Mon 20 Mar 24 99 08

Recap

Therm. cycles, efficiency, Carnot & Otto

Grand-canonical partition function

$$Z_g = \sum_i e^{-\beta(E_i - \mu N_i)} \qquad p_i = \frac{1}{Z_g} e^{-\beta(E_i - \mu N_i)}$$

Derived quantities from Z_g

Entropy $S(T,\mu) = -\sum_i p_i \log p_i$

Internal energy $\langle E\rangle(T,\mu) = \sum_i p_i E_i = \frac{1}{Z_g}\sum_i E_i\, e^{-\beta(E_i-\mu N_i)}$

Particle number $\langle N\rangle(T,\mu) = \sum_i p_i N_i = \frac{1}{Z_g}\sum_i N_i\, e^{-\beta(E_i-\mu N_i)}$

All related to derivatives of <u>grand-canonical potential</u> $\Phi(T,\mu)$

$$\Phi = -T\log Z_g \qquad Z_g = e^{-\Phi/T}$$

$$p_i = \frac{1}{Z_g} e^{-\beta(E_i-\mu N_i)} = e^{(\Phi - E_i + \mu N_i)/T}$$

(in therm. equil) "Landau free energy"

$$\frac{\partial}{\partial\mu}\Phi = \frac{-1}{\beta}\frac{\partial}{\partial\mu}\log Z_g = \frac{-1}{\beta Z_g}\sum_i \frac{\partial}{\partial\mu} e^{-\beta(E_i-\mu N_i)} = \frac{-1}{Z_g}\sum_i N_i\, e^{-\beta(E_i-\mu N_i)}$$

$$= -\sum_i p_i N_i = -\langle N\rangle$$

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$$\frac{\partial}{\partial T}\Phi = -\log Z_g - T\underbrace{\frac{\partial}{\partial T}\log Z_g}_{} \qquad \frac{\partial}{\partial T} = -\beta^2\frac{\partial}{\partial\beta}$$

$$\hookrightarrow \frac{-\beta^2}{Z_g}\sum_i \frac{\partial}{\partial\beta} e^{-\beta(E_i-\mu N_i)}$$

$$= +\beta^2\sum_i p_i(E_i - \mu N_i)$$

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$$\frac{\partial}{\partial T}\Phi = \frac{\Phi}{T} - T\left(\frac{\langle E\rangle - \mu\langle N\rangle}{T^2}\right) = \frac{\Phi - \langle E\rangle + \mu\langle N\rangle}{T}$$

$$S = -\sum_i p_i \log p_i = -\sum_i p_i\left(-\log Z_g - \beta E_i + \beta\mu N_i\right)$$

$$= \log Z_g + \beta\langle E\rangle - \beta\mu\langle N\rangle$$

$$= \frac{-\Phi + \langle E\rangle - \mu\langle N\rangle}{T} = -\frac{\partial}{\partial T}\Phi$$

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$$\langle N\rangle = \frac{-\partial}{\partial\mu}\Phi \qquad S = \frac{-\partial}{\partial T}\Phi$$

$$\langle E\rangle = -T^2\frac{\partial}{\partial T}\left(\frac{\Phi}{T}\right) - \mu\langle N\rangle$$

$$\Phi = -TS + \langle E\rangle - \mu\langle N\rangle$$

Generalized First law

Recall canonical $dE = TdS - PdV = Q + W$

Now have possible dN as well

Expand $dS = \left.\frac{\partial S}{\partial E}\right|_{V,N} dE + \left.\frac{\partial S}{\partial V}\right|_{E,N} dV + \left.\frac{\partial S}{\partial N}\right|_{V,E} dN$

$$= \frac{1}{T}dE + \left.\frac{\partial S}{\partial V}\right|_{E,N} dV + \frac{-\mu}{T}dN$$

Fixed $N \to$ canonical

Fixed $E \to$ $dE = TdS - PdV = 0$

$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

Generalized therm. identity

$$dE = TdS - PdV + \underbrace{\mu dN}_{\text{"chemical work"}}$$

[lots of info]

Fix N and V: $\quad dE = T\,dS \rightarrow \frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{N,V}$ ✓

Fix N and S: $\quad dE = -P\,dV \rightarrow P = -\left.\frac{\partial E}{\partial V}\right|_{N,S}$ ✓

Fix S and V $\quad dE = \mu\,dN \rightarrow \mu = \left.\frac{\partial E}{\partial N}\right|_{S,V}$

Recall $\Delta N > 0$ with fixed E naturally increases S

$\rightarrow$ reduce E to fix S $\quad (T>0)$

$\rightarrow \mu < 0$ for natural systems ✓

Quantum statistics

Recall we regulated ideal gases

by allowed only discrete momenta $\rightarrow$ energy levels

Assuming $\hbar \ll L\sqrt{mT}$ $\quad$ sum $\rightarrow$ integral over continuous energies

Now retain discrete energy levels

gives classical (non-quantum) Maxwell-Boltzmann statistics

& will reveal what is needed for true quantum statistics

Label energy levels as ε_ℓ with energy E_ℓ

Can have $E_m = E_n$ for different ε_m and ε_n, $m \neq n$

$\vec{p} = (1,0,0)\frac{\hbar\pi}{L}$ vs. $(0,0,1)\frac{\hbar\pi}{L}$

"Degenerate" energy levels

Label $E_m \leq E_n$ for $m < n$, $\quad E_\ell \geq E_0 \geq 0$

Organize micro-states by N_i

$$Z_g = \sum_i e^{-\beta(E_i - \mu N_i)} = \sum_{\substack{i \\ N_i=0}} e^{-\beta E_i} + \sum_{\substack{j \\ N_j=1}} e^{-\beta(E_j - \mu)} + \sum_{\substack{k \\ N_k=2}} e^{-\beta(E_k - 2\mu)} + \dots$$

$$= Z_0 + e^{\beta\mu} Z_1 + e^{2\beta\mu} Z_2 + \dots$$

$$= \sum_{N=0}^{\infty} (e^{\beta\mu})^N Z_N$$

Z_N: N-particle canonical part. func.

"fugacity" $\zeta = e^{\beta\mu} = e^{\mu/T}$

Recall $Z_N = \frac{1}{N!} Z_1^N$ for ideal systems (non-interacting particles)

$\frac{1}{N!}$: correcting for over-counting <u>indist'able</u> particles

$$Z_g = \sum_{N=0}^{\infty} \frac{1}{N!} (e^{\beta\mu} Z_1)^N = \exp[e^{\beta\mu} Z_1]$$

Z_1 → energy levels

Single particle can occupy each energy level once

$$Z_1 = \sum_{l=0}^{L} e^{-\beta E_l}$$

Gives <u>Maxwell-Boltzmann</u> g.c. part. func.

$$Z_g = \exp\left[e^{\beta\mu} \sum_l e^{-\beta E_l}\right] = \exp\left[\sum_l e^{-\beta(E_l - \mu)}\right] = \prod_l \exp\left[e^{-\beta(E_l - \mu)}\right]$$

Hidden (classical) assumption:

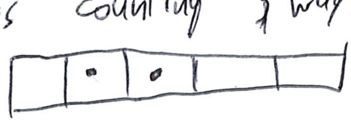
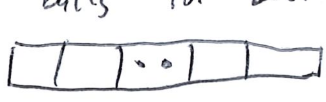
All particles occupy different energy level → $Z_N = \frac{1}{N!} Z_1^N$

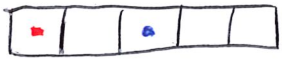
Illustration: Set $N=2$ $L=4$ all with $E_l = 0$

$$Z_1 = \sum_{l=0}^{4} e^{-\beta E_l} = \sum_l 1 = 5$$

Z_N counts micro-states

Same as counting # ways place N balls in $L+1$ boxes

Let $N=2$ particles be dist'able 

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$Z_D(N=2) = 5^2 = 25$

For indist'able $\rightarrow$ $Z_I = \frac{1}{2} 25 = 12.5$ ways of putting balls in boxes
cannot be correct

All 25 micro-states in Z_D

ROBOO	OROBO	BOROO	OBORO	20000
RBOOO	OROOB	BROOO	OBOOR	02000
ROOBO	OORBO	BOORO	OOBRO	00200
ROOOB	OOROB	BOOOR	OOBOR	00020
ORBOO	OOORB	OBROO	OOOBR	00002

$$\frac{1}{N!} = \frac{1}{2} \checkmark$$

No $\frac{1}{N!}$

Classical continuous energies $\rightarrow$ guarantees different energy levels

Let occupation number n_ℓ be # of particles in ε_ℓ
Rather than considering Z_1 for each particle
quantum statistics defines micro-states by summing over n_ℓ for each energy level ε_ℓ
$\rightarrow$ no over-counting

What occupation #s n_ℓ are possible
Two possibilities (in 3d)
1) Bosons can have $n_\ell = 0, 1, 2, \ldots$ (Higgs, photons pion, He^4)

2) Fermions can have $n_\ell = 0$ or $n_\ell = 1$ (electrons, protons)
"Pauli exclusion principle" $\rightarrow$ chemistry, life
(Feature of quantum physics, not repulsion)

Return to $N=2$ and $L=4$

How many micro-states for bosons?

11000	01010	20000
10100	01001	02000
10010	00101	00200
10001	00110	00020
01100	00011	00002

$\underbrace{\qquad\qquad}_{10\ w_i}$ for fermions

15 w_i for bosons

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both different from non-sensical 12.5

Different allowed micro-states
→ different quantum statistics

For bosons (Bose-Einstein statistics)

Sum over energy levels ε_ℓ, then over n_ℓ for each ε_ℓ

Single energy level ε_0 with energy E_0, occ. # n_0

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$$\boxed{\text{Micro-state energy } E_i = N_i E_0 = n_0 E_0}$$

g-c part. func.

$$Z_g = \sum_{n_0=0}^{\infty} e^{-\beta(n_0 E_0 - \mu n_0)} = \sum_{n_0}\left(e^{-\beta(E_0-\mu)}\right)^{n_0}$$

$$= \frac{1}{1-e^{-\beta(E_0-\mu)}}$$

Geometric series only converges for $e^{-\beta(E_0-\mu)} < 1$

$\beta > 0 \rightarrow E_0 - \mu > 0 \rightarrow E_{0,\ell} > \mu$

$(E_\ell \geq 0)$ $(\mu < 0)$ ✓

Generalize to ε_ℓ $\ell = 0, 1, \dots L$

$\{n_\ell\}$ define micro-state w_i

Non-interacting particles: $E_i = \sum_\ell n_\ell \varepsilon_\ell$ $N_i = \sum_\ell n_\ell$

$$Z_g = \sum_{n_0} \sum_{n_1} \cdots \sum_{n_L} \exp\left[-\beta \sum_{\ell} (E_\ell - \mu) n_\ell\right]$$

Factorizes

$$= \left(\sum_{n_0} e^{-\beta(E_0-\mu)n_0}\right)\left(\sum_{n_1} e^{-\beta(E_1-\mu)n_1}\right) \cdots \left(\sum_{n_L} e^{-\beta(E_L-\mu)n_L}\right)$$

$$= \prod_{\ell} \frac{1}{1-e^{-\beta(E_\ell-\mu)}}$$