Chap 9. Quantum Mechanical Description

9.2 Quantum Statistical Thermodynamics
Model :
Configuration space : basis (after partial trace)

- CM :
- QM (ket state) :
- QM (density state) :

One free particle : $\mathcal{H}_1 : \{|\vec{r}\rangle\}, \{|\vec{k}\rangle\}$

$$H = \qquad \rho =$$

$$H|\vec{k}\rangle =$$

$$P(\vec{k}) =$$

$$Z = Tr\ e^{-\beta H} =$$

Two free ptls : $\mathcal{H}_{1,2} =$

cf. CM, $\mathbb{R}^{12} = \mathbb{R}^6 \otimes \mathbb{R}^6$:

$$H =$$

$$|\vec{k}_1, \vec{k}_2\rangle =$$

$$H|\vec{k}_1, \vec{k}_2\rangle =$$

$$E =$$

$$\rho =$$

$$P(\vec{k}_1, \vec{k}_2) =$$

$$Z =$$

$$=$$

9.2.1 Exchange Operator

$\mathcal{H}_{1,2}$ is a subspace of $\mathcal{H}_1 \bigotimes \mathcal{H}_2$??

Exchange Operator: P_{12}

$$P_{12} f(x_1, x_2) =$$
$$H(x_2, x_1) =$$

$$P_{12} H - H P_{12} =$$

Exist basis vector set such that

$$H|x_1, x_2\rangle = \qquad \text{and} \qquad P|x_1, x_2\rangle =$$

Now we see that λ must be $+1$ or -1 since

$$P^2|x_1, x_2\rangle =$$
$$P^2|x_1, x_2\rangle = \qquad \Longrightarrow \qquad \lambda = \pm 1$$

Let $|x_1, x_2\rangle$ be an eigenstate of H [but not necessary for P]. Then we can make Co-Eigenstates of P and H by

$$|x_1, x_2\rangle_s =$$
$$|x_1, x_2\rangle_a =$$

Eigenstates of both P and H

$$|x_1, x_2\rangle_s \quad =$$
$$|x_1, x_2\rangle_a \quad =$$

$$P|x_1, x_2\rangle_s \quad =$$
$$H|x_1, x_2\rangle_a \quad =$$
$$H|x_1, x_2\rangle_{sa} \quad =$$

$$P|x_1, x_2\rangle_a \quad =$$
$$H|x_1, x_2\rangle_a \quad =$$

$$|\alpha, \beta\rangle_{SA} \quad =$$
$$\langle\vec{r}|\alpha, \beta\rangle_{SA}$$

$\mathcal{H}_{1,2} =$

The 2nd equality holds only for $N = 2$.

- $\mathcal{H}_s$:
- $\mathcal{H}_a$:

9.2.2 Boson & Fermion

For an N-ptl system : $\mathcal{H}_{1,\cdots,N} = \mathcal{H}_e \oplus \mathcal{H}_o \neq \bigotimes_\alpha \mathcal{H}_\alpha$. $\mathcal{H}_{1,\cdots,N}$ is a proper subspace of $\mathcal{H}_N$

$$
\begin{aligned}
|x_1, \cdots, x_N\rangle &= \\
P_{\alpha\beta}|x_1, \cdots, x_N\rangle &= \\
P_{\alpha\beta\gamma} &=
\end{aligned}
$$

$$
\begin{aligned}
|x_1, \cdots, x_N\rangle_s &= \\
|x_1, \cdots, x_N\rangle_a &= \\
S &= \\
A &=
\end{aligned}
$$

where p is the number of permutations

- boson :
- Fermion :

Properties of Quantum ideal gas [Ex. a two ptl system]

$$\rho \quad = \qquad\qquad Z^{S,A} \; =$$

For $\vec{k}_1 \neq \vec{k}_2$

$$\rho(kk) \quad \propto \quad {}_{sa}\langle \vec{k}_1, \vec{k}_2 | e^{-\beta H} | \vec{k}_1, \vec{k}_2 \rangle_{sa} \; =$$

$$=$$

For $\vec{k}_1 = \vec{k}_2$

$$\rho(kk) \quad \propto \quad {}_{sa}\langle \vec{k}_1, \vec{k}_2 | e^{-\beta H} | \vec{k}_1, \vec{k}_2 \rangle_{sa}$$

Since $|\vec{k}_1, \vec{k}_2\rangle_{sa} = |\vec{k}_2, \vec{k}_1\rangle_{sa}$ trace should count only half of the summation for $\vec{k}_1 \neq \vec{k}_2$;

$$\sum_{\vec{k}_1 > \vec{k}_2} =$$

$$Z^{S,A} \quad = \quad Tr\, e^{-\beta H}$$

$$Z^{S,A} = Tr\, e^{-\beta H}$$

The 2nd term goes to zero as $\hbar$ goes to zero and we get the classical result.

Diagonal term in real space representation

$$\rho(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) =$$

$$=$$

$$=$$

$$=$$

$$P(\vec{r}_1, \vec{r}_2) :=$$

$$U_e(\vec{r}_1, \vec{r}_2) =$$

Q. Draw $U(r)$ and interpretate it.

9.2.3 Quantum Statistics (2nd Quantization)

- $\langle \alpha, \beta|_{sa} = \pm \langle \beta, \alpha|_{sa}$: cannot distinguish, identical,
- Instead of describing each ptl, # of ptls in each state, i.e., discribe occupation number

Occupation number representation
Ex) Two ptls; one in the state α, the other in the the state β.

$$|\alpha, \beta\rangle_{SA} =$$
$$\langle \vec{r}|\alpha, \beta\rangle_{SA} =$$

$$|\alpha, \beta\rangle_{SA} =$$

$$Cf. \qquad [x, p] = i\hbar,$$

Occupation number representation

$$|n_1, n_2, \cdots\rangle_{BF} =$$

$$n_l = \begin{cases} 0, 1, \cdots, \infty \\ 0, 1 \end{cases}$$

Occupation number representation

$$|n_1, n_2, \cdots\rangle_{BF} \quad =$$

$$n_l \quad =$$

$$\hat{N}|n_1, n_2, \cdots\rangle_{BF} \quad =$$

$$H|n_1, n_2, \cdots\rangle_{BF} \quad =$$

$$N \quad = \qquad\qquad E \; =$$

cf.

$$H|x_1, \cdots, x_N\rangle_{sa} \quad =$$

$$E \quad =$$

9.2.4 Canonical Ensemble

$$\rho(n', n) =$$
$$=$$

$$Z =$$

where summation under

$$n_l = \begin{cases} 0, 1, \cdots, \infty & \text{Boson} \\ 0, 1 & \text{Fermion,} \end{cases} \quad \text{and} \quad \sum_l n_l = N.$$

Now partition functions for both Bosons and Fermions can be written as

$$Z^{BF} =$$

with

$$g^B(n_1, n_2, \cdots) = 1$$
$$g^F(n_1, n_2, \cdots) = \begin{cases} 1 & \text{all } n_l \in \{0, 1\} \\ 0 & \text{otherwise} \end{cases}$$

cf. MB-statistics (Classical identical ptls)

$$Z(T,V,N) =$$

$$=$$

Therefore we have $g^{MB}(n_1, n_2, \cdots) = \frac{1}{n_1!n_2!\cdots}$.

cf. For distingishable Classical ptls,

$$Z(T,V,N) =$$

$$=$$

we have

$$g^{DC}(n_1, n_2, \cdots) = \frac{N!}{n_1!n_2!\cdots}$$

$$Z = \sum_{\sum n_l = N} g(n_1, n_2, \cdots,) e^{-\beta \sum_l n_l \epsilon_l}$$

with g given by

$$\begin{aligned} g^B(n_1, n_2, \cdots) &= \\ g^F(n_1, n_2, \cdots) &= \begin{cases} 1 \\ 0 \end{cases} \\ g^{MB}(n_1, n_2, \cdots) &= \\ g^{DC}(n_1, n_2, \cdots) &= \end{aligned}$$

Not easy to calculate Z [for Boson and Fermion] due to the constraint $\sum_l n_l = N$

9.2.5 Grand Canonical Ensemble

- GCE : $\rho =$

$$\rho(n', n) =$$

$$Z_G =$$

Bose-Einstein Statistics

$$Z_G^{BE} =$$

$$=$$

Fermi-Dirac Statistics

$$Z_G^{FD} =$$

$$=$$

Maxwell-Boltzman Statistics

$$Z_G^{MB} =$$

$$=$$

$$Z_G^{BE} =$$

$$Z_G^{FD} =$$

$$Z_G^{MB} =$$

9.2.6 Quantum Statisitcal Theormodynamics
Grand Potential

$$\Phi(T, V, \mu) =$$
$$\Longrightarrow \quad PV =$$

What is $\ln Z_G$? We have

$$Z_G^{BE} = \qquad Z_G^{FD} =$$
$$Z_G^{MB} =$$

Therefore, we can write

$$\ln Z_G =$$

with

$$a = \left\{ \right.$$

$$\ln Z_G =$$

$$U =$$

$$=$$

$$N =$$

$$=$$

$$\langle n_l \rangle =$$

$$N = \qquad\qquad U =$$

$N = \sum \langle n_l \rangle$: Def. of μ for closed system

9.2.7 Occupation Number Statistics

$$\langle n_l \rangle = \frac{1}{e^{\beta(\epsilon_l - \mu)} + a}$$

$\circ \epsilon_l - \mu > T$
Figure $\langle n_l \rangle$ vs $x = (\epsilon_l - \mu)/T$

$\langle n_l \rangle \approx e^{-\beta(\epsilon_l - \mu)}$

$\circ \ |\epsilon_l - \mu| < T$

- Fermion