Kardar, 7.1

Ideal Quantum Gases

Quantum mechanical states of identical particles have probability distributions invariant under exchange of particles:

$$|\psi(\vec{x}_1, \vec{x}_2)|^2 = |\psi(\vec{x}_2, \vec{x}_1)|^2$$

If ψ is single-valued, then either

$$\underbrace{|\psi(1,2)\rangle = +|\psi(2,1)\rangle}_{\text{Boson}} \quad \text{or} \quad \underbrace{|\psi(1,2)\rangle = -|\psi(2,1)\rangle}_{\text{Fermion}}$$

N particles $\rightarrow N!$ permutations P

Every permutation of N labels can be obtained by a succession of pairwise exchanges.

Parity $(-1)^P$ of a permutation:

$$(-1)^P = \begin{cases} +1 & \text{if } P \text{ involves an } \underline{\text{even}} \text{ \# of pairwise exchanges} \\ -1 & \text{if } P \text{ involves an } \underline{\text{odd}} \text{ \# of pairwise exchanges} \end{cases}$$

Bosons: $P|\psi(1,\ldots,N)\rangle = +|\psi(1,\ldots,N)\rangle$

Fermions: $P|\psi(1,\ldots,N)\rangle = (-1)^P|\psi(1,\ldots,N)\rangle$

$\forall$ permutations P.

Identical particles have symmetric Hamiltonians $P\mathcal{H} = \mathcal{H}$.

N particles in box of volume V:

$$\mathcal{H} = \sum_{a=1}^{N} \mathcal{H}_a = \sum_{a=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_a^2\right) \quad \text{in coordinate rep.}$$

$\mathcal{H}_a$ eigenstates $|\vec{k}\rangle$ with $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$

product Hilbert space:

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

$$\langle \vec{x}_1, \ldots, \vec{x}_N | \vec{k}_1, \ldots, \vec{k}_N\rangle = \frac{1}{V^{N/2}} \exp\left(i \sum_{a=1}^{N} \vec{k}_a \cdot \vec{x}_a\right)$$

$$\mathcal{H}|\vec{k}_1, \ldots, \vec{k}_N\rangle = \sum_{a=1}^{N} \frac{\hbar^2 k_a^2}{2m} |\vec{k}_1, \ldots, \vec{k}_N\rangle$$

Symmetrized states:

Fermions: $|\vec{k}_1, \ldots, \vec{k}_N\rangle_- \equiv \frac{1}{\sqrt{N_-}} \sum_P (-1)^P P |\vec{k}_1, \ldots, \vec{k}_N\rangle$

antisymmetrized for fermions

$N_- = N!$

permutations of N particles

$$|\vec{k}_1, \vec{k}_2\rangle_- = \frac{|\vec{k}_1, \vec{k}_2\rangle - |\vec{k}_2, \vec{k}_1\rangle}{\sqrt{2}}$$

Bosons: $|\vec{k}_1, \ldots, \vec{k}_N\rangle_+ = \frac{1}{\sqrt{N_+}} \sum_P P |\vec{k}_1, \ldots, \vec{k}_N\rangle$

symmetrized for bosons

For fermions, any given $\vec{k}$ can appear in the state at most once.

For bosons, any $\vec{k}$ can appear an arbitrary number of times $n_{\vec{k}} \leq N$.

occupation number of mode $\vec{k}$.

If $\vec{k}$ appears $n_{\vec{k}}$ times, then

$\langle \{\vec{k}_a\} | P\{\vec{k}_a\} \rangle = 0$ unless the $\{\vec{k}_a\}$ are in the correct slot:

$$\langle \vec{k}_1, \vec{k}_2 | \vec{k}_1, \vec{k}_2 \rangle = 1$$

$$\langle \vec{k}_1, \vec{k}_2 | \vec{k}_2, \vec{k}_1 \rangle = 0$$

If $\vec{k}$ appears $n_{\vec{k}}$ times in the state, then there are $n_{\vec{k}}!$ permutations of the momenta that contribute to ${}_+\langle \{\vec{k}_a\} | \{\vec{k}_a\} \rangle_+$:

$$1 = {}_+\langle \{\vec{k}_a\} | \{\vec{k}_a\} \rangle_+ = \frac{1}{N_+} \sum_{P,P'} \langle P'\{\vec{k}_a\} | P \{\vec{k}_a\} \rangle$$

$$= \frac{N!}{N_+} \sum_{P} \langle \{\vec{k}_a\} | P \{\vec{k}_a\} \rangle$$

$$= \frac{N!}{N_+} \prod_{\vec{k}_a} n_{\vec{k}_a}! = 1$$

$$\Rightarrow \boxed{N_+ = N! \prod_{\vec{k}_a} n_{\vec{k}_a}!}$$

Example: State $|\alpha\rangle$ appears w/ $n_\alpha = 2$
$|\beta\rangle$ w/ $n_\beta = 1$

3-particle state:

$$|\alpha\alpha\beta\rangle_+ = \frac{1}{\sqrt{12}}\left(|\alpha\alpha\beta\rangle + |\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle + |\alpha\alpha\beta\rangle + |\beta\alpha\alpha\rangle + |\alpha\beta\alpha\rangle\right)$$
$$= \frac{1}{\sqrt{3}}\left(|\alpha\alpha\beta\rangle + |\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle\right)$$

For fermions or bosons write

$$|\{\vec{k}\}\rangle_\eta = \frac{1}{\sqrt{N_\eta}} \sum_P \eta^P P|\{\vec{k}\}\rangle, \text{ with } \eta = \begin{cases} +1 & \text{for bosons} \\ -1 & \text{for fermions} \end{cases}$$

$$N_{-1} = N!$$
$$N_{+1} = N! \prod_{\vec{k}_\alpha} n_{\vec{k}_\alpha}!$$

States are specified by occupation numbers $\{n_{\vec{k}}\}$

$$\sum_{\vec{k}_\alpha} n_{\vec{k}_\alpha} = N$$

Fermions: $n_{\vec{k}} = 0$ or 1

7.2 Canonical formulation

Density matrix ρ:

$$\sum_{\{\vec{k}\}}' = \sum_{\{\vec{k}\}} \frac{\prod_{\vec{k}} n_{\vec{k}}!}{N!}$$ so each state in the sum is counted once.

$$\langle\{\vec{x}'\}|\rho|\{\vec{x}\}\rangle_\eta = \frac{1}{N_\eta} \sum_{\{\vec{k}\}}' \sum_{P,P'} \eta^P \eta^{P'} \langle\{\vec{x}'\}|P'\{\vec{k}\}\rangle \rho(\{\vec{k}\}) \langle P\{\vec{k}\}|\{\vec{x}\}\rangle$$

$$\rho(\{\vec{k}\}) = \exp\left[-\beta \sum_{\alpha=1}^{N} \frac{\hbar^2 k_\alpha^2}{2m}\right] / Z_N$$

$\langle \{\vec{x}'\} | \rho | \{\vec{x}\} \rangle_\zeta$

$$= \sum_{\{\vec{k}\}} \frac{\prod_{\vec{k}} n_{\vec{k}}!}{N!} \cdot \frac{1}{N! \prod_{\vec{k}} n_{\vec{k}}!} \sum_{P,P'} \frac{\zeta^P \zeta^{P'}}{Z_N} \exp\left(-\beta \sum_{\alpha=1}^{N} \frac{\hbar^2 k_\alpha^2}{2m}\right)$$

$$\times \langle \{\vec{x}'\} | P'\{\vec{k}\} \rangle \langle P\{\vec{k}\} | \{\vec{x}\} \rangle$$

$$\xrightarrow{V\to\infty} \frac{1}{Z_N} \frac{1}{(N!)^2} \sum_{P,P'} \zeta^P \zeta^{P'} \int \prod_{\alpha=1}^{N} \frac{V\, d^3 k_\alpha}{(2\pi)^3} \exp\left(-\beta \frac{\hbar^2 k_\alpha^2}{2m}\right)$$

$$\times \frac{1}{V^N} \exp\left[-i \sum_{\alpha=1}^{N} \left(\vec{k}_{P\alpha} \cdot \vec{x}_\alpha - \vec{k}_{P'\alpha} \cdot \vec{x}'_\alpha\right)\right]$$

$$= \frac{1}{Z_N} \frac{1}{(N!)^2} \sum_{P,P'} \zeta^P \zeta^{P'} \prod_{\alpha=1}^{N} \int \frac{d^3 k_\alpha}{(2\pi)^3} \exp\left[-i \vec{k}_\alpha \cdot \left(\vec{x}_{P^{-1}\alpha} - \vec{x}'_{P'^{-1}\alpha}\right) - \beta \frac{\hbar^2 k_\alpha^2}{2m}\right]$$

$$= \frac{1}{Z_N \lambda^{3N}} \frac{1}{(N!)^2} \sum_{P,P'} \zeta^P \zeta^{P'} \exp\left\{-\frac{\pi}{\lambda^2} \sum_{\beta=1}^{N} \left(\vec{x}_\beta - \vec{x}'_{P'^{-1}P\beta}\right)^2\right\}$$

$\beta = P^{-1}\alpha$

Define permutation $Q \equiv P'^{-1}P$, use $\zeta^P = \zeta^{P^{-1}}$,
$\zeta^Q = \zeta^{P'^{-1}P} = \zeta^{P'}\zeta^P$

$$\Rightarrow \langle \{\vec{x}'\} | \rho | \{\vec{x}\} \rangle = \frac{1}{Z_N \lambda^{3N} N!} \sum_Q \zeta^Q \exp\left[-\frac{\pi}{\lambda^2} \sum_{\beta=1}^{N} \left(\vec{x}_\beta - \vec{x}'_{Q\beta}\right)^2\right]$$

Extra factor of $N!$ from $\sum_{P,P'} \to \sum_Q$

Normalization: $\mathrm{Tr}\, \rho = \int \prod_{\alpha=1}^{N} d^3 x_\alpha \langle \{\vec{x}_\alpha\} | \rho | \{\vec{x}_\alpha\} \rangle = 1$

$$\Rightarrow Z_N = \frac{1}{N! \lambda^{3N}} \int \prod_{\alpha=1}^{N} d^3 x_\alpha \sum_Q \zeta^Q \exp\left[-\frac{\pi}{\lambda^2} \sum_{\beta=1}^{N} \left(\vec{x}_\beta - \vec{x}_{Q\beta}\right)^2\right]$$

Term with $Q = 1$ contributes $Z_N \supset \left(\frac{V}{\lambda^3}\right)^N \frac{1}{N!}$

= classical result w/ factor $\frac{1}{N!}$ for identical particles.

High T: $\lambda \to 0$, $\exp\left[-\frac{\pi}{\lambda^2}(\vec{x}_a - \vec{x}_{Qa})^2\right] \to 0$ for $Q \neq 1$

$\to$ exchange contributions vanish

$\to$ classical behavior.

Quantum corrections at high T:

Exchange 2 particles $\sim$ factor $\eta \exp\left[-2\pi(\vec{x}_1 - \vec{x}_2)^2/\lambda^2\right]$

$\frac{N(N-1)}{2}$ different pairwise exchanges

$$\to Z_N = \frac{1}{N!\lambda^{3N}} \int \prod_{a=1}^{N} d^3x_a \left\{ 1 + \frac{N(N-1)}{2} \eta \exp\left[-2\pi(\vec{x}_1 - \vec{x}_2)^2/\lambda^2\right] + \cdots \right\}$$

Change variables $(\vec{x}_1, \vec{x}_2) \to \begin{cases} \vec{r}_{12} = (\vec{x}_2 - \vec{x}_1) \\ \vec{r}_{cm} = \frac{(\vec{x}_1 + \vec{x}_2)}{2} \end{cases}$

$$Z_N = \frac{1}{N!\lambda^{3N}} V^N \left[1 + \frac{N(N-1)}{2V} \eta \int d^3r_{12} \exp\left[-2\pi \vec{r}_{12}^{\,2}/\lambda^2\right] + \cdots \right]$$

$$= \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \left[1 + \frac{N(N-1)}{2V} \eta \left(\frac{2\pi\lambda^2}{4\pi}\right)^{3/2} + \cdots \right]$$

Free energy:

$$F = -k_B T \ln Z_N$$

$$= -N k_B T \ln\left[\frac{e}{\lambda^3}\frac{V}{N}\right] - \frac{k_B T N^2}{2V}\frac{\lambda^3}{2^{3/2}}\eta + \cdots$$

Pressure:

$$P = -\frac{\partial F}{\partial V}\bigg|_T = \frac{N}{V} k_B T \left(1 - \frac{\eta \lambda^3}{2^{5/2}} \frac{N}{V} + \cdots \right)$$

classical ideal gas

$\sim$ quantum corrections.

Quantum correction to pressure is negative for bosons,
positive for fermions.

— Degeneracy Pressure.

Grand Canonical Formulation

Occupation numbers satisfy $\sum_{\vec{k}} n_{\vec{k}} = N$. In the Grand Canonical Formulation N is not fixed.

Grand partition function:

$$Q_\eta(T,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\{n_{\vec{k}}\}}^{\sum n_{\vec{k}} = N} \exp\left[-\beta \sum_{\vec{k}} \varepsilon(\vec{k}) n_{\vec{k}}\right]$$

$$= \sum_{\{n_{\vec{k}}\}_\eta} \prod_{\vec{k}} \exp\left[-\beta(\varepsilon(\vec{k})-\mu) n_{\vec{k}}\right]$$

Fermions: Sum over $n_{\vec{k}} = 0$ or 1

Bosons: sum over $n_{\vec{k}} = 0, 1, 2, \dots$

$$Q_-(T,\mu) = \prod_{\vec{k}} \Big[\underbrace{1}_{n_{\vec{k}}=0} + \underbrace{\exp\left(-\beta(\varepsilon(\vec{k})-\mu)\right)}_{n_{\vec{k}}=1}\Big]$$

$$Q_+(T,\mu) = \prod_{\vec{k}} \left[1 - \exp\left(-\beta(\varepsilon(\vec{k})-\mu)\right)\right]^{-1}$$

summing geometric series.

$$\ln Q_\eta = -\eta \sum_{\vec{k}} \ln\left[1 - \eta \exp\left(\beta\mu - \beta\varepsilon(\vec{k})\right)\right]$$

$\eta = -1$ fermion or $+1$ boson.

$$\text{prob}(\{n_{\vec{k}}\}) = \frac{1}{Q_\eta} \prod_{\vec{k}} \exp\left[(\beta\mu - \beta\varepsilon(\vec{k}))\, n_{\vec{k}}\right]$$

Average Occupation number:

$$\langle n_{\vec{k}} \rangle_\eta = -\frac{\partial \ln Q_\eta}{\partial(\beta\varepsilon(\vec{k}))} = \frac{1}{e^{-\beta\mu} e^{\beta\varepsilon(\vec{k})} - \eta}$$

$$= \frac{1}{z^{-1} e^{\beta\varepsilon(\vec{k})} - \eta}$$

where $z = e^{\beta\mu}$

$$N_\eta = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle_\eta = \sum_{\vec{k}} \frac{1}{z^{-1} e^{\beta\varepsilon(\vec{k})} - \eta}$$

$$E_\eta = \sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}} \rangle_\eta = \sum_{\vec{k}} \frac{\varepsilon(\vec{k})}{z^{-1} e^{\beta\varepsilon(\vec{k})} - \eta}$$