Quantum Statistical Mechanics

Byungjoon Min

Department of Physics, Chungbuk National University

November 13, 2018

Pure and Mixed Ensembles

Let us consider spin 1/2 particles. In general, the state of the particle is given by

$$|\alpha\rangle = c_+|+\rangle + c_-|-\rangle.$$

If we describe an ensemble quantum mechanical, suppose that we have an physical system, 40% of $|\alpha\rangle$ 60% of $|\beta\rangle$. In order to deal with population probability, we introduce the concept of fractional population, such as

$$w_\alpha = 0.4, \quad w_\beta = 0.6.$$

Note that these two probabilities are essentially different.

Pure and Mixed Ensembles

- Pure ensemble: $|+\rangle$, $|-\rangle$, or $|\alpha\rangle$.
- Mixed ensemble: $\{w_+|+\rangle + w_-|-\rangle\}$ or $\{w_\alpha|\alpha\rangle + w_\beta|\beta\rangle\}$.

Because w is probability, they satisfy the normalization condition

$$\sum_i w_i = 1.$$

And, the ensemble average is given by

$$[A] = \sum_i w_i \langle i|A|i\rangle.$$

Note that the expectation value in quantum mechanics is

$$\langle A\rangle = \langle i|A|i\rangle.$$

Density Matrix

To cope with the ensemble average, we introduce the density matrix (operator) ρ as

$$\rho = \sum_i w_i |i\rangle\langle i|. \tag{1}$$

Then we have

$$\begin{aligned}
[A] &= \sum_i w_i \langle i|A|i\rangle && (2)\\
&= \sum_i w_i \langle i| \left(\sum_j |j\rangle\langle j| \right) A|i\rangle && (3)\\
&= \sum_i w_i \sum_j \langle j|A|i\rangle\langle i|j\rangle && (4)\\
&= \sum_j \langle j|A \left(\sum_i w_i |i\rangle\langle i| \right) |j\rangle && (5)\\
&= \sum_j \langle j|A\rho|j\rangle = \mathrm{Tr}(A\rho). && (6)
\end{aligned}$$

Pure Ensemble

A pure ensemble corresponds to $w_i = 1$ for some i and $w_i = 0$ for the others, and thus the density matrix is given by

$$\rho = |i\rangle\langle i|, \tag{8}$$

with no summation. Clearly, $\rho^2 = \rho$ and $\mathrm{Tr}(\rho) = 1$.
For instance, $|+\rangle$ for S_z with a spin 1/2 system,

$$\rho = |+\rangle\langle +| = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} \tag{9}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{10}$$

Pure Ensemble: $|S_x;\pm\rangle$

For instance, $|+\rangle$ for S_x,

$$\rho = |S_x;+\rangle\langle S_x;+| = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)\frac{1}{\sqrt{2}}(\langle +| + \langle -|) \tag{11}$$

$$= \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}. \tag{12}$$

Mixed Ensemble

An incoherent mixture of a spin-up and down with the equal probability:

$$\rho = \frac{1}{2}|+\rangle\langle+| + \frac{1}{2}|-\rangle\langle-| \tag{13}$$

$$= \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}, \tag{14}$$

$$[S_x] = [S_y] = [S_z] = 0. \tag{15}$$

Another example of a partially polarized beam: $w(S_z; +) = 3/4$ and $w(S_x; +) = 1/4$.

$$\rho = \frac{3}{4}|+\rangle\langle+| + \frac{1}{4}\frac{1}{2}(|+\rangle + |-\rangle)(\langle+| + \langle-|) \tag{16}$$

$$= \begin{pmatrix} 7/8 & 1/8 \\ 1/8 & 1/8 \end{pmatrix}, \tag{17}$$

$$[S_x] = \frac{\hbar}{8}, \quad [S_y] = 0, \quad [S_z] = \frac{3\hbar}{8}. \tag{18}$$

Time Evolution of Ensembles (Density Matrix)

Density matrix is given by

$$\rho = \sum_i w_i |i\rangle\langle i|. \tag{19}$$

Then, time evolution of the matrix is

$$\frac{\partial \rho}{\partial t} = \sum_i w_i \left(\frac{\partial |i\rangle}{\partial t} \langle i| + |i\rangle \frac{\partial \langle i|}{\partial t} \right). \tag{20}$$

The time evolutioin of state ket with Hamiltonian is given by Schödinger equation:

$$i\hbar \frac{\partial |i\rangle}{\partial t} = H|i\rangle, \quad -i\hbar \frac{\partial \langle i|}{\partial t} = \langle i|H. \tag{21}$$

Hence, we arrive at the quantum Liouville theorem

$$\frac{\partial \rho}{\partial t} = \sum_i w_i \frac{1}{i\hbar} \left(H|i\rangle\langle i| - |i\rangle\langle i|H \right) \tag{22}$$

$$= \frac{1}{i\hbar}(H\rho - \rho H) = \frac{1}{i\hbar}[H, \rho]. \tag{23}$$

The canonical distribution of a mixture of the energy state $|E_n\rangle$ with Boltzmann weights $exp(-\beta E_n)$. Hence, the density matrix ρ_{canon} is a diagonal form:

$$\rho_{canon} = \sum_n \frac{e^{-\beta E_n}}{Z} |E_n\rangle\langle E_n|, \tag{24}$$

where the partition function is

$$\begin{aligned} Z = \sum_n e^{-\beta E_n} &= \sum_n \langle E_n | e^{-\beta H} | E_n \rangle && (25) \\ &= \mathrm{Tr}\, e^{-\beta H}. && (26) \end{aligned}$$

Note that

$$e^{-\beta H} = \sum_n |E_n\rangle e^{-\beta H} \langle E_n| = \sum_n |E_n\rangle e^{-\beta E_n} \langle E_n|. \tag{27}$$

Identical Particles and Exchange Operator

In quantum mechanics, particles are in principle identical (thus, not distinguishable). We introduce exchange operator as

$$\hat{P}\psi(r_1, r_2) = \psi(r_2, r_1).$$

Since particles are identical, the Hamiltonian of a system and the exchange operator must commute each other as $[H, P] = 0$. Therefore, the eigenfunctions of the Hamiltonian should be the eigenfunctions of P simultaneously. In addition, the probability density of $\hat{P}\psi(r_1, r_2)$ should satisfy

$$|\psi(r_1, r_2)|^2 = |\psi(r_2, r_1)|^2.$$

Identical Particles and Exchange Operator

Consider the following eigenvalue equation,

$$\hat{P}\psi(r_1, r_2) = \lambda\psi(r_1, r_2).$$

Note that trivially

$$\hat{P}^2\psi(r_1, r_2) = \lambda^2\psi(r_1, r_2) = \psi(r_1, r_2),$$

and $\lambda = \pm 1$.
Hence, we have two possible wave functions: symmetric and antisymmetric.

- Symmetric: $\psi(r_2, r_1) = \psi(r_1, r_2)$.
- Antisymmetric: $\psi(r_2, r_1) = -\psi(r_1, r_2)$.

Boson and Fermion

We call the particles as boson when their wave functions are symmetric. And, we call the particles as fermion when their wave functions are antisymmetric. Also, note that the property of boson and fermion is determined by the spin of particles.

In summary,

- Boson, Symmetric: $\psi(r_2, r_1) = \psi(r_1, r_2)$ and $s = 0, 1, 2, \cdots$.
- Fermion, Antisymmetric: $\psi(r_2, r_1) = -\psi(r_1, r_2)$ and $s = 1/2, 3/2, 5/2, \cdots$.

Grand Canonical Ensemble

We slightly modify grand partition function as

$$Q(T, V, \mu) = \sum_k e^{-\beta(\epsilon_k - \mu)n_k}.$$

We consider each eigenstate as being populated independently from other eigenstates and exchanging particles with the external bath. We also define grand free energy as

$$\Phi = -kT \log Q.$$

Then, the number of particles in state k is

$$\langle n \rangle = -\frac{\partial \Phi}{\partial \mu}.$$

Bose-Einstein Distribution

For bosons, grand partition function is

$$\begin{aligned} Q_{BE} &= \sum_{n_k=0}^{\infty} e^{-\beta(\epsilon_k-\mu)n_k} \\ &= \sum_{n_k=0}^{\infty} \left(e^{-\beta(\epsilon_k-\mu)}\right)^{n_k} \\ &= \frac{1}{1-e^{-\beta(\epsilon_k-\mu)}}. \end{aligned}$$

The boson grand free energy is then

$$\Phi_k = -kT\log Q_{BE} = kT\log\left(1-e^{-\beta(\epsilon_k-\mu)}\right).$$

The number of bosons in state k is

$$\langle n_k\rangle_{BE} = -\frac{\partial \Phi_k}{\partial \mu} = \frac{1}{e^{\beta(\epsilon_k-\mu)}-1}.$$

Fermi-Dirac Distribution

For fermions, grand partition function is

$$Q_{FD} = \sum_{n_k=0}^{1} e^{-\beta(\epsilon_k-\mu)n_k}$$
$$= 1 + e^{-\beta(\epsilon_k-\mu)}.$$

The fermion grand free energy is then

$$\Phi_k = -kT \log Q_{FD} = -kT \log\left(1 + e^{-\beta(\epsilon_k-\mu)}\right).$$

The number of bosons in state k is

$$\langle n_k \rangle_{FD} = -\frac{\partial \Phi_k}{\partial \mu} = \frac{1}{e^{\beta(\epsilon_k-\mu)} + 1}.$$

Maxwell-Boltzmann Distribution

For classical but indistinguishable particles, we can derive similarly

$$Q_{MB} = \sum_N \frac{1}{N!} \left(\sum_k e^{-\beta \epsilon_k} \right)^N e^{N\beta\mu}$$
$$= \Pi_k \exp\left(e^{-\beta(\epsilon_k - \mu)} \right).$$

The grand free energy for a single particle is then

$$\Phi_k = -kT e^{-\beta(\epsilon_k - \mu)}.$$

The number of particles in state k is

$$\langle n_k \rangle_{MB} = -\frac{\partial \Phi_k}{\partial \mu} = e^{-\beta(\epsilon_k - \mu)}.$$

BE, FD, and MB Distribution

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon-\mu)} + \alpha},$$

- $\alpha = -1$: Bose-Einstein Distribution
- $\alpha = +1$: Fermi-Dirac Distribution
- $\alpha = 0$: Maxwell-Boltzmann Distribution

BE, FD, and MB Distribution

$$\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} + \alpha},$$

- $\alpha = -1$: Bose-Einstein Distribution
- $\alpha = +1$: Fermi-Dirac Distribution
- $\alpha = 0$: Maxwell-Boltzmann Distribution

For quantum gases,

$$\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1},$$

where $-$ for bosons and $+$ for fermions.

Number of Particles and Energy

Then, the number of total particles and energy are then

$$N = \sum_k \langle n_k \rangle = \int_0^\infty \frac{g(E)dE}{e^{\beta(E-\mu)} \pm 1},$$

$$E = \sum_k \langle n_k \rangle E_k = \int_0^\infty \frac{Eg(E)dE}{e^{\beta(E-\mu)} \pm 1},$$

where $g(E)$ is the density of states. And, defining the fugacity $z = e^{\beta\mu}$,

$$N = \sum_k \langle n_k \rangle = \int_0^\infty \frac{g(E)dE}{z^{-1}e^{\beta E} \pm 1},$$

$$E = \sum_k \langle n_k \rangle E_k = \int_0^\infty \frac{Eg(E)dE}{z^{-1}e^{\beta E} \pm 1}.$$

Density of States (Free Particles)

Consider particles in a box with $V = L \times L \times L$.

$$\Psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin(k_x x) \sin(k_y y) \sin(k_z z),$$

$$E_n = \frac{\hbar^2 k^2}{2m}, \quad k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L}, \quad k_z = \frac{n_z \pi}{L},$$

where n_x, n_y, and n_z are integer. Thus,

$$k^2 = \frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2) = \frac{\pi^2}{L^2} r^2.$$

where $r^2 = n_x^2 + n_y^2 + n_z^2 = \left(\frac{kL}{\pi}\right)^2$.

Density of States (Free Particles)

The total number of states $G(k)$ with k-vectors of magnitude between 0 and k is one-eighth (1/8) of the volume of the sphere of radius r,

$$G(k) = \frac{1}{8} \times \frac{4}{3}\pi r^3 = \frac{1}{8} \times \frac{4}{3}\pi \left(\frac{kL}{\pi}\right)^3 .$$

And, the density of states is

$$g(k)dk = \frac{dG(k)}{dk}dk = \frac{1}{8} \times 4\pi k^2 \left(\frac{L}{\pi}\right)^3 dk = \frac{Vk^2}{2\pi^2}dk.$$

Density of States (Electron)

Electrons in solids (metals) are fermions and are fixed in number. The density of states in k-space is the same as

$$g(k)dk = \frac{Vk^2}{2\pi^2}dk.$$

For the density of state in energy space,

$$\epsilon = \frac{\hbar^2 k^2}{2m}, \quad d\epsilon = \frac{\hbar^2}{2m}(2k)dk,$$

$$\begin{aligned} g(\epsilon)d\epsilon &= 2 \times \frac{Vk^2}{2\pi^2}\frac{m}{\hbar^2 k}d\epsilon = 2 \times \frac{V}{2\pi^2}\frac{m}{\hbar^2}kd\epsilon \\ &= 2 \times \frac{V}{2\pi^2}\frac{m}{\hbar^2}\frac{\sqrt{2m\epsilon}}{\hbar}d\epsilon = 2 \times \frac{mV}{2\pi^2\hbar^3}\sqrt{2m\epsilon}d\epsilon, \end{aligned}$$

where 2 is for two different spins.

Density of States (Photon)

The density of states in k-space is

$$g(k)dk = \frac{Vk^2}{2\pi^2}dk.$$

In order to obtain the density of state for photons in energy space,

$$\epsilon = \hbar\omega = \hbar ck, \quad d\epsilon = c\hbar dk,$$
$$g(\epsilon)d\epsilon = 2 \times \frac{V[\epsilon/(c\hbar)]^2}{2\pi^2}\frac{1}{c\hbar}d\epsilon = 2 \times \frac{V\epsilon^2}{2\pi^2(c\hbar)^3}d\epsilon,$$

where 2 is for two different polarizations. And, for the density of state in frequency space,

$$\omega = ck, \quad d\omega = cdk,$$
$$g(\omega)d\omega = 2 \times \frac{V\omega^2}{2\pi^2c^3}d\omega.$$

Density of States (Phonon)

Phonons are quantized thermal waves in a solid. They are bosons and are not fixed in number. The density of states in k-space is

$$g(k)dk = \frac{Vk^2}{2\pi^2}dk.$$

For the density of state in frequency space,

$$\epsilon = \hbar\omega, \quad \omega = vk, \quad d\omega = vdk,$$
$$g(\omega)d\omega = 3 \times \frac{V\omega^2}{2\pi^2 v^3}d\omega,$$

where 3 is for two different polarizations (2 transverse and 1 longitudinal).