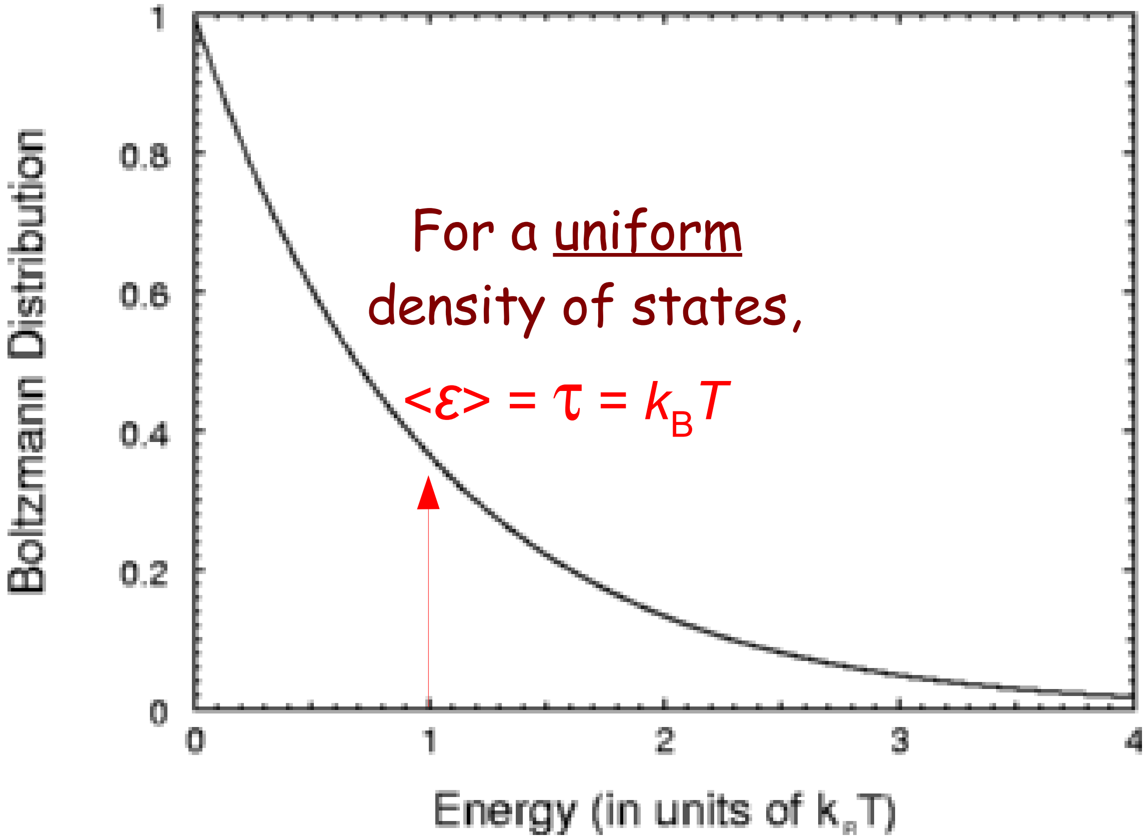
Averaging over the Boltzmann Distribution



For a uniform density of states,

$\langle \varepsilon \rangle = \tau = k_B T$

Looked at as a probability distribution over **energy** at a **fixed temperature**, the Boltzmann distribution is just an exponential decay. If we assume that the **density of states** (the number of states per unit energy interval) is **uniform**, then we find a **mean** energy $\langle \varepsilon \rangle = \tau = k_B T$.

But what if the density of states is not uniform? What if there are more **available** states per unit energy interval at low energy than at high energy (or vice versa)? Then we have to include another factor in our averages:

$\mathcal{D}(\varepsilon)$, the density of states.

Distributions & Averages

If "X" is a function of ε, $X(\varepsilon)$, and the **probability** of a state of energy ε being **occupied** is given by $\mathcal{P}(\varepsilon)$, and the **number** of such states per unit energy interval is given by the **density of states** $\mathcal{D}(\varepsilon)$, then the **average** value of "X" is given by

$$\langle X \rangle = \int X(\varepsilon)\, \mathcal{P}(\varepsilon)\, \mathcal{D}(\varepsilon)\, d\varepsilon \Big/ \int \mathcal{P}(\varepsilon)\, \mathcal{D}(\varepsilon)\, d\varepsilon$$

where the integral (or sum, in the case of discrete states) extends over the entire range of possible values of ε. The same formulation would hold mathematically for averages over momentum p or other properties, but the Boltzmann distribution gives us an explicit result for $\mathcal{P}(\varepsilon)$, so this one is easiest. Moreover, the simplest thing to take the average of is ε itself.

Note that **normalization** is accomplished by **dividing by** $\int \mathcal{P}(\varepsilon)\, \mathcal{D}(\varepsilon)\, d\varepsilon$.

Allowed Energies of a Particle in a 1D Box

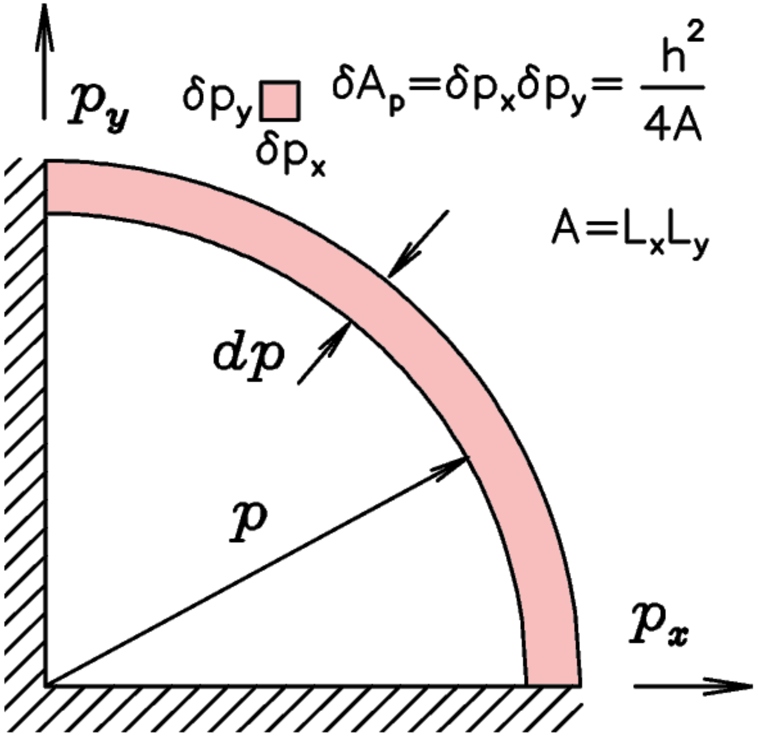
Recall that de Broglie's hypothesis implies a discrete set of allowed **modes** for a particle confined to a box of length L: those with $\lambda_n = 2L/n$ and so $p_n = h/\lambda_n = nh/2L$ and $E_n = p_n^2/2m = n^2 h^2/8mL^2$. Now, the allowed values of n range over all positive integers and are **uniformly distributed** -- i.e. $\mathcal{D}(n)$ = constant. But $E_n \equiv \varepsilon$ is not! The energy scales with n^2 and so there are **more** allowed energies per unit energy interval at **low** energies than at high energies. Mathematically we can write $\mathcal{D}(\varepsilon)\, d\varepsilon = \mathcal{D}(n)\, dn$ so $\mathcal{D}(\varepsilon) = \mathcal{D}(n)\, dn/d\varepsilon \propto dn/d\varepsilon$. Since $\varepsilon \propto n^2$, $n \propto \varepsilon^{1/2}$ and we have $dn/d\varepsilon \propto \varepsilon^{-1/2}$ or

$$\boxed{\mathcal{D}(\varepsilon) \propto \varepsilon^{-1/2}}$$

There, wasn't that easy? This is the result for a 1D box, where there is a **uniform** distribution of allowed n values. In higher dimensions it's a bit more complicated . . . .

Allowed Energies of a Particle in a 2D Box

Allowed modes for a particle confined to a 2D square box of width L are those with $p_x = n_x h/2L$, $p_y = n_y h/2L$ and $\varepsilon = p^2/2m = n^2\, h^2/8mA$, where $A = L^2$ and $n^2 = n_x^2 + n_y^2$. Both n_x and n_y range over all positive integers and are uniformly distributed, but now n is not: the number of allowed modes within dn of a given n is proportional to the area of an annulus of width dn and radius n in "n-space" -- namely $\mathcal{D}(n) \propto n$.



Now $\mathcal{D}(\varepsilon) = \mathcal{D}(n)\, dn/d\varepsilon \propto n\, dn/d\varepsilon$. We still have $n \propto \varepsilon^{1/2}$ and so $dn/d\varepsilon \propto \varepsilon^{-1/2}$, giving $\mathcal{D}(\varepsilon) \propto \varepsilon^{1/2} \cdot \varepsilon^{-1/2}$, or

$$\boxed{\mathcal{D}(\varepsilon) = \text{constant}}$$

in a **two** dimensional box.

In 3D we get $\mathcal{D}(n) \propto n^2$ by an analogous 3D "n-space" picture.

Allowed Energies of a Particle in a 3D Box

Allowed modes for a particle confined to a 3D cube of width L are those with $p_x = n_x h/2L$, $p_y = n_y h/2L$, $p_z = n_z h/2L$ and $\varepsilon = p^2/2m = n^2\, h^2/8mV$, where $V = L^3$ and $n^2 = n_x^2 + n_y^2 + n_z^2$. As before, n_x, n_y and n_z range over all positive integers and are uniformly distributed, but now the number of allowed modes within dn of a given n is proportional to the volume of a spherical shell of width dn and radius n in 3D "n-space" -- namely $\mathcal{D}(n) \propto n^2$. Now $\mathcal{D}(\varepsilon) = \mathcal{D}(n)\, dn/d\varepsilon \propto n^2\, dn/d\varepsilon$. We still have $n \propto \varepsilon^{1/2}$ and so $dn/d\varepsilon \propto \varepsilon^{-1/2}$, giving $\mathcal{D}(\varepsilon) \propto \varepsilon \cdot \varepsilon^{-1/2}$, or

$$\boxed{\mathcal{D}(\varepsilon) \propto \varepsilon^{1/2}}$$

in a **three** dimensional box (the kind we are most familiar with).

Now we can calculate **thermal averages** in 3D:

$$\langle X \rangle = \int X(\varepsilon)\, e^{-\varepsilon/\tau}\, \varepsilon^{1/2}\, d\varepsilon \Big/ \int e^{-\varepsilon/\tau}\, \varepsilon^{1/2}\, d\varepsilon$$

The Maxwellian Distribution of Speeds in a 3D Box

In 3D we have $\mathcal{D}(\varepsilon) \propto \varepsilon^{1/2}$ and $\varepsilon = \tfrac{1}{2} m v^2$ or $\varepsilon \propto v^2$ where v is the **speed** of a particle in the box. The usual distribution conversion gives $\mathcal{D}(v)\, dv = \mathcal{D}(\varepsilon)\, d\varepsilon$ so $\mathcal{D}(v) = \mathcal{D}(\varepsilon)\, d\varepsilon/dv \propto \varepsilon^{1/2}\, v \propto v^2$. This is all we need to write down the thermal distribution of **speeds** in a 3D box:

$$\boxed{\mathcal{P}(v)\, \mathcal{D}(v) \propto v^2\, e^{-\frac{1}{2} m v^2/\tau}}$$

This is the same as Eq. (22-14) on p. 503 of the textbook, except for the normalization factor that turns the $\propto$ sign into an $=$ sign, and of course the notation: $N(v) \equiv \mathcal{P}(v)\, \mathcal{D}(v)$.

The Maxwellian distribution is even simpler in 1D and 2D . . . .