Ab-Initio Phonon Coupling & optical Response of hot electrons in plasmonic Metals. 2016

$$g(\varepsilon) = \int \frac{dk}{(2\pi)^3} \sum_n \delta(\varepsilon - \varepsilon_{n,k}) \text{ (per unit volume)}$$

$$C_e(T_e) = \int_{-\infty} d\varepsilon \, g(\varepsilon)\, \varepsilon \, \frac{\partial f(\varepsilon, T_e)}{\partial T_e} ,$$

$$g(\varepsilon) = \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{2\pi^2} \sqrt{\varepsilon} \, , \; g(\varepsilon) \cong g(\varepsilon_F) + g'(\varepsilon_F)(\varepsilon - \varepsilon_F)$$

$$\frac{\partial f}{\partial T} = \frac{\partial}{\partial T} \frac{1}{e^{\varepsilon/k_B T}+1} = \frac{+(\varepsilon-\mu)}{k_B T^2} \frac{1}{\left(e^{(\varepsilon-\mu)/k_B T}+1\right)^2} \times e^{\varepsilon/k_B T} \Rightarrow$$

$$C(T_e) \cong \frac{\varepsilon_F (2m)^{3/2}}{\hbar^3} \frac{1}{2\pi^2} \frac{1}{2\sqrt{\varepsilon_F}} \int \frac{x}{(x+1)^2} \, d\varepsilon \, \frac{(\varepsilon-\mu)^2}{k_B T^2}$$

Check energy shift invariance:

$$\frac{x}{(x+1)^2} \text{ when } \varepsilon - \mu \to \mu - \varepsilon \quad \frac{1/x}{(1/x+1)^2} = \frac{x}{x^2(1/x+1)^2}$$

$$= \frac{x}{(x+1)^2}$$ ✓ Therefore, $f'(\varepsilon, T)$ (WRT temperature) is odd WRT $\boxed{\varepsilon = \mu}$ (as expected).

Now $$\int \frac{e^y}{(e^y+1)^2} k_B y^2 dy ,$$

Review: $$E(T) = E(T=0) + \underbrace{\left[g(\varepsilon_F) k_B T\right]}_{\text{\# of new electrons at excited ...}} k_B T$$

$$\Rightarrow \partial E \sim 2 g(\varepsilon_F) k_B^2 T \propto T$$ ✓

∂T

$N = \frac{2}{3} \varepsilon_F g(\varepsilon_F)$. Proof: $N = 2\sum_{k<k_F} 1 =$

$\frac{2V}{(2\pi)^3}\int_0^{k_F} d^3k = \frac{V}{4\pi^3}\left(\frac{4}{3}\pi k_F^3\right) = \frac{V}{3\pi^2} k_F^3$

$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m_e}$, $g(\varepsilon) \Rightarrow \frac{2V}{(2\pi)^3}(4\pi)k^2 dk \Rightarrow$

$\boxed{\frac{V}{\pi^2} k^2 = \frac{dN}{dk}}$, $\frac{dN}{d\varepsilon} = \frac{dN}{dk}\frac{dk}{d\varepsilon} = \frac{Vk^2}{\pi^2}\frac{1}{\frac{\hbar^2}{m}k} =$

$\frac{Vk}{\pi^2}\frac{m}{\hbar^2} = \frac{V}{\pi^2}\frac{m}{\hbar^2}\sqrt{\frac{2m}{\hbar^2}\varepsilon}$

$N = \frac{V}{3\pi^2}k_F^3 = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon_F}{\hbar^2}\right)^{3/2} \stackrel{?}{=} \frac{2}{3}\left(\frac{V}{\pi^2}\frac{m}{\hbar^2}\sqrt{\frac{2m\varepsilon}{\hbar^2}} \times \varepsilon\right)$

$\Rightarrow \frac{1}{3\pi^2}\frac{2^{3/2} m^{3/2} \varepsilon_F^{3/2}}{\hbar^3} = \frac{2^{3/2}}{3}\frac{1}{\pi^2}\frac{m^{3/2}\varepsilon_F^{3/2}}{\hbar^3}$ ✓

Heat capacity of free electron gas in 3D scales as T

Phonons: $D(\varepsilon) = \int \frac{dq}{(2\pi)^3}\sum_\alpha \delta(\varepsilon - \hbar\omega_q^\alpha) \Rightarrow$

Debye model: $\omega_{q\alpha} = v_\alpha q$ for $q \in (0, q_D) \rightarrow$

q_D

$$D(\varepsilon) = \int \frac{dq}{(2\pi)^3} \sum_{\alpha}' \delta(\varepsilon - \hbar v_\alpha q) =$$

$$\frac{1}{2\pi^2}\int_0^{q_D} q^2 \sum_{\alpha}' \delta(\varepsilon - \hbar v_\alpha q) = \frac{1}{2\pi^2 \hbar v_\alpha}\left(\frac{\varepsilon}{\hbar v_\alpha}\right)^2$$

$$= \frac{\varepsilon^2}{2\pi^2}\frac{1}{\hbar^3}\frac{1}{v_\alpha^3} \checkmark$$ (Must sum over different α branches in the end however)

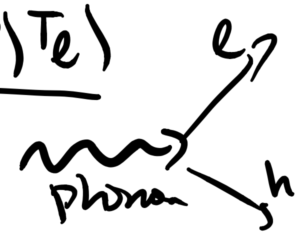
Rate of energy transfer from electrons to lattice:

$$\frac{dE}{dt} = \frac{2\pi}{\hbar}\int_{BZ} \frac{\Omega\, dk\, dk'}{(2\pi)^6} \sum_{n,n',\alpha}' \delta(\varepsilon_{k'n'} - \varepsilon_{kn} - \hbar\omega_{k-k',\alpha})$$

$$\times\, \hbar\omega_{k'-k,\alpha} \left|g^{k'-k,\alpha}_{k'n',kn}\right|^2 \left(f(\varepsilon_{kn},T_e) - f(\varepsilon_{k'n'},T_e)\right) \times$$

$$\underline{n(\hbar\omega_{k'-k,\alpha},T_e) - n(\hbar\omega_{k'-k,\alpha},T_e)}$$

Two processes are possible:



One

coupling is of form $\sum' c^\dagger_{k+q} c_k (b_q + b^\dagger_{-q}) g_q$

$\Longrightarrow$ now we know that $c_k^\dagger |\psi\rangle = \sqrt{1-f_k}\, |n_k+1\rangle$

$c_k|\psi\rangle = \sqrt{f_k}\, |\psi, n_k - 1\rangle$, and $b_q^\dagger |\psi\rangle = \sqrt{1+n_q}\, |n_q+1\rangle$

and $b_q |\psi\rangle = \sqrt{n_q}\ |n_q - 1\rangle$

Therefore, total energy transfer is given by:

$$\frac{2\pi}{\hbar} \sum_{k,k'} f_k(1-f_{k'})\ \hbar\omega_{k'-k} \left(1+n_q - n_{-q}\right)$$

Note that $\int \frac{dk\,dk'\,\Omega}{(2\pi)^6} = \frac{1}{\Omega} \iint dk\,dk' \frac{\Omega^2}{(2\pi)^6} =$

$$\frac{1}{\Omega}\left(\frac{1}{\Omega_{BZ}^2}\int dk\,dk'\right) = \frac{1}{\Omega}\ \underbrace{\frac{1}{N_k N_{k'}} \sum_{k,k'}}_{\text{averaging over Brillouin zone}}$$

The $\frac{1}{N_k}, \frac{1}{N_{k'}}$ come from matrix element.

$$V \int \frac{\Omega\, dk\, dk'}{(2\pi)^6} = N_k \Omega^2 \int \frac{dk\,dk'}{(2\pi)^6} = \frac{N_k}{\Omega_{BZ}^2} \iint =$$

$= \frac{1}{N_{k'}} \sum_{k,k'}$, The $1/N_{k'}$ comes from $|g|^2$

$$\operatorname{Im} \varepsilon(\omega) = \frac{4\pi\sigma_0}{\omega(1+\omega^2\tau^2)} + \operatorname{Im}\varepsilon_{direct}(\omega) + \operatorname{Im}\varepsilon_{phonon}(\omega)$$

Citation: Phonon assisted optical absorption in silicon from first principles. Cohen, Louie 2012

Si direct band gap: 3.4 eV. indirect bandgap: 1.1 eV

$$\alpha(\omega) = \frac{2\pi e^2}{\varepsilon_0 \omega c n(\omega)} \frac{1.\Omega}{\Omega} \int \frac{d^3k\, \delta^3}{(2\pi)^6} \left[\lambda \cdot (s_1 + s_2) \right]$$

$\times (n_{q,\nu} + 1/2 \pm 1/2)(f_{ik} - f_{j,k+q})$

<u>Check:</u> $H = \sum_i \frac{1}{2m} \left(p_i + e \underline{A(r_i,t)} \right)^2$

Note that since $A \sim e^{ik \cdot r_i} \hat{\varepsilon} (a_k + a_k^\dagger)$,

$\nabla \cdot A = 0 \Rightarrow \hat{k} \cdot \hat{\varepsilon} = 0$ ~~and $[p, A] = 0$~~

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in semi-classical approximation, we get

$$P_{\nu k_i s_i \to c, k_f, s_f} = \frac{2\pi}{\hbar} \left(\frac{eA_0}{mc} \right)^2 \delta_{s_i, s_f} \left| \langle \psi_{ck_f} | e^{iq \cdot r} e \cdot p | \psi_{ck_i} \rangle \right|^2$$

$\delta(\varepsilon_f - \varepsilon_i - \hbar\omega)$

Must have that $\boxed{k_f = k_i + q + h}$ reciprocal lattice vector

in quantized form, get something like

$$\frac{2\pi}{\hbar} \left(\frac{e}{mc} \right)^2 \left(\frac{1}{\varepsilon_0 V \hbar\omega} \right) \delta_{s_i, s_f} \left| \langle \psi_{ck_f} | e^{iq \cdot r} e \cdot p | \psi_{c,k} \rangle \right|^2$$

$\Rightarrow$ total absorption must integrate over ~~the~~ whole Brillouin zone:

$$\frac{2\pi}{\hbar} \left(\frac{e}{mc} \right)^2 \left(\frac{1}{\varepsilon_0 \hbar\omega} \right) \int \frac{d^3k}{(2\pi)^3} \left| \langle \psi_{ck} | \hat{\varepsilon} \cdot p | \psi_{\nu k} \rangle \right|^2$$

<u>Optical constants</u>: $\alpha = \frac{2k\omega}{c}$, $\alpha = \frac{\omega}{nc} \varepsilon_2$

$\alpha(\omega) = \frac{\hbar\omega\, W(\omega)}{u(c/n)}$ c/n is speed of light in medium, $u \sim \frac{\epsilon_0}{2}|E|$

Multiphoton processes:

$$\frac{2\pi}{\hbar}\left|\sum_m \frac{\langle f|V|m\rangle\langle m|V|i\rangle}{\varepsilon_m - \varepsilon_i - \hbar\omega}\right|^2 \delta(\varepsilon_f - \varepsilon_i - \hbar\omega)$$

where $\varepsilon_f, \varepsilon_i$ are electron energies of final, initial states, respectively.

$$\frac{2\pi}{\hbar}\left(\frac{eA_0^1}{mc}\right)^2\left(\frac{eA_0^2}{mc}\right)^2\left|\frac{e_2\cdot M_{c\beta}(k)\, e_1\cdot M_{\beta v}(k)}{E_\beta - E_v - \hbar\omega_1} + \frac{e_1\cdot M_{c\beta}\; e_2\cdot M_{\beta v}}{E_\beta - E_v - \hbar\omega_2}\right|^2 \delta(E_c - E_v - \hbar\omega_1 - \hbar\omega_2)$$

Energy density in $\frac{n^2E^2}{4\pi} = \epsilon_0 E^2$

Indirect Band to Band transitions:

List of materials: Silicon, Germanium, AgCl