

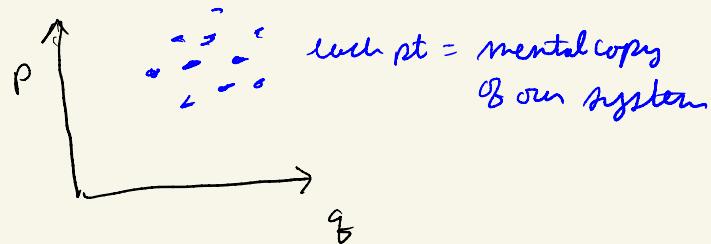
## Reminders

- ① Exam 1 Monday Oct 18 (STEM classroom)
- Thermodynamics
  - Stat. mech. fundamentals
- } HW 1-4  
≈ 3 more lectures

- ② HW 4 will be posted later today (due Friday 10/15)
- ③ Monday will be remote again (Sorry!)

## Recap from L12

### \* Ensembles in Classical Phase Space

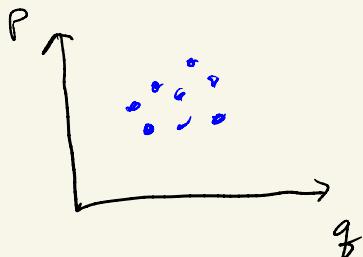


$$P(q, p; t) d\Gamma = \frac{\# \text{ of points in } d\Gamma}{d^{3N} p d^{3N} q} \text{ about } \{p_1, \dots, p_{3N}, q_1, \dots, q_{3N}\}$$

For any  $f(q, p)$ ,

$$\langle f \rangle = \frac{\int f(q, p) P(q, p; t) d\Gamma}{\int P(q, p; t) d\Gamma}$$

## \* Conditions for equilibrium P



How does the swarm of points evolve in time?



$$\frac{d}{dt} \rho = \frac{\partial \rho}{\partial t} + \{ \rho, H \}_{PB} = 0$$

Total derivative  
 (aka convective derivative)

Liouville's Theorem

$$\{ A, B \}_{PB} = \sum_{i=1}^{3N} \left( \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right)$$

(density doesn't change if you "ride along" with the trajectory of a given point as it evolves in time)

\* For equilibrium, should be no explicit t-dep.

$$\text{i.e., } \frac{\partial \rho}{\partial t} = 0$$

↓ Liouville

$$\{ \rho_{eq}, H \}_{PB} = 0$$

$$\Rightarrow \rho_{eq}(p, q) = \rho_{eq}(H(p, q))$$

Microcanonical: (all systems have  $E < Z(H_{(p,q)}) < E + \Delta E$   $\Delta E \ll E$ )

$$J(E) = \int \frac{d\Gamma}{\Gamma_0} \left[ \Theta(E + \Delta E - Z(H_{(p,q)})) - \Theta(E - Z(H_{(p,q)})) \right]$$

$$\begin{aligned}\Gamma_0 &= \text{phase space of 1 microstate} \\ &= (2\pi\hbar)^{3N} = h^{3N}\end{aligned}$$

$$\text{Canonical}: Z_{CE} = \frac{1}{N!} \int \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N}} e^{-\beta Z(H_{(p,q)})}$$

$$\text{Grand Canonical}: Z_{GCE} = \sum_N \frac{1}{N!} \int \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N}} e^{-\beta(Z(H_{(p,q)}) - \mu N)}$$

\*Thermodynamics calculated as before...

# Equipartition Theorem (Classical 2)

Simple form: Consider the thermal average of a single cartesian component  $\frac{P_x^2}{2m}$  of sp. KE

$$\langle \frac{P_x^2}{2m} \rangle = \frac{1}{(2\pi k_B T)^N} \int d\vec{p}_1 \dots d\vec{p}_N \frac{P_x^{(i)2}}{2m} e^{-\beta \sum_i \frac{P_i^2}{2m}} \int d\vec{r}_1 \dots d\vec{r}_N e^{-\beta \sum_{ij} \frac{P_{ij}^2}{2m}}$$

$$= \frac{1}{(2\pi k_B T)^N} \int d\vec{p}_1 \dots d\vec{p}_N e^{-\beta \sum_i \frac{P_i^2}{2m}} \int d\vec{r}_1 \dots d\vec{r}_N e^{-\beta \sum_{ij} \frac{P_{ij}^2}{2m}}$$

$$= \frac{\int dP_x^{(i)} \frac{P_x^{(i)2}}{2m} e^{-\beta \frac{P_x^{(i)2}}{2m}}}{\int dP_x^{(i)} e^{-\beta \frac{P_x^{(i)2}}{2m}}}$$

$$= \frac{1}{\int dP_x e^{-\beta P_x^2}} \times -\frac{\partial}{\partial \beta} \int dP_x e^{-\beta \frac{P_x^2}{2m}}$$

$$= \frac{1}{\sqrt{\frac{2m\pi}{\beta}}} - \frac{\partial}{\partial \beta} \sqrt{\frac{2m\pi}{\beta}}$$

$$= \sqrt{\frac{1}{2m\pi\beta}} \cdot \frac{1}{2} \sqrt{\frac{2m\pi}{\beta}} \frac{1}{\beta}$$

$$\Rightarrow \langle \frac{P_x^2}{2m} \rangle = \frac{k_B T}{2}$$

i.e., each DOF has avg KE =  $\frac{k_B T}{2}$

$$\left. \therefore \langle \sum_{i=1}^N \frac{P_i^2}{2m} \rangle = \frac{3}{2} N k_B T \right\}$$

## generalized form

\* Let  $\xi_i + \xi_j$  be any 2 components of  $(P_1, \dots, P_{3N}, q_1, \dots, q_{3N})$

$$\langle \xi_i \frac{\partial H}{\partial \xi_j} \rangle = \frac{\int d\Gamma e^{-\beta H} \xi_i \frac{\partial H}{\partial \xi_j}}{\int d\Gamma e^{-\beta H}}$$

\* Focus on the numerator:

$$\int d\Gamma e^{-\beta H} \xi_i \frac{\partial H}{\partial \xi_j} = \int d\Gamma \left( -\frac{1}{\beta} \frac{\partial}{\partial \xi_j} e^{-\beta H} \right) \xi_i$$

$$\stackrel{\text{partial integration}}{=} \underset{\text{Surface term}}{\cancel{\int d\Gamma e^{-\beta H}}} + \frac{1}{\beta} \int d\Gamma e^{-\beta H} \frac{\partial \xi_i}{\partial \xi_j}$$

$$\therefore \langle \xi_i \frac{\partial H}{\partial \xi_j} \rangle = \frac{1}{\beta} \delta_{ij} \frac{\int d\Gamma e^{-\beta H}}{\int d\Gamma e^{-\beta H}} = k_B T \delta_{ij}$$

Special case: 1)  $\xi_i = q_j = p_i \Rightarrow \langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i q_i \rangle = k_B T$

$$2) \xi_i = q_j = q_i = \langle q_i \frac{\partial H}{\partial q_i} \rangle = -\langle q_i p_i \rangle = k_B T$$

|| Summing over  $i = 1 \dots 3N$

$$\left\langle \sum_i p_i \frac{\partial H}{\partial p_i} \right\rangle = \left\langle \sum_i p_i q_i \right\rangle = 3N k_B T$$

$$\left\langle \sum_i q_i \frac{\partial H}{\partial q_i} \right\rangle = \left\langle -\sum_i q_i p_i \right\rangle = 3N k_B T$$

\* Now, in problems where  $H$  is a quadratic form  
 (or can be brought to one with a canonical transformation  
 $q_i, p_i \rightarrow Q_i, P_i$ )

$$H = \sum_j A_j P_j^2 + \sum_j B_j Q_j^2 \quad (\textcircled{X})$$

↓

$$\sum_j \left( P_j \frac{\partial H}{\partial P_j} + Q_j \frac{\partial H}{\partial Q_j} \right) = 2H$$

$\therefore \langle H \rangle = \frac{1}{2} f k_B T$

$f = \# \text{ of non-vanishing}$

Coefficients  $A_j + B_j$

in  $(\textcircled{X}) = \# \text{ of DOF}$



\* Corollary: Each quadratic term in  $Z$  makes a contribution of  $\frac{1}{2} k_B$  to  $C_v$

Remark:  $\textcircled{X} + C_v = \frac{f k_B}{2}$  only holds when all relevant DOF can be excited. at low  $T$ , some might be "frozen out" due to quantum effects  
 (Indeed, the mismatch of  $C_v$  at low temps was one of the early evidences for the failure of classical physics.)

## Virial Theorem

\* already showed in our derivation of the generalized equipartition theorem

$$\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = -3Nk_B T \quad \text{"Virial theorem"}$$

"Virial"

{ or since  $\dot{p}_i = F_i$

$$\left\langle \sum_{i=1}^{3N} q_i F_i \right\rangle = -3Nk_B T$$

ex: Derivation of ideal gas law

Force on the gas from  
the container walls

$$d\vec{F} = -P d\vec{S}$$



$$\begin{aligned} \therefore D &= \left\langle \sum_i q_i F_i \right\rangle = -P \oint_S \vec{r} \cdot d\vec{s} \\ &= -P \int_V (\vec{r} \cdot \vec{F}) dV = -3PV \end{aligned}$$

$$\therefore -3PV = -3Nk_B T \Rightarrow$$

$PV = Nk_B T$

## Excitation of internal DOF

- \* So far in our gas treatments, we've only looked at translational KE
- \* But for molecules you can have internal motions (e.g., rotational or vibrational)



- \* When these motions can be excited, the available microstates changes, which means so does  $Z$  + all derived TD properties
- \* Often, the internal excitations decouple from trans. motion, so

$$E_{\alpha}(\vec{p}) = E(\vec{p}) + E_{\alpha}$$

$\uparrow$

translational  
KE

$\uparrow$

intrinsic  
excitation

\* Re-tracing our derivation of  $Z_{CE}$  for the ideal gas,

$$Z_N = \frac{1}{N!} (Z_1)^N$$

↑  
partition function  
for 1 particle

$$Z_1 = \frac{V}{(2\pi k_B T)^3} \sum_{\alpha} \int d^3 p e^{-\beta(\frac{p^2}{2m} + E_{\alpha})}$$

$$= Z_1^{\text{trans}} \times Z_1^{\text{int}}$$

$$= \frac{V}{l_{\alpha}^3} \times \sum_{\alpha} e^{-\beta E_{\alpha}}$$

$$l_{\alpha} = \sqrt{\frac{2\pi k_B T}{m}}$$

$$\Rightarrow Z_N = \frac{1}{N!} \frac{V^N}{l_{\alpha}^{3N}} \times \left[ \sum_{\alpha} e^{-\beta E_{\alpha}} \right]^N = Z_N^{\text{trans}} \times Z_N^{\text{int}}$$

$$\therefore F = -\frac{1}{\beta} \log Z = F_{\text{trans}} + F_{\text{int}}$$

$$F_{\text{int}} = -k_B T N \log Z_1^{\text{int}}$$

$\Rightarrow$  all TD properties modified (take appropriate derivs. of F)

$$E_{\text{int}} = -N \frac{\partial}{\partial \beta} \log Z_i^{\text{int}}$$

$$P_{\text{int}} = 0$$

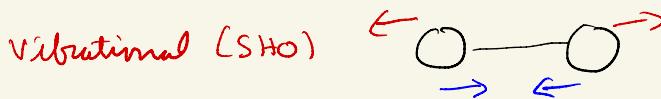
$$S_{\text{int}} = N \log Z_i^{\text{int}} + N k_B T \frac{1}{Z_i^{\text{int}}} \frac{\partial}{\partial T} Z_i^{\text{int}}$$

$$M_{\text{int}} = -k_B T \log Z_i^{\text{int}}$$

:

etc

Example: Diatomic gas



$$\begin{aligned} E &= (n + \frac{1}{2})\hbar\omega \quad \text{redefine zero of energy} \\ &= n\hbar\omega \quad n = 0, 1, 2, \dots \infty \end{aligned}$$

$$Z_i^{\text{int}} = \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega} = \sum_{n=0}^{\infty} [e^{-\beta \hbar \omega}]^n \quad \left( \sum_n x^n = \frac{1}{1-x} \right)$$

$$Z_i^{\text{int}} = \frac{1}{1 - e^{-\beta \hbar \omega}}$$

$\Rightarrow$  the vibrational correction to (say) the internal energy

$$\begin{aligned}\langle E \rangle &= \langle E_{\text{trans}} \rangle + \langle E_{\text{vib}} \rangle \\ &= \underbrace{\frac{3}{2} k_B T - N \frac{2}{2\pi} \log Z_1^{\text{int}}}_{\text{---}} \\ &\quad \frac{N \hbar \omega}{e^{\beta \hbar \omega} - 1} = \langle E_{\text{vib}} \rangle\end{aligned}$$

\*Look at high- + low-T limits

$$\left\langle \frac{E_{\text{int}}}{N} \right\rangle = \begin{cases} \hbar \omega e^{-\frac{\hbar \omega}{k_B T}} & k_B T \ll \hbar \omega \\ K_B T & K_B T \gg \hbar \omega \end{cases}$$

(Refer back to our earlier caveat about the equipartition theorem not being universally valid due to modes being frozen out at low T due to their quantum nature)

\*Note: at  $T \sim$  room temp, you don't "see" the vib. modes since  $\frac{\hbar \omega}{k_B} \sim 10^3 \text{ } ^\circ\text{K}$  for most molecules

\* Can play the same game with rotational modes

$$E_{\text{elm}} = \frac{\hbar^2}{2I} l(l+1) \quad I = \text{moment of inertia}$$

$$(m = -l \dots l)$$

$$\therefore Z_{\text{rot}}^{(1)} = \sum_l (2l+1) e^{-\frac{\hbar^2 l^2}{2I} l(l+1)}$$

\* For many molecules,  $\frac{\hbar^2}{2k_B I} \ll T_{\text{room}}$

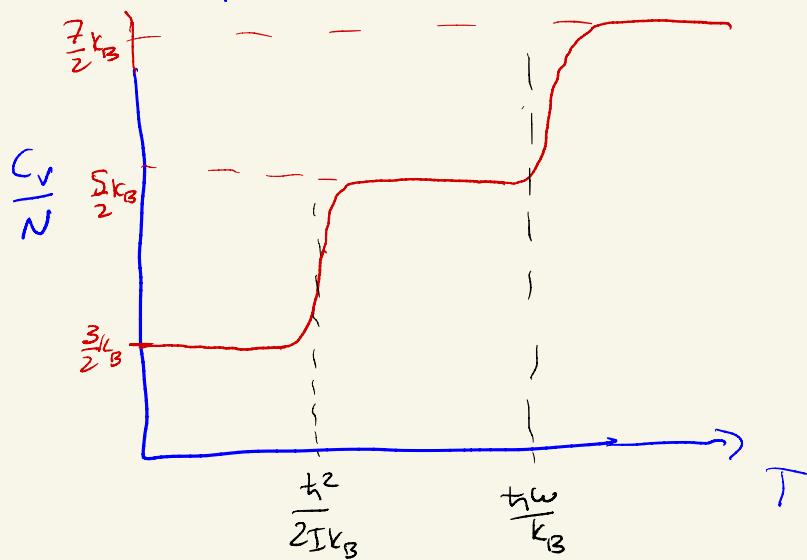
i.e. for  $T \gg \frac{\hbar^2}{2k_B I}$  can replace the sum by an integral

$$Z_{\text{rot}}^{(1)} \approx \int_0^\infty dl (2l+1) e^{-\frac{\hbar^2 l^2}{2I} l(l+1)} = \frac{2I/k_B T}{\hbar^2}$$

$$\langle E_{\text{rot}} \rangle = -N \frac{\partial}{\partial \beta} \log Z_{\text{rot}}^{(1)} = N k_B T$$

i.e. the 2 rotational modes of  
a rotor each contribute  $\frac{k_B T}{2}$   
as the EP theorem says.

Based on these 2 examples then, expect a "Staircase" behavior for  $\frac{C_V}{N}$  for diatomic gas



## Ensemble theory revisited

- \* I'd like to revisit the derivation of  $P_i$  of the canonical + grand canonical ensembles from a different perspective due to Gibbs, since it comes in use later on when we discuss bose/fermi distributions (+ also because it connects with ideas from other fields like information theory if we decide to explore that later on.)
- \* The key concept is a variational principle where the entropy is maximized under different constraints, depending on the ensemble.

→  $N_s$  mental copies of our system  
(i.e., # of copies in the ensemble)

→ each system can be in any of  $M$  different micro states

$$\rightarrow \left\{ \begin{array}{l} \# \text{ of arrangements} \\ \text{for } n_i \text{ systems} \\ \text{in microstate } i \end{array} \right. = W = \frac{n_s!}{n_1! n_2! \dots n_m!}$$

where  $\sum_{i=1}^M n_i = N_s$

\* Sometimes  $W$  is called "the ignorance" since larger values mean there are more possible configs. of the ensemble, so we know less about its state.

\* Following Gibbs, define

$$N_S S = \log W$$

$$= \log(N_S!) - \sum_i \log(n_i!)$$

\* Take the freedom to take  $N_S$  (+ hence  $n_i$ ) large  $\Rightarrow$  Stirling Approx.

$$N_S S = N_S \log N_S - N_S - \sum_i n_i \log n_i + \sum_i n_i$$

$$= (\sum_i n_i) \log N_S - \sum_i n_i \log n_i$$

$$= \sum_i n_i (\log N_S - \log n_i)$$

$$= - \sum_i n_i \log \frac{n_i}{N_S}$$

Since  $\frac{n_i}{N_S} = \text{fraction of system in state } i$

$\Rightarrow \boxed{S = - \sum_i \frac{n_i}{N_S} \log \frac{n_i}{N_S} = - \sum_i p_i \log p_i}$

\* Now we re-derive  $P_i$  for the different ensembles by maximizing  $S$  (entropy) under different constraints (treat  $P_i$  as variational parameters)

### (i) Microcanonical

$$\frac{\partial S}{\partial P_i} = 0 \quad \text{with constraint} \quad \sum_i P_i = 1$$

or  $\left( \sum_i P_i - 1 \right) = 0$

Reminder: If you want to maximize  $f(\vec{x})$  subject to some constraint  $g(\vec{x}) = 0$ , then you maximize without any constraint the modified function  $(f(\vec{x}) - \lambda g(\vec{x}))$  wrt  $\vec{x} + \lambda$

$$\text{i.e., } \frac{\partial}{\partial x_i} (f(\vec{x}) - \lambda g(\vec{x})) = 0$$

$$\frac{\partial}{\partial \lambda} (f(\vec{x}) - \lambda g(\vec{x})) = 0$$

\* if multiple constraints  $g_\alpha(\vec{x}) = 0 \quad \alpha = 1 \dots N$

$$\frac{\partial}{\partial x_i} (f(\vec{x}) - \sum_\alpha \lambda_\alpha g_\alpha(\vec{x})) = 0$$

$$\frac{\partial}{\partial \lambda_\beta} (f(\vec{x}) - \sum_\alpha \lambda_\alpha g_\alpha(\vec{x})) = 0 \quad \beta = 1 \dots N$$

$$\therefore \frac{\partial}{\partial p_j} \left( -\sum_i p_i \log p_i - \lambda (\sum_i p_i - 1) \right) = 0$$

$$\Rightarrow -\log p_j - 1 - \lambda = 0$$

$$= \log p_j = -\lambda - 1$$

$$\Rightarrow p_j = e^{-1-\lambda} \equiv p \text{ (constant)}$$

$$\text{Since } \sum_{i=1}^M p_i = 1 = pM$$

$$\Rightarrow p = \frac{1}{M} \text{ as before ( } M \rightarrow \infty \text{ )}$$

## ② Canonical

$$\frac{\partial S}{\partial p_i} = 0 \quad \text{w/ constraint} \quad \textcircled{1} \quad \sum_i p_i = 1$$

$$\textcircled{2} \quad \langle E \rangle = \sum_i p_i E_i$$

$$\Rightarrow \frac{\partial}{\partial p_j} \left[ -\sum_i p_i \log p_i - \lambda (\sum_i p_i - 1) - \beta \sum_i p_i E_i \right] = 0$$

$$= -\log p_j - 1 - \lambda - \beta E_j$$

$$\Rightarrow \log p_j = \log C - \beta E_j \quad (\log C = -1-\lambda)$$

$$p_j = C e^{-\beta E_j} ; \sum_j p_j = 1 \Rightarrow C = \frac{1}{\sum_j e^{-\beta E_j}}$$

\* Similarly, you can find  $p(i)$  for GCE by

$$\frac{\partial S}{\partial p_i} = 0 \quad \text{w/ constraints} \quad \begin{aligned} (1) \quad & \sum_i p_i = 1 \\ (2) \quad & \sum_i p_i N_i = \langle N \rangle \\ (3) \quad & \sum_i p_i E_i = \langle E \rangle \end{aligned}$$

where now  $\beta \mu$  appears as the Lagrange multiplier of the  $\sum_i p_i N_i = \langle N \rangle$  constraint.