Statistical Physics
Section 3: Fluctuations and Response

3. 1. Fluctuations in the energy of an assembly

Let us consider the Canonical Ensemble. The (internal) energy of an assembly fluctuates randomly about the fixed mean value $\overline{E}$.

First we note that the mean energy may be expressed in the Canonical Ensemble as

$$\begin{aligned} \overline{E} &= \sum_i p_i E_i = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} && (1) \\ &= -\frac{1}{Z_c}\frac{\partial Z_c}{\partial \beta} && (2) \\ &= -\frac{\partial \ln Z_c}{\partial \beta} \; . && (3) \end{aligned}$$

This is a very important idea: we can write the mean value of some observable (here the energy) as the 'logarithmic derivative of Z_c' (i.e. a derivative of $\ln Z_c$). You should make very sure you see how taking the derivative in (2) brings down E_i inside the sum in Z_c.

Now we wish to estimate the size of the mean-square fluctuation, and this is where we take an indirect route and consider the heat capacity C_V (at constant volume):

$$\begin{aligned} C_V &= \left(\frac{\partial \overline{E}}{\partial T}\right)_V = \frac{D\beta}{DT}\frac{\partial \overline{E}}{\partial \beta} \\ &= -\frac{1}{kT^2}\left[-\frac{1}{Z_c}\frac{\partial^2 Z_c}{\partial \beta^2} + \frac{1}{Z_c^2}\left(\frac{\partial Z_c}{\partial \beta}\right)^2\right] && (4) \end{aligned}$$

Where we have used the chain rule for differentiation and (2). Then using (1) and (2) and noting that two derivatives of Z_c with respect to β brings down E_i^2 inside the sum, we can write this as

$$C_V = -\frac{1}{kT^2}\left[-\sum_i E_i^2 p_i + \overline{E}^2\right]$$

and finally we obtain

$$C_V = \frac{1}{kT^2}[\overline{E^2} - \overline{E}^2]. \qquad (5)$$

If we consider the fluctuation of the energy from the mean given by

$$\Delta E = E - \overline{E}, \qquad (6)$$

then square the fluctuation, and take averages, we obtain the mean-square fluctuation as

$$\overline{\Delta E^2} = \overline{E^2 - 2E\overline{E} + \overline{E}^2} = \overline{E^2} - \overline{E}^2. \qquad (7)$$

Comparison of this result with equation (5) yields an explicit expression for the mean-square fluctuation, and taking the square-root of both sides leads to an expression for the root-mean-square fluctuation ΔE_{rms} as

$$\Delta E_{rms} = \left(\overline{\Delta E^2}\right)^{1/2} = (kT^2 C_V)^{1/2}.$$

Evidently the relative fluctuation, i.e. the rms fluctuation on the scale of the mean, may be written as

$$\frac{\Delta E_{rms}}{\overline{E}} = \frac{\sqrt{kT^2 C_V}}{\overline{E}} \sim \frac{1}{N^{1/2}}, \tag{8}$$

where the last step follows from the fact that both $\overline{E}$ and C_V are extensive quantities and therefore depend linearly on N. For Avogadro-sized assemblies, we have $N \sim 10^{24}$ and hence the relative fluctuation in the energy has a root-mean-square value of about $\sim 10^{-12}$. This is less than any experimental precision could detect so the value of the energy is *sharp*.

The property (8) is often referred to as the **equivalence** of the Canonical and Microcanonical Ensembles i.e. in the Microcanonical Ensemble the energy is strictly fixed and only microstates with the same energy are available whereas in the Canonical Ensemble microstates of all energy are available but are sampled with the Canonical probabilities which depend on E_i. The result is that the actual energy fluctuations vanish in the large N limit and one expects that the physical properties of the Microcanonical and Canonical Ensembles are the same in this limit.

3. 2. Magnetisation Fluctuations

Let us consider an assembly in an applied external magnetic field H and write the energy of a microstate as

$$E_i = E_i(H=0) - \mu_0 M_i H \tag{9}$$

where M_i is the magnetisation of the assembly in microstate i and μ_0 is a constant (nothing to do with chemical potential). Thus H is the external field conjugate to the macroscopic observable M.

The mean magnetisation may be expressed in the Canonical Ensemble as

$$\overline{M} = \sum_i p_i M_i = \frac{\sum_i M_i \exp(-\beta E_i(0) + \beta\mu_0 M_i H)}{Z_c} \tag{10}$$

$$= \frac{1}{\beta\mu_0 Z_c}\frac{\partial Z_c}{\partial H} = \frac{1}{\beta\mu_0}\frac{\partial \ln Z_c}{\partial H} \tag{11}$$

Again we see the idea of writing the expectation value of an observable (here M) as the derivative of $\ln Z_c$ with respect to the conjugate field (here H). Again you should make sure you have this at your fingertips.

In the tutorial you are invited to show that

$$\overline{\Delta M^2} = \frac{kT}{\mu_0}\chi \tag{12}$$

where

$$\chi = \left(\frac{\partial \overline{M}}{\partial H}\right)_{T,V} \tag{13}$$

is the isothermal susceptibility.

3. 3. Density fluctuations

Let us now consider an assembly in the Grand Canonical Ensemble and study the fluctuations in the number of particles— the number of particles in an assembly in the Grand

Canonical Ensemble will fluctuate about the mean value $\overline{N}$. We can obtain an indication of the significance of such fluctuations by deriving an expression for the rms value of the fluctuation $\Delta N = N - \overline{N}$.

We begin by noting how we may express $\overline{N}$:

$$\begin{aligned} \overline{N} &= \sum_{i,N} N p_{i,N} = \frac{\sum_{i,N} N \exp(-\beta(E_{i,N} - \mu N)}{\sum_{i,N} \exp(-\beta(E_{i,N} - \mu N))} && (14) \\ &= \frac{1}{\beta}\frac{1}{\mathcal{Z}_{gc}}\frac{\partial \mathcal{Z}_{gc}}{\partial \mu} = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}_{gc}}{\partial \mu} && (15) \end{aligned}$$

We see, this time in the GCE, how we express the mean of a macroscopic property (here particle number) as the derivative of the logarithm of the Grand Canonical partition function with respect to the conjugate 'field' μ.

Recalling the Grand Canonical bridge equation $\Phi = -kT \ln \mathcal{Z}_{gc}$ we can write this as

$$\overline{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \tag{16}$$

which recovers a thermodynamic relationship (see definition of Φ in section 2).

Now from (15) we have

$$\begin{aligned} \frac{\partial \overline{N}}{\partial \mu} &= \frac{1}{\beta}\frac{\partial^2 \ln \mathcal{Z}_{gc}}{\partial^2 \mu} && (17) \\ &= \frac{1}{\beta}\left[\frac{1}{\mathcal{Z}_{gc}}\frac{\partial^2 \mathcal{Z}_{gc}}{\partial \mu^2} - \frac{1}{\mathcal{Z}_{gc}^2}\left(\frac{\partial \mathcal{Z}_{gc}}{\partial \mu}\right)^2\right] && (18) \\ &= \beta\left[\overline{N^2} - \overline{N}^2\right] . && (19) \end{aligned}$$

Finally we have

$$\overline{\Delta N^2} = kT\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} . \tag{20}$$

Since we expect the rhs to be extensive we have

$$\frac{\Delta N_{rms}}{\overline{N}} \sim \frac{1}{\overline{N}^{1/2}} . \tag{21}$$

Thus the typical particle number fluctuation vanishes on the scale of the mean, for large assemblies. Again this is referred to as the equivalence of the Grand Canonical and Canonical Ensembles in the thermodynamic limit.

3. 4. General Theorem

If we have some macroscopic observable A with conjugate field f we can write the energy of a microstate as

$$E_i = E_i(0) - A_i f \tag{22}$$

where A_i is the value of the observable in microstate i and $E_i(0)$ is the energy at $f = 0$ i.e. this term does not involve f.

Let us work on the Canonical Ensemble (a similar general theorem can be deduced for the Grand Canonical). Following the development of subsection 3.1 we deduce

$$\beta\overline{A} = \frac{\partial \ln Z_c}{\partial f} \tag{23}$$

and

$$\chi_{AA} \equiv \frac{\partial \overline{A}}{\partial f} = \beta\overline{\Delta A^2} \tag{24}$$

Notes

1. χ_{AA} is a 'generalised susceptibility' i.e. it is the *response* of observable A to a change in the field conjugate to A, hence the two subscripts.

2. Since we expect

$$\chi_{AA} \propto N \tag{25}$$

   we have

$$\frac{\left(\overline{\Delta A^2}\right)^{1/2}}{N} = \frac{\Delta A_{rms}}{N} \sim \frac{1}{N^{1/2}} \,. \tag{26}$$

   Therefore the typical fluctuation on the scale of the mean vanishes in the large N limit. Thus thermodynamic observables are sharply defined in the large N limit and this is why it is referred to as the thermodynamic limit. As we have discussed the vanishing of fluctuations (on the scale of the mean) also implies the equivalence of ensembles.

3. Although we expect $\chi_{AA} \propto N$, it is possible for the coefficient of proportionality to diverge at some parameter values. In this case the above argument for vanishing fluctuations breaks down and we would have large scale fluctuations. This is realised at certain parameter values where *phase transitions* occur.