Review of Last Lecture

- Seebeck effect
- Peltier effect
- Thomson effect
- Device analysis
- Figure of merit ZT
- Applications

Thermoelectric Figure of Merit

Electrical Conductivity

Seebeck Coefficient

$$ZT = \frac{\sigma S^2 T}{k} = \frac{\sigma S^2 T}{k_p + k_e}$$

Thermal Conductivity

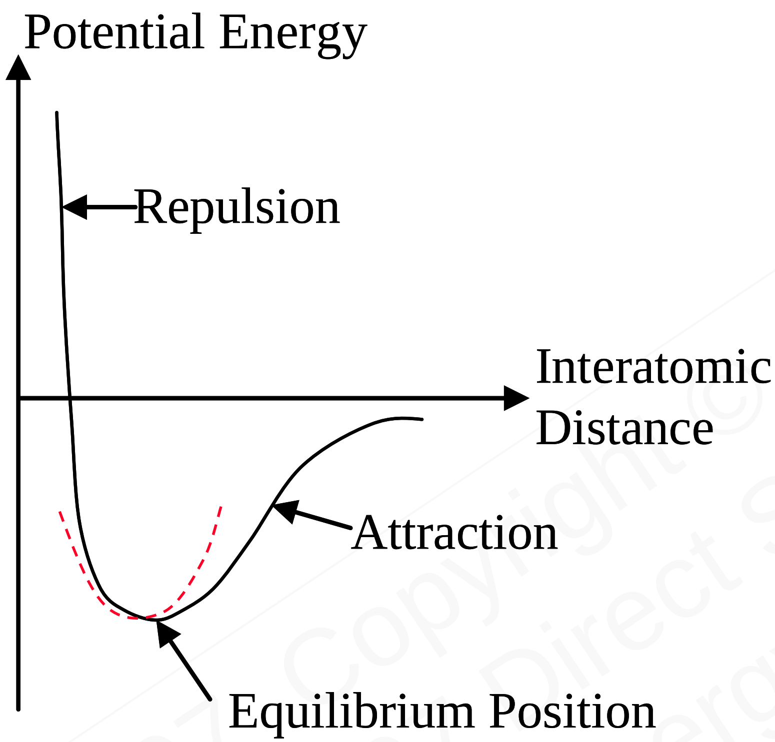
Phonon Contribution

Electron Contribution

Microscopic Formulation of Thermoelectric Properties

- Review of basic concepts in solid states
- Simple kinetic formulation
- Results from formal transport theory

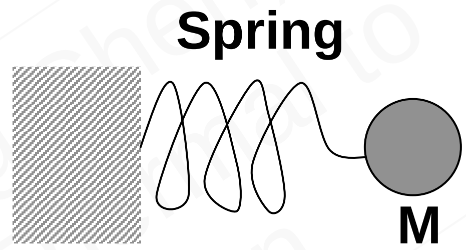
Atomic Vibration



$$U \approx U_o + K\left(x - x_o\right)^2$$

$$F = -\frac{dU}{dx} = -K(x - x_o)$$

- **Classical Oscillator**



Natural Frequency

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{M}}$$

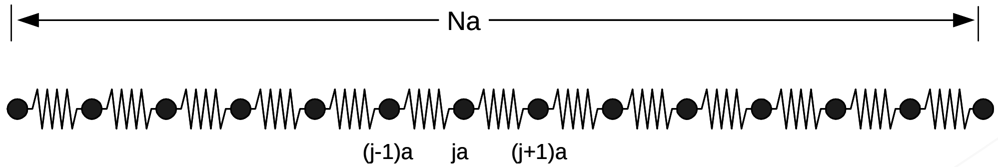
- **From Quantum Mechanics Energy of Mode**

$$E = \left(n + \frac{1}{2}\right)h\nu \quad \mathrm{n} = 0, 1, 2...$$

- **Basic vibrational energy quanta hν is called a phonon**

1D Atomic Chain

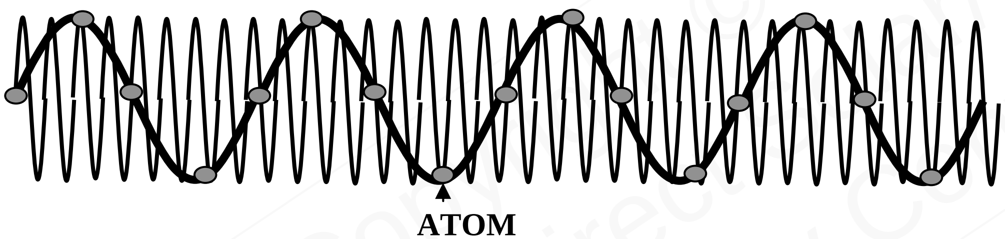
Monatomic



Allowable wavelength $$Na = \frac{\lambda}{2}, 2\frac{\lambda}{2}, \ldots\ldots,$$

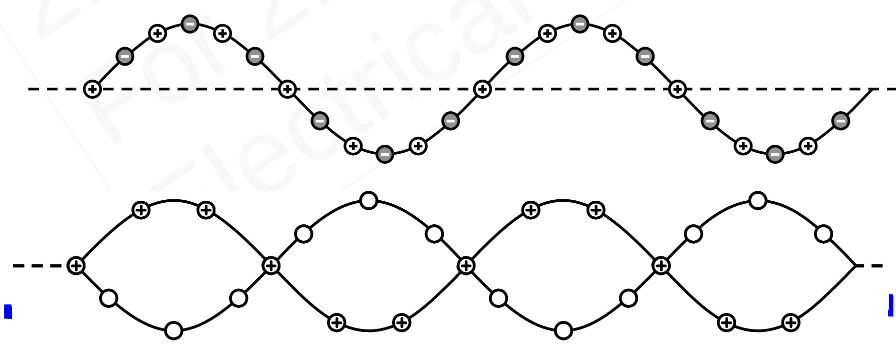
$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{2Na}, \ldots\ldots, \frac{(N-1)a\pi}{2Na}, \frac{\pi}{2a}, \ldots\ldots$$

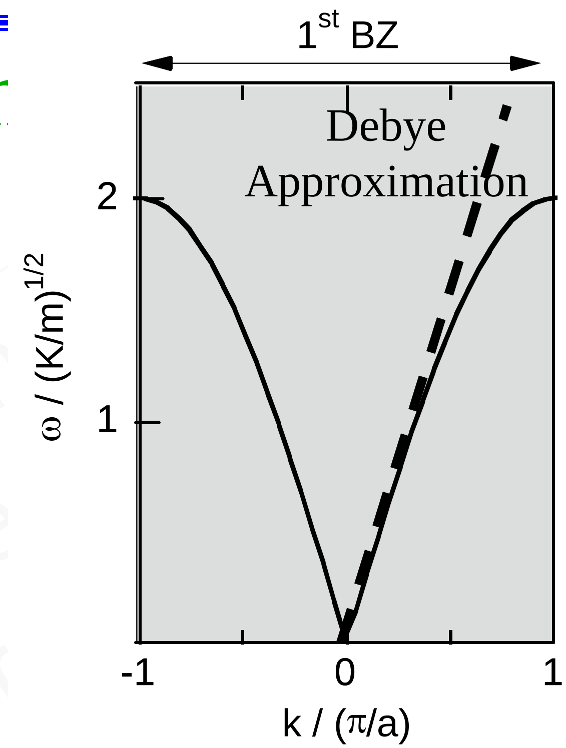
Standing Wave Picture

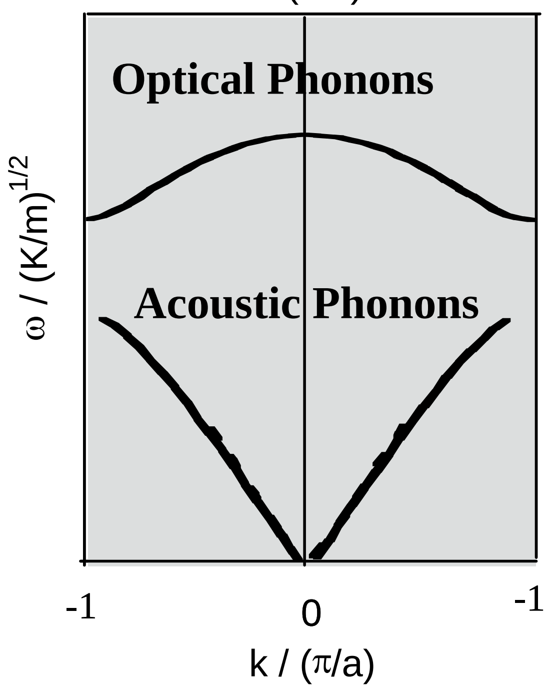


$$k = \frac{2\pi}{\lambda} = -\frac{\pi}{a}, -\frac{(N-1)a\pi}{Na}, \ldots\ldots, \frac{(N-1)a\pi}{Na}, \frac{\pi}{a}$$

Diatomic

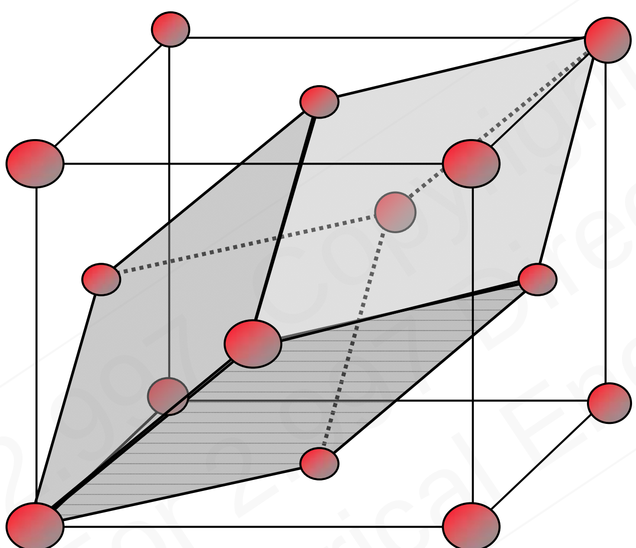






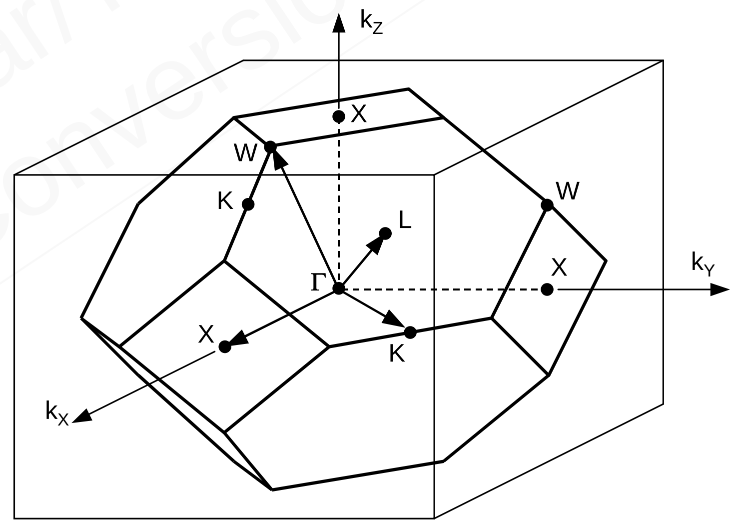
Unit Cell in Real and Reciprocal Spaces

- Periodic signal in time with period T, Fourier transform gives a frequency $\nu=2\pi/T$,
- Periodic signal in space with wavelength λ, Fourier transform gives $2\pi/\lambda$.



Crystal unit cell in real space

Fourier Transform

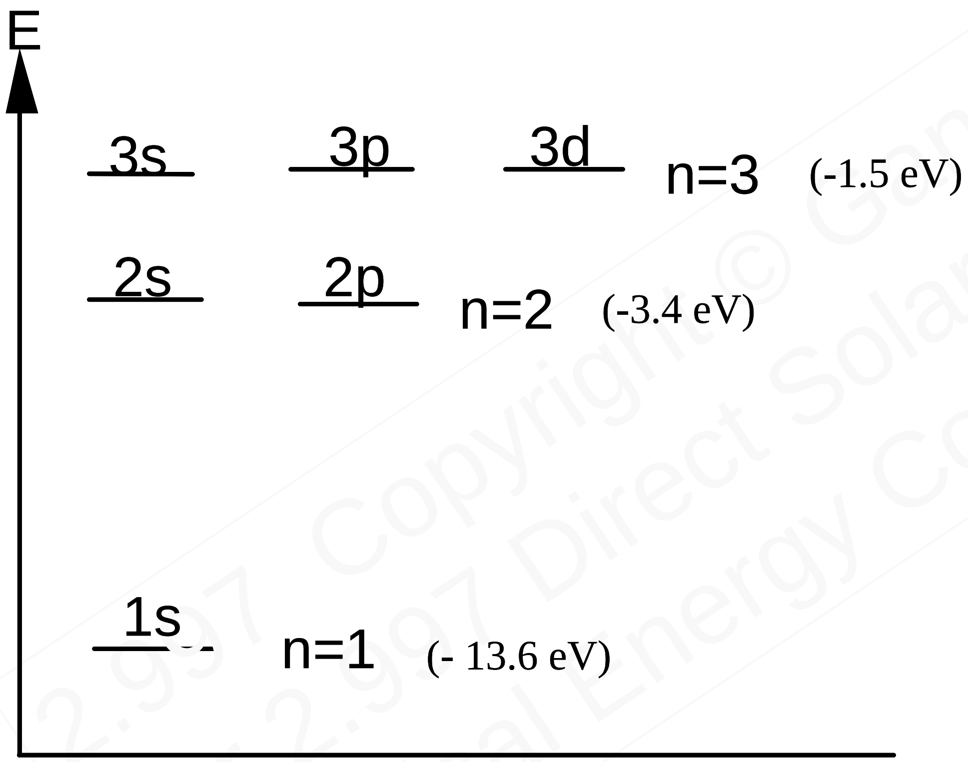


Reciprocal Space

Phonons Dispersion in Crystals

Image removed due to copyright restrictions.
Please see Fig. 1a and 2a in Giannozzi, Paolo, et al.
"*Ab initio* Calculation of Phonon Dispersions in Semiconductors."
Physical Review B 43 (March 1991): 7231-7242.

Electronic Energy Levels



Hydrogen Atom

- **Wavefunction**

$$\Psi_{n\ell ms}(r,\theta,\varphi)$$

$$n = 1, 2, 3, \ldots$$

$$\ell < \mathrm{n}$$

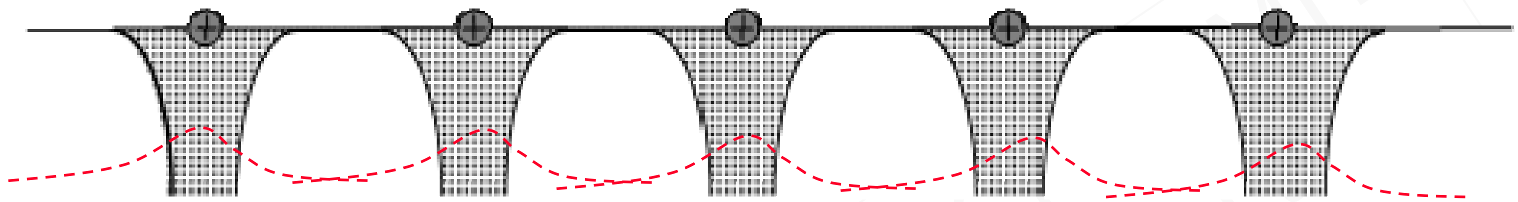
$$|\mathrm{m}| \le \ell$$

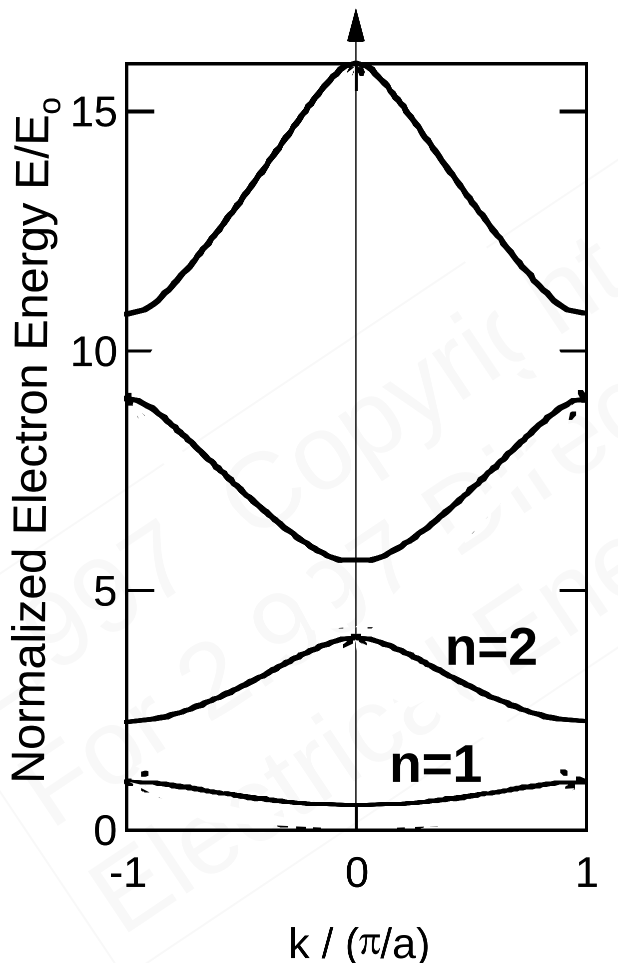
$$s = \pm\frac{1}{2}$$

- **Degeneracy**

$$D = 2n^2$$

Electrons in an Atomic Chain



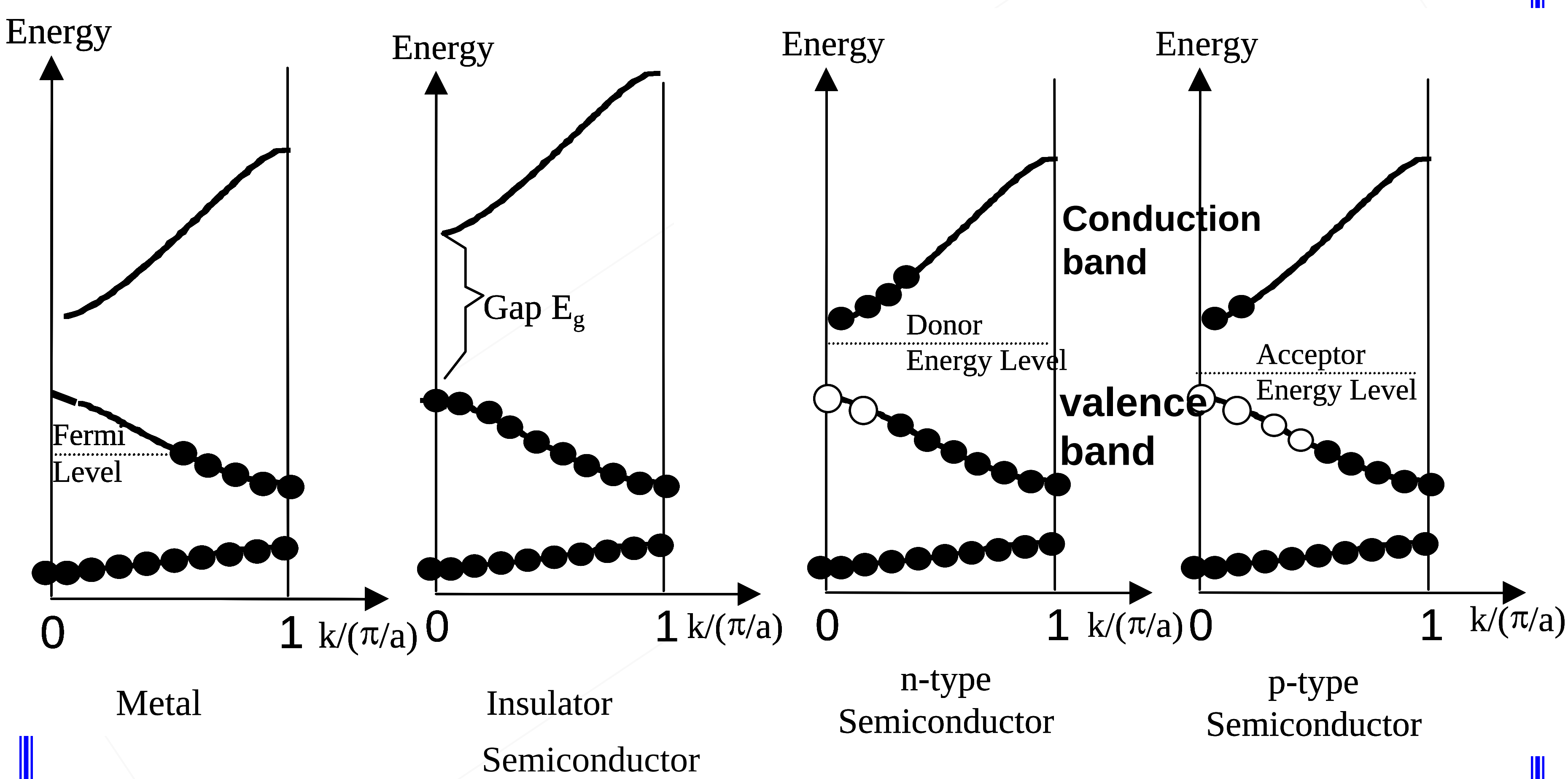


$$\Psi_{ns}(k,x)$$

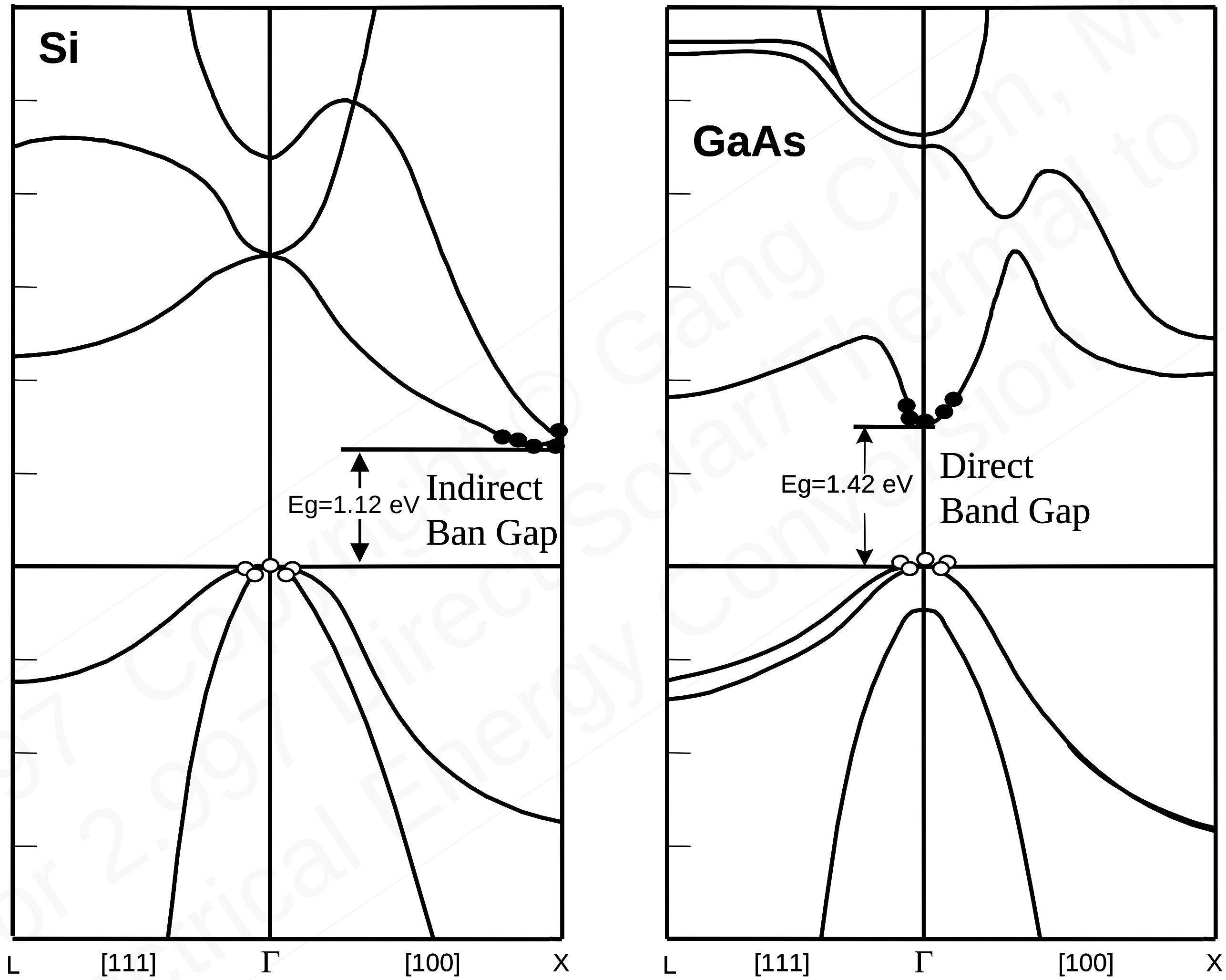
$$k = \frac{2\pi}{\lambda} = -\frac{\pi}{a}, -\frac{(N-1)a\pi}{Na}, \ldots, \frac{(N-1)a\pi}{Na}, \frac{\pi}{a}$$

k has N discrete values between (-N/2,N/2)

Different Solids



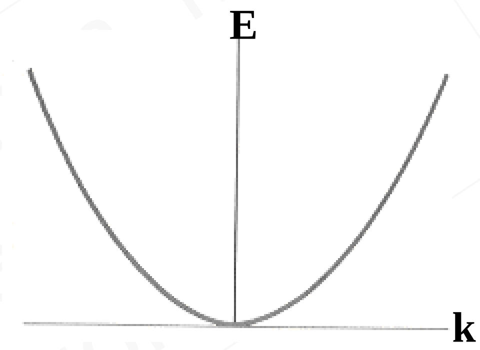
Electronic Band Structures of Real Crystals

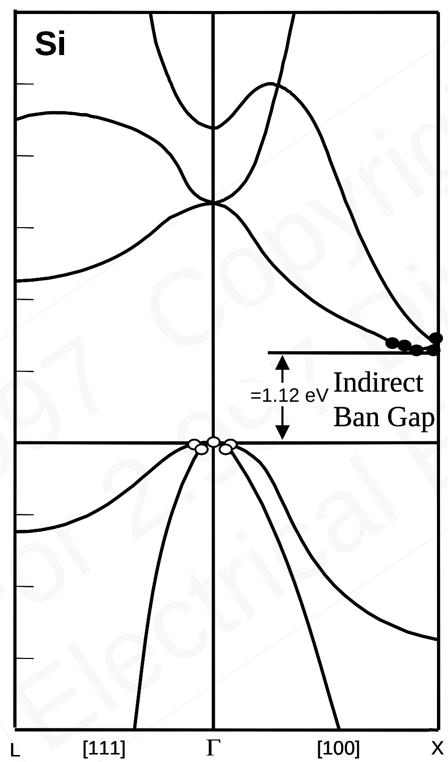


Parabolic Band Approximation

- **Free Electrons**

$$E = mv^2/2 = p^2/2m = \hbar \mathbf{k}^2/2m$$





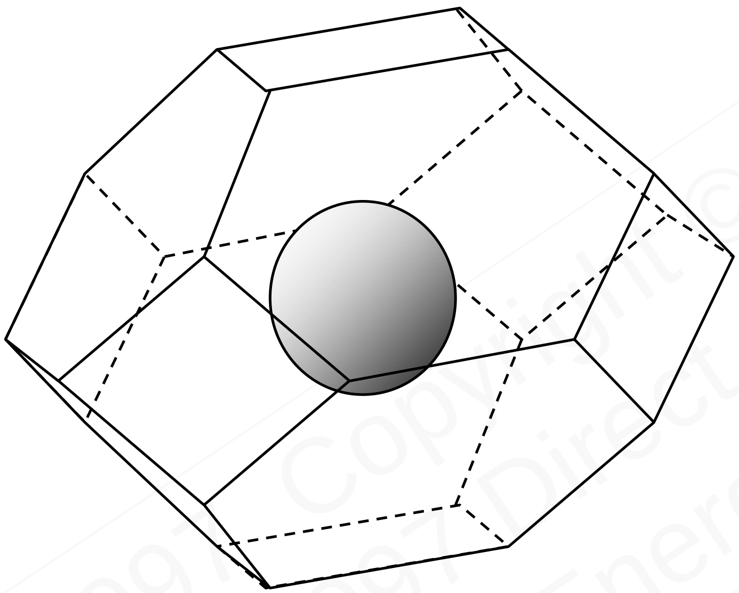
- **Near Minimum (Maximum)**

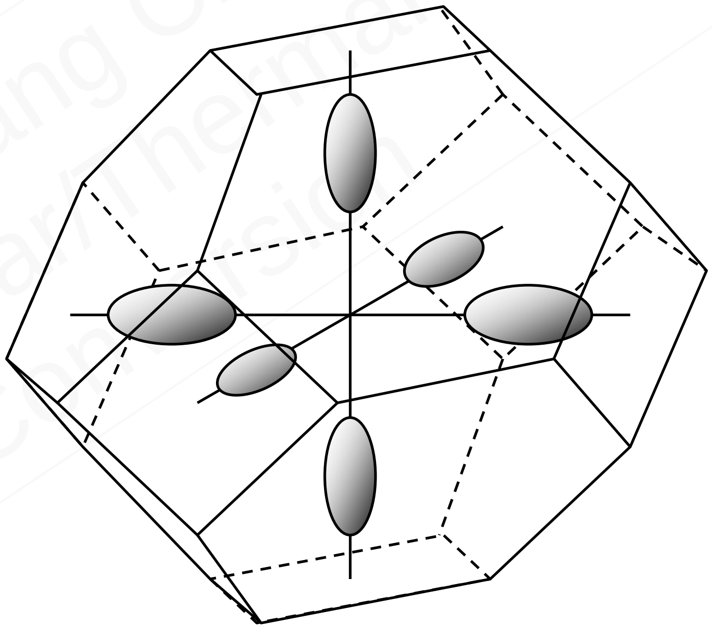
$$E - E_c = \frac{\hbar^2}{2}\left(\frac{k_x^2}{m_{11}} + \frac{k_y^2}{m_{22}} + \frac{k_z^2}{m_{33}}\right)$$

Effective mass

$$m_{ij} = \hbar^2 \Big/ \left(\partial^2 E / \partial k_i \partial k_j\right)$$

Constant Energy Surface





Statistical Distributions

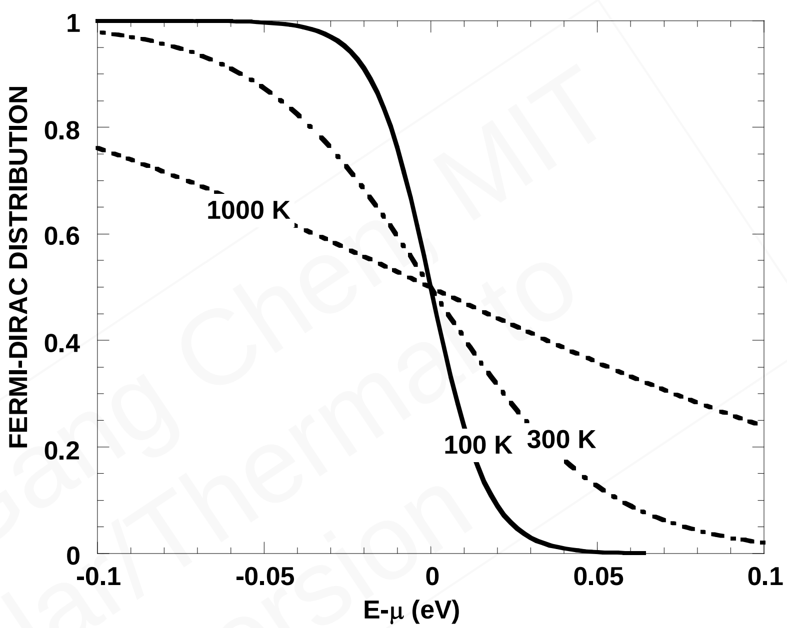
Average Number of Particles in a Quantum State

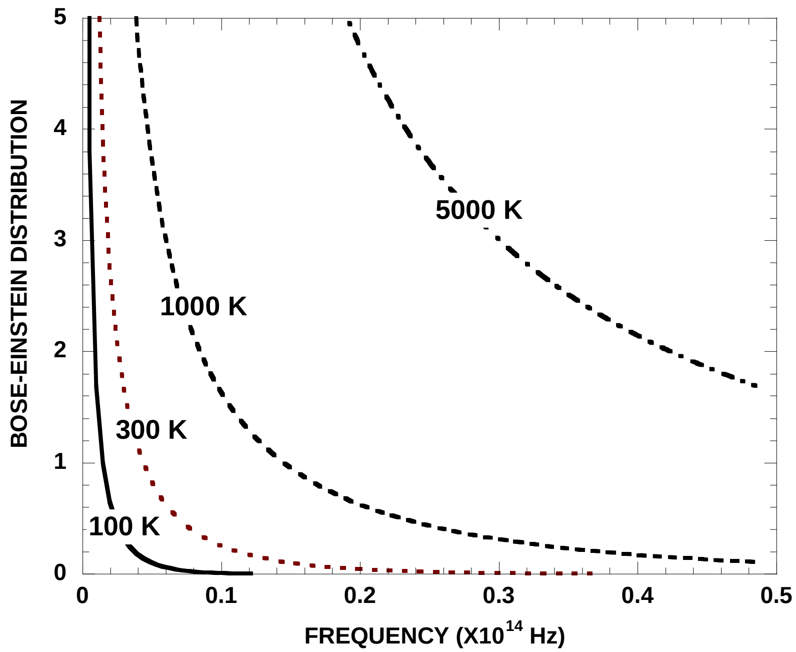
Fermi-Dirac

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

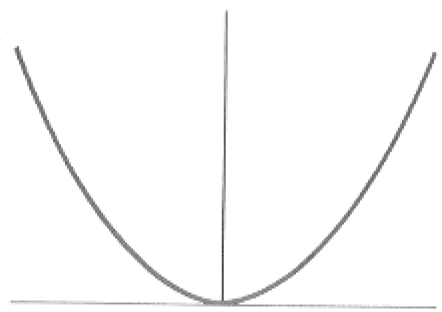
Bose-Einstein

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





Electron Density



$$E - E_c = \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2m}$$

$$N = 2\sum_{-N_x/2}^{N_x/2}\sum_{-N_y/2}^{N_y/2}\sum_{-N_z/2}^{N_z/2} f(E,T)$$

$$= 2\int_{-\pi/a}^{\pi/a}\frac{dk_x}{(2\pi/L_x)}\int_{-\pi/a}^{\pi/a}\frac{dk_y}{(2\pi/L_y)}\int_{-\pi/a}^{\pi/a}\frac{dk_z}{(2\pi/L_z)} f(E,T)$$

$$= \frac{2V}{8\pi^3}\int_{-\pi/a}^{\pi/a}\int_{-\pi/a}^{\pi/a}\int_{-\pi/a}^{\pi/a} dk_x dk_y dk_z \exp\left[-\frac{E-\mu}{k_B T}\right]$$

Electron Density

$$n = \frac{N}{V} = \frac{2V}{8\pi^3}\int_{E_c}^{\infty} 4\pi k^2 dk \exp\left[-\frac{E-\mu}{k_B T}\right]$$

$$= \frac{1}{\pi^2}\int_{E_c}^{\infty}\left(\frac{2m(E-E_c)}{\hbar^2}\right) d\sqrt{\left(\frac{2m(E-E_c)}{\hbar^2}\right)} \exp\left[-\frac{E-\mu}{k_B T}\right]$$

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

$$= 2\left(\frac{2\pi m^* \kappa_B T}{h^2}\right)^{3/2}\exp\left(-\frac{E_c-\mu}{k_B T}\right)$$

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

Density of States D(E): Number of quantum states per unit volume and per energy interval

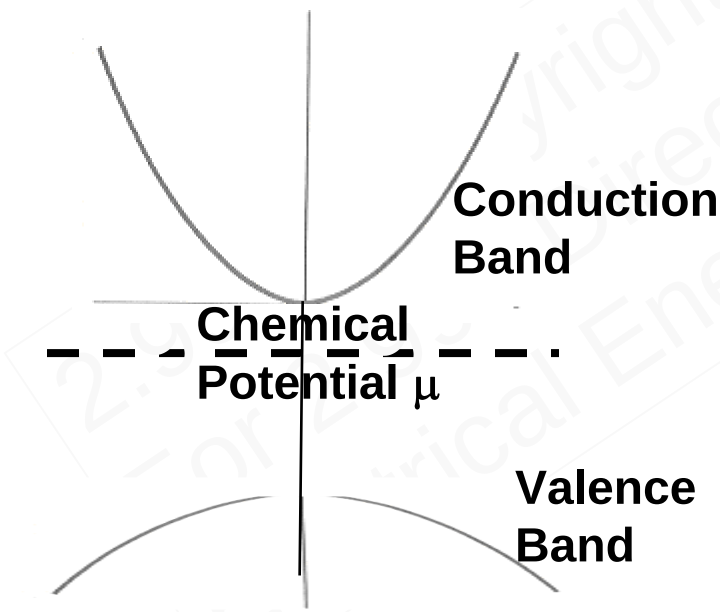
Electron Density

General:

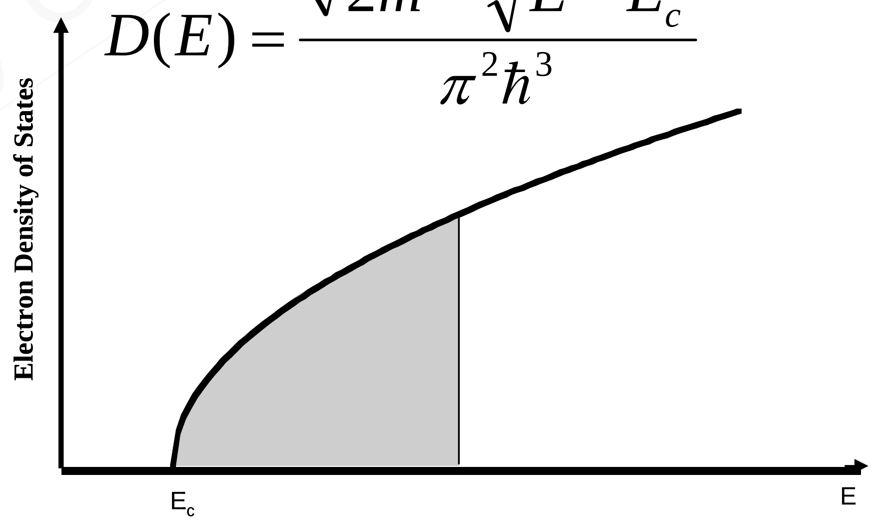
$$n = \int_{E_c}^{\infty} D(E) f(E,\mu,T)\, dE$$

$$n = 2\left(\frac{2\pi m^* \kappa_B T}{h^2}\right)^{3/2} \exp\left(-\frac{E_c-\mu}{k_B T}\right) = N_c \exp\left(-\frac{E_c-\mu}{k_B T}\right)$$

Under Boltzmann Statistics



$$D(E) = \frac{\sqrt{2} m^{3/2} \sqrt{E-E_c}}{\pi^2 \hbar^3}$$



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