Maxwell-Boltzmann distribution of speeds of molecules in an ideal gas at temp. T.

equipartition theorem: $\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_B T$

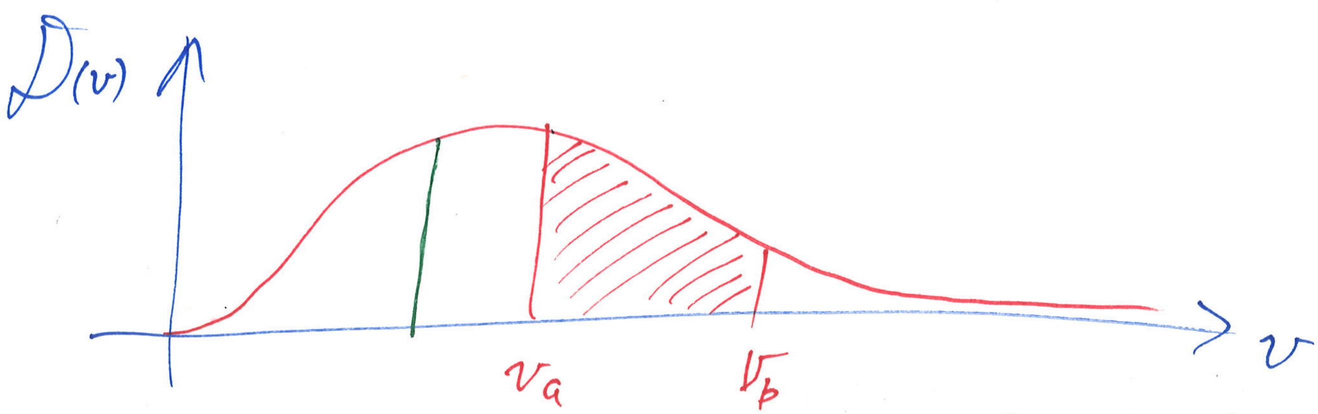
$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$

↑ root mean square

We Seek a probabity density function

$$\frac{dP}{dv} = \mathcal{D}(v)$$ The integral over $\mathcal{D}(v)$ gives the probability

$$P(v_a \le v \le v_b) = \int_{v_a}^{v_b} \mathcal{D}(v)\,dv = \int_{v_a}^{v_a} \frac{dP}{dv}\,dv = \int_{v_a}^{v_b} dP$$

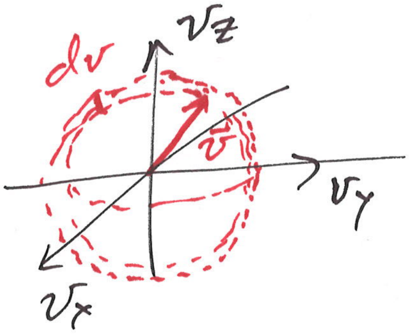


What is the probability that a molecule has speed exactly $4.0000\ldots$ m/s $= 0 \quad \int_4^4 \mathcal{D}(v)\,dv$

$$\mathcal{D}(v)\,dv = \left(\text{Normalization}\right)\left(\begin{array}{c}\text{Probability of}\\ \text{molecules having}\\ \text{speed } v\end{array}\right)\underbrace{\left(\begin{array}{c}\text{number of}\\ \text{vectors } \vec{v}\\ \text{corresponding to}\\ \text{speed } v \text{ in}\\ \text{3 dimensions}\end{array}\right)}_{\begin{array}{l}\text{degeneracy}\\ = \text{multiplicity}\\ = \#\text{ of microstates}\end{array}}$$

3-dimensional

$$= N_3 \cdot e^{-\frac{\frac{1}{2} m v^2}{k_B T}} \cdot 4\pi v^2 dv$$



$$|\vec{v}| = v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

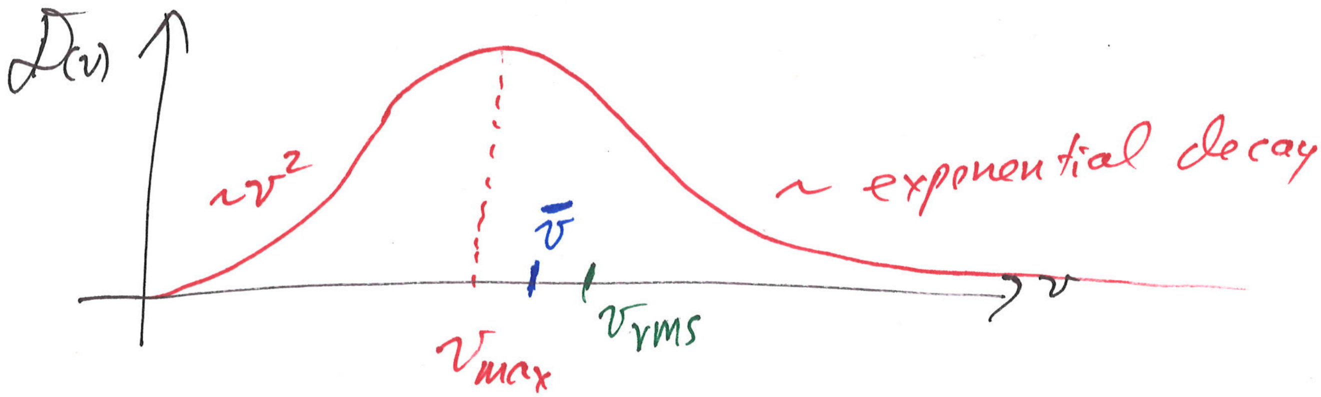
Get N from unitarity

$$P(0 \le v \le \infty) = 1 = \int_{v=0}^{\infty} \mathcal{D}(v)\,dv$$

$$\Rightarrow 1 = \int_{v=0}^{\infty} N_3 \exp\left[\frac{-\frac{1}{2} m v^2}{k_B T}\right] 4\pi v^2\,dv$$

$$N_3 = \left(\frac{m}{2\pi k_B T}\right)^{3/2}$$

$$\mathcal{D}(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[\frac{-\frac{1}{2}mv^2}{k_B T}\right] 4\pi v^2$$



$$\frac{d\mathcal{D}(v)}{dv} \stackrel{!}{=} 0 \Rightarrow v_{max} = \sqrt{\frac{2k_B T}{m}} \quad \text{(3-dimension)}$$

most likely speed – ~~median~~ mode

$$\langle v \rangle = \bar{v} = \int_{v=0}^{\infty} v\,\mathcal{D}(v)\,dv = \sqrt{\frac{8}{\pi}\frac{k_B T}{m}}$$

"Average" speed

Mean speed

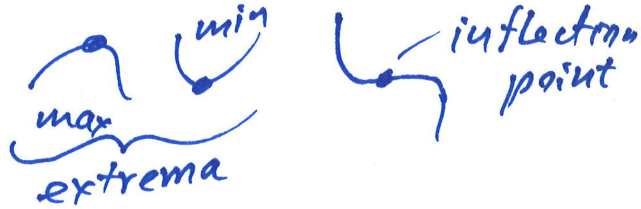
RMS speed $$v_{rms} = \sqrt{\int_{v=0}^{\infty} v^2 \mathcal{D}(v)\,dv} = \sqrt{\frac{3k_B T}{m}}$$

$$= \sqrt{\langle v^2 \rangle}$$

II. Statistical Mechanics

Lagrange Multiplier Refresher

find stationary point:

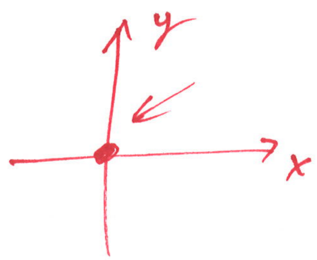


"Easy" way to find stationary solutions subjects to constraints.

Mechanics: minimize Action $S = \int_{t_1}^{t_2} L \, dt$ ← $L = T - V$

Thermodynamics: maximize Entropy S

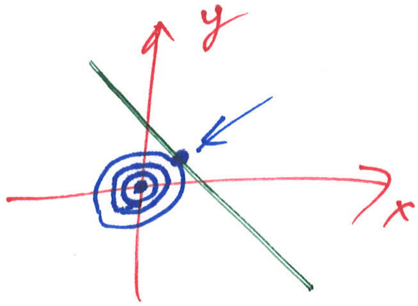
Example: Mathematics: minimize $(x^2 + y^2) \equiv g(x,y)$



but subject to the constraint

$f = x + 2y - 1 = 0$

↗ straight line : $y = -\frac{1}{2}x + \frac{1}{2}$



"Hard" way $x = 1 - 2y$

$$g(x,y) = (x^2+y^2) = (1-2y)^2 + y^2 = 1 - 4y + 5y^2 \equiv h(y)$$

$$\frac{d}{dy} h(y)\Big|_{y=y_0} \overset{!}{=} 0 = (10y-4)\Big|_{y=y_0} = 0 \Rightarrow y_0 = \frac{2}{5}$$

$$x_0 = 1 - 2y_0 = 1 - 2\left(\frac{2}{5}\right) = \frac{1}{5} \Rightarrow (x_0, y_0) = \left(\frac{1}{5}, \frac{2}{5}\right)$$

"Easy" way with the constraint + Lagrange multiplier

Minimize: $g(x,y) + \beta f = x^2 + y^2 + \beta(x + 2y - 1)$

$$\frac{\partial}{\partial x}\left[x^2+y^2+\beta(x+2y-1)\right] \overset{!}{=} 0 \Rightarrow 2x + \beta = 0 \Rightarrow x = -\frac{\beta}{2}$$

$$\frac{\partial}{\partial y}\left[x^2+y^2+\beta(x+2y-1)\right] \overset{!}{=} 0 \Rightarrow 2y + 2\beta = 0 \Rightarrow y = -\beta$$

Choose β to satisfy the constraint

$$0 = f = x + 2y - 1 = -\frac{\beta}{2} + 2(-\beta) - 1 = 0 \Rightarrow \beta = -\frac{2}{5}$$

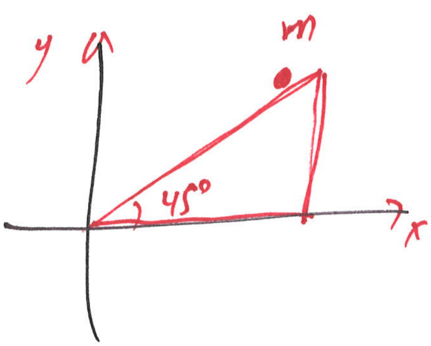
$$x = -\frac{\beta}{2} = -\left(-\frac{2}{5}\right)/2 = +\frac{1}{5}, \quad y = -\beta = \frac{2}{5}$$

Example from Mechanics

Particle of mass m in 2 dimensions, with gravity, sliding down a frictionless ramp,

$$\dot{x} \equiv \frac{dx}{dt}$$

ramp $y = x$



Kinetic Energy

$$T = \frac{m}{2}(\dot{x}^2 + \dot{y}^2)$$

Potential Energy

$$V = mgy + \cancelto{0}{\text{constant}}$$

Constraint: $f = y - x = 0$

Lagrangian: $L = T - V + \lambda f$

Minimize the action: $S = \int_{t_1}^{t_2} L \, dt$

$$S = \int_{t_1}^{t_2} \Big[\underbrace{\frac{m}{2}\dot{x}^2 + \frac{m}{2}\dot{y}^2 - mgy + \lambda(y - x)}_{L} \Big] dt$$

Euler-Lagrange Equations

$$\frac{\partial L}{\partial x} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) = 0 \Rightarrow -\lambda - \frac{d}{dt}(m\dot{x}) = 0$$

$$\Rightarrow -\lambda - m\ddot{x} = 0$$

$$\frac{\partial L}{\partial y} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{y}}\right) = 0 \Rightarrow -mg + \lambda - \frac{d}{dt}(m\dot{y}) = 0$$

$$\Rightarrow -mg + \lambda - m\ddot{y} = 0$$

Constraint : $y = x \Rightarrow \dot{y} = \dot{x} \Rightarrow \ddot{y} = \ddot{x}$

$$m\ddot{y} = m\ddot{x} \Rightarrow -\lambda = -mg + \lambda \Rightarrow \lambda = \frac{mg}{2}$$

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① $-\lambda - m\ddot{x} = 0 \Rightarrow -\frac{mg}{2} = m\ddot{x} \Rightarrow \ddot{x} = \frac{-g}{2}$

② $-mg + \lambda = m\ddot{y} \Rightarrow -mg + \left(\frac{mg}{2}\right) = m\ddot{y} \Rightarrow \ddot{y} = \frac{-g}{2}$

Suppose there is a relation among $\{x, y, z\}$.

e.g. $\frac{x^2\sqrt{y}}{z} = 3$, $x\tan(x) + \ln\left(\frac{y}{z}\right) = 10$

$x(y, z)$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$y(x, z)$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

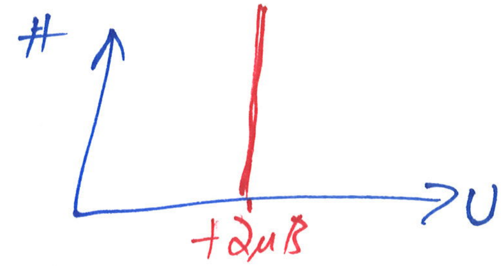
$$dx = \underbrace{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z}_{1} dx + \underbrace{\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right]}_{0} dz$$

$$0 = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y$$

multiply by $\left(\frac{\partial z}{\partial x}\right)_y$

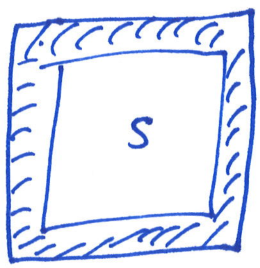
$$-\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \implies -1 = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y$$

Ensembles



1) Microcanonical Ensemble

Isolated system



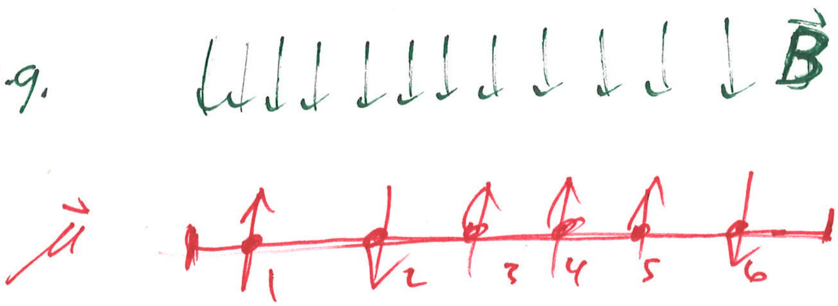
Know: N, V, U

Energy is exactly known.

Fundamental Assumption of thermodynamics

All states are equally likely.

e.g.



$U = -\vec{\mu}\cdot\vec{B}$

$N = 6$

$U = +2\mu B$

distinguishable

\# of microstate Ω dduuuu, duduuu....

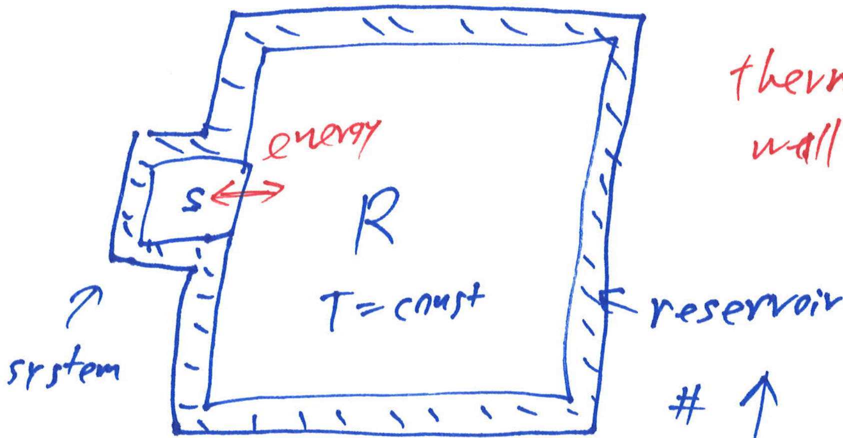
$\Omega = \binom{6}{2}$ - six take two $= \frac{6!}{2!\,(6-2)!} = \frac{6!}{2!\,4!} = 15$

$P(uuuudd) = \frac{1}{15}$, $P(uuduud) = \frac{1}{15}$

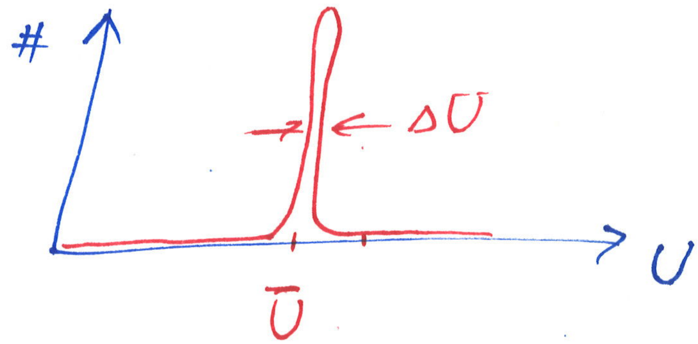
$P = \frac{1}{\Omega}$ entropy: $k_B \ln(\Omega) = S$

temp. $T = \left(\frac{\partial U}{\partial S}\right)_{NV} = ?$

② Canonical Ensemble – specify N, V, T for system



thermally conducting (diathermal) wall between S & R.



All states not equally likely

Boltzmann weighting

$$p \propto e^{-\frac{E_i}{k_B T}}$$

$(S+R)$ is microcanonical

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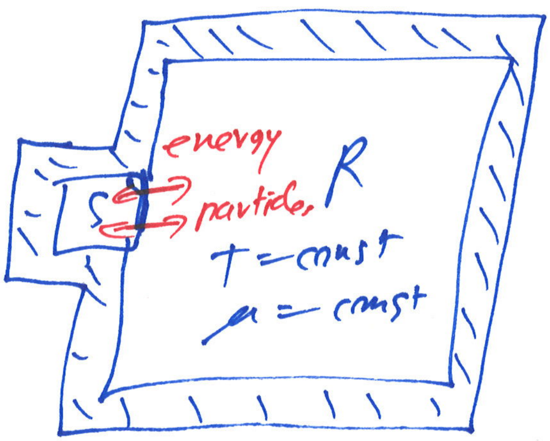
③ Grand Canonical Ensemble – specify μ, V, T



$(S+R)$ is microcanonical

States are Gibbs weighted

$$p \propto e^{-\frac{E_i - \mu N_i}{k_B T}}$$