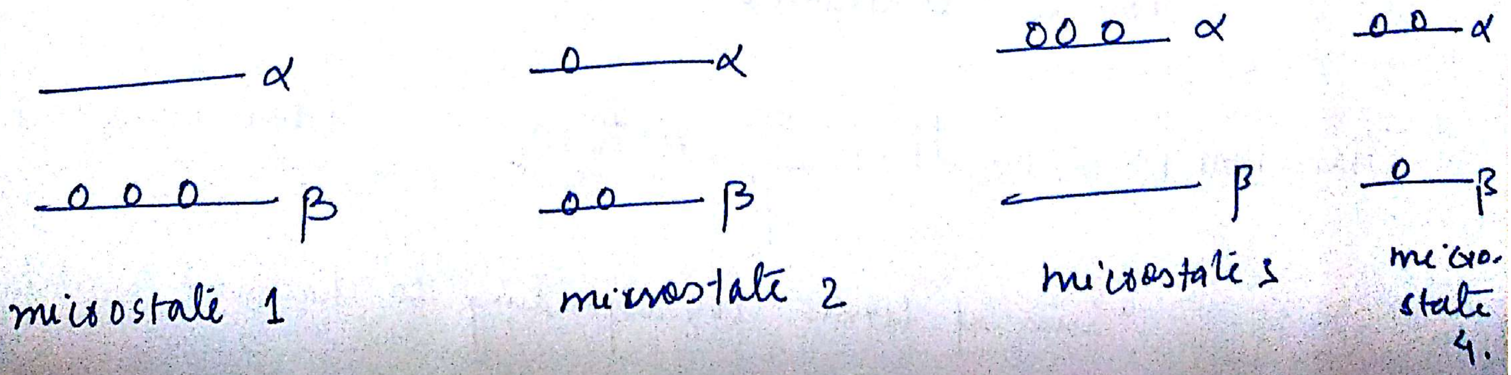
Chapter 3 Quantum Statistics.

- Quantum system of N- particles.
- This is specified by a wavefunction : $\psi_\nu(r_1, r_2, \ldots r_N)$
- ψ_ν is the ν^{th} eigen solution for an N- particle system.
- If particles are non-interacting (ideal) ψ_ν ~~is~~ can be expressed as symmetrized (anti-symmetrized for Fermions) product of single particle wavefunctions, $\phi_1(r), \phi_2(r) \ldots$
- For a particular microstate ν (say), $\psi_\nu(r_1, r_2 \ldots r_N)$ will be a product containing n_1 particles in single particle wavefunction ϕ_1, n_2 particles in ϕ_2. and so on.
- Hence n_i is called the occupation no. of single particle state i



Scanned by CamScanner

$\nu = (n_1, n_2, \ldots n_j, \ldots) \equiv \nu^{th}$ microstate

$N = \sum_j n_j$ = total no. of particles in ν^{th} state

ϵ_j be the energy of j^{th} single particle state.

then,

$$E_\nu = \sum_j \epsilon_j n_j \equiv \text{energy in the } \nu^{th} \text{ state.}$$

Note: Particles with half integer spins : $n_i = 0, 1$ (Fermions)

" " integer spins : $n_i = 0, 1, 2, \ldots$ (Bosons)

*. Fermions & Bosons follow Fermi-Dirac & Bose-Einstein statistics respectively.

*. Photon gas: This is a Boson system

Eg. Electromagnetic field in thermal equilibrium with a container.

Hamiltonian : $\mathcal{H} = \sum_j n_j \hbar w_j$ (Ignoring zero pt. energy)

"Sum of terms corresponding to harmonic oscillator"

$n_i \hbar \omega_i$ is the energy of i^{th} oscillator. n_i is the excitation and ω_i corresponds to frequency.

We can interpret n_i as the no. of photons in i^{th} single particle state of energy $\hbar\omega_i$ -

Photons obey Bose-Einstein statistics.

Canonical partition function:

$$e^{-\beta F} = Z = \sum_{\nu} e^{-\beta H_\nu} = \sum_{\{n_i\}} e^{-\beta \sum_j n_j \hbar \omega_j}$$

$$= \sum_{\{n_i\}} e^{-\beta \sum_j n_j \epsilon_j} \qquad \epsilon_j = \hbar \omega_j$$

$$= \prod_j \left[\sum_{n_j=0}^{\infty} e^{-\beta n_j \epsilon_j} \right]$$

$$= \prod_j \left[\frac{1}{1 - e^{-\beta \epsilon_j}} \right]$$

We can construct all thermodynamic properties from this bridge.

For eg. average occupation no. $\langle n_j \rangle$

$$\langle n_j \rangle = \frac{\sum_{\nu} n_j \, e^{-\beta \sum_i n_i \epsilon_i}}{Z} = \frac{\frac{\partial}{\partial(-\beta\epsilon_j)} Z}{Z} = \frac{\partial}{\partial(-\beta\epsilon_j)} \ln Z$$

$$\therefore \quad \langle n_j \rangle = \frac{\partial}{\partial(-\beta\epsilon_j)} \sum_k -\ln\left(1 - e^{-\beta\epsilon_k}\right)$$

$$= \cancel{\frac{1}{1/\beta}} \quad \frac{1}{1 - e^{-\beta\epsilon_j}} \cdot e^{-\beta\epsilon_j}$$

$$\langle n_j \rangle = \frac{1}{e^{\beta\epsilon_j} - 1}$$

This is Planck distribution

Ex. For a photon gas, derive a formula for the correlation function $\langle \delta n_i \cdot \delta n_j \rangle$ where $\delta n_i = n_i - \langle n_i \rangle$

Ex. Using the formula for $\langle n_i \rangle$, show that the energy density of a photon gas is σT^4, where σ is a constant.

Scanned by CamScanner

Vibrations of a solid: Phonon gas at low T

quantum of vibrations.

At low T, atoms are close to equilibrium positions.

This allows us to expand U in powers of displacement:

$$U = U_0 + \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\alpha,\beta=\{x,y,z\}} d\vec{r}_{i\alpha}\, d\vec{r}_{j\beta} \frac{\partial^2 U}{\partial \vec{r}_{i\alpha}\, \partial \vec{r}_{j\beta}} + O(|d\vec{r}|^3)$$

Now the 1st derivative of U is zero as we are close to equilibrium. This is a Harmonic approximation.

The second derivative $\frac{\partial^2 U}{\partial \vec{r}_{i\alpha} \partial \vec{r}_{j\beta}} = K_{i\alpha j\beta}$ is the spring constant

$K_{i\alpha j\beta}$ is also called the Hessian matrix. Being symmetric in nature $K_{i\alpha j\beta}$ is readily diagonalized yielding dN eigen (normal) modes. Note: $K_{i\alpha j\beta}$ has a size $dN \times dN$

Thus energy of a low T solid can be written as sum of dN harmonic oscillators.

$\therefore$ Hamiltonian $\mathcal{H} = \sum_{\alpha} (n_\alpha + 1/2)\hbar\omega_\alpha$

$\therefore$ Canonical partition f^n: $Z(N,V,T) = \sum_{\{n_i\}=0}^{\infty} e^{-\beta \sum_{\alpha} (n_\alpha + 1/2)\hbar\omega_\alpha}$

i.e $$Z(N,V,T) = \sum_{n_1, n_2, \ldots = 0}^{\infty} e^{-\beta(n_1+1/2)\hbar\omega_1} \cdot e^{-\beta(n_2+1/2)\hbar\omega_2} \cdots$$

$$= \prod_{j=1}^{dN} \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega_j}$$

$$= \prod_{j=1}^{dN} \left(\frac{1}{1 - e^{-\beta\hbar\omega_j}} \cdot e^{-\beta\hbar\omega_j/2} \right)$$

$$\therefore \ln Z = -\sum_{j=1}^{dN} \ln \left[\exp(\beta\hbar\omega_j/2) - \exp(-\beta\hbar\omega_j/2) \right]$$

the sum over phonon states can be partitioned by.. using

$g(\omega)\,d\omega$ = No. of phonon states in the frequency interval $[\omega, \omega + d\omega]$

$$\therefore -\ln Z = \int_0^{\infty} d\omega \, g(\omega) \ln \left[\exp(\beta\hbar\omega/2) - \exp(-\beta\hbar\omega/2) \right]$$

Note 'ω' has no subscript now!

Ideal gas of real particles:

Bosons: Consider a system of N non-interacting Bosons.

The canonical partition function is

$$Z(N,V,T) = \sum_{\nu} e^{-\beta H_\nu}$$

For a fixed no. of particles, the canonical partition function is a constrained sum

$$Z(N,V,T) = \underbrace{\sum_{n_1, n_2, \ldots n_j, \ldots}} \exp\left(-\beta \sum_j n_j \epsilon_j\right)$$

constraint : $\sum_i n_i = N$

Here n_i is the occupation no. of i^{th} energy level.

The above constrained sum is difficult to evaluate.

We resolve this problem by doing this problem in the grand canonical ensemble i.e (μ, V, T)

$$\therefore \mathcal{Z}(\mu,V,T) = \sum_{n_1, n_2, \ldots} \exp\left(-\beta \underbrace{\left(\sum_j n_j \epsilon_j - \mu n_j\right)}_{E_\nu - \mu N_\nu}\right)$$

$$E_\nu = \sum_j n_j \epsilon_j$$

$$N_\nu = \sum_j n_j$$

Now the const N restriction is gone as we are dealing in grand-canonical ensemble with const μ.

$$\therefore \mathcal{Z}(\mu, V, T) = e^{\beta PV} = \prod_j \left\{ \sum_{n_j=0}^{\infty} e^{-\beta(n_j \epsilon_j - \mu n_j)} \right\}$$

$$= \prod_j \left\{ \frac{1}{1-e^{\beta(\mu-\epsilon_j)}} \right\}$$

$$\Rightarrow \beta PV = \ln \mathcal{Z} = \sum_j -\ln\left(1-e^{\beta(\mu-\epsilon_j)}\right)$$

the average occupation no. is then,

$$\langle n_j \rangle = \frac{\frac{\partial \mathcal{Z}}{\partial(-\beta\epsilon_j)}}{\mathcal{Z}} = \frac{\partial}{\partial(-\beta\epsilon_j)} \ln \mathcal{Z}$$

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

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j-\mu)}-1}$$

Hence $\epsilon_j - \mu$ must be always positive to make $\langle n_j \rangle$ +ve for all T.

At $\epsilon_j = \mu$, there is a singularity i.e $\langle n_j \rangle \xrightarrow[\epsilon_j \to \mu]{} \infty$

This is Bose condensation - a mechanism for super-fluidity.

According to the formula just derived, the chemical potential of an ideal photon gas is zero as also the chemical potential of an ideal phonon gas.

Fermions: Consider an ideal gas of Fermions.

Under grand canonical setting, the partition function is

$$Z(\mu, V, T) = \sum_{n_1, n_2, \ldots} \exp\left(-\beta \sum_j n_j(\epsilon_j - \mu)\right)$$

$$= \prod_j \sum_{n_j = 0,1} \exp\left(-\beta n_j (\epsilon_j - \mu)\right)$$

$$= \prod_j \left\{ \exp\left(-\beta(\epsilon_j - \mu)\right) + 1 \right\}$$

$$\therefore \beta PV = \ln Z = \sum_j \ln\left(1 + \exp\left(\beta(\mu - \epsilon_j)\right)\right)$$

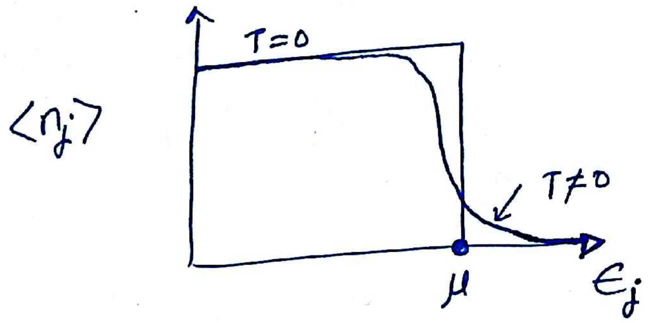
$\therefore$ the average occupation number is given by

$$\langle n_j \rangle = \frac{\partial}{\partial(-\beta \epsilon_j)} \ln \mathcal{Z}$$

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

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

This is the Fermi-distribution or Fermi-Dirac distribution.



In summary,

$$\langle n_j \rangle_{\substack{F.D.\\B.E.}} = \frac{1}{e^{\beta(\epsilon_j - \mu)} \pm 1}$$

Since the occupation n_i can be either 0 or 1,

$\langle n_i n_j \rangle$ = joint probability of that a particle is in state i and a particle is in state j!