

Statistical Mechanics: Lecture 8

Energy in Grand Canonical Ensemble

As in canonical ensemble, the energy of the system in the grand canonical ensemble too, is not constant. The system constantly exchanges energy with the heat-bath. As exchange of particles is also allowed, it too affects the energy of the system. Average energy, in the grand canonical ensemble, can be written as

$$\langle E \rangle = \frac{1}{\Delta} \int E(p, q) \rho(p, q) dp dq = \frac{1}{\Delta} \frac{1}{\mathcal{Z}} \int E e^{-(E-\mu N)/kT} dp dq, \quad (1)$$

where $E(p, q)$ and $N(p, q)$ are functions of p, q . Also, it should be kept in mind that q, p involves coordinates and momenta of all the particles in the system. Derivative of $e^{-\beta(E-\mu N)}$ with respect to β will pull down $-E + \mu N$.

$$\begin{aligned} \frac{1}{\Delta} \frac{1}{\mathcal{Z}} \int -\frac{\partial}{\partial \beta} e^{-\beta(E-\mu N)} dp dq &= \frac{1}{\Delta} \frac{1}{\mathcal{Z}} \int (E - \mu N) e^{-\beta(E-\mu N)} \\ &= \frac{1}{\Delta} \frac{1}{\mathcal{Z}} \int E e^{-\beta(E-\mu N)} - \mu \frac{1}{\Delta} \frac{1}{\mathcal{Z}} \int N e^{-\beta(E-\mu N)} \\ &= \langle E \rangle - \mu \langle N \rangle, \end{aligned} \quad (2)$$

where $\langle N \rangle$ is the ensemble average of the number of particles in the system. The above relation simplifies to

$$\langle E \rangle - \mu \langle N \rangle = -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \frac{1}{\Delta} \int e^{-\beta(E-\mu N)} dp dq = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} \quad (3)$$

Thus the average energy of the system is given by

$$\boxed{\langle E \rangle = -\frac{\partial \log \mathcal{Z}}{\partial \beta} + \mu \langle N \rangle} \quad (4)$$

The above relation has a very simple interpretation. The first term on the right arises because of heat exchange between the system and the heat-bath, and is identical to the average energy in canonical ensemble. Since chemical potential, by definition, is the increase in the energy of the system, when one particle is added to it, $\langle N \rangle$ particles being added to the system, increases its energy by $\mu \langle N \rangle$. Thus, the second term represents the change in energy of the system due to exchange of particles.

Average number of particles

Average number particles of the system is defined as

$$\langle N \rangle = \frac{1}{\Delta} \int N(p, q) \rho(p, q) dp dq = \frac{1}{\Delta} \frac{1}{\mathcal{Z}} \int N e^{-(E-\mu N)/kT} dp dq, \quad (5)$$

Derivative of $e^{-\beta(E-\mu N)}$ with respect to μ will pull down βN . Using this fact, the above equation can be written as

$$\begin{aligned}\langle N \rangle &= \frac{1}{\mathcal{Z}} \frac{1}{\Delta} \int \frac{1}{\beta} \frac{\partial}{\partial \mu} e^{-\beta(E-\mu N)} dpdq \\ &= \frac{1}{\mathcal{Z}} \frac{1}{\beta} \frac{\partial}{\partial \mu} \frac{1}{\Delta} \int e^{-\beta(E-\mu N)} dpdq \\ &= \frac{1}{\mathcal{Z}} \frac{1}{\beta} \frac{\partial \mathcal{Z}}{\partial \mu}\end{aligned}\quad (6)$$

Thus the average number of particles in the system is given by

$$\boxed{\langle N \rangle = \frac{1}{\beta} \frac{\partial \log \mathcal{Z}}{\partial \mu}} \quad (7)$$

Entropy and grand potential

The entropy can be generally written as

$$S = -k \sum_i \rho_i \log [\rho_i] \quad (8)$$

where $\rho(p, q)$ is the density function in the grand canonical ensemble, and Δ is the phase volume corresponding to one microstate. Substituting the grand canonical form of $\rho(p, q)$ in the above equation, we get

$$\begin{aligned}S &= -k \sum_i \rho_i \log \rho_i \\ &= -k \sum_i \frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}} \log \left(\frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}} \right) \\ &= -k \sum_i \frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}} (-\beta E_i + \beta \mu N_i - \log \mathcal{Z}) \\ &= \beta k \sum_i \frac{E_i e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}} - \mu \beta k \sum_i \frac{N_i e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}} + \frac{k}{\mathcal{Z}} \log \mathcal{Z} \sum_i e^{-\beta E_i + \mu N_i} \\ &= \beta k \langle E \rangle - \mu \beta k \langle N \rangle + \frac{k}{\mathcal{Z}} \log(\mathcal{Z}) \mathcal{Z} \\ &= \beta k \langle E \rangle - \mu \beta k \langle N \rangle + k \log(\mathcal{Z})\end{aligned}\quad (9)$$

where $\langle E \rangle$ is the ensemble average of the energy of the system, and $\langle N \rangle$ is the average number of particles in it. The above equation can be rewritten as

$$\langle E \rangle - TS - \mu \langle N \rangle = -kT \log \mathcal{Z} \quad (10)$$

The quantity $\Phi \equiv U - TS - \mu N = F - \mu N$, in thermodynamics, is called the grand potential, or sometimes, *Landau potential* or *Landau free energy*. Thus, in statistical mechanics, the grand potential can be written as

$$\boxed{\Phi \equiv \langle E \rangle - TS - \mu \langle N \rangle = -kT \log \mathcal{Z}} \quad (11)$$

Particle number fluctuations

Since the number of particles in a system is not constant in grand canonical ensemble, apart from calculating its average, we will also be interested in knowing how much the particle number deviates from its average value. A good measure of it is the particle number *fluctuation*, defined as

$$\Delta N \equiv \sqrt{\langle (N - \langle N \rangle)^2 \rangle} = \sqrt{\langle N^2 \rangle - \langle N \rangle^2}, \quad (12)$$

where the angular brackets denote thermal average or ensemble average. Square of particle number fluctuation can now be written as

$$\begin{aligned} (\Delta N)^2 &= \langle N^2 \rangle - \langle N \rangle^2 \\ &= \frac{1}{\Delta} \frac{1}{\mathcal{Z}} \int N^2 e^{-\beta(E-\mu N)} dpdq - \langle N \rangle^2 \\ &= \frac{1}{\Delta} \frac{1}{\mathcal{Z}} \int \left(\frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \right) e^{-\beta(E-\mu N)} dpdq - \langle N \rangle^2 \\ &= \frac{1}{\mathcal{Z}} \left(\frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \right) \frac{1}{\Delta} \int e^{-\beta(E-\mu N)} dpdq - \langle N \rangle^2 \\ &= \frac{1}{\mathcal{Z}} \frac{1}{\beta^2} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \langle N \rangle^2 \\ &= \frac{1}{\mathcal{Z}} \frac{1}{\beta^2} \frac{\partial}{\partial \mu} \frac{\partial \mathcal{Z}}{\partial \mu} - \langle N \rangle^2 \\ &= \frac{1}{\mathcal{Z}} \frac{1}{\beta} \frac{\partial}{\partial \mu} \left(\mathcal{Z} \frac{1}{\beta} \frac{\partial \mathcal{Z}}{\partial \mu} \right) - \langle N \rangle^2 \\ &= \frac{1}{\mathcal{Z}} \frac{1}{\beta} \frac{\partial}{\partial \mu} (\mathcal{Z} \langle N \rangle) - \langle N \rangle^2 \\ &= \frac{1}{\mathcal{Z}} \frac{1}{\beta} \frac{\partial \mathcal{Z}}{\partial \mu} \langle N \rangle + \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} - \langle N \rangle^2 \\ &= \langle N \rangle \langle N \rangle + \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} - \langle N \rangle^2 \\ &= \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} = kT \frac{\partial \langle N \rangle}{\partial \mu} \end{aligned} \quad (13)$$

A better measure of fluctuation would be the relative fluctuation given by $\Delta N / \langle N \rangle$. The above equation can thus be written as

$$\frac{(\Delta N)^2}{\langle N \rangle^2} = \frac{kT}{\langle N \rangle^2} \frac{\partial \langle N \rangle}{\partial \mu} \quad (14)$$

We can rewrite the above equation in terms of average volume per particle, given by $v = V / \langle N \rangle$

$$\begin{aligned} \frac{(\Delta N)^2}{\langle N \rangle^2} &= \frac{kT}{\langle N \rangle^2} \frac{\partial (V/v)}{\partial \mu} \\ &= - \frac{kT}{\langle N \rangle^2} \frac{V}{v^2} \frac{\partial v}{\partial \mu} \\ &= - \frac{kT}{V} \frac{\partial v}{\partial \mu} \end{aligned} \quad (15)$$

Change in chemical potential μ can be related to the change in pressure by the following thermodynamic relation

$$Nd\mu = VdP - SdT$$

or

$$d\mu = vdP - \frac{S}{N}dT$$

So, at constant temperature, $d\mu$ is just equal to vdP . Putting this form in (15), we get

$$\frac{(\Delta N)^2}{\langle N \rangle^2} = -\frac{kT}{V} \frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \quad (16)$$

But $-\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$ is just the isothermal compressibility, denoted by κ_T . Thus we get our final result

$$\boxed{\frac{(\Delta N)^2}{\langle N \rangle^2} = \frac{kT}{V} \kappa_T} \quad (17)$$

If we define average particle density as $\bar{n} = \langle N \rangle / V$, particle density fluctuation will be given by $(\Delta n)^2 \equiv \frac{\langle N^2 \rangle}{V^2} - \frac{\langle N \rangle^2}{V^2} = \frac{(\Delta N)^2}{V^2}$. We can now write a similar relation for *relative particle-density fluctuations*

$$\boxed{\frac{(\Delta n)^2}{\bar{n}^2} = \frac{kT}{V} \kappa_T} \quad (18)$$

Thus we see that particle density fluctuations, which spontaneously happen because of interaction with a heat-bath, are intimately related to a thermodynamic property of the system, namely the isothermal compressibility.

Relation between canonical and grand canonical ensembles

We look at the relative particle number fluctuation in the thermodynamic limit, namely when $V \rightarrow \infty$, $\langle N \rangle \rightarrow \infty$.

$$\lim_{V \rightarrow \infty} \frac{\Delta N}{\langle N \rangle} \propto \lim_{V \rightarrow \infty} \frac{1}{\sqrt{V}} = 0 \quad (19)$$

So, in the thermodynamic limit, the fluctuations are negligible, and the number of particles remains practically constant. If the number of particles is almost constant, one can also safely use canonical ensemble to describe the system, where particle number is fixed. So we conclude that in the thermodynamic limit ($V \rightarrow \infty$), canonical and grand canonical ensembles should give similar results.

