

Quantum Mechanical Ensembles

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If the micro-state energy is not continuous, but discrete, the macro-state properties of material must be treated using discrete energy functions. These macro properties include thermal radiation, sound wave in a crystal lattice (phonons), heat capacity of solids, heat capacity of metals, paramagnetism, and diamagnetism etc. This article reviews ensembles with discrete micro-state energies.

Density of State

In quantum mechanics, particles are not distinguishable; the energy levels however are still distinct. Therefore, to integrate over all the states, the counting variable needs to be converted from dn to dE and dn/dE is called the density of state, $g(E)$. Computing the energy density, one uses the relativistic energy formula that connects the energy E to the wave vector k of the quanta:

$$E = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$$

$$k = \frac{\sqrt{E^2 - m^2 c^4}}{\hbar c}$$

Therefore,

$$dE = \frac{\hbar^2 c^2 k dk}{\sqrt{\hbar^2 k^2 c^2 + m^2 c^4}}$$

$$dn = \frac{4\pi V}{(2\pi)^3} k^2 dk = \frac{4\pi V}{(2\pi)^3} \frac{kE}{\hbar^2 c^2} dE = \frac{VE}{2\pi^2 \hbar^3 c^3} \sqrt{E^2 - m^2 c^4} dE$$

For massless particles, the density of state is:

$$g(E) = \frac{VE^2}{2\pi^2 \hbar^3 c^3}$$

Photons

For a massless photon with a specific frequency $\omega = 2\pi c/\lambda = kc$, its energy is:

$$E = \hbar\omega$$

Photons have two polarization states and the density of state becomes:

$$g(E)dE = \frac{VE^2}{\pi^2 \hbar^3 c^3} dE \Rightarrow g(\omega)d\omega = \frac{V\omega^2}{\pi^2 c^3} d\omega$$

Since the number of photons is not conserved (due to emission), the energy of a state with n photons is $n\hbar\omega$, and one must sum all the n possible states for the partition function (where n is large):

$$Z(\omega) = \sum_{j=0}^n e^{-\beta j \hbar \omega} \underset{n \rightarrow \infty}{=} \frac{1}{1 - e^{-\beta \hbar \omega}}$$

The partition function is a product of $Z(\omega)$ of all ω 's, or $\log Z$ is the sum of $\log Z(\omega)$:

$$\log Z = \int_0^\infty g(\omega) \log Z(\omega) d\omega = \frac{V}{\pi^2 c^3} \int_0^\infty -\omega^2 \log(1 - e^{-\beta \hbar \omega}) d\omega$$

The average energy of photons is:

$$E = -\frac{\partial}{\partial \beta} \log Z = \frac{V \hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta \hbar \omega} - 1} d\omega$$

The photonic energy between ω and $\omega + d\omega$ is

$$\frac{V \hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta \hbar \omega} - 1} d\omega$$

This is called the Planck distribution. The energy density is the integral over the frequency range:

$$\frac{E}{V} = \frac{\beta^4}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

The integration in above equation is $\pi^4/15$. Therefore,

$$\frac{E}{V} = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} T^4$$

and the energy flux (per unit area in a given time) is known as the Stefan-Boltzmann equation:

$$\frac{V}{St} = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} T^4$$

Phonons

A solid is made of atoms bonded together, thus not as loosely as photons in photonic “gas.” However, the energy of a solid is primarily reflected as the movements of atoms around their equilibrium sites in the solid. Such movements can be described as a combination of sound waves and the energy of the sound waves is quantized as $E = \hbar \omega$ known as phonons. The differences between phonons and photons are 1) there is a minimum wavelength (λ_D) that cannot exceed the atomic spacing in the solid, 2) the conversion from wavelength to frequency is by the speed of sound in the solid, c_s , and 3) phonons have three polarization states instead of two for photons. The density of state becomes:

$$g(\omega) d\omega = \frac{3V \omega^2}{2\pi^2 c_s^3} d\omega$$

Likewise, the logarithmic partition function is the sum of $\log Z(\omega)$:

$$\log Z = \int_0^{\omega_D} g(\omega) \log Z(\omega) d\omega = \frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D} \omega^2 \log(1 - e^{-\beta \hbar \omega}) d\omega$$

The average energy of phonons is:

$$E = -\frac{\partial}{\partial \beta} \log Z = \frac{3V\hbar}{2\pi^2 c_s^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta \hbar \omega} - 1} d\omega = \frac{3V k_B^4 T^4}{2\pi^2 \hbar^3 c_s^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

where T_D is the “Derby temperature”:

$$T_D = \frac{\hbar \omega_D}{k_B} = \left(\frac{6\pi^2 N}{V} \right)^{1/3} \frac{c_s \hbar}{k_B}$$

At T much less than T_D , the heat capacity of solid is proportional to T^3 .

$$C_V = \frac{\partial E}{\partial T} = \frac{2\pi^2 V k_B^4}{5 \hbar^3 c_s^3} T^3 = N k_B \frac{12\pi^4}{5} \left(\frac{T}{T_D} \right)^3$$

Bosons

Quantum particles are falling into two classes: bosons and fermions. Boson particles have integer spins, but fermion particles have half integer spins. The spin characteristics determine the particle wave function as either symmetric (boson) or antisymmetric (fermion). As such, for a given energy state, many boson particles can fill in a single state; yet fermion can either not fill the state or only one particle is permitted at the state. The grand canonical ensemble partition functions are used for the conservation of the number of particles. For a state, r , the partition function of bosons is:

$$Z(r) = \sum_{n_r} e^{-\beta n_r (E_r - \mu)} = \frac{1}{1 - e^{-\beta (E_r - \mu)}}$$

where n_r is the number (very large) of particle at state, r , and μ the chemical potential. To ensure convergence of the summation, it is necessary that $E_r - \mu > 0$.

The logarithmic partition function of boson particles is the summation of $\log Z(r)$ for all r .

$$\log Z = \sum_r \log \left(e^{-\beta (E_r - \mu)} - 1 \right)$$

$$N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z = \sum_r \frac{1}{e^{\beta (E_r - \mu)} - 1}$$

Let $z = e^{\beta \mu}$, we have the Bose-Einstein distribution at given energy E :

$$\frac{1}{z^{-1} e^{\beta E} - 1}$$

Using the density of state function $g(E)$:

$$N = \int \frac{g(E)dE}{z^{-1}e^{\beta E} - 1}$$

$$E = \int \frac{g(E)EdE}{z^{-1}e^{\beta E} - 1}$$

$$pV = \frac{\log Z}{\beta} = -\frac{1}{\beta} \int g(E)dE \log(1 - ze^{-\beta E}) = \frac{2}{3} \int \frac{Eg(E)dE}{z^{-1}e^{\beta E} - 1} = \frac{2}{3}E$$

Fermions

The grand canonical ensemble partition function for fermion has only two terms: either the state, r , is not occupied ($n_r = 0$) or the state is occupied ($n_r = 1$):

$$Z(r) = e^{-\beta 0(E_r - \mu)} + e^{-\beta 1(E_r - \mu)} = 1 + e^{-\beta(E_r - \mu)} = \frac{1}{e^{\beta(E_r - \mu)} + 1} = \frac{1}{z^{-1}e^{\beta E_r} + 1}$$

This is the Fermi-Dirac distribution. Likewise,

$$N = \int \frac{g(E)dE}{z^{-1}e^{\beta E} + 1}$$

$$E = \int \frac{g(E)EdE}{z^{-1}e^{\beta E} + 1}$$

$$pV = \frac{\log Z}{\beta} = -\frac{1}{\beta} \int g(E)dE \log(1 + ze^{-\beta E}) = \frac{2}{3} \int \frac{Eg(E)dE}{z^{-1}e^{\beta E} + 1} = \frac{2}{3}E$$

As temperature approaches absolute zero, the Fermi-Dirac distribution becomes a step function where a state is either filled ($E < \mu$) or not filled ($E > \mu$). The chemical potential at $T = 0$ is called the Fermi energy which is computed by integrating particles from 0 to E_F as the total number of particles N :

$$E_F = \mu(T = 0) = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{g_s V} \right)^{2/3}$$

where g_s is the degeneracy factor when counting the number of spin states. For electrons, $g_s = 2$. For all states with energies less than E_F , the distribution function is 1:

$$E = \int_0^{E_F} Eg(E)dE = \frac{3}{5}NE_F$$

$$pV = \frac{2}{5}NE_F$$