The "correct" enumeration of the microstates

In the preceding section we saw that an ad hoc diminution in the entropy of an N-particle system by an amount kln(N!),

$$S_{New} = S_{Old} - k \ln N!$$

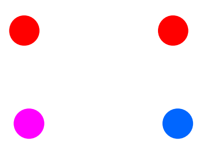
which implies an ad hoc reduction in the number of microstates accessible to the system by a factor (N!),

$$\Gamma_{New} = \frac{\Gamma_{old}}{N!}$$

was able to correct the unphysical features of some of our former expressions.

It is now natural to ask: why, in principle, should the number of microstates, computed in Sec. 1.4, be reduced in this manner?

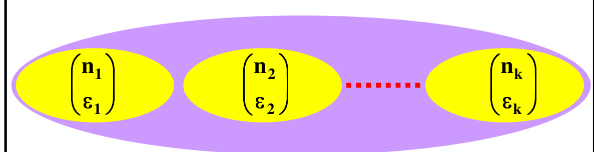
The physical reason for doing so is that the particles constituting the given system are not only identical but also indistinguishable.



accordingly, it is unphysical to label them as No. 1, No. 2, No. 3, etc., and to speak of their being individually in the various single-particle states ε_i.

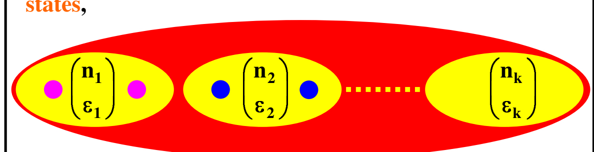
All we can sensibly speak of is their distribution over the states ε_i by numbers, e.g. n_1 particles being in the state ε_1, n_2 in the state ε_2, and so on.

$$E = \sum_i n_i \varepsilon_i$$



Thus, the correct way of specifying a microstate of the system is through the distribution numbers $\{n_i\}$, and not through the statement as to "which particle is in which state".

To elaborate the point, we may say that if we consider two microstates which differ from one another merely in an interchange of two particles in different energy states,



then according to our original mode of counting we would regard these microstates as distinct; in view of the indistinguishability of the particles, however, these microstates are not distinct (for, physically, there exists no way of distinguishing between them).

Combination

$$C(m,n)=\binom{n}{m}=\frac{n!}{m!(n-m)!}$$

ترکیب که در آن نظم یا ترتیب اهمیت ندارد.

تمایزناپذیری ذرات

مکانیک کوانتمی

Permutation

$$P(m,n)=(n)_m=\frac{n!}{(n-m)!}$$

ترتیب که در آن نظم یا ترتیب اهمیت دارد.

تمایزپذیری ذرات

مکانیک کلاسیک

به چند طریق می توان دو تا از سه تا عدد ۳و۲و۱ را کنار هم نوشت؟

1, 2, 3

$$1\begin{cases}1 & 2 & 1\\ 2 & 1 & 2\end{cases}\qquad 2\begin{cases}1 & 3 & 3\\ 3 & 1 & 4\end{cases}\qquad 3\begin{cases}2 & 3 & 5\\ 3 & 2 & 6\end{cases}$$

$$C(m,n)=\binom{n}{m}=C(2,3)=\binom{3}{2}=\frac{3\,!}{2\,!(3-2)!}=3$$

تمایز ناپذیر

$$P(m,n)=(n)_m=P(2,3)=(3)_2=\frac{3\,!}{(3-2)!}=6$$

تمایز پذیر

تعداد حالتهایی که می توان N شیی را که شامل n_1 شیی از یک نوع n_2 شیی از یک نوع دیگر و ... n_k شیی از نوع دیگر هستند را کنار هم نوشت:

$$\begin{pmatrix}\{n_1\} & \{n_2\} & \ldots & \{n_k\}\\ & n_1+n_2+\ldots+n_k=N & & \end{pmatrix}\qquad \begin{pmatrix}E=\sum_i n_i\varepsilon_i\\ N=\sum_i n_i\end{pmatrix}$$

$$\frac{N\,!}{n_1\,!n_2\,!\ldots n_k\,!}$$

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1 2 3 4 5 6 7 8 9 10 11

1 2 3

1 2 3

1 2

1 2

1

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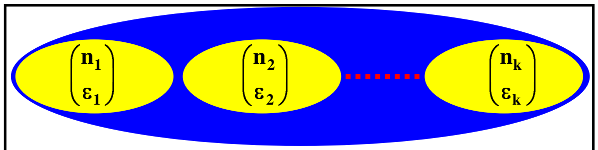
$$\frac{11\,!}{3\,!3\,!2\,!2\,!1\,!}=277200$$



$$\begin{pmatrix} E = \sum_i n_i \varepsilon_i \\ N = \sum_i n_i \end{pmatrix} \qquad \frac{N!}{n_1!\,n_2!\ldots n_k!}$$

If for each i we have $n_i=1$, then everything is okay with the Gibbs correction, for in this case the total number of microstates simplifies as follows:

$$\frac{N!}{1!1!\ldots 1!} = N!$$

Therefore, Gibbs correction yields correct weight factor of one:

$$\frac{1}{N!}\frac{N!}{1!2!\ldots 3!} = \frac{1}{N!}N! = 1$$

However, if this is not so, i.e. $n_i \neq 1$, then weight factor does not simplify to one:

$$\frac{1}{N!}\frac{N!}{n_1!\,n_2!\ldots n_k!} = \frac{1}{n_1!\,n_2!\ldots n_k!}$$

This non unit weight factor indicates that n_i particles with energies ε_i are not similar to n_j particles with different energies ε_j, which means that they are distinguishable.

However, for sure this cannot be true in quantum mechanics, for in quantum one cannot label the electrons, as they are indistinguishable particles.

Therefore, even employing Gibbs correction we cannot state that the problem is solved completely, for the weight factor remains:

$$W\{n_i\} = \frac{1}{n_1!\,n_2!\ldots n_k!}$$

We cannot change the above weight factor to unit, for we are not aware about the occupation numbers of n_1, $n_2,\ldots,n_k$.

We shall back to this point in chapter 5, where within quantum mechanics we will fix the problem improving the weakness of the Gibbs paradox.