NANO 705-Notes

Density of States

The hamiltonian for a electron in an isotropic electronic band of a material depends on the band-edge energy of E_C and an effective mass m_C

$$\hat{H} = E_C + \frac{\hat{p}^2}{2m_C}$$

In any number of dimensions, the dispersion relation is

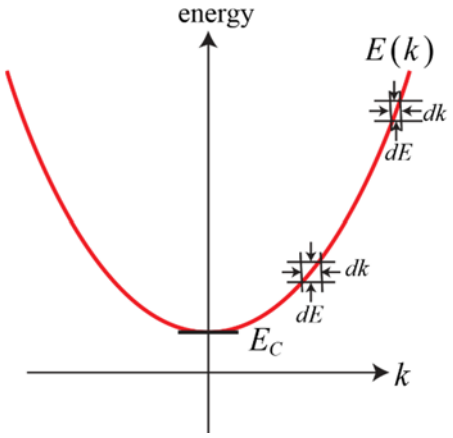
$$E(k) = E_C + \frac{\hbar^2 k^2}{2m_C}$$

The electronic band is described as "parabolic". For a particular energy $E \geq E_C$, the wavenumber can be either of two values:

$$k(E) = \pm \frac{\sqrt{2m_C}}{\hbar} \sqrt{E - E_C}$$

Assuming $k \geq 0$, the wavenumber changes with energy as

$$\frac{dk}{dE} = \frac{\sqrt{m_C/2}}{\hbar} (E - E_C)^{-1/2}$$



Often, it is useful to know the number of states per unit energy, called the density of states (or DOS), D. In any number of dimensions, we can use

$$D = \frac{dk}{dE} \cdot \frac{dN}{dk} = \frac{\sqrt{m_C/2}}{\hbar} (E - E_C)^{-1/2} \cdot \frac{dN}{dk}$$

where N is the number of states having wavevector with length less than than $k = |\mathbf{k}|$. This will depend on the number of macroscopic dimensions in which the electron is free.

1-D case

The eigenfunctions in any macroscopic dimensions are plane waves. So in 1-D

$$\phi_k(x) = A \cdot e^{ikx}$$

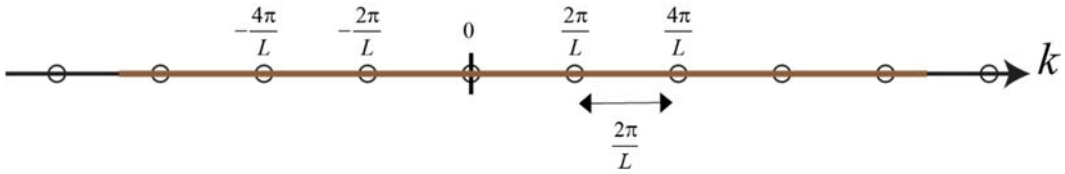
where any real value of k is allowed. It is useful to assume periodic boundary conditions within a box of size L, so that the wavefunctions in the macroscopic dimension x satisfy

$$\phi_k(x+L) = e^{ikL} \cdot \phi_k(x) = \phi_k(x)$$

We then have $e^{ikL} = 1$, which tells us that $k_n = (2\pi/L) \cdot n$, with $n \in \mathbb{Z}$. We can choose to normalize these wave functions over the size of the box, i.e.

$$\phi_n(x) = \frac{1}{\sqrt{L}} \cdot e^{2\pi i n x/L}$$

Apparently, the separation in reciprocal space between adjacent states is $\Delta k = k_{n+1} - k_n = 2\pi/L$, so we have one state per $2\pi/L$ in reciprocal space.



In 1-D, the number of states for which $k_n < |k|$ is

$$N_{1D}(k) = \frac{2|k|}{\frac{2\pi}{L}} = \frac{|k|L}{\pi}$$

The number of states per unit length with wavevector less than k is

$$\frac{N_{1D}(k)}{L} = \frac{|k|}{\pi}$$

Assuming $k \geq 0$, the number of states per unit length of wave vector is

$$\frac{1}{L}\frac{dN_{1D}}{dk} = \frac{1}{\pi}$$

So the DOS per unit length is

$$\frac{D_{1D}(E)}{L} = \begin{cases} \frac{\sqrt{m_C/2}}{\pi\hbar}(E - E_C)^{-1/2}, & E_C \leq E \\ 0, & E < E_C \end{cases}$$

This can be simplified using the step function Θ;

$$\frac{D_{1D}(E)}{L} = \frac{\sqrt{m_C/2}}{\pi\hbar}(E - E_C)^{-1/2} \cdot \Theta(E - E_C)$$

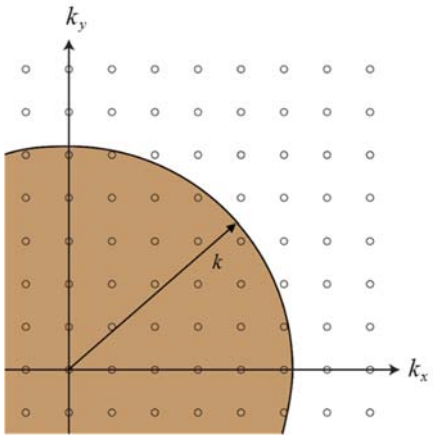
2-D case

In a 2-D box with area $S = L_x \times L_y$, the wave functions are

$$\phi_{k_x,k_y}(x,y)=\left(\frac{1}{\sqrt{L_x}}\cdot e^{ik_x x}\right)\cdot\left(\frac{1}{\sqrt{L_y}}\cdot e^{ik_y x}\right)$$

The length squared of wave vector is $k^2=k_x{}^2+k_y{}^2$, so the number of states within a circle about the origin of radius k is

$$N_{2D}(k)=\frac{\pi k^2}{\left(\frac{2\pi}{L_x}\right)\cdot\left(\frac{2\pi}{L_y}\right)}=\frac{Sk^2}{4\pi}$$



The rate of increase of the number of states per unit area with increasing wavevector is

$$\frac{1}{S}\frac{dN_{2D}}{dk}=\frac{k}{2\pi}$$

The DOS per unit area is

$$\frac{D_{2D}(E)}{S}=\frac{m_C}{2\pi\hbar^2}\cdot\Theta(E-E_C)$$

3-D case

In a 3-D box with volume $V=L_x\times L_y\times L_z$, we can write the wavefunction as

$$\phi_{\mathbf{k}}(\mathbf{r})=\frac{1}{\sqrt{V}}\cdot e^{i\mathbf{k}\cdot\mathbf{r}}$$

The number of states inside a sphere of radius k is

$$N_{3D}(k)=\frac{\frac{4}{3}\pi k^3}{\frac{(2\pi)^3}{V}}=\frac{Vk^3}{6\pi^2}$$

The rate of increase of the number of states per unit volume with increasing wavevector is

$$\frac{1}{V}\frac{dN_{3D}}{dk}=\frac{k^2}{2\pi^2}$$

The DOS per unit volume is

$$\frac{D_{3D}(E)}{V}=\frac{\sqrt{m_C{}^3/2}}{\pi^2\hbar^3}\cdot\sqrt{E-E_C}\cdot\Theta(E-E_C)$$

DOS for real-world nanostructures

Real nanostructures exist in a 3-D world, so we will have quantum confinement in some dimensions and no confinement in others. We can describe these as follows.

Quantum well

In the real, 3-D world, a quantum well has one nanoscale dimension and two bulk dimensions. Assuming particle-in-a-box confinement in the z-direction only, the wavenumbers in that direction will be limited to discrete values. The dispersion relation within this subband is

$$E_{n_z}(k)=E_C+\frac{\hbar^2k^2}{2m_C}+n_z{}^2\cdot\varepsilon_z$$

where $n_z\in\mathbb{Z}^+$. We can apply the analysis of the 2-D case above to each subband. The DOS above the edge $E_C+n_z{}^2\cdot\varepsilon_z$ of each subband is constant. For example

$$\frac{D_{n_z}(E)}{S}=\frac{m_C}{2\pi\hbar^2}\cdot\Theta\left[E-\left(E_C+n_z{}^2\cdot\varepsilon_z\right)\right]$$

So the total DOS for all subbands is

$$\frac{D(E)}{S}=\frac{m_C}{2\pi\hbar^2}\cdot\sum_{n_z}\Theta\left[E-\left(E_C+n_z{}^2\cdot\varepsilon_z\right)\right]$$

Quantum wire

A real quantum wire has two nanoscale dimensions and one bulk dimension. Assuming the cross-section of the wire is rectangular, the eigenvalue problem is separable in cartesian coordinates. We can have particle-in-a-box confinement in x and y directions, and 1-D dispersion in the z direction, so that the dispersion within a subband is

$$E_{n_x,n_y}(k)=E_C+\frac{\hbar^2k^2}{2m_C}+\varepsilon_{n_x,n_y}$$

We have defined $\varepsilon_{n_x,n_y}=n_x{}^2\cdot\varepsilon_x+n_y{}^2\cdot\varepsilon_y$ and $(n_x,n_y)\in\left(\mathbb{Z}^+\right)^2$. The previous 1-D analysis applies to each subband. So the total DOS per unit length of quantum wire is

$$\frac{D(E)}{L}=\frac{\sqrt{m_C/2}}{\pi\hbar}\cdot\sum_{n_x,n_y}\left[E-\left(E_C+\varepsilon_{n_x,n_y}\right)\right]^{-1/2}\cdot\Theta\left[E-\left(E_C+\varepsilon_{n_x,n_y}\right)\right]$$

Quantum dot

A quantum dot has confinement in all three nanoscale dimensions, with zero bulk dimensions. We would find solutions of the form

$$E_{n_x,n_y,n_z} = E_C + \varepsilon_{n_x,n_y,n_z}$$

where $(n_x, n_y, n_z) \in \left(\mathbb{Z}^+\right)^3$. Since we have no macroscopic dimensions, there is no dispersion within these subbands, so that total DOS is

$$D(E) = \sum_{n_x,n_y,n_z} \delta\left[E - \left(E_C + \varepsilon_{n_x,n_y,n_z}\right)\right]$$

Electron Concentration

To specify the electron concentration, we need to know not only the DOS, but the probability that each state is occupied, as given by the fermi function. This can be approached from a microscopic perspective if we know all of the energy eigenstates. Assume some set of quantum numbers α specifies each eigenstate, which have wavefunctions $\phi_\alpha(\mathbf{r})$ and energy eigenvalues ε_α. Then

$$n(\mathbf{r}) = 2 \cdot \sum_\alpha |\phi_\alpha(\mathbf{r})|^2 \cdot f_0(\varepsilon_\alpha - \mu)$$

where the initial factor of 2 is for the possible spin states. We assume the energy eigenstates are formed from the electronic band described previously. If the region of interest is macroscopic in one or more dimensions, we can apply periodic boundary conditions and, the allowed energies form a continuous spectrum. But if the region is nanoscopic, we will impose infinite barriers at the boundaries, causing the spectrum to become discrete.

3-D (bulk) material

Since we have no nanoscale dimensions, we can apply periodic boundary conditions in all dimensions. Thus, there is no physical boundary, and the magnitude-squared of the wave function is constant

$$|\phi_\alpha(\mathbf{r})|^2 = \frac{1}{V}$$

We previously found the number of states per unit radius of wavevector, per unit volume, so the sum of states becomes an integral

$$\sum_\alpha \rightarrow \int_{k=0}^{\infty} dk \cdot \left(\frac{dN_{3D}}{dk}\right)$$

Now we have

$$n = 2\int_{k=0}^{\infty} dk \cdot \left(\frac{1}{V}\frac{dN_{3D}}{dk}\right) \cdot f_0\left(E_C + \frac{\hbar^2 k^2}{2m_C} - \mu\right)$$

Specifically

$$n = \frac{1}{\pi^2} \cdot \int_{k=0}^{\infty} \frac{dk \cdot k^2}{1 + e^{(E_C-\mu)/k_BT} \cdot e^{\hbar^2 k^2/2m_C k_B T}}$$

Defining

$$y^2 = \frac{\hbar^2 k^2}{2m_C k_B T}, \text{ so } k^2 = \left(\frac{2m_C k_B T}{\hbar^2}\right) \cdot y^2 \text{ and } dk = \left(\frac{2m_C k_B T}{\hbar^2}\right)^{1/2} \cdot y$$

We can write this as

$$n = 2 \cdot N_C \cdot \left[\frac{4}{\sqrt{\pi}} \cdot \int_{y=0}^{\infty} \frac{dy \cdot y^2}{1 + \mathrm{e}^{(E_C - \mu)/k_B T} \cdot \mathrm{e}^{y^2}} \right]$$

We define the function

$$\Im_{3\mathrm{D}}(x) = \frac{4}{\sqrt{\pi}} \cdot \int_{y=0}^{\infty} \frac{dy \cdot y^2}{1 + \mathrm{e}^{x} \cdot \mathrm{e}^{y^2}}$$

We have used the "effective" conduction-band DOS

$$2N_C = 2 \cdot \left(\frac{m_C}{m_0} \right)^{3/2} \cdot N_0$$

where, at $k_B T = 0.026$ eV,

$$2N_0 = 2\left(\frac{m_0 k_B T}{2\pi\hbar^2} \right)^{3/2} = 2.51 \times 10^{19} \ \mathrm{cm}^{-3}$$

One can condense further using

$$n = 2 \cdot f_{3D}(E_C - \mu)$$

where

$$f_{3D}(E_C - \mu) = N_C \cdot \Im_{3\mathrm{D}} \left(\frac{E_C - \mu}{k_B T} \right)$$

Quantum well

In this case, we will have only a z-dependence on the magnitude squared of the wave function

$$|\phi_\alpha(\mathbf{r})|^2 = \frac{1}{S} |\phi_{n_z}(z)|^2$$

We cannot eliminate the sum in n_z, but we can still replace the sums in x and y

$$\sum\nolimits_\alpha \ \rightarrow \sum\nolimits_{n_z} \int_{k=0}^{\infty} dk \cdot \left(\frac{dN_{2\mathrm{D}}}{dk} \right)$$

Now

$$n = 2 \sum\nolimits_{n_z} |\phi_{n_z}(z)|^2 \int_{k=0}^{\infty} dk \cdot \left(\frac{1}{S} \frac{dN_{2\mathrm{D}}}{dk} \right) \cdot f_0 \left(E_C + \frac{\hbar^2 k^2}{2m_C} + \varepsilon_{n_z} - \mu \right)$$

This gives

$$n = \frac{1}{\pi} \sum\nolimits_{n_z} |\phi_{n_z}(z)|^2 \cdot \int_{k=0}^{\infty} \frac{dk \cdot k}{1 + \mathrm{e}^{(E_C + \varepsilon_{n_z} - \mu)/k_B T} \cdot \mathrm{e}^{\hbar^2 k^2 / 2 m_C k_B T}}$$

Using

$$y^2 = \frac{\hbar^2 k^2}{2m_C k_B T}\text{, so } k^2 = \left(\frac{2m_C k_B T}{\hbar^2}\right)\cdot y^2 \text{ and } k\cdot dk = \left(\frac{2m_C k_B T}{\hbar^2}\right)\cdot y\cdot dy$$

We can write this as

$$n = 2\sum\nolimits_{n_z} |\phi_{n_z}(z)|^2 \cdot {N_C}^{2/3} \cdot \left[2\int_{y=0}^{\infty} \frac{dy\cdot y}{1+\mathrm{e}^{(E_C+\varepsilon_{n_z}-\mu)/k_B T}\cdot \mathrm{e}^{y^2}}\right]$$

using the same definition of N_C as in the 3-D case. Now we can define

$$\begin{aligned}\Im_{2D}(x) &= 2\cdot\int_{y=0}^{\infty}\frac{dy\cdot y}{1+\mathrm{e}^{x}\cdot\mathrm{e}^{y^2}}\\ &= 2\cdot\int_{y=0}^{\infty}\frac{dy\cdot y\cdot \mathrm{e}^{-y^2}}{\mathrm{e}^{-y^2}+\mathrm{e}^{x}}\\ &= -\ln\left(\mathrm{e}^{-y^2}+\mathrm{e}^{x}\right)\Big|_{y=0}^{\infty}\\ \Im_{2D}(x) &= \ln\left(1+\mathrm{e}^{-x}\right)\end{aligned}$$

If we also define

$$f_{2D}(E-\mu) = {N_C}^{2/3}\cdot\Im_{2D}\left(\frac{E-\mu}{k_B T}\right)$$

we can further condense to

$$n = 2\sum\nolimits_{n_z} |\phi_{n_z}(z)|^2 \cdot f_{2D}(E_C+\varepsilon_{n_z}-\mu)$$

Quantum-wire

In this case, we will have both x and y-dependence on the magnitude squared of the wave function

$$|\phi_\alpha(\mathbf{r})|^2 = \frac{1}{L}|\phi_{n_x,n_y}(x,y)|^2$$

We change the z sum to an integral

$$\sum\nolimits_\alpha \rightarrow \sum\nolimits_{n_x,n_y}\int_{k=0}^{\infty} dk\cdot\left(\frac{dN_{1D}}{dk}\right)$$

Now

$$n = 2\sum\nolimits_{n_x,n_y}|\phi_{n_x,n_y}(x,y)|^2\int_{k=0}^{\infty}dk\cdot\left(\frac{1}{L}\frac{dN_{1D}}{dk}\right)\cdot f_0\left(E_C+\frac{\hbar^2k^2}{2m_C}+\varepsilon_{n_x,n_y}-\mu\right)$$

which becomes

$$n = \frac{2}{\pi}\sum\nolimits_{n_x,n_y}|\phi_{n_x,n_y}(x,y)|^2\int_{k=0}^{\infty}\frac{dk}{1+\mathrm{e}^{\left(E_C+\varepsilon_{n_x,n_y}-\mu\right)/k_B T}\cdot\mathrm{e}^{\hbar^2k^2/2m_C k_B T}}$$

Using

$$y^2 = \frac{\hbar^2 k^2}{2m_C k_B T}, \text{ so } k^2 = \left(\frac{2m_C k_B T}{\hbar^2}\right)\cdot y^2 \text{ and } dk = \left(\frac{2m_C k_B T}{\hbar^2}\right)^{1/2}\cdot dy$$

we can write this as

$$n = 2\sum_{n_x,n_y}\left|\phi_{n_x,n_y}(x,y)\right|^2 \cdot N_C{}^{1/3}\cdot\left[\frac{2}{\sqrt{\pi}}\int_{y=0}^{\infty}\frac{dy}{1+\mathrm{e}^{(E_C+\varepsilon_{n_x,n_y}-\mu)/k_BT}\cdot\mathrm{e}^{y^2}}\right]$$

Let's define

$$\Im_{1D}(x) = \frac{2}{\sqrt{\pi}}\int_{y=0}^{\infty}\frac{dy}{1+\mathrm{e}^{x}\cdot\mathrm{e}^{y^2}}$$

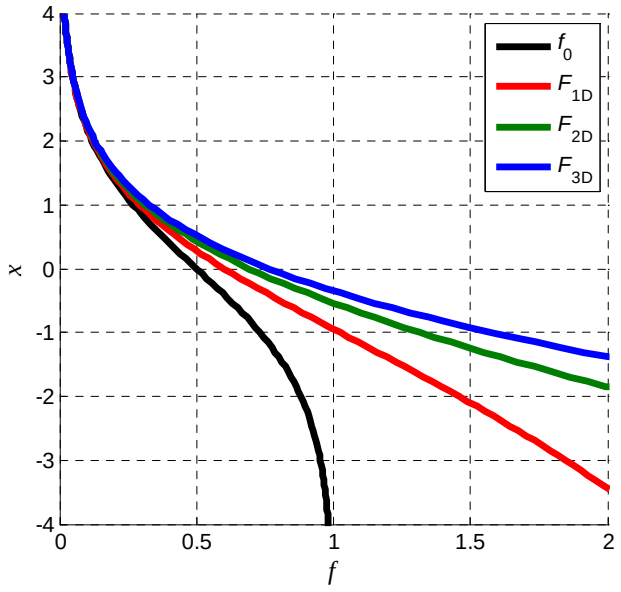
and

$$f_{1D}(E-\mu) = N_C{}^{1/3}\cdot\Im_{1D}\left(\frac{E-\mu}{k_BT}\right)$$

Finally,

$$n = 2\sum_{n_x,n_y}\left|\phi_{n_x,n_y}(x,y)\right|^2 \cdot f_{1D}\left(E_C+\varepsilon_{n_x,n_y}-\mu\right)$$

The functions $f_0(x)$ $\Im_{1D}(x)$, $\Im_{2D}(x)$, and $\Im_{3D}(x)$ are plotted below. Whereas the fermi function is limited to the range $0 \le f_0 \le 1$, the functions we have defined have no upper limits.



Quantum dot

A quantum dot has confinement in all three nanoscale dimensions, with zero bulk dimensions. Assuming all faces of the box are rectangular, the eigenvalue problem is separable in cartesian coordinates, and we would find solutions $\phi_{n_x,n_y,n_z}(\mathbf{r})$ for $(n_x,n_y,n_z)\in\left(\mathbb{Z}^+\right)^3$. The equilibrium electron concentration is

$$n(\mathbf{r}) = 2 \cdot \sum_{n_x,n_y,n_z} \left|\phi_{n_x,n_y,n_z}(\mathbf{r})\right|^2 \cdot f_0\left(E_C + \varepsilon_{n_x,n_y,n_z} - \mu\right)$$

Non-degenerate cases

The preceding analysis is sufficiently general that it would apply regardless of the relative position of the chemical potential with respect to the conduction-band edge. If the chemical potential lies close to the band edge or within the band, the electron concentration is called "degenerate". In semiconductors, we usually have the situation where the chemical potential is well below the conduction band edge, such that $E_C - \mu \gg k_B T$. This case is called "non-degenerate". For the functions defined above, this corresponds to the limit where $e^x \cdot e^{y^2} \gg 1$, so $1 + e^x \cdot e^{y^2} \approx e^x \cdot e^{y^2}$, which allows simplification of the expressions we obtained.

Bulk material

In the 3D case,

$$\mathfrak{I}_{3D}(x) \approx e^{-x} \frac{4}{\sqrt{\pi}} \cdot \int_{y=0}^{\infty} dy \cdot y^2 \cdot e^{-y^2}$$

The integral is easily found as follows: Say we want to know

$$I_0 = \int_{y=0}^{\infty} dy \cdot e^{-\alpha y^2}$$

So

$$2I_0 = \int_{y=-\infty}^{\infty} dy \cdot e^{-\alpha y^2}$$

The square of this is

$$\begin{aligned}(2I_0)^2 &= \left(\int_{x=-\infty}^{\infty} dx \cdot e^{-\alpha x^2}\right)\left(\int_{y=-\infty}^{\infty} dy \cdot e^{-\alpha y^2}\right) \\ &= \int_{x=-\infty}^{\infty} dx \int_{y=-\infty}^{\infty} dy \cdot e^{-\alpha\left(x^2+y^2\right)}\end{aligned}$$

We can switch to polar coordinates

$$\begin{aligned}(2I_0)^2 &= \int_{\phi=0}^{2\pi} d\phi \int_{r=0}^{\infty} dr \cdot r \cdot e^{-\alpha r^2} \\ &= 2\pi \cdot \int_{r=0}^{\infty} dr \cdot r \cdot e^{-\alpha r^2} \\ &= -\frac{\pi}{\alpha} \cdot e^{-r^2}\Big|_{r=0}^{\infty}\end{aligned}$$

$$(2I_0)^2 = \frac{\pi}{\alpha}$$

So

$$I_0 = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

Now we want to find

$$I_2 = \int_{y=0}^{\infty} dy \cdot y^2 \cdot \mathrm{e}^{-\alpha y^2}$$

We can observe that

$$I_2 = -\frac{\partial}{\partial \alpha} I_0 = \frac{1}{4}\sqrt{\frac{\pi}{\alpha^3}}$$

For $\Im_{3D}(x)$, we have $\alpha = 1$, so $\Im_{3D}(x) \approx \mathrm{e}^{-x}$. In this limit

$$n = 2 \cdot N_C \cdot \mathrm{e}^{-(E_C - \mu)/k_B T}$$

Quantum well

The expression for the quantum well is easily simplified. For example, we can repeat the integral in this limit

$$\Im_{2D}(x) \approx \mathrm{e}^{-x} \cdot 2 \cdot \int_{y=0}^{\infty} dy \cdot y \cdot \mathrm{e}^{-y^2} = \mathrm{e}^{-x}$$

Now we can write the electron concentration as

$$\begin{aligned} n &= 2\sum\nolimits_{n_z} \left|\phi_{n_z}(z)\right|^2 \cdot {N_C}^{2/3} \cdot \mathrm{e}^{-(E_C + \varepsilon_{n_z} - \mu)/k_B T} \\ &= 2 \cdot {N_C}^{2/3} \cdot \mathrm{e}^{-(E_C - \mu)/k_B T} \cdot \sum\nolimits_{n_z} \left|\phi_{n_z}(z)\right|^2 \cdot \mathrm{e}^{-\varepsilon_{n_z}/k_B T} \end{aligned}$$

Quantum wire

In this case, we again have

$$\Im_{1D}(x) \approx \mathrm{e}^{-x} \cdot \frac{2}{\sqrt{\pi}} \int_{y=0}^{\infty} dy \cdot \mathrm{e}^{-y^2} = \mathrm{e}^{-x}$$

leading to

$$\begin{aligned} n &= 2\sum\nolimits_{n_x, n_y} \left|\phi_{n_x, n_y}(x, y)\right|^2 \cdot {N_C}^{1/3} \cdot \mathrm{e}^{-\left(E_C + \varepsilon_{n_x, n_y} - \mu\right)/k_B T} \\ &= 2 \cdot {N_C}^{1/3} \cdot \mathrm{e}^{-(E_C - \mu)/k_B T} \cdot \sum\nolimits_{n_x, n_y} \left|\phi_{n_x, n_y}(x, y)\right|^2 \cdot \mathrm{e}^{-\varepsilon_{n_x, n_y}/k_B T} \end{aligned}$$