5.1: Statistical Mechanics of Noninteracting Quantum Systems

Bose and Fermi systems in the grand canonical ensemble

A noninteracting many-particle quantum Hamiltonian may be written as[1]

$$\hat{H}=\sum_\alpha \varepsilon_\alpha\,\hat{n}_\alpha\ , \tag{5.1.1}$$

where $\hat{n}_\alpha$ is the number of particles in the quantum state α with energy ε_α. This form is called the *second quantized representation* of the Hamiltonian. The number eigenbasis is therefore also an energy eigenbasis. Any eigenstate of $\hat{H}$ may be labeled by the integer eigenvalues of the $\hat{n}_\alpha$ number operators, and written as $\big|\,n_1\,,\,n_2\,,\,\ldots\,\big\rangle$. We then have

$$\hat{n}_\alpha\,\big|\,\vec{n}\,\big\rangle = n_\alpha\,\big|\,\vec{n}\,\big\rangle \tag{5.1.2}$$

and

$$\hat{H}\,\big|\,\vec{n}\,\big\rangle = \sum_\alpha n_\alpha\,\varepsilon_\alpha\,\big|\,\vec{n}\,\big\rangle\ . \tag{5.1.3}$$

The eigenvalues n_α take on different possible values depending on whether the constituent particles are *bosons* or *fermions*, *viz.*

$$\begin{aligned} \textsf{bosons:}\quad & n_\alpha\in\big\{0\,,\,1\,,\,2\,,\,3\,,\,\ldots\big\}\\ \textsf{fermions:}\quad & n_\alpha\in\big\{0\,,\,1\big\}\ .\end{aligned}$$

In other words, for bosons, the occupation numbers are nonnegative integers. For fermions, the occupation numbers are either 0 or 1 due to the *Pauli principle*, which says that at most one fermion can occupy any single particle quantum state. There is no Pauli principle for bosons.

The N-particle partition function Z_N is then

$$Z_N=\sum_{\{n_\alpha\}} e^{-\beta\sum_\alpha n_\alpha\varepsilon_\alpha}\,\delta_{N,\sum_\alpha n_\alpha}\ , \tag{5.1.4}$$

where the sum is over all allowed values of the set $\{n_\alpha\}$, which depends on the *statistics* of the particles. Bosons satisfy *Bose-Einstein* (BE) statistics, in which $n_\alpha\in\{0\,,\,1\,,\,2\,,\,\ldots\}$. Fermions satisfy *Fermi-Dirac* (FD) statistics, in which $n_\alpha\in\{0\,,\,1\}$.

The OCE partition sum is difficult to perform, owing to the constraint $\sum_\alpha n_\alpha=N$ on the total number of particles. This constraint is relaxed in the GCE, where

$$\begin{aligned}\Xi&=\sum_N e^{\beta\mu N}\,Z_N\\ &=\sum_{\{n_\alpha\}} e^{-\beta\sum_\alpha n_\alpha\varepsilon_\alpha}\,e^{\beta\mu\sum_\alpha n_\alpha}\\ &=\prod_\alpha\Bigg(\sum_{n_\alpha} e^{-\beta(\varepsilon_\alpha-\mu)\,n_\alpha}\Bigg)\ .\end{aligned}$$

Note that the grand partition function Ξ takes the form of a product over contributions from the individual single particle states.

We now perform the single particle sums:

$$\begin{aligned}\sum_{n=0}^\infty e^{-\beta(\varepsilon-\mu)\,n}&=\frac{1}{1-e^{-\beta(\varepsilon-\mu)}}\qquad\textsf{(bosons)}\\ \sum_{n=0}^1 e^{-\beta(\varepsilon-\mu)\,n}&=1+e^{-\beta(\varepsilon-\mu)}\qquad\textsf{(fermions)}\ .\end{aligned}$$

Therefore we have

\begin{split} \XBE&=\prod_\alpha {1\over 1-e^{-(\ve\ns_\alpha-\mu)/\kT}}\\ \OBE&=\kT\sum_\alpha\ln\!\Big(1-e^{-(\ve\ns_\alpha-\mu)/\kT}\Big) \end{split}

and

\begin{split} \XFD&=\prod_\alpha \Big(1+e^{-(\ve\ns_\alpha-\mu)/\kT}\Big)\\ \OFD&=-\kT\sum_\alpha\ln\!\Big(1+e^{-(\ve\ns_\alpha-\mu)/\kT}\Big). \end{split}

We can combine these expressions into one, writing

$$\Omega(T,V,\mu)=\pm k_B T\sum_\alpha \ln\!\Big(1\mp e^{-(\varepsilon_\alpha-\mu)/k_BT}\Big), \tag{5.1.5}$$

where we take the upper sign for Bose-Einstein statistics and the lower sign for Fermi-Dirac statistics. Note that the average occupancy of single particle state α is

$$\langle\hat{n}_\alpha\rangle=\frac{\partial\Omega}{\partial\varepsilon_\alpha}=\frac{1}{e^{(\varepsilon_\alpha-\mu)/k_BT}\mp 1}, \tag{5.1.6}$$

and the total particle number is then

$$N(T,V,\mu)=\sum_\alpha\frac{1}{e^{(\varepsilon_\alpha-\mu)/k_BT}\mp 1}. \tag{5.1.7}$$

We will henceforth write $n_\alpha(\mu,T)=\langle\hat{n}_\alpha\rangle$ for the thermodynamic average of this occupancy.

Quantum statistics and the Maxwell-Boltzmann limit

Consider a system composed of N noninteracting particles. The Hamiltonian is

$$\hat{H}=\sum_{j=1}^N \hat{h}_j\ . \tag{5.1.8}$$

The single particle Hamiltonian $\hat{h}$ has eigenstates $|\alpha\rangle$ with corresponding energy eigenvalues ε_α. What is the partition function? Is it

$$Z\ \text{to}1\overset{?}{0}pt{=}\sum_{\alpha_1}\cdots\sum_{\alpha_N} e^{-\beta\left(\varepsilon_{\alpha_1}+\varepsilon_{\alpha_2}+\ldots+\varepsilon_{\alpha_N}\right)}=\zeta^N\ , \tag{5.1.9}$$

where ζ is the single particle partition function,

$$\zeta=\sum_\alpha e^{-\beta\varepsilon_\alpha}\ . \tag{5.1.10}$$

For systems where the individual particles are *distinguishable*, such as spins on a lattice which have fixed positions, this is indeed correct. But for particles free to move in a gas, this equation is *wrong*. The reason is that for *indistinguishable particles* the many particle quantum mechanical states are specified by a collection of *occupation numbers* n_α, which tell us how many particles are in the single-particle state $\,|\,\alpha\,\rangle$. The energy is

$$E=\sum_\alpha n_\alpha\,\varepsilon_\alpha \tag{5.1.11}$$

and the total number of particles is

$$N=\sum_\alpha n_\alpha\ . \tag{5.1.12}$$

That is, each collection of occupation numbers $\{n_\alpha\}$ labels a unique many particle state $\,\big|\,\{n_\alpha\}\,\big\rangle$. In the product ζ^N, the collection $\{n_\alpha\}$ occurs many times. We have therefore *overcounted* the contribution to Z_N due to this state. By what factor have we overcounted? It is easy to see that the overcounting factor is

$$\text{degree of overcounting} \quad = \quad \frac{N!}{\prod_\alpha n_\alpha!} \quad ,$$

which is the number of ways we can rearrange the labels α_j to arrive at the same collection $\{n_\alpha\}$. This follows from the multinomial theorem,

$$\bigg(\sum_{\alpha=1}^K x_\alpha\bigg)^{\!N} = \sum_{n_1}\sum_{n_2}\cdots\sum_{n_K}{N!\over n_1!\,n_2!\cdots n_K!}\,x_1^{n_1}\,x_2^{n_2}\cdots x_K^{n_K}\,\delta_{N,n_1+\ldots+n_K}\ . \tag{5.1.13}$$

Thus, the correct expression for Z_N is

$$\begin{split} Z_N&=\sum_{\{n_\alpha\}}\,e^{-\beta\sum_\alpha n_\alpha\varepsilon_\alpha}\,\delta_{N,\sum_\alpha n_\alpha} \\ &=\sum_{\alpha_1}\sum_{\alpha_2}\cdots\sum_{\alpha_N}\bigg({\prod_\alpha n_\alpha!\over N!}\bigg)\,e^{-\beta(\varepsilon_{\alpha_1}+\varepsilon_{\alpha_2}+\ldots+\varepsilon_{\alpha_N})}\ . \end{split}$$

In the high temperature limit, almost all the n_α are either 0 or 1, hence

$$Z_N\approx {\zeta^N\over N!}\ . \tag{5.1.14}$$

This is the classical *Maxwell-Boltzmann limit* of quantum statistical mechanics. We now see the origin of the $1/N!$ term which is so important in the thermodynamics of entropy of mixing.

Finally, starting with the expressions for the grand partition function for Bose-Einstein or Fermi-Dirac particles, and working in the low density limit where $n_\alpha(\mu,T)\ll 1$, we have $\varepsilon_\alpha-\mu\gg k_BT$, and consequently

\begin{split} \Omega\ns_{\ssr{BE}/\ssr{FD}}&=\pm\kT\,\sum_\alpha\ln\!\Big(1\mp e^{-(\ve\ns_\alpha-\mu)/\kT}\Big)\\ &\longrightarrow-\kT\sum_\alpha e^{-(\ve\ns_\alpha-\mu)/\kT}\equiv \Omega\ns_\ssr{MB}\ . \end{

This is the Maxwell-Boltzmann limit of quantum statistical mechanics. The occupation number average in the Maxwell-Boltzmann limit is then

$$\langle\,\hat n_\alpha\rangle = e^{-(\varepsilon_\alpha-\mu)/k_BT}\ . \tag{5.1.15}$$

Single particle density of states

The single particle density of states per unit volume $g(\varepsilon)$ is defined as

$$g(\varepsilon)={1\over V}\sum_\alpha\delta(\varepsilon-\varepsilon_\alpha)\ . \tag{5.1.16}$$

We can then write

$$\Omega(T,V,\mu)=\pm Vk_BT\int\limits_{-\infty}^\infty\!\!d\varepsilon\; g(\varepsilon)\,\ln\!\Big(1\mp e^{-(\varepsilon-\mu)/k_BT}\Big)\ . \tag{5.1.17}$$

For particles with a dispersion $\varepsilon({\mathbf k})$, with ${\mathbf p}=\hbar{\mathbf k}$, we have

$$\begin{split} g(\varepsilon)&={\mathsf g}\!\int\!{d^d\!k\over (2\pi)^d}\,\delta(\varepsilon-\varepsilon({\mathbf k}))\\ &={{\mathsf g}\,\Omega_d\over (2\pi)^d}\,{k^{d-1}\over d\varepsilon/dk}\ . \end{split}$$

where ${\mathsf g}=2S+1$ is the spin degeneracy, and where we assume that $\varepsilon({\mathbf k})$ is both isotropic and a monotonically increasing function of k. Thus, we have

$$g(\varepsilon)={{\mathsf g}\,\Omega_d\over (2\pi)^d}\,{k^{d-1}\over d\varepsilon/dk}=\begin{cases} {{\mathsf g}\over\pi}\,{dk\over d\varepsilon} & d=1 \\ \\ {{\mathsf g}\over 2\pi}\,k\,{dk\over d\varepsilon} & d=2 \\ \\ {{\mathsf g}\over 2\pi^2}\,k^2\,{dk\over d\varepsilon} & d=3\ . \end{cases} \tag{5.1.18}$$

In order to obtain $g(\varepsilon)$ as a function of the energy ε one must invert the dispersion relation $\varepsilon=\varepsilon(k)$ to obtain $k=k(\varepsilon)$.

Note that we can equivalently write

$$g(\varepsilon)\,d\varepsilon={\mathsf g}\,{d^d\!k\over(2\pi)^d}={{\mathsf g}\,\Omega_d\over (2\pi)^d}\,k^{d-1}\,dk \tag{5.1.19}$$

to derive $g(\varepsilon)$.

For a spin-S particle with ballistic dispersion $\varepsilon({\mathbf k})=\hbar^2{\mathbf k}^2/2m$, we have

$$g(\varepsilon)={2S+1\over\Gamma(d/2)}\bigg({m\over 2\pi\hbar^2}\bigg)^{\!d/2}\varepsilon^{{d\over 2}-1}\,\Theta(\varepsilon), \tag{5.1.20}$$

where $\Theta(\varepsilon)$ is the step function, which takes the value 0 for $\varepsilon<0$ and 1 for $\varepsilon\ge 0$. The appearance of $\Theta(\varepsilon)$ simply says that all the single particle energy eigenvalues are nonnegative. Note that we are assuming a box of volume V but we are ignoring the quantization of kinetic energy, and assuming that the difference between successive quantized single particle energy eigenvalues is negligible so that $g(\varepsilon)$ can be replaced by the average in the above expression. Note that

$$n(\varepsilon,T,\mu)=\frac{1}{e^{(\varepsilon-\mu)/k_BT}\mp 1}. \tag{5.1.21}$$

This result holds true independent of the form of $g(\varepsilon)$. The average total number of particles is then

$$N(T,V,\mu)=V\!\int\limits_{-\infty}^{\infty}\!\!d\varepsilon\,g(\varepsilon)\,\frac{1}{e^{(\varepsilon-\mu)/k_BT}\mp 1}, \tag{5.1.22}$$

which does depend on $g(\varepsilon)$.