GCE: Occupation number representation

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We now discuss the occupation number representation for the grand canonical ensemble. This representation is very useful in quantum statistics.

1. Occupation number representation

With ε_r the energy in the single-particle state $|r\rangle$, the total energy E of the system is

$$E = n_0\varepsilon_0 + n_1\varepsilon_1 + n_2\varepsilon_2 + ... + n_i\varepsilon_i + \dots \tag{1}$$

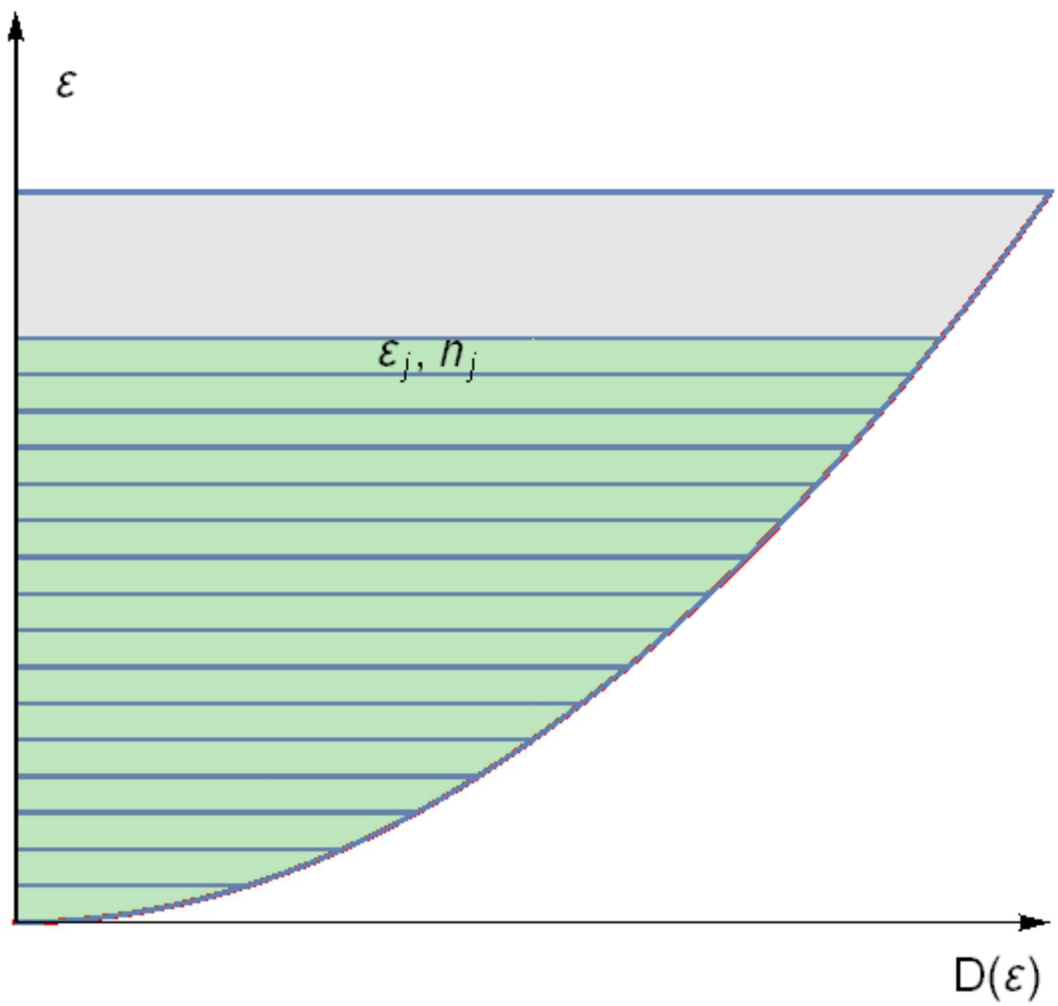


Fig. The number of states vs one-particle energy.

The number of particles N in the system is given by

$$N = n_0 + n_1 + n_2 + ... + n_i + ... \qquad (2)$$

We note that

$$\begin{aligned} \exp[\beta(\mu N - E)] &= \exp[\beta\mu(n_0 + n_1 + ...) - \beta(\varepsilon_0 n_0 + \varepsilon_1 n_1 + ...)] \\ &= \exp[\beta(\mu - \varepsilon_0)n_0]\ \exp[\beta(\mu - \varepsilon_1)n_1].... \\ &= \prod_{i=0}^{\infty} \exp[\beta(\mu - \varepsilon_i)n_i] \end{aligned}$$

Then the partition for the grand canonical ensemble

$$Z_G = \sum_{N=0}^{\infty}(\sum_{n_0=0}^{\infty}\sum_{n_1=0}^{\infty}...\prod_{i=0}^{\infty}\exp[\beta(\mu - \varepsilon_i)n_i]\,\delta_{N,n_0+n_1+n_2+...})$$

The factor $\delta_{N,n_0+n_1+n_2+...}$ is required for the condition of the fixed N such that

$$N = n_0 + n_1 + n_2 + ... + n_i + ...$$

In order to simplify this expression, we just discuss the mathematics using the two problems. These problems are discussed in Widom's textbook on statistical mechanics.

B. Widom, Statistical Mechanics, A Concise Introduction for Chemists (Cambridge, 2002).

((**Problem-1**))
Compare the two double sums

$$S_1 = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} x^m y^n , \qquad S_2 = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} x^m y^n \delta_{m+n,6}$$

where in S_1 the summations over *m* and *n* are independent while in S_2 they are not: in each term of the double sum S_2 the sum of *m* and *n* is required to be 6. Show that

$$S_1 = S_2$$

((**Solution**))

$$S_1 = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} x^m y^n = \frac{1}{1-x}\cdot\frac{1}{1-y}$$

$$\begin{aligned} S_2 &= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} x^m y^n \delta_{m+n,6} \\ &= y^6 + xy^5 + x^2y^4 + x^3y^3 + x^4y^2 + x^5y^1 + x^6 \\ &= \frac{y^7 - x^7}{y - x} \end{aligned}$$

Note that S_1 can be written out as the product

$$S_1 = \frac{1}{1-x}\cdot\frac{1}{1-y} = (1 + x + x^2 + x^3 + ...)(1 + y + y^2 + y^3 + ...)\,,$$

which is then expanded, it is seen that all the terms

$$y^6 + xy^5 + x^2y^4 + x^3y^3 + x^4y^2 + x^5y^1 + x^6$$

of S_2 appear among the terms in that expansion, as a small subset of them.

((**Problem-2**))
Show by explicitly evaluating

$$S_3 = \sum_{N=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty} x^m y^n \delta_{m+n,N}$$

that it is identical to the

$$S_1 = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} x^m y^n = \frac{1}{1-x}\cdot\frac{1}{1-y}$$

((**Solution**))
S_3 can be evaluated as follows.

$$S_3=\sum_{N=0}^{\infty}\left(\frac{y^N-x^N}{y-x}\right)$$
$$=\frac{1}{y-x}\sum_{N=0}^{\infty}\left(y^N-x^N\right)$$
$$=\frac{1}{y-x}[\frac{1}{1-y}-\frac{1}{1-x}]$$
$$=\frac{1}{(1-y)(1-x)}$$

which is equal to S_1.

It can follow from the above examples that

$$Z_G=\sum_{N=0}^{\infty}(\sum_{n_0=0}^{\infty}\sum_{n_1=0}^{\infty}...\prod_{i=0}^{\infty}\exp[\beta(\mu-\varepsilon_i)n_i]\ \delta[N-(n_0+n_1+n_2+...)])$$
$$=\sum_{n_0=0}^{\infty}\sum_{n_1=0}^{\infty}...\prod_{i=0}^{\infty}\exp[\beta(\mu-\varepsilon_i)n_i]$$
$$=\prod_{i=0}^{\infty}\sum_{n_i=0}^{\infty}\exp[\beta(\mu-\varepsilon_i)n_i]$$

where we use the mathematical equivalence

$$\sum_{N=0}^{\infty}(\sum_{n_0=0}^{\infty}\sum_{n_1=0}^{\infty}...\ \delta[N-(n_0+n_1+n_2+...)])=\sum_{n_0=0}^{\infty}\sum_{n_1=0}^{\infty}...$$

For the boson system (n_i = 0, 1, 2, …, ∞)

$$Z_G=\prod_{i=0}^{\infty}\frac{1}{1-e^{\beta(\mu-\varepsilon_i)}}$$

For the fermion system n_i = 0, 1)

$$Z_G=\prod_{i=0}^{\infty}[1+e^{\beta(\mu-\varepsilon_i)}]$$

2. Relation between the Grand canonical ensemble and canonical ensemble

The grand canonical ensemble can be expressed in terms of the canonical ensemble

$$Z_G = \sum_{N=0}^{\infty} z^N Z_{CN} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_{CN}$$

where Z_{CN} is the N-particle partition function of canonical ensemble, and is defined by

$$Z_{CN} = \sum_{i[N]} \exp[-\beta E_i(N)]$$

and

$$z = e^{\beta\mu} \qquad \text{(the fugacity).}$$

Thus the partition function of the grand canonical ensemble is expressed by

$$\begin{aligned}
Z_G &= \sum_{N=0}^{\infty}\sum_{i[N]} \exp[\beta(\mu N - E_i(N)] \\
&= \sum_{N=0}^{\infty}\sum_{i[N]} z^N \exp[-\beta E_i(N)] \\
&= \sum_{N=0}^{\infty} z^N Z_{CN}
\end{aligned}$$

We note that

$$\begin{aligned}
\frac{\partial}{\partial z} Z_G &= \frac{\partial}{\partial z}\sum_{N=0}^{\infty} z^N Z_{CN} \\
&= \sum_{N=0}^{\infty} N z^{N-1} Z_{CN} \\
&= \frac{1}{z}\sum_{N=0}^{\infty} N z^N Z_{CN}
\end{aligned}$$

or

$$\langle N \rangle_G = \frac{1}{Z_G}\sum_{N=0}^{\infty} N z^N Z_{CN} = \frac{z}{Z_G}\frac{\partial}{\partial z} Z_G = z\frac{\partial}{\partial z}\ln Z_G$$

3. Derivation of the Fermi-Dirac distribution function

Using the relation,

$$\ln Z_G = \sum_i \ln[1 + e^{\beta(\mu-\varepsilon_i)}] = \sum_i \ln[(+ze^{-\beta\varepsilon_i})$$

we get

$$\begin{aligned}
\langle N \rangle &= z\frac{\partial}{\partial z}\ln Z_G \\
&= \sum_i \frac{ze^{-\beta\varepsilon_i}}{1+ze^{-\beta\varepsilon_i}} \\
&= \sum_i \frac{1}{\frac{1}{z}e^{\beta\varepsilon_i}+1} \\
&= \sum_i \langle n_i \rangle
\end{aligned}$$

or

$$\langle n_i \rangle = \frac{1}{\frac{1}{z}e^{\beta\varepsilon_i}+1} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}+1}$$

Fermi-Dirac distribution function.

4. Derivation of the Bose-Einstein distribution function

Using the relation,

$$\ln Z_G = -\sum_i \ln[1 - e^{\beta(\mu-\varepsilon_i)}] = -\sum_i \ln(1 - ze^{-\beta\varepsilon_i})$$

we get

$$\begin{aligned}
\langle N \rangle &= z\frac{\partial}{\partial z}\ln Z_G \\
&= -\sum_i \frac{(-z)e^{-\beta\varepsilon_i}}{1-ze^{-\beta\varepsilon_i}} \\
&= \sum_i \frac{1}{\frac{1}{z}e^{\beta\varepsilon_i}-1} \\
&= \sum_i \langle n_i \rangle
\end{aligned}$$

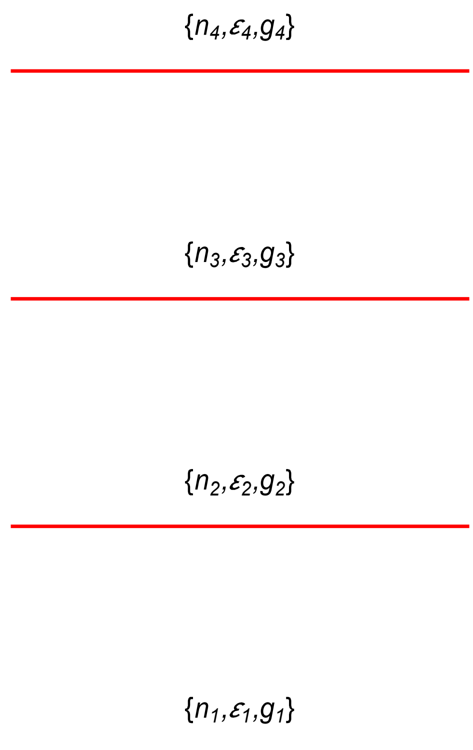
or

$$\langle n_i \rangle = \frac{1}{\frac{1}{z}e^{\beta\varepsilon_i} - 1} = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}$$

Bose-Einstein distribution function

5. Example

We discuss the relation between the partition function of the grand canonical ensemble and that of the canonical ensemble using a simple example.



For example, we use $N = 6$. We need to calculate the following partition function.

$$Z_G(N) = \sum_{\{n1,n2,n3,n4\}} \frac{N!}{n_1!n_2!n_3!n_4!}(g_i z)^{n_i} e^{-\beta n_i \varepsilon_i} \delta(n_1 + n_2 + n_3 + n_4, N)$$

$$Z_G(N) = [Z(1)]^N = z^N (Z_{C1})^N$$

where

$$
\begin{aligned}
Z_G(1) &= g_1 z e^{-\beta\varepsilon_1} + g_2 z e^{-\beta\varepsilon_2} + g_3 z e^{-\beta\varepsilon_3} + g_4 z e^{-\beta\varepsilon_4} \\
&= z(g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2} + g_3 e^{-\beta\varepsilon_3} + g_4 e^{-\beta\varepsilon_4}) \\
&= z Z_{C1}
\end{aligned}
$$

where Z_{C1} is the on-particle partition function of the canonical ensemble

$$
Z_{C1} = g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2} + g_3 e^{-\beta\varepsilon_3} + g_4 e^{-\beta\varepsilon_4}
$$

The partition function of the grand canonical ensemble:

$$
\begin{aligned}
Z_G &= 1 + Z_G(1) + Z_G(2) + ... \\
&= 1 + z Z_{C1} + z^2 (Z_{C1})^2 + ... \\
&= \frac{1}{1 - z Z_{C1}}
\end{aligned}
$$

((**Mathematica**))

```
Clear["Global`*"];
J2[N1_] :=
 Sum[N1!/(n1! n2! n3! n4!) (g1 z)^n1 Exp[-β (n1 E1)] (g2 z)^n2
   Exp[-β (n2 E2)] (g3 z)^n3 Exp[-β (n3 E3)]  (g4 z)^n4
   Exp[-β (n4 E4)] KroneckerDelta[n1 + n2 + n3 + n4 - N1],
  {n1, 0, N1}, {n2, 0, N1}, {n3, 0, N1},
  {n4, 0, N1}] // Simplify;
J2[6]
```

$$
e^{-6 (E1+E2+E3+E4) \beta} \left(e^{(E2+E3+E4) \beta} g1 + e^{(E1+E3+E4) \beta} g2 + e^{(E1+E2+E4) \beta} g3 + e^{(E1+E2+E3) \beta} g4\right)^6 z^6
$$

REFERENCES

C. Kittel, Elementary Statistical Physics (John Wiley & Sons, 1958).

B. Widom, Statistical Mechanics, A Concise Introduction for Chemists (Cambridge, 2002).