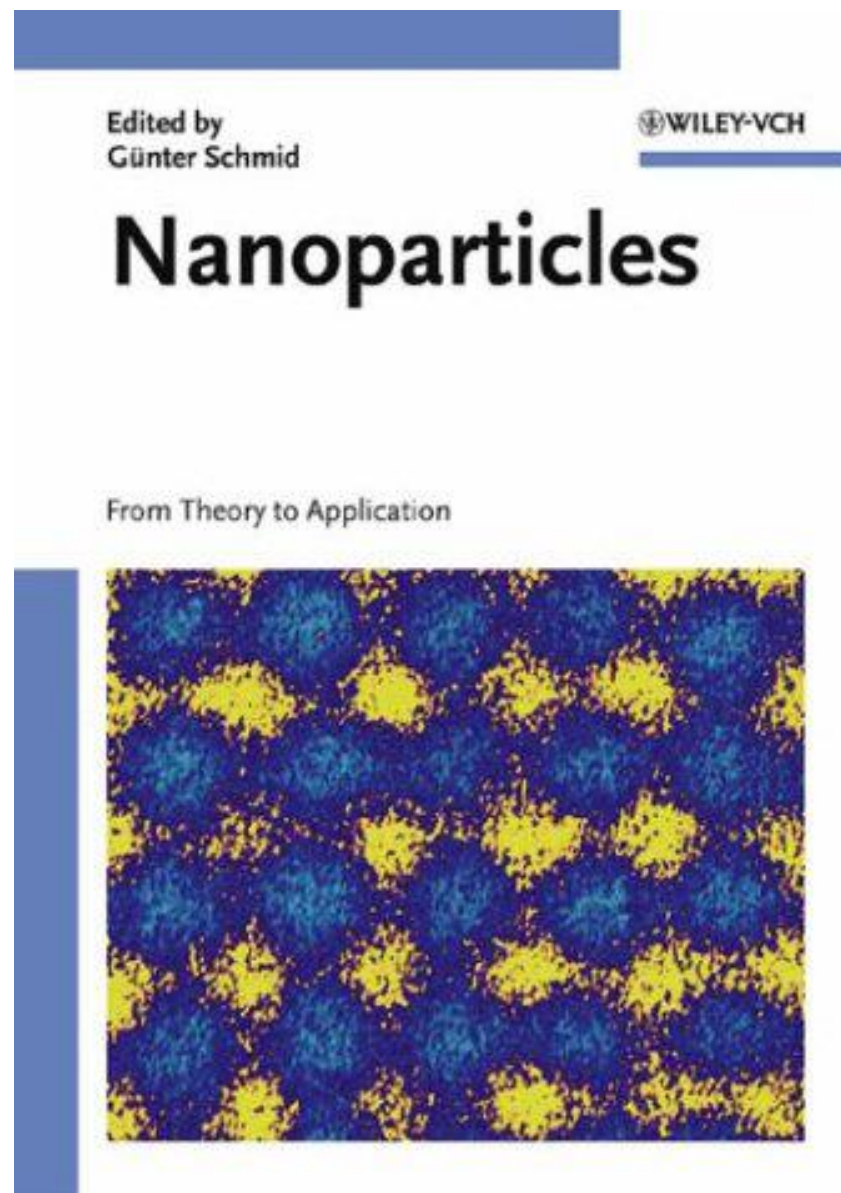


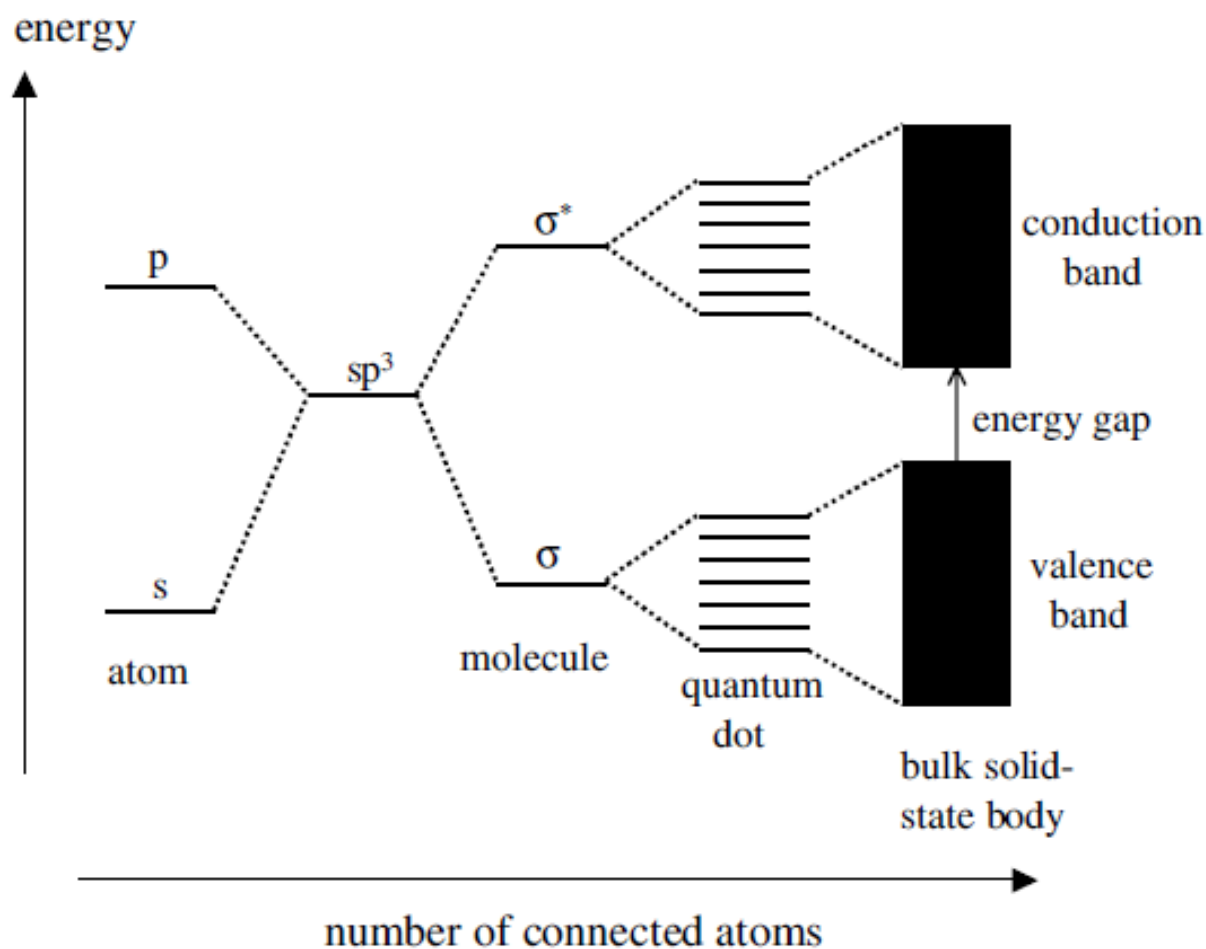
Electronic Structure

CML102

Nanoparticles: From Theory to Applications



bottom-up: atoms-molecules-nanomaterials-bulk



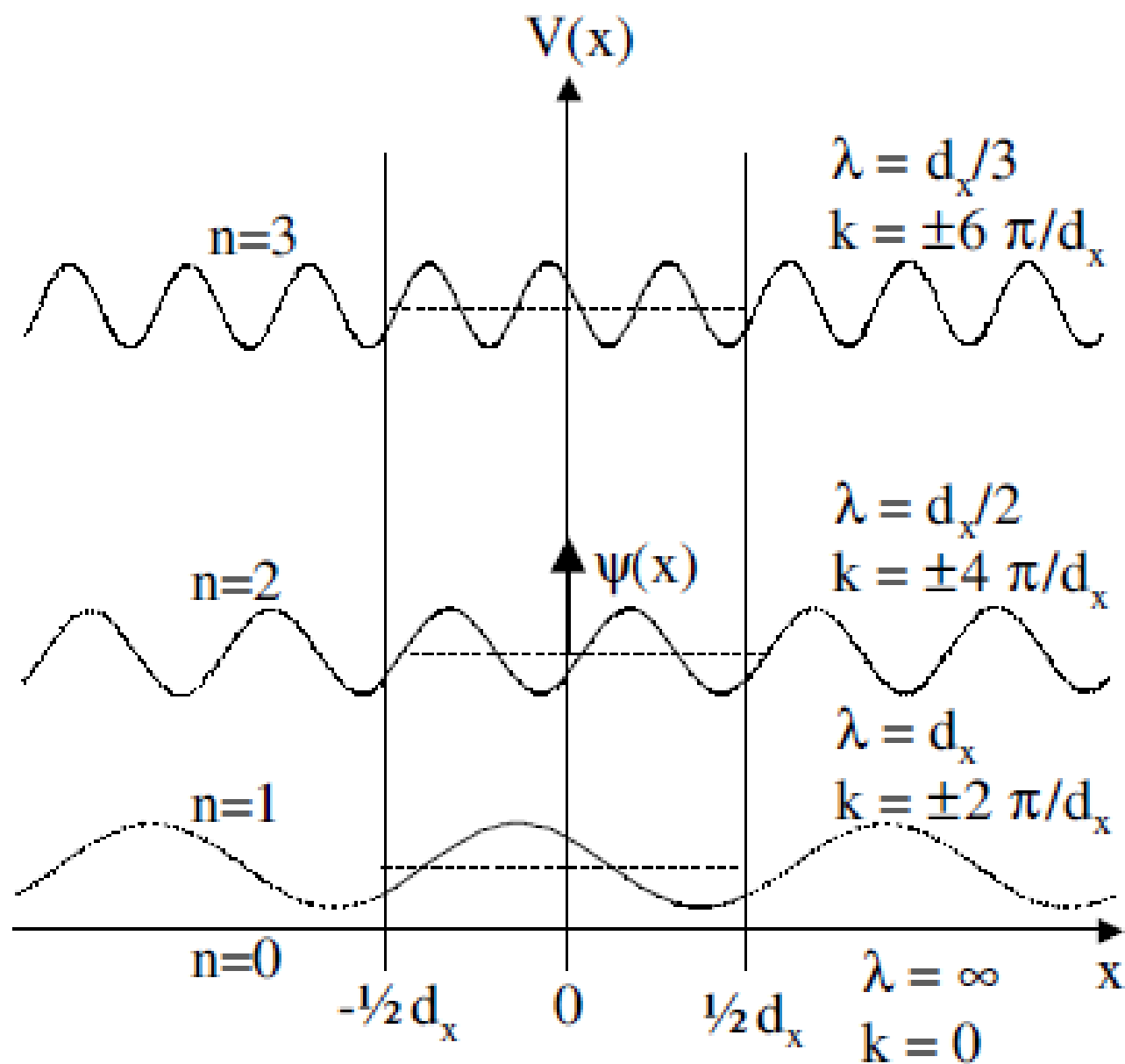
3D system

- solid of sides d_x, d_y, d_z containing N free electrons
- assumption – neglect e-e and e-crystal interactions – free electron gas
- use effective mass m^*
- energy of electron $E = \frac{1}{2} m \vec{v}^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$. Two electrons can have the same energy i.e. be in the same state, two spins
- wave vector $\vec{k} = (k_x, k_y, k_z)$,
- $\vec{p} = m\vec{v} = \hbar\vec{k} = h \frac{\vec{k}}{2\pi} = h/\lambda$
- $\pm k = |\vec{k}| = \pm 2\pi/\lambda$
 - $\sim$ nm long wave
- periodic boundary conditions – to simulate an infinite solid
 - $\psi(x, y, z) = \psi(x + d_x, y, z) = \psi(x, y + d_y, z) = \psi(x, y, z + d_z)$
 - $\psi(x, y, z) = \psi(x)\psi(y)\psi(z)$
 - soln $\psi(x) = A e^{ik_x x} e^{ik_y y} e^{ik_z z}$
 - $k_x = \pm n\Delta k = \pm n2\pi/d_x \dots$
 - two e-s ($m_s = \pm \frac{1}{2}$) in each state
- all states are equally distributed

... contd



periodic boundary condition 1D



periodic boundary conditions

- all states are equally distributed
 - 2 e-s in $k_x = 0$
 - 2 e-s in $k_x = +\Delta k, -\Delta k$ ($v_x = \pm\Delta v$)
 - 2 e-s in $k_x = +2\Delta k, -2\Delta k$ ($v_x = \pm2\Delta v$)
- In 3D bulk material
 - 2 e-s in $(k_x, k_y, k_z) = (\pm n_x \Delta k, \pm n_y \Delta k, \pm n_z \Delta k_z)$
 - sphere for large values of n
 - At 0 K
 - k_F radius of sphere
 - Fermi velocity v_F
 - Fermi energy $E_F \propto k_F$, $E < E_F$ occupied, $E > E_F$ vacant
 - Separation between states, $\Delta k = \pm n 2\pi / d_{x,y,z}$
 - bulk material, $d_{x,y,z}$ is large, Δk small, quasicontinuously filled levels
 - nanomaterials Δk is large



- Density of states, DOS $D_{3d}(k)$ – number of states per unit interval of wavenumbers
 - $D_{3d}(k)\Delta k$ is the number of electrons with wavenumber between k and Δk
 - # of e-s with wavenumber $< k_{max}$

$$N(k_{max}) = \int_0^{k_{max}} D_{3d}(k) dk$$

- G.S. all e-s have $k < k_F$

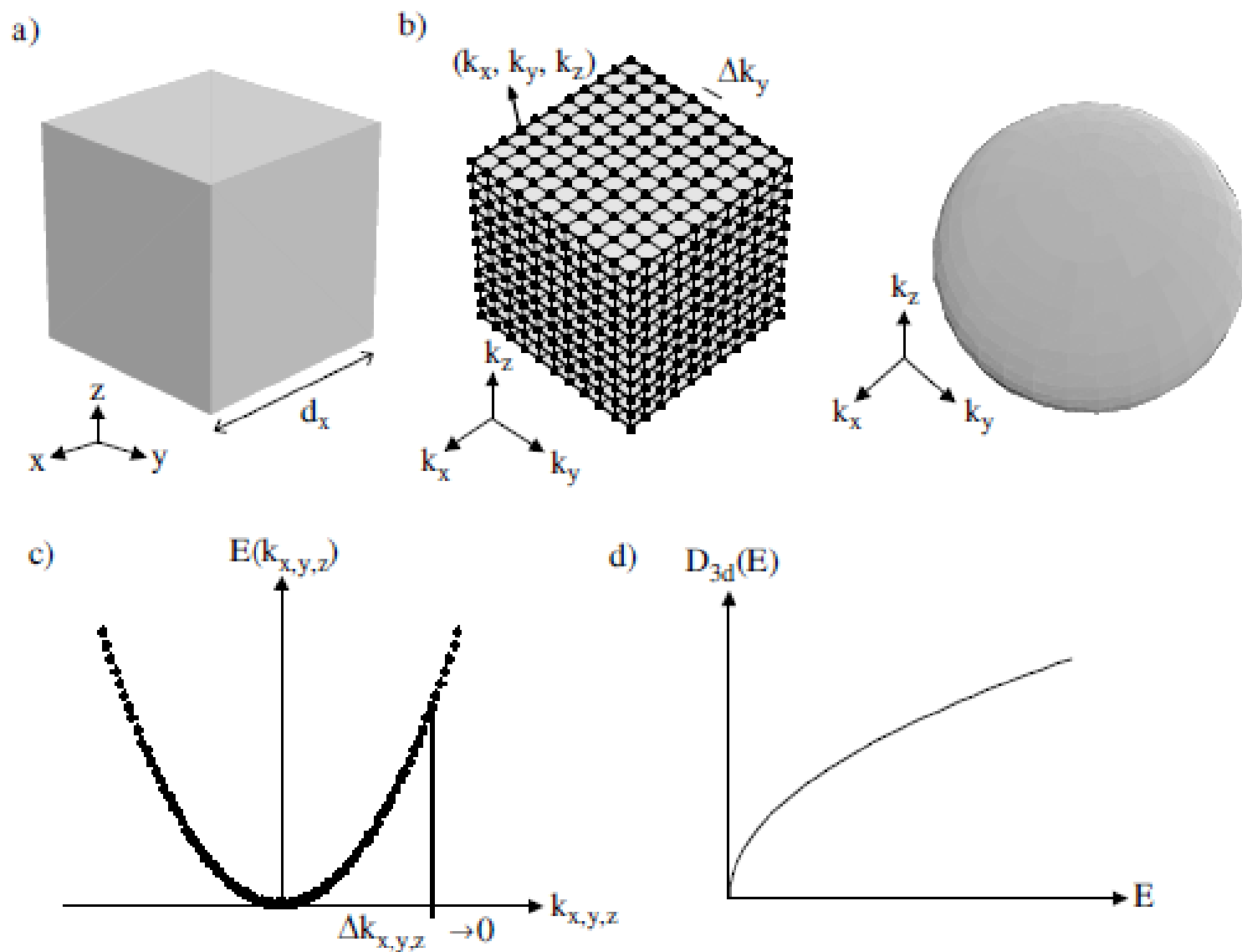
$$D_{3d}(k) = \frac{dN(k)}{dk} \propto k^2$$

- $E(k) \propto k^2$

$$D_{3d}(E) = \frac{dN(E)}{dE} = \frac{dN(k)}{dk} \cdot \frac{dk}{dE} \propto E \cdot 1/\sqrt{E} \propto \sqrt{E}$$

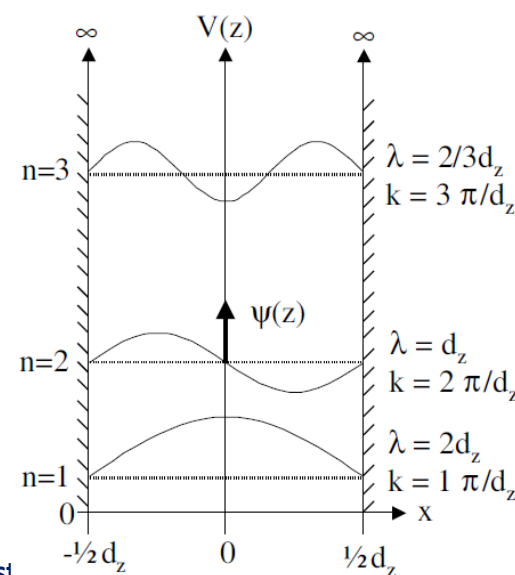


electrons in 3D bulk



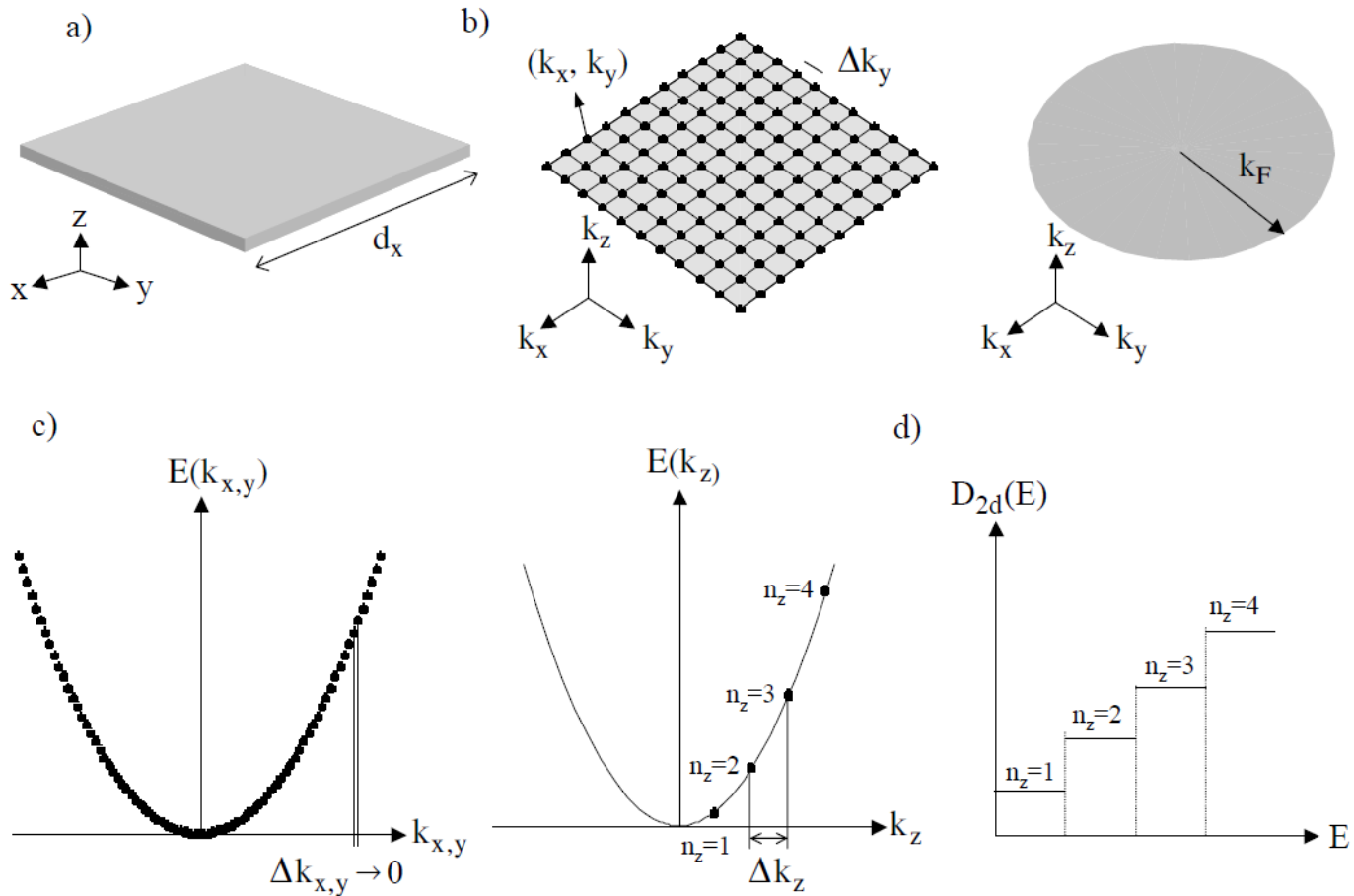
2D sheet

- extended in x- and y- directions, few nm thick in z-direction
- free electrons in xy-plane, quantized along z
 - 2DEG
- infinite high potential walls at $z = \pm \frac{1}{2} d_z$
- solutions $\rightarrow$ PIB,
 - $E_{n_z} = \hbar^2 k_z^2 / 2m = h^2 k_z^2 / 8\pi^2 m = h^2 n_z^2 / 8m d_z^2$, $n_z = 1, 2, 3 \dots$
 - similar to $k_z = n \Delta k_z$, $\Delta k_z = \pi / d_z$
- distribution of states in $k_x k_y$ plane remains quasi-continuous
- visualize this as planes in $k_x k_y$ with a separation Δk_z between the planes in k_z direction. label individual planes with n_z
- within one plane # of states is quasicontinuous
 - $\therefore$ # of states $\propto$ area of plane
 - i.e. # of states $\propto k^2 = k_x^2 + k_y^2$
 - in a ring, # states $\propto k \cdot \Delta k$
 - integration over all rings = total area of plane



DOS 2D

- $D_{2d}(k) = \frac{dN(k)}{dk} \propto k$
- $D_{2d}(E) = \frac{dN(E)}{dE} = \frac{dN(k)}{dk} \frac{dk}{dE} \propto \sqrt{E} \cdot 1/\sqrt{E} \propto 1$



DOS 1D

- $D_{1d}(E) = 1/\sqrt{E}$

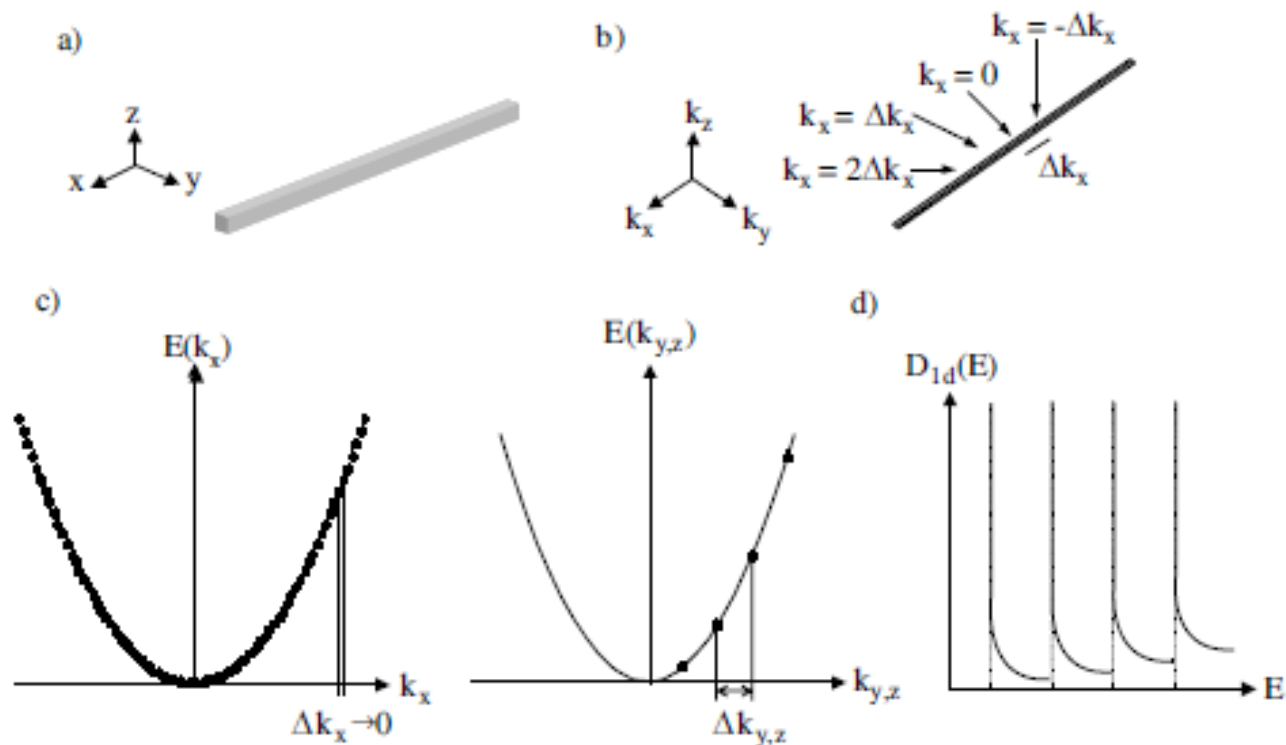


Fig. 2-6 (a) One-dimensional solid. (b) The allowed (k_x, k_y, k_z) -states can be visualized as lines parallel to the k_x -axes in the three-dimensional k -space. In this figure only one line is shown as an example. Within each line, the distribution of states is quasi-continuous, since $\Delta k_x \rightarrow 0$. The arrangement of the individual lines is discrete, since only certain discrete k_y - and k_z -states are allowed. (c) This

can also be seen in the dispersion relations. Along the k_x -axes the energy band $E(k_x, k_y, k_z)$ is quasi-continuous, but along the k_y - and k_z -axes only certain energies exist. (d) The density of states within one line along the k_x -axes is proportional to $E^{-1/2}$. Each of the hyperbolas shown in the D_{1d} -diagram corresponds to an individual (k_y, k_z) -state.

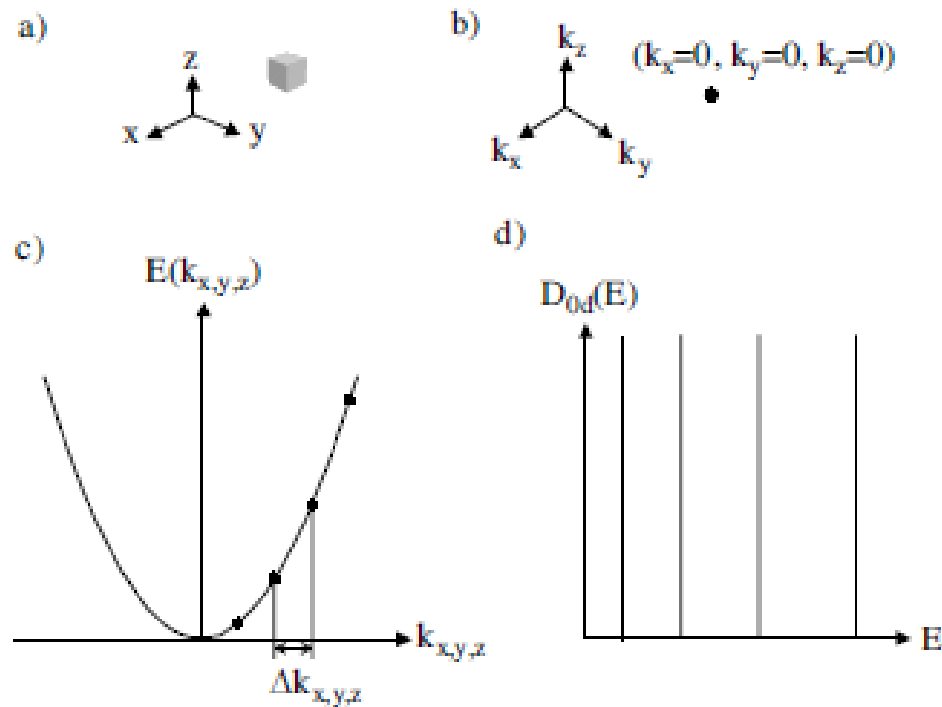


Fig. 2-7 A zero-dimensional solid. (a) The solid is shrunk in all three dimensions to a thickness that is comparable to the De Broglie wavelength of its charge carriers. (b) Because of such confinement, all states (k_x, k_y, k_z) are discrete points in the three-dimensional k -

space. (c) Only discrete energy levels are allowed. (d) The one-dimensional density of states $D_{0d}(E)$ contains delta peaks, which correspond to the individual states. Electrons can occupy only states with these discrete energies.

- Energy level spacing $\delta \propto E_F/N$ i.e. the highest occupied energy divided by the number of electrons
- $E_F \propto \rho (= N/V)$
- Fermi energy depends only on the density of electrons, not on the number
=> E_F is independent of particle size
- $\delta \propto 1/V \propto 1/L^3$
- The size of the particle decreases, energy level spacing increases



Quantum dots

- $E_{well,1D} = \frac{1}{8} \frac{h^2}{m^* d^2}$

- $E_{well,3D} = \frac{3}{8} \frac{h^2}{m^* d^2}$

- $E_{sphere} = \frac{1}{2} \frac{h^2}{m^* d^2}$

- $\frac{1}{m^*} = \frac{1}{m_h^*} + \frac{1}{m_e^*}$

- $E_{Coul} = \frac{-1.8 e^2}{2\pi\epsilon d}$

- $E_g(dot) = E_g(bulk) + E_{well} + E_{Coul}$

- $E_g(d) = E_g(bulk) + \frac{h^2}{2d^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8 e^2}{2\pi\epsilon d}$

