Lecture 7 Canonical Ensemble

Have learned about fundamental eq in different representations, how EOS + $C_p^\circ(T)$ can be used to recover thermodynamic differences, and specific examples of EOS's. Where does this all come from, microscopically. To answer that, have to return to microscopic thinking.

microcanonical ensemble $S(U,V,N)$

two state systems

canonical ensemble $F(T,V,N)$

Boltzmann distribution $e^{-\varepsilon\beta}$ $\beta = 1/k_B T$
relative probability to have energy ε

$q(T,V) = \sum e^{-\varepsilon(V)\beta}$ single particle partition function
sum over all energy states

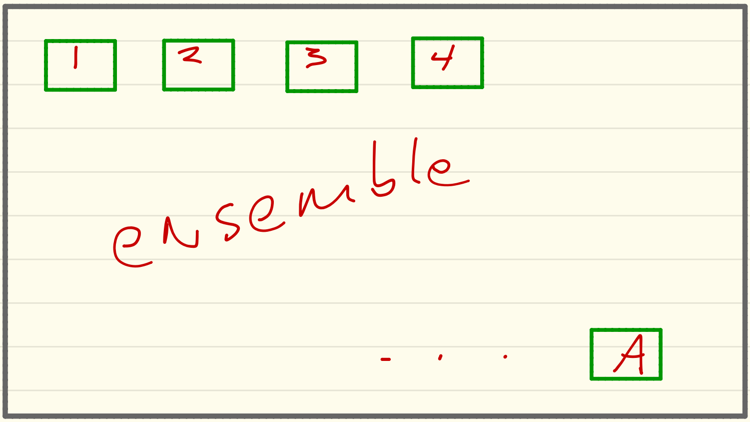
many independent particles

$Q(T,V,N) = q(T,V)^N$ distinguishable

$= q(T,V)^N/N!$ indistinguishable

If we know these sums, we know all about a system! Eg

$$F(T,V,N) = -k_B T \ln Q$$



A systems, all identical and at thermal equilibrium.

QM tells us energy is discrete

Each system has some energy E_i

Let # of systems w/ E_i be a_i

$$\sum a_i = A$$

Relative # of a_i + a_j can depend only on E_i and E_j:

$$a_i/a_j = f(E_i, E_j) = f(E_j - E_i)$$

Because energies are relative, can only depend on E difference

Must hold for any pair of energies:

$$\frac{a_i}{a_j} = f(E_j - E_i) \qquad \frac{a_j}{a_k} = f(E_k - E_j)$$

$$\frac{a_i}{a_k} = \frac{a_i}{a_j} \cdot \frac{a_j}{a_k}$$

$$f(E_k - E_i) = f(E_j - E_i)\, f(E_k - E_j)$$

Hmm, what f has this property?

$$f(a+b) = f(a) \cdot f(b)\ ?$$

$$e^{a+b} = e^a e^b \ !$$

$$f(E) = e^{\beta E} !!$$

$$f(E_j - E_i) = e^{\beta(E_j - E_i)} = a_i / a_j$$

$$\boxed{a_i \propto e^{-\beta E_i}}$$!! Boltzmann ftn

$$p_i = \frac{a_i}{\Sigma a} = \frac{a_i}{Q} \qquad \boxed{Q = \sum_i e^{-\beta E_i}}$$

Partition function!

What's the average energy of a system?

$$U = \sum_j p_j E_j = \sum_j \frac{E_j e^{-E_j \beta}}{Q}$$

$$\boxed{U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}}$$

We imagine each system has the same volume V + # of particles N. What if we infinitesimally change V?

$$dU = \sum_j p_j \, dE_j + \sum_j E_j \, dp_j$$

$$dU = \sum_j p_j \left(\frac{\partial E_j}{\partial V}\right) dV + \sum_j E_j \, dp_j$$

$$= -P \, dV + T \, dS$$

$$= đW_{qs} + đq_{qs}$$

Quasi-static work is infinitesimal change in energy states @ const. probability

Quasi-static heat is change in the probabilities

From this can get

$$\boxed{P = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}}$$

How many ways can we have a_1 of energy E_1, a_2 of E_2, ... ?

$$\Omega(a_1, a_2, \ldots) = \frac{A!}{a_1!\, a_2! \cdots} = \frac{A!}{\prod a_j!}$$

Eg $a_1 = A$, $a_2 = a_3 = \cdots = 0 \longrightarrow \Omega = 1$

What's entropy of an arrangement?

$$S_{ensemble} = k \ln \Omega$$

$$= k\left[\ln A! - \sum \ln a_j!\right]$$

Stirling's approximation

$$= k\left[A \ln A - A - \sum a_j \ln a_j + \cancel{\sum} a_j\right]$$

A

$$= k\left[A \ln A - \sum a_j \ln a_j\right]$$

$$S_{system} = \frac{S_{ensemble}}{A} = k\left[\ln A - \sum \left(\frac{a_j}{A}\right) \ln a_j\right]$$

$$= -k \sum \frac{a_j}{A} \ln \frac{a_j}{A}$$

$$\boxed{S_{sys} = -k \sum p_j \ln p_j}$$

If ensemble is large, this average will overwhelm all else.

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$$S = -k \sum \frac{e^{-\beta E_j}}{Q}\left(-\beta E_j - \ln Q\right) \qquad p_j = e^{-E_j\beta}/Q$$

$$= \beta k_B \sum_j \frac{E_j e^{-E_j\beta}}{Q} + \frac{k_B \ln Q}{\cancel{Q}} \cancel{\sum_j e^{-E_j\beta}}$$

$$\boxed{S = \beta k_B U + k_B \ln Q}$$

Still don't know what β is!

$$dS = -k \sum_j \left(dp_j + \ln p_j\, dp_j\right)$$

$$\sum p_j = 1 \qquad \sum dp_j = 0$$

$$dS = -k \ln p_j\, dp_j$$

$$= -k_B \sum_j \left(-\beta E_j - \ln Q\right) dp_j$$

$$= k_B \beta \sum_j E_j\, dp_j + k_B \ln Q \cancel{\sum_j dp_j}^{\,0}$$

$$dS = k_B \beta \sum_j E_j\, dp_j = dq_{rev}/T$$

$$k_B \beta = 1/T \Rightarrow \boxed{\therefore\ \beta \equiv 1/k_B T}$$

$$A = U - TS = U - T\left(\beta k_B U + k_B \ln Q\right)$$

$$= -k_B T \ln Q = \boxed{-\frac{\ln Q}{\beta} = A}$$

$Q(N, V, T)$ is the canonical partition ftn

The natural representation of the Helmholtz potential.

Other ensembles

Fluctuations

Example

2 state $N=3$

			E
0	0	0	0
1	0	0	ε
0	1	0	
0	0	1	
0	1	1	2ε
1	0	1	
1	1	0	
1	1	1	3ε

$$Q = e^{-0\beta} + 3e^{-\varepsilon\beta} + 3e^{-2\varepsilon\beta} + e^{-3\varepsilon\beta}$$

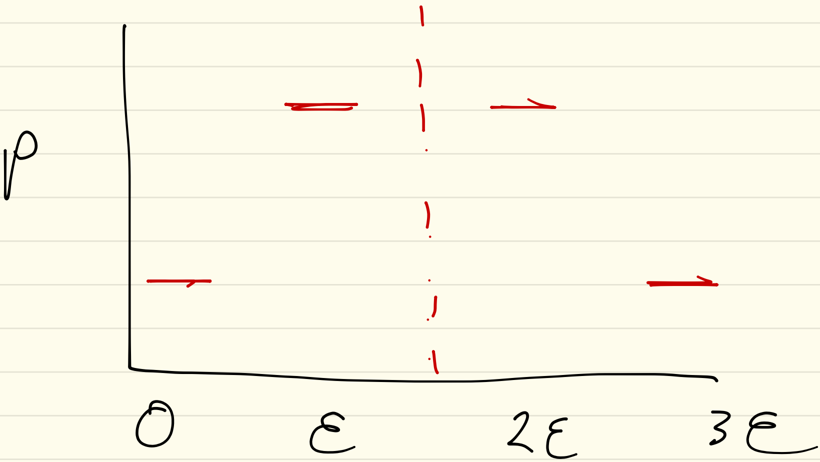
Sum over μ states vs sum over energies

$$Q = \sum_{\text{states}} e^{-E\beta}$$

$$= \sum_{\text{energies}} \Omega(E)\, e^{-E\beta}$$

$$P(E=0) = 1/Q$$

$$(E=1) = 3e^{-\varepsilon\beta}/Q$$



Fluctuations + determinism

Width of distribution
look at standard deviation

$$\sigma_u^2 = \langle \varepsilon_j^2 \rangle - \langle \varepsilon_j \rangle^2$$

$$= \sum_j \varepsilon_j^2 p_j - \left(\sum_j \varepsilon_j p_j\right)^2 \qquad p_j = e^{-\varepsilon_j/kT}$$

$$= k_B T^2 \left(\frac{\partial u}{\partial T}\right)_{V,N}$$

$$\sigma_u = \left(k_B T^2 C_v\right)^{1/2}$$

$$\frac{\sigma_u}{u} = \left(\frac{k_B T^2 C_v}{u^2}\right)^{1/2}$$

$$= \frac{1}{\sqrt{N}}\left(\frac{k_B T^2 c_v}{u^2}\right)^{1/2}$$ width goes as $\sqrt{N}$ relative to energy

Observation of width gives C_v

$$\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$\left(\frac{\partial u}{\partial T}\right)_{V,N} = \sum_j \varepsilon_j \left(\frac{\partial p_j}{\partial T}\right)$$

$$p_j = e^{-\varepsilon_j \beta}/Q = e^{-\varepsilon_j/kT}$$

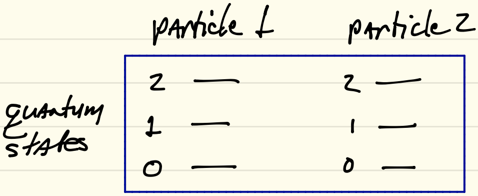
$$\partial p_j/\partial T = \frac{\partial p_j}{\partial \beta}\frac{\partial \beta}{\partial T} = \frac{Q(-\varepsilon_j)e^{-\varepsilon_j\beta} - e^{-\varepsilon_j\beta}(\partial Q/\partial\beta)}{Q^2}\left(-\frac{1}{k_B T^2}\right)$$

$$\Rightarrow \frac{1}{k_B T^2}\left\{\sum_j \varepsilon_j^2 e^{-\varepsilon_j\beta}/Q + \sum_j \varepsilon_j e^{-\varepsilon_j\beta}/Q\,(\partial \ln Q/\partial\beta)\right\}$$

$$= \frac{1}{k_B T^2}\left\{\langle \varepsilon_j^2 \rangle - \langle \varepsilon_j \rangle^2\right\}$$

Seperability / energy factoring

Often our system is composed of many individual elements that are (at least approximately) independent, as in an ideal gas. In that case, can write



distinguishable	
0, 0	$\varepsilon_0 + \varepsilon_0$
0, 1	$\varepsilon_0 + \varepsilon_1$
1, 0	$\varepsilon_1 + \varepsilon_0$
0, 2	$\varepsilon_0 + \varepsilon_2$
2, 0	$\varepsilon_2 + \varepsilon_0$
1, 1	$\varepsilon_1 + \varepsilon_1$
1, 2	$\varepsilon_1 + \varepsilon_2$
2, 1	$\varepsilon_2 + \varepsilon_1$
2, 2	$\varepsilon_2 + \varepsilon_2$

9 possibilies

$$Q = \sum_j e^{-E_j \beta} \qquad E_j = \varepsilon_l^1 + \varepsilon_m^2$$

$$\sum_l \sum_m e^{-(\varepsilon_l^1 + \varepsilon_m^2)\beta} = \sum_l \sum_m e^{-\varepsilon_l^1 \beta} e^{-\varepsilon_m^2 \beta}$$

$$= \left(\sum_l e^{-\varepsilon_l \beta}\right)\left(\sum_m e^{-\varepsilon_m \beta}\right)$$

identical!

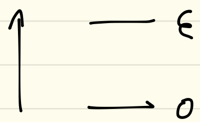
$$= q^2 \qquad q = \sum_i e^{-\varepsilon_i \beta}$$

In general $Q = q^N$ if distinguishable particles

Try it! $q = e^{-\varepsilon_0 \beta} + e^{-\varepsilon_1 \beta} + e^{-\varepsilon_2 \beta}$

$Q = q^2 = e^{-(\varepsilon_0 + \varepsilon_0)\beta} + \cdots$ 9 terms

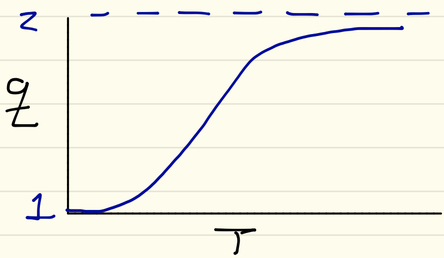
Two-state example returns



$$q = \sum_i e^{-\varepsilon_i \beta}$$
$$= \underline{1 + e^{-\varepsilon\beta}}$$

$\beta \to 0 \quad T \to \infty \quad q \to 2$

$\beta \to \infty \quad T \to 0 \quad q \to 1$

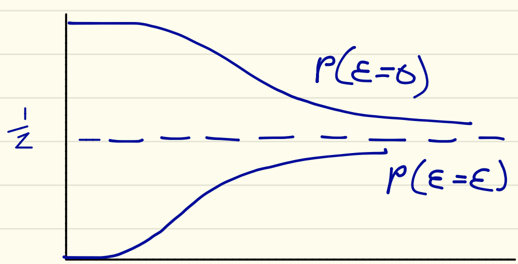


Reflects # of accessible states

$$P(\varepsilon = 0) = \frac{e^{-0\beta}}{q} = \frac{1}{1 + e^{-\varepsilon\beta}}$$

$$P(\varepsilon = \varepsilon) = \quad = \frac{e^{-\varepsilon\beta}}{1 + e^{-\varepsilon\beta}}$$

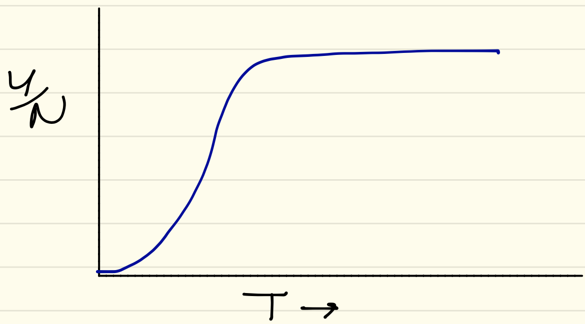
	$\beta \to \infty$	$\beta \to 0$
$P(\varepsilon = 0)$	1	1/2
$P(\varepsilon = \varepsilon)$	0	1/2



$$U/N = -\left(\frac{\partial \ln q}{\partial \beta}\right) = -\frac{1}{q}\frac{\partial q}{\partial \beta}$$

$$= -\frac{1}{q}\left(-\varepsilon e^{-\varepsilon\beta}\right) = \frac{\varepsilon e^{-\varepsilon\beta}}{1+e^{-\varepsilon\beta}}$$

$\beta \to \infty \quad U/N \to 0 \qquad \beta \to 0 \quad U/N \to \varepsilon/2$



$$C_v = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right) = -k_B\beta^2\left(\frac{\partial U}{\partial \beta}\right) = \frac{-\varepsilon^2 e^{\varepsilon\beta}}{(1+e^{\varepsilon\beta})^2}$$

Useful to think about in terms of $\partial T/\partial U$.

Helmholtz energy $\quad A/N = -\ln q/\beta = -\dfrac{\ln(1+e^{-\varepsilon\beta})}{\beta}$

$\beta \to \infty \quad T \to 0 \quad A/N \to 0$

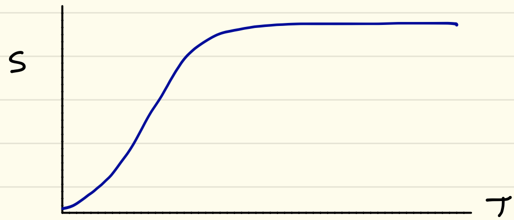
$\beta \to 0 \quad T \to \infty \quad A/N \to -\infty$

Entropy - $S/N = U/NT + k_B \ln q$ (distinguishable)

$$= k_B \left(\frac{\beta\epsilon}{1+e^{\epsilon\beta}} + \ln\left(1+e^{-\epsilon\beta}\right) \right)$$

$\beta \to \infty \quad T \to 0 \quad S/N \to 0$ 3rd Law!

$\beta \to 0 \quad T \to \infty \quad S/N \to k_B \ln 2$ compare $k_B \ln \Omega$



If indistinguishable, more subtle.

For non-bizarre conditions

$$Q = q^N / N!$$

refer to canonical ensemble equation sheet

Other ensembles

UVN $\quad p_j = 1/\Omega(U,V,N)$ μcanonical

TVN $\quad p_j = e^{-U_j\beta}/Q(T,V,N)$ canonical/Helmholtz

TPN $\quad p_j(U_j,V) = e^{-U_j\beta}\, e^{-PV\beta} / \Delta(T,P,N)$ Gibbs isobaric/isothermal

$$G(T,P,N) = -kT\ln(\Delta(T,P,N))$$

$$\Delta(T,P,N) = \int_V Q(T,V,N)\, e^{-PV\beta}\, dV$$

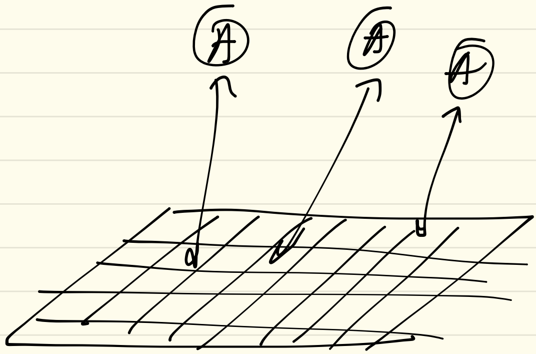
$TV\mu$ $\quad p_j(U_j,N) = e^{-U_j\beta}\, e^{\mu N\beta} / \Xi(T,V,\mu)$ grand canonical

$$\Psi(T,V,\mu) = -kT\ln\Xi$$

$$\Xi = \sum_N Q(T,V,N)\, e^{\mu N\beta}$$

Langmuir adsorption

How many adsorbates at a given T + μ?



A sites
N adsorbates

Some energy ε associated w/ each adsorption

~~$q_{site} = 1 + e^{-\varepsilon\beta}$~~ $\quad q_{site} = \sum$ internal DOFs of A

$$Q(T,A,N) = q_{site}^N \cdot {}_A C_N$$
$$= q_{site}^N \cdot \frac{A!}{N!\,(A-N)!}$$

$$\Xi(T,A,\mu) = \sum_{N=0}^{A} Q(T,A,N)\, e^{N\mu\beta}$$
$$= \sum_{N=0}^{A} q_{site}^N\, e^{N\mu\beta} \frac{A!}{N!\,(A-N)!}$$
$$= \left(1 + q_{site}\, e^{\mu\beta}\right)^A$$

$$\Psi(T,A,\mu) = -A k_B T \ln\left(1 + q_{site}\, e^{\mu\beta}\right)$$

$$N = -\left(\frac{\partial \Psi}{\partial \mu}\right)_{A,T}$$

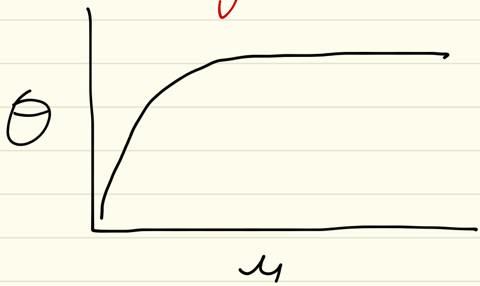
$$= + A \cancel{k_B T} \cdot \frac{1}{1 + q_{site} e^{\mu\beta}} \cdot \cancel{\beta}\, q_{site} e^{\mu\beta}$$

$$\frac{N}{A} = \theta = \frac{q_{site}(T) e^{\mu\beta}}{1 + q_{site}(T) e^{\mu\beta}}$$

Langmuir isotherms

$\mu \to -\infty \quad \theta \to 0$

$\mu \to \infty \quad \theta \to 1$



ideal gas reservoir

$$\mu = \mu^\circ(T) + RT \ln P/P^\circ$$

$$\theta = \frac{q_{site}(T) e^{\mu_0(T)\beta} \cdot P/P_0}{1 + q_{site}(T) e^{\mu_0(T)\beta} \cdot P/P_0}$$

$$\boxed{\theta = \frac{K(T)\, P}{1 + K(T)\, P}} \qquad K(T) = \frac{q_{site}(T)}{e^{-\mu_0\beta}}$$

$$q_{site} = e^{-\mu_{site}\beta} \qquad K(T) = e^{-(\mu_{site} - \mu_0)\beta}$$

indistinguishable particles

fermions - 1/2 integer spin
MUST have unique quantum states

ex electrons $\uparrow\downarrow$ is one possibility, not 2

bosons - integer spin
may have same quantum state, but still indistinguishable

Both cases more subtle to treat exactly
Sums above don't factor nicely

(see Fermi and Bose-Einstein statistics)

In the limit that the number of energy states available to a particle are much much greater than the number of particles, then the vast majority of terms are the $\varepsilon_0 + \varepsilon_1$, $\varepsilon_1 + \varepsilon_2$, ..., type, and we just have to make sure we don't count both $\varepsilon_0 + \varepsilon_1$ and $\varepsilon_1 + \varepsilon_0$

For a given set of unique QN, $N!$ ways of assigning them to N particles

$$q = \sum_i e^{-\varepsilon_i \beta} \qquad Q \approx q^N / N!$$

if indistinguishable and unique states dominate.

	particle 1	particle 2
quantum states	2 —	2 —
	1 —	1 —
	0 —	0 —

distinguishable		fermions	bosons
0, 0	$\varepsilon_0+\varepsilon_0$		$\varepsilon_0+\varepsilon_0$
0, 1	$\varepsilon_0+\varepsilon_1$	$\varepsilon_0+\varepsilon_1$	$\varepsilon_0+\varepsilon_1$
1, 0	$\varepsilon_1+\varepsilon_0$		
0, 2	$\varepsilon_0+\varepsilon_2$	$\varepsilon_0+\varepsilon_2$	$\varepsilon_0+\varepsilon_2$
2, 0	$\varepsilon_2+\varepsilon_0$		
1, 1	$\varepsilon_1+\varepsilon_1$	$\varepsilon_1+\varepsilon_2$	$\varepsilon_1+\varepsilon_1$
1, 2	$\varepsilon_1+\varepsilon_2$		$\varepsilon_1+\varepsilon_2$
2, 1	$\varepsilon_2+\varepsilon_1$		
2, 2	$\varepsilon_2+\varepsilon_2$		$\varepsilon_2+\varepsilon_2$
9 possibilies		3 possibilites	6 possibilities

$$Q=\sum_j e^{-E_j\beta} \qquad E_j=\varepsilon_l^1+\varepsilon_m^2$$

$$\sum_l\sum_m e^{-(\varepsilon_l^1+\varepsilon_m^2)\beta} = \sum_l\sum_m e^{-\varepsilon_l^1\beta}e^{-\varepsilon_m^2\beta}$$

$$= \left(\sum_l e^{-\varepsilon_l\beta}\right)\left(\sum_m e^{-\varepsilon_m\beta}\right)$$

identical !

$$= q^2 \qquad q=\sum_i e^{-\varepsilon_i\beta}$$

In general $Q=q^N$ if distinguishable particles

Try it! $q=e^{-\varepsilon_0\beta}+e^{-\varepsilon_1\beta}+e^{-\varepsilon_2\beta}$

$Q=q^2=e^{-(\varepsilon_0+\varepsilon_0)\beta}+\cdots$ 9 terms