

QUANTUM STATISTICAL MECHANICS

A summary for non-interacting particles

Density of states

The no. of states available to a particle of spin s in a cell in phase space $dV dV_p$ is

$$d\mathcal{N} = g \frac{dV dV_p}{h^3}$$

where the spin degeneracy $g = 2s + 1$ for massive particles, 2 for massless ones.

For non-interacting particles, we may integrate over 5 of the 6 variables to obtain

$$d\mathcal{N} = \frac{gV4\pi}{h^3} p^2 dp \quad g(p) dp$$

This is often changed by use of the energy-momentum relationship to the form

$$d\mathcal{N} = \frac{d\mathcal{N}}{dE} dE \quad g(E) dE \quad (1)$$

by using the energy-momentum relationship. For nonrelativistic particles, $E = \frac{p^2}{2m}$ and

$$d\mathcal{N} = \frac{gV2\pi}{h^3} (2m)^{3/2} E^{1/2} dE = g(E) dE \quad (2)$$

Distribution of particles

The number of particles is

$$dN = F d\mathcal{N}$$

where $F(E)$ is the average number of particles occupying states of energy E . The occupancy factor F depends on the temperature T and the number density N/V , but it is usually expressed as a function of T and the chemical potential μ . When we express the density of states as in equation (1), we obtain

$$dN = F g(E) dE \quad (3)$$

Thermodynamic properties

From equation (3) many of the thermodynamic properties of the many-particle system may be obtained:

- a) The total number of particles¹

$$N = \int_0^\infty F g(E) dE \quad (4)$$

[Actually, this is usually used to obtain $\mu(N/V, T)$].

¹ but N_0 must be added to this for very low temperature bosons.

b) The total energy of the system

$$U = \int E dN = \int_0^\infty E F g(E) dE \quad (5)$$

c) The heat capacity of the system

$$C_v = \frac{\partial U}{\partial T} \quad (N, V \text{ held constant}) \quad (6)$$

d) The pressure of the system (at $T = 0$)

$$P = -\frac{\partial U}{\partial V} \quad \text{at } T = 0 \quad (7)$$

The occupancy factors

The factor F , defined above as the average number of particles occupying a single state at energy E , can be derived from three different initial assumptions.

a) **For distinguishable particles**

$$F_{MB} = B e^{-E/kT} \quad \text{MAXWELL-BOLTZMANN} \quad (8)$$

b) **For indistinguishable particles with no restrictions on occupancy of states**

$$F_{BE} = \frac{1}{e^{(E-\mu)/kT} - 1} \quad \text{BOSE-EINSTEIN} \quad (9)$$

c) **For indistinguishable particles obeying the Pauli exclusion principle—no two may occupy the same state.** (This requires that $F \leq 1$ always.)

$$F_{FD} = \frac{1}{e^{(E-\mu)/kT} + 1} \quad \text{FERMI-DIRAC} \quad (10)$$

It is easily seen that if $e^{-\mu/kT} \gg 1$ then both F_{FD} and F_{BE} approach F_{MB} . This occurs at high T and low number density N/V . More precisely, for non-relativistic particles, the MB distribution may be used if

$$\frac{N}{V} \ll \frac{1}{\lambda_{th}^3} \quad \text{where the thermal wavelength } \lambda_{th} = \frac{h}{\sqrt{2\pi m k T}}$$

A note on notation

Many books contain variations of the above notation. For example, I defined the distribution so that the integral $\int dN = N =$ total no. of particles. Some books define a distribution so that the total integral equals 1 or even N/V . I have defined the chemical potential μ in equations (9) and (10) as used in most statistical mechanics texts. When dealing with fermions, many authors use the symbol E_F for this quantity and call it the Fermi energy. Nearly all call it the Fermi energy when the temperature $T = 0$. When dealing with bosons it is common to replace μ with a quantity $\alpha = -\mu/kT$. It is common to start with equations (9) and (10) and then show that both reduce to equation (8) with $B = e^{-\alpha}$ whenever $\alpha \gg 1$.