{SS}$$

The equations of motion then become:

$$i\omega M_x = \gamma M_y H_z - M_x/\tau_{SS}$$

Bloch loc. cit
and PR, 69, 127

$$i\omega M_y = \gamma(M_z H_x - M_x H_z) - M_y/\tau_{ss}$$

$$i\omega M_z = -\gamma M_y H_x - (M_z - M_0)/\tau_{sl} \quad (H_0 \text{ applied } \parallel^{l} \text{ to } z)$$

Whence $\chi = \chi' + - i\chi''$, $\chi' = \frac{1}{2}\chi_0 \omega_L \tau_{ss} \frac{(\omega_L - \omega)\tau_{ss}}{\left(1 + (\omega_L - \omega)^2 \tau_{ss}^2 + \gamma^2 H_0^2 \tau_{sl}\tau_{ss}\right)}$

and $\chi'' = \frac{1}{2}\chi_0 \omega_L \tau_{ss} \frac{1}{\left(1 + (\omega_L - \omega)^2 \tau_{ss}^2 + \gamma^2 H_0^2 \tau_{sl}\tau_{ss}\right)}$.

If H is small, so that $\gamma^2 H^2 \tau_{sl}\tau_{ss} \ll 1$, $M_z = \chi_0 H_0$. This means that τ_{sl} small enough to depopulate levels as fast as RF absorption throws spins into them.

When $\gamma^2 H^2 \tau_{sl}\tau_{ss} \sim 1$, $M_z < \chi_0 H_0$. Now the above cannot happen. Spin temperature > lattice temperature ∵ RF energy absorbed faster than lattice can sop it up.

The Weiss Theory of Ferromagnetism.

The two important successes of the Weiss $\textcircled{th}^{y}$ are its production of a critical point or "Curie temperature", given by $\Theta = N\mu^2\lambda/3k$, and its prediction of the correct form of dependence of the saturation magnetisation with temperature below $T = \Theta$. It is seen that, using variables $\zeta = M/N\mu$ and $\tau = T/\Theta$, there is for all substances a variation $\zeta = f(\tau)$ which is the same function in every case. The universality of the ζ-τ curve is an example of the Law of Corresponding states. In obtaining the form of this universal curve, the applied field $\underline{H}$ is neglected in comparison with the Weiss field $\lambda\underset{\sim}{M}$ in the argument of the Brillouin function. It might be objected that the full magnetisation is never reached without applying <u>some</u> field $\underset{\sim}{H}$, so that $\underset{\sim}{H} = 0$ is not really an allowable approximation, but the point is that the value of the necessary field is minimal compared with the resulting induction.

The problem in hand is the explanation of the Weiss field. The most obvious explanation is a simple dipole-dipole magnetic interaction, whose potential is known classically to be

$$V_{ij} = \frac{\mu_i \cdot \mu_j}{r_{ij}^3} - 3\frac{(\mu_i \cdot r_{ij})(\mu_j \cdot r_{ij})}{r_{ij}^5}$$

There are two strong reasons why this cannot be the solution, however. Firstly, it is far too weak to provide the Weiss coupling. λ could not be greater than 4π for such an interaction, whereas the fitting of the Weiss model in practice requires $\lambda \sim 10^5$. Further, the interaction is anisotropic (this may be seen from the observation that, if $\mu_{i,j}$ ∥ to r_{ij}, $\mu_i = \mu_j$ gives the minimum V_{ij}, whereas if $\mu_{ij} \perp r_{ij}$, $\mu_i = -\mu_j$ gives V_{ij} minm.), and so the saturation intensities of magnetisation should be strongly anisotropic. This is evidently not the case for most ferromagnetics, although the fields necessary to produce this magnetisation vary with direction. Put another way, Θ would be far too small on this model, and would also depend on the crystallographic orientation of the material w.r.t. $\underline{H}$. (Note that with electric dipoles the coupling is much stronger, and ferroelectricity could arise from dipolar interactions alone).

The application of quantum mechanics (which introduced the Brillouin fn. mentioned above) to ferromagnetism also provides a description of the origin of the coupling. According to Heisenberg, there exists an apparent spin-spin coupling between overlapping electronic orbitals giving a potential energy of the form

$$V_{ij} = -2J_{ij}\,\hat{S}_i \cdot \tilde{S}_j$$

This interaction is not however directly spin-spin. It enters when orbital wave functions overlap, and arises from the dependence of the orbital energy on the symmetry of these functions. The spins are involved only through the correlation between the symmetries of orbital and spatial parts of the wave-function, and the forces involved are e/s rather than magnetic. Both of the essential points about the Weiss field appear in this interaction. Firstly, J_{ij} can be very large, as required to meet the experimental results, and secondly the term $S_i . S_j$ is isotropic symmetric w.r.t. r_{ij}. Thus in the first approximation ferromagnetic materials should be magnetically isotropic. The small anisotropy of magnetic properties that is observed may result from dipole-dipole interaction, but the effects of spin-orbit coupling and incomplete orbital quenching are also involved no doubt.

The total exchange energy can be found by summing over all pairs of atoms in the crystal. If it is assumed that J_{ij} is zero for non-neighbouring atoms, and equals J for all neighbouring atoms,

$$V_{total} = -2J \sum S_i . S_j$$

To find the susceptibility associated with this interaction term, we must make the approximation that the instantaneous values of neighbouring spins may be replaced by their time-averages. Thus, per nearest-neighbour pair, $V = 2J\left(S_{xi}\langle S_{xj}\rangle + S_{yi}\langle S_{yj}\rangle + S_{zi}\langle S_{zj}\rangle\right)$

Assuming M to be along Oz, $\langle S_{xj}\rangle = \langle S_{yj}\rangle = 0$, $\langle S_{zj}\rangle = M/g_L N\mu_B$

$$\therefore \; V_{ij} = -2JS_{zi}M/g_L N\mu_B$$

Now if this is equated with the Weiss field, $= -g_L S_{zi}\mu_B \lambda M$ for the presence of the same spin S_i,

$$\lambda = 2J/Ng_L^2\mu_B^2$$

If there are z nearest neighbours,

$$\lambda = 2zJ/Ng_L^2\mu_B^2$$

This procedure obviously represents only an approximation, which is tantamount to saying that all fluctuations in the molecular field are negligible. Néel has demonstrated that it is just such fluctuations which distinguish between the paramagnetic & ferromagnetic Curie Points.

In order to have ferromagnetism, it is obvious that the exchange integral must be positive. There is no suggestion that the exchange integral might be actually computed for a ferromagnetic. The interatomic forces no doubt distort the d electrons very badly, and even calculations based on free atoms would be very tricky anyway, so the matter is one of great technical difficulty. Slater has given the rule that the integral will only be sufficiently positive if the atomic radius is small compared with the interatomic distance.

Slater PR <u>35</u>, 509; <u>36</u>, 57

Ferromagnetic Domains

Evidence for existence of domains is 2 fold, i) the nature of the hysteresis loop (magnetisation curve) of the material, which is well accounted for by postulating a domain structure for the ferromagnetic material in the "non-magnetised" state, and ii) more direct evidence from Bitter patterns. Find that colloidal ferromagnetic particles tend to congregate in certain regions on the surface of a ferromagnetic, and interpret this as being due to v. strong fields at domain boundaries. Can obtain dirn. of magnetisation by scratching surface and then doing the above. Max. aggregation of colloid in scratch when it is ⊥r to $\underline{H}$. Vector direction of magnetisation obvious from study of movement in applied $\underline{H}_{ext}$.

Origin of domains is energetics of xstal. Balance of magnetic self energy, wall energy + anisotropy energy. ≡m between these three attained in macroscopic specimen. Closure domains "eliminate magnetic poles". No external field due to the magnetisation and minimum energy. In anisotropic material (e.g. hexagonal with only 1 "easy direction") these must be ⊥ to easy direction, so therefore they are energetic + balancing still $\underline{N}$. For cubic material magnetostrictive strain fields due to ↑ → orientation give the energy to be balanced.

Will not get domain formation in v. small specimens as they become energetically unfavourable (Too much of specimen is domain wall). Thus can make a magnetically hard material by mixture of v. small grains. Then each grain always sat. mag. as single domain, and magnetisation or demagnetisⁿ must take place thru rotⁿ of magnetisⁿ of particle as a whole. ∴ high coercive force.

Coercive forces in general vary widely ($\cup \times 10^5$) strongly dependent on physical state of material, impurities, lattice imperfections, internal strains. Idea that domain walls sit in potential wells in Ξm. and have to be moved over barriers by field. This idea supported by fact that coercive force > with impurity (ppm >. Also as internal strains removed by slow annealing.

Estimation of the Width of a Bloch Wall

The width of a Bloch wall may be estimated as follows. Represent energies as sum of contribns. of exchange and anisotropy energies.

$$\varepsilon_{wall} = \varepsilon_{exchange} + \varepsilon_{anisot}$$

$\varepsilon_{exch} \sim JS^2\Phi_D^2/N$, where Φ_D is change of angle between domains, N = no. of steps in wall, this per line of spins. Now if a is lattice constant, per unit wall area there are $1/a^2$ such lines, $\varepsilon_{exch}/\text{area} = JS^2\Phi_D^2/Na^2$.

Take $\sigma_{an} = KNa$ where K is anisotropy constant

$$\sigma_{wall} = \frac{JS^2\Phi_D^2}{Na^2} + KNa$$

$$\partial\sigma_w/\partial N = -\frac{JS^2\Phi_D^2}{N^2a^2} + Ka$$

$= 0$ when $N = \sqrt{JS^2\Phi_D^2/Ka^3} \sim 1000$ Å for iron.

The origin of the anisotropy energy was referred to earlier. It is thought to be the combined effect of spin-orbit interaction and the partial quenching of the orbital L, by xstal fields & by orbital overlap.

Gyromagnetic Ratio of Iron (Scott PR $\underline{82}$, 542)

Wind cylinder with uniform magnetising coil and support as a torsional pendulum rotating about magnetic axis with a long period and very low damping. In this condition, assuming negligible damping, if the angular momentum of the pendulum is changed by ΔL as it crosses centre of swing, change in amplitude is $\Delta\theta = \Delta L\,\tau / 2\pi I$, where τ is period of pendulum, I mt. of inertia. $\Delta\theta$ observed by ballistic spot-and-scale method.

Reverse magnetising current periodically. Correct for change in angular momentum of the winding.

Now need to find ΔM (magnetic moment). For linear relationship $M = \alpha i + b$, $\Delta M = \alpha \Delta i$. Must correct for change in magnetic moment of coil, $\Delta M_{coil} = \Delta i \sum A$, where A = loop area. After correcting for the ΔL & ΔM of the coil, the required gyromagnetic ratio follows as

$$\frac{\Delta L}{\Delta M} = \frac{1}{G}.$$

Gives $G \sim 1.9$, $\therefore$ electron spins are the important moments.

Discussion of Methods Employed in Band Theory of Metals.

Concerned with approx. method of solving Schrödinger Eqn. for a large no. of particles which interact with one another. Restrict discussion to a perfect xtal, & neglect effects of motion of atomic nuclei. The situation is still far too complicated to be capable of a rigorous discussion & we adopt an approximation method. The one-electron method seeks to express the wave function Ψ of the entire electronic system as a combination of functions ψ_i, each of which involves the co-ordinates of only one electron. Equivalently, this means that each electron sees, in addition to the nuclear potential, only the average potential due to all the other electrons, and moves as an independent entity through the xtal. In throwing away electron correlations at the outset in this manner we automatically exclude such phenomena as superconductivity from the domain of the problem.

The one-electron method has the success that it relates the electronic structure of a solid to xtal structure.

Within the one-electron method there are two lines of attack, the Heitler-London approach via localised atomic orbitals, which is valid when the electrons can be regarded as spending most of their time in the vicinity of one particular ion or atom, and the Bloch scheme, in which

Holes.

Consider a full Brillouin zone. Each electron contributes a current $\underset{\sim}{i}_j = -e\underset{\sim}{v}_j$ to the current carried by the zone in the absence of an applied electric field. Then $\underset{\sim}{i}_{tot} = -e\sum_j \underset{\sim}{v}_j = 0$. Let one electron, the k'th, be singled out for special attention, then

$$i_{tot} = -e\underset{\sim}{v}_k - e\sum_{j\neq k}{}' \underset{\sim}{v}_j = 0.$$

Now if the k'th electron is not there, the current in the zone is

$$i_{res} = -e\sum{}'_{j\neq k} \underset{\sim}{v}_j = +e\underset{\sim}{v_k}$$

This current is exactly the current we should find in an otherwise empty zone with one positive electron added. The way in which this current varies under the action of an applied field is given by

$$\frac{di_{res}}{dt} = +e\frac{dv_k}{dt}$$

Now for the quantum state k, m^*_k is negative, as it will be at the top of the band, so that $\frac{dv_k}{dt} = \frac{+e\mathcal{E}}{m^*_k}$

Thus $\frac{di_{res}}{dt} = +\frac{e^2\mathcal{E}}{m^*_k}$, so that $\underset{\sim}{i}_{res}$ increases in the direction of $+\underset{\sim}{\mathcal{E}}$.

If $i=0$ at $t=0$, $\quad i(t) = \frac{e^2\mathcal{E}t}{m^*k}$

The power delivered to the material is $\mathcal{E} i(t) = + \dfrac{e^2 \mathcal{E} t}{m_k^*}$

Suppose that we now attempt to explain this behaviour in terms of a charge e' and mass m'. The power supplied to the material must have a positive sign, and we would write it as

$$P(t) = \frac{+e'^2 \mathcal{E} t}{m'}$$

Whatever the sign of e', we must agree that $P(t)$ is positive, and so we are committed to putting m' +ve. Then for the velocity to increase with time as

$$\frac{dv}{dt} = \frac{e' \mathcal{E}}{m'}$$ we must make e' positive also.

The choice e' negative and m' negative could be made but for the sign of the power equation.

Electron Correlation in Metals.

Hartree calculation neglects all correlations of electron motions, due to Coulomb interaction or Pauli Principle, & its qualitative & occasional quantitative success in describing metallic behaviour suggests that corrections to independent-electron model might be small. If try to include corrections for Coulomb interactions and Pauli, agreement bet. Θ^y & expr. destroyed. If try to include Coulomb interactions via pertbn. Θ^y. find that corrections diverge, difficulties due to long range of Coulomb interactions, so that the interaction is in principle capable of affecting motions of many electrons simultaneously.

If include Coulomb interaction from outset, correlated motion → collective oscillations of system as a whole, cf. plasma. For phenomena involving distances $\gg$ inter-particle spacing, system behaves collectively & is best described by set of harmonic oscillators which rep. the plasma oscillations. Can see however that the independent-electron model is not too bad an approximation in some cases. Key to this dualism is the effective law of interaction between electrons. Find that eff. law of force is screened Coulomb with screening distance ~ av. inter-electron spacing in metal. ∴ Phys. plausible to treat electron system as a group of almost independent particles once long-range correlations which lead to screening have been taken in by introduction of plasma oscillations. Indep. - particle model then becomes math. plausible ∵ find that correlations brought in by P-Pt. & effective short range screened interaction do represent a relatively small correction.

The plasma oscillations have high ν — $h\nu > E_F$. ∴ the oscns. do not figure prominently in metallic behaviour under normal circumstances. Scattering of kev electrons by thin films can → info.

Failure of Hartree.

Falls down on cohesive energies of metals. Hartree-Fock does give some cohesion where Hartree fails completely, but inclusion of an exchange term in this ruins the exptal agreement on sp.hts. and most predictions go for the worse.

Collective Description of Electron Interactions.

Begin by founding on Coulomb interaction - this is as diametrically opposed to one-electron model as possible, but ends up by justifying it to some extent! Regard electrons as a plasma, classical analogue, here plasma density $\sim 10^{23}$/cc. Plasma tends to remain in neutral field-free state ∵ of screening action of highly mobile electrons. Also capable of sustaining oscillations about ≡m. cond^n. Screening & osc^n can be characterised by 2 parameters, λ (screening distance) and ω (plasma freq.).

Screening results thus: ∵ ε's are highly mobile they are particularly sensitive to slight charge imbalance. If introduce such, electrons rush to affected area in attempt to restore ≡m. In this they are hindered by KE of thermal motion. ∴ For distances which are too short electrical forces are insufficient to overcome thermally induced motion. ∴ get characteristic length → measures screening action. Estimate this as follows:- Consider charge q introduced at origin of plasma. This → change in ε density $\delta\rho$ and eff. potl. φ. These related by Poisson Eqn:

$$\nabla^2\varphi = 4\pi q - 4\pi e\,\delta\rho$$

If electrons in $\equiv$m. at temp. T, for small potls, $e\varphi \ll KT$

$$\delta\rho = n_0\exp[e\varphi/KT] - n_0 \sim n_0 e\varphi/KT$$

$$\therefore \nabla^2\varphi + \frac{4\pi n_0 e^2\varphi}{KT} = 4\pi q$$

Whence $\varphi = \dfrac{q}{r}e^{-r/\lambda}$, $\lambda = \left\{\dfrac{KT}{4\pi n_0 e^2}\right\}^{1/2}$

$$= \left\{\frac{m\langle v^2\rangle}{12\pi n_0 e^2}\right\}^{1/2}$$

$\therefore$ Response of electrons to introduced charge is to screen field within distance λ. Screening reps. compromise of effects of ke and pe on electronic motion. High temperatures obv. reduce it, high densities encourage it. The ke with which electrons rush to counteract local imbalance → overshoot. Suppose charge imbalance results from displac$^{\text{t}}$ of slab thin distance ξ. If plasma otherwise unaffected, slab behaves like condenser, $\underset{\sim}{\mathcal{E}}$ set up which acts to restore charge balance. $|\mathcal{E}| = 4\pi\sigma$. Now σ = xs $\underset{\text{density}}{\overset{\text{surface}}{\text{charge}}}$ $= n_0 e\xi$

$$\therefore m\ddot{x} = m\ddot{\xi} = -e\mathcal{E} = -4\pi n_0 e^2\xi$$

Slab ∴ does SHM with $\omega = \{4\pi n_0 e^2/m\}^{1/2}$

If alternatively analyse motion in terms of density fluctuations of independent electron gas, find that can have oscillations $\sim$ at ω for long wavelengths. Begin to get transition from collective to individual particle behaviour with wave vectors $\sim 1/\lambda$.

If construct =n. of motion of density fluct^{ns}, find that this has harmonic form but non-oscillatory terms arise significantly for $\lambda_s \ll \lambda$. For $\lambda_s < \lambda$ collective oscillations cannot be sustained. Motion can be described as that of individual electrons surrounded by co-moving clouds of charge, which arise ∵ ε in gas tends to repel the others. General physical picture ∴ that ε's capable of both collective & indiv. particle behaviour, λ functioning as indicator of which to expect. Although these conclusions come from classical analysis, do carry over into cons. domains of metals. Fermi statistics does not have much effect ∵ we deal with phenomena involving distances long w.r.t. de Broglie λ.

Occurrence of Superconductivity.

No strict regularity, but a few general trends. State in $\boxed{1960}$:-

i) No monovalent metal found superconducting

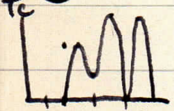
* ii) Conjectured that high internal magnetic field of **strongly** ferromagnetic materials may make them non-s/cond.

iii) S/conductors in regions of intermediate atomic volume, as far as els. go. Note that Au (too small), Bi (too large)$^{\phi}$ are both non/s, but Au_2Bi is s/cond.

iv) Depce. on xstal structure. White tin s/cond, grey non-s/cond. S/cond property ∴ property of ε energy spectrum of metal?

Transition Temperatures. (T_c)

~0.5°K to 18°K. Many metals have been investigated to below 0.1°K, but no transition temps $0.1°K < T < 0.5°K$ yet fd.



Correlation bet T_c and no. of valence for transition metals electrons. Sharp maxima for 3, 5, 7 ε's/at. Also correl. with high γ-values for elect. sp. ht. T_c increases as high power of at. vol & as 1/at. mass.

Exps. have shown ranges of T_c for same material,

* - S/cond found in weak ferromagnetics (but perhaps not in same domain)

φ - remarks on next page

particularly for metals with high M-Pts. May be due to diffr. samples being in diffr. states of internal strain or even difft xstal modifications.

ϕ Bi becomes s/cond at $\sim$ 20,000 atm, poss due to change in xstal structure.

Nature of the Phase Transition.

The disappearance of resistance takes place very suddenly (~0.001 °K) if strain and measuring current are both small. Extrapolate expt'l data :- for single xstal & zero measuring current, transition completely discont's at definite temperature T_c.

Msring current broadens trans'n & puts it at lower temp. Similarly, ext. mag. field will do same. Silsbee's hypothesis : current and ext. field effect are same. On this I_c is that ⇒ H_c at surface. For wire rad. r,

$$I_c = \tfrac{1}{2} r H_c ,$$ exptally ver.

Work with H_c ∵ I_c effect cplx, e/dyn.

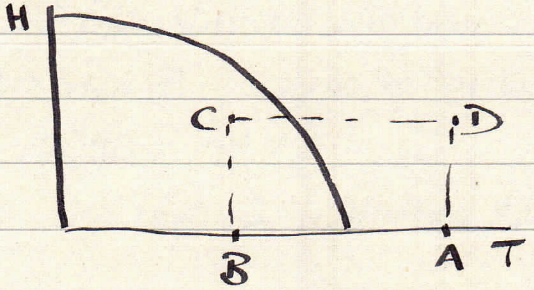
H_c-T curves same form for all s/conds. Approx. parab^c

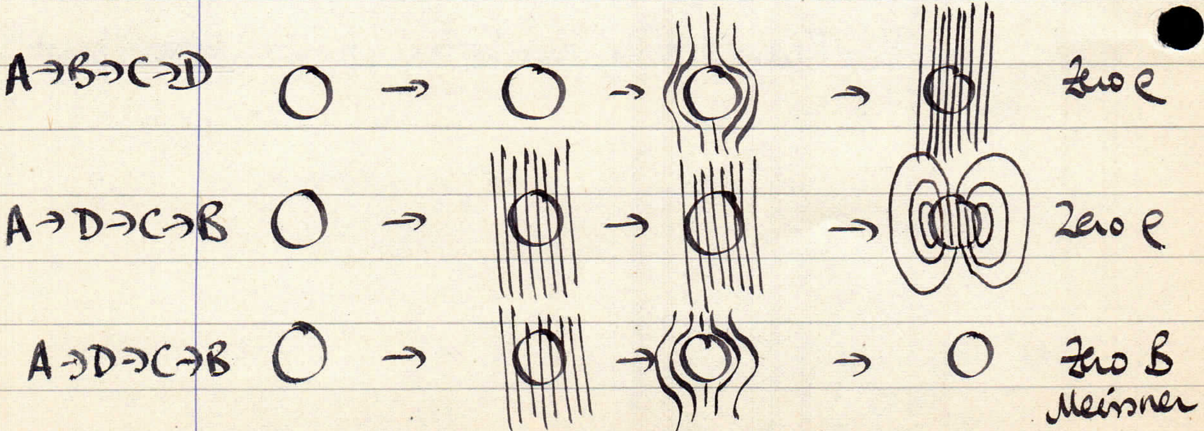
Meissner Effect. (Meissner-Ochsenfeld)

$$\rho = 0 \not\Rightarrow B = 0 \text{ but } \dot{B} = 0 \text{ by Maxwell.}$$

∴ Could get "frozen-in" flux. Found to be so exptally at first.

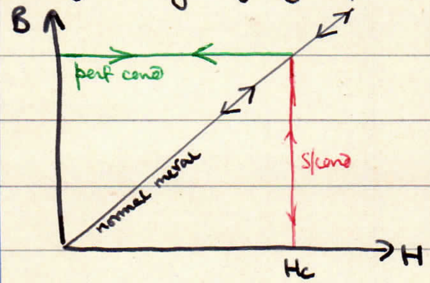
Therm^{d}. rev. $\not\Rightarrow$ diffr. states depr. on past history. Meissner Effect:- $B = 0$. This gives conclusion that final state of s/conductor does not depend on path of change or order of T, H variations.





i) and iii) → therm^{dc} rev.

Can illustrate this by giving B(H) curves for perfect conductor and s/conductor, taking case of long cyl. spec. ∥ $\underset{\sim}{H}$.



Vanishing of $\underset{\sim}{B}$ is basic property of ideal s/cond. material. Independent of conductivity of body, so that if have s/cond. with hole, field lines go thru hole. Magnetic props of specimen then det. by rel. size of diam of ring to diam of hole.

Origin of this perfect diamagnetism? Electron currents, not spin, ∵ expt. shows $g_L = 1$.

"Magnetic Supercooling".

Can sometimes reduce H well below H_c without $B \to 0$. Due to energy req^{d} in forming s/cond phase bdry. Occurs in v. pure samples cont. no inhomogeneities at which new bdry. pref^{ly} formed.

Thermodynamics of Superconductors.

Applicability of thermodynamics rests on Meissner Effect, which gives the necessary grounds for assuming reversibility. Begin from condition that two phases are in Em. when their Gibbs free energies are equal. Then we put

$$G_S(\underset{\sim}{H}) = G_S(0) - \int_0^V dV \int_0^H \underset{\sim}{M}(\underset{\sim}{H})\, d\underset{\sim}{H}$$

If $\underset{\sim}{M}(\underset{\sim}{H})$ is uniform (ellipsoid) this simplifies to

$$\boxed{G_S(\underset{\sim}{H}) = G_S(0) - V\int_0^H \underset{\sim}{M}(\underset{\sim}{H})\, d\underset{\sim}{H}}$$

The last term gives the work done on the specimen by the field $\underset{\sim}{H}$. Now the critical field is not too sharply defined in magnitude, except for the proverbial infinite thin cylinder. For all realisable shapes of specimen, the transition proceeds via an intermediate state that is a mixture of the superconducting and normal states. We assume that the normal state is non-magnetic, though, so that "magnetic work" is performed solely on the superconducting parts. In this case, whatever the shape of the specimen, the total magnetic work we do in bringing a volume V from $\underset{\sim}{H} = 0$ to $\underset{\sim}{H} = \underset{\sim}{H}_c$ is

$$-V\int_0^{H_c} \underset{\sim}{M}(\underset{\sim}{H})\,d\underset{\sim}{H} = W_{magn.}$$

<u>Now the Meissner Effect implies that in the superconducting state</u> $\underset{\sim}{M}(\underset{\sim}{H}) = -\frac{1}{4\pi}\underset{\sim}{H}$, so that

$$W_M = +\frac{H_c^2}{8\pi}V$$

In the normal state $G_n(\underset{\sim}{H_c}) = G_n(0)$ if it is non-magnetic, so that, from the $\equiv$m. cond^n. defining $\underset{\sim}{H}_c$, viz

$$\underline{G_n(H_c) = G_s(H_c)}$$

we get

$$\boxed{G_n(0) - G_s(0) = +H_c^2V/8\pi}$$

Now $G = \underset{-HM}{H'} - TS$, $\quad dG = -VdP \underset{-MdH}{-} SdT$, $\therefore S = -\left(\partial G/\partial T\right)_{P,H}$

$$\therefore\ S_n(0) - S_s(0) = -\frac{V}{8\pi}\frac{\partial H_c^2}{\partial T}$$

$$= -\frac{V}{4\pi}H_c\frac{\partial H_c}{\partial T}$$

At $T = T_c$, $H_c = 0$, and $S_n = S_s$. Thus <u>the entropies of the two phases are equal at zero field strength for $T = T_c$.</u>

For $T < T_c$, $H_c > 0$ and experimental evidence shows that

$dH_c/dT < 0$. This implies that below T_c $S_s < S_n$, so that the superconducting state is in some sense more ordered than the normal one. As at $T=0$ S_s and S_n must be equal again, by 3LT, it follows that either $H_c \to 0$ with $T \to 0$ or $dH_c/dT \to 0$ with $T \to 0$. The latter is in fact the case.

Note that there is no latent heat for a s/conducting transition in zero field.

Now $C = T\left(\partial S/\partial T\right)$ so that:

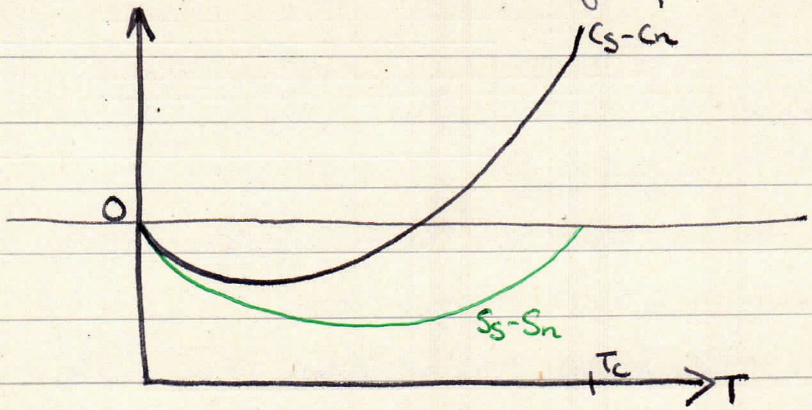
$$C_s - C_n = \frac{VT}{4\pi}\left\{\left(\partial H_c/\partial T\right)^2 + H_c\left(\partial^2 H_c/\partial T^2\right)\right\}$$

Thus at $T=T_c$, $H_c=0$, $\boxed{\Delta C = \left(\frac{VT_c}{4\pi}\right)\left(\partial H_c/dT\right)^2_{T=T_c} > 0.}$

The observed specific heat discontinuity thus appears in the thermodynamic treatment straight away.

How do these formulae describe the real situation? We start from an experimental determination of $H_c(T)$, as indicated above. It should also be noted that the assumption of a "complete" Meissner effect, ($\underset{\sim}{B}=0$) has been taken for a starting-point, and so we *cannot expect to apply these formulae to small specimens*, in which the penetration depth is comparable with the main dimensions. Also, many materials show only a very incomplete Meissner effect anyway, and data from these cannot be considered.*

The comparison with the specific heat curves in cases not eliminated by the above considerations is then inaccurate insofar as it requires double differentiation of the experimental results. Bearing this in mind, the agreement is quite reasonable where it has been validly looked into. The expression for $\overset{T=T_c}{\Delta C}$ only requires single differentiation of the $H_c(T)$ curve and has been well verified for Sn, Pb & Ta.



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* Data from zero-resistance measurements are similarly invalid, as perfect conductivity can persist even above the $H_{external}$ required to cause flux-penetration. The only acceptable $H_c(T)$ data is that derived from susceptibility measurements.

The relationship for $\Delta C(T=T_c)$ [Rutger's Relation], and its confirmation by experiment, provide good experimental evidence for the assumption of reversibility, and give some strength to the idea of using thermodynamics in the first place. The treatment shows how closely interwoven are the thermal and magnetic properties of these materials, for instance the relation between the observation that $dH_c/dT < 0$, quite regardless of the detailed form of $H_c(T)$, and the greater order of the superconducting state.

A Simple Two-Fluid Model of a Superconductor.

The success of a two-fluid model in describing the behaviour of liquid helium 4 at low temperatures, and the obvious phenomenological analogy between the superfluidity (non-viscous flow) of this substance and the superfluidity (non-resistive flow) of electrons in a superconductor, suggests that a two-fluid model of a superconductor might be a profitable consideration. Two postulates must be made.

1. The superconducting state is characterised by order (this is an experimental deduction). Let the amount of this order be specified by the fraction φ which will be considered to denote the proportion of the total system in an ordered state at a given temperature. We have that $\varphi(T_c) = 0$ and $\varphi(0) = 1$.

2. The entire entropy of the system is caused by the disordered state, whose characteristics will be assumed to be identical with those of the normal state above $T = T_c$.

We then have, similarly to the Tisza model of He^4, a fraction φ of "superconducting", "ordered" electrons, and a fraction $(1-\varphi)$ of "normal", "disordered" electrons.

The physics of this segregation, and its meaningfulness, is not to be questioned for the moment. It is an empirical, phenomenological model of an essentially coarse-grained nature. It may however throw some light on the correlation between various observed properties.

The free energy per unit volume of the "normal" electrons will be that of electrons in a normal metal, viz

$$g_n(t) = -\tfrac{1}{2}\gamma T^2$$

where γ is the Sommerfeld specific heat constant.

The Critical Field as a Function of Temperature

The Clapeyron analogue can be re-written as

$$v_s \frac{\partial}{\partial T}(\mathcal{H}_c^2) = 8\pi\left\{\frac{1}{3}\alpha T^3 - \frac{1}{3}\beta T^3 - \gamma T\right\}$$

$$\therefore v_s . \mathcal{H}_c^2 = 8\pi\left\{\frac{1}{12}\alpha T^4 - \frac{1}{12}\beta T^4 - \frac{1}{2}\gamma T^2\right\} + v_s \mathcal{H}_0^2$$

where $\mathcal{H}_0 = \mathcal{H}_c$ for $T = 0$.

$$v_s . \mathcal{H}_c^2 = \frac{8\pi}{4}\left\{\frac{1}{3}\alpha T^4 - \frac{1}{3}\beta T^4 - 2\gamma T^2\right\} + v_s \mathcal{H}_0^2$$

$$= \gamma . 2\pi\left\{\frac{\alpha - \beta}{3\gamma} T^4 - 2T^2\right\} + v_s \mathcal{H}_0^2$$

$$= 2\pi\gamma\left\{\frac{T^4}{T_c^2} - 2T^2\right\} + v_s . \mathcal{H}_0^2$$

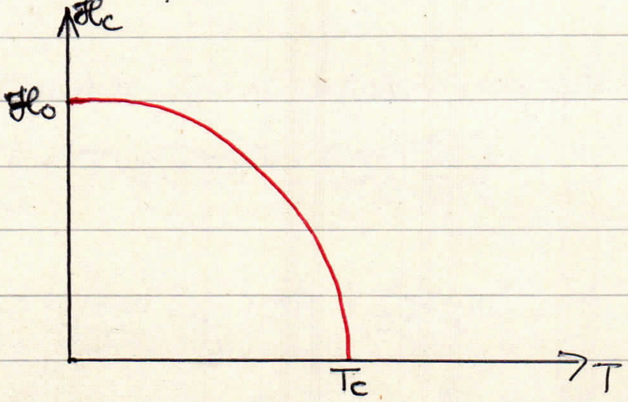
When $\mathcal{H}_c = 0$, $T = T_c$, so that

$$T_c^2 . 2\pi\gamma = v_s \mathcal{H}_0^2 , \quad \mathcal{H}_0 = T_c\sqrt{2\pi\gamma / v_s}$$

Then $\cancel{v_s} . \mathcal{H}_c^2 = \frac{\cancel{v_s}\mathcal{H}_0^2}{T_c^2}\left\{\frac{T^4}{T_c^2} - 2T^2 + T_c^2\right\}$

$$\boxed{\mathcal{H}_c = \mathcal{H}_0\left\{1 - T^2 / T_c^2\right\}}$$

This predicts the parabolic $\mathcal{H}_c : T$ plot found in practice.



Because we have considered the equilibrium condition of the material, and discussed the phase diagram boundary between the two states, $\mathcal{H}$ here = $\mathcal{H}_c$, the critical magnetic field above which no phase transition to the superconducting state will occur at the temperature T. The temperature T_c is defined as the temperature for which $\mathcal{H}_c = 0$.

The Clausius - Clapeyron analogue derived with the assumptions stated can be used as the starting-point for a number of calculations about the phase transition. We need a model for the specific heats, however, and the theory can be developed on the following basis.

For the superconducting phase: assume $\boxed{C_p = \alpha T^3}$. For the normal phase, assume $\boxed{C_p = \beta T^3 + \gamma T}$. At the low temperatures at which superconductivity is observed, the latter form expresses the Debye T^3 dependence with the electronic specific heat added. The former removes the electronic term.

This approach is not really very sat. Can develop results from more general grounds. See below.

Transition Temperature In Zero Field.

In zero field, writing the Clapeyron analogue as

$$V_S \mathcal{H} \left.\frac{\partial \mathcal{H}}{\partial T}\right)_P = 4\pi (S_S - S_n),$$

it is clear that $\underline{S_S = S_n}$ at the transition-point.

Now $C_P = T\left(\frac{dS}{dT}\right)_P$, $\therefore S_S = \int_0^T C_{PS}/T \, dT$

$$= \int_0^T \alpha T^2 \, dT$$

Using the Third Law of Thermodynamics at $T=0$, $S(0)=0$

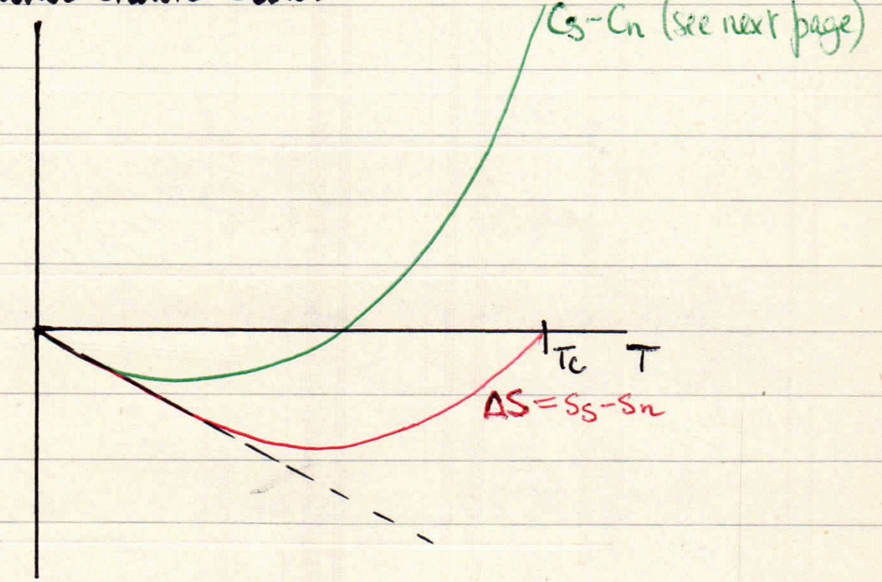
$$\left.\begin{aligned} \therefore \; S_S &= \tfrac{1}{3}\alpha T^3 \\ \text{Similarly, } S_n &= \tfrac{1}{3}\beta T^3 + \gamma T \end{aligned}\right\} \text{these must be equal at transition temp. for } \mathcal{H}=0$$

$$\therefore \tfrac{1}{3}\alpha T_c^3 = \tfrac{1}{3}\beta T_c^3 + \gamma T_c, \quad (T = T_c \text{ for } \mathcal{H}_c = 0)$$

$$\therefore \boxed{T_c = (3\gamma/\alpha-\beta)^{1/2}}$$

$$\therefore \quad \boxed{S_n - S_s = -\left[\frac{\mathcal{H}_c}{4\pi}\right]\frac{d\mathcal{H}_c}{dT}\cdot V_s} \quad \text{at const. P.}$$

If we differentiate $\mathcal{H}_c$ v T curve for typical s/cond^r, get the ΔS v T curve shown below:



ΔS = 0 at T=0 expected from 3LT. ΔS=0 at T_c ⇒ transn. in zero field does not involve latent heat.

$$\boxed{Q = T\Delta S = -T\left(\frac{\mathcal{H}_c}{4\pi}\right)\left(\frac{d\mathcal{H}_c}{dT}\right)V_s \text{ , heat of transition.}}$$

Exptal agreement for tin v. good.

Note that ΔS v T extrapolates linearly to zero of temp. Remember

that for normal metal C_V (electronic) = γT ∴ $S_{elect} = \gamma T$
As $S_S < S_n$ (s/cond more ordered) can hypothesise that
$S_S \to 0$ at reasonably high temps and the T depce. of ΔS
is due to γT electronic entropy.

$T \to 0$, $\Delta S = S_S - S_n = -\gamma T$ good fit for Tin

$C = T(dS/dT)$,

$$\therefore \boxed{C_S - C_n = \frac{T}{4\pi}\left\{\mathcal{H}_c \frac{d^2\mathcal{H}_c}{dT^2} + \left(\frac{d\mathcal{H}_c}{dT}\right)^2\right\} V_S}$$

Comparison with expt. difficult here as it involves diff^{n}.
$\mathcal{H}_c$-T curve 2ce.

At T_c, $\mathcal{H}_c = 0$, ∴ 1st term vanishes.

$$\boxed{C_S - C_n = \frac{T_c}{4\pi}\left\{\frac{d\mathcal{H}_c}{dT}\right\}^2_{T=T_c} V_S}$$

Difficulties of applying these formulae:

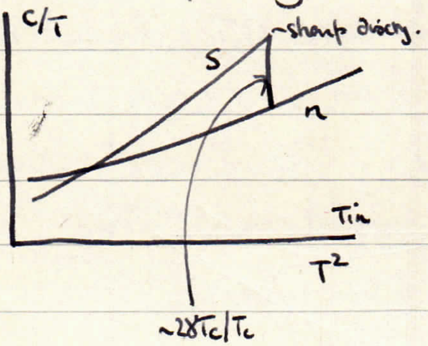
$\mathcal{H}_c$ msts. from disappearance of resistance are not reliable ∵ zero resistance can persist above flux-penetration $\mathcal{H}_{ext}$. Must use $\mathcal{H}_c$ values derived from susc. msts in thermodynamic formulae ∵ we assumed $\mathcal{B} = 0$.

Electronic Sp. Ht. in S/Cond State - The Energy Gap.

T^3 dependance of $C_{elect.}$ in s/cond. follows N from parabolic $H_c(T)$ plot. Accurate recent work* suggests a form

$$C_{es} = a\gamma T_c e^{-bT_c/T}$$

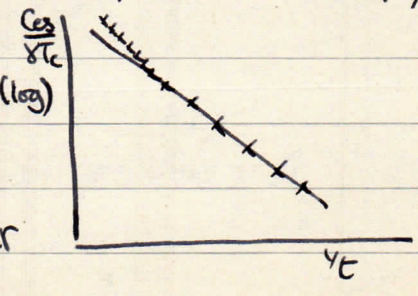
Corresponding devns. from $H_c(T)$ parabola found.



Plot of C/T v T^2 determines constants in $C = \gamma T + A(T/\Theta)^3$. Assume $C_{lattice}$ same in s/ & n/., reasonable in view of electronic nature of phenomenon. Also borne out by absence of any change in lattice parameters, and only v. small changes in elastic properties. Then we have to agree that

$$C_{es} - C_{en} = C_s - C_n$$

, so that all of diffce is in electronic sp. ht. Get $C_s - C_n$ from above, measure C_{en} sep., ↲



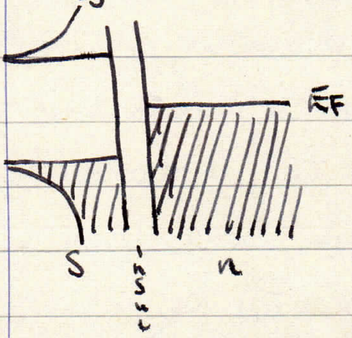
Suggests ∃ energy gap across which electrons must be therm. excited. Story is not simple, ∵ variations now known - suggest that gap is in fact

* Corak & Satterthwaite PR 99, 1660

anisotropic.

Had been noted for long time that LF behaviour of s/c not accompanied by HF behaviour of similar kind. Would expect v. high reflectivity, but no visible diffce. Found that at 0°K, normal resistance persisted for $\nu \sim 10^{13}$ c/s, but remained zero for $\nu \sim 10^{10}$ c/s. If electron gap were to explain sp. ht. varn., should be $\sim k_B T_c$, which puts $h\nu \sim 10^{11} - 10^{12}$ c/s! An awkward range for exptal. investig^n.

Giaever measured gap with voltmeter! Observe tunnel effect bet s/cond & normal metal. Finite chance of tunnelling if there is a state allowed of equal or smaller energy on other side.



In s/cond, filled up to $E_F - \varepsilon$, & gap of 2ε. Apply potl diffce, tunnelling suddenly sets in when applied voltage = ε. Subsequent varn. of tunnelling current with app. voltage → density of states of s/cond. above gap. Do it with 2 s/conds with diff. T_c's (Al & Pb, say)

Fröhlich's One-Dimensional Model.

We know that an external sinusoidal potential of wave number w_0 yields in 1-d case gap in electronic energy spectrum at $k_0 = w_0/2$. States below gap are depressed. States above it have energies increased. Most favourable potl.: that for which all occupied states depressed & all unocc. lifted. ∴ k_0 = Fermi w-n. This potl. will occur if the lattice vibn $w_0 = \pm 2k_0$ is excited.

Fröhlich uses pert^n. Θ^y to show that these can be highly excited. $\pm 2k_0$ mode interacts with av. electron density, elects. move in av. field of mode $\pm 2k_0$. Amplitudes β, β^* of mode turn out to be large. Elect. density & latt. vibn maintain one another. Strong interaction → large gap.

∞ly long lattice } The periodic potential is not fixed to the lattice. System of ε's + vibns. moves with vely v. Single particle excitations must overcome gap $\Delta(v)$. For $v \neq 0$, persistent current.

Cf. insulator : ε-fns fixed to periodic positions of ions

here : fixed to periodic vibrations

As temp. increases, electrons excited across the gap. Exponential depce. of $C_v(T)$ and also: electron excitation facilitates ε-density fluctuations, which then reduce gap width → facilitates excitation. Co-operative breakdown.

Co-op. effects $\rightsquigarrow$ 2-order transn.

Superconductive Electrodynamics.

Zero resistance $\not\Rightarrow$ Meissner Effect. Londons give $\operatorname{curl} \Lambda \underset{\sim}{j_s} = -\frac{1}{c}\underset{\sim}{H}$, $\underset{\sim}{j_s}$ is s/cond current density, Λ a characteristic const.

This =n. replaces acc^n. =n of normal conductor; assoc^n. with $\underset{\sim}{H}$, not $\underset{\sim}{E}$ via Ohm's Law.

Gradual increase in H_c as T lowered and fact that no latent heat (S discty.) at T_c suggest that "no. of s/cond electrons" increases from zero at T_c to 100% at $T=0$. Doubtful meaning of distinction, but analog with liq. He 2-fluid idea. Here the 2 types of electron obey diff. e/dynamic eqns. tho'.

$$\underset{\sim}{j} = \underset{\sim}{j_n} + \underset{\sim}{j_s} \qquad \underset{\sim}{j_n} = \sigma \underset{\sim}{E}$$

Need another relation also

$$\frac{d}{dt}(\Lambda \underset{\sim}{j_s}) = \underset{\sim}{E}$$

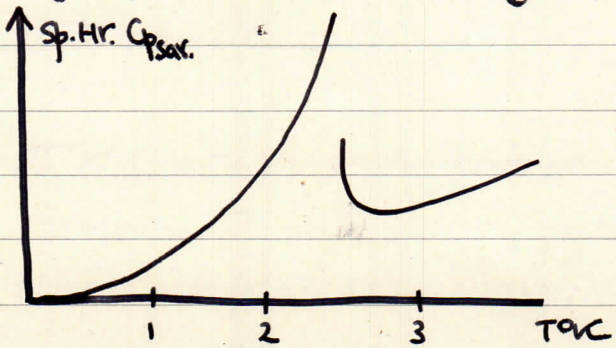
Penetration Depth.

$\lambda = c\sqrt{\Lambda/4\pi}$ for fields to go to 1/e th.
Perfect diamagnetism thus only for large specimens.
$\lambda \sim 10^{-5}$ cm. Effects of finite penetration ∴ noticeable for a colloid → method of finding λ.
Temp. depce. from χ of macroscopic specimens

$$\lambda = \lambda_0 \left\{ 1 - \left(\frac{T}{T_c}\right)^4 \right\}^{-1/2}$$

Liquid Helium - the λ transition

See Below: Sp. ht. msd by finding temp. rise when heat supplied to known mass of liq. thermally isolated by vacuum.



Similar behaviour in order-disorder transition in alloys, and ferromagnetic Curie point. Detailed mechanisms differ among these, but all are co-operative phenomena, involving strong interactions bet. units undergoing change. Msd. sp. ht. and that in diagram = sp. ht. under sat^n vap. press.

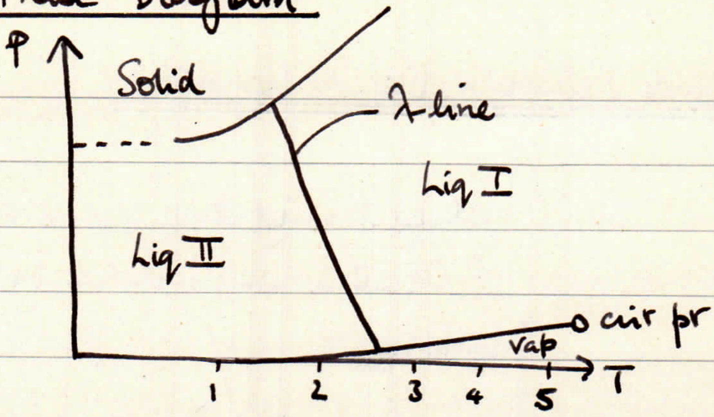
$$C_{sat} = C_p - TV\alpha\left(\frac{\partial p}{\partial T}\right)_{vap.\ pres.\ curve}$$

α being the coefficient of expansion.

Density goes to maximum at λ-pt.

No latent heat at λ-transition.

Full Phase Diagram



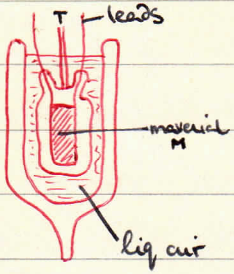
X-ray investigations show that both II and I are liquids. Large anomaly in sp.ht. corresponds to rapid drop in entropy of liq. as T > below λ-pt. Salient feature is rapid approach to perfect order in liquid structure.

∴ $dp/dT = \Delta S/\Delta V$, as $\Delta S \to 0$ (liquid order → solid ~~[illegible]~~ order), so $dp/dT \to 0$. This explains change of dirn. of melting curve across λ-line. At $T=0$, can melt or freeze helium by doing or abstracting work at the melting pressure. Since zero change in entropy involved, there is no latent heat and process is purely mechanical. Type of excitation approached via spec. ht.

Below 0.7°K, $C \sim T^3$ phonon

Above 0.7°K $C \sim T^{6.2}$ see below

Measurements of Specific Heats at Low Temperatures



Insulated coil of Pt. wire wound on block of material & suspended by leads in vacuo. All mounted in liq air, liq. H_2 or liq He. Vessel containing material can be filled with gaseous He or evacuated thru T. M cooled by gaseous condn. to temp of bath, then inner vessel evacuated. Known quantities of heat supplied to M by passing current through Pt coil for given times (stop-watch controlled circuit) & corresponding temp changes msd. by corresponding resistance changes in coil.

Seperate htr. & thermometer coils nowadays.

Difficulties: radiative heat exchange above liq H_2 temps. Poor vacuum below liq H_2 temps. Former can be controlled by surrounding M with a shield made to follow temp. of M acc. by servo means. Servos actuated by diff. thermocouples bet M & shield.

Vacuum difficulties arise ∵ He adsorbed on walls of container. Overcome by not using He gas but mechanical heat exchange (pressed metal surfaces).

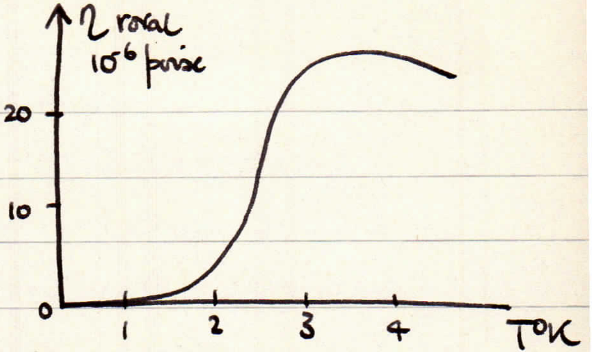
Measurements Below 1°K

Substance mixed with p/mag salt, which acts as cooling agent & thermometer. Demagnetise → heat by γ-rays, or electric heater. Temp. changes msd. thru χ changes of salt & sp. ht. of subst. follows from total C_v − salt C_v. Knowledge of sp. ht. of salt & its $T-T^*$ reln. abv. req^d. Only satisfactory if $C_{material} \simeq C_{salt}$.

Temperature Waves.

Pass periodically changing heat current. Propag^n. det. by $K/C\rho$. Measure $K \to C$.

Viscosity & Superfluidity.



Below λ-pt. quite diff. vals. of η obtainable, depd. on method employed. Osc. disc, η falls gradually with decr. temp. to ~ 10^{-6} poise at 1.3°K.
Flow through narrow capillary → < 10^{-11} poise just below λ-pt. Not a limiting case of ordinary viscous behaviour. Expts with diff-sized capillaries → anomalous character more pronounced in v. fine capillaries. In narrowest channels, flow becomes indept. of pressure head & channel length, depd. only on temperature.
In large capillaries flow becomes complicated, being a mixture of superflow & normal viscous flow.

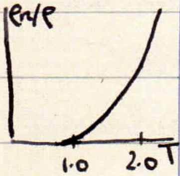
These effects → 2-fluid model, cf. s/cond. No physical reality suggested. Think of progressively greater fraction of s/fluid as T→0, remainder being identical with He I

$$\rho = \rho_n + \rho_s$$

Props. of normal cpt. those of gradually diluted He I. S/fluid supposed to have no thermal excitations & incapable of participating in dissipation processes. Set up hydrodynamics separately.

Superflow carries no entropy and does not interact with normal flow carrying excitations. Expt → not always true but is so below a certain vely. of flow.

Exptal. det. of rel. proportions.

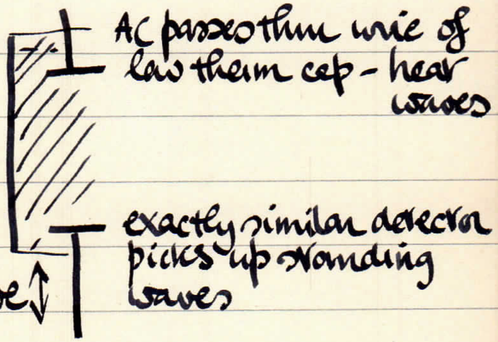


Mt. of inertia of stack of closely-packed discs osc. in He II. As T >, Mt. > ∴ less and less normal fluid carried along in gaps bet. plates.

Liquid Helium: "Second Sound".

In "first sound", normal & s/fluid cpts move in phase with one another. Total density ∴ varies from pt. to pt. but rel. concs. do not (to same order) ∴ propagn. of acoustic wave. In "second sound" cpts move out of phase in opposite directions. Density does not change but rel. concs. do. ∴ s/fluid "cold" and normal "hot"; increase in s/fluid lowers temp. at pt. ½λ away, increase in normal raises temp. ∴ Thermal wave.

Detection of Second Sound:
Vely of second sound ∼ 20 cm/sec. First sound ∼ 250 cm/sec. ∴ definitely a new phenomenon.



Important Properties of He^4.

i) Remains liquid under own vap. pres. down to $T=0$.
Solidifies under external pressure, when ats. brought close enough together for cohesion > zero-pt energy.

ii) λ-phenomenon. See below.

iii) Viscosity almost non-temp dept in He I. Below 2.6°K, η drops rapidly in same temp region as sp. ht. anomaly. η is always small ($\sim 3 \times$ that of gas).

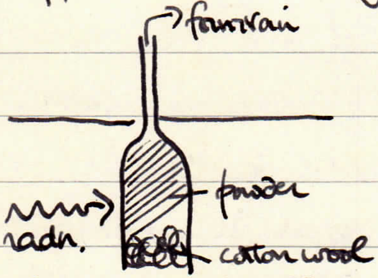
iv) Thermo-mechanical Effects. See below.

Thermal Effects.

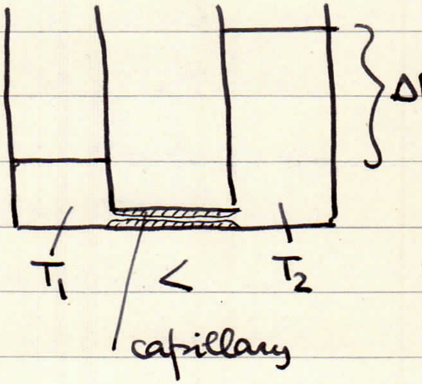
Fine capillary acts as "entropy filter". Liquid coming out colder than that going in. Not suitable for low temp. prodn. ∵ entropy of liq. He falls v. rapidly with decr. temp.

Thermo-mechanical Effect.

2 vols. of liq He connected by capillary, heat supplied to one → flow towards heat supply.



Thermo-mech. effect
"Fountain"



Explicable by 2 fluid model again. Any T characterised by certain value of ρ_n/ρ When heat is supplied, s fluid excited into normal state & ρ_n increases. This is compensated by a flow of ~~normal~~ super fluid through capillary in dirn. of higher temp. Return flow of normal fluid is prevented by capillary resistance and ∴ a thermomechanical pressure develops.

System ≡ heat engine. Level of He in right hand column can be raised by applicⁿ of heat. Liq. can then do work by dropping back to level of l.h. column. Assuming complete reversibility, $\frac{\Delta p}{\Delta T} = \rho \Delta S$.

where Δp = therm/mech pres. diffce ≡ ΔT, ΔS = diffce in entropy bet. liq. flowing in capillary & bulk liquid rer. from higher to lower level.

London's. **Proof**. Consider 2 containers of const. vols. V_A & V_B entirely filled with liq He & connected by ext. fine capillaries. Only s/fluid can pass. Then S_A & S_B are sep. constant. ≡m det. by minimum of total energy $U(M_A, M_B)$ where M_A & M_B masses of He in 2 containers. Here we can exchange mass but not entropy bet. containers.

$$\text{In } \equiv\text{m.,} \quad 0 = \delta U = \delta(M_A u_A) + \delta(M_B u_B)$$

$$① \quad 0 = u_A \delta M_A + u_B \delta M_B + M_A\left[\left(\frac{\partial u}{\partial S}\right)_A \delta S_A + \left(\frac{\partial u}{\partial V}\right)_A \delta V_A\right] + M_B\left[\qquad\qquad\right]$$

For each ctr. $\delta(M_i s_i)$ & $\delta(M_i v_i) = 0$.

$$\therefore \quad M_i \delta s_i + s_i \delta M_i = 0 \Rightarrow \delta s_i = \frac{s_i \delta M_i}{M_i}$$

$$M_i \delta v_i + v_i \delta M_i = 0 \Rightarrow \delta v_i = \frac{v_i \delta M_i}{M_i}$$

Now $\left(\frac{\partial u}{\partial s}\right)_v = T$, $\left(\frac{\partial u}{\partial v}\right)_s = -P$ from 1LT,

① ⇒ $\therefore \sum_{A,B} u_i \delta M_i + T_i s_i \delta M_i - P_i v_i \delta M_i = 0$

Now $\delta M_A = -\delta M_b$, $u - sT - vP = g$.

$$\therefore \left(g_a - g_B\right)\delta M_A = 0, \quad \therefore g(P_A, T_A) = g(P_B, T_B)$$

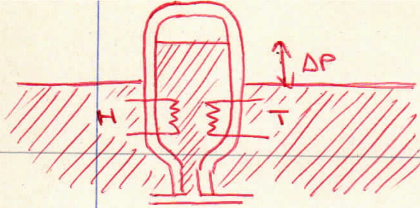
Thus for small ΔT, ΔP,

$$\frac{\partial g}{\partial T}\Delta T + \frac{\partial g}{\partial P}\Delta P = 0, \qquad \underline{\underline{\Delta P = \rho S \Delta T}}$$

Heat of transport $\underline{N}$ to bring unit quant. of liq. He from left to right is $Q_T = T\Delta S = T\Delta p/\rho\Delta T$. Kapitza showed that heat supplied per gram of He pumped into container lie strictly on curve of [redacted] TS v T for liq He S obtained from sp. ht. msts. ∴ Heat supplied to produce small temp diffce bet containers just that $\underline{N}$ to raise same amount of liq He from $T=0$ to $T=$ temp. in question. Also msd. vals of $\frac{T}{\rho}\frac{\Delta P}{\Delta T}$ lie exactly on same curve.

∴ Confⁿ. of i) reversibility

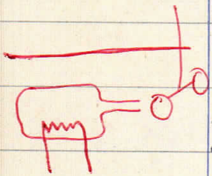
ii) zero entropy in afflow.



Apparatus for an experiment of Kapitza type.

Heat Conductivity

He I normal th. cond., heat transport in He II can be 10^3 × that in copper. Evidenced by stoppage of boiling of He under reduced pressure as λ-pt. gone through. Conductivity so great that all evapn. must take place from surface. Detailed effects v. complicated, dept. on temp. gradient & geometry.



Explanation on 2-fluid model. Counterflow of 2 fluids through a narrow gap. Heating causes inflow of s fluid as in previous exx., but now no space for rise and normal ejected, as proved by Kapitza with suspended vanes.

$$\dot{Q} = \rho_n v_n \times TS$$

$$= \rho_n \frac{\Delta p \pi a^4}{8 \eta_n l} . TS$$

Mass flow must balance $\rho_s v_s = \rho_n v_n$

$$\frac{\Delta T}{\dot{Q}} = \frac{\eta_n 8 l}{\pi a^4} \Big/ \rho^2 S^2 T$$

This mechanism would be indept. of temp. gradient & is ∴ oversimplified. Works for small velys.