6.730 Physics for Solid State Applications

Lecture 25: Chemical Potential and Non-equilibrium

Outline

- Fermi Integrals and Approximations
- Rate Equations for Non-equilibrium Electrons
- Quasi-Fermi Levels

Counting and Fermi Integrals

3-D Conduction Electron Density

$$N = \int_{E_c}^{\infty} \rho_c(E) f(E) dE$$

$$f(E) = \frac{1}{1 + \exp\left(\frac{E-\mu}{k_B T}\right)}$$

$$\rho_c(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_c}$$

$$N = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\int_{E_c}^{\infty}\frac{\sqrt{E}}{1 + \exp\left(\frac{E-\mu}{k_B T}\right)} dE$$

$$= \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\int_{E_c}^{\infty}\frac{\sqrt{y}\sqrt{k_B T}}{1 + e^{y-v}}\, k_B T dy$$

$$y = \frac{E - \mu}{k_B T}$$

$$v = \frac{\mu - E_c}{k_B T}$$

$$= \frac{2}{\sqrt{\pi}} 2\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2}\int_{E_c}^{\infty}\frac{\sqrt{y}}{1 + e^{y-v}}\, dy$$

$$= \frac{2}{\sqrt{\pi}} N_c F_{1/2}$$

Counting and Fermi Integrals

3-D Hole Density

$$P = \int_{-\infty}^{E_v} \rho_v(E)(1 - f(E))dE$$

$$P_{hh} = \frac{2}{\sqrt{\pi}} 2 \left(\frac{m_{hh}^* k_B T}{2\pi\hbar^2}\right)^{3/2} F_{1/2}\left(\frac{E_v - \mu}{k_B T}\right)$$

$$P_{lh} = \frac{2}{\sqrt{\pi}} 2 \left(\frac{m_{lh}^* k_B T}{2\pi\hbar^2}\right)^{3/2} F_{1/2}\left(\frac{E_v - \mu}{k_B T}\right)$$

$$m_{hh}^*|_{\mathrm{GaAs}} = 0.51\, m \qquad m_{lh}^*|_{\mathrm{GaAs}} = 0.087\, m$$

$$\frac{P_{lh}}{P_{hh}} = \left(\frac{m_{hh}^*}{m_{lh}^*}\right)^{3/2} \approx \left(\frac{0.51}{0.87}\right)^{3/2} = 13.7$$

$$(m_{\mathrm{eff}}^*)^{3/2} = (m_{hh}^*)^{3/2} + (m_{lh}^*)^{3/2}$$

Boltzmann Approximation

$$N_o = \frac{2}{\sqrt{\pi}} N_c F_{1/2}\left(\frac{E_{F_o} - E_c}{k_B T}\right) = \frac{2}{\sqrt{\pi}} N_c F_{1/2}(v)$$

Boltzmann Approximation: $F_{1/2}(v) \approx \frac{\sqrt{\pi}}{2} e^v$

$$N_o = \frac{2}{\sqrt{\pi}} N_c F_{1/2}\left(\frac{E_{F_o} - E_c}{k_B T}\right) \rightarrow N_c \exp\left(\frac{-(E_c - E_{F_o})}{k_B T}\right)$$

$$P_o = \frac{2}{\sqrt{\pi}} N_v F_{1/2}\left(\frac{E_v - E_{F_o}}{k_B T}\right) \rightarrow N_v \exp\left(\frac{-(E_{F_o} - E_v)}{k_B T}\right)$$

$$N_o P_o = N_c N_v \exp\left(\frac{-(E_c - E_v)}{k_B T}\right) = N_c N_v \exp\left(\frac{-E_g}{k_B T}\right) = N_i^2$$

Approximations for Fermi Integrals

3-D Carrier Densities

$$N_o = \frac{2}{\sqrt{\pi}} N_c F_{1/2}\left(\frac{E_{F_o} - E_c}{k_B T}\right) = \frac{2}{\sqrt{\pi}} N_c F_{1/2}(v) \qquad v = \frac{E_{F_o} - E_c}{k_B T}$$

Sommerfeld Approximation:

$$F_{1/2}(v) \approx \frac{2}{3} v^{3/2} \left[a_1 + a_2 v^{-2} + \ldots\right]$$

$$a_1 = 1 \qquad a_2 = \frac{\pi^2}{8} \approx 1.2337$$

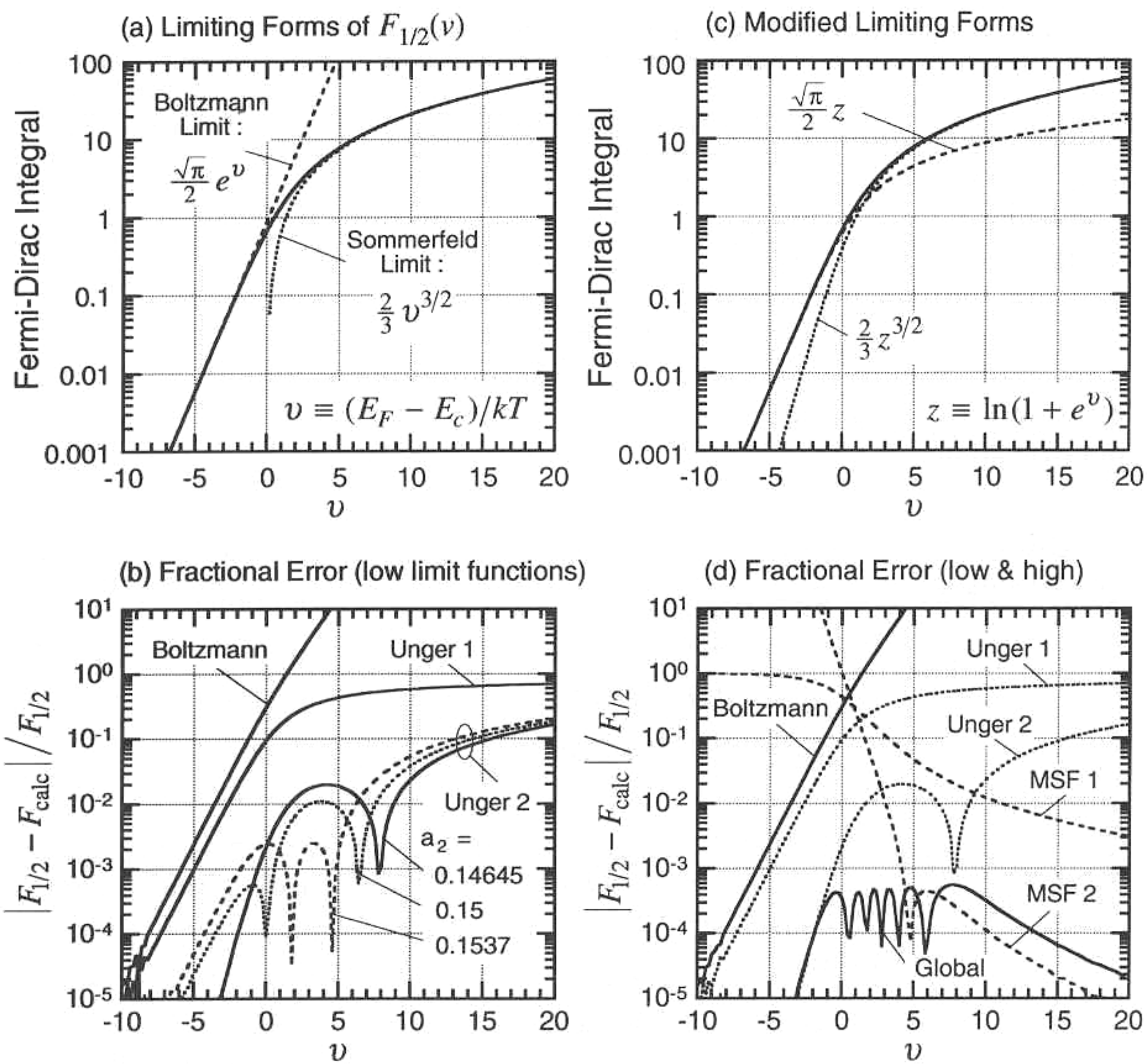
Unger Approximation:

$$F_{1/2}(v) \approx \frac{\sqrt{\pi}}{2} z \left[a_1 + a_2 z + \ldots\right] \quad \text{where} \quad z = \ln(1 + e^v)$$

$$a_1 = 1 \qquad a_2 = \frac{1}{2}\left(1 - \frac{1}{\sqrt{2}}\right) \approx 0.14645$$

Approximations for Fermi Integrals

3-D Carrier Densities



Approximations for Inverse Fermi Integrals

$$r = \frac{N}{N_c} \qquad v = \frac{E_{F_o} - E_c}{k_B T}$$

Inverse First-order Sommerfeld Approximation:

$$v \approx \left(\frac{3\sqrt{\pi}}{4} r\right)^{3/2} \qquad v > 20$$

for 0.04 error

Inverse Second-order Unger Approximation:

$$v \approx \ln(\exp(\frac{1}{2a_2}(\sqrt{1 + 4a_2 r} - 1)) - 1)$$

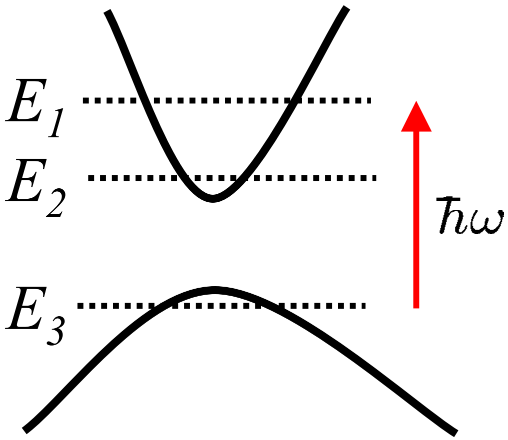
$$a_2 = 0.146545 \qquad v < 2.8$$

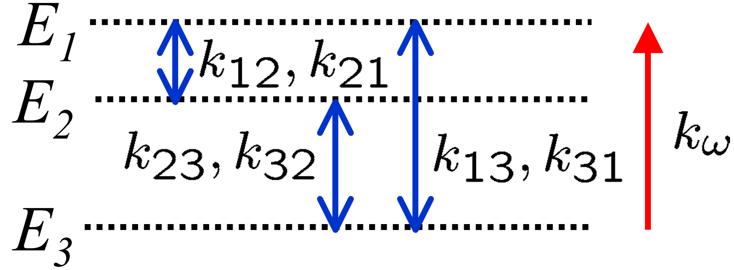
$$a_2 = 0.15 \qquad v < 7.4$$

for 0.04 error

Near Equilibrium Electron Distributions

Optical Excitation





k_{12}, k_{21}	Intraband scattering:	electron-electron electron-acoustic phonon
k_{23}, k_{32} k_{13}, k_{31}	Interband scattering:	electron-hole electron-phonon with defects

What are f_1, f_2, & f_3 under illumination (non-equilibrium) ?

Rate Equation Formalism

number of electrons = number of states x probability of occupancy

$$n_1 = N_1 f_1 \qquad n_2 = N_2 f_2 \qquad n_3 = N_3 f_3$$

$$\frac{dn_1}{dt} = -k_{12} N_1 f_1 N_2(1-f_2) + k_{21} N_2 f_2 N_1(1-f_1)$$

$$-k_{13} N_1 f_1 N_3(1-f_3) + k_{31} N_3 f_3 N_1(1-f_1) + k_\omega N_3 f_3 N_1(1-f_1)$$

$$\frac{dn_2}{dt} = +k_{12} N_1 f_1 N_2(1-f_2) - k_{21} N_2 f_2 N_1(1-f_1)$$

$$-k_{23} N_2 f_2 N_3(1-f_3) + k_{32} N_3 f_3 N_2(1-f_2)$$

$$\frac{dn_3}{dt} = -\left(\frac{dn_1}{dt} + \frac{dn_2}{dt}\right)$$

assume total number of electrons in N_1, N_2, & N3 is contant

Rate Constants in Equilibrium

Detailed Balance

In equilibrium: $f^o(E) = \dfrac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$

Detailed balance:

In equilibrium, each scattering process balances with its inverse

$$k_{12}\, N_1 f_1^o\, N_2 (1 - f_2^o) = k_{21}\, N_2 f_2^o\, N_1 (1 - f_1^o)$$

$$k_{21} = k_{12} \frac{f_1^o}{(1 - f_1^o)} \frac{(1 - f_2^o)}{f_2^o}$$

$$= k_{12}\, e^{-(E_1 - E_F)/k_B T}\, e^{(E_2 - E_F)/k_B T}$$

$$= k_{12}\, \underbrace{e^{-(E_1 - E_2)/k_B T}}_{A_{12}}$$

$$k_{21} = k_{12}\, A_{12} \qquad k_{32} = k_{23}\, A_{23} \qquad k_{31} = k_{13}\, A_{13}$$

Rate Equations

Assume the rate constants don't change out of equilibrium…

$$N_1 \frac{df_1}{dt} = -k_{12}\, N_1\, N_2\, [f_1(1 - f_2) + A_{12}\, f_2\, (1 - f_1)]$$

$$-k_{13}\, N_1\, N_3\, [f_1(1 - f_3) + A_{13}\, f_3\, (1 - f_1)] + k_\omega\, N_3\, N_1 f_3 (1 - f_1)$$

$$N_2 \frac{df_2}{dt} = +k_{12}\, N_1 N_2\, [f_1\, (1 - f_2) - A_{12}\, f_2\, (1 - f_1)]$$

$$-k_{23}\, N_2\, N_3\, [f_2(1 - f_3) + A_{23}\, f_3\, (1 - f_2)]$$

Steady-State Solutions
Non-equilibrium

$$\frac{dn_3}{dt} = \frac{dn_1}{dt} = \frac{dn_2}{dt} = 0$$

$$\frac{f_1\,(1-f_2) - A_{12}\,f_2\,(1-f_1)}{f_2(1-f_3) + A_{23}\,f_3\,(1-f_2)} = \frac{k_{23}}{k_{12}}\frac{N_3}{N_1}$$

For example when intraband scattering is much faster than interband scattering…

$$N_1 \sim N_3 \qquad\qquad k_{12} \gg k_{31}, k_{23}$$

$$f_1\,(1-f_2) - A_{12}\,f_2\,(1-f_1) \approx 0$$

$$\frac{f_1}{(1-f_1)} \approx A_{12}\frac{(1-f_2)}{f_2}$$

Steady-State Solutions

Non-equilibrium

Equilibrium Fermi-Dirac distribution:

$$f^o(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$$

Non-equilibrium Quasi-Fermi-Dirac distribution:

$$f_i(E_i) = \frac{1}{1 + \exp\left(\frac{E_i - E_{F_i}}{k_B T}\right)}$$

$$\frac{f_1}{(1 - f_1)} \approx A_{12} \frac{(1 - f_2)}{f_2}$$

$$e^{-(E_1 - E_{F_1})/k_B T} \approx e^{-(E_1 - E_2)/k_B T} \, e^{(E_2 - E_{F_2})/k_B T}$$

$$E_{F_1} \approx E_{F_2}$$

Intraband states have same chemical potential

→ in ‘equilibrium’ with each other because of fast intraband scattering

Steady-State Solutions

Non-equilibrium

$$N_1 \frac{df_1}{dt} \to 0 = -k_{12}\, N_1\, N_2\, [f_1(1 - f_2) + A_{12}\, f_2\, (1 - f_1)]$$

$$-k_{13}\, N_1\, N_3\, [f_1(1 - f_3) + A_{13}\, f_3\, (1 - f_1)] + k_\omega\, N_3\, N_1 f_3 (1 - f_1)$$

$$E_{F_3} = E_{F_1} - k_B T \ln \left[\frac{k_\omega e^{(E_1 - E_3)/k_B T} + A}{A} \right]$$

$$A = k_{13} + \frac{N_2}{N_1} k_{21} e^{(E_1 - E_2)/k_B T}$$

Interband states have different chemical potentials

unless $k_\omega \to 0$ $E_{F_3} = E_{F_1}$

Counting in Non-equilibrium Semiconductors

Equilibrium

$$N_o = N_c \exp\left(\frac{-(E_c - E_{F_o})}{k_B T}\right)$$

$$P_o = N_v \exp\left(\frac{-(E_{F_o} - E_v)}{k_B T}\right)$$

$$N_o P_o = N_c N_v \exp\left(\frac{-E_g}{k_B T}\right) = N_i^2$$

Quasi-equilibrium

$$N \approx N_c \exp\left(\frac{-(E_c - E_{F_c})}{k_B T}\right)$$

$$P \approx N_v \exp\left(\frac{-(E_{F_v} - E_v)}{k_B T}\right)$$

$$NP = N_i^2 \exp\left(\frac{-(E_{F_c} - E_{F_v})}{k_B T}\right)$$