The equivalence: microcanonical, canonical, and grand canonical ensembles

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Here we show the equivalence of three ensembles; micro canonical ensemble, canonical ensemble, and grand canonical ensemble. The neglect for the condition of constant energy in canonical ensemble and the neglect of the condition for constant energy and constant particle number can be possible by introducing the density of states multiplied by the weight factors [Boltzmann factor (canonical ensemble) and the Gibbs factor (grand canonical ensemble)]. The introduction of such factors make it much easier for one to calculate the thermodynamic properties.

((Microcanonical ensemble))

In the micro canonical ensemble, the macroscopic system can be specified by using variables *N*, *E*, and *V*. These are convenient variables which are closely related to the classical mechanics. The density of states $\Omega(N,E,V)$ plays a significant role in deriving the thermodynamic properties such as entropy and internal energy. It depends on *N*, *E*, and *V*. Note that there are two constraints. The macroscopic quantity *N* (the number of particles) should be kept constant. The total energy *E* should be also kept constant. Because of these constraints, in general it is difficult to evaluate the density of states.

((Canonical ensemble))

In order to avoid such a difficulty, the concept of the canonical ensemble is introduced. The calculation become simpler than that for the micro canonical ensemble since the condition for the constant energy is neglected. In the canonical ensemble, the system is specified by three variables (*N*, *T*, *V*), instead of *N*, *E*, *V* in the micro canonical ensemble. The introduction of *T* indicates that the energy of the system is not constant. There exists the energy fluctuation around the average energy. The specification of the fixed *T* leads to the energy fluctuation around an average energy $\langle E\rangle$. In this ensemble, the number of particles is specified and is kept constant. The quantity $\Omega(N,E,V)e^{-\beta E}$ has a sharp peak around the average energy $\langle E\rangle$. So the canonical ensemble consists of a collection of micro canonical ensemble weighted by the Boltzmann factor $e^{-\beta E}$. The average energy $\langle E\rangle$ is given by

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z_C(\beta),$$

with the partition function defined by

$$Z_C(\beta) = \sum_i e^{-\beta E_i} .$$

The energy fluctuation ΔE is evaluated as

$$\frac{\Delta E}{\langle E \rangle} \approx \frac{1}{\sqrt{N}} .$$

In the thermodynamic limit ($N \to \infty$), the ratio $\Delta E / \langle E \rangle$ reduces to zero. This implies that the average energy $\langle E \rangle$ derived from the canonical ensemble is the same as that defined in the micro canonical ensemble. In other words, $\Omega(N, E, V) e^{-\beta E}$ has a very sharp peak centered at $E = \langle E \rangle$. The energy fluctuation is negligibly small.

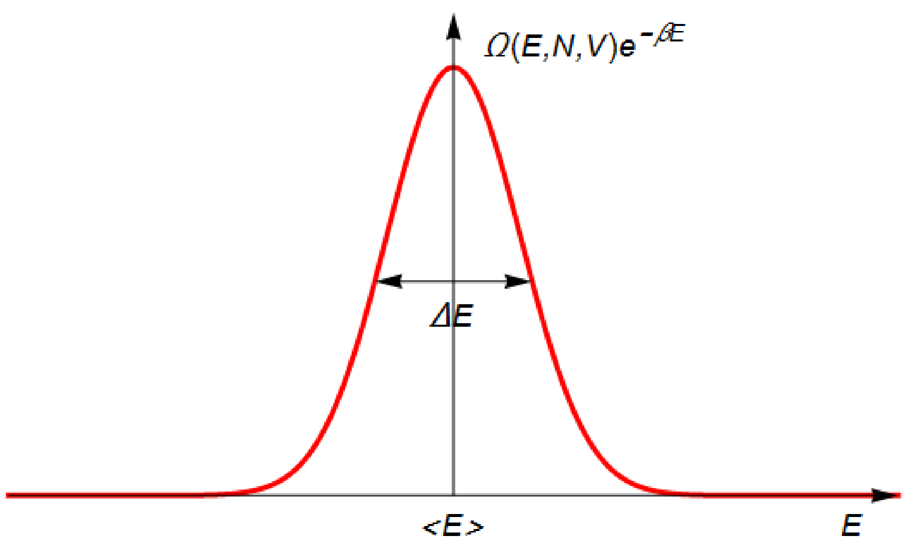

Fig. The plot of $\Omega(N, E, V) e^{-\beta E}$ as a function of E. The Gaussian shape with $E = \langle E \rangle$ and the energy fluctuation δE .

((**Grand canonical ensemble**))

In the grand canonical ensemble, the chemical potential is used instead of the particle number N. This leads to the particle number fluctuation ΔN around the average value $\langle N \rangle$. In this ensemble, the condition of constant energy and constant particle number are neglected. The macroscopic state is denoted by three variables, μ, T, V . The quantity

$\Omega(N,E,V)e^{-\beta E}e^{\beta\mu N}$ has a sharp peak around the average number $\langle N\rangle$ as well as around the average energy $\langle E\rangle$. So the ground ensemble consists of a collection of micro canonical ensemble weighted by the Boltzmann factor $e^{-\beta E}e^{\beta\mu N}$.

In the grand canonical ensemble, the average energy $\langle N\rangle$ is given by

$$\langle N\rangle = k_B T\frac{\partial}{\partial\mu}\ln Z_G.$$

with the grand partition function defined by

$$Z_G(\beta,\mu)=\sum_{N=0}^{\infty}\sum_{i[N]}\exp[-\beta E_i(N)+\beta\mu N]$$

The energy fluctuation ΔN is evaluated as

$$\frac{\Delta N}{\langle N\rangle}\approx\frac{1}{\sqrt{N}}.$$

In the thermodynamic limit ($N\to\infty$), the ratio reduces to zero. This means that the average number $\langle N\rangle$ derived from the grand canonical ensemble is the same as that derived from the micro canonical ensemble *N*. In other words, $\Omega(N,E,V)e^{-\beta E}$ has a very sharp peak centered at $E=\langle E\rangle$ and $N=\langle N\rangle$.

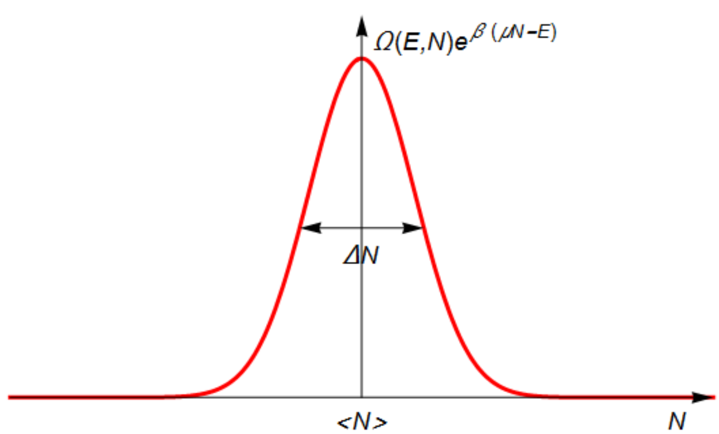

Fig. The plot of $\Omega(N,E,V)e^{\beta(\mu N-E)}$ as a function of *N*. The Gaussian shape with $N=\langle N\rangle$ and the energy fluctuation ΔN.

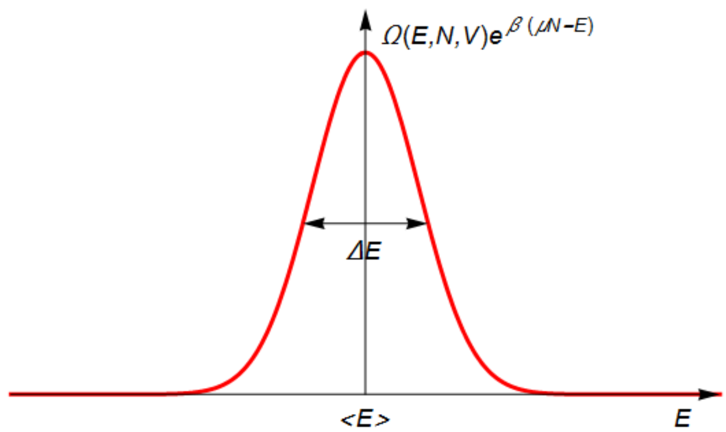

Fig. The plot of $\Omega(N,E,V)e^{\beta(\mu N-E)}$ as a function of *E*. The Gaussian shape with $E=\langle E\rangle$ and the energy fluctuation ΔE.

((**Note**)) **Explanation by Widom on the grand canonical ensemble**
B. Widom, *Statistical Mechanics A Concise Introduction for Chemists* (Cambridge, 2002).

The fluctuations are about the average energy $\langle E\rangle$ and about the average particle number $\langle N\rangle$. The fluctuations ΔE and ΔN are highly improbable. While the extensive $\langle E\rangle$ is proportional to the size of the system, the fluctuation ΔE is very much smaller, of the order only of the square-root of the system size ($\sqrt{N}$). The fluctuation ΔN is only of order $\sqrt{N}$, much less than $\langle N\rangle$. On the scale of the averages $\langle E\rangle$ and $\langle N\rangle$, then, the fluctuations ΔE and ΔN are minute: *E* and *N* are very narrowly distributed about their means. This has two important consequences. First, the means $\langle E\rangle$ and $\langle N\rangle$ may be identified with the most probable *E* and *N*; i.e., with the *E* and *N* at which the respective probability distributions have their maxima. Second, since the fluctuations are too small to be macroscopically discernible, the $\langle E\rangle$ and $\langle N\rangle$ at which the distributions peak may be identified as the thermodynamic *E* at the given *T, V*, and *N* (the micro canonical ensemble) and the thermodynamic *N* at the given *T, V* , and μ, respectively.