Grand Canonical Ensemble

Consider a system of interest which is in contact with both a thermal and a particle reservoir.

System of interest $E, V, N$

Wall allows exchange of energy and particles

Reservoir $E_R, V_R, N_R$

One way such a situation may arise physically is if the "system of interest" is just a certain volume immersed in a much larger volume of the same "stuff", and the walls around the "system of interest" are just our mental constructs.

Gas in a box

Reservoir is the rest of the gas

System of interest is some interior region of the gas. Dashed lines are mental construct—not physical walls!

The energy $E$ and number of particles $N$ in the region of interest are not fixed but fluctuate as energy + particles flow between the region and the rest of the gas.
The reservoir is so large, that no matter how much energy or particles the system of interest transfers to it, its temperature $T_R$ and chemical potential $\mu_R$ do not change — this is what we mean by it being a reservoir.

We see this as we argued before. If heat $dQ = T dS$ is transferred to the reservoir, then the change in $T_R$ is

$$\Delta T_R = \frac{\partial T_R}{\partial S_R} dS_R = (\frac{\partial^2 E_R}{\partial S_R^2}) dS_R \sim \frac{N}{N_R} \frac{T_R}{T_R} \text{ as } E_R, S_R \sim N_R, dS \sim N \text{ at most}$$

So if $N \ll N_R$, $\Delta T_R \ll T_R$

Similarly, if $dN$ is transferred to the reservoir,

$$\Delta N_R = \frac{\partial N_R}{\partial N_R} dN = (\frac{\partial^2 E_R}{\partial N_R^2}) dN_R \sim \frac{N}{N_R} \frac{\mu_R}{N_R} \text{ as } E_R, N_R \sim N_R, dN \sim N \text{ at most}$$

So if $N \ll N_R$, $\Delta \mu_R \ll \mu_R$

So we regard $T_R$ and $\mu_R$ of the reservoir as fixed.

Now because the system of interest is in equilibrium with the reservoir, we have $T = T_R$, and $\mu = \mu_R$.
Now \( N + N_T = N_f \) or fixed, \( E + E_R = E_f \) or fixed.

Similarly to what we had for the canonical ensemble, the density of states for the total system of reservoir + system of interest is

\[
g_T(E_f, V, V_R, N_T) = \int dE \sum_{N} g(E, V, N) g_R(E_f - E, V_R, N_T - N)
\]

or for the number of states \( S_2 = g \Delta \) (in small energy interval as before)

\[
S_T(E_f, V, V_R, N_T) = \int dE \sum_{\Delta} S(E, V, N) \sum_{N} S_R(E_f - E, V_R, N_T - N)
\]

\[
= \int dE \sum_{\Delta} S(E, V, N) e^{S_R(E_f - E, V_R, N_T - N) / k_B}
\]

Probability density for system to have \( E \) and \( N \) is

\[
P(E, N) \propto S(E, V, N) e^{S_R(E_f - E, V_R, N_T - N) / k_B}
\]

\[
= S_R - \frac{E}{T} + \mu N
\]

\[
P(E, N) \propto \sum_{\Delta} S(E, V, N) e^{-(E - \mu N) / k_B T}
\]

Normalized

\[
P(E, N) = \frac{\sum_{\Delta} S(E, V, N) e^{-E / k_B T}}{\sum_{N} \int dE \sum_{\Delta} S(E, V, N) e^{-E / k_B T}}
\]
Probability density

\[ P(E, N) = \frac{\Omega(E, V, N)}{\sum_N \Omega_N(V, T) z^N} e^{-\frac{(E - \mu N)}{k_B T}} \]

Normalized such that

\[ \sum_N \int dE P(E, N) = 1 \]

where \( z = e^{\mu/k_B T} \) is called the fugacity.

Define the grand canonical partition function

\[ Z(z, V, T) = \sum_{N=0}^{\infty} z^N \Omega_N(V, T) \]

\[ = \sum_N \int dE \Omega(E, V, N) e^{-\frac{(E - \mu N)}{k_B T}} \]

More generally, if the states of the system are labeled by an index \( i \), and state \( i \) has energy \( E_i \) and particle number \( N_i \), then

\[ Z(z, V, T) = \sum_i z^{N_i} e^{-\frac{(E_i - \mu N_i)}{k_B T}} \]

and

\[ P_i = \frac{e^{-\frac{(E_i - \mu N_i)}{k_B T}}}{Z(z, V, T)} \]

Note: These expressions make no reference to the reservoir.
Alternatively, for classical indistinguishable particles:

Consider system + reservoir to be a fixed $T$ in a canonical ensemble.

Canonical partition function for system + reservoir, with

volume $V_T = V + V_R$ and number particles $N_T = N + N_R$, is

$$Q_{N_T}(T, V_T) = \frac{1}{\hbar^{3N_T} N_T!} \prod_{i=1}^{3N_T} \int_{\frac{V}{V_T}} \frac{\hat{p}_i}{\frac{V}{V_T}} \frac{\hat{V}_i}{\frac{V}{V_T}} e^{-\beta \hat{H}_T}$$

$\hat{H}_T$ is total Hamiltonian.

Imagine dividing the combined system into the "system of interest" with $N$ particles in $V$, and the reservoir with $N_R$ particles in $V_R$.

The system of interest is weakly interacting with the reservoir, so

$$\hat{H}_T = \hat{H} + \hat{H}_R$$

and

$$\prod_{i=1}^{3N_T} \int_{\frac{V}{V_T}} \frac{\hat{p}_i}{\frac{V}{V_T}} \frac{\hat{V}_i}{\frac{V}{V_T}} e^{-\beta \hat{H}_T}$$

$$Q_{N_T}(T, V_T) = \frac{1}{\hbar^{3N_T} N_T!} \prod_{i=1}^{3N_T} \int_{\frac{V}{V_T}} \frac{\hat{p}_i}{\frac{V}{V_T}} \frac{\hat{V}_i}{\frac{V}{V_T}} e^{-\beta \hat{H}_T} e^{-\beta \hat{H}_R}$$

Expand out the product of factors—each term will correspond to a certain number $N$ particles in $V$, and the remainder $N_R = N_T - N$ in $V_R$. 
Because the particles are indistinguishable, it does not matter which \( N \) of the \( N_T \) are in \( V \) and which \( N_R \) are in \( V_R \). Each such term contributes the same amount. We can therefore consider just one such term, and multiply it by the number of ways to put \( N \) in \( V \), with the remainder in \( V_R \).

The number of such ways is \( \frac{N_T!}{N! \cdot N_R!} \).

\[
Q_{N_T}(T, V_T) = \frac{1}{h^{3N_T N_T}} \sum_{N=0}^{N_T} \frac{N_T!}{N! \cdot N_R!} \left( \prod_{i=1}^{3N_T} \int d\mathbf{q}_i \int d\mathbf{p}_i e^{-\beta H} \right) \left( \prod_{j=1}^{3N_R} \int d\mathbf{q}_j \int d\mathbf{p}_j e^{-\beta H_R} \right)
\]

\[
= \sum_{N=0}^{N_T} \left( \prod_{i=1}^{3N} \int d\mathbf{q}_i \int d\mathbf{p}_i e^{-\beta H} \right) \frac{1}{h^{3N_R}} \frac{1}{h^{3N_T}} \left( \prod_{j=1}^{3N_R} \int d\mathbf{q}_j \int d\mathbf{p}_j e^{-\beta H_R} \right)
\]

\[
Q_{N_T}(T, V_T) = \sum_{N=0}^{N_T} Q_N(T, V) Q_{N R}(T, V_R) \frac{N_T!}{N! \cdot N_R!}.
\]

The probability that there are \( N \) particles in \( V \) is therefore proportional to the weight this term has in the above sum.

\[
\Phi(N) \propto Q_N(T, V) Q_{N R}(T, V_R) = Q_N(T, V) e^{-A_R(T, V_R, N)/\hbar}
\]

Expand

\[
A_R(T, V_R, N_R) = A_R(T, V_R, N_T - N)
\]

\[
= A_R(T, V_R, N_T) - \left( \frac{\partial A_R}{\partial N} \right)_{T, V_R} N
\]

\[
= \text{const} - \mu N
\]

\[
\mu = \partial A_R / \partial N \bigg|_{T, V_R}
\]

\[
\mu_R = \mu
\]

\[
\text{indep of } N
\]
So

\[
P(N) \propto Q_N(T, V) e^{\frac{MN}{k_B T}}
\]

\[
P(N) = \frac{Q_N(T, V)e^{\frac{MN}{k_B T}}}{\sum_{N=0}^{\infty} Q_N(T, V)e^{\frac{MN}{k_B T}}}
\]

where we set \( N_T \to \infty \) in upper limit of sum

Define \( \Xi = e^{\frac{\mu}{k_B T}} \)

Grand canonical partition function

\[
Z(\Xi, T, V) = \sum_{N=0}^{\infty} Q_N(T, V) e^{\frac{MN}{k_B T}}
\]

Substitute for \( Q_N \) to get

\[
P(N) = \frac{\int_{\Delta} \Xi \Omega(E) e^{-\frac{E}{k_B T}} e^{\frac{MN}{k_B T}}}{Z} \]

or \( P(E, N) = \frac{\Omega(E) e^{-\frac{(E-MN)}{k_B T}}}{Z} \)

as before.
Next we want to show that \( z \) is related to the Grand Potential \( \Sigma(T, V, \mu) = E - TS - \mu N \)

Legendre transform of \( E \)

First note:

\[
-\frac{\partial}{\partial \beta} \langle \ln Z \rangle_{N,V,T} = -\frac{\partial}{\partial \beta} \langle \frac{1}{2} \sum_i \frac{e^{-\beta (E_i - \mu N_i)}}{\sum_i e^{-\beta (E_i - \mu N_i)}} \rangle_{N,V,T} = \langle E \rangle - \mu \langle N \rangle \quad (1)
\]

\[
\frac{1}{\beta} \frac{\partial}{\partial \mu} \langle \ln Z \rangle_{N,V,T} \quad (2)
\]

\[
= \frac{1}{\beta} \frac{\partial}{\partial \mu} \langle \frac{1}{2} \sum_i \frac{e^{-\beta E_i} e^{\beta \mu N_i}}{\sum_i e^{-\beta E_i}} \rangle_{N,V,T}
\]

\[
= \frac{\sum_i N_i e^{-\beta (E_i - \mu N_i)}}{\sum_i e^{-\beta (E_i - \mu N_i)}}
\]

\[
= \langle N \rangle
\]

\[
\int \frac{1}{\beta} \frac{\partial}{\partial \mu} \langle \ln Z \rangle_{N,V,T} = \langle N \rangle
\]
Next from Thermodynamics

\[ \Sigma = E - TS - \mu N \]

so \[ E - \mu N = \Sigma + TS = \Sigma - T \left( \frac{\partial \Sigma}{\partial T} \right)_{V, \mu} = \Sigma \left( \frac{\partial \Sigma}{\partial \beta} \right)_{V, \beta} \]

\[ \Rightarrow E - \mu N = \frac{\partial (\beta \Sigma)}{\partial \beta} \]

(see corresponding result in discussion of \( A = -k_B T \ln Q_N \))

Also

\[ \frac{\partial \Sigma}{\partial N} = -N \]

Company these last two results with (1) ad (2) we conclude

As we did in discussion of canonical ensemble, we here equated the averages \( \langle E \rangle \) and \( \langle N \rangle \) in the grand canonical ensemble with the thermodynamic \( E \) ad \( N \).

Note: From the Euler relation \( E = TS - pV + \mu N \), and the Legendre transform \( \Sigma = E - TS - \mu N \), we have

\[ \Sigma = -pV \quad \text{grand potential} = -pV \]

\[ \Rightarrow \text{pressure} \quad P = \frac{k_B T}{V} \ln L(T, V, \mu) \]
That, analogous to what we did for the canonical ensemble, one can show that in the thermodynamic limit, \( N \to \infty \), computing in the grand canonical ensemble, with a fixed \( \mu \) determining an average \( \langle N \rangle \), gives the same result as computing in the canonical ensemble with fixed \( N = \langle N \rangle \).

One can use the grand canonical ensemble even if the physical system of interest is not in contact with a reservoir. Just choose a \( T \) and a \( \mu \) to give the desired \( E \) and \( N \) via eqs. (1) and (2). Because, as \( N \to \infty \), the prob. for a state in the grand canonical ensemble to have some \( E', N' \) is so sharply peaked about the averages \( \langle E \rangle, \langle N \rangle \), the difference from using a micro canonical ensemble at the fixed \( E = \langle E \rangle \) and \( N = \langle N \rangle \) is negligible.
Fluctuations - We want to show that the grand canonical distribution is indeed sharply peaked about the average \( \langle N \rangle \) and \( \langle \rangle \)

\[ \langle N \rangle = \frac{1}{\beta} \frac{2}{\partial \mu} \left( \text{ln } x \right) \]

\[ \Rightarrow \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} \bigg|_{T,N} = \frac{1}{\beta^2} \frac{2}{\partial \mu^2} \left( \text{ln } x \right) \]

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

Now \[ \frac{1}{\beta} \frac{2}{\partial \mu} = \frac{1}{\beta} \frac{2}{\partial \mu} \text{ln } x = \langle N \rangle \]

\[ \frac{1}{\beta^2} \frac{2}{\partial \mu^2} \text{ln } x = \langle N \rangle \]

And \[ \frac{1}{\beta^2} \frac{2}{\partial \mu^2} = \frac{1}{\beta^2} \frac{2}{\partial \mu^2} \left( \frac{1}{\beta} \sum_i \epsilon_i e^{\beta \epsilon_i} \epsilon_i N \right) \]

\[ \frac{1}{\beta^2} \frac{2}{\partial \mu^2} \sum_i \epsilon_i e^{\beta \epsilon_i} \epsilon_i N = \langle N^2 \rangle \]

So \[ \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} \bigg|_{T,N} = \frac{1}{\beta^2} \frac{2}{\partial \mu^2} \text{ln } x = \langle N^2 \rangle - \langle N \rangle^2 \]

\[ \sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} \bigg|_{T,N} \sim N \text{ as } \mu, \beta \text{ intensive} \]

So \[ \frac{\sigma_N}{\langle N \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0 \text{ as } N \to \infty \]

Fluctuations in \( N \) vanish as \( N \to \infty \)
We can write $\sigma^2_N$ in terms of more familiar response functions as follows:

\[ \sigma^2_N = \frac{1}{\beta} \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \]

write $\nu = \nu_N \Rightarrow N = \nu/\nu$

\[ \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \left( \frac{\partial \left( \nu/\nu \right)}{\partial \mu} \right)_{T,V} = -\frac{\nu}{\nu^2} \left( \frac{\partial \nu}{\partial \mu} \right)_{T,V} \]

By Gibbs-Duhem relation $N d\mu = V d\nu - S dT$

\[ d\mu = \nu d\nu - (S/N) dT \]

\[ \Rightarrow \text{at constant } T, \quad d\mu = \nu d\nu \]

\[ \Rightarrow \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = -\frac{\nu}{\nu^2} \left( \frac{\partial \nu}{\partial \mu} \right)_{T,V} = -\frac{N^2}{V} \frac{1}{\nu} \left( \frac{\partial \nu}{\partial p} \right)_{T,V} \]

Now, since both $\nu$ and $p$ are intensive, they are independent of $V, N \Rightarrow \left( \frac{\partial \nu}{\partial p} \right)_{T,V} = \left( \frac{\partial \nu}{\partial p} \right)_{T,N} = \left( \frac{\partial \left( \nu N \right)}{\partial p} \right)_{T,N} = \frac{1}{N} \left( \frac{\partial \nu}{\partial p} \right)_{T,N}$

so \[ \frac{1}{\nu} \left( \frac{\partial \nu}{\partial p} \right)_T = \frac{N}{\nu} \left( \frac{\partial \nu}{\partial p} \right)_T = \frac{1}{V} \left( \frac{\partial \nu}{\partial p} \right)_T = -k_T \]

So \[ \frac{\sigma^2_N}{\langle N \rangle^2} = \frac{1}{\beta N^2} \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{k_B T}{N^2} \frac{N^2}{V} k_T \]

\[ \frac{\sigma_N}{\langle N \rangle} = \sqrt{\frac{k_B T k_T}{V}} \]

$k_T$ is isothermal compressibility or const except perhaps at a phase transition.
\[ \text{Energy} \]

Write \( Z = \sum_i e^{-\beta (E_i - \mu N_i)} = \sum_i e^{-\beta E_i} z^{N_i} \).

Then:
\[
-\left( \frac{\partial \ln Z}{\partial \beta} \right)_{Z,V} = -\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right)_{Z,V} = \frac{1}{Z} \sum_i E_i e^{-\beta E_i} z^{N_i} = \langle E \rangle
\]

and
\[
\left( \frac{2 \ln Z}{\partial \beta} \right)_{Z,V} = -\left( \frac{2 \langle E \rangle}{\partial \beta} \right)_{Z,V} = \frac{1}{Z} \left( \frac{2 \partial Z}{\partial \beta} \right)_{Z,V} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)_{Z,V}^2
\]

Now:
\[
\frac{1}{Z} \left( \frac{2 \partial Z}{\partial \beta} \right)_{Z,V} = \frac{1}{Z} \sum_i E_i^2 e^{-\beta E_i} z^{N_i} = \langle E^2 \rangle
\]

\[
\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right)_{Z,V}^2 = \langle E \rangle^2
\]

So,
\[
-\left( \frac{2 \langle E \rangle}{\partial \beta} \right)_{Z,V} = k_B T^2 \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{Z,V} = \langle E^2 \rangle - \langle E \rangle^2 = \sigma_E^2
\]

Above expression involves derivative at constant \( \frac{Z}{e^\beta} \).

We want to convert it to an expression at constant \( N \).

\[
\left( \frac{2 \langle E \rangle}{\partial T} \right)_{Z,V} = \left( \frac{2 \langle E \rangle}{\partial T} \right)_{N,V} + \left( \frac{2 \langle E \rangle}{\partial N} \right)_{T,V} \left( \frac{\partial N}{\partial T} \right)_{Z,V}
\]

Above follows from regarding \( E \) as a function of \( T, N, V \) and \( N \) as a function of \( Z, V, T \), and then applying the chain rule to differentiate

\[ E(T, N, V) = E(T, N(z, V, T), V) \]
\[
\left( \frac{\partial \langle E \rangle}{\partial T} \right)_{z,V} = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{\mu,V} + \left( \frac{\partial \langle E \rangle}{\partial N} \right)_{T,N} \left( \frac{\partial N}{\partial T} \right)_{z,V}
\]

\[\uparrow\]

\[= C_V\]

This term is the same

This term is the extra fluctuation in energy

one we had for energy

fluctuations in the canonical ensemble

due to fluctuations in \( N \)
in the grand canonical ensemble.

To rewrite the second term above, one can show that

\[
\left( \frac{\partial N}{\partial T} \right)_{z,V} = \frac{1}{T} \left( \frac{\partial \langle E \rangle}{\partial \mu} \right)_{T,V} = \frac{1}{k_B T^2} \left[ \langle EN \rangle - \langle E \rangle \langle N \rangle \right]
\]

proof left to the reader

Then:

\[
\left( \frac{\partial \langle E \rangle}{\partial \mu} \right)_{T,V} = \left( \frac{\partial \langle E \rangle}{\partial N} \right)_{T,V} \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \left( \frac{\partial \langle E \rangle}{\partial N} \right)_{T,V} \beta \sigma_N^2
\]

last step comes from our earlier calculation of \( \sigma_N \)

So finally

\[
\sigma_E^2 = k_B T^2 \left[ C_V + \left( \frac{\partial \langle E \rangle}{\partial N} \right)_{T,N} \frac{1}{T} \left( \frac{\partial \langle E \rangle}{\partial N} \right)_{T,V} \beta \sigma_N^2 \right]
\]

\[
\sigma_E^2 = k_B T^2 C_V + \left( \frac{\partial \langle E \rangle}{\partial N} \right)_{T,N}^2 \sigma_N^2
\]

\[
\text{Note: } C_V \sim N \quad \frac{\partial \langle E \rangle}{\partial N} \sim N^{-1} \quad \sigma_N^2 \sim N
\]

\[\Rightarrow\]

\[\sigma_E^2 \sim N \quad \sigma_E \sim \sqrt{N} \sim \frac{1}{\sqrt{N}}\]