Chapter 3

Canonical Ensemble

Often we have a system in contact with a thermal reservoir, with which it can exchange energy. The canonical formalism allows us to calculate the probability that the system is in a particular energy state in this case.

3.1   Boltzmann Distribution

Consider a small system in thermal contact with a large heat reservoir. The total energy of the system is U, and we transfer a small amount of energy ϵ to the system, hence the reservoir has energy $U - \epsilon$. What is the probability that the system has energy ϵ? We will assume that the system is non-degenerate, so only has one way of having energy ϵ. The number of ways the system can have energy ϵ is equal to the nuber of ways the reservoir can have the rest of the energy, i.e. $U - \epsilon$. We can compute this as follows.

$$
\begin{aligned}
\ln W_{\text{res}}(U - \epsilon) &= \ln W_{\text{res}}(U) - \epsilon \frac{d}{dU} \ln W_{\text{res}}(U) + \ldots & (3.1) \\
&\approx \ln W_{\text{res}}(U) - \frac{\epsilon}{k_B T} & (3.2)
\end{aligned}
$$

where W_{res} denotes the number of microstates in the reservoir, and we have used Taylor's theorem to expand the expression on the right hand side, as well as the result $\frac{\partial S}{\partial U} = k_B \frac{\partial \ln W}{\partial U} = \frac{1}{T}$. Hence (by exponentiating the previous equation) the probability that the system has energy ϵ is

$$
P(\epsilon) \propto W_{\text{res}}(U - \epsilon) = \exp\left(-\frac{\epsilon}{k_B T}\right) \tag{3.3}
$$

This is called the *Boltzmann factor*. To calculate the probability distribution we require a normalisation factor, given by

$$
Z = \sum_j \exp\left(-\frac{\epsilon_j}{k_B T}\right) \tag{3.4}
$$

where j represents a sum over all states of the system, including any degeneracy. This expression is called the *partition function*, and plays a crucial role in statistical physics. The Boltzmann (probability) distribution is then given by

$$
P(\epsilon_j) = \exp\left(-\frac{\epsilon_j}{k_B T}\right) / Z \tag{3.5}
$$

Examples

1. Isothermal atmosphere model – in the atmosphere air molecules are acted upon by gravity, but also have some thermal energy. Their height distribution (assuming that the temperature in the atmosphere is uniform) should follow a Boltzmann distribution, so the density $\rho(h)$ is

$$\rho(h) \propto \exp\left(-\frac{mgh}{k_B T}\right) \tag{3.6}$$

This gives a basic explanation as to why the atmosphere thins at the top of mountains.

2. Maxwell-Boltzmann distribution for gas velocity – can be worked out from the Boltzmann factor. Each particle in the gas has kinetic energy $E = \frac{1}{2}m\mathbf{v}^2$. If we put this into the Boltzmann probability distribution we find

$$P(v_x, v_y, v_z)dv_x dv_y dv_z \propto \exp\left(-\frac{mv_x^2 + mv_y^2 + mv_z^2}{2k_B T}\right)dv_x dv_y dv_z. \tag{3.7}$$

This is the probability that a gas particle is found with velocity component v_x to $v_x + dv_x$, and similarly for v_y and v_z. To calculate the distribution of the *magnitude* of the velocities we convert to spherical polar coordinates, and hence work in terms of the magnitude v, and the angular coordinates of the velocity vector θ and ϕ. By integrating over all possible angles (i.e. the surface of a sphere) we find the distribution for the magnitude is

$$P(v)dv \propto \exp\left(-\frac{mv^2}{2k_B T}\right)4\pi v^2 dv. \tag{3.8}$$

This probability distribution can be normalised to give

$$P(v) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \tag{3.9}$$

Here the factor v^2 can be thought of as a degeneracy factor (the number of states with velocity v).

3.2   The two level system

An important example that illustrates many of the principles of Statistical Physics is the two level system. Here we suppose that a system with two energy levels 0 and ϵ is in contact with a heat reservoir at a temperature T. The partition function for the system is (summing over the Boltzmann factors for the two states)

$$Z = 1 + \exp\left(-\frac{\epsilon}{k_B T}\right) \tag{3.10}$$

The probability of the occupation of the lower and upper levels are

$$p(0) = \frac{1}{Z} \;\; ; \;\; p(\epsilon) = \frac{1}{Z}\exp\left(-\frac{\epsilon}{k_B T}\right) \tag{3.11}$$

The average energy of the system (this is the internal energy, U, in thermodynamics) is

$$U = \langle E \rangle = \sum_i \epsilon_i p_i = \epsilon p(\epsilon) = \frac{\epsilon}{1 + \exp\left(\frac{\epsilon}{k_B T}\right)}. \tag{3.12}$$

Hence at high temperature $(k_B T \gg \epsilon)$ $\langle E \rangle \to \frac{\epsilon}{2}$ and the levels are equally occupied. However, at low temperature $(k_B T \ll \epsilon)$ the occupation of the upper level is suppressed by the Boltzmann factor and $\langle E \rangle \to \epsilon \exp\left(-\frac{\epsilon}{k_B T}\right)$. The heat capacity of the system can be calculated from the derivative of the energy

$$C_V = \frac{d}{dT} U = k_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{\exp\left(\frac{\epsilon}{k_B T}\right)}{\left[1 + \exp\left(\frac{\epsilon}{k_B T}\right)\right]^2} \tag{3.13}$$

At high temperature $(k_B T \gg \epsilon)$, $C_V \to k_B \left(\frac{\epsilon}{k_B T}\right)^2$, i.e. the heat capacity becomes very small. This is because the system cannot absorb any more heat as both levels are equally occupied. At low temperature $(k_B T \ll \epsilon)$ the heat capacity rises from zero very quickly, and consequently there is a peak in the heat capacity at approximately $k_B T = 0.42\epsilon$. This is known as a Schottky hump or Schottky anomaly. A maximum like this occurring in experimental data is indicative of a pair of low lying energy states.

3.3 The partition function, Z

The partition function can be used to calculate averages, standard deviations, and the free energy of the system. Hence, once we have calculated the partition function, we can work out all the properties of the system we require. One way to see this is from the Gibbs expression for the entropy. Substitution of the Boltzmann probability distribution into this gives

$$\begin{aligned} S &= -k_B \sum_i p_i \ln p_i & (3.14) \\ &= -k_B \sum_i p_i \left(-\frac{\epsilon_i}{k_B T} - \ln Z\right) & (3.15) \\ &= \frac{1}{T} \underbrace{\sum_i p_i \epsilon_i}_{=\langle E \rangle} + k_B \underbrace{\sum_i p_i \ln Z}_{=1} & (3.16) \\ &= \frac{\langle E \rangle}{T} + k_B \ln Z & (3.17) \\ \Rightarrow F &= \langle E \rangle - TS = -k_B T \ln Z & (3.18) \end{aligned}$$

This link between the Helmholtz free energy F and the partition function Z provides a bridge between thermodynamic quantities, and the microscopic description of statistical physics.

An alternative way of working out average quantities is by differentiating the partition function. For example, the average energy of the system is given by

$$\langle E \rangle = \sum_i p_i \epsilon_i \tag{3.19}$$

However, if we differentiate the partition function with respect to $\beta = \frac{1}{k_B T}$ then

$$\frac{\partial}{\partial \beta} Z = \frac{\partial}{\partial \beta} \sum_i e^{-\beta \epsilon_i} = -\sum_i \epsilon_i e^{-\beta \epsilon_i} = -Z \sum_i \epsilon_i \underbrace{\frac{e^{-\beta \epsilon_i}}{Z}}_{p_i} = -Z \langle E \rangle \tag{3.20}$$

$$\Rightarrow \langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \tag{3.21}$$

This method can also be used for higher moments of the energy too, for example

$$
\langle E^2 \rangle \quad = \quad \sum_i p_i \epsilon_i^2 \tag{3.22}
$$

$$
= \quad \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} \sum_i e^{-\beta \epsilon_i} \tag{3.23}
$$

$$
= \quad \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z \tag{3.24}
$$

$$
= \quad \frac{\partial^2}{\partial \beta^2} \ln Z + \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 \tag{3.25}
$$

This expression is the key for calculating fluctuations of the energy, and illustrates how fluctuations can be calculated in general. We can rearrange it to read

$$
\langle E^2 \rangle - \langle E \rangle^2 \quad = \quad \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z - \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 \tag{3.26}
$$

$$
= \quad \frac{\partial^2}{\partial \beta^2} \ln Z \tag{3.27}
$$

$$
= \quad \frac{\partial^2}{\partial \beta^2} (-\beta F) \tag{3.28}
$$

It can be shown that $C_v = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$, and hence that the fluctuations in the energy are given by

$$
\langle E^2 \rangle - \langle E \rangle^2 = \langle (\Delta E)^2 \rangle = k_B T^2 C_V \tag{3.29}
$$

Microscopic meaning of heat and work

The Gibbs entropy provides us with a microscopic connection to the work done by a system. The differential of the Gibbs entropy is given by

$$
dS = -k_B \sum_i dp_i (\ln p_i + dp_i) \tag{3.30}
$$

If we substitute into this the Boltzmann probability distribution then

$$
dS \quad = \quad -k_B \sum_i \left(dp_i \left(-\frac{\epsilon_i}{k_B T} - \ln Z \right) + 0 \right) \tag{3.31}
$$

$$
= \quad k_B \sum_i \frac{\epsilon_i dp_i}{k_B T} \tag{3.32}
$$

$$
\Rightarrow T dS \quad = \quad \sum_i \epsilon_i dp_i \tag{3.33}
$$

where we have used the fact that $\sum_i dp_i = 0$, as $\sum_i p_i = 1$. This is the heat supplied, $đQ$. If we use the expression for the average energy $U = \sum_i \epsilon_i p_i$, we can find the work done

$$
dU = \underbrace{\sum_i d\epsilon_i p_i}_{đW} + \underbrace{\sum_i \epsilon_i dp_i}_{đQ} \tag{3.34}
$$

Hence the microscopic definitions of heat and work are given by

$$\dbar W = \sum_i d\epsilon_i p_i \quad \text{and} \quad \dbar Q = \sum_i \epsilon_i dp_i \tag{3.35}$$

i.e. heat corresponds to a change in the probability distribution, but the underlying levels remain unchanged. Work corresponds to a systematic shift in the energy levels, with a fixed probability distribution.

3.4   Classical statistical physics

The ideas of statistical physics can be applied to both quantum systems, where typically we have a discrete set of quantised energy levels, classical systems, where we have a continuum of energy levels. The idea of summing over all states is rather more complicated in classical physics, as things soon get messy when summing over a continuum of states. We will mention a few details of classical statistical mechanics here, so we can derive an important result: the principle of equipartition of energy.

To do statistical mechanics of classical systems, we need to define the probability distribution $\rho(p_i, x_i)$, where p_i and x_i are momentum and position coordinates of each particle in the system. This probability distribution is defined over the space of position and momentum (p_i, x_i), known as *phase space*. For a closed system, we must have a total energy between U and $U + dU$, and all states in this interval are equally likely (by the principle of equal a priori probabilities), whilst those outside it have probability zero. The entropy is then calculated by integrating overall of these states

$$S = -k_B \int \rho \ln \rho d\Omega \tag{3.36}$$

where $d\Omega = \Pi_i dx_i dp_i$. The Boltzmann distribution and the partition function follow in exactly the same way as before

$$\rho = \frac{e^{-E/(k_B T)}}{Z} \tag{3.37}$$

$$Z = \int e^{-E/(k_B T)} d\Omega \tag{3.38}$$

The principle of equipartition of energy

Equipartition of energy is arises from calculating the average energy of a quadratic degree of freedom using the Boltzmann distribution. Consider a degree of freedom such as the momentum that can take on a continuum of values (at least classically). Its energy is given by

$$\epsilon = \frac{p^2}{2m} \tag{3.39}$$

So the Boltzmann probability distribution is

$$\rho(p) = \frac{e^{-\frac{p^2}{2mk_B T}}}{Z} \tag{3.40}$$

where $Z = \int_{-\infty}^{\infty} e^{-\frac{p^2}{2mk_B T}} dp = \sqrt{2\pi m k_B T}$.

If we calculate the mean energy using the Boltzmann probability distribution we obtain

$$\langle \epsilon \rangle = \int_{-\infty}^{\infty} \frac{p^2}{2m} e^{-\frac{mv^2}{2k_B T}} dp \sqrt{\frac{1}{2\pi m k_B T}} = \frac{k_B T}{2} \tag{3.41}$$

This is a *classical* result and relies on the fact that the energy levels form a continuum. It breaks down in the quantum limit, where the discreteness of energy levels becomes apparent.

The heat capacity of a classical system can be evaluated by counting up the degrees of freedom and then differentiating the average energy with respect to temperature

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \tfrac{1}{2} k_B \text{ per degree of freedom per particle.} \tag{3.42}$$

This assumption breaks down for quantum systems as we shall now see.

3.5   Simple harmonic oscillator

Consider a quantum system, with an infinite number of discrete energy levels in contact with a heat reservoir of temperature T. For example the quantum simple harmonic oscillator with frequency ω has equally spaced energy levels given by $\epsilon_n = \hbar\omega(n + \frac{1}{2})$. The partition function in this case is

$$Z = \sum_n \exp\left(-\frac{\hbar\omega(n+\frac{1}{2})}{k_B T}\right) = \frac{\exp\left(-\frac{\hbar\omega}{2k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \tag{3.43}$$

where we have summed up the geometric series. The probability of occupation of energy level ϵ_n is thus

$$p_n = \frac{\exp\left(-\frac{\hbar\omega(n+\frac{1}{2})}{k_B T}\right)}{Z} \tag{3.44}$$

At low temperatures, when $\hbar\omega \gg k_B T$ then the discreteness of the level spacing is apparent, and the excited states are very rarely populated. At high temperatures $\hbar\omega \ll k_B T$, the levels look like a continuum, and they have the continuous thermal distribution of occupancy. The average energy is given by

$$\langle E \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/(k_B T)} - 1}. \tag{3.45}$$

The first term in this expression is the zero point energy of the oscillator. In the high temperature limit where $\hbar\omega \ll k_B T$ we can expand the exponential in the denominator $exp\left(\frac{\hbar\omega}{k_B T}\right) \approx 1 + \frac{\hbar\omega}{k_B T}$, and hence we recover the classical limit from the equipartition theorem $\langle E \rangle \approx k_B T$ (Note: an oscillator has 2 degrees of freedom, hence we expect $2 \times \frac{1}{2} k_B T$). However, in the low temperature limit where the exponential factor is very large the equipartition theorem does not hold, and the oscillator only has the zero point energy.

3.6   Heat capacity of a hetero-nuclear diatomic gas

If the total energy of a system is made up of various (non-interacting) parts, we can write the energy of the ith microstate as $\epsilon_i = \epsilon_i^{(1)} + \epsilon_i^{(2)} + \ldots$. In this case the partition function can be separated out into a sum for each component

$$Z = \sum_i \exp\left(-\frac{\epsilon_i^{(1)} + \epsilon_i^{(2)} + \ldots}{k_B T}\right) = \sum_i \exp\left(-\frac{\epsilon_i^{(1)}}{k_B T}\right) \sum_i \exp\left(-\frac{\epsilon_i^{(2)}}{k_B T}\right) \ldots \tag{3.46}$$

$$= Z^{(1)} Z^{(2)} \ldots \tag{3.47}$$

The Helmholtz free energy then similarly breaks up into a sum over the different components

$$F = -k_B T \ln Z^{(1)} - k_B T \ln Z^{(2)} - \ldots \tag{3.48}$$

An important example of this is the ideal gas. Here there are contributions to the energy from the three translational modes of the whole molecule, vibrational modes and rotational modes. In principle there are also contributions from the electronic modes and nuclear modes but we will not consider those here. For simplicity we will focus on a diatomic molecule, but the considerations here apply to more complex molecules.

Vibrational modes

The vibrational modes can be modelled as a simple harmonic oscillator with equally spaced energy levels $\hbar\omega$. The contribution to the partition function is as we saw in Eq. (3.43). If we ignore the zero point energy (as it does not affect the heat capacity) then

$$Z_{\text{vib}} = \frac{1}{1 - e^{-\hbar\omega/(k_B T)}} \tag{3.49}$$

We have seen earlier that for $k_B T \ll \hbar\omega$ this does not contribute to the heat capacity. At $k_B T \approx \hbar\omega$ there is a step change in the heat capacity, and C_V has an additional k_B per molecule. The characteristic vibrational temperatures $T_{\text{vib}} \sim \hbar\omega/k_B$ depend on the stiffness of the interatomic bond and the atomic masses, but range from several thousand kelvin (6300K for H_2) to several hundred kelvin (309K for Br_2).

Rotational modes

The rotational motion of the molecule has an associated energy

$$E_{\text{rot}} = \tfrac{1}{2} I \dot{\theta}^2 \tag{3.50}$$

where I is the moment of inertia of the molecule. This expression has a quantum mechanical analog

$$E_{\text{rot}} = \frac{\hbar^2}{2I} \ell(\ell+1) \tag{3.51}$$

where $\ell = 0, 1, 2, \ldots$ is the quantum number associated with angular momentum. Each of these energy levels has a degeneracy of $(2\ell+1)$. The characteristic separation of the energy levels gives a temperature of $T_{\text{rot}} \sim \frac{\hbar^2}{2Ik_B}$. For molecules with a large I (heavy with a large separation) then this temperature is low, but for light molecules this temperature is much higher. For example for HCl the characteristic temperature is $15K$.

The partition function is rather more tricky to calculate as the degeneracy must be factored in

$$Z_{\text{rot}} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\hbar^2/(2Ik_B T)\ell(\ell+1)} \tag{3.52}$$

If we are at a high temperature then we can evaluate this by setting $x = \ell(\ell+1)$ and approximating the sum as an integral

$$Z_{\text{rot}} \approx \int_0^{\infty} e^{-\hbar^2/(2Ik_B T)x} dx = \frac{2Ik_B T}{\hbar^2} \tag{3.53}$$

Hence the average energy is $k_B T$ in this limit.

Translational modes

The translational part of the partition function is a little more subtle to calculate. We shall for the moment ignore quantum effects, and assume that the energy levels form a continuum. The classical

recipe for the partition function then requires integrating over all the points in phase space. For a single particle this is

$$z_{\text{tr}} = \frac{1}{h^3} \iiint dx\,dy\,dz \iiint dp_x\,dp_y\,dp_z\, e^{-\mathbf{p}^2/(2mk_BT)} \tag{3.54}$$

$$= \frac{V}{h^3}[2\pi m k_B T]^{3/2} \tag{3.55}$$

where the h^3 factor defines the volume of one quantum state in phase space. The contribution to the heat capacity for one particle is then $C_V = \frac{3}{2}k_B$.

If we have N identical particles then naively we would expect a partition function $Z = z_{\text{tr}}^N$. However, this assumes that the particles are indistinguishable, and hence makes a subtle over counting error. The partition function should include a factor of $N!$ as all the particles are identical. Hence

$$Z_{\text{tr}} = \frac{1}{N!}z_{\text{tr}}^N \tag{3.56}$$

The Helmholtz free energy (after using Stirling's approximation) is then

$$F = -k_B T \ln Z = -N k_B T \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] - N k_B T \tag{3.57}$$

3.7 Heat capacity of a solid

Einstein Model

This model assumes that each of the N atoms in the crystal behave independently and focuses on their vibrational motion. The electronic, nuclear, and other types of excitation are ignored. Each atom is bound to its equilibrium position by a harmonic spring, with natural frequency ω. Hence there are $3N$ vibrational modes, each with mean energy

$$\frac{\hbar\omega}{e^{\hbar\omega/(k_BT)} - 1} \tag{3.58}$$

The quantity $\hbar\omega/k_B$ is of the same order of magnitude as the melting temperature, and is called the Einstein temperature. The heat capacity of the solid is thus

$$C_v = \frac{d}{dT}\left(3N \frac{\hbar\omega}{e^{\hbar\omega/(k_BT)} - 1} \right) \tag{3.59}$$

$$= 3Nk_B \left(\frac{\hbar\omega}{k_BT} \right)^2 \frac{e^{\hbar\omega/(k_BT)}}{(e^{\hbar\omega/(k_BT)} - 1)^2}. \tag{3.60}$$

In the high temperature limit, this recovers Dulong-Petit law based on the equipartition theorem, and so reproduces the result of classical physics. However, in the low temperature limit it predicts an exponential dependence of the heat capacity, rather than the $\sim T^3$ behaviour expected from experiment.

Debye Model

The Debye model improves on the Einstein model of heat capacity by counting the energy associated with N longitudinal wavelike modes, and $2N$ transverse modes (known as *phonons*). This example illustrates the use of the *density of states* for counting the degeneracy of energy levels in a system.

Instead of counting the degeneracy of each energy level, we calculate a function $D(E)$ which gives the number of states in an interval E to $E + dE$. Once we have computed the density of states then our averages can be simplified

$$\langle X \rangle = \sum_i X p_i \quad \rightarrow \quad \langle X \rangle = \int_0^\infty X D(E) dE \tag{3.61}$$

The density of states can be computed by counting number of wave modes we can fit in the system. For a cubic box of side L these modes must have an integer number of half wavelengths in each direction, i.e. $n\frac{\lambda}{2} = L$. The corresponding wave vectors is $k = 2\pi/\lambda = \frac{\pi n}{L}$ in each direction. If we plot all the allowed values of the wave vector $\mathbf{k}$, then we have a set of lattice points in $3 - D$, with each point occupying a volume π^3/V. Hence the number of modes dN between a wave vector k and $k + dk$ is

$$dN = \frac{V}{8\pi^3} 4\pi k^2 dk \tag{3.62}$$

If we convert this expression from a wave vector to a frequency using $\omega = ck$ where c is the wave velocity, then we obtain

$$D(\omega) d\omega = \frac{V}{2\pi^2} \omega^2 \frac{1}{c^3} d\omega$$

as the number of modes between ω and $\omega + d\omega$. We have assumed here that the dispersion relation between ω and k is linear. However, the total number of modes should not exceed $3N$ as there are no more degrees of freedom in the system. Hence when we integrate over all the modes in the system we should obtain

$$3N \quad = \quad \int_0^{\omega_{\max}} \frac{V}{2\pi^2} \omega^2 \frac{1}{c^3} d\omega \tag{3.63}$$

$$\Rightarrow D(\omega) \quad = \quad \frac{9N}{\omega_{\max}^3} \omega^2 \tag{3.64}$$

The total energy of the system can be obtained by integrating the energy of each mode over the density of states

$$U = \int_0^{\omega_{\max}} \frac{\hbar\omega}{e^{\hbar\omega/(k_B T)} - 1} \frac{9N}{\omega_{\max}} \omega^2 d\omega \tag{3.65}$$

From this average energy we can compute the heat capacity. In the high temperature limit it again recovers the Dulong-Petit law. In the low temperature limit we find that $C_V \propto T^3$.

3.8 Fluctuations

For systems containing a large number of particles we have seen that the most likely state is typically overwhelmingly more likely than any other state. The associated probability distribution is very narrow. As a result the fluctuations in the pressure, or the energy of the system are expected to be very small. Under some circumstances (near phase transitions) fluctuations become very important, and hence it is useful to quantify them.

We have seen a method of calculating the average energy from the Boltzmann distribution. If we have a variable $\mathcal{X}$ appearing in the energy then we can use a similar method to calculate the fluctuations. Typically it will appear in the combination $\mathcal{F}\mathcal{X}$ where $\mathcal{F}$ is the conjugate force. The averages can

then be calculated just as for the average energy

$$\langle \mathcal{X} \rangle = \frac{1}{Z} \sum_i \mathcal{X}_i e^{-\mathcal{F}\mathcal{X}_i/(k_B T)} = -k_B T \left(\frac{\partial \ln Z}{\partial \mathcal{F}} \right)_T \tag{3.66}$$

$$\langle \mathcal{X}^2 \rangle = \frac{(k_B T)^2}{Z} \left(\frac{\partial^2 Z}{\partial \mathcal{F}^2} \right)_T \tag{3.67}$$

$$\Rightarrow \langle (\Delta \mathcal{X})^2 \rangle = k_B T \left(\frac{\partial^2 \ln Z}{\partial \mathcal{F}^2} \right)_T = k_B T \left(\frac{\partial \langle \mathcal{X} \rangle}{\partial \mathcal{F}} \right)_T \tag{3.68}$$

We will seem some examples of this in lectures. Typically $\langle (\Delta \mathcal{X})^2 \rangle \propto N$ (system size) and so the root mean square fluctuation $\frac{\sqrt{\langle (\Delta \mathcal{X})^2 \rangle}}{\langle \mathcal{X} \rangle} \propto \frac{1}{\sqrt{N}}$, and hence for systems with a large number of particles, the fluctuations are very small.