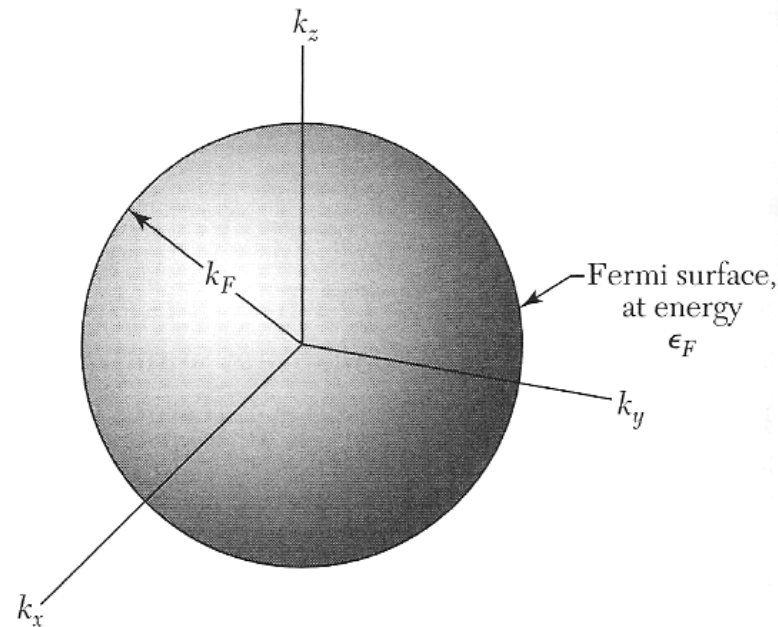**Technische Universität Graz**

19. Electrons, Electron Bands

June 5, 2018

Internal energy

$$u = \int_{-\infty}^{\infty} ED(E)f(E)dE$$

Sommerfeld Expansion: internal energy

$$\int_{-\infty}^{\infty} H(E)f(E)dE = K(\mu) + \frac{\pi^2}{6}(k_BT)^2 \left.\frac{dH(E)}{dE}\right|_{E=\mu} + \frac{7\pi^4}{360}(k_BT)^4 \left.\frac{d^3H(E)}{dE^3}\right|_{E=\mu} + \cdots$$

$$u = \int_{-\infty}^{\infty} ED(E)f(E)dE$$

$$H(E) = ED(E)$$

$$K(\mu) = \int_{-\infty}^{\mu} ED(E)dE$$

$$\left.\frac{dH}{dE}\right|_{E=\mu} = D(\mu) + \mu\frac{dD(\mu)}{dE} \approx D(E_F) + E_F\frac{dD(E_F)}{dE}$$

$$u = \int_{-\infty}^{\mu} ED(E)dE + \frac{\pi^2}{6}(k_BT)^2 (D(E_F) + E_F D'(E_F)) + \cdots$$

Sommerfeld Expansion: internal energy

$$u = \int_{-\infty}^{\mu} ED(E)dE + \frac{\pi^2}{6}(k_BT)^2 (D(E_F) + E_F D'(E_F))$$

$$u = \int_{-\infty}^{E_F} ED(E)dE + (\mu - E_F)E_F D(E_F) + \frac{\pi^2}{6}(k_BT)^2 (D(E_F) + E_F D'(E_F))$$

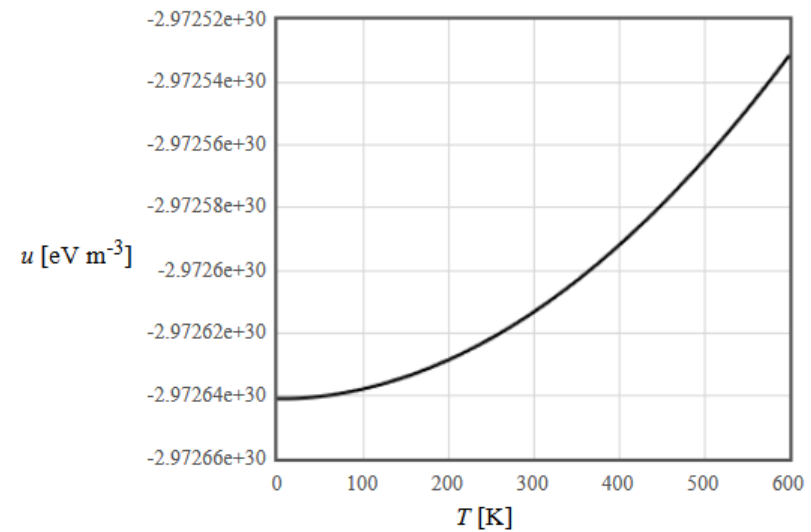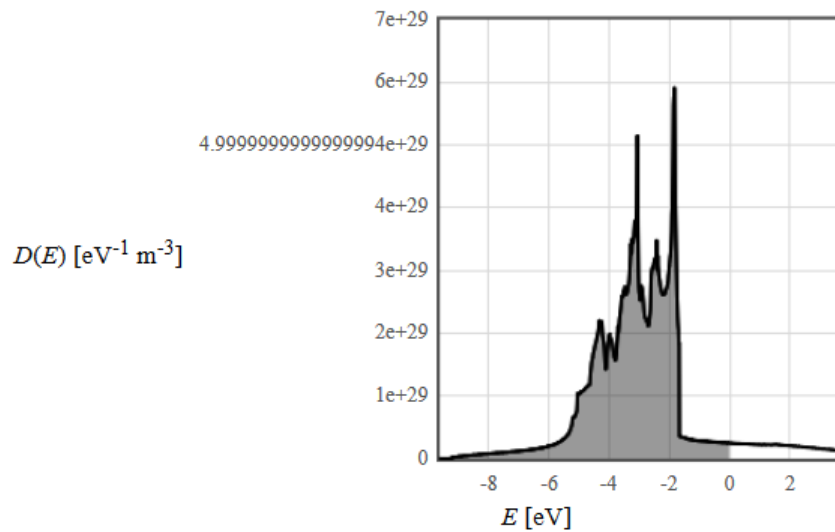$$\mu \approx E_F - \frac{\pi^2}{6}(k_BT)^2 \frac{D'(E_F)}{D(E_F)}$$

$$u = \int_{-\infty}^{E_F} ED(E)dE + (E_F - \frac{\pi^2}{6}(k_BT)^2 \frac{D'(E_F)}{D(E_F)} - E_F)E_F D(E_F) + \frac{\pi^2}{6}(k_BT)^2 (D(E_F) + E_F D'(E_F))$$

$$\boxed{u \approx \int_{-\infty}^{E_F} ED(E)dE + \frac{\pi^2}{6}(k_BT)^2 D(E_F)}$$

Free electrons: $\quad u \approx \dfrac{3}{5}nE_F + \dfrac{\pi^2 D(E_F)}{6}(k_BT)^2 = \dfrac{\hbar^2}{10m}(\pi^4 3^5 n^5)^{\frac{1}{3}} + \dfrac{m(3\pi^2 n)^{\frac{1}{3}}}{6\hbar^2}(k_BT)^2 \quad$ J m^{-3}

Sommerfeld Expansion: internal energy

$$u \approx \int_{-\infty}^{E_F} E D(E) dE + \frac{\pi^2}{6} \left(k_B T \right)^2 D(E_F)$$
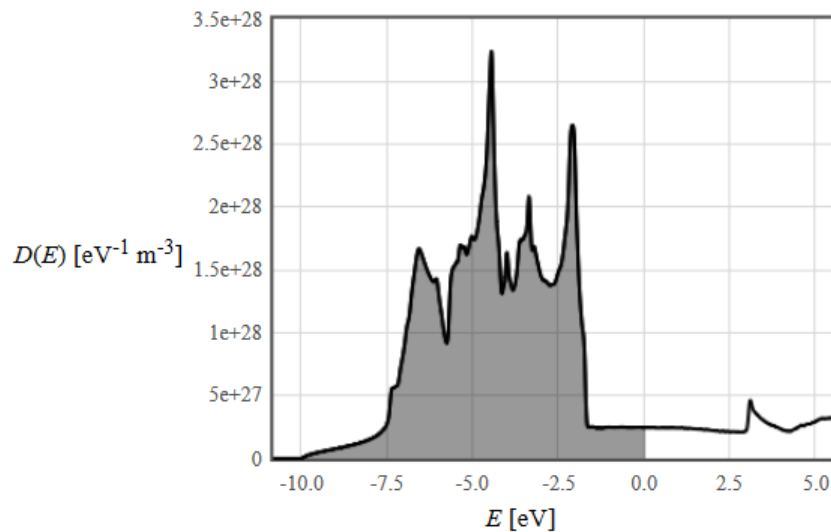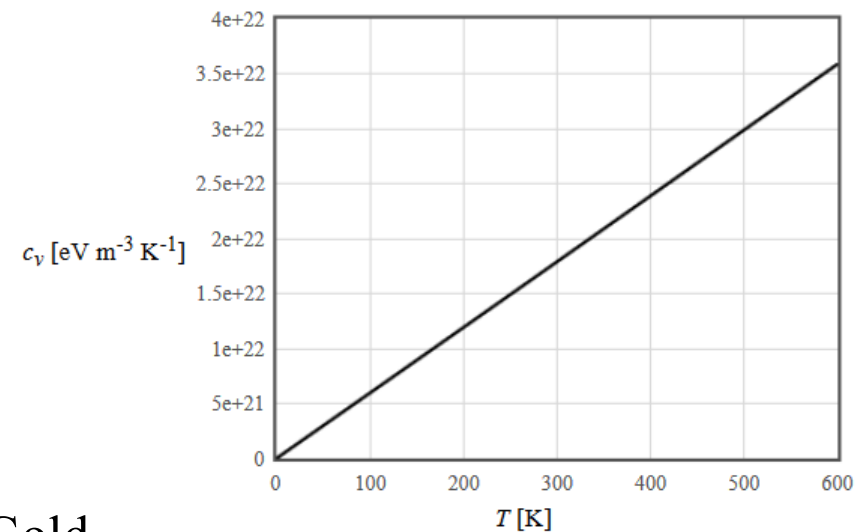

Copper

Sommerfeld Expansion: specific heat

$$c_v = \frac{du}{dT} \approx \frac{d}{dT}\left(u(T=0) + \frac{\pi^2}{6}\left(k_B T\right)^2 D(E_F) \right) = \frac{\pi^2 D(E_F)}{3} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$$

free electrons: $\approx \left(\dfrac{\pi}{3}\right)^{\frac{2}{3}} \dfrac{mn^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$
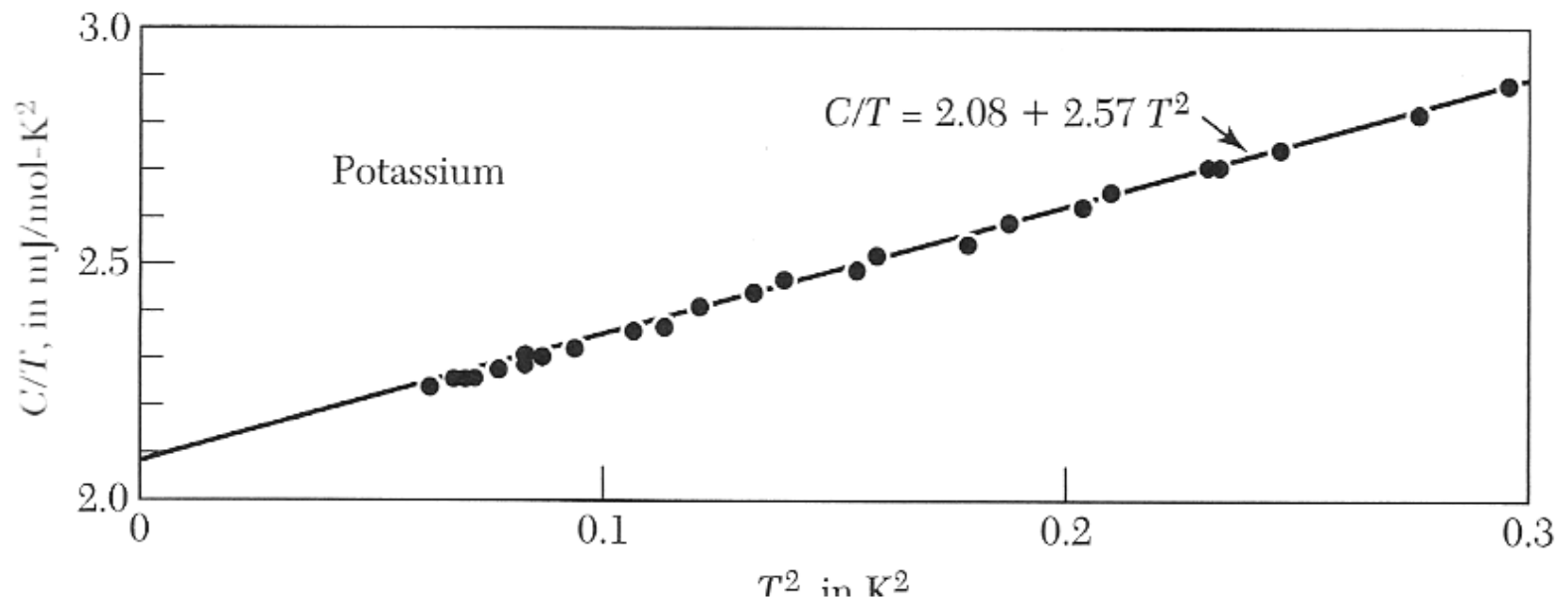

Gold

The electronic specific heat is linear in temperature

Electronic specific heat

$$c_{v,electrons} = \frac{du}{dT} \approx \left(\frac{\pi}{3}\right)^{\frac{2}{3}} \frac{mn^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$$

$$c_{v,total} = \gamma T + AT^3$$

electrons   phonons

Effective mass

$$c_{v,electrons} = \frac{du}{dT} \approx \left(\frac{\pi}{3}\right)^{\frac{2}{3}} \frac{mn^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$$

$$C_v = \gamma T + AT^3$$

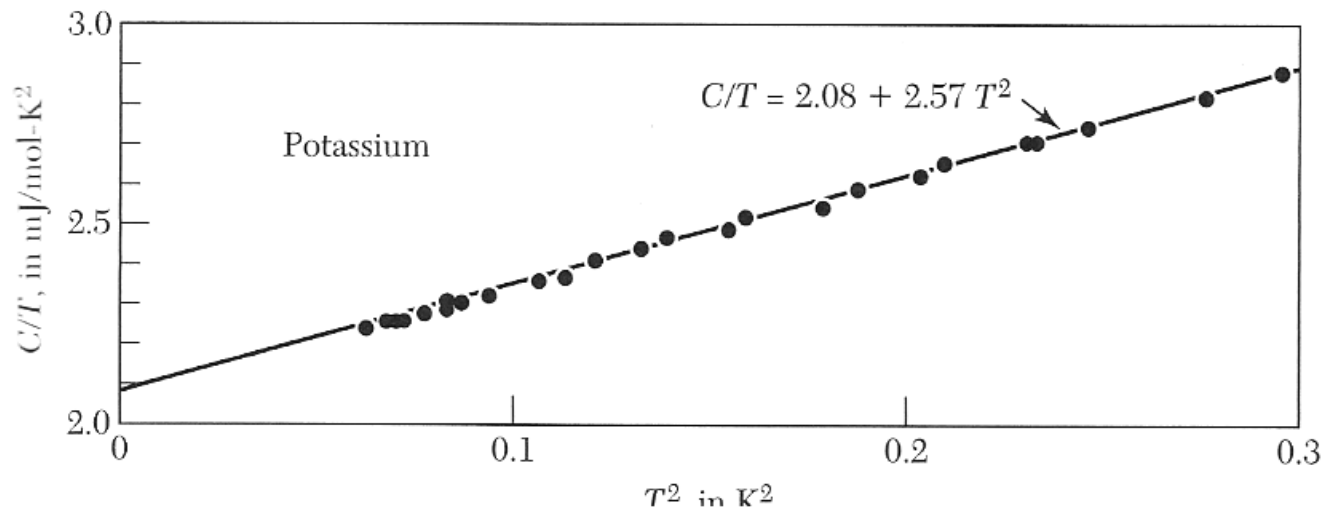$$\frac{m^*}{m} = \frac{\gamma_{observed}}{\gamma} = \frac{D(E_F)_{observed}}{D(E_F)_{free\ electron}}$$

Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).)

Observed γ in mJ mol^{-1} K^{-2}.
Calculated free electron γ in mJ mol^{-1} K^{-2}
m_{th}/m = (observed γ)/(free electron γ).

Li	Be											B	C	N
1.63	0.17													
0.749	0.500													
2.18	0.34													

Na	Mg											Al	Si	P
1.38	1.3											1.35		
1.094	0.992											0.912		
1.26	1.3											1.48		

K	Ca	Sc	Ti	V	Cr	Mn(γ)	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
2.08	2.9	10.7	3.35	9.26	1.40	9.20	4.98	4.73	7.02	0.695	0.64	0.596		0.19
1.668	1.511									0.505	0.753	1.025		
1.25	1.9									1.38	0.85	0.58		

Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (w)	Sb
2.41	3.6	10.2	2.80	7.79	2.0	—	3.3	4.9	9.42	0.646	0.688	1.69	1.78	0.11
1.911	1.790									0.645	0.948	1.233	1.410	
1.26	2.0									1.00	0.73	1.37	1.26	

Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg(α)	Tl	Pb	Bi
3.20	2.7	10.	2.16	5.9	1.3	2.3	2.4	3.1	6.8	0.729	1.79	1.47	2.98	0.008
2.238	1.937									0.642	0.952	1.29	1.509	
1.43	1.4									1.14	1.88	1.14	1.97	

from Kittel

Heavy Fermions

$$\frac{m^*}{m} = \frac{\gamma_{observed}}{\gamma}$$

Heavy fermions are materials that have effective masses 100 - 1000 times larger than the value expected from the free-electron theory. Examples are $CeCu_6$, the UBe_{13}, and $CeAl_3$. The last two are superconductors.

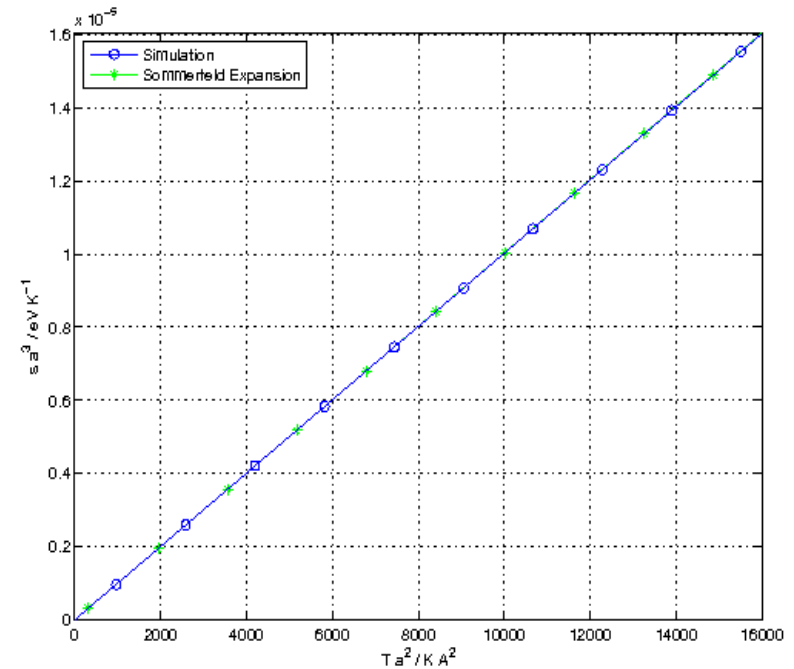Something goes seriously wrong with the free electron model in these materials.

Entropy

$$c_v = \frac{du}{dT} \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$$

$$\frac{c_v}{T} = \left.\frac{\partial s}{\partial T}\right|_{N,V} \approx \frac{\pi^2 D(E_F)}{3} k_B^2 \quad \text{J K}^{-1}\text{m}^{-3}$$

free electrons: $s \approx \left(\dfrac{\pi}{3}\right)^{\frac{2}{3}} \dfrac{m n^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$

Entropy density

Helmholtz free energy

$$s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 \text{T} \quad \text{J K}^{-1}\text{m}^{-3}$$

$$\text{free electrons: } \approx \left(\frac{\pi}{3}\right)^{\frac{2}{3}} \frac{mn^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \text{J K}^{-1}\text{m}^{-3}$$

Helmholtz free energy density

$$f = u - Ts \approx \int_{-\infty}^{E_F} ED(E)dE - \frac{\pi^2 D(E_F)}{6}\left(k_B T\right)^2 \quad \text{J m}^{-3}$$

$$\text{free electrons: } f \approx \frac{\hbar^2}{10m}\left(\pi^4 3^5 n^5\right)^{\frac{1}{3}} - \frac{m\left(3\pi^2 n\right)^{\frac{1}{3}}}{6\hbar^2}\left(k_B T\right)^2 \quad \text{J m}^{-3}$$

Results of the quantization of the Schrödinger equation for free fermions in 1, 2, and 3 dimensions.

A simple model for metals is the free electron model where the potential energy of the electrons is zero and the electron-electron interactions are ignored. This is equivalent to any system of noninteracting fermions with zero potential energy. In this model the thermodynamic properties only depend on one parameter, the particle density n. In the table below, n denotes the number of particles per meter in one-dimension, the number of particle per square meter in two-dimensions, and the number of particles per cubic mter in three dimensions.

	1-D Schrödinger equation for a free particle $$i\hbar\frac{d\psi}{dx}=-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$$	2-D Schrödinger equation for a free particle $$i\hbar\frac{d\psi}{dx}=-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}\right)$$	3-D Schrödinger equation for a free particle $$i\hbar\frac{d\psi}{dx}=-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}\right)$$
Eigenfunction solutions	$A_k\exp\left(i\left(kx-\omega t\right)\right)$	$A_{\vec{k}}\exp\left(i\left(\vec{k}\cdot\vec{r}-\omega t\right)\right)$	$A_{\vec{k}}\exp\left(i\left(\vec{k}\cdot\vec{r}-\omega t\right)\right)$
Dispersion relation	$E=\hbar\omega=\dfrac{\hbar^2 k^2}{2m}$ J	$E=\hbar\omega=\dfrac{\hbar^2 k^2}{2m}$ J	$E=\hbar\omega=\dfrac{\hbar^2 k^2}{2m}$ J
Density of states	$D(k)=\dfrac{2}{\pi}$	$D(k)=\dfrac{k}{\pi}$ m^{-1}	$D(k)=\dfrac{k^2}{\pi^2}$ m^{-2}
Density of states $D(E)=D(k)\dfrac{dk}{dE}$	$D(E)=\dfrac{1}{\pi\hbar}\sqrt{\dfrac{2m}{E}}=\dfrac{n}{2\sqrt{E_F E}}$ J^{-1}m^{-1}	$D(E)=\dfrac{m}{\pi\hbar^2}=\dfrac{n}{E_F}$ J^{-1}m^{-2}	$D(E)=\dfrac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\sqrt{E}=\dfrac{3n}{2E_F^{3/2}}\sqrt{E}$ J^{-1}m^{-3}
Fermi energy E_F $n=\displaystyle\int_{-\infty}^{E_F}D(E)dE$	$E_F=\dfrac{\pi^2\hbar^2 n^2}{8m}$ J	$E_F=\dfrac{\pi\hbar^2 n}{m}$ J	$E_F=\dfrac{\hbar^2}{2m}\left(3\pi^2 n\right)^{\frac{2}{3}}$ J
$D(E_F)$	$D(E_F)=\dfrac{4m}{\pi^2\hbar^2 n}$ J^{-1}m^{-1}	$D(E_F)=\dfrac{m}{\pi\hbar^2}$ J^{-1}m^{-2}	$D(E_F)=\dfrac{m(3n)^{\frac{1}{3}}}{\pi^{\frac{4}{3}}\hbar^2}$ J^{-1}m^{-3}
$D'(E_F)=\dfrac{dD}{dE}\Big|_{E=E_F}$	$D'(E_F)=\dfrac{-16m^2}{\pi^4\hbar^4 n^3}$ J^{-2}m^{-1}	$D'(E_F)=0$ J^{-2}m^{-2}	$D'(E_F)=\dfrac{m^2}{\hbar^4\sqrt[3]{3\pi^8 n}}$ J^{-2}m^{-3}
Chemical potential μ $n=\displaystyle\int_{-\infty}^{\infty}D(E)f(E)dE$	$\mu\approx E_F-\dfrac{\pi^2}{6}(k_B T)^2\dfrac{D'(E_F)}{D(E_F)}$ J $\approx\dfrac{\pi^2\hbar^2 n^2}{8m}+\dfrac{2m}{3\hbar^2 n^2}(k_B T)^2$ J	$\mu=k_B T\ln\left(\exp\left(\dfrac{E_F}{k_B T}\right)-1\right)$ J $=k_B T\ln\left(\exp\left(\dfrac{\pi\hbar^2 n}{mk_B T}\right)-1\right)$ J	$\mu\approx E_F-\dfrac{\pi^2}{6}(k_B T)^2\dfrac{D'(E_F)}{D(E_F)}$ J $\approx\dfrac{\hbar^2}{2m}\left(3\pi^2 n\right)^{\frac{2}{3}}-\dfrac{\pi^{\frac{2}{3}}m}{\dots+2\dots^{\frac{1}{3}}\dots}(k_B T)^2$ J

Band Theory, Kittel chapter 7

Calculate the dispersion relation for electrons in a crystal
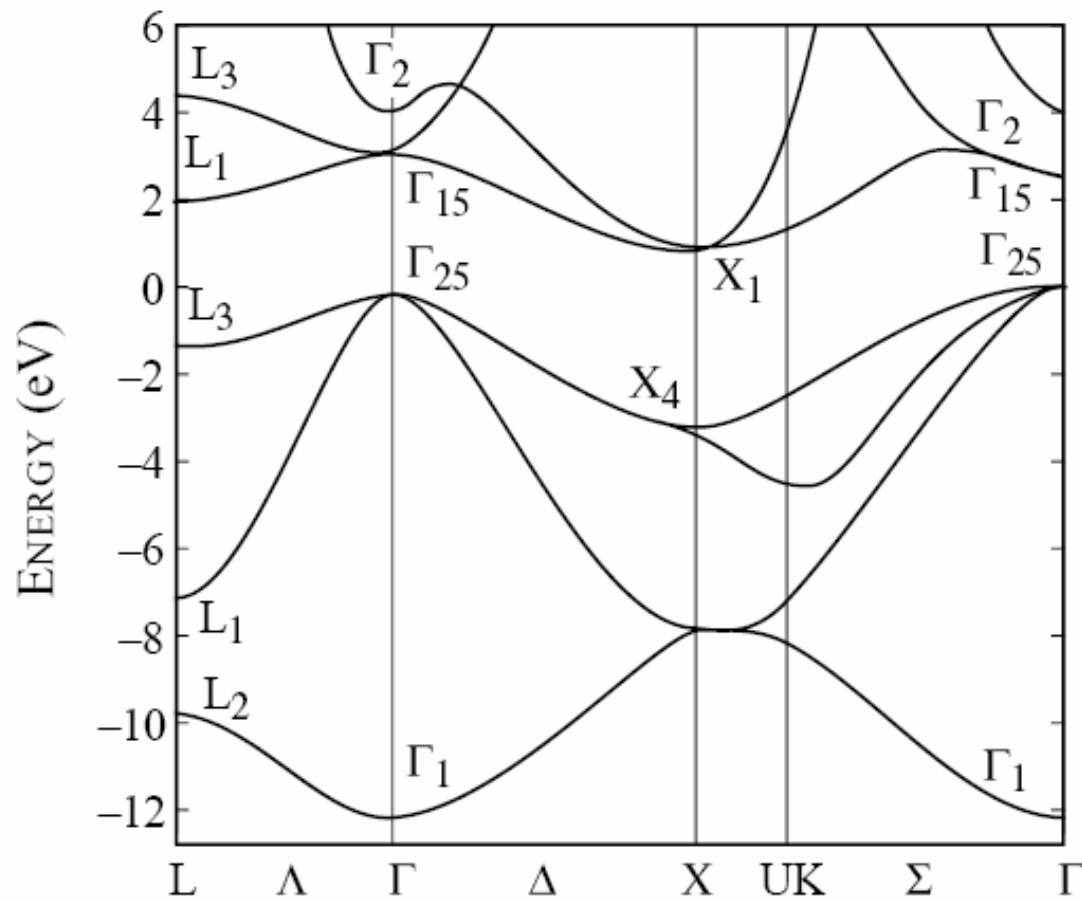
silicon

Empty lattice approximation

Extended   Repeated   Reduced
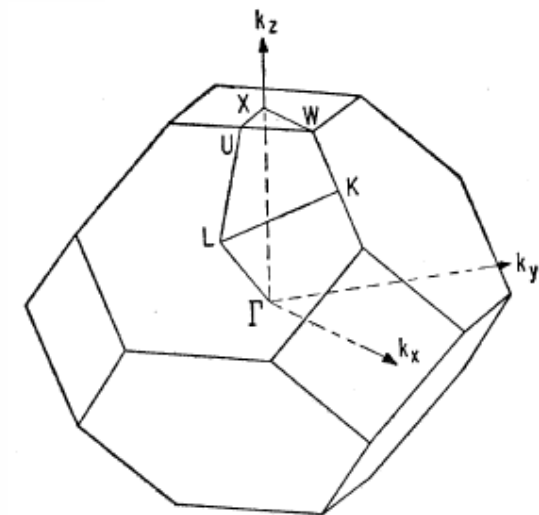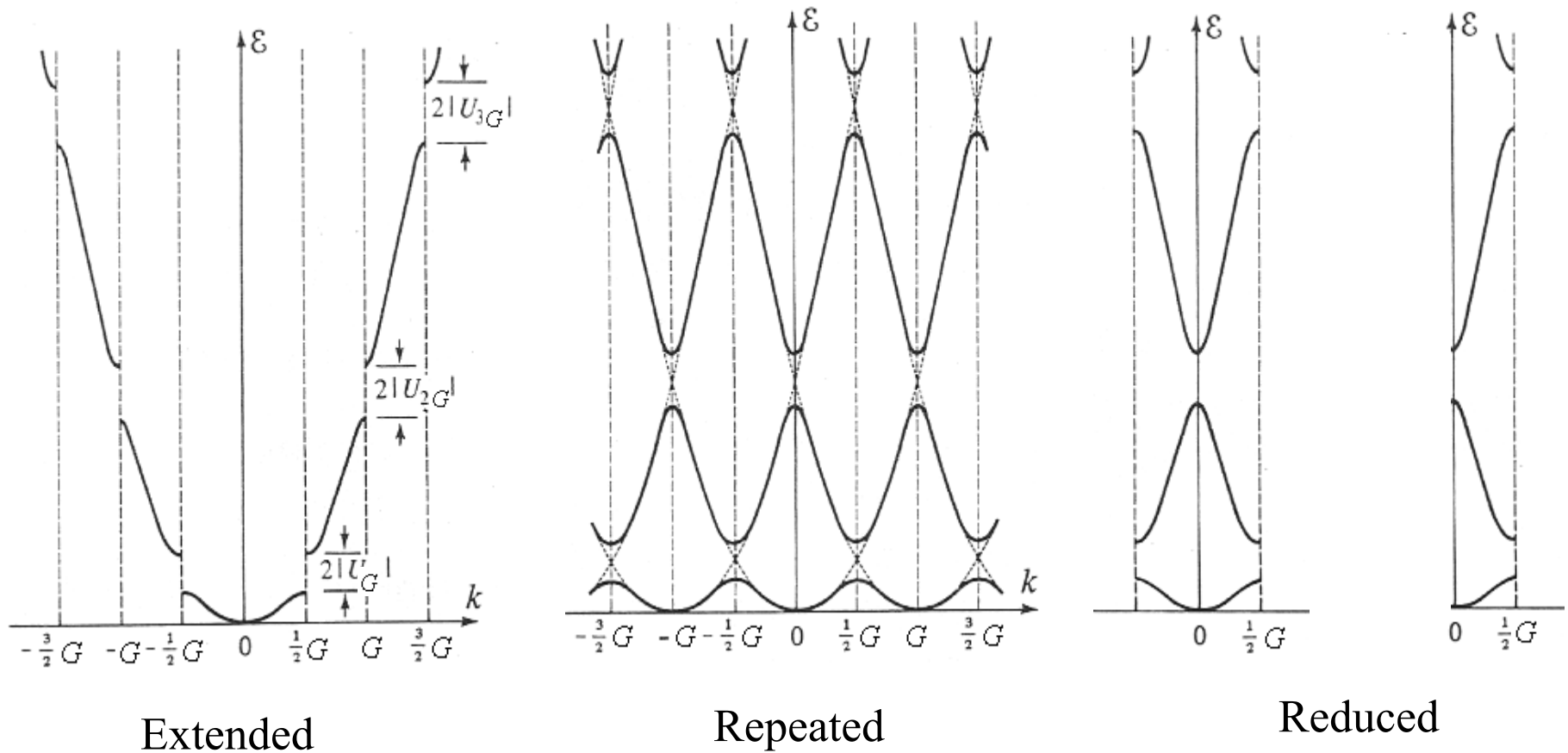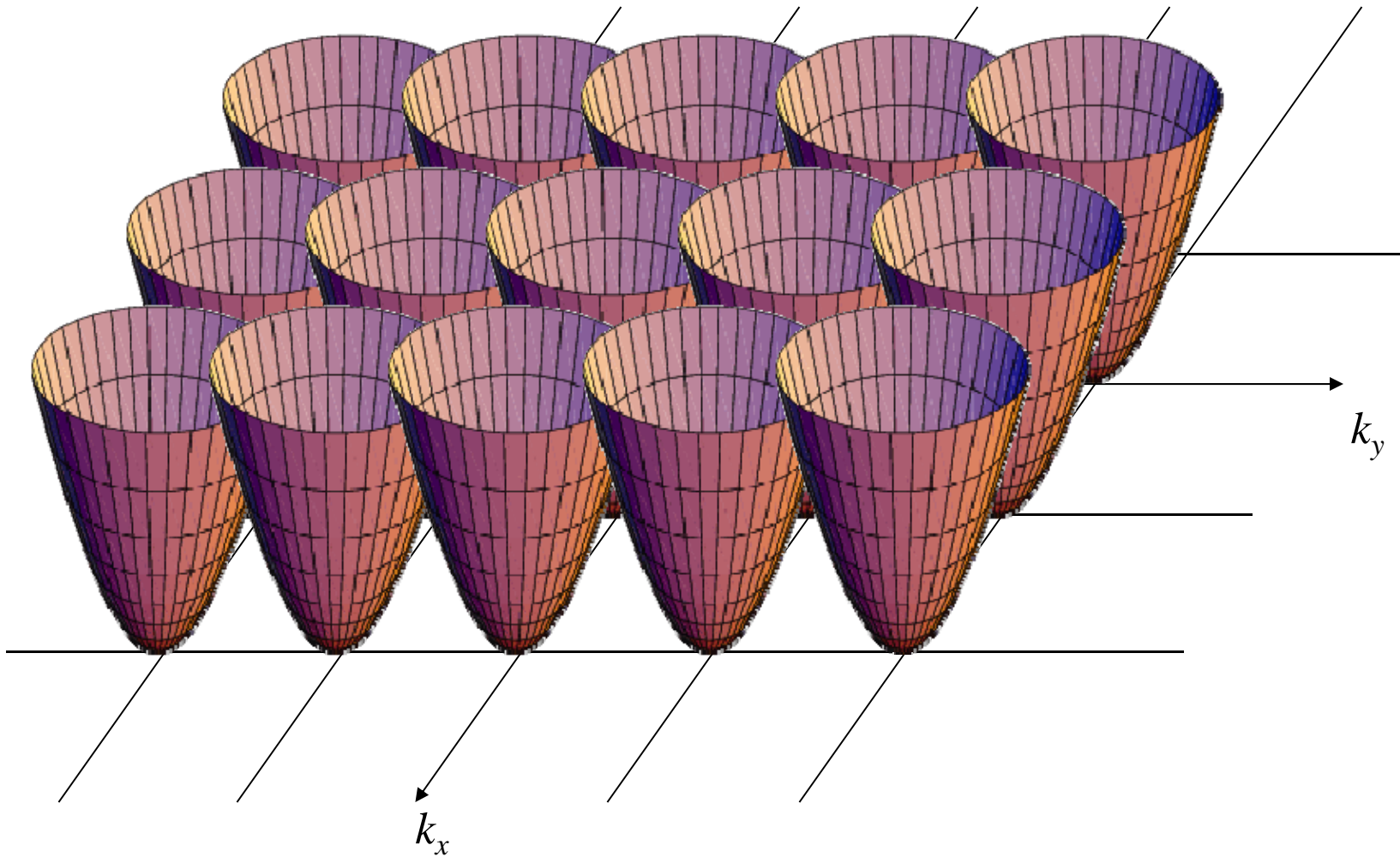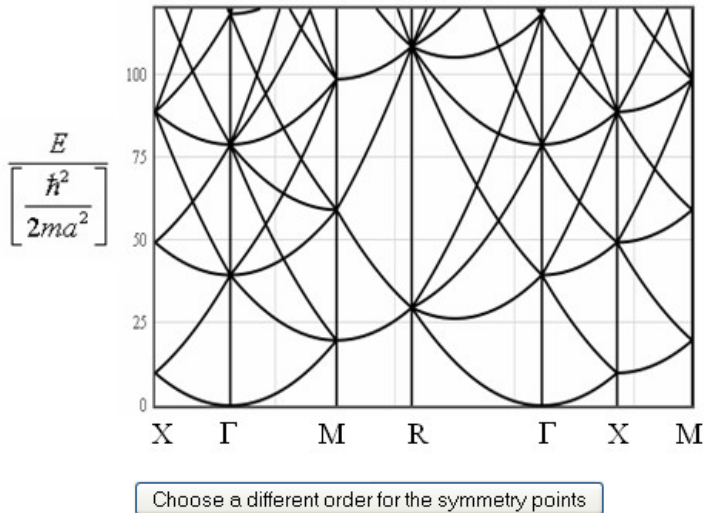
$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}} \underbrace{e^{i\vec{G}_0\cdot\vec{r}} e^{-i\vec{G}_0\cdot\vec{r}}}_{1} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = e^{i(\vec{k}+\vec{G}_0)\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i(\vec{G}-\vec{G}_0)\cdot\vec{r}}$$

Empty lattice approximation

k_y

k_x

Empty lattice approximation

Simple cubic

$\dfrac{E}{\left[\dfrac{\hbar^2}{2ma^2}\right]}$

X   Γ   M   R   Γ   X   M

Choose a different order for the symmetry points

Face centered cubic

$\dfrac{E}{\left[\dfrac{\hbar^2}{2ma^2}\right]}$

L   Γ   X   U   K   Γ   W

Choose a different order for the symmetry points

Body centered cubic

$\dfrac{E}{\left[\dfrac{\hbar^2}{2ma^2}\right]}$

H   Γ   P   Γ   H   P

Hexagonal

$\dfrac{E}{\left[\dfrac{\hbar^2}{2ma^2}\right]}$
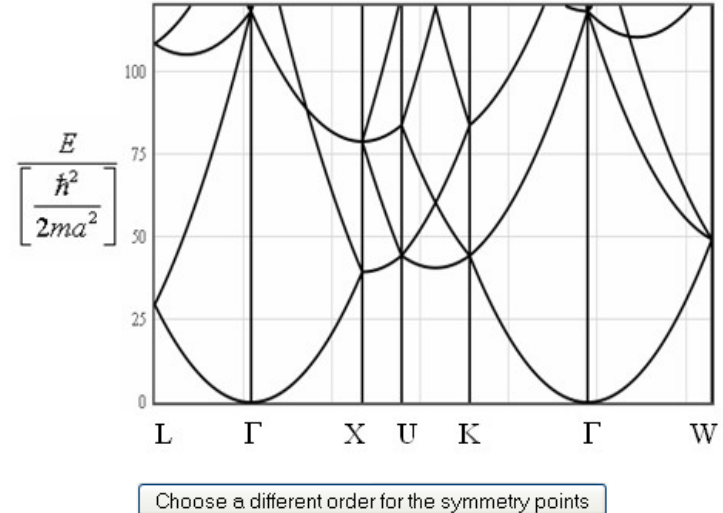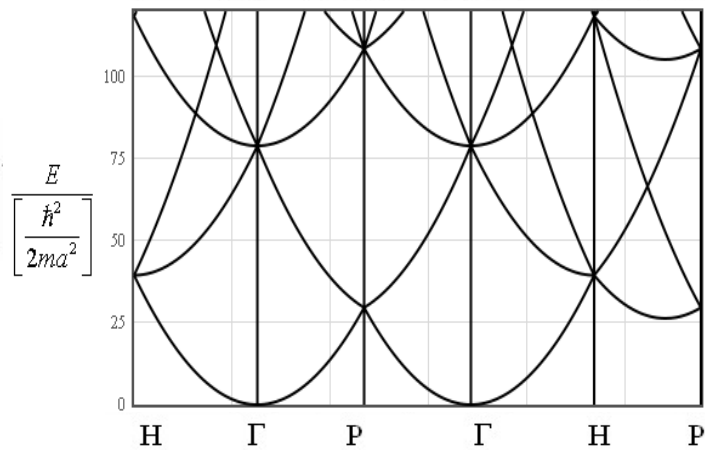
K   Γ   A   H   M   Γ   L
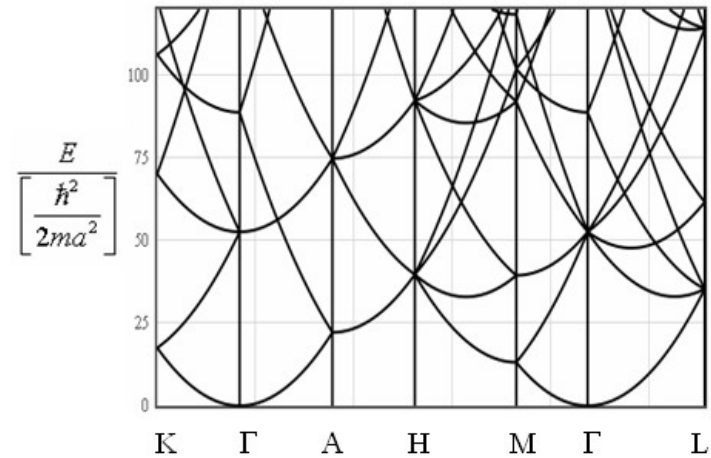
Band Structure of Aluminum

WALTER A. HARRISON

General Electric Research Laboratory, Schenectady, New York
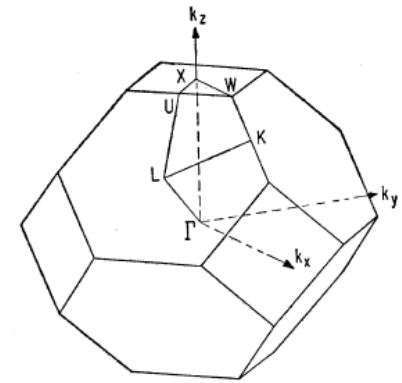
empty lattice approximation
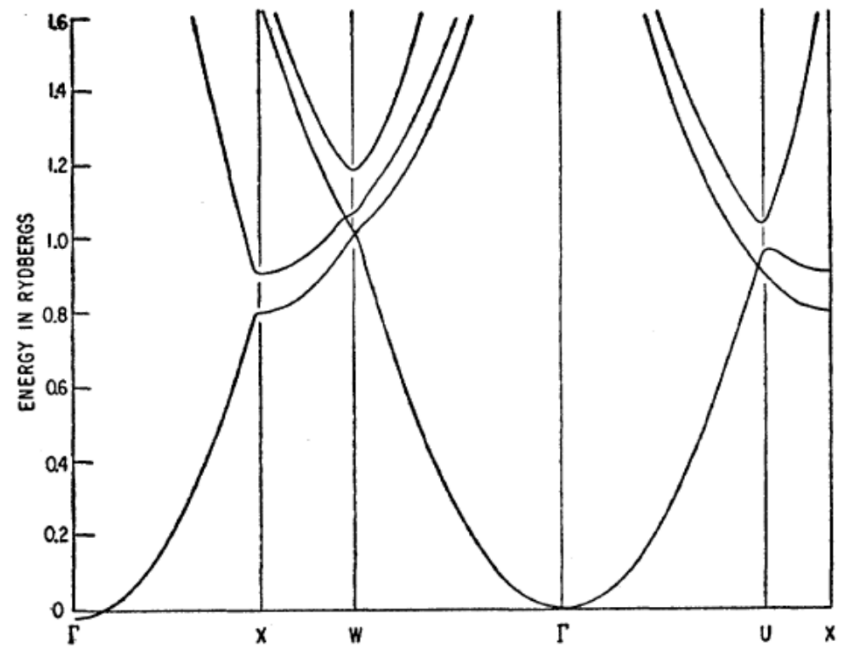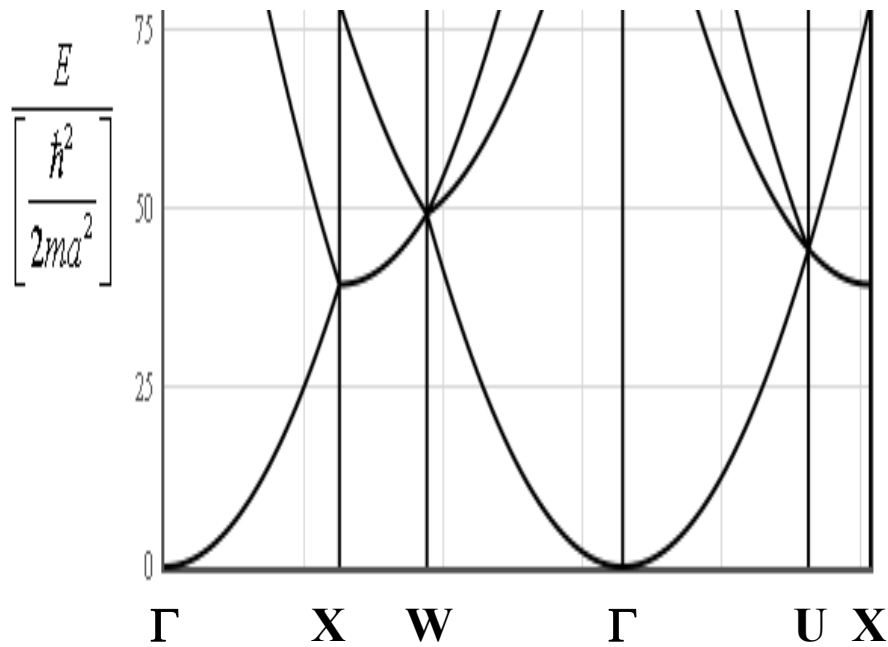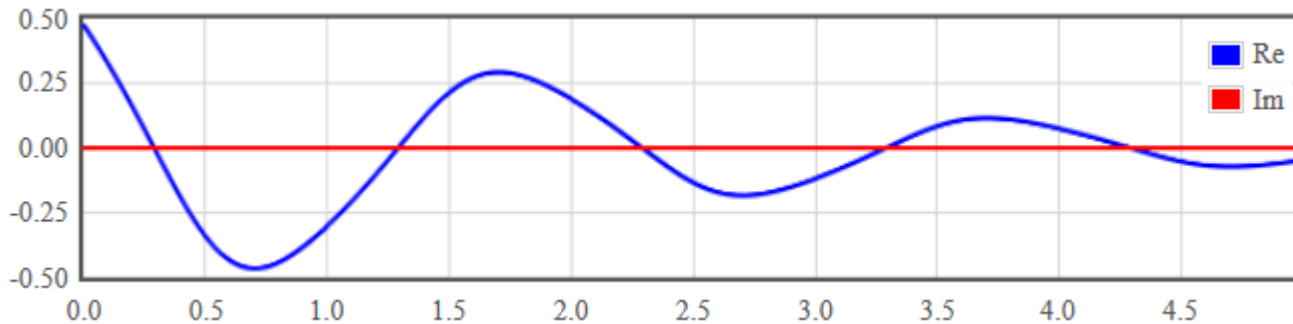
Kronig-Penney model
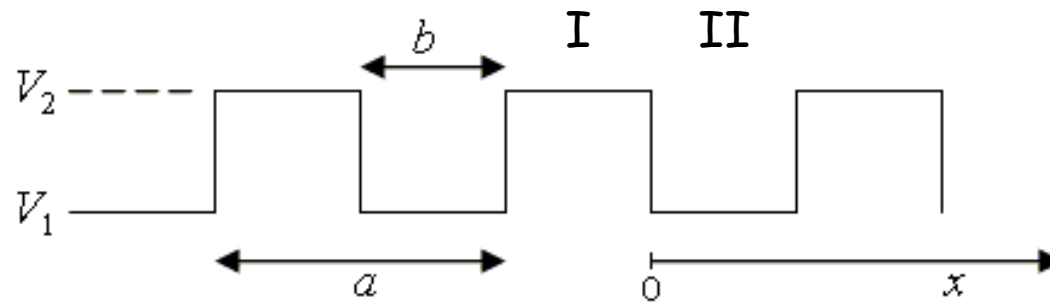
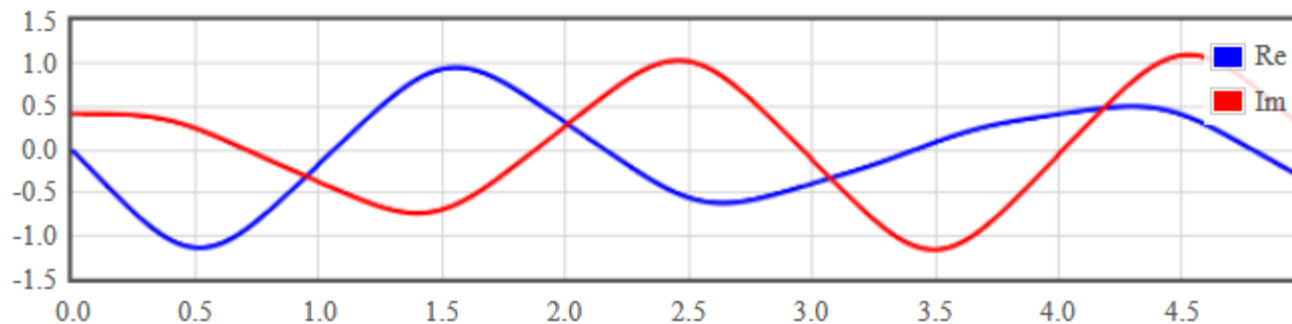$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

Solutions can be found in region I and region II
Match boundary conditions

Linear differential equations with periodic coefficients

Have exponentially decaying solutions,
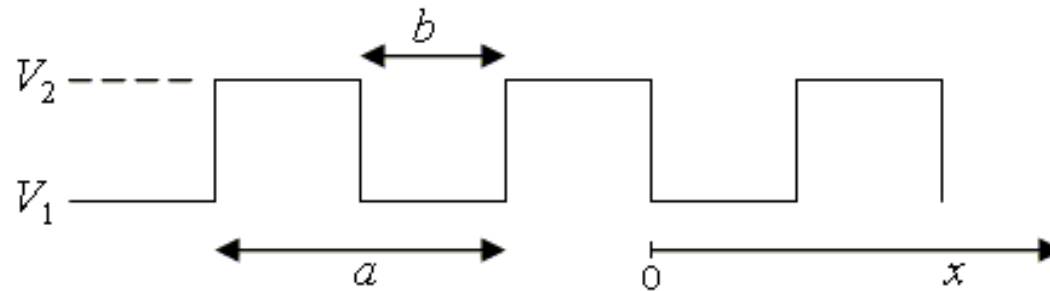

or solutions of the form $e^{ikx}u_k(x)$

$$T\psi = \lambda\psi$$

$$Te^{ikx}u_k(x) = e^{ik(x+a)}u_k(x+a) = e^{ika}e^{ikx}u_k(x) = e^{ika}\psi$$

$$\lambda = e^{ika}$$
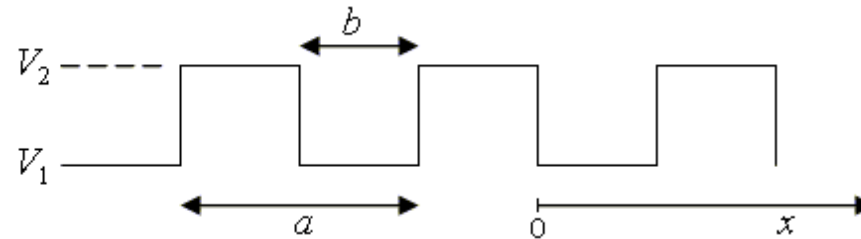
Kronig-Penney model

Solutions can be found that are simultaneous eigenfunctions of the Hamiltonian and the translation operator.

Eigenfunctions of the translation operator can be found in terms of any two linearly independent solutions. A convenient choice is:

$$\psi_1(0)=1, \qquad \frac{d\psi_1}{dx}(0)=0, \qquad \psi_2(0)=0, \qquad \frac{d\psi_2}{dx}(0)=1.$$

Kronig-Penney model

for $0 < x < b$

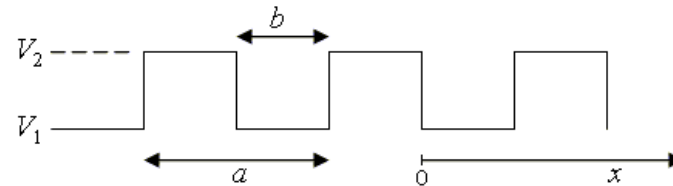$$\psi_1(x) = \cos(k_1 x), \qquad\qquad \psi_2(x) = \frac{\sin(k_1 x)}{k_1}$$

for $b < x < a$

$$\psi_1(x) = \cos(k_2(x-b))\cos(k_1 b) - \frac{k_1 \sin(k_2(x-b))\sin(k_1 b)}{k_2},$$

$$\psi_2(x) = \frac{\cos(k_2(x-b))\sin(k_1 b)}{k_1} + \frac{\sin(k_2(x-b))\cos(k_1 b)}{k_2}.$$

Except for the coefficients, these are the same solutions as we found for light in a layered material.

Kronig-Penney model

at $x = a$

$$\psi_1(a) = \cos(k_2(a-b))\cos(k_1b) - \frac{k_1 \sin(k_2(a-b))\sin(k_1b)}{k_2},$$

$$\psi_2(a) = \frac{\cos(k_2(a-b))\sin(k_1b)}{k_1} + \frac{\sin(k_2(a-b))\cos(k_1b)}{k_2}.$$

The translation operator translates the function a distance a.

$$\begin{bmatrix} \psi_1(x+a) \\ \psi_2(x+a) \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix}.$$

The elements of the translation operator can be evaluated at $x = a$.

Kronig-Penney model

$$\begin{bmatrix} \psi_1(x+a) \\ \psi_2(x+a) \end{bmatrix} = \begin{bmatrix} \psi_1(a) & \dfrac{d\psi_1}{dx}(a) \\ \psi_2(a) & \dfrac{d\psi_2}{dx}(a) \end{bmatrix} \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix}$$
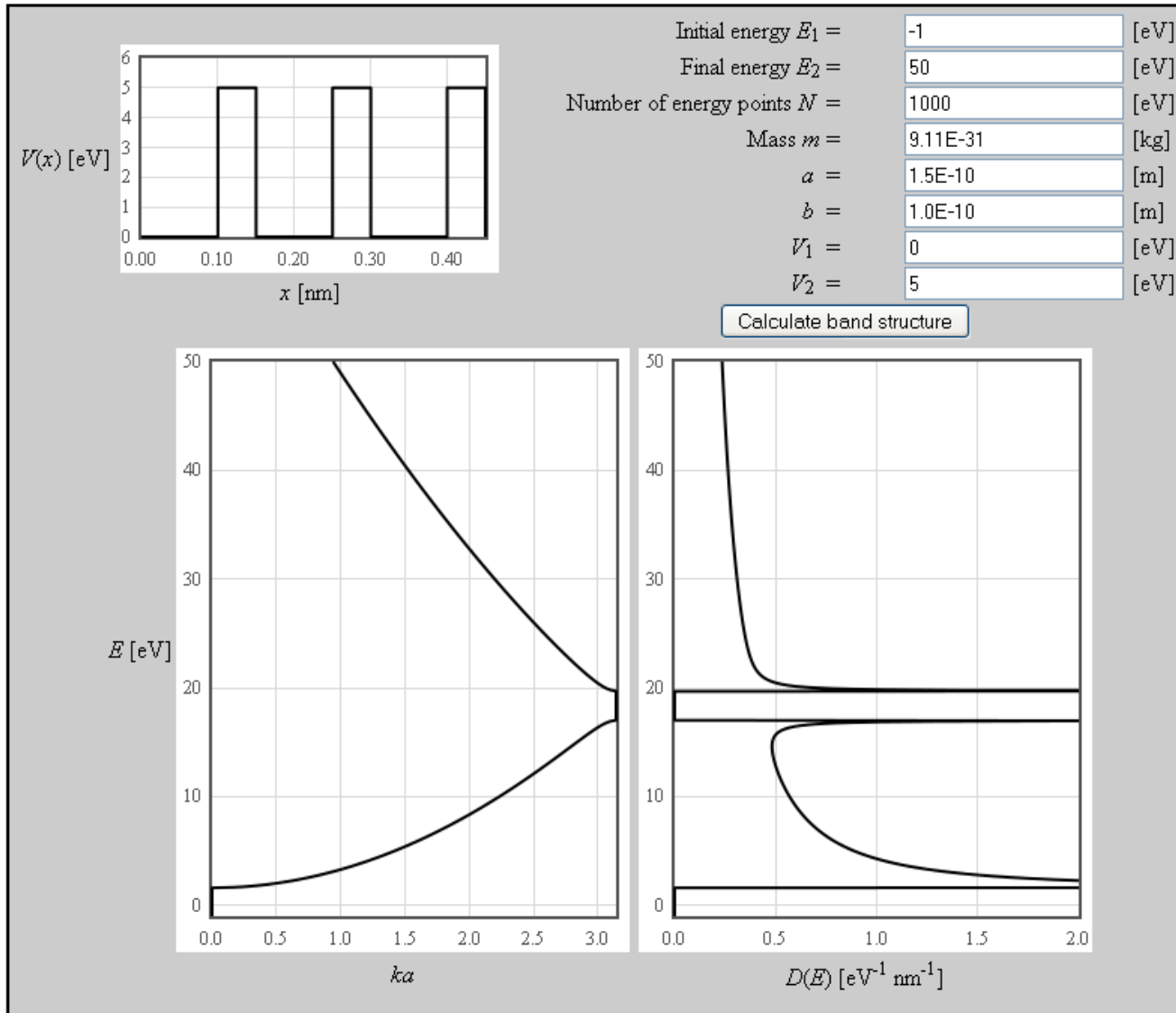
The eigen functions and eigen values are

$$\psi_\pm(x) = \frac{2\psi_2(a)}{\dfrac{d\psi_2(a)}{dx} - \psi_1(a) \pm \delta} \psi_1(x) + \psi_2(x), \qquad \lambda\pm = \frac{1}{2}(\alpha \pm \delta),$$

$$\delta = \sqrt{\alpha^2 - 4}$$

$$\alpha = \psi_1(a) + \frac{d\psi_2(a)}{dx} = 2\cos\big(k_2(a-b)\big)\cos(k_1 b) - \left(\frac{k_2}{k_1} + \frac{k_1}{k_2}\right)\sin\big(k_2(a-b)\big)\sin(k_1 b).$$

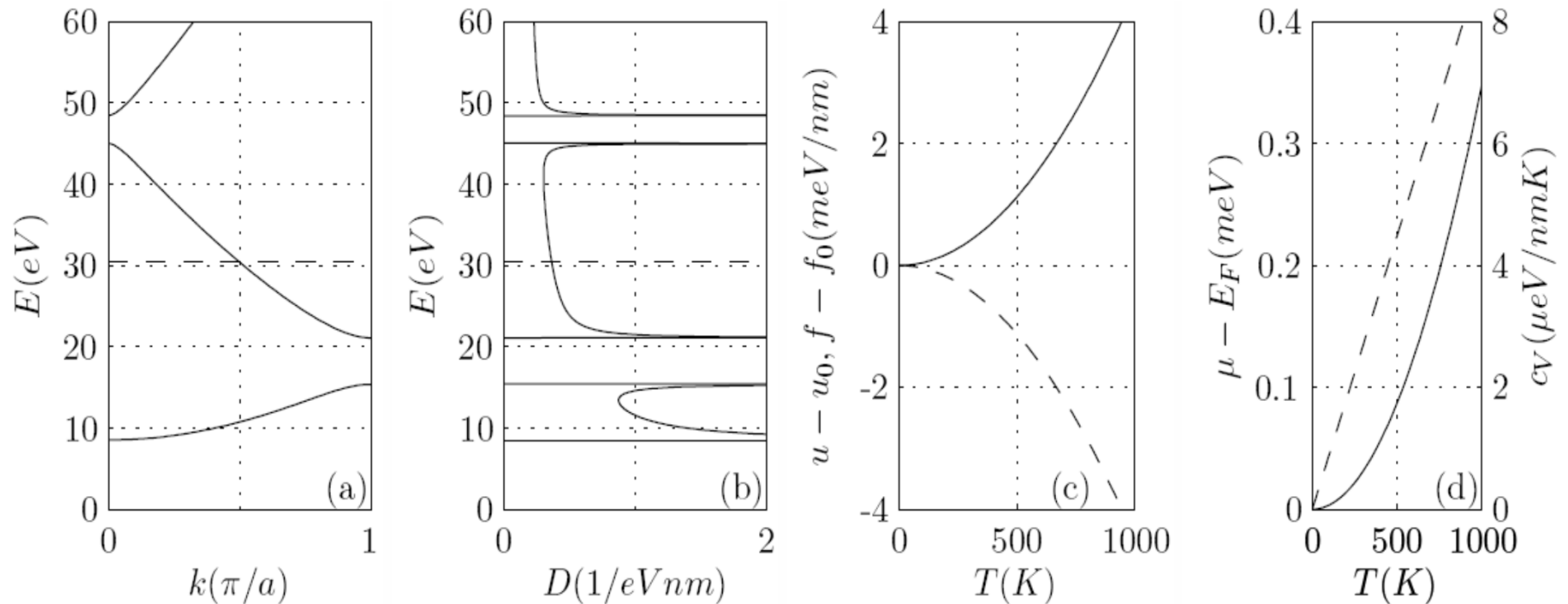If $\alpha > 2$, the potential acts like a mirror for electrons

Kronig-Penney model

Initial energy E_1 = -1 [eV]
Final energy E_2 = 50 [eV]
Number of energy points N = 1000 [eV]
Mass m = 9.11E-31 [kg]
a = 1.5E-10 [m]
b = 1.0E-10 [m]
V_1 = 0 [eV]
V_2 = 5 [eV]

Calculate band structure

$$\alpha(E, V_1, V_2, a, b)$$

$$k = \pm \frac{1}{a} \tan^{-1}\left(\frac{\sqrt{4-\alpha^2}}{\alpha} \right)$$

Kronig-Penney model

(a) The energy-wave number dispersion relation. The dashed line is the Fermi energy. (b) The density of states. (c) The internal energy density (solid line) and Helmholtz free energy density (dashed line). (d) The chemical potential (solid line) and the specific heat (dashed line). All of the plots were drawn for a square wave potential with the parameters: $V = 12.5$ eV, $a = 2 \times 10^{-10}$ m, $b = 5 \times 10^{-11}$ m, and an electron density of $n = 3$ electrons/primitive cell.
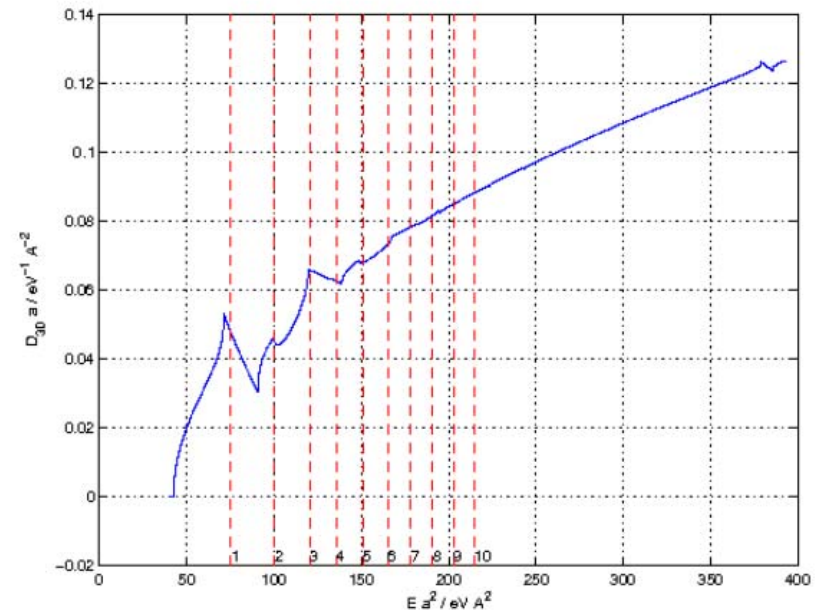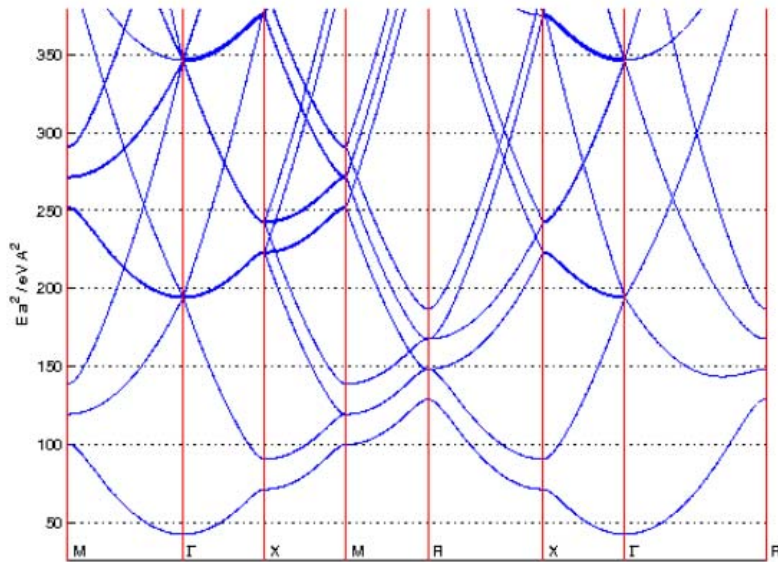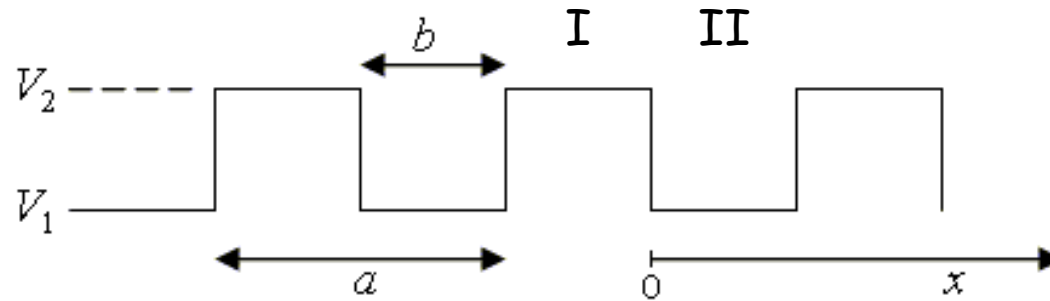
A separable potential
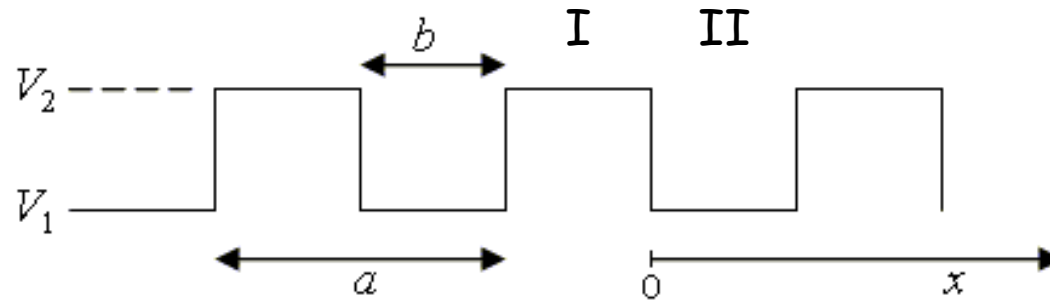
$$-\frac{\hbar^2}{2m}\nabla^2\Psi + (V(x)+V(y)+V(z))\Psi = E\Psi$$

Ψ is the product of the solutions to the Kronig-Penney model.

$$\Psi(x,y,z) = \psi_{KP}(x)\psi_{KP}(y)\psi_{KP}(z)$$

A separable potential

http://lampx.tugraz.at/~hadley/ss1/separablecrystals/thermo.html