CHM 421/621
Statistical Mechanics

Lecture 29 Quantum Statistics of Identical Particles

Applications of Statistical Mechanics

Lecture Plan

Permutation symmetry of identical particles

Quantum statistics of identical particles

Fermi-Dirac Statistics

Bose-Einstein Statistics

Perfect Fermi Gas (Electrons in a metal)

Molecules and Solids

Normal modes of vibrations in a crystal

Debye model: In this model it is assumed that the frequencies in a crystal are continuously distributed in the range $0 < \nu < \nu_m$

The number of oscillators with frequencies between $\nu \text{ to } \nu + d\nu$ is taken to be

$$g(\nu)d\nu = \left(\frac{9N}{\nu_m^3}\right)\nu^2 d\nu$$ (see McQuarrie)

assuming that they all correspond to an *acoustic* branch of lattice vibrations.

$$\bar{\epsilon} = \left(\frac{9N}{\nu_m^3}\right)\int_0^{\nu_m} d\nu\ \nu^2 \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} \implies C_V = \left(\frac{9N}{\nu_m^3}\right)\int_0^{\nu_m} d\nu\ \nu^2 \frac{(\beta h\nu/2)^2}{\sinh(\beta h\nu/2)^2}$$

$$= 3Nk_b D\left(\frac{\Theta_D}{T}\right)$$

Molecules and Solids

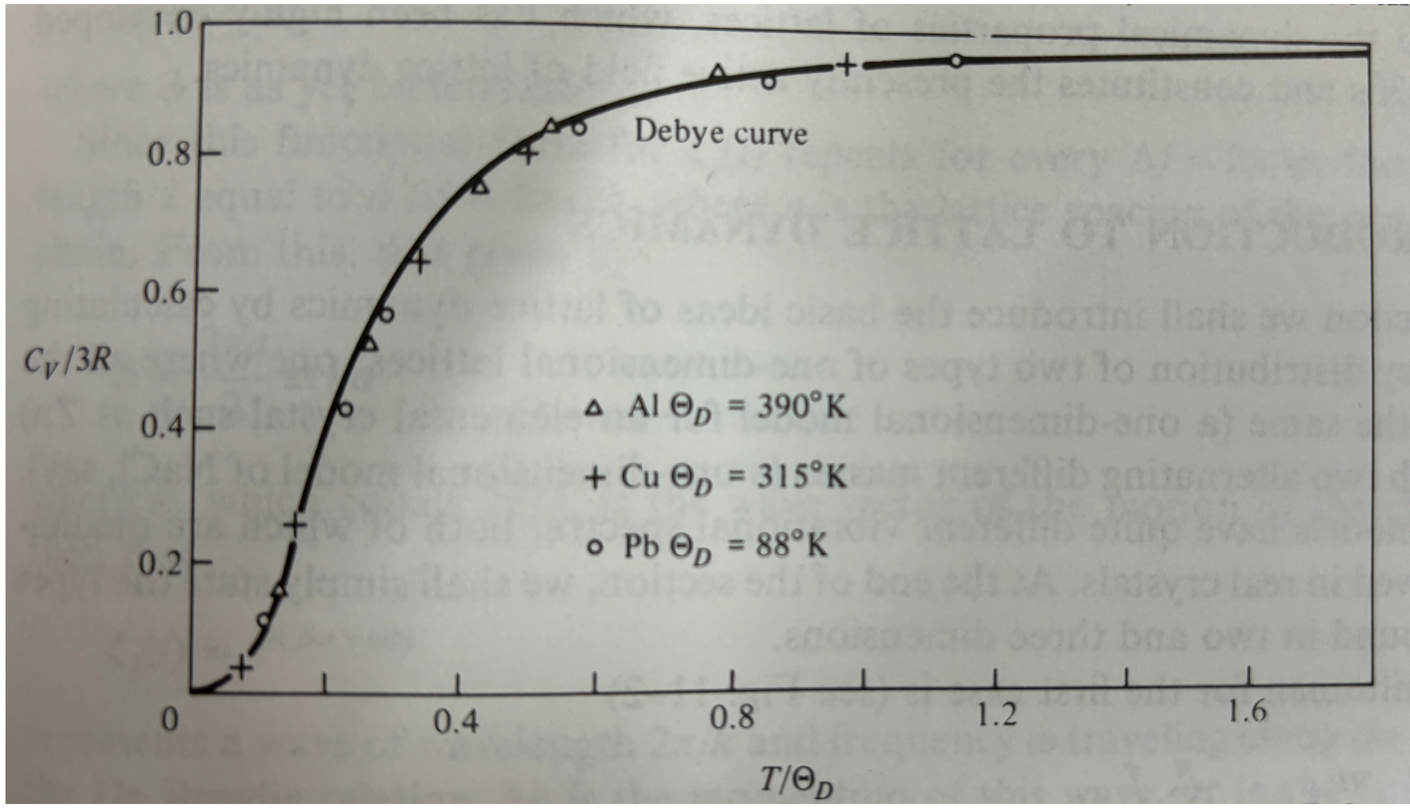
Normal modes of vibrations in a crystal

$$D\left(\frac{T}{\Theta_D}\right) = 3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2}$$

$$D\left(\frac{T}{\Theta_D}\right) \to 1$$ High temperatures

$$\to 3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15}$$

Low temperatures



Hence, at low temperatures we have

$$C_V \propto \left(\frac{T}{\Theta_D}\right)^3$$ Debye T^3 law

Applications

Permutation symmetry of identical particles

Permuting the coordinates of two identical particles in a system does not change any measurable properties of its state

In quantum mechanics this translates to invariance of the probability density of the system to permutation of the particles' coordinates

$$|\Psi(x_1, x_2, ...)|^2 = |\Psi(x_2, x_1, ...)|^2$$

$$x_i = (\vec{r}_i, \sigma_i)$$

Spatial and spin variables

If P_{12} is the permutation operator then we can write

$$P_{12}\Psi(x_1, x_2) \equiv \Psi(x_2, x_1) \quad \text{and} \quad P_{12}^2\Psi(x_1, x_2) \equiv \Psi(x_1, x_2)$$

Since P_{12} is a symmetry in the system we can consider the wavefunction to be an eigenfunction of the operator

$$P_{12}\Psi(x_1, x_2) \equiv \lambda\Psi(x_1, x_2)$$

Applications

Permutation symmetry of identical particles

Using the previous relations we can easily show that $\lambda = \pm 1$ corresponding to symmetric and antisymmetric wave functions, respectively.

Symmetric wave functions -> Bosons (photons, phonons, etc.)

Anti-symmetric wave functions -> Fermions (electrons, protons, etc.)

In the case of independent particles it can be shown that no two fermions can occupy the same (single-particle) state.

However, bosons do not have such a restriction.

Applications

Quantum statistics of identical particles

We have seen that if there are *N* identical non-interacting particles in a system at temperature *T* the canonical partition function is given by

$$Z(N,V,T) = \sum_{n_1,n_2,n_3,\ldots} e^{-\beta \sum_{i=1}^{\infty} n_i \epsilon_i}$$

With the restriction $$N = \sum_{i=1}^{\infty} n_i$$

The restriction makes this sum hard to obtain. So we can try a different strategy.

Applications

Quantum statistics of identical particles

Consider the system to be open and able to exchange particles with a reservoir with chemical potential μ

$$Z_g(V,T,\mu) = \sum_{N=0}^{\infty} \sum_{n_1,n_2,\ldots} \lambda^N e^{-\beta \sum_{i=1}^{\infty} n_i \epsilon_i}$$

$$\lambda = e^{\beta\mu}$$

absoulte activity

Each internal sum is restricted to yield a sum of particles equal to *N*.
However, since *N* itself can be anything, we can rewrite the above as the unrestricted sum

$$Z_g(V,T,\mu) = \sum_{n_1=0}^{n_{max}} \sum_{n_2=0}^{n_{max}} \sum_{n_3=0}^{n_{max}} \cdots \lambda^N e^{-\beta \sum_{i=1}^{\infty} n_i \epsilon_i}$$

$$= \prod_{i=1}^{\infty} \left(\sum_{n_i=0}^{n_{max}} \lambda^{n_i} e^{-\beta n_i \epsilon_i} \right)$$

n_{max} is the maximum number of particles in each level

Applications

Fermi-Dirac Statistics

For fermions n_{max} = *1*. So we get

$$Z_g^{FD}(V,T,\mu) = \prod_{i=1}^{\infty}\left(\sum_{n_i=0}^{1}\lambda^{n_i}e^{-\beta n_i\epsilon_i}\right)$$

$$= \prod_{I=1}^{\infty}(1+\lambda e^{-\beta\epsilon_i})$$

Average number of particles in the system is

$$\overline{N} = \frac{1}{\beta}\frac{\partial \ln Z_g^{FD}}{\partial\mu} = \lambda\frac{\partial \ln Z_g^{FD}}{\partial\lambda}$$

$$= \sum_{i=1}^{\infty}\frac{\lambda e^{-\beta\epsilon_i}}{1+\lambda e^{-\beta\epsilon_i}} \equiv \sum_{i=1}^{\infty}\overline{n}_i$$

Average number of particles in level *i*

$$\overline{n}_i = \frac{\lambda e^{-\beta\epsilon_i}}{1+\lambda e^{-\beta\epsilon_i}}$$
$$= \frac{1}{e^{-\beta(\mu-\epsilon_i)}+1}$$

Applications

Bose-Einstein Statistics

For bosons $n_{max} = \infty$. So we get

$$Z_g^{BE}(V,T,\mu) = \prod_{i=1}^{\infty}\left(\sum_{n_i=0}^{\infty} \lambda^{n_i} e^{-\beta n_i \epsilon_i}\right)$$
$$= \prod_{i=1}^{\infty}(1-\lambda e^{-\beta\epsilon_i})^{-1} \qquad (\lambda e^{-\beta\epsilon_i} < 1)$$

Average number of particles in the system is

$$\overline{N} = \frac{1}{\beta}\frac{\partial \ln Z_g^{BE}}{\partial \mu} = \lambda \frac{\partial \ln Z_g^{BE}}{\partial \lambda}$$

$$= \sum_{i=1}^{\infty} \frac{\lambda e^{-\beta\epsilon_i}}{1-\lambda e^{-\beta\epsilon_i}} \equiv \sum_{i=1}^{\infty} \overline{n}_i$$

Average number of particles in level *i*

$$\overline{n}_i = \frac{\lambda e^{-\beta\epsilon_i}}{1-\lambda e^{-\beta\epsilon_i}}$$
$$= \frac{1}{e^{-\beta(\mu-\epsilon_i)} - 1}$$

Applications

Summary of Quantum Statistics

$$Z_g = \prod_{i=0}^{\infty} \left(1 \pm e^{\beta(\mu - \epsilon_i)}\right)^{\pm 1}$$

$$\overline{n}_i = \frac{1}{e^{-\beta(\mu - \epsilon_i)} \pm 1}$$

+ Fermi-Dirac

- Bose-Einstein

Classical limit: High temperature or low density $\lambda \to 0$

$$\overline{n}_i \approx \lambda e^{-\beta \epsilon_i} \quad \Rightarrow \quad \frac{\overline{n}_i}{N} = \frac{e^{-\beta \epsilon_i}}{z}$$