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Consider matrix $\begin{pmatrix} a & b \\ b & d \end{pmatrix}$:

$$\left|\begin{pmatrix} a-\lambda & b \\ b & d-\lambda \end{pmatrix}\right| = 0$$

$$(a-\lambda)(d-\lambda) - b^2 = 0$$
$$\lambda^2 - (a+d)\lambda + (ad - b^2) = 0$$

$$\lambda_\pm = \frac{1}{2}\left[(a+d) \pm \sqrt{(a+d)^2 - 4(ad-b^2)}\right] =$$

$$= \frac{1}{2}\left[(a+d) \pm \sqrt{(a-d)^2 + 4b^2}\right]$$

For $\lambda_+ > 0$ need $(a+d) > 0$

For $\lambda_- > 0$ need $(a+d)^2 > (a-d)^2 + 4b^2$

$$\Longrightarrow ad > b^2$$

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Thus, stability conditions

$$\frac{\partial^2 E_1}{\partial S_1^2} > 0 \quad ; \quad \frac{\partial^2 E_1}{\partial V_1^2} > 0$$

$$\frac{\partial^2 E_1}{\partial S_1^2}\frac{\partial^2 E_1}{\partial V_1^2} - \left(\frac{\partial^2 E_1}{\partial S_1 \partial V_1}\right)^2 > 0$$

$$\left(\frac{\partial^2 E_1}{\partial S_1^2}\right)_V = \left(\frac{\partial T_1}{\partial S_1}\right)_V = \frac{(\partial T_1/\partial E_1)_V}{(\partial S_1/\partial E_1)_V} = \frac{T_1}{C_V} > 0$$

For $T_1 > 0 \Rightarrow \boxed{C_V > 0}$

$$\left(\frac{\partial^2 E_1}{\partial V_1^2}\right)_S = -\left(\frac{\partial P_1}{\partial V_1}\right)_S = \frac{1}{V K_S} > 0$$

where $K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ ← adiabatic compressibility

$$\Longrightarrow \boxed{K_S > 0}$$

Last condition:

$$ad > b^2 \Rightarrow \frac{T}{V K_S C_V} > \left(\frac{\partial T}{\partial V}\right)_S^2$$

Quantum Statistics

Consequences of QM approach:

(1) Energy levels are discrete

(2) Pauli exclusion principle:
fermions vs bosons

(3) particles are indistinguishable
$\Rightarrow$ combinatorial factors differ from $N!$

* From E-discreteness:

$$Z_e = \sum_i g_i e^{-\beta E_i}$$ for canonical and grandcanonical ensembles

where i – over all E-levels

* Combinatorial factors:
for BE or FD statistics from Schrodinger eq., FD
or additional symmetrization (BE)

Blackbody Radiation

* gas of photons (spinless)
* total number of photons is not conserved

$\Rightarrow n_i$ can be anything!

$$E = \sum_i n_i \epsilon_i \quad \text{where} \quad \epsilon_i = \hbar\omega$$

$$\boxed{\ln Z = -\sum_i \ln(1 - e^{-\beta\epsilon_i})}$$

(ignoring polarization)

$$Z = \sum_{\{n_i\}} e^{-\beta \sum_i n_i \epsilon_i} = \prod_i \left(\sum_{n=0}^{\infty} e^{-\beta n_i \epsilon_i} \right) \overset{\text{sum of geometrical progres}}{=}$$

$$= \prod_i \frac{1}{1 - e^{-\beta\epsilon_i}} = e^{-\beta A}$$

$$\Rightarrow \boxed{\beta A = \sum_i \ln\left(1 - e^{-\beta\epsilon_i}\right)}$$

Enumeration of states:

$$\begin{cases} \text{momentum} & \vec{p} = \dfrac{2\pi\hbar}{L}\vec{n} \\ \text{polarization} & \pm \text{ for each } \vec{k} \\ \text{energy} & \epsilon_p = p^2/2m \end{cases}$$

Consider radiation in a box of size L:

wave function $e^{-i\vec{k}\cdot\vec{x}}$

$$k_a = \frac{2\pi \vec{n}_a}{L} \quad \text{where } \vec{n}_a = 0, \pm 1, \pm 2, \ldots$$

De Broglie: $$p_a = \hbar k_a = \frac{2\pi\hbar n_a}{L}$$

Photon dispersion:

$$\epsilon = c\sqrt{p_1^2 + p_2^2 + p_3^2} \quad \text{where } 1,2,3 \to x,y,z$$

So, $\displaystyle\sum_i = 2 \sum_{n_1} \sum_{n_2} \sum_{n_3}$

In the limit $L \to \infty$ where $L^3 = V$

$\Rightarrow \vec{p} \to$ continuum and

$$\sum_{n_1} \to \left(\frac{L}{2\pi\hbar}\right) \int dp_1$$

So, $$\boxed{\beta A = \frac{2V}{h^3} \int d^3p \, \ln\left(1 - e^{-\beta c|\vec{p}|}\right)}$$

$2 \to$ from polarization

Average energy:

$$\langle E \rangle = \frac{\partial}{\partial \beta} \overbrace{\sum_i \ln\left(1 - e^{-\beta \epsilon_i}\right)}^{Z} =$$

$$= \sum_i (-1) \frac{(-\epsilon_i) e^{-\beta \epsilon_i}}{1 - e^{-\beta \epsilon_i}} = \sum_i \frac{\epsilon_i}{e^{\beta \epsilon_i} - 1} = \sum_i \hbar\omega \langle n_i \rangle$$

$$\Rightarrow \boxed{\langle n_i \rangle = \frac{1}{e^{\beta \epsilon_i} - 1}}$$

+ factor 2 for ± polarization

$\Rightarrow$ the average occupation nu. for photons of momentum $\vec{k}$, regardless of polarization

In $L \to \infty$ limit, need to get nu. of states in the range

$$(\vec{P}, \vec{P} + d\vec{P})$$

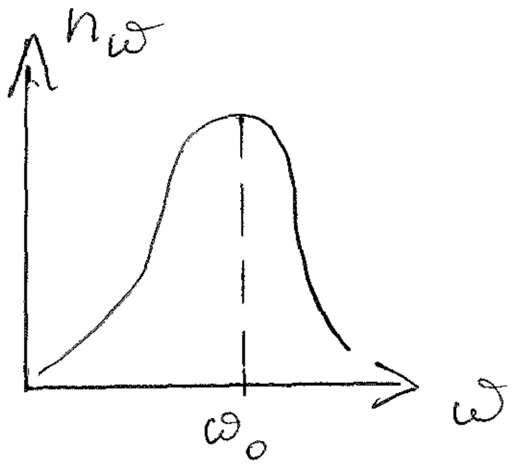
$$\langle n_{\vec{P}} \rangle d\vec{P} = \frac{1}{e^{\beta c|P|} - 1} \, dp_x \, dp_y \, dp_z$$

To find occupation number of photons of some energy range

$$\epsilon = \hbar\omega = |P| c$$

$$\boxed{n_\epsilon = 4\pi |P|^2 dP \, \frac{1}{e^{\beta\hbar\omega} - 1}}$$

i.e. $$\boxed{n_\omega \sim \frac{\omega^2 d\omega}{e^{\beta\hbar\omega} - 1}}$$



$$\omega_0 \sim \frac{1}{\beta\hbar} \Rightarrow \lambda_{max} T = \text{const.}$$

Free Fermions

Most fermions have a conserved particle number e.g. baryon nu.
lepton nu.

For non-relativistic fermions this nu. is equal to nu. of particles

Thus, the occupation nu. obey

$$\sum_{i=1}^{s} n_i = N$$

Using grand canonical ensemble,

$$Z_G = \sum_{N=0}^{\infty} \Bigg(\sum_{\substack{\{n_i = 0,1\} \\ \sum n_i = N}} e^{-\beta \sum n_i \epsilon_i + \beta \mu \sum n_i} \Bigg)$$

However, since we sum over all N, the restriction on the n_i sum is not present $\Rightarrow$ free sum over all $\{n_i\}$

$$Z_G = \sum_{\{n_i = 0,1\}} e^{-\beta \sum n_i (\epsilon_i - \mu)} = \prod_{i=2}^{s} \Bigg(\sum_{n=0}^{1} e^{-\beta n (\epsilon_i - \mu)} \Bigg)$$

$$Z_G = \prod_{i=1}^{s} \left(1 + e^{-\beta(\epsilon_i - \mu)} \right)$$

This leads to

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i-\mu)}+1}$$

The grand canonical ensemble will describe our system for large $\langle N \rangle$:

$$\langle N \rangle = \sum_i \frac{1}{e^{\beta(\epsilon_i-\mu)}+1} = N$$

This determines $\mu(N,\beta)$.

For $\beta \to \infty$, $\langle N \rangle = 0$ unless $\epsilon_i < \mu(N,\infty)$

Call $\underbrace{\mu(T=0)}_{\beta\to\infty} \equiv \epsilon_F$

For finite β

$$n(\epsilon) = \begin{cases} 0 & \epsilon > \mu(N,\infty) \equiv \epsilon_F \\ 1 & \epsilon < \epsilon_F \end{cases}$$