Tuesday 28 Feb 716 099

Applications of canonical ensemble

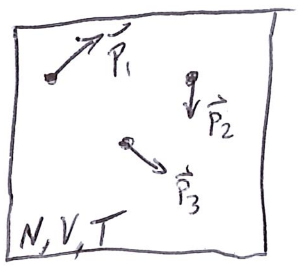
Dist'able vs. indist'able spins

→ physical effects from info content

Classical non-rel. ideal gases in volume $V = L^3$

Start with partition function / free energy

derive internal energy $\langle E \rangle$, entropy S



Problem: Continuous $E = \frac{1}{2m} \sum_n p_n^2$

vs. $Z = \sum_i e^{-E_i/T}$

Regulate to get countable micro-states

then limit of sum → integral

Ansatz of discrete momenta $\vec{p} = \hbar \frac{\pi}{L} (k_x, k_y, k_z)$ with $k = 0, 1, 2, \ldots$

→ Discrete energies $E_k = \frac{\hbar^2 \pi^2}{2mL^2} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 \pi^2 k^2}{2mL^2}$

Unlike energy levels of spin systems, not evenly spaced

$k^2 = 6$ for $\vec{k} = (2, 1, 1)$ + perms

$k^2 = 8$ for $\vec{k} = (2, 2, 0)$ + perms.

no $k^2 = 7$

First consider single particle $N=1$

$$Z_1 = \sum_i e^{-E_i/T} = \sum_{\vec{p}} \exp\left[-\frac{p^2}{2mT}\right] = \sum_{n_{xyz}=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2}{2mTL^2}(n_x^2+n_y^2+n_z^2)\right]$$

$$= \left(\sum_{n_i=0}^{\infty} \exp\left[\frac{-\hbar^2\pi^2}{2mTL^2} n_i^2\right]\right)^3$$

Now approximate sum by <u>integral</u>

Classical $\rightarrow$ T, L large compared to $\hbar$

Non-rel. $\rightarrow$ m large compared to $\hbar$

$$\frac{\hbar^2\pi^2}{2mTL^2} \ll 1$$

$\rightarrow$ Terms vary very smoothly for n_i^2 small

As $n_i \rightarrow \infty$, terms $\rightarrow 0$

$$\sum_{n_i=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2 n_i^2}{2mTL^2}\right] \approx \frac{1}{2}\int_{-\infty}^{\infty} d\hat{n}_i \exp\left[\frac{-\hbar^2\pi^2\hat{n}_i^2}{2mTL^2}\right]$$

continuous

$$p_i = \hbar\frac{\pi}{L}\hat{n}_i$$

$$\frac{L}{2\pi\hbar}\int_{-\infty}^{\infty} dp_i \exp\left[\frac{-p_i^2}{2mT}\right]$$

$$Z_1 = \left(\frac{L}{2\pi\hbar}\right)^3 \int d^3p \exp\left[\frac{-p^2}{2mT}\right] \qquad p^2 = p_x^2+p_y^2+p_z^2$$

Generalize to N (distinguishable) particles

$$Z_D = \left(\frac{L}{2\pi\hbar}\right)^{3N} \int d^{3N}p \exp\left[-\sum_{n=1}^{N}\frac{p_n^2}{2mT}\right]$$

3N independent gaussian integrals

$$\int dp_i \exp\left[\frac{-p_i^2}{2mT}\right] = \sqrt{2\pi mT}$$

$$Z_D = \left(\frac{L}{2\pi\hbar}\right)^{3N}(2\pi mT)^{3N/2} = \left(\frac{mTL^2}{2\pi\hbar^2}\right)^{3N/2}$$

$$Z_D = \left(\frac{L^2}{\lambda_{th}^2(T)}\right)^{3N/2}$$

for convenience, define $\lambda_{th}(T) = \sqrt{\frac{2\pi\hbar^2}{mT}}$

(thermal ~~de~~ de Broglie wavelength)

$$Z_D = \left(\frac{V}{\lambda_{th}^3}\right)^N \qquad \lambda_{th}^3 \ll L^3 = V$$

Dependence on volume of gas, along with N and T

What about indist'able case?

$N=2$ particles $\rightarrow$ half as many micro-states

$N=3$ particles

$\vec{p}_1$	A	A	B	B	C	C	single indist'able w
$\vec{p}_2$	B	C	A	C	B	A	$\rightarrow 6 = 3!$ dist'able w_i
$\vec{p}_3$	C	B	C	A	A	B	

page 59

(Assume $\vec{p}_i \neq \vec{p}_k$ for $i \neq k$)

In general, same integrals over momenta

but $N!$ fewer micro-states without labeling

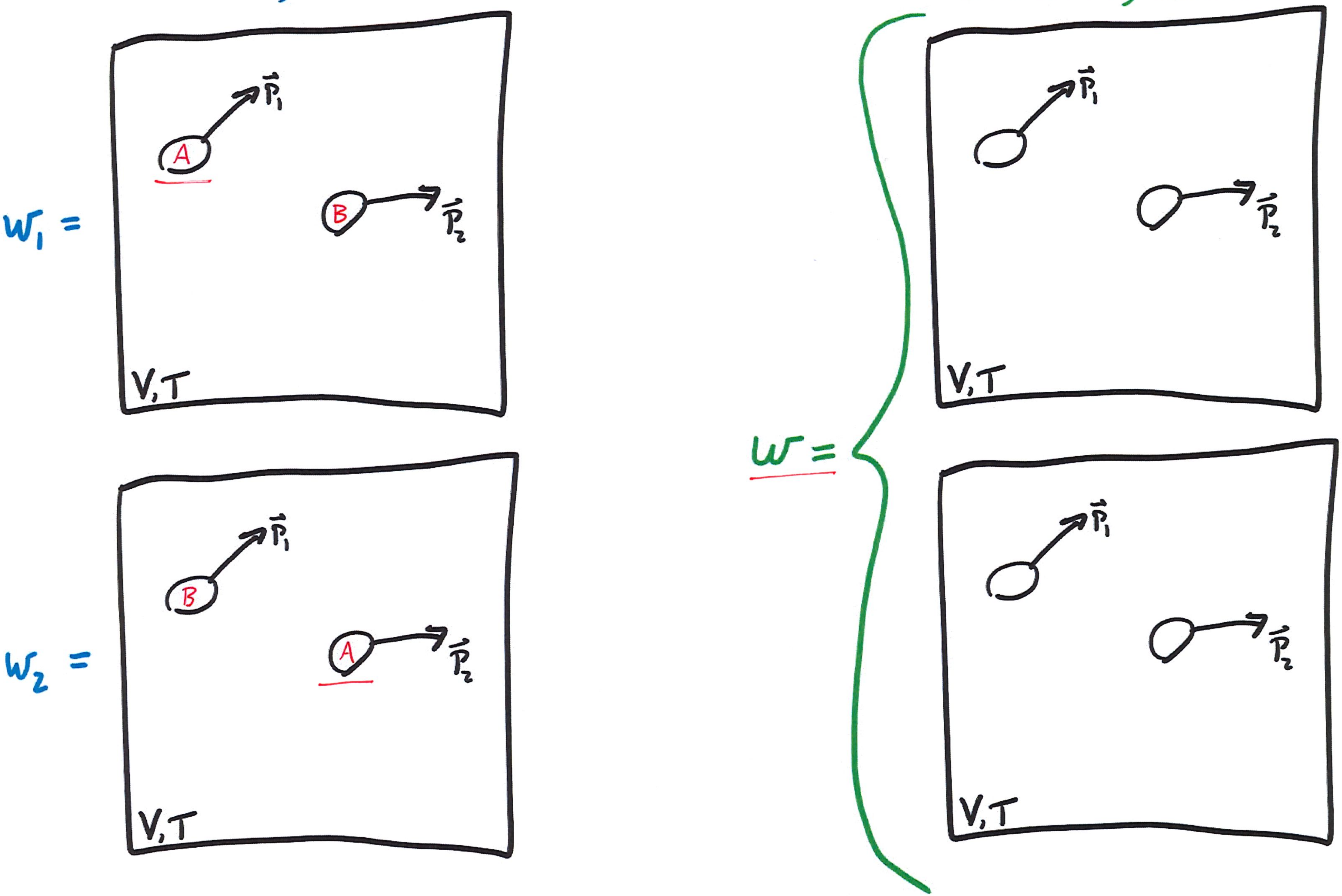
$$\rightarrow Z_I = \frac{1}{N!} Z_D = \frac{1}{N!} Z_1^N = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N = \frac{1}{N!}\left(\frac{mTL^2}{2\pi\hbar^2}\right)^{3N/2}$$

Helmholtz free energy $F_I = -T \log Z_I$

$$= T\log(N!) - \frac{3NT}{2}\log\left(\frac{mTL^2}{2\pi\hbar^2}\right)$$

Distinguishable

Indistinguishable



Average internal energy

$$\langle E\rangle_I = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right) = -T^2\frac{\partial}{\partial T}\left(-\frac{3N}{2}\log(T) + T\text{-independent}\right)$$

$$= \frac{3}{2}NT$$

Macroscopic relation from microscopic energy

Entropy ~~relative~~

$$S_I = \frac{\langle E\rangle_I - F_I}{T} = \frac{3}{2}N + \frac{3}{2}N\log\left(\frac{L^2}{\lambda_{th}^2}\right) - \underbrace{\log(N!)}_{N\log N - N}$$

$$= \frac{5}{2}N + N\log\left(\frac{V}{N\lambda_{th}^3}\right)$$

Writing down for dist'able case

$$\boxed{\begin{aligned} F_D &= -\frac{3NT}{2}\log\left(\frac{mTL^2}{2\pi\hbar^2}\right) \\ \langle E\rangle_D &= \frac{3}{2}NT \\ S_D &= \frac{3}{2}N + N\log\left(\frac{V}{\lambda_{th}^3}\right) \end{aligned}}$$

page 61