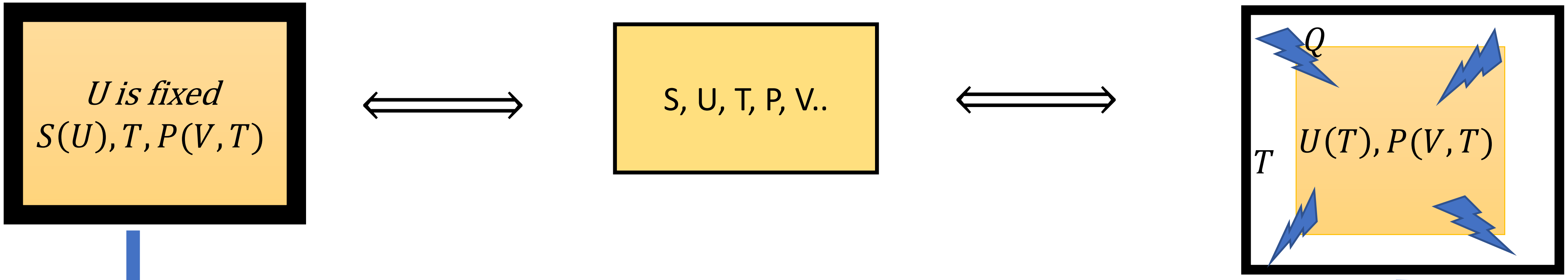
Lecture 15

31.09.2018

Ideal gas in a thermal bath

Equilibrium thermodynamic state



Statistical mechanics

$\Omega(U)$ counts all **equally-likely** accessible microstates

$$P(s) = \frac{1}{\Omega(U)}$$

✓ $S(U) = -k \sum_s P(s) \, ln \, P(s) = k \ln \Omega \quad (U)$

✓ $T = \left(\frac{\partial S}{\partial U}\right)^{-1}_{V,N}$

✓ $F = U - TS$

Isolated system

$\Longleftrightarrow$

$Z(T) = \sum_s e^{-\beta E_s}$ counts the microstates when they don't have the same probability at a given T

$$P(s) = \frac{1}{Z(T)} e^{-\beta E_s}$$

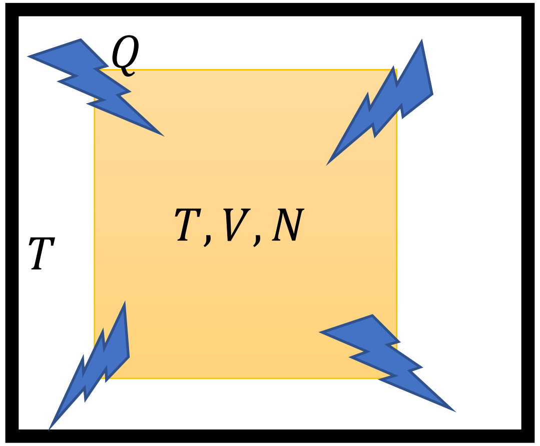
✓ $\mathbf{F = -kT \ln Z(\mathit{T})}$

System in a thermal bath

✓ $U = \langle E_s \rangle = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{V,N}$

✓ $S = -k \sum_s P(s) \ln P(s) = \frac{U-F}{T}$

System in contact with a thermal bath: Partition function $Z(T, V, N)$



- One particle in a thermal bath

$$Z_1(T) = \sum_{\{s\}} e^{-\frac{E(s)}{kT}}, \qquad \text{so that } P_1(s) = \frac{1}{Z_1} e^{-\beta E(s)}, \qquad \beta = \frac{1}{kT}$$

- *N-**distinguishable, identical and independent*** classical particles

$$Z_N(T, V) = \sum_{\{s_1, s_2 \cdots s_N\}} e^{-\frac{E_N(s_1, \cdots s_N)}{kT}}$$

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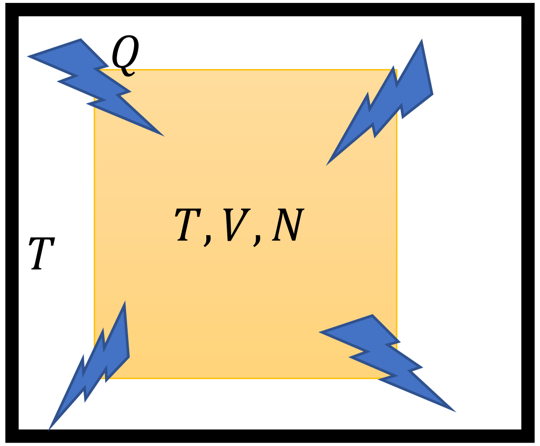
$$Z_N(T, V) = \left(\sum_{s_1} e^{-\beta\, E_1(s_1)}\right)\left(\sum_{s_2} e^{-\beta E_1(s_2)}\right) \cdots \left(\sum_{s_N} e^{-\beta E_1(s_N)}\right)$$

$$Z_N(T, V) \; = Z_1^N(T, V)$$

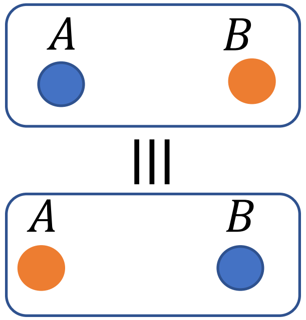
System in contact with a thermal bath: Partition function $Z(T,V,N)$



- One particle in a thermal bath

$$\boldsymbol{Z_1(T) = \sum_{\{s\}} e^{-\frac{E(s)}{kT}}, \qquad so\ that\ P_1(s) = \frac{1}{Z_1}\, e^{-\beta E(s)}, \qquad \beta = \frac{1}{kT}}$$

- *2-**indistinguishable, identical and independent*** particles in 2 states

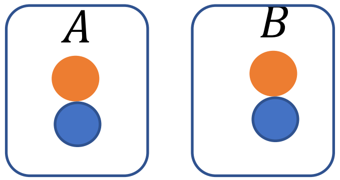


$$\boldsymbol{Z_2 = \tfrac{1}{2} Z_1^2 = \tfrac{1}{2}\left(e^{-\beta E(s_A)} + e^{-\beta E(s_B)}\right)^2}$$

$$\boldsymbol{Z_2 = \frac{1}{2} e^{-\beta E(s_A)} + e^{-\beta E(s_A)}\, e^{-\beta E(s_B)} + \frac{1}{2} e^{-\beta E(s_B)}}$$

  - **Configurations in which the two particles are in the same state are also «double-counted». The probability that two particles are in the same state is very low for dilute ideal gas , so this error is very small.**

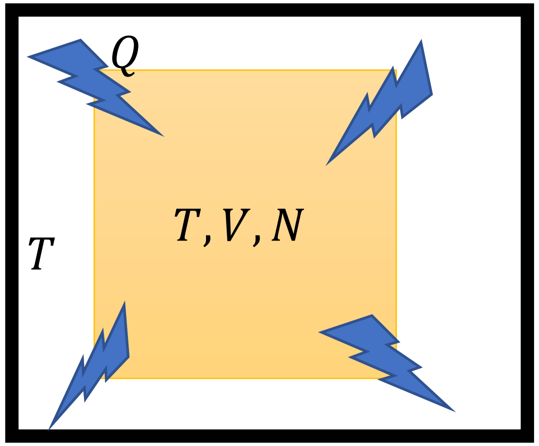
- *N-**indistinguishable, identical and independent*** classical particles



$$\color{red}{\boldsymbol{Z_N(T,V) = \tfrac{1}{N!} Z_1^N(T,V)}}$$

So, if we know $Z_1(T)$, we know the partition function of N independent, identical particles $Z_N(T)$

$\ln Z$ and F



- 1- particle

$$F_1(T) = -kT \ln Z_1(T)$$

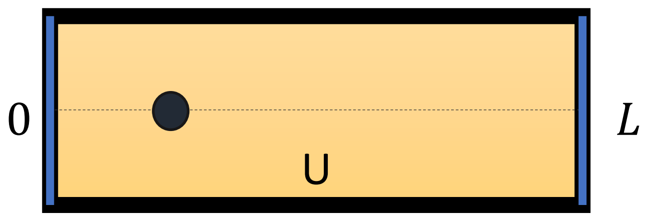
- *N-**distinguishable, identical and independent*** classical particles

$$F_N(T) = -kT \ln Z_N(T) = -NkT \ln Z_1(T)$$

- *N-**indistinguishable, identical and independent*** classical particles

$$F_N(T) = -kT \ln \frac{Z_1^N(T)}{N!} =_{N\gg 1} -NkT \left[\ln\left(\frac{Z_1}{N}\right) - 1 \right]$$

One isolated free particle in 1D



- Consider **one free quantum** particle in a 1D box of «volume» L
- Quantum states are *standing waves* with wavelengths $\lambda_{n_x} = \frac{2L}{n_x}$, with $n_x = 1,2,\cdots$ is the state number
- Standing waves are superposition of travelling waves in opposite directions with the same momentum in magnitute

$$p_x = \frac{h}{\lambda_n} = \frac{h}{2L}\, n_x$$

- The energy levels of a free particle in 1D are

$$\epsilon_{n_x} = \frac{p_x^2}{2m} \to \boldsymbol{\epsilon_{n_x} = \frac{h^2}{8mL^2} n_x^2} \to n_x(\epsilon_n) = \frac{2L}{h}\sqrt{2m\epsilon_n}$$

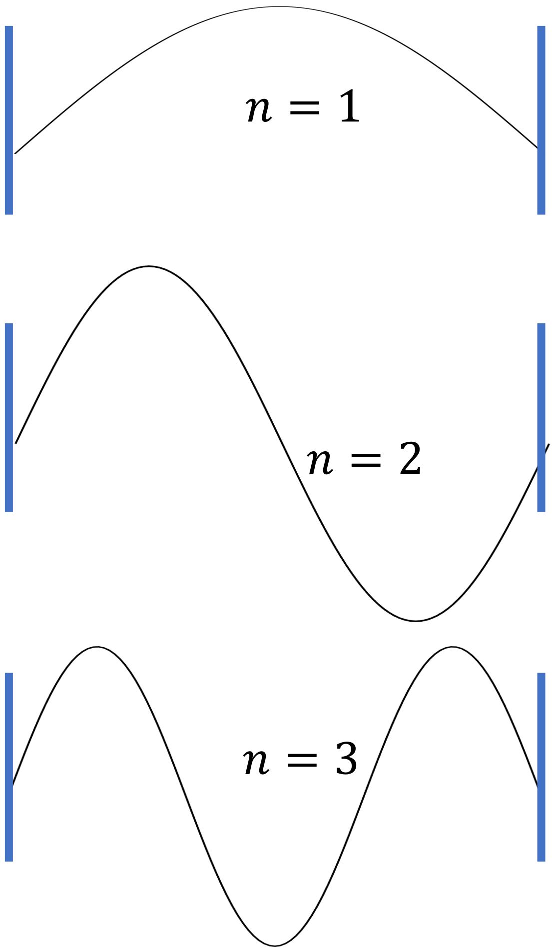
- Multiplicity $\Omega_1^{1D}(U,L)$ is given by the state number corresponding to the fixed energy U **(number of microstates with energies $\le U$)**

$$\Omega_1^{1D}(U,L) = n(\epsilon_n = U) \to \boldsymbol{\Omega_1^{1D}(U,L) = \frac{2L}{h}\sqrt{2mU}}$$

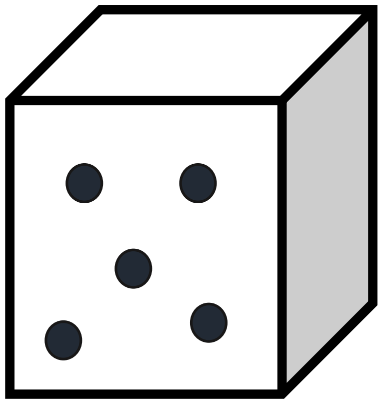
(technically it should just be one microstate, but that will lead to inconsistent thermodynamics)

$$\boldsymbol{S = k\, ln\, \Omega_1^{1D} \to \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right) = \frac{k}{2U} \to U = \frac{kT}{2}}$$

!! For many particles, counting all the states with energy $\le U$ is more or less the same as counting the states with energy U, and all is good!



N isolated free particles in 3D

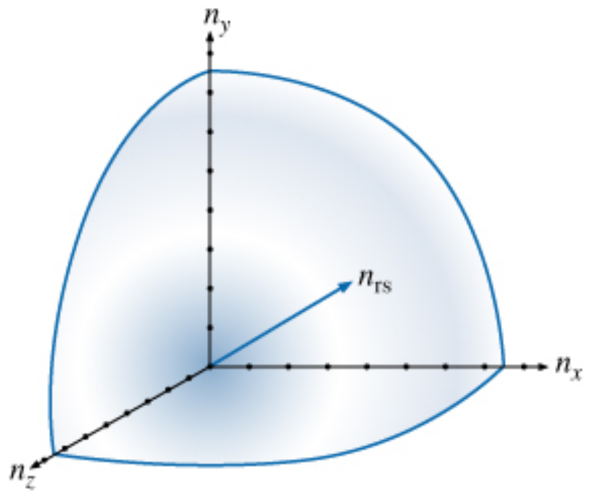


- Consider **N independent and free** quantum particles in a 3D box of volume $V = L^3$
- The energy levels for each free particle in 3D are

$\epsilon_{n_i} = \frac{\vec{p_i} \cdot \vec{p_i}}{2m} = \frac{h^2}{8mL^2}(n_{x,i}^2 + n_{y,i}^2 + n_{z,i}^2),\ where\ n_{k,i} = 0,1,2,\cdots$ is the state number for $\mathrm{k} =$ x, y, z of each particle $i = 1, \cdots N$

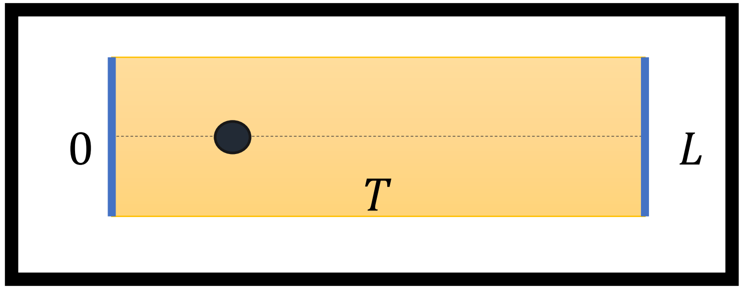
- Multiplicity Ω_N^{3D} is the volume of the hyperspehere in the **3N-dimensional «$\boldsymbol{n}$-space»** corresponding to a fixed energy $U = \sum_{i=1}^{N} \epsilon_{n_i}$
- Hyper-surface in the «n-space» with equal energy is described by the quadratic form

$$\sum_{i}^{N} n_{x,i}^2 + n_{y,i}^2 + n_{z,i}^2 = \frac{8mL^2 U}{h^2} = R_n^2$$



- $\boldsymbol{\Omega_N^{3D}(U, V) = \frac{1}{N!\left(\frac{3N}{2}-1\right)!} V^N \left(\frac{2\pi m U}{h^2}\right)^{\frac{3N}{2}}}$
- $\boldsymbol{S = k\ ln\ \Omega_N^{3D} \rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right) = \frac{3Nk}{2U} \rightarrow U = \frac{3NkT}{2}}$

One free particle in 1D in a thermal bath

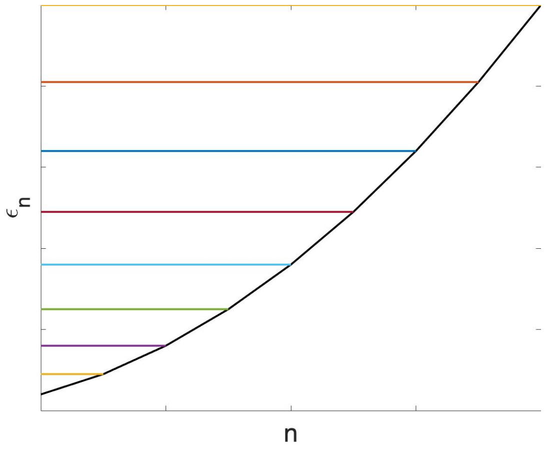


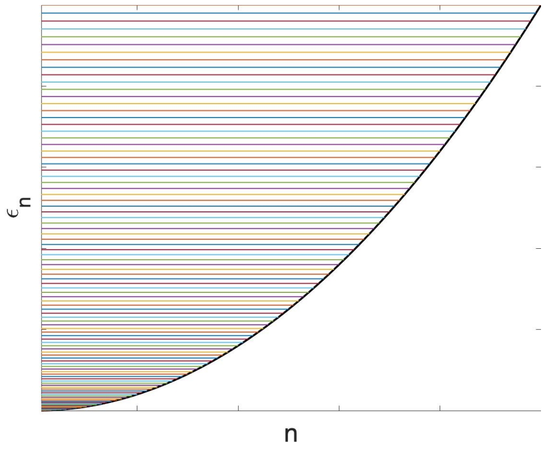
- Given the particle's energy levels in 1D

$$\epsilon_{n_x} = \frac{h^2}{8mL^2} n_x^2, \qquad n_x = 1, 2, \cdots$$

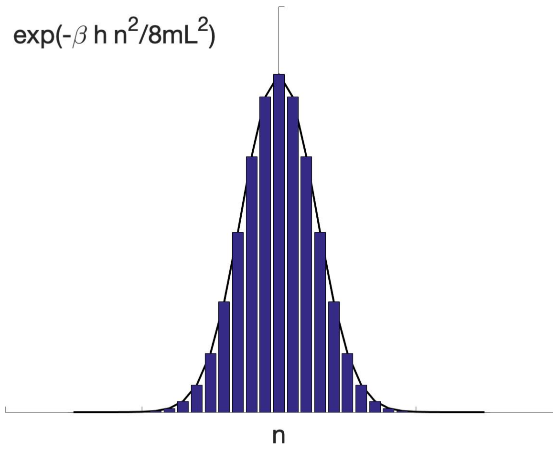
- One-particle partition function

$$Z_1^{1D}(T) = \sum_n^{\infty} e^{-\beta \epsilon_n} = \sum_n^{\infty} e^{-\beta \frac{h^2}{8mL^2} n^2}$$



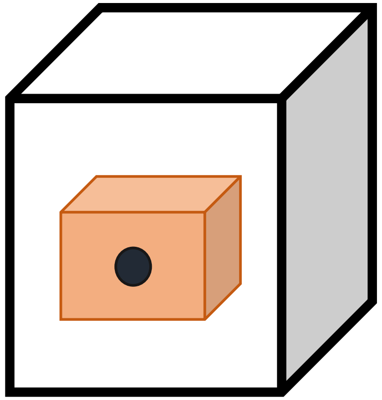


$$Z_1^{(1D)}(T) \approx_{n \gg 1} \int_0^{\infty} dn\ e^{-\beta \frac{h^2}{8mL^2} n^2} = \frac{1}{2} \int_{-\infty}^{\infty} dn\ e^{-\beta \frac{h^2}{8mL^2} n^2} = \frac{\sqrt{\pi}}{2} \sqrt{\frac{8mL^2}{\beta h^2}}$$



$$Z_1^{(1D)}(T) = \sqrt{\frac{2\pi mkT}{h^2}}\, L = \frac{L}{\Lambda(\mathrm{T})}, \quad \Lambda(\mathrm{T}) = \sqrt{\frac{h}{2\pi mkT}} \text{ (quantum length)}$$

One free particle in 3D in a thermal bath



- Given the energy levels of a free particle in 3D

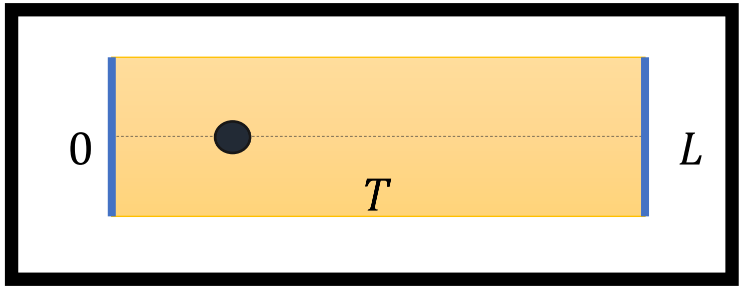
$$\epsilon_n = \frac{\vec{p}\cdot\vec{p}}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2), \quad n_k = 0,1,2,\cdots \text{ are the state numbers for } \mathrm{k} = x, y, z$$

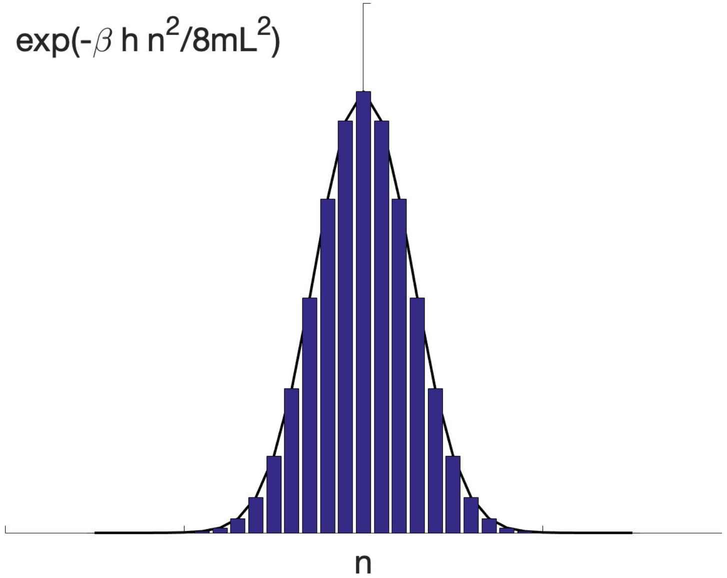
- One-particle partition function

$$Z_1(T,V) = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta\epsilon_n} = \left(\sum_{n_x} \boldsymbol{e}^{-\boldsymbol{\beta}\frac{\boldsymbol{h}^2}{8\boldsymbol{m}\boldsymbol{L}^2}\boldsymbol{n}_x^2}\right)\left(\sum_{n_y} \boldsymbol{e}^{-\boldsymbol{\beta}\frac{\boldsymbol{h}^2}{8\boldsymbol{m}\boldsymbol{L}^2}\boldsymbol{n}_y^2}\right)\left(\sum_{n_z} \boldsymbol{e}^{-\boldsymbol{\beta}\frac{\boldsymbol{h}^2}{8\boldsymbol{m}\boldsymbol{L}^2}\boldsymbol{n}_z^2}\right)$$

$$Z_1(T,V) = \left(\sum_{n} \boldsymbol{e}^{-\boldsymbol{\beta}\frac{\boldsymbol{h}^2}{8\boldsymbol{m}\boldsymbol{L}^2}\boldsymbol{n}^2}\right)^3 = \left(\frac{L}{\Lambda(T)}\right)^3 = \frac{V}{\Lambda^3(T)}$$

Quantum length $\Lambda(T)$ $[textbook - l_Q]$





- One-particle partition function counts the number of quantum volumes that fit into the box of size $L \times L \times L$

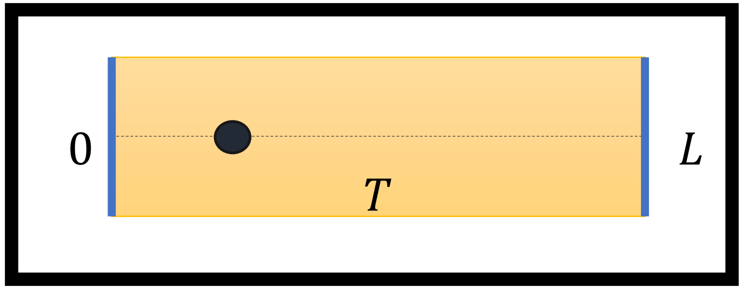
$$Z_1(T) = \frac{L^3}{\Lambda^3(\mathrm{T})}, \qquad \Lambda(\mathrm{T}) = \sqrt{\frac{h^2}{2\pi mkT}}$$

- **One N_2 molecule at room temperature $T_0 = 300K$ has $\Lambda(\mathrm{T_0}) \approx 2 \times 10^{-2} nm$. So, if the molecule is confined to a box of length $L = 1\ cm$, its partition function would $\mathrm{Z_1} = \left(\frac{\mathrm{L}}{\Lambda(\mathrm{T_0})}\right)^3 = 5^3 \times 10^{24}!$**

- **Unless T is close absolute zero or the box size is on atomic scale, the quantum length (proportial to the de Broglie wavelength) of the particle is much smaller than any other lengthscale**

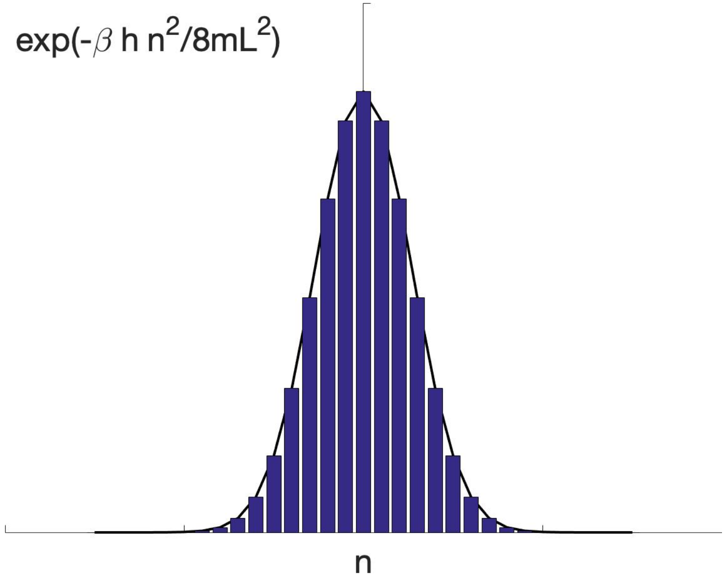
- **Classical limit**

Average kinetic energy of one particle in 1D



- One-particle partition function (1D) counts the number of quantum lengths that fit into the box of size L

$$Z_1(T,L) = \frac{L}{\Lambda(T)}, \qquad \Lambda(T) = \sqrt{\frac{h^2}{2\pi mkT}}$$



- **Energy of the particle will fluctuation due to thermal fluctuations about an average**

$$\langle \epsilon \rangle = -\frac{\partial \ln Z_1(T,L)}{\partial \beta} = \frac{d}{d\beta} \ln \Lambda(\beta) = \frac{d}{d\beta} \ln\sqrt{\beta} = \frac{1}{2} kT$$

- **Equipartition of energy for one *translational* degree of freedom**

When does the equipartition of energy apply? (revisit)

- Quadratic degrees of freedom ($E(q) = cq^2$):

  translations $E_{kin}(v) = \frac{1}{2}mv^2$

  rotations $E_{rot}(\dot{\theta}) = \frac{1}{2}I\dot{\theta}^2$

  oscillations $H = \frac{1}{2}mv^2 + \frac{1}{2}m\omega^2 x^2$

- Sufficiently large number of distinct microstates with significant probability (that are thermally accessible) («high temperature limit»): $Z_1(T) = \frac{1}{2}\int_{-\infty}^{+\infty} dq\ e^{-c\beta q^2} \sim \sqrt{kT}$

  - ***1D free particle has*** $\langle\epsilon\rangle = \frac{1}{2}kT$***, in the limit of a continuous spectrum of available energies (so at sufficiently low temperatures and in the quantum world this will not be valid)***

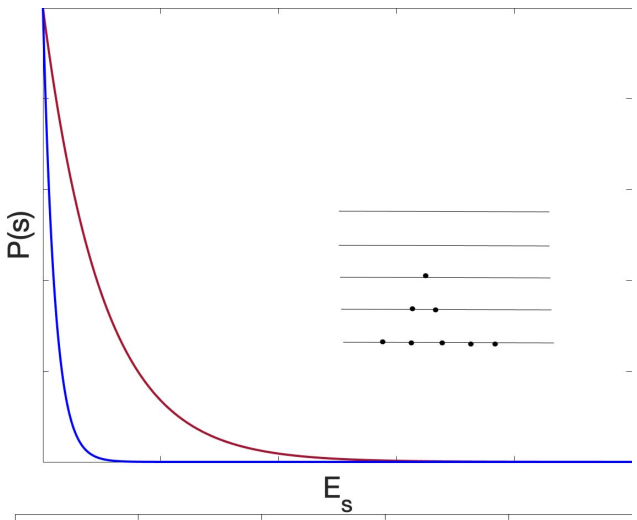
  - ***Harmonic oscillator has*** $\frac{\hbar\omega}{e^{\beta\hbar\omega}-1} \rightarrow_{T\rightarrow\infty} kT$

Maxwell-Bolzmann distribution (revisit)

- Equilibrium distribution of particles in a gas between (non-degenerate) energy levels E_s at a given T

Probability distribution of a particle between energy levels E_s

$$P(s) = \frac{1}{Z}\, e^{-E_s}$$

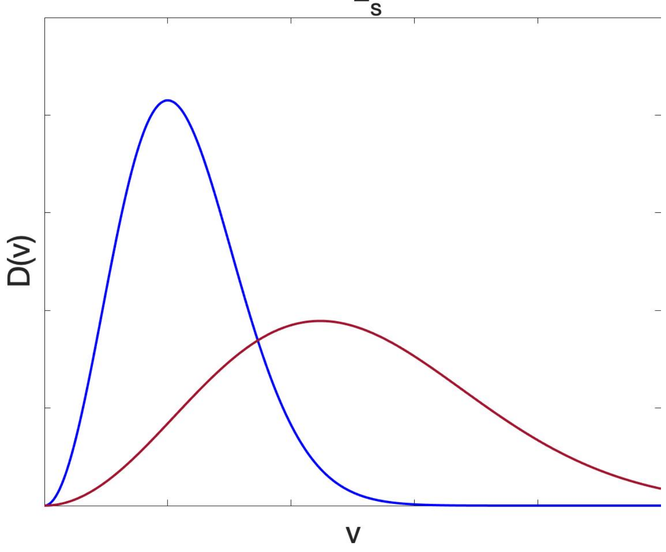


- Equilibrium distribution particles in a gas with speeds between v and $v + dv$ at a given T

Probability that a particles moves with a speed between v and $v + dv$

$$\boldsymbol{D^{(1D)}(v)dv = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{m}{2kT}v^2} 2\, dv}$$

$$\boldsymbol{D^{(3D)}(v)dv = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}v^2} 4\pi v^2 dv}$$



Maxwell-Bolzmann velocity distribution (revisit)

- Probability of a free particle to have a velocity along one direction between v_x *and* $v_x + dv_x$

$$P(v_x) \sim e^{-\beta E(v_x)} \sim e^{-\frac{m}{2kT}v_x^2}$$

Using the normalization condition $\int_{-\infty}^{+\infty} dv_x\, P(v_x) = 1 \rightarrow \int_{-\infty}^{+\infty} dv_x\, e^{-\frac{m}{2kT}v_x^2} = \sqrt{\frac{2\pi kT}{m}}$

$$P(v_x) = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m}{2kT}v_x^2}$$

- Velocity statistics

$$\langle v_x \rangle = \int_{-\infty}^{+\infty} dv_x\, v_x\, P(v_x) = 0$$

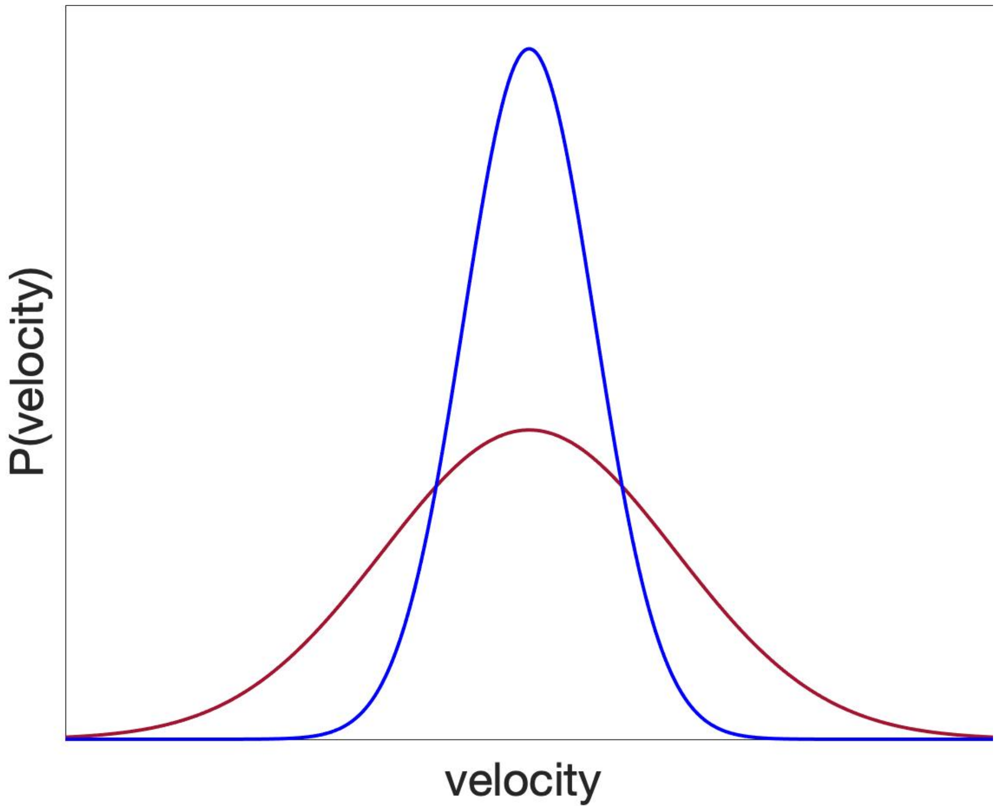
$$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} dv_x\, v_x^2\, P(v_x) = \frac{kT}{m}$$

$$\langle |v_x| \rangle = 2\int_{0}^{+\infty} dv_x\, v_x\, P(v_x) = \sqrt{\frac{2kT}{\pi m}}$$

Maxwell-Bolzmann velocity distribution (revisit)

Probability of a free particle to have a velocity along one direction between $\vec{v}_x$ *and* $\vec{v}_x + d\vec{v}_x$

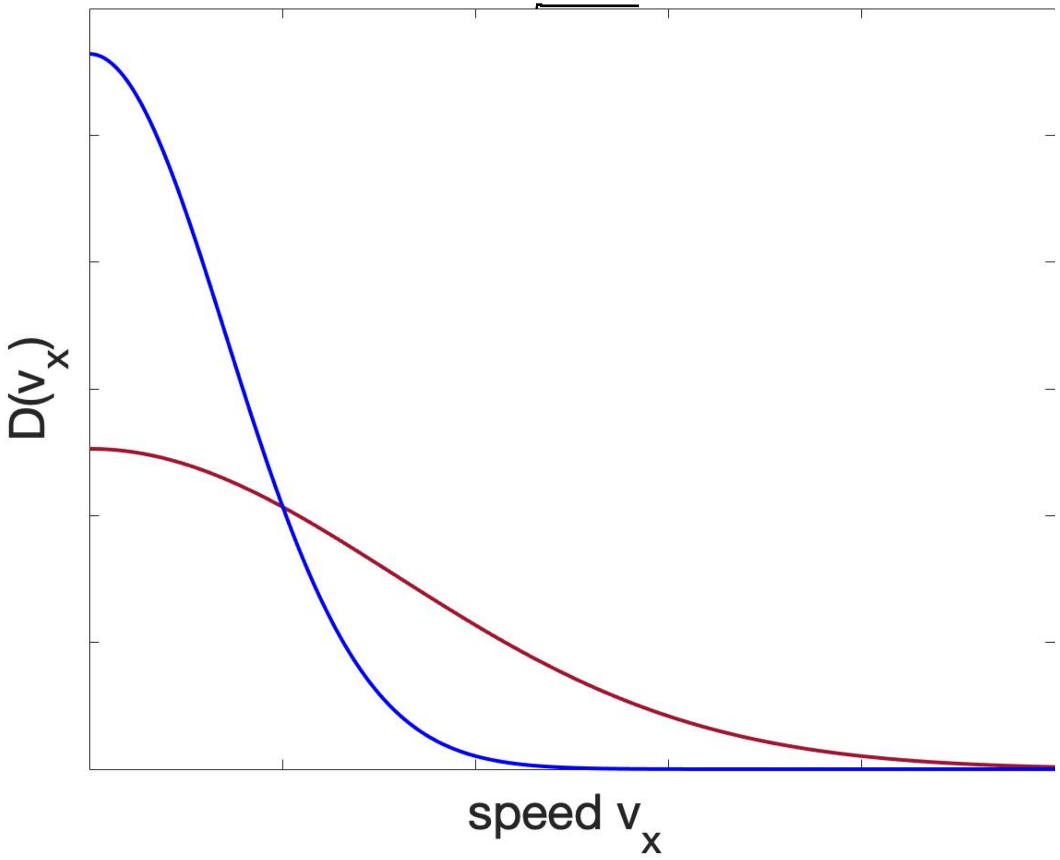
$$P(\vec{v}_{\boldsymbol{x}})d\vec{v}_{\boldsymbol{x}} = \sqrt{\frac{m}{2\pi kT}}e^{-\frac{m}{2kT}v_x^2}d\vec{v}_{\boldsymbol{x}}$$



Maxwell-Bolzmann velocity distribution (revisit)

Probability density of a free particle to have a *speed* along one direction between v_x *and* $v_x + dv_x$

$$D(v_x) = (prob\ to\ have\ a\ vector\ \vec{v}_x)\times(\#\ of\ vectors\ \vec{v}_x\ with\ speed\ v_x)$$

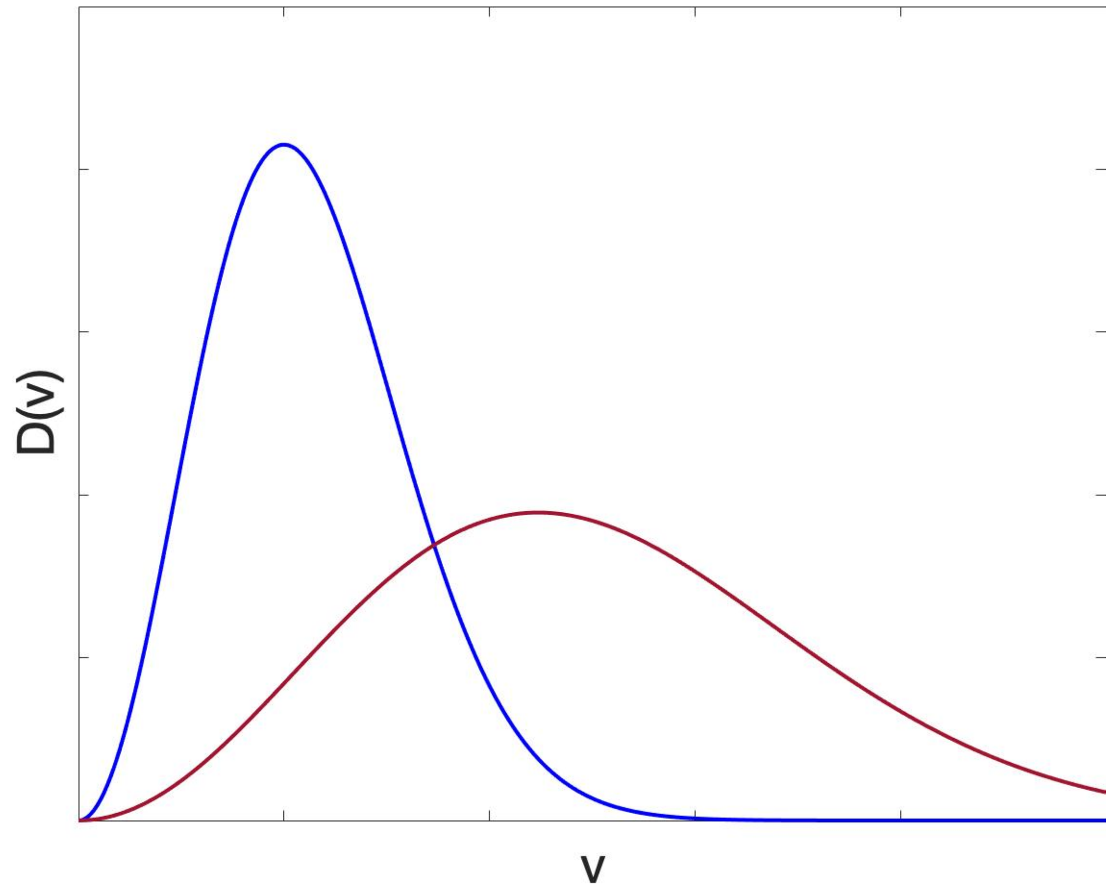


Maxwell-Bolzmann velocity distribution (revisit)

Probability density of a free particle in 3D to have a *speed* between v *and* $v + dv$ $\quad (v^2 = v_x^2 + v_y^2 + v_z^2)$

$$D(v)dv$$
$$= (prob\ to\ have\ a\ vector\ \vec{v}) \times (\#\ of\ vectors\ \vec{v}\ with\ speed\ v)$$

$$D(v)dv = \left(\sqrt{\frac{m}{2\pi kT}}\right)^3 e^{-\frac{m}{2kT}v^2} \times 4\pi v^2 dv$$



Maxwell-Bolzmann velocity distribution (revisit)

Probability density of a free particle in 3D to have a *speed* between v *and* $v + dv$ $\quad (v^2 = v_x^2 + v_y^2 + v_z^2)$

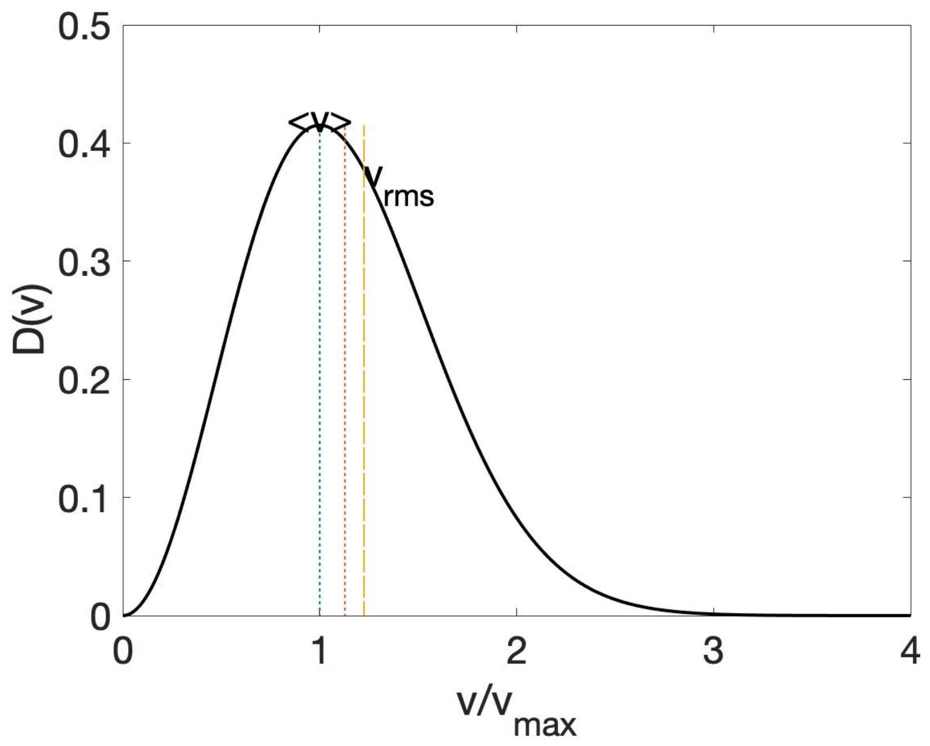
$$D(v) = \left(\sqrt{\frac{m}{2\pi kT}}\right)^3 4\pi v^2 e^{-\frac{m}{2kT}v^2}$$

Speed statistics : $\quad \langle v \rangle = \int_0^{+\infty} dv\, v\, D(v) = \sqrt{\frac{8kT}{\pi m}}$

$$\langle v^2 \rangle = \int_0^{+\infty} dv\, v^2\, D(v) = \frac{3kT}{m}$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

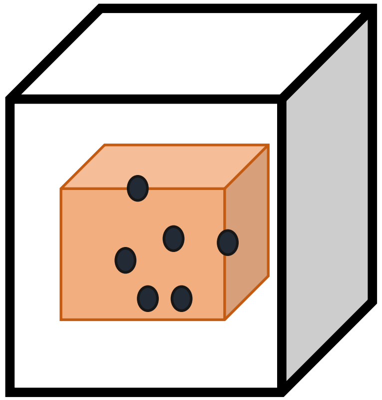
$$v_{max} = \sqrt{\frac{2kT}{m}} \quad (\, v \; for \max D(v)\,)$$



$$\mathbf{v_{max}} \quad < \langle v \rangle < v_{rms}$$

So the most likely speed is actuallty smaller than the average speed! (Non-Gaussian distribution!)

N-free particles in a thermal bath



- One-particle partition function

$$Z_1(T,V) = \left(\sum_n e^{-\beta \frac{h^2}{8mL^2} n^2}\right)^3 = \left(\frac{L}{\Lambda(T)}\right)^3 = \frac{V}{\Lambda^3(T)}$$

- N-particle partition function

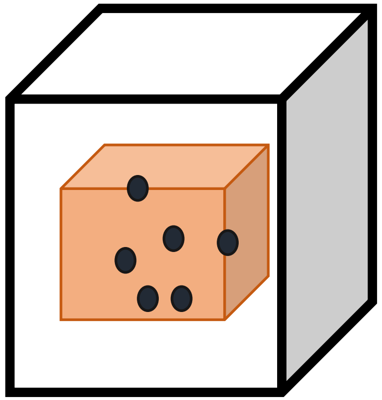
$$Z_N(T,V) = \frac{Z_1^N}{N!} = \frac{1}{N!}\left(\frac{V}{\Lambda^3(T)}\right)^N$$

- Helmholtz free energy

$$F_N(T,V) = -kT\, ln\, Z_N(T,V) = -NkT\left[ln\left(\frac{Z_1}{N}\right) - 1\right]$$

$$F_N(T,V) = -NkT\left[ln\left(\frac{V}{N\Lambda^3(T)}\right) - 1\right]$$

N-free particles in a thermal bath



- N-particle partition function

$$Z_N(T,V) = \frac{Z_1^N}{N!} = \frac{1}{N!}\left(\frac{V}{\Lambda^3(T)}\right)^N, \qquad \Lambda(T) = \sqrt{\frac{h^2}{2\pi m k T}}$$

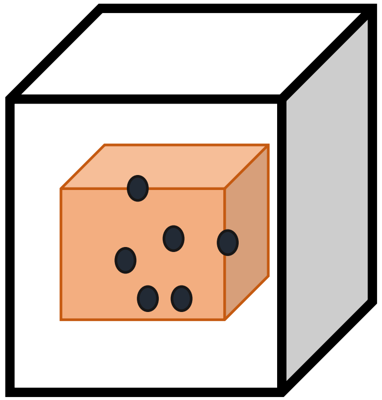
- Energy energy

$$U = -\frac{\partial}{\partial\beta} ln\, Z_N(T,V) = 3N\frac{d}{d\beta}\, ln\,\Lambda(\beta) = \frac{3\mathrm{N}}{2}\mathrm{kT}$$

- Entropy

$$S = \frac{U-F}{T} = \frac{3\mathrm{N}k}{2} + Nk + Nk\left[ln\left(\frac{V}{N\Lambda^3(T)}\right)\right] = Nk\left[ln\left(\frac{V}{N\Lambda^3(T)}\right) + \frac{5}{2}\right]$$

N-free particles in a thermal bath



- N-particle partition function

$$Z_N(T,V) = \frac{Z_1^N}{N!} = \frac{1}{N!}\left(\frac{V}{\Lambda^3(T)}\right)^N , \qquad \Lambda(T) = \sqrt{\frac{h^2}{2\pi mkT}}$$

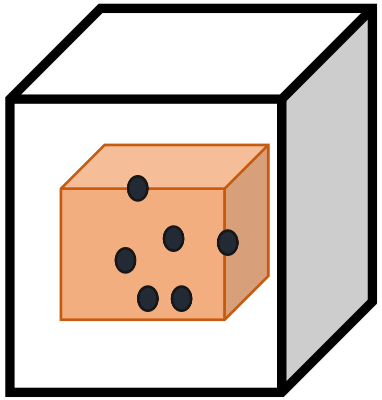
- Energy energy

$$U = -\frac{\partial}{\partial \beta} ln\, Z_N(T,V) = 3N\frac{d}{d\beta}\, ln\, \Lambda(\beta) = \frac{3\mathrm{N}}{2}\mathrm{kT}$$

- Heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3\mathrm{N}k}{2}$$

N-free particles in a thermal bath



- Helmholtz free energy

$$F_N(T,V) = -NkT\left[ln\left(\frac{V}{N\Lambda^3(T)}\right) - 1\right]$$

- **Equation of state**

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{kT}{V}$$

- **Chemical potential**

$$\mu(T,V) = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ ln\left(\frac{V}{N\Lambda^3(T)}\right)$$

$$\mu(T,V) = kT\ ln\,\rho - \frac{3}{2}kT\ ln\left(\frac{2\pi mkT}{h^2}\right)$$