

Figure 3.7 An  $N$  particle system of free particles with one particle in each of  $N$  boxes. The energy is  $N$  times that for one particle in one box.

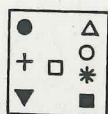


Figure 3.8 Atoms of different species in a single box.

If we have one atom in each of  $N$  distinct boxes (Figure 3.7), the partition function is the product of the separate one atom partition functions:

$$Z_{N \text{ boxes}} = Z_1(1) Z_1(2) \cdots Z_1(N), \quad (66)$$

because the product on the right-hand side includes every independent state of the  $N$  boxes, such as the state of energy

$$\varepsilon_\alpha(1) + \varepsilon_\beta(2) + \cdots \varepsilon_\zeta(N), \quad (67)$$

where  $\alpha, \beta, \dots, \zeta$  denote the orbital indices of atoms in the successive boxes. The result (66) also gives the partition function of  $N$  noninteracting atoms all of different species in a single box (Figure 3.8):

$$Z_\alpha(\bullet) Z_\beta(\square) Z_\gamma(*) \cdots Z_\zeta(\triangle),$$

this being the same problem because the energy eigenvalues are the same as for (67). If the masses of all these different atoms happened to be the same, the total partition function would be  $Z_1^N$ , where  $Z_1$  is given by (62).

When we consider the more common problem of  $N$  identical particles in one box, we have to correct  $Z_1^N$  because it overcounts the distinct states of the  $N$  identical particle system. Particles of a single species are not distinguishable: electrons do not carry registration numbers. For two labeled particles  $\bullet$  and  $*$  in a single box, the state  $\varepsilon_\alpha(\bullet) + \varepsilon_\beta(*)$  and the state  $\varepsilon_\alpha(*) + \varepsilon_\beta(\bullet)$  are distinct states, and both combinations must be counted in the partition function. But for two identical particles the state of energy  $\varepsilon_\alpha + \varepsilon_\beta$  is the identical state as  $\varepsilon_\beta + \varepsilon_\alpha$ , and only one entry is to be made in the state sum in the partition function.