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Abbreviation:

$$Z(T,\mu) = \sum_{i=1}^{\mathcal{N}} e^{-\beta E_i + \beta \mu' N_i}$$

grand canonical "partition function"

$$S = k_B \ln Z(T,\mu) + \frac{U}{T} - \frac{\mu' N}{T}$$

$$\Rightarrow -k_B T \ln Z(T,\mu) = U - TS - \mu' N = \Omega \quad \text{"grand potential"}$$

connection to canonical partition function:

canonical N-particle partition function

$$Z_N(T) = \sum_{i \text{ with } N_i = N} e^{-\beta E_i}$$

$$Z(T,\mu) = \sum_{N=0}^{\infty} \sum_{i \text{ with } N_i=N} e^{-\beta E_i + \beta\mu' N_i} = \sum_{N=0}^{\infty} Z_N(T)\, e^{\beta\mu' N}$$

$$= \sum_{N=0}^{\infty} Z_N(T) \left(e^{\beta\mu'}\right)^N$$

$e^{\beta\mu'}$: fugacity

V.4.2 General framework (continuous system)

Setup:

For each N $\vec{x}^N = (\vec{q}_1, -, \vec{q}_N, \vec{p}_1, -, \vec{p}_N)$

system described by probability density

$\rho(N, \vec{x}^N)$

$\rho(N, \vec{x}^N) d\vec{x}^N$ = probability to find system with N particles and in phase space volume $(\vec{x}^N, \vec{x}^N + d\vec{x}^N]$

energy $H(N, \vec{x}^N)$ of each phase space point

correspondence (no derivation given → analogous to microcanonical & canonical)

$i \to (N, \vec{x}^N)$ $\qquad p_i \to \rho(N, \vec{x}^N)$

$$\sum_i \to \sum_{N=0}^{\infty} \int \frac{d\vec{x}^N}{C_N}$$

$$\Rightarrow \rho(N, \vec{x}^N) = \frac{e^{-\beta H(N,\vec{x}^N) + \beta\mu' N}}{C_N \sum_{\tilde{N}=0}^{\infty} \int \frac{d\vec{x}^{\tilde{N}}}{C_{\tilde{N}}} e^{-\beta H(\tilde{N}, \vec{x}^{\tilde{N}}) + \beta\mu' \tilde{N}}}$$

$$Z(\mu, T) = \sum_{N=0}^{\infty} \int \frac{d\vec{x}^N}{C_N} e^{-\beta H(N, \vec{x}^N) + \beta\mu' N}$$

$$\Omega = -k_B T \ln Z(\mu, T)$$

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V.4.3 Example: pressure of a photon gas (black body radiation)

cubic box of volume $V = L^3$
contains photons
photons massless $\rightarrow \mu' = 0$

possible photon modes = possible standing waves in the box

$$\omega^2_{(l_x, l_y, l_z)} = c^2\left[\left(\frac{l_x \pi}{L}\right)^2 + \left(\frac{l_y \pi}{L}\right)^2 + \left(\frac{l_z \pi}{L}\right)^2\right]$$

$$l_x, l_y, l_z = 1, 2, \ldots$$

state of the system:

$\{n_{(l_x, l_y, l_z, i)}\}$ numbers of photons in mode (l_x, l_y, l_z, i)

$i = 1, 2$ (two polarizations)

total number of photons in state $\{n_{(l_x, l_y, l_z, i)}\}$

$$N_{\{n_{(l_x, l_y, l_z, i)}\}} = \sum_{l_x l_y l_z i} n_{(l_x, l_y, l_z, i)}$$

total energy of state $\{n_{(l_x, l_y, l_z, i)}\}$

$$E_{\{n_{(l_x, l_y, l_z, i)}\}} = \sum_{l_x l_y l_z i} \hbar \omega_{(l_x, l_y, l_z)} n_{(l_x, l_y, l_z, i)}$$

$$Z(\mu' = 0, T) = \sum_{\{n_{(l_x, l_y, l_z, i)}\}} \exp(-\beta \mathbf{E}_{\{n_{(l_x, l_y, l_z, i)}\}})$$

$$= \sum_{\{n_{(l_x, l_y, l_z, i)}\}} \exp\left\{-\beta\hbar \sum_{l_x l_y l_z i} n_{(l_x, l_y, l_z, i)} \omega_{(l_x, l_y, l_z)}\right]$$

$$= \prod_{l_x l_y l_z i} \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega_{(l_x, l_y, l_z)}}$$

$$= \prod_{l_x, l_y, l_z, i} \frac{1}{1 - e^{-\beta\hbar\omega(l_x, l_y, l_z)}} = \prod_{l_x, l_y, l_z} \left(\frac{1}{1 - e^{-\beta\hbar\omega(l_x, l_y, l_z)}} \right)^2$$

$$\Omega = -k_B T \ln Z(\mu' = 0, T) = 2 k_B T \sum_{(l_x, l_y, l_z)} \ln(1 - e^{-\beta\hbar\omega(l_x, l_y, l_z)})$$

$$= 2 k_B T \int_0^\infty d\omega \, n(\omega) \ln(1 - e^{-\beta\hbar\omega})$$

$n(\omega)$: density of modes at frequency ω

# of modes at frequency below ω:

$$\left| \left\{ (l_x, l_y, l_z) \text{ positive integers} \;\middle|\; l_x^2 + l_y^2 + l_z^2 \leq \frac{L^2\omega^2}{c^2\pi^2} \right\} \right| = \frac{1}{8} \frac{4}{3}\pi \left(\frac{L\omega}{c\pi} \right)^3 = \frac{V}{6c^3\pi^2}\omega^3$$

$$\Rightarrow n(\omega) = \frac{d}{d\omega} \quad '' \quad = \frac{V}{2c^3\pi^2}\omega^2$$

$$\Omega = \frac{V k_B T}{c^3\pi^2} \int_0^\infty d\omega \, \omega^2 \ln(1 - e^{-\beta\hbar\omega}) = \frac{V k_B T}{c^3\pi^2\beta^3\hbar^3} \underbrace{\int_0^\infty dx \, x^2 \ln(1 - e^{-x})}_{= -\frac{\pi^4}{45}}$$

$$= -\frac{k_B^4 T^4 \pi^2}{45 c^3 \hbar^3} V$$

$$\Omega = -PV \Rightarrow P = \frac{k_B^4 \pi^2}{45 c^3 \hbar^3} T^4$$

Stefan - Boltzmann law of black-body radiation

Energy density:

$$\frac{U}{V} = \frac{1}{V} \left(\frac{\partial}{\partial\beta} \frac{\Omega}{k_B T} \right)_{\mu'=0} = \frac{1}{c^3\pi^2} \int_0^\infty d\omega \, \omega^2 \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$= \int_0^\infty d\omega \underbrace{\frac{\hbar}{c^3\pi^2} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}}$$

energy density of blackbody radiation at frequency ω

$\rightarrow$ Planck radiation formula

IV.4.3 Second reading assignment

1) Why do photons ~~with~~ mass 0 have chemical potential zero? → $E = mc^2$ ⇒ creation or annihilation of photons does not cost anything

2) ~~How~~ How many photon modes are there?

2 $\vec{E} \perp \vec{k}$ in an electromagnetic wave,

two independent polarizations of light

3) $\Omega = XY$ general? Yes, see last quarter,

$$U = TS + XY + \sum \mu_i N_i$$

$$\Omega = U - TS - \sum \mu_i N_i = XY$$

4) Conversion from sum to integral, factor of 2, density of states

any parameter α, each state has α_i

$\nu(\alpha) = \#$ states with $\alpha_i \leq \alpha$

$\frac{d\nu(\alpha)}{d\alpha} =$ ~~density~~ states with $\alpha_i = \alpha$

$$\Rightarrow \sum_i \ldots = \int \frac{d\nu(\alpha)}{d\alpha} \ldots \, d\alpha$$

factor 2 in example comes from 2 photon modes

$\Rightarrow \nu(\alpha) = 2\,\nu'(\alpha)$

number of quantum numbers below freq. ω

V.5 Summary

concepts:

canonical ensemble
partition function
Einstein solid
Debeye solid
models for magnetic systems
Ising model
grand canonical ensemble

facts:

p_i and $\rho(\vec{x}^N)$ in canonical ensemble
$F = -k_B T \ln Z(T)$
$U = -\left(\frac{\partial \ln Z(T)}{\partial \beta}\right)$
heat capacity of a solid
phase diagram of Ising model
p_i and $\rho(N, \vec{x}^N)$ in grand canonical ensemble
$\Omega = -k_B T \ln Z(\mu', T)$

tools:

Lagrange multipliers
functional derivatives
~~tran~~sfer matrix
mean-field approximation