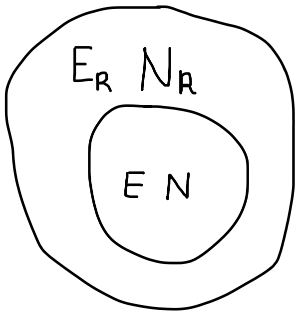
Grand-canonical ensemble

Consider a system of interest in contact with a thermal and particle reservoir – a system separated from the reservoirs by a permeable wall which is thermally conducting as well as allow the particles to transfer. Let E, N be the energy and number of particles of the system, and $E_T - E$ and $N_T - N$ be the energy and number of particles, respectively, of the reservoir. Total energy E_T is fixed. Then,



$$\Omega_T(\mathrm{E}_T, \mathrm{N}_T) = \int \frac{dE}{\Delta}\, \Omega(\mathrm{E}, \mathrm{N})\, \Omega_R(\mathrm{E}_T - \mathrm{E}\,,\ \mathrm{N}_T - \mathrm{N})$$

Here, $\Omega(\mathrm{E})$ is the total number of microstates of the system and $\Omega_R(\mathrm{E}_T - \mathrm{E},\ \mathrm{N}_T - \mathrm{N})$ is the total number of microstates of the reservoir.

Note that $\mathrm{E}_T = \mathrm{E}_R + \mathrm{E}$ is the total energy, i.e., system + reservoir. Similarly, $\mathrm{N}_T = \mathrm{N}_R + \mathrm{N}$. In the above equation, the integration is over all the available energy of the system.

The probability that the system has energy E with the number of particles N is therefore,

$$\mathrm{P}(\mathrm{E}, \mathrm{N}) \propto \Omega(\mathrm{E}, \mathrm{N})\, \Omega_R(\mathrm{E}_T - \mathrm{E}\,,\ \mathrm{N}_T - \mathrm{N}) = \Omega(\mathrm{E}, \mathrm{N})\, e^{S_R(\mathrm{E}_T - \mathrm{E}\,, \mathrm{N}_T - \mathrm{N})/k_B}$$

Where we have used that $S_R = k_B \ln \Omega_R(\mathrm{E}_T - \mathrm{E}\,,\ \mathrm{N}_T - \mathrm{N})$. This implies

$$\Omega_R(\mathrm{E}_T - \mathrm{E}\,,\ \mathrm{N}_T - \mathrm{N}) = e^{S_R(\mathrm{E}_T - \mathrm{E}\,,\, \mathrm{N}_T - \mathrm{N})/k_B}.$$

Since the reservoir is large $\mathrm{E} \ll \mathrm{E}_T$ and $\mathrm{N} \ll \mathrm{N}_T$, we can expand $\Omega_R(\mathrm{E}_T - \mathrm{E}\,,\ \mathrm{N}_T - \mathrm{N})$ (Taylor expansion) at the point $(\mathrm{E}_T, \mathrm{N}_T)$

$$\Omega_R(\mathrm{E}_T - \mathrm{E}\,, \mathrm{N}_T - \mathrm{N}) \approx \exp\left\{\frac{1}{k_B}\left[S_R(E_T\,, N_T) - \frac{\partial S_R}{\partial E_R}\, E - \frac{\partial S_R}{\partial N_R}\, N + higher\ order\ terms\right]\right\}$$

$$\Omega_R(\mathrm{E}_T - \mathrm{E}\,, \mathrm{N}_T - \mathrm{N}) \approx \exp\left\{\frac{1}{k_B}\left[S_R(E_T\,, N_T) - \frac{E}{T} + \frac{\mu N}{T}\right]\right\}$$

$$\Omega_R(\mathrm{E}_T - \mathrm{E}\,, \mathrm{N}_T - \mathrm{N}) \approx \exp\left\{\frac{1}{k_B}\left[S_R(E_T\,, N_T) - \frac{(E - \mu N)}{T}\right]\right\} = Constant\ \exp\left\{-\frac{E - \mu N}{k_B\, T}\right\}$$

So,

$$\mathrm{P}(\mathrm{E}, \mathrm{N}) = \frac{\frac{\Omega(\mathrm{E}, \mathrm{N})}{\Delta}\, e^{-\frac{E - \mu N}{k_B T}}}{\mathrm{Z}}$$

Where the grand canonical partition function is

$$\mathrm{Z}_g = \sum_{N=0}^{\infty} \int \frac{dE}{\Delta}\, \Omega(\mathrm{E,N})\ e^{-\frac{E-\mu N}{k_B T}}$$

It can be expressed as

$$\mathrm{Z}_g = \sum_{N=0}^{\infty} \int \frac{dE}{\Delta}\, \Omega(\mathrm{E,N})\ e^{-\frac{E}{k_B T}}\, e^{\frac{\mu N}{k_B T}} = \sum_{N=0}^{\infty} Z_{Canonical}\, e^{\frac{\mu N}{k_B T}}$$

$$\mathrm{Z}_g = \sum_{N=0}^{\infty} Z_{Canonical}\, \zeta^N$$

where ζ^N is called fugacity, it is a convenient measure of chemical potential.

Consider the following

$$-\frac{\partial\left(\ln \mathrm{Z}_g\right)_{V,\mu}}{\partial\beta} = -\frac{1}{\mathrm{Z}_g}\frac{\partial\, \mathrm{Z}_g}{\partial\beta} = -\frac{1}{\sum_{N=0}^{\infty}\int \frac{dE}{\Delta}\, \Omega(\mathrm{E})\ e^{-\frac{E-\mu N}{k_B T}}}\ \frac{\partial}{\partial\beta}\left[\sum_{N=0}^{\infty}\int \frac{dE}{\Delta}\, \Omega(\mathrm{E})\ e^{-\frac{E-\mu N}{k_B T}}\right]$$

$$-\frac{\partial\left(\ln \mathrm{Z}_g\right)_{V,\mu}}{\partial\beta} = \frac{\sum_{N=0}^{\infty}\int \frac{dE}{\Delta}\, \Omega(\mathrm{E})\ (E-\mu N)\, e^{-\frac{E-\mu N}{k_B T}}}{\sum_{N=0}^{\infty}\int \frac{dE}{\Delta}\, \Omega(\mathrm{E})\ e^{-\frac{E-\mu N}{k_B T}}}$$

$$-\frac{\partial\left(\ln \mathrm{Z}_g\right)_{V,\mu}}{\partial\beta} = \langle E\rangle - \mu\,\langle N\rangle \qquad (1)$$

This is one of the useful relations.

Now, consider the following

$$\frac{1}{\beta}\frac{\partial\left(\ln \mathrm{Z}_g\right)}{\partial\mu} = \frac{1}{\beta}\frac{1}{\mathrm{Z}_g}\frac{\partial\, \mathrm{Z}_g}{\partial\mu} = \frac{1}{\beta}\ \frac{1}{\sum_{N=0}^{\infty}\int \frac{dE}{\Delta}\, \Omega(\mathrm{E})\ e^{-\frac{E-\mu N}{k_B T}}}\ \frac{\partial}{\partial\mu}\left[\sum_{N=0}^{\infty}\int \frac{dE}{\Delta}\, \Omega(\mathrm{E})\ e^{-\frac{E-\mu N}{k_B T}}\right]$$

$$\frac{1}{\beta}\frac{\partial\left(\ln \mathrm{Z}_g\right)}{\partial\mu} = \frac{\sum_{N=0}^{\infty}\int \frac{dE}{\Delta}\, \Omega(\mathrm{E})\ N\, e^{-\frac{E-\mu N}{k_B T}}}{\sum_{N=0}^{\infty}\int \frac{dE}{\Delta}\, \Omega(\mathrm{E})\ e^{-\frac{E-\mu N}{k_B T}}}$$

$$\frac{1}{\beta}\frac{\partial\left(\ln \mathrm{Z}_g\right)}{\partial\mu} = \langle N\rangle \qquad (2)$$

From Thermodynamics, the grand potential is

$$\Xi = \mathrm{E} - \mathrm{T\,S} - \mu\,\mathrm{N}$$

$$\mathrm{E} - \mu\,\mathrm{N} = \Xi + \mathrm{T\,S} = \Xi - \mathrm{T}\left(\frac{\partial\,\Xi}{\partial T}\right)_{V,\mu} = \frac{\partial\,(\beta\,\Xi)_{V,\mu}}{\partial\beta}$$

$$\mathrm{E} - \mu\, \mathrm{N} = \frac{\partial\, (\beta\, \Xi)_{V,\mu}}{\partial \beta} \qquad (3)$$

Also,

$$\left(\frac{\partial\, \Xi}{\partial \mu}\right)_{T,V} = -N \qquad (4)$$

Comparing (1) & (3) and (2) & (4) we get

$$\Xi = -\mathrm{k}_B\, \mathrm{T} \ln \mathrm{Z}_g$$

As we did before in the canonical ensemble, here we equated the $\langle E \rangle$ and $\langle N \rangle$ in the grand canonical ensemble with the thermodynamic E and N.

From the Euler's relation $E = T\,S - P\,V + \mu\,\mathrm{N}$, and the grand potential $\Xi = \mathrm{E} - \mathrm{T\,S} - \mu\,\mathrm{N}$, we get

$$\Xi = -\mathrm{P\,V}$$

This implies, the pressure is given by

$$\mathrm{P} = \frac{\mathrm{k}_B\, \mathrm{T}}{V} \ln \mathrm{Z}_g \quad or \quad \mathrm{P} = \frac{1}{V\,\beta} \ln \mathrm{Z}_g$$

Note that the grand canonical in the thermodynamic limit $N \to \infty$, computing in the grand canonical ensemble, with a fixed μ, determining an average ⟨N⟩, gives the same result as computing in the canonical ensemble with fixed $N = \langle \mathrm{N} \rangle$.

Grand canonical partition function for distinguishable and indistinguishable particles

We have

$$\mathrm{Z}_g = \sum_{N=0}^{\infty} Z_{Canonical}\, \zeta^N$$

For indistinguishable particles we saw that

$$Z_{Canonical} = \frac{1}{N\,!}\, [Q_1(T,V)]^N$$

For distinguishable particles we saw that

$$Z_{Canonical} = [Q_1(T,V)]^N$$

Where $Q_1(T,V)$ is the single particle partition function.

Thus, for indistinguishable particles

$$\mathrm{Z}_g = \sum_{N=0}^{\infty} \frac{1}{N!}\, Z_{Canonical}\, \zeta^N = \sum_{N=0}^{\infty} \frac{(Q_1\, \zeta)^N}{N\,!} = e^{Q_1\, \zeta}$$

For distinguishable particles

$$Z_g = \sum_{N=0}^{\infty} Z_{Canonical}\, \zeta^N = \sum_{N=0}^{\infty} (Q_1\, \zeta)^N = \frac{1}{1 - Q_1\, \zeta}$$

Here, $Q_1\, \zeta < 1$ for series to converge.

For the ideal gas we have

$$Q_1 = \frac{V}{h^3}\, (2\, m\, \pi\, k_B T)^{\frac{3}{2}}$$

$$Q_1 = \frac{V}{\lambda^3}$$

Here, $\lambda(T) = \sqrt{h^2/(2\, m\, \pi\, k_B T)}$ or $\lambda(\beta) = \sqrt{\beta\, h^2/(2\, m\, \pi\,)}$ is the thermal wavelength.

Consider the case of indistinguishable particles, i.e., $Z_g = e^{Q_1\, \zeta} = e^{V\, \zeta/\lambda^3}$. The average particle number is expressed as

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial(\ln Z_g)}{\partial \mu} = \frac{1}{\beta}\frac{\partial \zeta}{\partial \mu}\frac{\partial(\ln Z_g)}{\partial \zeta} = \frac{1}{\beta}\, \zeta\, \frac{\partial(\ln Z_g)}{\partial \zeta} = V\, \zeta/\lambda^3$$

So, using the relation

$$\mathrm{PV} = \mathrm{k}_B\, \mathrm{T} \ln Z_g$$

$$\mathrm{PV} = \mathrm{k}_B\, \mathrm{T}\, V \frac{\zeta}{\lambda^3} = \langle N \rangle\, \mathrm{k}_B\, \mathrm{T}$$

Similarly,

$$\langle E \rangle = \mu\, \mathrm{N} - \frac{\partial(\ln Z_g)}{\partial \beta} = \frac{3\, V\, \zeta}{\lambda^4}\frac{\partial \lambda}{\partial \beta}$$

$$\langle E \rangle = \frac{3}{2}\, \langle N \rangle\, \mathrm{k}_B\, \mathrm{T}$$

We can calculate the corresponding entropy for the system which will be same as that we have obtained for Microcanonical and Canonical ensembles as it should be.

Number fluctuations

We have

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial(\ln Z_g)}{\partial \mu}$$

Consider

$$\frac{1}{\beta}\frac{\partial \langle N \rangle}{\partial \mu} = \frac{1}{\beta^2}\frac{\partial^2(\ln Z_g)}{\partial \mu^2}$$

$$= \frac{1}{\beta^2} \frac{\partial}{\partial \mu}\left(\frac{1}{Z_g}\frac{\partial Z_g}{\partial \mu}\right)$$

$$= \frac{1}{\beta^2}\left[\frac{1}{Z_g}\frac{\partial^2 Z_g}{\partial \mu^2} - \frac{1}{{Z_g}^2}\left(\frac{\partial Z_g}{\partial \mu}\right)^2\right]$$

Here,

$$\langle N \rangle = \frac{1}{\beta Z_g}\frac{\partial Z_g}{\partial \mu}$$

and we can easily show that

$$\langle N^2 \rangle = \frac{1}{\beta^2 Z_g}\frac{\partial^2 Z_g}{\partial \mu^2}$$

So, the number fluctuations are

$$\frac{1}{\beta}\frac{\partial\langle N \rangle}{\partial \mu} = \langle N^2 \rangle - \langle N \rangle = {\sigma_N}^2$$

This can be written as

$$\frac{{\sigma_N}^2}{\langle N \rangle^2} = \frac{k_B\, T}{\langle N \rangle^2}\ \frac{\partial\langle N \rangle}{\partial \mu} = \frac{k_B\, T}{\langle N \rangle^2}\ \frac{\partial(V/v)}{\partial \mu}$$

Where we have expressed $v = \frac{V}{\langle N \rangle}$

$$\frac{{\sigma_N}^2}{\langle N \rangle^2} = -\ \frac{k_B\, T}{\langle N \rangle^2}\ \frac{V}{v^2}\ \frac{\partial\, v}{\partial \mu}$$

$$= -\ \frac{k_B\, T}{V}\ \frac{\partial\, v}{\partial \mu}$$

Using Gibbs-Duhem relation, $N\, d\mu = V\, dp - S\, dT$, we can write $d\mu = v\, dp$ at constant temperature. Using it, we get

$$\frac{{\sigma_N}^2}{\langle N \rangle^2} = -\ \frac{k_B\, T}{V}\ \frac{1}{v}\ \frac{\partial\, v}{\partial p}$$

$$\frac{{\sigma_N}^2}{\langle N \rangle^2} = \frac{k_B\, T}{V}\ k_T$$

Where k_T is called Isothermal compressibility which is defined as $k_T = -\ \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$. This is an important relation related to the phase transitions.