Grand Canonical Ensemble

The ensemble of systems immersed in a particle-heat reservoir at constant temperature T, pressure P, and chemical potential μ.

1. Consider an ensemble of M identical systems (M = 1, 2, 3, ...M).
2. They are mutually sharing the total number of particles $M<N>$ and total energy $M<E>$.
3. Let $n_{r,s} \equiv$ number of systems that have, at any time, the number N_r of particles and the amount E_s of energy (r, s = 0, 1, 2, ...).
4. The ensemble has the following constrains:

$$\sum_{r,s} n_{r,s} = \mathcal{N},$$

$$\sum_{r,s} n_{r,s} N_r = \mathcal{N}\overline{N},$$

And

$$\sum_{r,s} n_{r,s} E_s = \mathcal{N}\overline{E}.$$

Define $W\{n_{r,s}\}$ number of different ways that any set $\{n_{r,s}\}$ of the numbers nr,s satisfy the above conditions. Then

$$W\{n_{r,s}\} = \frac{\mathcal{N}!}{\prod_{r,s}(n_{r,s}!)}.$$

To calculate the most probable mode of distribution $\{ n^*_{r,s} \}$ as the one that maximize $W\{n_{r,s}\}$, one can defines the function

$$\ln W = \ln M! - \ln \prod_{r,s}(n_{r,s}!) = \ln M! - \sum_{r,s} n_{r,s}(\ln n_{r,s} - 1).$$

Using $\frac{\partial \ln W}{\partial n_{r,s}}$, and eqautions (1), (2) and (3) $\Rightarrow$

$$\sum_{r,s} (-\ln n_{r,s} - \gamma - \alpha N_r - \beta E_s)\delta n_{r,s} = 0$$

This gives

$$n^*_{r,s} = c e^{-\alpha N_r - \beta E_s}$$

Consequently $P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{Z_G}$, $\qquad Z_G = \sum_{r,s} e^{-\alpha N_r - \beta E_s}$.

Define the grand canonical potential $\Psi(\alpha,\beta,V) = \log Z_G$, then $\langle N \rangle, \langle E \rangle$, and the pressure P are given by the derivatives of Ψ :

$$\langle N\rangle = -\frac{\partial \Psi}{\partial \alpha}, \quad \langle E\rangle = -\frac{\partial \Psi}{\partial \beta}, \quad P = \frac{1}{\beta}\frac{\partial \Psi}{\partial V}$$

In the grand canonical ensemble, the entropy is defined by

$$S = \sum_{r,s} P_{r,s} \log P_{r,s}$$

which gives

$$S = k\beta\langle E\rangle + k\ln Z_G - k\beta\mu\langle N\rangle$$

as compared with the thermodynamics:

$$dS = k\beta d\langle E\rangle - k\beta P dV - k\beta\mu d\langle N\rangle$$

It is easy to prove that:

$$\boxed{PV = kT\log Z_G = kT\Psi}$$

Comparing with the canonical ensemble ($F = -kT\ln Z_C \Rightarrow Z_C = e^{-\beta F}$)

$$P_i = \frac{e^{-\beta E}}{Z_C} = e^{\beta(F-E)}$$

Now use $F = \mu N - PV$, then $Z_G = e^{\beta PV}$, which gives the grand canonical relation. The following relations would be useful to calculate the equations of state and other thermodynamics functions:

$$P = \left(\frac{\partial(PV)}{\partial V}\right)_{T,\mu}$$

$$S = \left(\frac{\partial(PV)}{\partial T}\right)_{V,\mu}$$

$$\bar{N} = \left(\frac{\partial(PV)}{\partial \mu}\right)_{T,V}$$

where in grand canonical ensemble $PV = kT\log Z_G$.

Example:- Derive the equations of state of a **monatomic ideal gas**, using classical mechanics and the grand canonical ensemble.

Solution The Hamiltonian function for an *N*-particle monatomic gas is

$$H_N = \sum_{n=1}^{N} \frac{p_n^2}{2m}$$

To derive equations of state, one first calculates the grand partition function, defined as

$$Z_G(\alpha,\beta,V) = \sum_{N=0}^{\infty} e^{-\alpha N} Z_C(N), \qquad Z_C(N) = \frac{V^N}{N! h^{3N}} \int e^{-\beta H_N} d^{3N}p = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{e^{-\alpha}V}{\lambda^3}\right)^N = \exp\left[\frac{e^{-\alpha}V}{\lambda^3}\right]$$

where $\lambda = \dfrac{h}{\sqrt{2\pi mkT}}$ is the thermal de-Broglie wavelength, also $e^{-\alpha N} = (e^{-\alpha})^N$. The grand canonical potential Ψ is the logarithm of Z_G.

$$\Psi(\alpha,\beta,V) = \frac{e^{-\alpha}V}{\lambda^3}$$

$\overline{N}$, $\overline{E}$, and P are given by the derivatives of Ψ.

$$\overline{N} = -\frac{\partial \Psi}{\partial \alpha} = \frac{e^{-\alpha} V}{\lambda^3}$$

$$\overline{E} = -\frac{\partial \Psi}{\partial \beta} = \frac{3}{2\beta} \frac{e^{-\alpha} V}{\lambda^3}$$

$$P = \frac{1}{\beta} \frac{\partial \Psi}{\partial V} = \frac{1}{\beta} \frac{e^{-\alpha}}{\lambda^3}$$

Using the last three equations, one obtains the desired equations of state

$$\frac{E}{N} = \frac{3}{2} kT \qquad \text{and} \qquad PV = NkT$$

1. Density Fluctuation in Grand Canonical Ensemble:

Define the ***fugacity*** (absolute ***activity***) of the system as

$$z \equiv e^{-\alpha} = e^{\mu\beta}$$

then

$$Z_G(z, V, T) = \sum_{N_r=0}^{\infty} z^{N_r} Z_{N_r}(V, T), \qquad (\text{with } Z_0 \equiv 1).$$

and

$$\bar{N} = \sum_i N_i P_i = \frac{kT}{Z_G} \left(\frac{\partial Z_G}{\partial \mu}\right)_{V,T}$$

$$\overline{N^2} = \sum_i N_i^2 P_i = \frac{(kT)^2}{Z_G} \left(\frac{\partial^2 Z_G}{\partial \mu^2}\right)_{V,T}$$

Using the identity

$$\frac{\partial}{\partial \mu} \left\{ \frac{1}{Z_G} \left(\frac{\partial Z_G}{\partial \mu}\right) \right\}_{V,T} = \left\{ \frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} - \frac{1}{Z_G^2} \left(\frac{\partial Z_G}{\partial \mu}\right)^2 \right\}_{V,T}$$

$$\overline{(\Delta N)^2} = \overline{N^2} - \bar{N}^2 = kT \left\{ \frac{\partial \bar{N}}{\partial \mu} \right\}_{V,T} = kT \left\{ \frac{\partial (e^{\beta\mu} Z)}{\partial \mu} \right\}_{V,T} = Z e^{\beta\mu} = \bar{N}$$

The mean fractional fluctuation of the number of systems is defined as

$$F = \sqrt{\frac{\overline{(\Delta N)^2}}{\bar{N}^2}} = \frac{1}{\sqrt{\bar{N}}}$$

In general, $\left\{ \frac{\partial \overline{N}}{\partial \mu} \right\}_{V,T} = \frac{\kappa_T}{V}$, where κ_T is the isothermal compressibility of the system. 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. This is negligible except in a situation accompanying phase transitions.

2. **Energy Fluctuation**:

In the **canonical ensemble**, fluctuations occur in energy because the system is in equilibrium with the reservoir, it has been proven that

$$(\Delta E)^2 = \frac{\partial^2 \log Z}{\partial \beta^2} = -\frac{\partial}{\partial \beta}\left(\frac{\partial \log Z}{\partial \beta^2}\right) = -\frac{\partial}{\partial \beta}\langle E\rangle = -\frac{\partial T}{\partial \beta}\frac{\partial}{\partial T}\langle E\rangle = \frac{1}{k\beta^2}\frac{\partial}{\partial T}\langle E\rangle = kT^2 C_v$$

In **grand canonical ensemble**, with the same technique, one can show that (using the following)

$$\bar{E} = \sum_i E_i P_i = \frac{kT}{Z_G}\left(\frac{\partial Z_G}{\partial \mu}\right)_{V,T}$$

$$\overline{E^2} = \sum_i E_i^2 P_i = \frac{(kT)^2}{Z_G}\left(\frac{\partial^2 Z_G}{\partial \mu^2}\right)_{V,T}$$

That

$$\overline{(\Delta E)^2_{Gcan}} = \overline{E^2} - \bar{E}^2 = kT^2\left\{\frac{\partial U}{\partial T}\right\}_{z,V}.$$

With

$$\left\{\frac{\partial U}{\partial T}\right\}_{z,V} = \left\{\frac{\partial U}{\partial T}\right\}_{N,V} + \left\{\frac{\partial U}{\partial N}\right\}_{T,V}\left\{\frac{\partial N}{\partial T}\right\}_{z,V}.$$

Using the expressions:

$$\left\{\frac{\partial U}{\partial N}\right\}_{T,V} = \mu + T\left\{\frac{\partial S}{\partial N}\right\}_{T,V} = \mu - T\left\{\frac{\partial \mu}{\partial T}\right\}_{N,V}.$$

$$\begin{aligned}\left\{\frac{\partial N}{\partial T}\right\}_{z,V} &= \left\{\frac{\partial N}{\partial T}\right\}_{\mu,V} + \left\{\frac{\partial N}{\partial \mu}\right\}_{T,V}\left\{\frac{\partial \mu}{\partial T}\right\}_{z,V} \\ &= -\left\{\frac{\partial N}{\partial \mu}\right\}_{T,V}\left\{\frac{\partial \mu}{\partial T}\right\}_{N,V} + \frac{\mu}{T}\left\{\frac{\partial N}{\partial \mu}\right\}_{T,V} \\ &= \frac{1}{T}\left\{\frac{\partial N}{\partial \mu}\right\}_{T,V}\left\{\mu - T\left\{\frac{\partial \mu}{\partial T}\right\}_{N,V}\right\}.\end{aligned}$$

Then

$$\begin{aligned}\overline{(\Delta E)^2_{Gcan}} &= kT^2 C_v + kT\left\{\frac{\partial N}{\partial \mu}\right\}_{T,V}\left\{\left\{\frac{\partial U}{\partial N}\right\}_{T,V}\right\}^2 \\ &= \overline{(\Delta E)^2}_{can} + \overline{(\Delta N)^2}\left\{\left\{\frac{\partial U}{\partial N}\right\}_{T,V}\right\}^2.\end{aligned}$$

Last equation tells us that the mean square fluctuation in the energy of GCE is equal to the value in the canonical *plus* a contribution arising from the fluctuation in the number of particles *N*. This also a negligible value except at the phase transition.

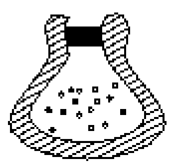
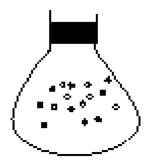
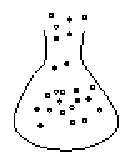
Relation between canonical and grand canonical ensembles

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

$$\lim_{V\to\infty} \frac{\Delta N}{\langle N \rangle} \propto \lim_{V\to\infty} \frac{1}{\sqrt{V}} = 0.$$

What is this means?
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 the in the thermodynamic limit $(V \to \infty)$, canonical and grand canonical ensembles should give similar results.

Summary

	ensemble		
	microcanonical	canonical	grand canonical
characteristic system	isolated	closed	open
Example	 micro-canonical	 canonical	 grand-canonical
characteristic system	isolated	closed	open
independent variables	N, E, V	N, β, V	α, β, V
distribution function	$\rho_i = C = \frac{1}{W}$	$\rho_i = e^{-\psi - \beta E_i} = \frac{e^{-\beta E_i}}{Z_C}$	$\rho_{i,N} = e^{-\varsigma - \alpha N - \beta E_i} = \frac{e^{-\alpha N - \beta E_i}}{Z_G}$
partition function	$W(N, E, V)$	$Z_C = e^{\psi} = \sum_i e^{-\beta E_i}$	$Z_G = \sum_N \sum_i e^{-\alpha N - \beta E_i}$
basic thermodynamic relations	$S = k \ln W$	$F = -kT \ln Z_C$	$\Psi = -kT \ln Z_G$

(4) Relation between three ensembles

In the canonical ensemble the most probable energy E* is identical to the mean value of all energies and corresponds to the fixed given energy of the micro canonical ensemble.

The deviations (fluctuations) of energy from the mean value in the canonical ensemble become smaller and smaller with increasing particle numbers. It means that at a given temperature, the system can assume (up to very small deviations) only a certain energy, which coincides with the total energy of micro canonical ensemble.