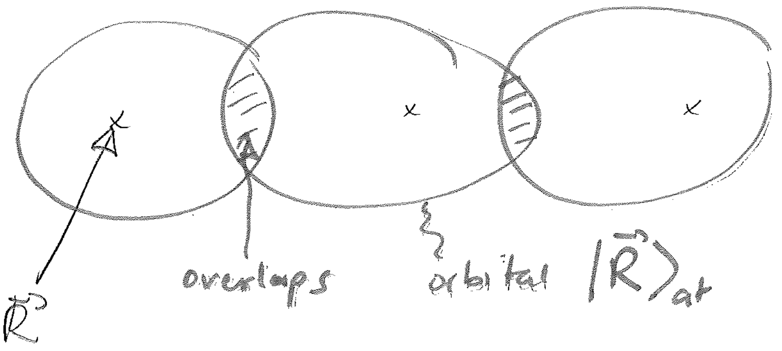
Tight-binding description

solids $\approx$ well localized "atomic" orbitals
+ electrons hopping between them



$$\langle \vec{r} | \vec{R} \rangle_{at} = \varphi_{at}(\vec{r}-\vec{R}) \qquad \varphi_{at}: \text{atomic orbitals}$$

- simplest case: H-crystal $\Rightarrow$ only one s-orbital per atom

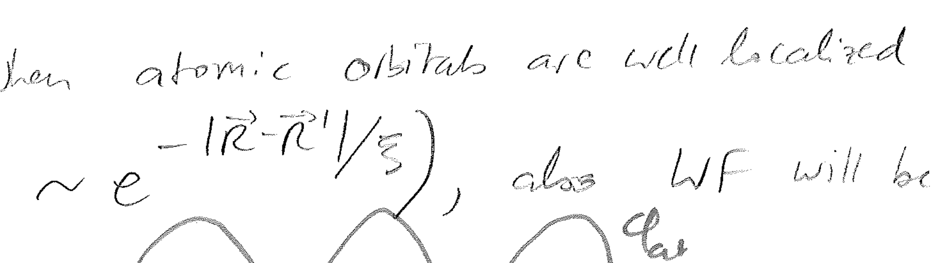
$\Rightarrow$ diagonalize $\hat{H} = -\frac{\hbar^2 \vec{\nabla}^2}{2m} + V(\vec{r})$ in subset $\{|\vec{R}\rangle_{at}\}$

"Problem": atomic orbitals at different sites not orthogonal (overlaps) : ${}_{at}\langle \vec{R} | \vec{R}' \rangle_{at} \neq \delta_{RR'}$

$\Rightarrow$ construct $|\vec{R}\rangle \equiv \sum_{\vec{R}'} U_{RR'} |\vec{R}'\rangle_{at}$ (with suitable choice of $\underline{U}$) another basis with $\langle \vec{R} | \vec{R}' \rangle = \delta_{RR'}$

$\Rightarrow$ Wannier basis

- when atomic orbitals are well localized $\left({}_{at}\langle R | R' \rangle_{at} \sim \sim e^{-|\vec{R}-\vec{R}'|/\xi} \right)$, also WF will be localized



- Representation of Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})$$

$$\hat{H} = \sum_{RR'} |R\rangle \underbrace{\langle R|\hat{H}|R'\rangle}_{h_{R-R'}} \langle R'|$$

Matrix element for tunneling between Wannier orbitals

- if Wannier orbitals are well localized, $h_{R-R'}$ falls off exponentially

Simplest approximation:

$$h_{R-R'} = \begin{cases} \varepsilon & R=R' \\ -J & R,R' \text{ nearest neighbors} \\ 0 & \text{else} \end{cases}$$

- band structure:

Bloch state $|\psi_k\rangle = \frac{1}{\sqrt{L}}\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}|\vec{R}\rangle$

[check: $\psi_k(\vec{r}) = e^{i\vec{k}\vec{r}}\underbrace{\left\{\frac{1}{\sqrt{L}}\sum_k w(r-R)e^{ik(R-r)}\right\}}_{\text{periodic}}$]

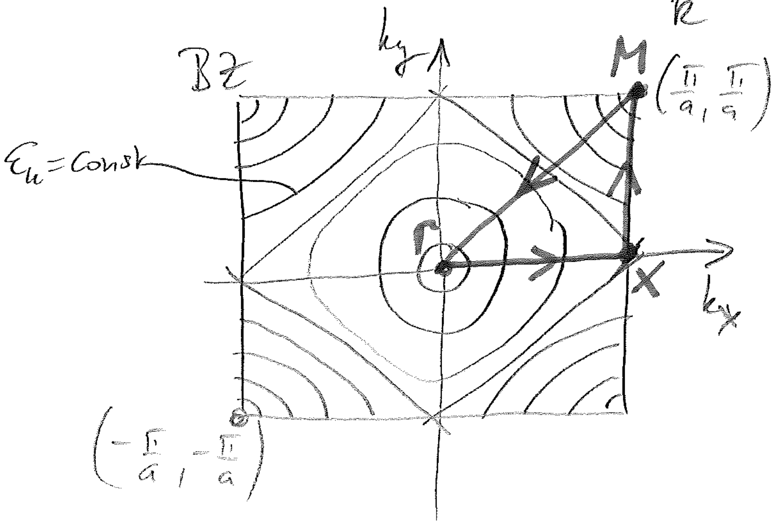
$\hat{H}$ is diagonalized by the Bloch functions

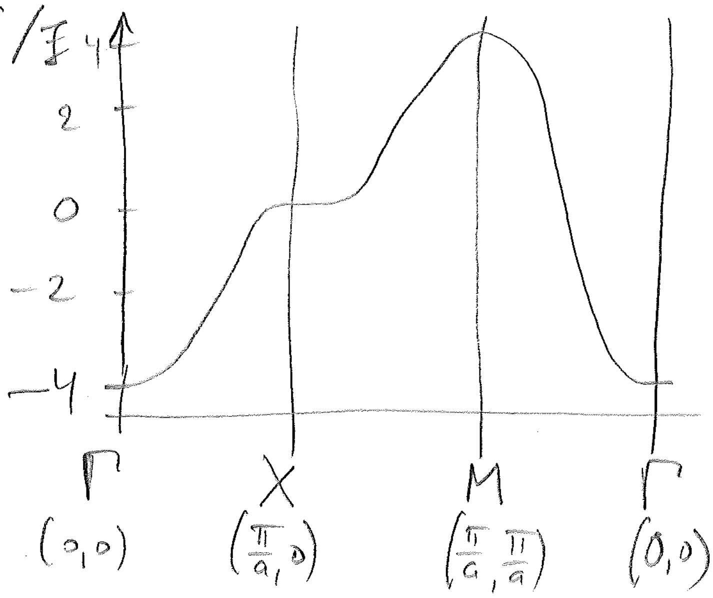
$$|\psi_k\rangle = \frac{1}{\sqrt{L}}\sum_k e^{i\vec{k}\vec{R}}|\vec{R}\rangle$$

$$\hat{H}|\psi_k\rangle \underset{2D}{=} \frac{1}{\sqrt{L}}\sum_k e^{i\vec{k}\vec{R}}\left\{\varepsilon|\vec{R}\rangle - J|\vec{R}+\vec{a}_1\rangle - J|\vec{R}-\vec{a}_1\rangle - J|\vec{R}+\vec{a}_2\rangle - J|\vec{R}-\vec{a}_2\rangle\right\}$$

$$= \frac{1}{\sqrt{L}} \sum_R e^{i\vec{k}\vec{R}} |\vec{R}\rangle \left\{ \varepsilon - J e^{-i\vec{k}\vec{a}_1} - J e^{+i\vec{k}\vec{a}_1} - J e^{-i\vec{k}\vec{a}_2} - J e^{+i\vec{k}\vec{a}_2} \right\}$$

$$\boxed{H|\psi_k\rangle = [\underbrace{\varepsilon - 2J\cos(k_x a) - 2J\cos(k_y a)}_{\varepsilon_k}]|\psi_k\rangle}$$





Dynamics of Bloch electrons

3) Screening in dielectrics & metals

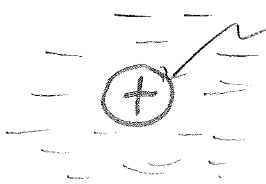
<u>Solid:</u> Long-ranged Coulomb interaction screened by mobile charges (fast!)

$\Rightarrow$ effectively short-ranged interaction between charges

$\oplus$

$$\phi(r) = \frac{q}{r}$$

"bare charge"



accumulation of charge with opposite sign

<u>Motivation:</u>

- relation to dielectric response $\Rightarrow$ <u>optical conductivity</u>
- understand <u>effective interactions</u> between (quasi)particles in the solid (e.g., attractive interactions which lead to superconductivity)
- response functions $\Leftrightarrow$ excitation spectrum, <u>collective excitations</u>

- <u>Macroscopic description</u>

<u>Maxwell:</u> (cgs)

$$\vec{\nabla} \cdot \vec{E} = 4\pi\rho \qquad \vec{\nabla} \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$$

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c}\vec{j} + \frac{1}{c}\frac{\partial \vec{E}}{\partial t} \qquad \vec{\nabla} \cdot \vec{B} = 0$$

$\rho, \vec{j}$: microscopic charges, currents: "external + induced"

$\Updownarrow$

macroscopic Maxwell equations:

$$\left.\begin{aligned} \vec{\nabla}\cdot\vec{D} &= 4\pi \rho_{ext} \\ \vec{\nabla}\times\vec{H} &= \frac{4\pi}{c}\vec{j}_{ext} + \frac{1}{c}\frac{\partial \vec{D}}{\partial t} \end{aligned}\right\} \quad \rho_{ext}, \vec{j}_{ext}: \text{ external charges}$$

+ linear response $\vec{D} = \varepsilon \vec{E}$, $\vec{B} = \mu \vec{H}$

Note: linear-response relations in general non-local in space and time

$$D_\alpha(\vec{r},t) = \underbrace{\int_{-\infty}^{t}}_{\text{causal!}} dt' \, \underbrace{\tilde{\varepsilon}_{\alpha\beta}}_{\text{tensor}}(\vec{r}-\vec{r}\,', t-t') E_\beta(\vec{r}\,', t')$$

retarded response

$\Rightarrow$ Fourier: $\vec{D}(\vec{r},t) = \int d^3q \int d\omega \, e^{i(\vec{q}\vec{r}-\omega t)} \vec{D}(\vec{q},\omega)$

$$\boxed{\vec{D}(\vec{q},\omega) = \overleftrightarrow{\varepsilon}(\vec{q},\omega)\,\vec{E}(\vec{q},\omega)}$$

- Interpretation of dielectric function ε

Consider some "bare" potential due to "external" charge density:

$$-\vec{\nabla}^2 \phi_{ext} = 4\pi \rho_{ext}$$

$$4\pi\rho_{ext} = \vec{\nabla}\cdot\vec{D} = \vec{\nabla}(\varepsilon\cdot\vec{E}) \overset{\text{transl. invariance}}{=} \varepsilon \vec{\nabla}\cdot\vec{E} = -\varepsilon \vec{\nabla}^2 \phi$$

$$\Rightarrow \quad \boxed{\phi(\vec{q},\omega) = \frac{\phi_{ext}(\vec{q},\omega)}{\varepsilon(\vec{q},\omega)}}$$

$\Rightarrow$ phenomenologically ε describes screening

- Relation to conductivity:

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{j}_{ext} + \frac{1}{c} \frac{\partial \vec{D}}{\partial t}$$

nonmagnetic material: $\vec{j}_{ext} = 0$

$$\vec{\nabla} \times \vec{B} = -\frac{i\omega}{c} \vec{D} \quad (\text{Fourier: } \partial_t \to -i\omega)$$

$$= -\frac{i\omega\varepsilon}{c} \vec{E} \quad (*)$$

Microscopic: $\vec{j}$ = induced current

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \underbrace{\vec{j}}_{\sigma \vec{E}} - \frac{i\omega}{c} \vec{E}$$

$\sigma \vec{E} \longleftarrow$ definition of conductivity

$$= -\frac{i\omega}{c} \left(1 + i \frac{4\pi\sigma(\omega)}{\omega}\right) \vec{E}$$

Compare with $(*)$:

$$\boxed{\varepsilon(\omega) = 1 + i \frac{4\pi\sigma(\omega)}{\omega}} \qquad \left(1 + i\frac{\sigma}{\omega} \text{ in SI units}\right)$$

Optical response: measurement at $q \cong 0$
($\lambda_{visible} \gg$ atomic spacing)

- Relation to charge response function:

Define $\delta n = \chi \, \delta V_{ext}$

Response of density to external potential energy $\quad (\rho = -e\,\delta n \;,\; V = -e\phi)$

Poisson: $\quad \underbrace{\phi}_{\frac{\phi_{ext}}{\varepsilon}} = \underbrace{\frac{4\pi}{q^2}\,(\rho_{ext} + \rho_{induced})}_{\phi_{ext}}$

$$\boxed{\frac{1}{\varepsilon(q,\omega)} = 1 + \frac{4\pi e^2}{q^2}\,\chi(q,\omega)}$$

Usually difficult to compute $\chi = \frac{\delta n}{\delta V_{ext}}$ for interacting many-particle system

Often used: mean-field (random phase) approximation = RPA

$$\delta n = \chi\,\delta V_{ext} \simeq \chi_{free}(\delta V_{ext} + \delta V_{ind})$$

response of interacting electrons to external potential ≅ response χ_{free} of <u>non</u>-interacting electrons to full potential (external + induced)

with $\quad \delta V_{ind} = -e\,\phi_{ind} \overset{\text{Poisson}}{=} \frac{4\pi e^2}{q^2}\,\delta n$

$$\Rightarrow \delta n = \chi_{free}\left(\delta V_{ext} + \frac{4\pi e^2}{q^2}\,\delta n\right)$$

$$\Rightarrow \delta n = \chi_{RPA}\,\delta V_{ext} \quad \text{with}$$

$$\boxed{\chi_{RPA}(q,\omega) = \frac{\chi_{free}(q,\omega)}{1 - \frac{4\pi e^2}{q^2}\,\chi_{free}(q,\omega)}}$$

<u>RPA</u> mean-field susceptibility

Implications of denominator (see below)

- pole at $\omega > 0$: collective excitations
- pole at $\omega \to 0$: Instability (charge-density wave, @ $q \neq 0$) etc.

Static screening: Thomas-Fermi model

Simplest model for χ_{free}:

Density $n(\vec{r}_0)$ at given point $\vec{r}_0 \cong$ Density of homogeneous electron gas in potential $V \equiv V(\vec{r}_0)$ ("local density approximation")

homogeneous electron gas: $\left(n_F(x) = \frac{1}{e^{x/k_B T} + 1} \text{ Fermi fct.} \right)$

$$n(V) = \int \frac{d^3k}{(2\pi)^3} \, n_F\left(\frac{\hbar^2 k^2}{2m} + V - \mu \right)$$

$$\Rightarrow \boxed{\chi_{free} \cong -\frac{\partial n}{\partial \mu} \quad \text{Thomas-Fermi}}$$

note: $\frac{\partial n}{\partial \mu}$ = Compressibility

- dielectric function:

$$\varepsilon = \frac{1}{1+\frac{4\pi e^2}{q^2}\chi} = \quad \chi = \frac{\chi_{free}}{1-\frac{4\pi e^2}{q^2}\chi_{free}}$$

$$= 1 - \frac{4\pi e^2}{q^2}\chi_{free} \underset{\text{Thomas-Fermi}}{=} 1 + \frac{4\pi e^2 \frac{\partial n}{\partial \mu}}{q^2}$$

Define Thomas-Fermi wave vector

$$k_{TF}^2 \equiv 4\pi e^2 \frac{\partial n}{\partial \mu} \Rightarrow \boxed{\varepsilon_{TF} = 1 + \frac{k_{TF}^2}{q^2}}$$

- at $T=0$:

$$n = \int_{|k|<k_F} \frac{d^3k}{(2\pi)^3} \quad \text{with} \quad \frac{\hbar^2 k_F^2}{2m} = \mu$$

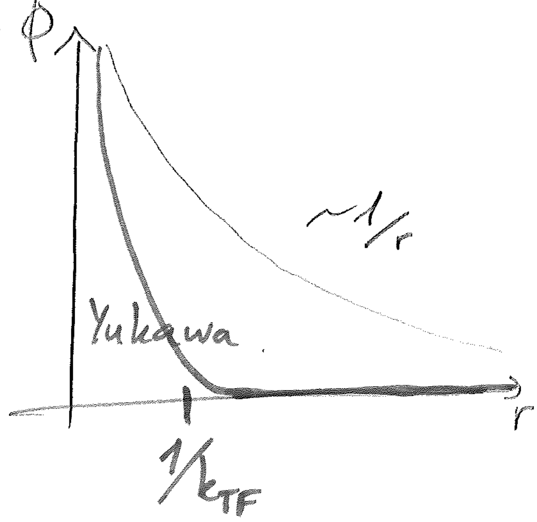
$$\Rightarrow \ldots \quad k_{TF}^2 = \frac{4me^2}{\pi\hbar^2} k_F \Rightarrow$$

$$\frac{1}{k_{TF}} = \mathcal{O}(\text{few Å})$$ for typical densities of mobile electrons in metals

- screened potential of extra point charge (impurity atom, defect in crystal, ...)

$$\phi(\vec{q}) = \underbrace{\frac{4\pi Q}{q^2}}_{\phi_{ext}} \cdot \frac{1}{\varepsilon(\vec{q})} \underset{TF}{=} \frac{4\pi Q}{k_{TF}^2 + q^2}$$

Fourier $\Rightarrow$ $$\boxed{\phi(\vec{r}) = \frac{Q}{r} e^{-r \cdot k_{TF}}}$$



<u>Yukawa potential</u>, screening length $1/k_{TF}$

- more accurate: $\chi_{free}(\vec{q})$: exact response of homogeneous electron gas: <u>Lindhard theory</u>

$s = q/k_F$

$$\chi_{free}(\vec{q}, \omega=0) \overset{d=3}{=} -\frac{2m}{\hbar^2} \frac{k_F}{2\pi^2} \left\{1 - \frac{s}{4}\left(1-\frac{4}{s^2}\right) \ln\left|\frac{s+2}{s-2}\right|\right\}$$

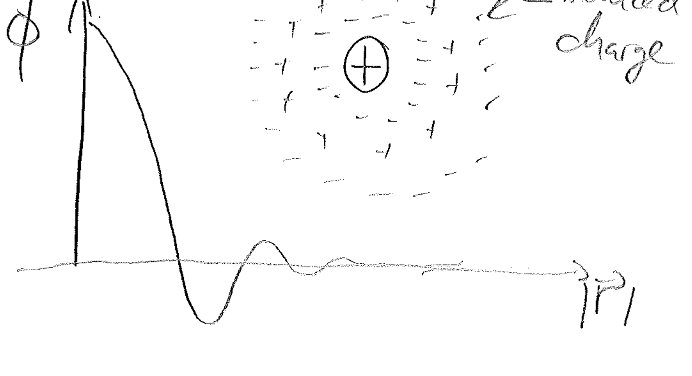
$$\chi_{free}(\vec{q}, \omega=0) \overset{d=2}{=} -\frac{2m}{\hbar^2} \frac{1}{2\pi} \left\{1 - \left(1-\frac{4}{s^2}\right) \Theta(s-2)\right\}$$

$$\chi_{free}(\vec{q}, \omega=0) \overset{d=1}{=} -\frac{2m}{\hbar^2} \frac{1}{2\pi q} \left\{\ln\left|\frac{s+2}{s-2}\right|\right\}$$

$\Rightarrow$ more and more singular at $|q| = 2k_F$ for lower d ($\rightsquigarrow$ instability for $d=1$)

$\Rightarrow$ interference effects (Friedel oscillations)

In $d=3$ @ $T=0$: $$\phi(\vec{r}) = c\,\frac{\cos(2k_F r)}{r^3}$$



Dynamic (frequency-dependent) screening

- Some general properties of response functions

linear response $\hat{H} = \hat{H}_0 + \hat{A} \cdot f(t)$ ← field

(e.g., $\hat{A} = e\hat{n}$ density, $f = \phi_{ext}$)

$$\langle \hat{A}(t) \rangle = \int_{-\infty}^{t'} dt' \, \chi(t-t') f(t')$$

1) Causality $\chi(t) = 0$ for $t<0$

$\Rightarrow$ FT defined for z with $\mathrm{Im}\, z > 0$

$$\chi(\omega) = \lim_{\delta \to 0^+} \chi(\omega + i\delta) = \lim_{\delta \to 0^+} \int_0^\infty dt \, \chi(t) e^{i(\omega + i\delta)t}$$

Meaning: response to perturbation $f(t) = f(\omega) e^{-i\omega t} e^{\delta t}$

$\hat{=}$ adiabatic switch on of field

2) Analytic properties

$\chi(z)$ analytic for $\mathrm{Im}\, z > 0$,

$\chi(z) \to 0$ for $|z| \to \infty$,

imply relation between Re and Im

$$\boxed{\begin{aligned} \chi'(\omega + i0^+) &= \frac{1}{\pi} \fint d\omega' \frac{\chi''(\omega' + i0^+)}{\omega' - \omega} \\ \chi''(\omega + i0^+) &= -\frac{1}{\pi} \fint d\omega' \frac{\chi'(\omega' + i0^+)}{\omega' - \omega} \end{aligned}}$$

Kramers-Kronig relation

example: $\chi = \frac{1}{\omega + i0^+} \Rightarrow \begin{aligned} \chi'' &= -\pi \delta(\omega) \\ \chi' &= \frac{1}{\omega}, \; \omega \neq 0 \end{aligned}$

3) Im χ $\Longleftrightarrow$ energy absorption

Consider $f(t) = e^{\delta t}\left(f(\omega)e^{-i\omega t} + f^{*}(\omega)e^{i\omega t}\right)$

$$E(t) = \langle \hat{H}_0 + \hat{A} f(t) \rangle$$

$$\frac{dE}{dt} \overset{(*)}{=} \left\langle \frac{d\hat{H}}{dt} \right\rangle = \frac{df}{dt} \underbrace{\langle \hat{A}(t) \rangle}_{\chi \cdot f}$$

(*) : Hellmann-Feynman theorem

... insert χ, f ... average over period:

$$\boxed{\frac{d\bar{E}}{dt} = \frac{1}{T}\int_0^T dt\, \frac{dE}{dt} = -2\omega\, \chi''(\omega)\, |f(\omega)|^2}$$

(*) : Hellmann-Feynman:

$$\frac{d}{dt}\langle \psi(t) | \hat{H}(t) | \psi(t) \rangle = \left. \begin{array}{l} \underbrace{\frac{d\langle\psi|}{dt}}_{i\langle\psi|\hat{H}} \hat{H} |\psi(t)\rangle \\ + \langle\psi| \hat{H} \underbrace{\frac{d|\psi\rangle}{dt}}_{-i\hat{H}|\psi\rangle} \end{array} \right\} = 0$$

$$+ \langle \psi | \frac{d\hat{H}}{dt} | \psi \rangle$$

4) Absorption $\Longleftrightarrow$ excitation spectrum

Fermi's golden rule ($T=0$, $\omega>0$):

$$\frac{d\bar{E}}{dt} = \sum_n W_{0\to n}\,(E_f - E_0) \qquad |n\rangle : \text{final states}$$

$$W_{0\to n} = \frac{2\pi}{\hbar} |\langle n|\hat{A}|0\rangle|^2\, \delta(\omega + E_0 - E_n) \qquad \hbar = 1$$

Compare with absorption (incl. $\omega<0$)

$$\chi''(\omega+i0) = -\pi \sum_n |\langle n|\hat{A}|0\rangle|^2 \left[\delta(\omega+E_0-E_n)-\delta(\omega+E_n-E_0)\right]$$

$\underline{T>0:}$

$$\boxed{\chi''(\omega) = -\pi \sum_{nm} \frac{e^{-\beta E_n}-e^{-\beta E_m}}{Z} |\langle n|\hat{A}|m\rangle|^2 \delta(\omega+E_n-E_m)}$$

$\Leftarrow$ Kubo formula

Z: partition function $Z \equiv \sum_n e^{-\beta E_n}$

5) Fluctuations $\longleftrightarrow$ response / dissipation

auto correlator $\langle (A(t)-\langle A\rangle)(A(t')-\langle A\rangle)\rangle$

$$= \langle A(t)\,A(t')\rangle - \langle A\rangle^2$$

$$C(t) \equiv \langle A(t)\,A(0) + A(0)\,A(t)\rangle$$

$$C(\omega) = -2\chi''(\omega)\coth\left(\frac{\beta\omega}{2}\right)$$

Fluctuation-dissipation theorem

universal ratio between fluctuations and response

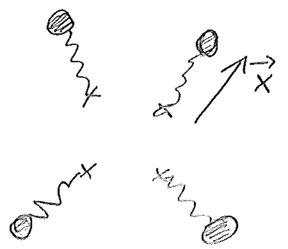
$\Longrightarrow$ "thermometer", fundamentally defines

thermal equilibrium

Back to density response $\quad \chi = \delta n / \delta V_{ext}$

Example 1: **oscillator model**

density n_0 of oscillators



$$m\ddot{\vec{x}} = -m\omega_0^2 \vec{x} + \underbrace{\vec{f}_{ext}}_{-\vec{\nabla} V_{ext}}$$

$$\vec{x}\,(\omega_0^2-\omega^2) = -\frac{1}{m}\vec{\nabla} V_{ext}$$

density: $\quad \delta n / n_0 = -\vec{\nabla}\cdot\vec{x} = \quad \uparrow$

Fourier: $\quad \delta n / n_0 = -i\vec{q}\cdot\vec{x}$

$$\vec{x} = -\frac{1}{m(\omega_0^2-\omega^2)}\, i\vec{q}\, V_{ext}$$

$$\Rightarrow \quad \delta n = \underbrace{q^2 \frac{n_0/m}{\omega^2-\omega_0^2}}_{\chi_{free}} V_{ext}$$

"free": no Coulomb interaction between oscillators, just harmonic potential; OK for low density

$$\chi_{free} = \frac{q^2 n_0}{m}\left(\frac{1}{\omega-\omega_0} - \frac{1}{\omega+\omega_0}\right)\frac{1}{2\omega_0}$$

Really. $\quad \omega \to \omega + i0^+ \quad$ (see above)

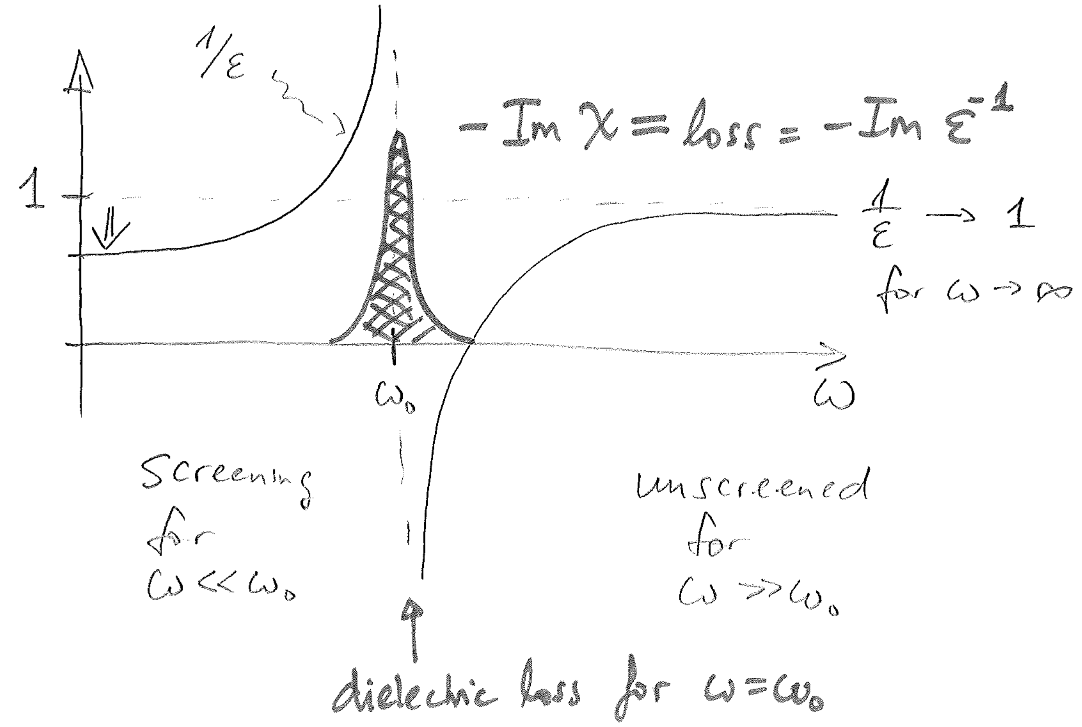
$$\operatorname{Im} \chi_{free}(\omega+i0^+) = -\pi\frac{q^2 n_0}{m}\left[\delta(\omega-\omega_0) - \delta(\omega+\omega_0)\right]$$

$\Rightarrow$ excitation spectrum: excitation of oscillator "quantum" $\hbar\omega_0$

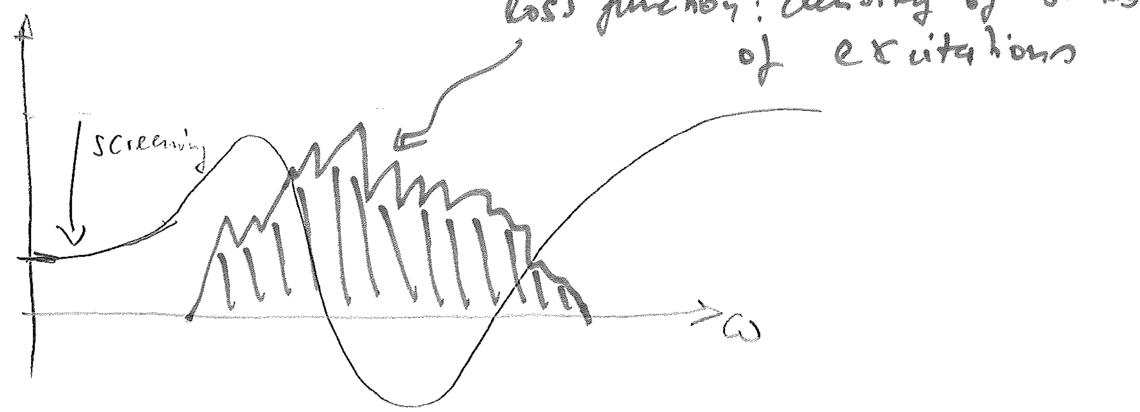
$$\frac{1}{\varepsilon(q,\omega)} = 1 + \frac{4\pi e^2}{q^2} \chi_{free} = 1 + \frac{4\pi e^2 n_0/m}{\omega^2 - \omega_0^2}$$

$4\pi e^2 n_0/m$ has unit $\left[\frac{1}{time^2}\right]$

$4\pi e^2 n_0/m \equiv \omega_p^2$ $\quad$ ω_p : plasma frequency



Real material (insulator) : → dielectrics



=> only true when all particles are bound
(no fully mobile electrons)

"unbound" particles $\omega_0 = 0$

(e.g., electrons in metals)

$$\chi_{free} = q^2 \frac{n_0/m}{\omega^2} \Rightarrow \text{absorption only at } \omega = 0 \text{ ?}$$

with <u>interaction</u> between particles:

$$\chi = \frac{\chi_{free}}{1 - \frac{4\pi e^2}{q^2}\chi_{free}} = \frac{q^2 n_0/m}{\omega^2\left(1 - \frac{4\pi e^2 n_0/m}{\omega^2}\right)}$$

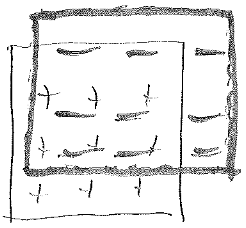
$$= \frac{q^2 n_0/m}{\omega^2 - \omega_p^2}$$

$\omega_p^2 \equiv 4\pi e^2 n_0/m$

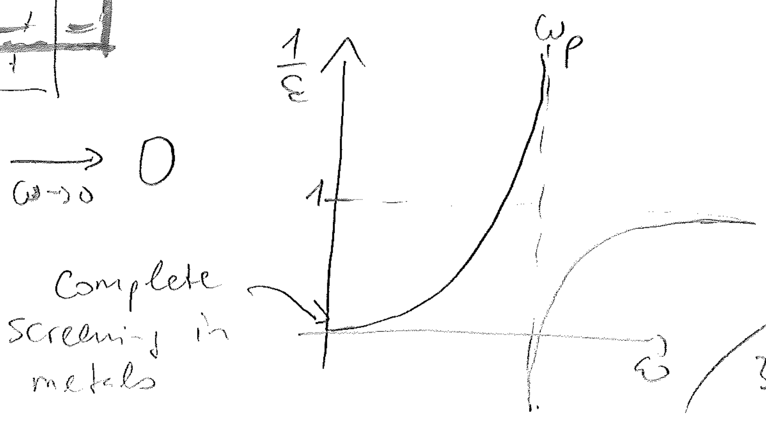
$$\boxed{\chi''(\omega) = -\pi \frac{q^2 n_0/m}{2\omega_p}\left[\delta(\omega-\omega_p) - \delta(\omega+\omega_p)\right]}$$

$\Rightarrow$ new "<u>collective excitation</u>" in system, present <u>only due to e-e interaction</u>

- corresponds to long-lived excitation (oscillation) of mobile electrons against positively charged background

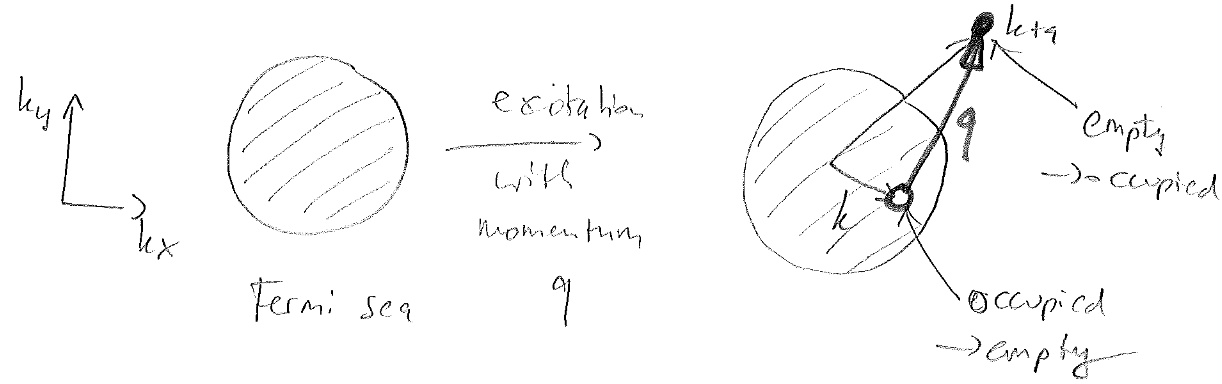


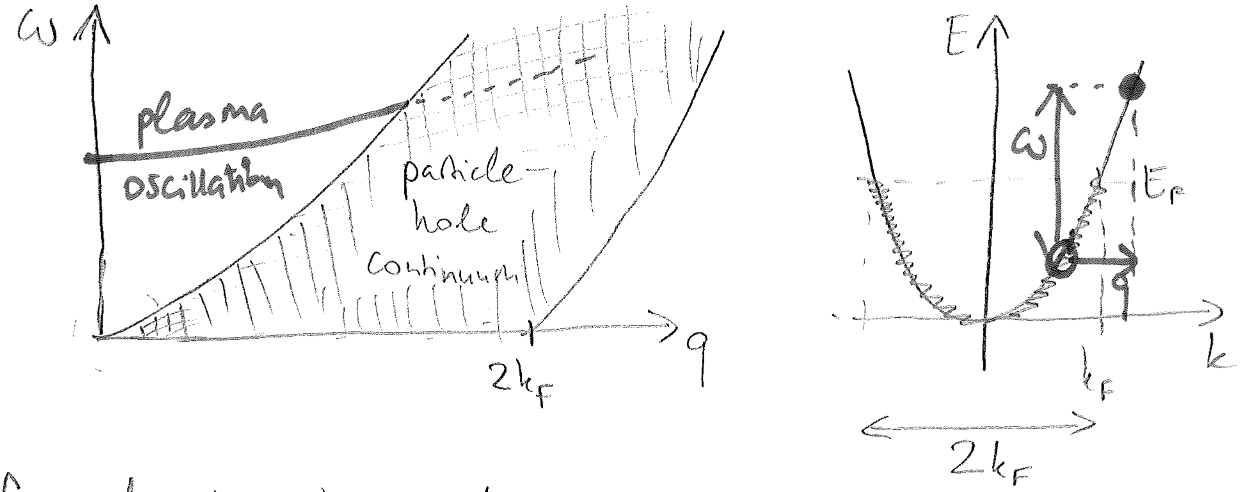
- check: $\frac{1}{\varepsilon} = \frac{\omega^2}{\omega^2 - \omega_p^2} \xrightarrow{\omega \to 0} 0$



• "particle-hole continuum"

Density of particle-hole excitations in solid





for densities of good metals: $\omega_p \sim$ several eV

⇒ short-ranged (well-screened) interaction OK for low-energy processes

Note: Form of collective excitation crucially depends on interaction

What changes when interaction between particles is short-ranged?

e.g., $\phi(r) = \frac{e^{-r/\lambda}}{r} \Leftrightarrow \phi(q) = \frac{4\pi}{q^2 + 1/\lambda^2}$

back to mean-field formula (RPA)

$$\delta n = \chi\, \delta V_{ext} \stackrel{\wedge}{=} \chi_{free} \left(\delta V_{ext} + \delta V_{ind}\right)$$

<u>now:</u> $$V_{ind} = \frac{4\pi e^2}{q^2 + 1/\lambda^2}\, \delta n$$

Solution of Poisson eq. with extra screening

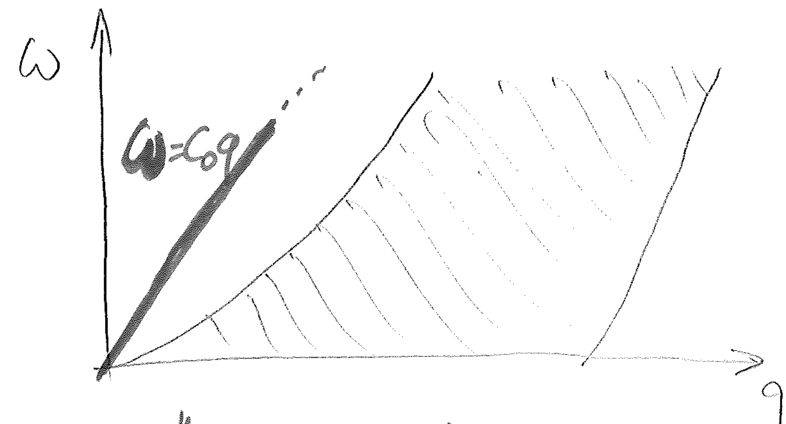
$$\chi = \frac{\chi_{free}}{1 - \frac{4\pi e^2 \lambda^2}{(q\lambda)^2 + 1} \chi_{free}} \xrightarrow{q \to 0} \frac{\chi_{free}}{1 - \frac{4\pi e^2 \lambda^2 q^2 n_0/m}{\omega^2}}$$

$$= \frac{q^2\, n_0/m}{\omega^2 - 4\pi e^2 \lambda^2 (n_0/m)\, q^2}$$

$\Rightarrow$ now there is a <u>pole</u> at $\omega = c_0 |q|$

$$c_0 = \sqrt{4\pi e^2 (n_0/m) \lambda^2} = \omega_p \lambda$$

$\Rightarrow$ sound-like dispersion



<u>"zero sound"</u> $\stackrel{\wedge}{=}$ collective excitation in Fermi system with short-ranged interaction