Occupation Numbers

single-particle state

Hamiltonian: $H_1 = \frac{1}{2m}\vec{P}^2$

orthonormal basis of energy eigenstates: $|i\rangle$

energy: $H_1|i\rangle = \varepsilon_i |i\rangle$

orthonormal: $\langle i'|i\rangle = \delta_{ii'}$

completeness: $\sum_i |i\rangle\langle i| = \mathbb{1}$

sum over single particle state

multi-particle states with N particles

Hamiltonian for non-interacting particles

$$H_N = \sum_{n=1}^{N} \frac{1}{2m}\vec{P}_n^2$$

N distinguishable particles

orthonormal basis: $|i_1, i_2, \ldots, i_N\rangle$

energy: $E = \sum_{n=1}^{N} \varepsilon_{i_n}$

for N identical fermions or N identical bosons, basis states can also be specified by listing occupation numbers for all single-particle states

N identical fermions

$$\frac{1}{\sqrt{N!}} \sum_P (-1)^P P \, | i_1, i_2, \ldots, i_N \rangle \qquad i_1, i_2, \ldots, i_N \text{ all distinct}$$

$$= | i_1 : 1, i_2 : 1, \ldots, i_N : 1, \text{all others} : 0 \rangle$$

$$\text{energy: } E = \sum_{n=1}^{N} \varepsilon_{i_n}$$

N identical bosons

$$\frac{1}{\sqrt{N!}} \sum_P P \, | i_1, i_2, \ldots, i_N \rangle \qquad i_1, i_2, \ldots, i_N \text{ all distinct}$$

$$= | i_1 : 1, i_2 : 1, \ldots, i_N : 1, \text{all others} : 0 \rangle$$

$$\frac{1}{2\sqrt{(N-2)!}} \sum_P P \, | i_1, i_1, i_3, \ldots, i_N \rangle \qquad i_1 = i_2, i_3, \ldots, i_N \text{ all distinct}$$

$$= | i_1 : 2, i_3 : 1, \ldots, i_N : 1, \text{all others} : 0 \rangle$$

$\vdots$

$$| i_1, i_1, \ldots, i_1 \rangle = \frac{1}{N!} \sum_P P \, | i_1, i_1, \ldots, i_1 \rangle$$

$$= | i_1 : N, \text{all others} : 0 \rangle$$

occupation number representation
for basis states of identical particles

enumerate the infinitely many
single-particle basis states

$|i_1\rangle, |i_2\rangle, |i_3\rangle, \ldots$

orthonormal basis for identical fermions

$|i_1 : n_1, i_2 : n_2, i_3 : n_3, \ldots\rangle \qquad n_i = 0, 1$

particle number: $N = \sum_i n_i$

energy: $E = \sum_i n_i \varepsilon_i$

sum over single-particle states

orthonormal basis for identical bosons

same except $n_i = 0, 1, 2, \ldots$

Microcanonical Ensemble with N particles
total energy U

number of microstates:

$\Omega(N,U)$ = number of distinct lists $(n_1, n_2, n_3, \dots)$ of occupation numbers

$$= \left(\sum_{n_1}\sum_{n_2}\sum_{n_3}\cdots\right)' 1$$

sums constrained by $\sum_i n_i = N$
$\sum_i n_i \varepsilon_i = E$

Canonical Ensemble with N particles
temperature $T = 1/\beta$

$Z(N,T) = \mathrm{Tr}\left(e^{-\beta \hat{H}}\right)$ trace over states with N particles

$$= \left(\sum_{n_1}\sum_{n_2}\sum_{n_3}\cdots\right)' e^{-\beta \sum_{i=1}^{\infty} n_i \varepsilon_i}$$

sums constrained by $\sum_i n_i = N$

Grand Canonical Ensemble

with temperature $T = \frac{1}{\beta}$
chemical potential μ

grand partition function

$$Q = \mathrm{Tr}\left(e^{-\beta(\hat{H} - \mu \hat{N})}\right)$$

$$= \left(\sum_{n_1} \sum_{n_2} \sum_{n_3} \cdots\right) \exp\left(-\beta\left(\sum_i n_i \varepsilon_i\right) + \beta\mu\left(\sum_i n_i\right)\right)$$

$$= \prod_i \sum_{n_i} \exp\left(-\beta n_i(\varepsilon_i - \mu)\right)$$

no constraints!

sum over occupation numbers of state i

product over single particle states

identical bosons

occupation numbers: $n_i = 0, 1, 2, \ldots$

$$Q = \prod_i \sum_{n_i = 0}^{\infty} \exp\left(-\beta n_i(\varepsilon_i - \mu)\right)$$

$$= \prod_i \frac{1}{1 - e^{-\beta(\varepsilon_i - \mu)}}$$

identical fermions

occupation numbers: $n_i = 0, 1$

$$Q = \prod_i \sum_{n_i = 0}^{1} \exp\left(-\beta n_i(\varepsilon_i - \mu)\right)$$

$$= \prod_i \left(1 + e^{-\beta(\varepsilon_i - \mu)}\right)$$

Thermodynamics

grand potential. $\Phi = U - ST - \mu N$

$$Q = e^{-\beta \Phi}$$

thermodynamic relation: $d\Phi = -S\,dT - N\,d\mu - P\,dV + \cdots$

entropy: $S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu, V, \ldots}$

particle number: $N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T, V, \ldots}$

average energy: $U = \frac{1}{Q}\left(\prod_{i'} \sum_{n_{i'}} \exp(-\beta n_{i'}(\epsilon_{i'} - \mu))\right) \sum_i n_i \varepsilon_i$

$$= \sum_i \varepsilon_i \frac{1}{\sum_{n_i} \exp(-\beta n_i(\epsilon_i - \mu))} \sum_{n_i} \exp(-\beta n_i(\epsilon_i - \mu))\, n_i$$

$$= \sum_i \langle n_i \rangle \varepsilon_i$$

average occupation number

$$\langle n_i \rangle = \frac{1}{\sum_n \exp(-\beta n(\epsilon_i - \mu))} \sum_n n \exp(-\beta n(\epsilon_i - \mu))$$

bosons: $n = 0, 1, 2, \ldots$ $\qquad \langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$

fermions: $n = 0, 1$ $\qquad \langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$