

## 5. Free energy minimisation

*See Mandl 2.6*

### 5.1. Energy and its fluctuations

We have seen that the energy of a system connected to a heat bath exhibits thermal fluctuations controlled by the Boltzmann distribution. Here we calculate the mean and variance of these fluctuations. The mean energy is defined as usual as:

$$\overline{E} = \sum_i E_i P_i$$

where  $P_i$  is the probability of the system being in microstate  $i$ . Inserting the Boltzmann distribution yields:

$$\overline{E} = \frac{1}{Z} \sum_i E_i \exp(-\beta E_i) = -\frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} \exp(-\beta E_i) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

Note the trick of using the derivative to bring down  $E_i$  from the argument of the exponential. A further manipulation to note is:

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

and we find:

$$\overline{E} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{dT}{d\beta} \frac{\partial \ln Z}{\partial T} = kT^2 \frac{\partial \ln Z}{\partial T}$$

Now we consider fluctuations of the energy. The variance is:

$$\overline{(\Delta E)^2} = \overline{(E - \overline{E})^2} = \overline{E^2} - \overline{E}^2$$

It turns out that this variance is related to the heat capacity  $C$  defined by

$$C \equiv \frac{\partial \overline{E}}{\partial T} = \frac{d\beta}{dT} \frac{\partial \overline{E}}{\partial \beta} = -\frac{1}{kT^2} \frac{\partial \overline{E}}{\partial \beta}$$

The relationship (derived below) is

$$C = -\frac{1}{kT^2} \left[ \overline{E^2} - \overline{E}^2 \right] = \frac{(\overline{\Delta E})^2}{kT^2}$$

### Open to see derivation

In order to demonstrate the relation of the energy fluctuations to the heat capacity, we write out the final expression for  $C$  above using the Boltzmann distribution:

$$C = -\frac{1}{kT^2} \frac{\partial}{\partial \beta} \left( \frac{\sum_i E_i \exp(-\beta E_i)}{Z} \right) = -\frac{1}{kT^2} \left[ -\frac{\sum_i E_i \exp(-\beta E_i)}{Z^2} \frac{\partial Z}{\partial \beta} - \frac{\sum_i E_i^2 \exp(-\beta E_i)}{Z} \right]$$

which recalling:

$$\sum_i E_i \exp(-\beta E_i) = \overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\sum_i E_i^2 \exp(-\beta E_i) = \overline{E^2}$$

yields:

$$C = \frac{1}{kT^2} \left[ \overline{E^2} - \overline{E}^2 \right] = \frac{(\overline{\Delta E})^2}{kT^2}$$

It is interesting to pause and think what this means. The heat capacity can be thought of as the response of a macroscopic variable (the energy) to changing an external variable (the temperature). Thus, the response is related to the fluctuations of the macroscopic variable.

Since  $E$  is proportional to  $N$ , so will be  $C = \partial \overline{E} / \partial T$ . Therefore:

$$\overline{(\Delta E)^2} \propto N$$

and the fractional deviation:

$$\frac{(\overline{\Delta E})^2}{\overline{E}} \propto \frac{1}{\sqrt{N}}$$

From this, we see that for a system in equilibrium with a heat bath, although the energy is a free macroscopic variable, it takes on a sharply defined value  $\overline{E}$ . A consequence is that a large system in equilibrium with a heat bath should have essentially the same behavior as a large isolated system with fixed energy  $\overline{E}$ .

## 5.2. Energy distribution, entropy, and free energy

Since, in the Boltzmann distribution, the energy is a free macroscopic variable, we can label the macrostates of the system by their energy, and the weight of the macrostate of energy  $E$  is  $\Omega(E)$ , the number of microstates with energy  $E$ .

As in chapter 3, we can use the Planck relation to determine the entropy of a macrostate:

$$S(E) = k \ln \Omega(E)$$

We now return to the question of the sharpness of  $E$ . Let us consider again:

$$\bar{E} = \frac{1}{Z} \sum_i E_i \exp(-\beta E_i)$$

Generally, for a system of large  $N$ , we expect many of the microstates to have the same energy. Therefore, rather than sum over all microstates, it is more convenient to sum over the possible values of the energy:

$$\bar{E} = \frac{1}{Z} \sum_E \Omega(E) E \exp(-\beta E)$$

To understand this, realize that we are simply grouping together microstates with the same energy  $E$  of which there are  $\Omega(E)$ .

The same idea of grouping microstates with the same energy gives the probability of the system having energy  $E$ :

$$P(E) = \frac{1}{Z} \Omega(E) \exp(-\beta E)$$

Since we expect  $E \sim N$ ,  $\exp(-\beta E)$  is a sharply decreasing function. Also,  $\Omega(E)$  is exponentially large in  $N$  and  $\Omega$  is a sharply increasing function of  $E$ . The two conspire to give as a product a sharply peaked probability distribution around  $\bar{E}$ . This is plotted in Figure 1

To go further, we rewrite  $P(E)$  and use the Planck relation:

$$P(E) = \frac{1}{Z} \exp\left(-\beta\left(E - \frac{\ln \Omega}{\beta}\right)\right) = \frac{1}{Z} \exp(-\beta(E - TS)) = \frac{1}{Z} \exp(-\beta F)$$

where:

$$F(E) \equiv E - TS(E)$$

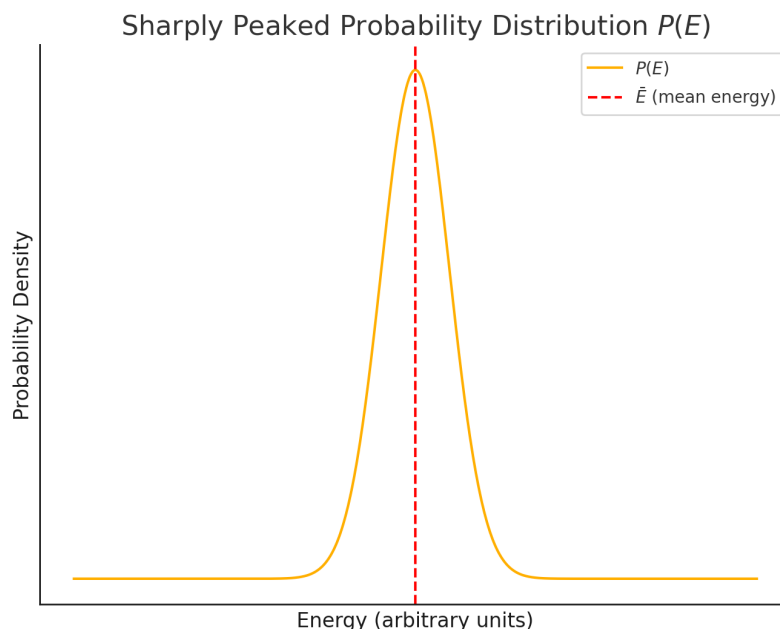


Figure 1: Sharply peaked probability distribution of the energy

$F$  is the Helmholtz free energy, which is often referred to in statistical mechanics simply as the free energy.

Now the peak of  $P(E)$  occurs when the argument of the exponential is maximized. Thus, we see that the equilibrium value of the energy  $E$  is determined by minimizing the free energy. This is a profound and general concept:

**💡 Key Point 11:**

The equilibrium values of the macroscopic properties  $E, \{\alpha\}$  of a system in equilibrium are such as to minimize the free energy  $F(E, \{\alpha\}) \equiv E - TS(E, \{\alpha\})$ .

We write equilibrium values as  $S(T)$ ,  $F(T)$ , etc.

### 5.3. Free energy: The energy–entropy competition

First, consider low  $T$ : here  $F$  is dominated by  $E$ , therefore minimizing  $F$  corresponds to minimizing  $E$  (exactly so for  $T = 0$ ).

Now consider high  $T$ : here  $F$  is dominated by  $S$ , therefore minimizing  $F$  corresponds to maximizing  $S$  (exactly so for  $T = \infty$ ).

Thus, one has a competition between energy and entropy, the arbiter of which is temperature.

However, it should always be borne in mind that equilibrium is such as to maximize the entropy of the universe under the constraint that energy is conserved. For example, in an isolated system, the energy is constant, therefore we just maximize the entropy. For a system in equilibrium with its environment, the energy is free to vary. Thus, the minimization of the free energy for a system in equilibrium tells us the best way to distribute energy between the system and the universe such that the entropy of the universe is maximized.

We now begin to understand the different phases in question 2.5:

- At low temperatures, ice forms. The crystal structure is energetically favorable and releases energy (latent heat of fusion) to the environment, which maximizes the entropy of the universe, i.e., from the viewpoint of the system, energy considerations win.
- At higher temperatures, storing more energy in the system gives the liquid phase (water), which has a high entropy and allows the entropy of the universe to be maximized. From the point of view of the system, entropy wins.

#### 5.4. Utility of the partition function

Let us first write  $Z$  as

$$Z = \sum_E \Omega(E) \exp(-\beta E)$$

In the same way as  $P(E)$  is an extremely sharp function, the summand is very sharply peaked at  $\bar{E}$  and of width  $N^{1/2}$  about the peak. Therefore, we can write

$$Z \approx \Omega(\bar{E}) \exp(-\beta \bar{E}) \times O(N^{1/2})$$

$$= \exp(-\beta F(T)) \times O(N^{1/2})$$

(since  $F(T) = F(\bar{E})$  for a large system in equilibrium). Thus

$$\ln Z = -\beta F(T) + O(\ln N^{1/2})$$

We see the last term can be ignored since we are in the ‘large  $N$ ’ regime where  $N \gg \ln N$ . Thus, the equilibrium value of the free energy

$$F(T) = \bar{E} - TS(T) = -kT \ln Z$$

This is a very important formula.

Also, the expression can be written in terms of the entropy

$$S(T) = k \ln Z + \frac{\overline{E}}{T}$$

Therefore, for a system in equilibrium at temperature  $T$ , all the thermodynamic properties can be obtained from  $Z$  from the following formulae:

💡 Key Point 12:

$$F = -kT \ln Z, \quad \overline{E} = kT^2 \frac{\partial}{\partial T} \ln Z, \quad S = k \ln Z + \frac{\overline{E}}{T}$$