

3

The Standard and the Super-standard (*Canonical and Grand Canonical*) Ensembles

3-1 Introducing the Standard (Canonical) Ensemble

Like I said before, the homogeneous ensemble is not so handy after all as a working tool. It is conceptually easy, but does not lend itself to a straightforward calculation of thermodynamic quantities. In particular, it is a precondition that the system be very large in order that any explicit result may at all be arrived at. Thus, we had to cover a lot of ground to arrive at the entropy of as simple a system as the classical ideal gas, and then too we had to assume that the gas is close to the thermodynamic limit.

A much better approach, if less fundamental from the conceptual point of view, is to use what may be termed the *standard ensemble* (usually called the *canonical ensemble*), based on the *temperature specification* of the system under consideration.

The temperature specification corresponds to a situation in which the system is not isolated from its surroundings, but is instead kept in thermal contact with a ‘reservoir’ at some specified temperature, say, T .

In thermodynamics and statistical mechanics, a reservoir means a large body, large compared to the system or systems under consideration, that can exchange heat with these systems without undergoing any appreciable change in temperature. For instance, the atmosphere plays the role of a reservoir for bodies of not too large dimensions, in numerous situations of practical interest.

Just as a body isolated from its surroundings goes over, in the long run, to an equilibrium configuration characterised by some specific value of

It is more useful to write this equality in terms of logarithms:

$$\ln P(\Psi(E)) = \ln C + \ln W(\mathcal{E} - E), \quad (3-2)$$

and then to expand the second term on the right hand side in a Taylor's series :

$$\ln P(\Psi(E)) = \ln C + \ln W(\mathcal{E}) - \frac{d \ln W(\mathcal{E})}{d \mathcal{E}} E. \quad (3-3)$$

The subsequent terms in the series are really insignificant since, \mathcal{R} being much larger than \mathcal{S} , E is on the average infinitesimally small compared to \mathcal{E} .

The second term on the right-hand side of (3-3) does not refer to the system \mathcal{S} , and so we lump it together with the first term so as to obtain, say,

$$\ln P(\Psi(E)) = \ln A - \frac{d \ln W(\mathcal{E})}{d \mathcal{E}} E, \quad (3-4)$$

where A is some new constant. In accordance with the second fundamental postulate (1-44), $\ln W(\mathcal{E})$ is just k_B^{-1} times $S^{(\mathcal{R})}(\mathcal{E})$, the entropy of \mathcal{R} at internal energy \mathcal{E} , and thus the derivative in (3-4) is nothing but $(k_B T)^{-1}$, T being the temperature of the reservoir, and *also* the temperature of the system \mathcal{S} .

If \mathcal{S} happens to be a small system so that thermodynamic functions do not make sense for it, then we *define* its temperature to be the temperature with which it is in equilibrium.

We thus arrive at

$$P(\Psi(E)) = A \exp(-E/(k_B T)). \quad (3-5a)$$

In this equation, A can evidently be looked upon as a normalisation constant, to be determined from the fact that the total probability of occurrence of all the distinct states of the system is to be 1. The quantity $(k_B T)^{-1}$ is so all-pervasive in equations of statistical mechanics that it is only fair to reserve a separate symbol for it. Since (2-62) tells us that it is just the undetermined multiplier β of Chapter 2, we write

$$P(\Psi(E)) = A \exp(-\beta E). \quad (3-5b)$$

Summing over all the distinct states Ψ of the system and noting that the summed probability must be unity, we find

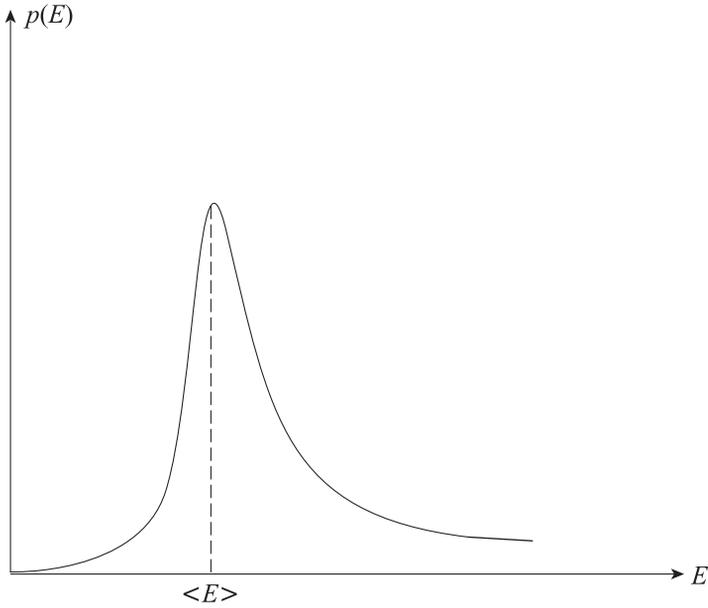


Fig. 3-1 Illustrating the way the energy distribution function $p(E)$ is peaked around an energy value approximately equal to the mean energy.

Since $p(E)$ gives the probability in the ensemble for energy E , we have,

$$\begin{aligned}
 \langle E^2 \rangle &= \sum_{\substack{\text{all energy} \\ \text{values}}} E^2 p(E) \\
 &= \sum_{\substack{\text{all} \\ \text{states}}} E^2 \exp(-\beta E) / Z \\
 &= Z^{-1} \frac{\partial^2}{\partial \beta^2} \sum_{\text{all states}} \exp(-\beta E) \\
 &= Z^{-1} \frac{\partial^2 Z}{\partial \beta^2} \\
 &= \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 \\
 &= -\frac{\partial \langle E \rangle}{\partial \beta} + \langle E \rangle^2,
 \end{aligned} \tag{3-25}$$

where (3-9c) has been made use of.

or, with the help of (3-48b), to

$$\tilde{S} = T^{-1}\langle E \rangle - T^{-1}\tilde{\Gamma} - \mu T^{-1}\langle N \rangle. \quad (3-49b)$$

This relation is analogous to the relation between the entropy, the internal energy, the super-potential, and the number of particles of a thermodynamic system.

Show further that for a thermodynamic system, (3-48b) yields,

$$\tilde{\Gamma} = \Gamma. \quad (3-50)$$

Finally, noting that for a thermodynamic system $\langle E \rangle$ and $\langle N \rangle$ reduce respectively to the internal energy U and the particle number N , show that in the thermodynamic limit (3-49b) leads to

$$\tilde{S} = S \quad (3-51)$$

Thus, the super-potential Γ for a thermodynamic system is related to the super-partition function as

$$\exp(-\beta\Gamma) = \mathcal{Z}, \quad (3-52a)$$

or,
$$\Gamma = -\beta^{-1} \ln \mathcal{Z}, \quad (3-52b)$$

which are relations of fundamental importance for the statistical mechanics of a thermodynamic system in the super-standard ensemble.

3-8.4 Fluctuations in the particle number

The mean squared particle number in the super-standard ensemble is

$$\langle N^2 \rangle = \mathcal{Z}^{-1} \sum_{\Psi} N^2 \exp(-\beta(E - \mu N)). \quad (3-53)$$

Problem 3-10

Prove that (3-53) can be written in the alternative form

$$\langle N^2 \rangle = \mathcal{Z}^{-1} \beta^{-2} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2}, \quad (3-54)$$

and then use (3-40b) to derive, for the fluctuation in particle number,

$$(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 = \beta^{-1} \frac{\partial \langle N \rangle}{\partial \mu}. \quad (3-55)$$
