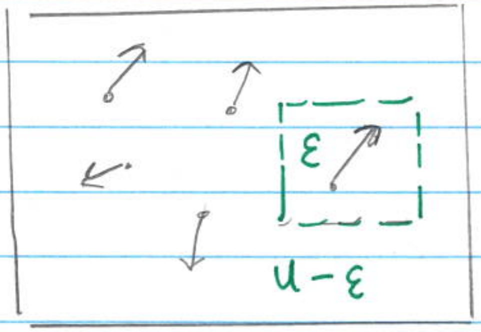
# The Boltzman Factor and Partition Fcns.

- This is based on Sect. 4.6. We will return to Chapter 4 later. Our goal is to give only an initial understanding of partition fcns.

- Consider a system with total energy U



- System has energy U
- Subsystem has energy ε
- Rest has energy U−ε

- Pick a small subsystem which is independent of the larger system except through the exchange of energy. In the case of an ideal gas, each molecule is independent of all others, and can be considered an independent subsystem.

- What is the probability that the subsystem will be in a state s with energy $\varepsilon_s$?

For instance, it is possible, though extremely unlikely, that the one molecule (subsystem) will have all of the energy of the gas.

- The probability to find a subsystem with in a state s with energy $\varepsilon_s$ is

$$P_s \propto e^{-\varepsilon_s/kT} \longleftarrow \text{This is the Boltzmann factor}$$

- If you a set of microscopic states $s = 1, \dots N$, then since $\sum_s P_s = 1$, we can deduce the normalization

Call the normalization constant $1/Z$. So:

$$P_s = \frac{e^{-\varepsilon_s/kT}}{Z(T)}$$

$Z(T)$ is a function of temperature and is called the partition fcn

Then

$$\sum_s \frac{1}{Z} e^{-\varepsilon_s/kT} = 1, \quad \text{and so} \quad Z = \sum_s e^{-\varepsilon_s/kT}$$

Finally we get tired of writing $1/kT$ and define $\beta \equiv 1/kT$

$$\boxed{Z(\beta) = \sum_s e^{-\beta \varepsilon_s}} \qquad \boxed{\beta \equiv \frac{1}{kT}}$$

and the probality to find the system in a state r is

$$\boxed{P_r = \frac{e^{-\beta \varepsilon_r}}{Z(\beta)}}$$

## Example 1

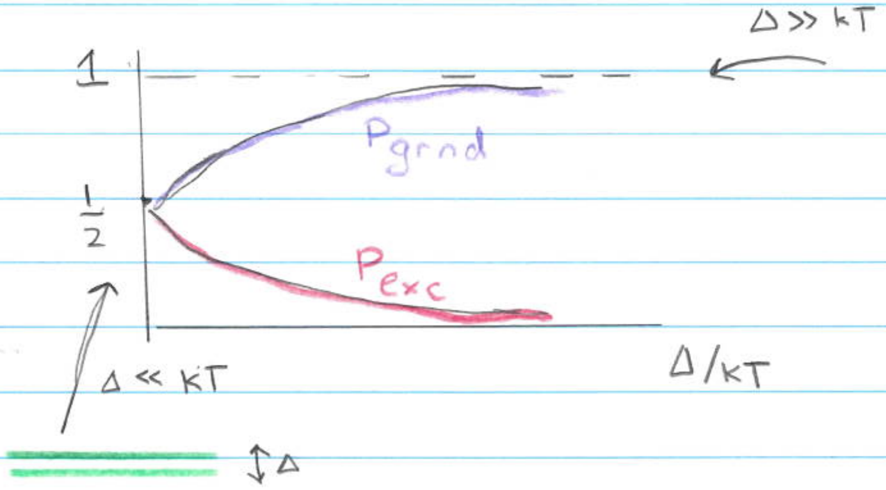
Consider an "atom" consisting of a ground state of energy 0 and an excited state of energy $\Delta$. At temperature T determine the probalilities to be in the ground and excited states

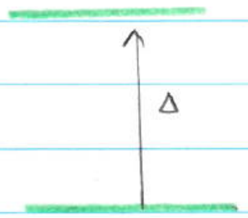
Then $Z(\beta) = \sum_s e^{-\beta \varepsilon_s} = e^{-0} + e^{-\beta\Delta} = 1 + e^{-\beta\Delta}$

So

$$P_{grnd} = \frac{e^{-\beta 0}}{Z} = \frac{1}{1+e^{-\beta\Delta}}$$

$$P_{exc} = \frac{e^{-\beta\Delta}}{Z} = \frac{e^{-\beta\Delta}}{1+e^{-\beta\Delta}}$$



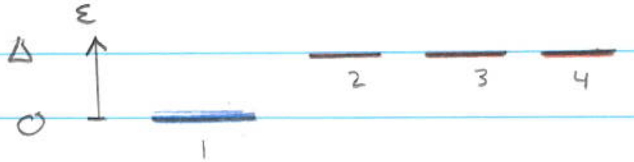


For small $\Delta$ compared to kT, the system can easily jump from the grnd state to the exc. state and back. Thus $P \simeq 1/2$

for large $\Delta$ compared to kT the system does not have enough thermal energy to jump to the higher state, and thus all atoms are in the grnd state $P_{grnd} \simeq 1$

## Ex 2

- Sometimes there are more than one state with the same energy level. This is called degeneracy. So if the excited state is 3-fold degenerate, $g = 3$



Then $$Z = \sum_{s=1}^{4} e^{-\beta \varepsilon_s} = 1 + g e^{-\beta\Delta}$$

- The probability to be in the 4-th state is $e^{-\beta\Delta}/Z(\beta)$. But the probability to be in an excited state (states 2, 3, 4) is

$$P_{exc} = P_2 + P_3 + P_4 = g e^{-\beta\Delta}/Z(\beta)$$

## Ex 3

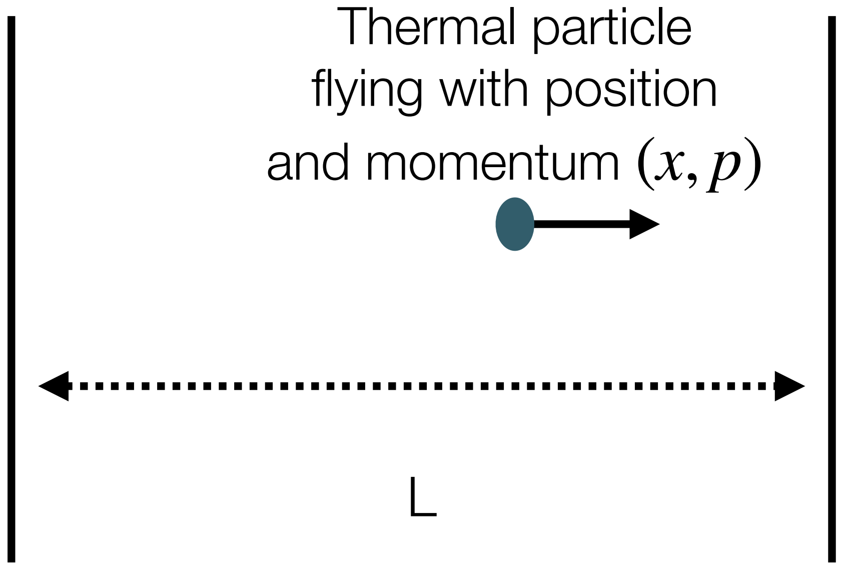
- What about a classical particle? How do I list the states? How do I sum over them?

(see slide for overview)

- Lets consider a particle in a box in one dimension. The state of a particle is labelled by its position and momentum $(x, p)$. The equations of motion advance the state to the next moment

$$\left.\begin{aligned} dx/dt &= p/m \\ \frac{dp}{dt} &= F(x) \end{aligned}\right\} \quad \text{The energy } \varepsilon = \frac{p^2}{2m}$$

# Classical thermal particle in a box of size L in 1D



Thermal particle flying with position and momentum $(x, p)$

The energy is

$$\varepsilon(p) = \frac{p^2}{2m}$$

Partition Function?

- Then we lay out $(x,p)$ on a grid called phase-space. The sum over states becomes an integral over classical configurations $\int dx\,dp$. The volume of phase space is proportianal to the number of states. To count configurations we need to define a cell size, $\Delta x \Delta p$, and the number is:

(see slide!)

$$\sum_{\text{states}} = \boxed{\begin{matrix}\#\text{ of states}\\ \text{in phase}\\ \text{space region}\end{matrix} = \int \frac{dx\,dp}{\Delta x\,\Delta p} = \int \frac{dx\,dp}{h} \xleftarrow{} \begin{matrix}\text{sets}\\ \text{units.}\end{matrix}}$$

- Classically $h = \Delta x \Delta p$ was aribitrary. Quantum mechanically the uncertainty principle says $\Delta x \Delta p \geq \hbar/2$. To have agreement with quantum mechanics, we must have $\Delta x \Delta p = h$, with $h$ planck's constant. We will show this later. $h$ matters only when comparing classical + quantum systems.

- The probability to be in a given cell of phase space is

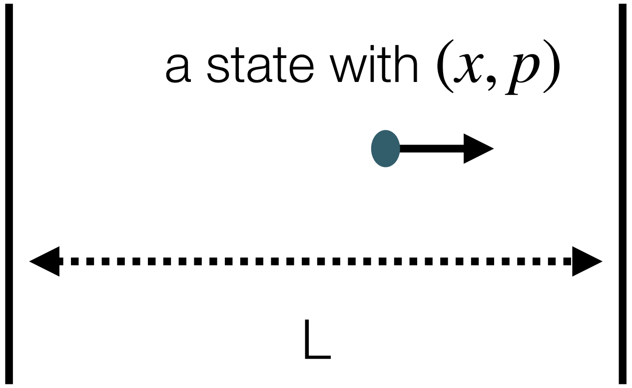
$$\boxed{d\mathcal{P} = \frac{1}{Z_1}\, e^{-\beta \varepsilon}\, \frac{dx\,dp}{h}}$$

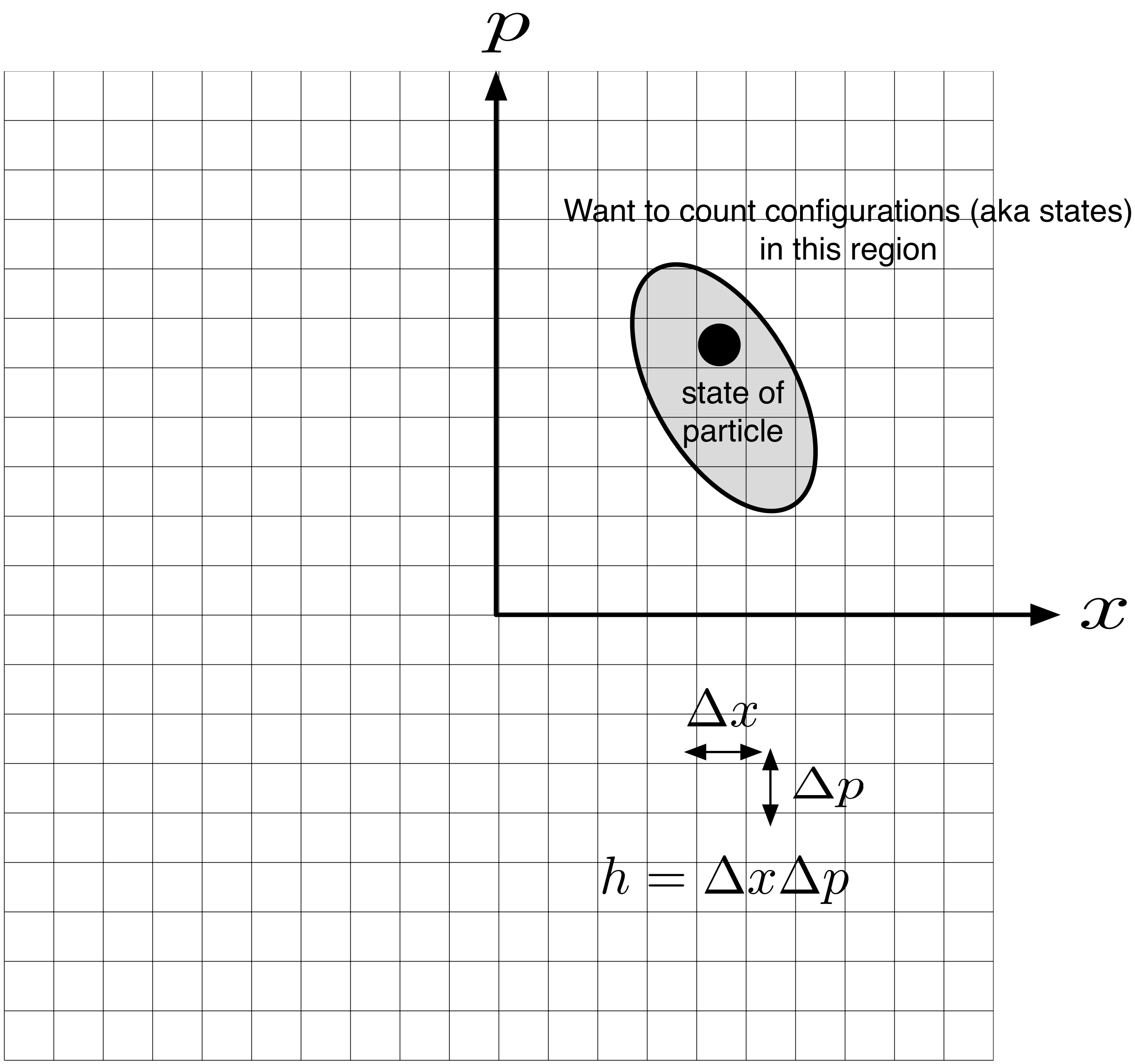
$\frac{dx\,dp}{h}$ is like $g$ in Example 2

This is the probality to have position between $x$ and $x+dx$, and momentum between $p$ and $p+dp$, or briefly to have $[x, dx]$ and $[p, dp]$.

$Z_1$ sets the overall normalization.

# Phase Space in One Dimension


a state with $(x, p)$


Want to count configurations (aka states) in this region

$$h = \Delta x \Delta p$$

The partition fcn sets the normalization. From $\int d\mathcal{P} = 1$ :

$$Z_1 = \int \frac{dx\,dp}{h}\; e^{-p^2/2mkT}$$

① The integral over x just gives the box size L

$$= \frac{L}{h} \int_{-\infty}^{\infty} dp\; e^{-p^2/2mkT}$$

② The integral over p is gaussian with $\sigma^2 = mkT$

$$= L\,\frac{(2\pi mkT)^{1/2}}{h}$$

$$\equiv \frac{L}{\lambda_{th}}$$

③ We note for later that $Z_1 = L/\lambda_{th}$ where $\lambda_{th}$ is the thermal debroglie wavelength.

$$\lambda_{th} = h/(2\pi mkT)^{1/2}$$

So

$$d\mathcal{P} = \frac{1}{\dfrac{L\,(2\pi mkT)^{1/2}}{\cancel{h}}}\; e^{-p^2/2mkT}\; \frac{dx\,dp}{\cancel{h}}$$

← cell size cancels, we are not comparing to quantum system

$$\boxed{d\mathcal{P} = \frac{dx}{L}\; \frac{e^{-p^2/2mkT}}{(2\pi mkT)^{1/2}}\; dp}$$

This is the probability of finding the particle per dx and dp. Lets express in terms of $v = p/m$ $dv = dp/m$

$$\boxed{d\mathcal{P} = \frac{dx}{L} \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{1}{2}mv^2/kT}\; dv}$$

## Comments

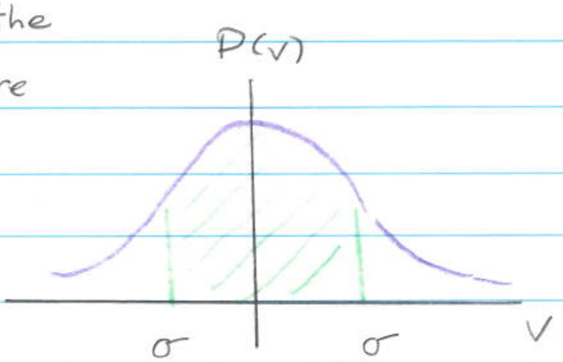
- The probability density factorizes, so the coordinates and velocity distributions are independent

$$d\mathcal{P} = P(x,v)\, dx\, dv$$

$$= P(x)\, dx \quad P(v)\, dv$$

$$= \underbrace{\left(\frac{1}{L}\, dx\right)}_{P(x)dx} \underbrace{\left(\sqrt{\frac{m}{2\pi kT}}\; e^{-\frac{1}{2}mv^2/kT}\, dv\right)}_{P(v)\,dv}$$

the energy and thus the probality are indep of x



P(v) is a gaussian with width $\sigma^2 = \frac{kT}{m}$

65% of the time the particle will have $|v| < \sqrt{\frac{kT}{m}}$

- In higher dimension say two dimensions, the notion of phase space is extended straightforwardly.

$$\sum_{\text{states}} = \int \frac{dx\, dp_x}{h} \frac{dy\, dp_y}{h} = \int \frac{d^2x\, d^2p}{h^2}$$

## Example 4

- For a particle in a 3D Box of Volume $L^3$

$$d\mathcal{P}_{\vec{r},\vec{p}} = \frac{1}{Z_1} e^{-p^2/2mkT} \frac{d^3\vec{r}\, d^3\vec{p}}{h^3}$$ ← prob to be in cell of $d^3\vec{r}$ and $d^3\vec{p}$.

with

$$\boxed{Z_1 = \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3} e^{-p^2/2mkT}}$$

the normalization constant will be important later.

So

$$d\mathcal{P}_{\vec{r},\vec{p}} \propto e^{-p^2/2mkT} \underbrace{\frac{dx\,dy\,dz}{V}}_{\text{inserted for convenience}} dp_x\, dp_y\, dp_z$$

- So if we don't care about the position we can integrate over $\vec{r}$:

$\mathcal{E}$ is independent of position

$$d\mathcal{P}_{\vec{p}} = \int_{\vec{r}} d\mathcal{P}_{\vec{r},\vec{p}}$$

$$\propto e^{-p^2/2mkT} dp_x\, dp_y\, dp_z$$

Use $\int \frac{dx\,dy\,dz}{V} = 1$

We usually care about velocity $v_x = p_x/m$ $dp_x = m\,dv_x$

So

$$\boxed{d\mathcal{P}_{\vec{v}} \propto e^{-\frac{1}{2}mv^2/kT} dv_x\, dv_y\, dv_z}$$ ← We will study this next