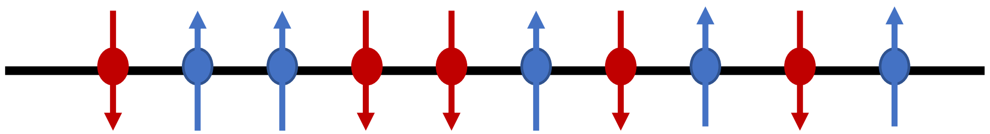
Lecture 6

Multiplicity of the ideal gas

05.09.2018

Two-state systems: Recap



- <u>Paramagnets:</u>

Multiplicity of a macrostate with $N_\uparrow$ out of N spins

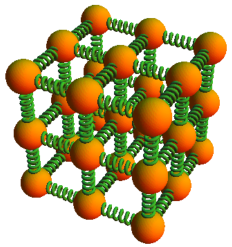
$$\Omega(N, N_\uparrow) = \frac{N!}{N_\uparrow!\,(N - N_\uparrow)!} \approx_{N \gg 1} \frac{N^N}{N_\uparrow^{N_\uparrow}(N - N_\uparrow)^{N - N_\uparrow}}$$

Macrostate with maximum multiplicity is $\Omega_{\max}(N) = \Omega(N, N/2) \approx 2^N$ and is the most likely state (largest probability)

Macrostates away from the most likely one have a probability that falls of very rapidly (*Gaussian tail*)

$$\boldsymbol{\Omega(N, N_\uparrow) \approx \Omega_{max}\, e^{-\frac{\left(N_\uparrow - \frac{N}{2}\right)^2}{\frac{N}{2}}} \rightarrow_{N\rightarrow\infty} \Omega_{max}\,\delta\left(N_\uparrow - \frac{N}{2}\right)}$$

Two-state systems: Recap



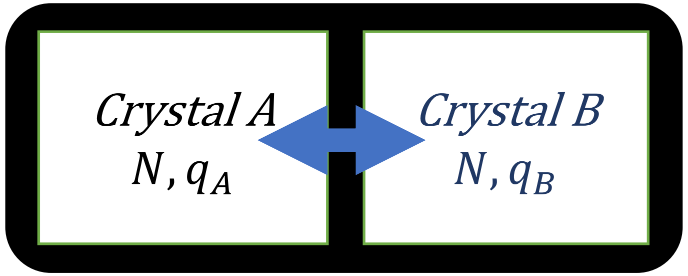
- <u>Einstein crystal</u>

Multiplicity of a macrostate with q units of energy distributed among N identical oscillators

$$\boldsymbol{\Omega(q,N) = \frac{(N-1+q)!}{q!\,(N-1)!} \approx_{q \gg N \gg 1} \left(\frac{eq}{N}\right)^{N}}$$

- <u>Two-interacting crystals</u>:

Total multiplicity of a composite system of crystals of the same N and for which crystal A has q_A energy units out of a total of q



$$\boldsymbol{\Omega_t = \Omega_A \cdot \Omega_B \approx \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N}$$

The most likely macrostate has a maximum multiplicity of the macrostate with $q_A = q_B = q/2$

$$\boldsymbol{\Omega_t^{max} = \left(\frac{eq}{2N}\right)^{2N}}$$

Macrostates away from the most likely one have a probability that falls of very rapidly (*Gaussian tail)*

$$\boldsymbol{\Omega_t(q_A) \approx \Omega_t^{max}\, e^{-\frac{4N}{q^2}\left(q_A - \frac{q}{2}\right)^2} \rightarrow_{N\to\infty} \Omega_t^{max}\,\delta\left(q_A - \frac{q}{2}\right)}$$

Counting of microstates for 1 particles in 1D

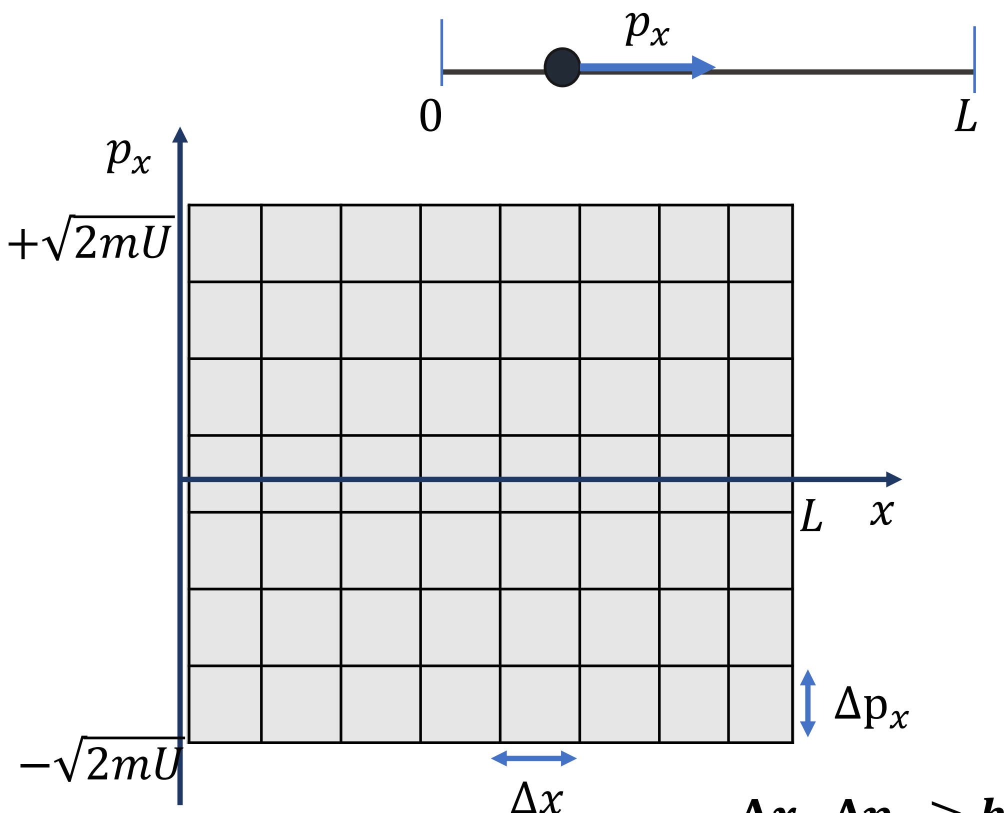
- Consider 1 **free classical** particle with kinetic energy

$U = \frac{p_x^2}{2m}$ in a 1D «box» of «volume» $V \equiv L$

- What is the number of microstates at fixed U and V for 1 free particle, $\Omega_1^{1D}(U, V)$?

- Multiplicity Ω_1^{1D} is equal to the number of microstates in the phase space (x, p_x)

$$\Omega_1^{1D}(U, L) = \frac{L \cdot 2\sqrt{2mU}}{\Delta x \cdot \Delta p_x} = \frac{2L\sqrt{2mU}}{h}$$



$\boldsymbol{\Delta x \cdot \Delta p_x \geq h}$

Counting of microstates for 1 particles in 1D

- Consider **one free quantum** particle with wavelength $\lambda_n = \frac{2L}{n_x}$ and momentum $p_x = \frac{h}{\lambda_n} = \frac{h}{2L}\ n_x$ in a 1D «box» of «volume» $V \equiv L$

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

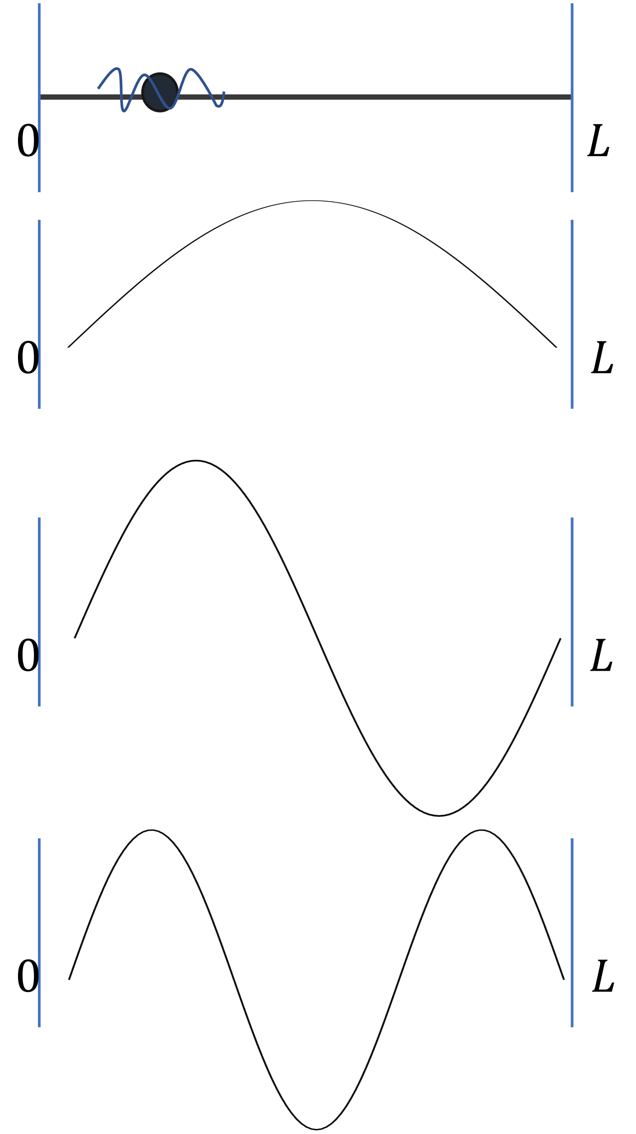
$$\epsilon_n = \frac{p_x^2}{2m} = \frac{h^2}{8mL^2} n_x^2,\ where\ n_x = 0,1,2,\cdots \text{ is the state number}$$

$$n(\epsilon_n) = \frac{2L}{h}\sqrt{2m\epsilon_n}$$

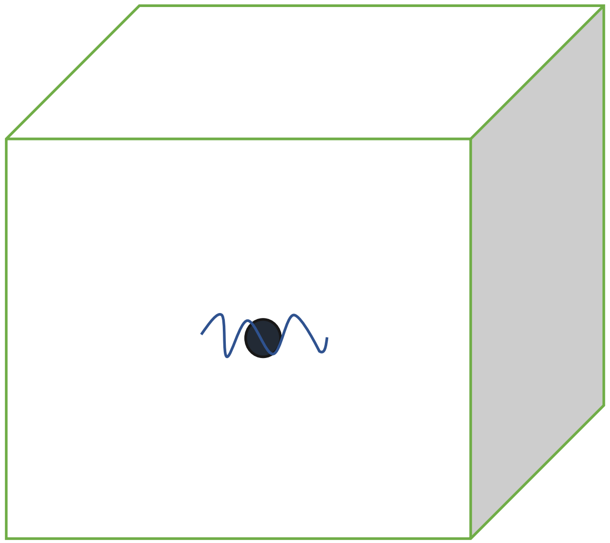
- What is $\Omega_1^{1D}(U,V)$ the number of microstates at fixed U and V for 1 free quantum particle ?

- Multiplicity Ω_1^{1D} is equal to the number of microstates in the «n-space» equals the maximum state number for a fixed energy U

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



Counting of microstates for 1 particles in 3D



- Consider **one free quantum** particle with momentum $\vec{p} = \frac{h}{2L}\vec{n}$ in a 3D box of volume $V = L^3$
- The energy levels of a free particle in 3D are

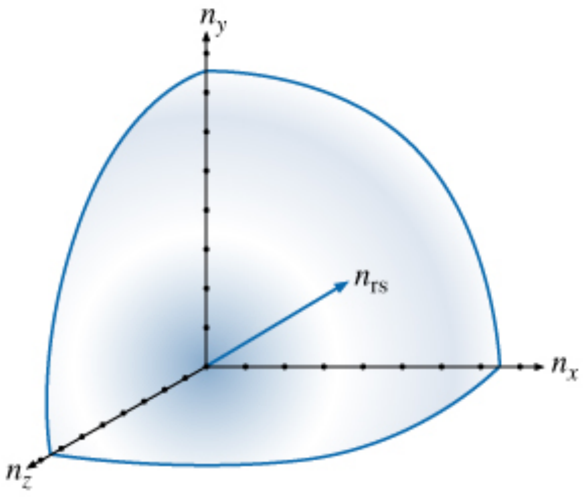
$$\epsilon_n = \frac{\vec{p}\cdot\vec{p}}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2),\ \ where\ n_k = 0{,}1{,}2,\cdots \text{ is the state number for k} = x, y, z$$

- Multiplicity Ω_1^{3D} is equal to the number of microstates in the «n-space» corresponding to a fixed energy $\epsilon_n = U$
- Surface in the «n-space» with equal energy

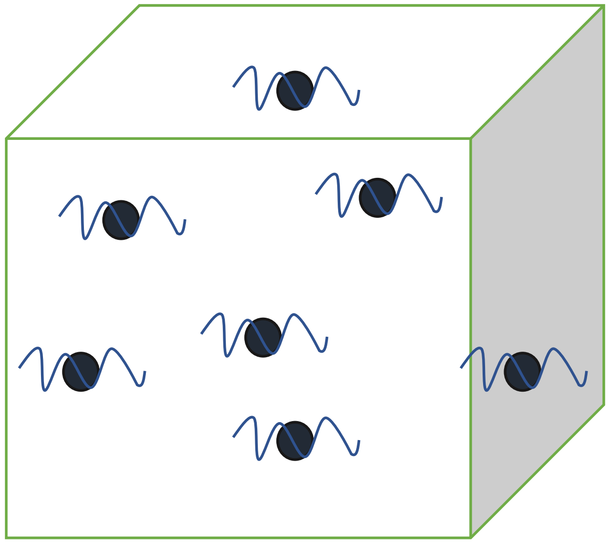
$$n_x^2 + n_y^2 + n_z^2 = \frac{8mL^2U}{h^2} = R_n^2$$

which has the area equal to $A_n = 4\pi R_n^2 = 4\pi\frac{8mL^2U}{h^2}$. We have to devide by the number of «quadrants» 2^3, since we consider only positive-valued state numbers $n_x, n_y, n_z \geq 0$ (positive quandrant). Hence, the multiplicity is 1/8th of the area

$$\Omega_1^{3D}(U,V) = \frac{1}{8}A_n \rightarrow \boldsymbol{\Omega_1^{3D}(U,V) = 4\pi\frac{mV^{\frac{2}{3}}U}{h^2}}$$



Counting of microstates for N 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 $i = 1, \cdots N$

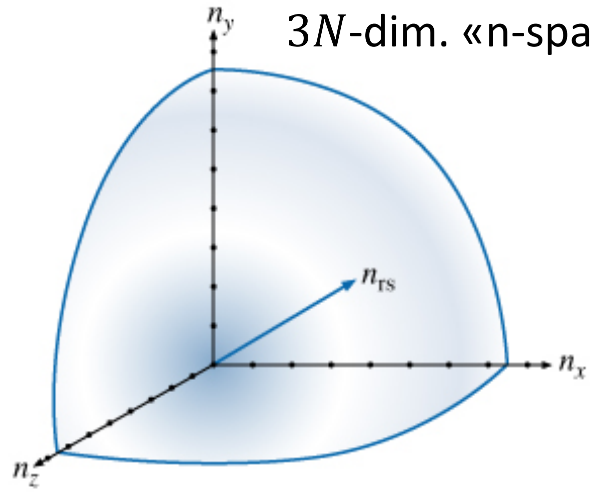
- Multiplicity Ω_N^{3D} is equal to the number of microstates in the **3N-dimensional «*n*-space»** corresponding to a fixed energy $U = \sum_{i=1}^{N} \epsilon_{n_i}$
- Hyper-surface in the «n-space» with equal energy is described by the quadratic form

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

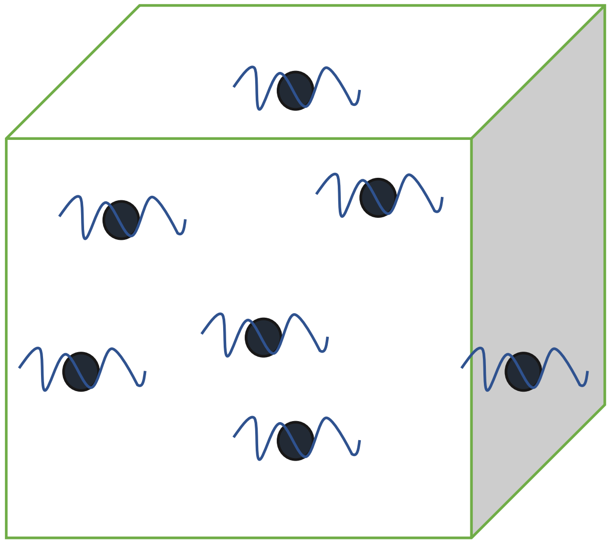
- Using the formula for the area of a d-dimensional sphere is $A = \frac{2\,\pi^{d/2}}{\left(\frac{d}{2}-1\right)!}\ r^{d-1}$

$$d = 2 \rightarrow A = 2\pi r, \qquad d = 3 \rightarrow A = \frac{2\pi^{3/2}}{(1/2)!}r^2 = \frac{4\pi^{3/2}}{\sqrt{\pi}}r^2 = 4\pi r^2$$

3N-dim. «n-space»



Counting of microstates for N particles in 3D



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

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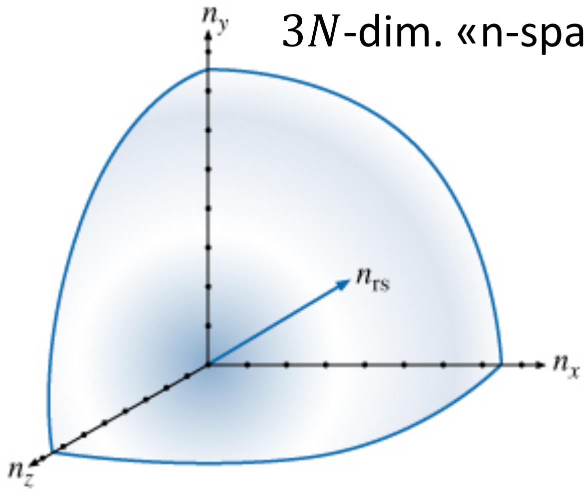
- Multiplicity Ω_N^{3D} is equal to the number of microstates in the **3N-dimensional «$\boldsymbol{n}$-space»** corresponding to a fixed energy $U = \sum_{i=1}^{N} \epsilon_{n_i}$
- Hyper-surface in the «n-space» with equal energy is described by the quadratic form

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



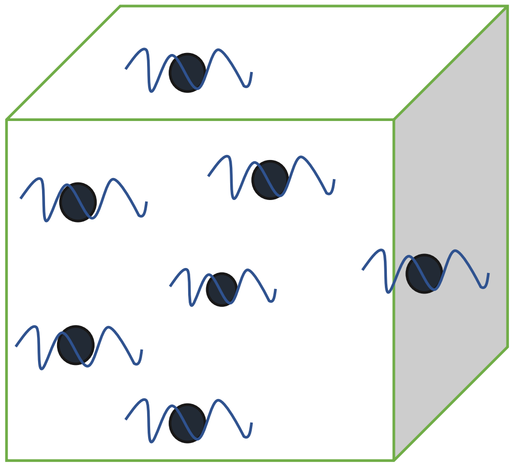
$3N$-dim. «n-space»

- Using the formula for the area of a d-dimensional sphere is $A = \frac{2\,\pi^{d/2}}{\left(\frac{d}{2}-1\right)!}\, r^{d-1}$, with $d = 3N$ and dividing by the number of «quadrants» 2^{3N}

$$\widetilde{\Omega}_N^{3D}(\boldsymbol{U},\boldsymbol{V}) = \frac{\mathbf{1}}{\mathbf{2}^{3N}}\boldsymbol{A_n} \to \widetilde{\Omega}_N^{3D}(\boldsymbol{U},\boldsymbol{V}) = \frac{\mathbf{1}}{\mathbf{2}^{3N}}\frac{\mathbf{2}\,\boldsymbol{\pi}^{3N/2}}{\left(\frac{\mathbf{3N}}{\mathbf{2}}-\mathbf{1}\right)!}\left(\frac{\mathbf{2L}}{\boldsymbol{h}}\sqrt{\mathbf{2mU}}\right)^{\mathbf{3N-1}}$$

Multiplicity function for N particles in 3D

$$\tilde{\Omega}_N^{3D}(U,V) = \frac{1}{2^{3N}} \frac{2\,\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \left(\frac{2L}{h}\sqrt{2mU}\right)^{3N-1}$$



$$\tilde{\Omega}_N^{3D}(U,V) = \frac{1}{2^{3N}} \frac{2\,\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \frac{2^{3N-1}}{h^{3N-1}} V^{\frac{3N-1}{3}} (2mU)^{\frac{3N-1}{2}} = \frac{\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!\,h^{3N-1}} V^{\frac{3N-1}{3}} (2mU)^{\frac{3N-1}{2}}$$

For large N, $N-1 \approx N$ and ***area*** scales like the ***volume***

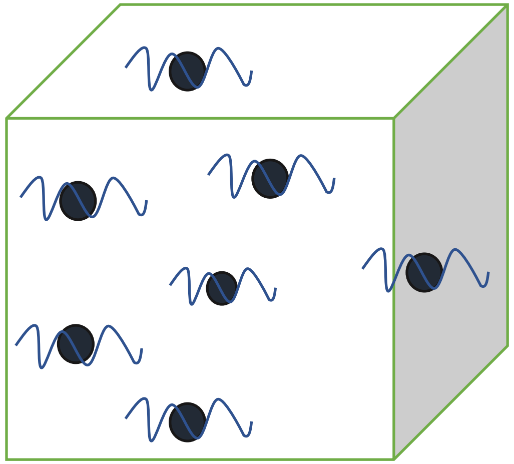
$$\tilde{\Omega}_N^{3D}(U,V) = \frac{1}{\left(\frac{3N}{2}-1\right)!} V^N \left(\frac{2\pi mU}{h^2}\right)^{\frac{3N}{2}}$$

In addition, for ***indistinguishable*** particles the multiplicity is reduced by their number of permutations, $N!$

$$\Omega_N^{3D}(U,V) = \frac{\tilde{\Omega}_N^{3D}(U,V)}{N!} \rightarrow \Omega_N^{3D}(U,V) = \frac{1}{N!\left(\frac{3N}{2}-1\right)!} V^N \left(\frac{2\pi mU}{h^2}\right)^{\frac{3N}{2}}$$

Multiplicity function for N particles in 3D

$$\boldsymbol{\Omega_N^{3D}(U,V) = \frac{1}{N!\left(\frac{3N}{2}-1\right)!} V^N \left(\frac{2\pi m U}{h^2}\right)^{\frac{3N}{2}}}$$



Generic expression when we consider only the U and V dependence

$$\boldsymbol{\Omega_N^{3D}(U,V) = f(N) V^N U^{\frac{3N}{2}}}$$

The multiplicity depends on the accessible volume in the coordinate space V and momentum space V_p for each particle, $\Omega_{\mathrm{N}}^{\mathrm{3D}}(\mathrm{U},\mathrm{V}) \sim (\mathrm{V} \cdot V_p)^{\mathrm{N}}$. The volume in the momentum space scales like $V_p \sim U^{\frac{3}{2}}$ for the sphere (quadratic form).

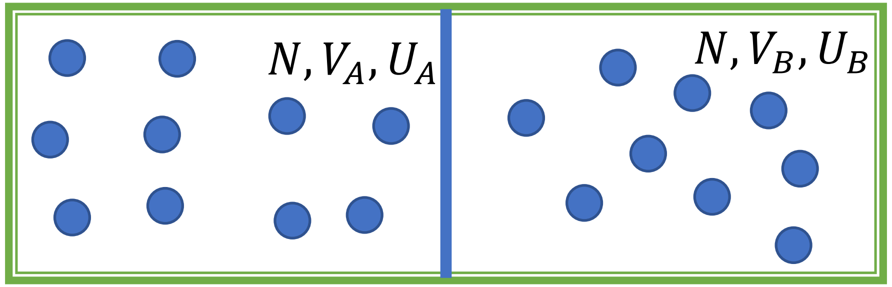
For f quadratic degrees of freedom, the multiplicity scales as $\Omega_{\mathrm{N}}^{\mathrm{3D}}(\mathrm{U}) \sim U^{\frac{fN}{2}}$

Two weakly interacting ideal gases

- $\Omega_N = f(N) V^N U^{\frac{3N}{2}}$ for each gas A and B

- Total multiplicity: $\Omega_{total} = \Omega_N^A \cdot \Omega_N^B = f(N)^2 (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$

- Macrostate with the maximum multiplicity:



$U = U_A + U_B$
$V = V_A + V_B$

$U_A = U_B = \frac{U}{2}$ and $V_A = V_B = \frac{V}{2}$

$$\Omega_{total}^{max} = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left(\frac{U}{2}\right)^{3N}$$

What is the shape of the multiplicity for states near the most likely state?

Two weakly interacting ideal gases

- Total multiplicity: $\Omega_{total} = f(N)^2 (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$

- States near the most likely state by varying U

$U_A = \frac{U}{2} + x, U_B = \frac{U}{2} - x \; with \; x \ll U/2$, while $V_A = V_B = \frac{V}{2}$

$$\Omega_{total} = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left[\left(\frac{U}{2}\right)^2 - x^2\right]^{\frac{3N}{2}}$$

Taking the logarithm and looking only at the U-dependence

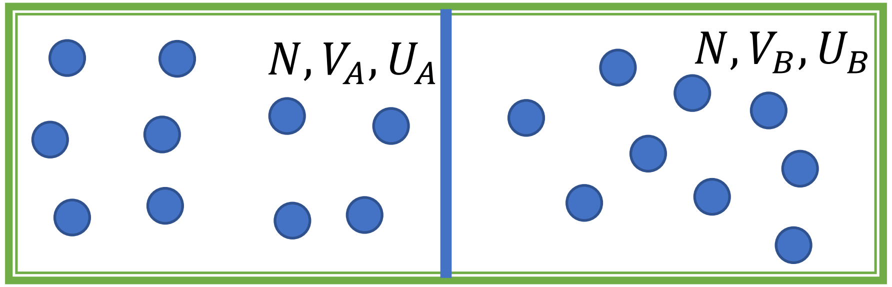
$$\ln \Omega_{total} \sim \frac{3N}{2} \ln\left[\left(\frac{U}{2}\right)^2 - x^2\right] = 3N \ln\left(\frac{U}{2}\right) + \frac{3N}{2} \ln\left[1 - \left(\frac{2x}{U}\right)^2\right]$$

$$\ln \Omega_{total} \sim 3N \ln\left(\frac{U}{2}\right) - \frac{3N}{2}\left(\frac{2x}{U}\right)^2$$

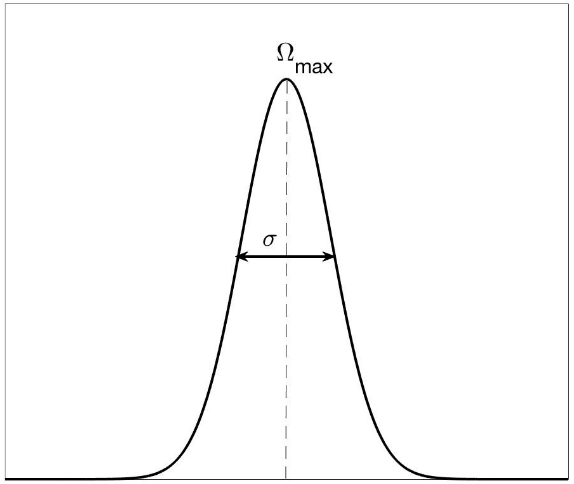
$$\Omega_{total}\left(x = U_A - \frac{U}{2}\right) = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left(\frac{U}{2}\right)^{3N} \cdot \exp\left(-\frac{3N}{2}\left(\frac{2x}{U}\right)^2\right)$$

$$\Omega_{total}(U_A) = \Omega_{total}^{max} \cdot \exp\left(-\frac{3N}{2}\left(\frac{2}{U}\right)^2 \left(U_A - \frac{U}{2}\right)^2\right)$$

The width scales as $\boldsymbol{\sigma_U = 2 \cdot \frac{U}{2}\sqrt{\frac{2}{3N}} = \frac{U}{\sqrt{\frac{3N}{2}}} \to 0 \quad as \quad N \to \infty}$



$U = U_A + U_B$
$V = V_A + V_B$



$U/2$

Two weakly interacting ideal gases

- Total multiplicity: $\Omega_{total} = f(N)^2 (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$

- States near the most likely state by varying V

$V_A = \frac{V}{2} + y, V_B = \frac{V}{2} - y \; with \; y \ll V/2$, while $U_A = U_B = \frac{U}{2}$

$$\Omega_{total} = f(N)^2 \left(\frac{U}{2}\right)^{3N} \left[\left(\frac{V}{2}\right)^2 - y^2\right]^N$$

Taking the logarithm and looking only at the V-dependence

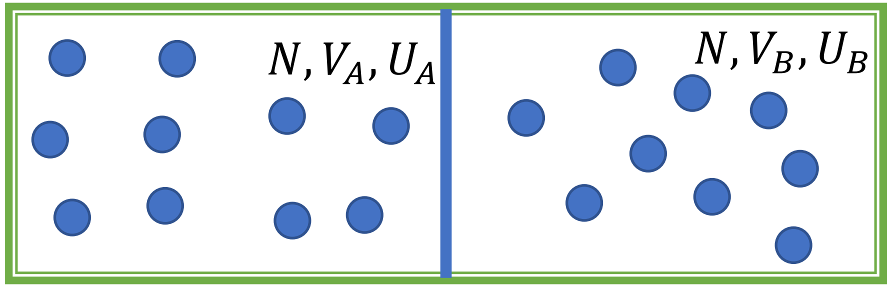
$$\ln \Omega_{total} \sim N \ln \left[\left(\frac{V}{2}\right)^2 - y^2\right] = N \ln \left(\frac{V}{2}\right) + N \ln \left[1 - \left(\frac{2y}{V}\right)^2\right]$$

$$\ln \Omega_{total} \sim N \ln \left(\frac{V}{2}\right) - N \left(\frac{2y}{V}\right)^2$$

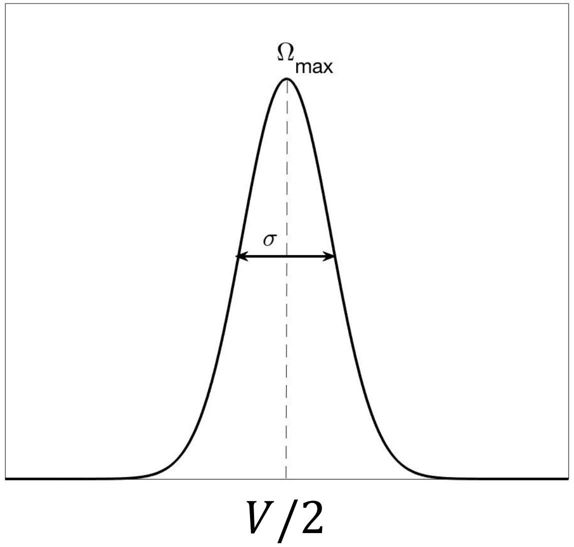
$$\Omega_{total}\left(y = V_A - \frac{V}{2}\right) = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left(\frac{U}{2}\right)^{3N} \cdot \exp\left(-N\left(\frac{2y}{V}\right)^2\right)$$

$$\Omega_{total}(V_A) = \Omega_{total}^{max} \cdot \exp\left(-N\left(\frac{2}{V}\right)^2 \left(V_A - \frac{V}{2}\right)^2\right)$$

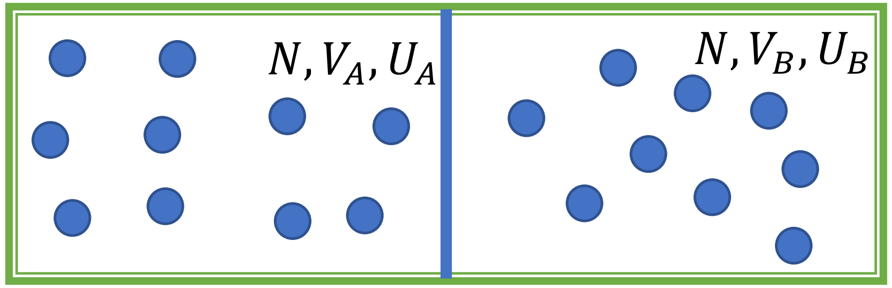
The width scales as $\boldsymbol{\sigma_V = 2 \cdot \frac{V}{2}\sqrt{\frac{1}{N}} = \frac{V}{\sqrt{N}} \to 0 \quad as \quad N \to \infty}$



$$U = U_A + U_B$$
$$V = V_A + V_B$$



Two weakly interacting ideal gases



- Macrostates near the most likely state

$$\Omega_{total}(V_A, U_A)$$
$$= \Omega_{total}^{max} \cdot \exp\left(-N\left(\frac{2}{V}\right)^2\left(V_A - \frac{V}{2}\right)^2\right) \cdot \exp\left(-\frac{3N}{2}\left(\frac{2}{U}\right)^2\left(U_A - \frac{U}{2}\right)^2\right)$$

$$U = U_A + U_B$$
$$V = V_A + V_B$$