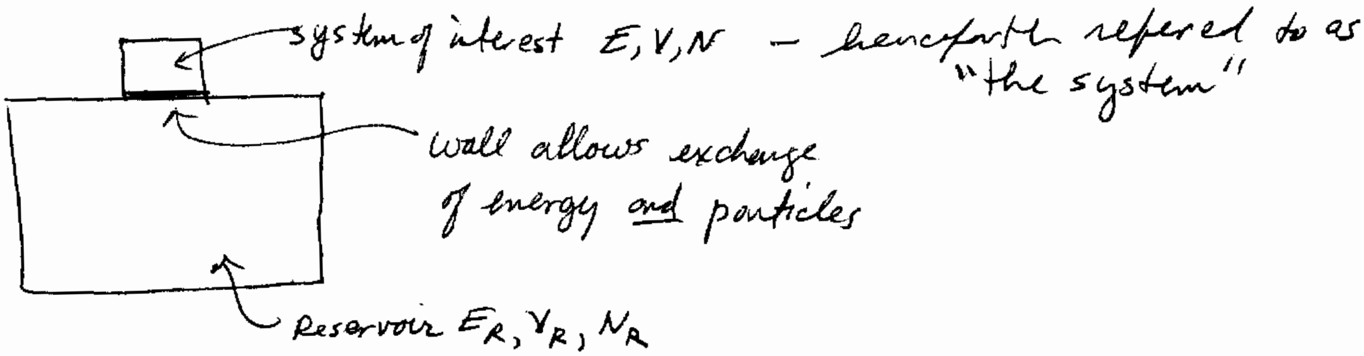
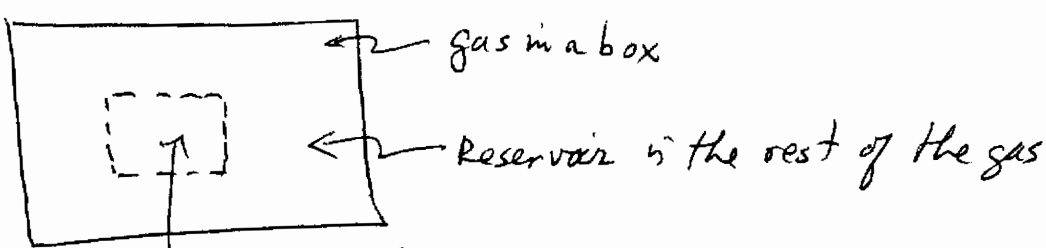
Grand Canonical Ensemble

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



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 ~~at~~ around the "system of interest" are just our mental constructs



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 μ_R do not change – this is what we mean by it being a reservoir.

We see this as we argued before. If heat $dQ = TdS$ is transfered to the reservoir then the change in T_R is

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

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

Similarly, if dN is transfered to the reservoir

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

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

So we regard T_R and μ_R of the reservoir as fixed

Now because the "system of interest" is in equilib with the reservoir, we have $T = T_R$, and $\mu = \mu_R$

Now $N + N_R = N_T$ is fixed, $E + E_R = E_T$ is fixed
V, V_R are fixed

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

$$g_T(E_T, V, V_R, N_T) = \int dE \sum_N g(E,V,N)\, g_R(E_T - E, V_R, N_T - N)$$

or for the number of states $\Omega = g\Delta$ (Δ is small energy interval as before)

$$\Omega_T(E_T, V, V_R, N_T) = \int \frac{dE}{\Delta} \sum_N \Omega(E,V,N)\, \Omega_R(E_T - E, V_R, N_T - N)$$

$$= \int \frac{dE}{\Delta} \sum_N \Omega(E,V,N)\, e^{S_R(E_T - E, V_R, N_T - N)/k_B}$$

probability density for system to have E and N is proportional to the number of states (of the total system) that have the system with E and N

$$P(E,N) \propto \frac{\Omega}{\Delta}(E,V,N)\, e^{S_R(E_T - E, V_R, N_T - N)/k_B}$$

expand

$$S_R(E_T - E, V_R, N_T - N) \simeq S_R(E_T, V_R, N_T) + \frac{\partial S_R}{\partial E_R}(-E_R) + \left(\frac{\partial S_R}{\partial N_R}\right)(-N)$$

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

$$P(E,N) \propto \frac{\Omega}{\Delta}(E,V,N)\, e^{-(E - \mu N)/k_B T}$$

Normalize

$$P(E,N) = \frac{\frac{\Omega}{\Delta}(E,V,N)\, e^{-(E - \mu N)/k_B T}}{\sum_N \int \frac{dE}{\Delta} \Omega(E,V,N)\, e^{-E/k_B T}\, e^{\mu N/k_B T}}$$

probability density for system to have E and N

$$P(E,N) = \frac{\frac{\Omega(E,V,N)}{\Delta}\, e^{-(E-\mu N)/k_BT}}{\sum_N \int \frac{dE}{\Delta}\, \Omega(E,V,N)\, e^{-(E-\mu N)/k_BT}}$$

$P(E,N)$ is normalized, ie $\sum_N \int dE\, P(E,N) = 1$

the denominator in the above expression for $P(E,N)$ defines the grand canonical partition function

$$\boxed{\begin{aligned}\mathcal{Z}(T,V,\mu) &\equiv \sum_N \left[\int \frac{dE}{\Delta}\, \Omega(E,V,N)\, e^{-E/k_BT}\right] e^{\mu N/k_BT} \\ &= \sum_N Q_N(T,V)\, z^N\end{aligned}}$$

where we define the fugacity $z \equiv e^{\mu/k_BT}$

If we can label the microscopic states of the system by the index i, such that state i has total energy E_i and contains N_i particles, then we can write

$$Q_N(T,V) = \sum_{\substack{i \text{ such} \\ \text{that } N_i = N}} e^{-E_i/k_BT}$$

and so

$$\mathcal{Z} = \sum_N \left[\sum_{\substack{i \text{ such that} \\ N_i = N}} e^{-E_i/k_BT}\right] e^{\mu N/k_BT}$$

$$\mathcal{Z} = \sum_i e^{-(E_i - \mu N_i)/k_BT}$$

where now sum on i is over all states with no restriction on N_i

Return now to probability density

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

since Ω just counts the number of states *of the system* with energy E and number of particles N, and all these states are equally likely, the probability to be in any particular state i is just

$$\boxed{P_i = \frac{e^{-(E_i - \mu N_i)/k_B T}}{\mathcal{L}}}$$

This is the obvious generalization of what we had earlier for the canonical ensemble

Note: these expressions for $\mathcal{L}$, P_i, $P(E,N)$ etc, make NO reference to the reservoir!

Alternatively - for classical indistinguishable particles

Consider system + reservoir to be a 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

$$Q_{N_T}(T, V_T) = \frac{1}{h^{3N_T} N_T!} \prod_{i=1}^{3N_T} \int_{V_T} dq_i \int dp_i \, e^{-\beta \mathcal{H}_T}$$

$\mathcal{H}_T$ 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

$$\mathcal{H}_T = \underbrace{\mathcal{H}}_{\text{system of interest}} + \underbrace{\mathcal{H}_R}_{\text{Reservoir}}$$

and $$\int_{V_T} dq_i = \int_{V+V_R} dq_i = \int_V dq_i + \int_{V_R} dq_i$$

$$Q_{N_T}(T, V_T) = \frac{1}{h^{3N_T} N_T!} \prod_{i=1}^{3N_T} \underbrace{\left(\int_V dq_i + \int_{V_R} dq_i \right)}_{} \int dp_i \, e^{-\beta \mathcal{H}} e^{-\beta \mathcal{H}_R}$$

expand out this 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 <u>indistinguishable</u>, it does not matter <u>which</u> 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 $\dfrac{N_T!}{N!\,N_R!}$

$$Q_{N_T}(T,V_T) = \frac{1}{h^{3N_T} N_T!}\sum_{N=0}^{N_T} \frac{N_T!}{N!\,N_R!}\left(\prod_{i=1}^{3N}\int_V dq_i \int dp_i\, e^{-\beta H}\right)\left(\prod_{j=1}^{3N_R}\int_{V_R} dq_j \int dp_j\, e^{-\beta H_R}\right)$$

$$= \sum_{N=0}^{N_T}\left(\frac{1}{h^{3N}N!}\prod_{i=1}^{3N}\int_V dq_i \int dp_i\, e^{-\beta H}\right)\left(\frac{1}{h^{3N_R}N_R!}\prod_{j=1}^{3N_R}\int_{V_R} dq_j \int dp_j\, e^{-\beta H_R}\right)$$

$$Q_{N_T}(T,V_T) = \sum_{N=0}^{N_T} Q_N(T,V)\, Q^R_{N_R}(T,V_R)$$

probability that there are N particles in V is therefore proportional to the weight this term has in the above sum

$$P(N) \propto Q_N(T,V)\, Q^R_{N_R}(T,V_R) = Q_N(T,V)\, e^{-A_R(T,V_R,N_R)/k_BT}$$

expand

$$A_R(T,V_R,N_R) = A_R(T,V_R,N_T-N)$$
$$\simeq A_R(T,V_R,N_T) - \left(\frac{\partial A_R}{\partial N}\right)_{T,V_R} N$$
$$= \underset{\substack{\uparrow\\ \text{indep of } N}}{\text{const}} - \mu N$$

$$\left(\frac{\partial A_R}{\partial N}\right)_{T,V_R} = \mu_R = \mu$$

So

$$P(N) \propto Q_N(T,V)\, e^{\mu N/k_B T}$$

$$P(N) = \frac{Q_N(T,V)\, e^{\mu N/k_B T}}{\sum_{N=0}^{\infty} Q_N(T,V)\, e^{\mu N/k_B T}}$$

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

Define $z = e^{\mu/k_B T}$

Grand canonical partition function

$$\mathcal{L}(z,T,V) \equiv \sum_{N=0}^{\infty} Q_N(T,V)\, e^{\mu N/k_B T}$$

Substitute for Q_N to get

$$P(N) = \frac{\int \frac{dE}{\Delta}\, \Omega(E)\, e^{-E/k_B T}\quad e^{\mu N/k_B T}}{\mathcal{L}}$$

or $$P(E,N) = \frac{\Omega(E)\, e^{-(E-\mu N)/k_B T}}{\mathcal{L}}$$

as before.

Relation between $\mathcal{L}$ and the grand Potential Σ

Elegant way:

$$\Sigma = E - TS - \mu N$$

$$\Rightarrow \quad -\frac{\Sigma}{T} = S - \left(\frac{1}{T}\right)E + \left(\frac{\mu}{T}\right)N$$

$-\frac{\Sigma}{T}$ is the Legendre transform of $S(E,V,N)$ with respect to E and N.

$\left(\frac{1}{T}\right)$ is the conjugate variable to E

$\left(-\frac{\mu}{T}\right)$ is the conjugate variable to N

Let us define $\beta \equiv \left(\frac{1}{k_B T}\right)$, $\alpha \equiv \left(\frac{\mu}{k_B T}\right)$

Then we can write $-\frac{\Sigma}{T}$ as a function of (β, V, α), with

$$\left(\frac{\partial\left(-\frac{\Sigma}{T}\right)}{\partial \beta}\right)_{V,\alpha} = k_B \left(\frac{\partial\left(-\frac{\Sigma}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_{V,\alpha} = -k_B E$$

$$\left(\frac{\partial\left(-\frac{\Sigma}{T}\right)}{\partial \alpha}\right)_{\beta,V} = -k_B \left(\frac{\partial\left(-\frac{\Sigma}{T}\right)}{\partial\left(-\frac{\mu}{T}\right)}\right) = -k_B(-N) = k_B N$$

where above follows since $\frac{1}{T}$ and $\frac{-\mu}{T}$ are conjugate to E and N

we conclude that

$$\left(\frac{\partial\left(-\frac{\Sigma}{k_B T}\right)}{\partial \beta}\right)_{V,\alpha} = -E$$

$$\left(\frac{\partial\left(-\frac{\Sigma}{k_B T}\right)}{\partial \alpha}\right)_{\beta,V} = N$$

Now consider $\ln \mathcal{Z}$. We have

$$\mathcal{Z} = \sum_i e^{-(E_i - \mu N_i)/k_B T}$$

$$= \sum_i e^{-\beta E_i} e^{\alpha N_i}$$

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{V,\alpha} = \frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{V,\alpha} = \frac{1}{\mathcal{Z}} \sum_i e^{-\beta E_i} e^{\alpha N_i} (-E_i)$$

$$= \frac{1}{\mathcal{Z}} \sum_i e^{-(E_i - \mu N_i)/k_B T} (-E_i)$$

$$= -\sum_i P_i E_i = -\langle E \rangle$$

prob to be in state i

average energy in grand canonical ensemble

Similarly,

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \alpha}\right)_{\beta,V} = \frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \alpha}\right)_{\beta,V} = \frac{1}{\mathcal{Z}}\sum_i e^{-\beta E_i} e^{\alpha N_i} N_i$$

$$= \sum_i P_i N_i = \langle N \rangle$$

← average number of particles in grand canonical ensemble

Comparing this to our results for $-\frac{\Sigma}{T}$, we identify:

$$-\frac{\Sigma}{k_B T} = \ln \mathcal{Z}$$

or

$$\boxed{\Sigma = -k_B T \ln \mathcal{Z}}$$

this is analogous to

$$A = -k_B T \ln Q$$

for the canonical ensemble.

Note: From the Euler relation $E = TS - pV + \mu N$ and Legendre transf $\Sigma = E - TS - \mu N$ we have

$$\Sigma = -pV$$

$$\Rightarrow \boxed{p = \frac{k_B T}{V} \ln \mathcal{Z}(T, V, \mu)}$$

Note: taking a derivative at constant $\alpha = \frac{\mu}{k_B T} = \ln z$ ($z = e^{\mu/k_B T}$ is the fugacity) is NOT the same as taking a derivative at constant μ.

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{V,\mu} = \frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{V,\mu} = \frac{1}{\mathcal{Z}} \sum_i \frac{\partial}{\partial \beta} e^{-\beta(E_i - \mu N_i)}$$

$$= \frac{1}{\mathcal{Z}} \sum_i e^{-\beta(E_i-\mu N_i)} (-)(E_i - \mu N_i) = -\langle E \rangle + \mu \langle N \rangle$$

so $\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{V,\mu} = -\left(\langle E \rangle - \mu \langle N \rangle\right)$

whereas $\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{V,z} = -\langle E \rangle$

fixed fugacity

Also $\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V} = \frac{1}{\mathcal{Z}} \sum_i \frac{\partial}{\partial \mu} e^{-\beta(E_i - \mu N_i)}$

$$= \frac{1}{\mathcal{Z}} \sum_i e^{-\beta(E_i-\mu N_i)} \beta N_i = \beta \langle N \rangle$$

so $\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V} = \langle N \rangle$

Another way to show the relation between $\mathcal{Z}$ and Σ

$$\Sigma = E - TS - \mu N$$

$$\Rightarrow E - \mu N = \Sigma + TS = \Sigma - T\left(\frac{\partial \Sigma}{\partial T}\right)_{V,\mu}$$

$$= \left(\frac{\partial(\beta\Sigma)}{\partial \beta}\right)_{V,\mu}$$

$\left\{ \begin{array}{l} \text{see similar result} \\ \text{in discussion of} \\ A = -k_B T \ln Q \end{array} \right.$

Also $\left(\frac{\partial \Sigma}{\partial \mu}\right)_{T,V} = -N$

Compare these to results on previous page:

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

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V} = \beta\langle N\rangle$$

we conclude that $\ln \mathcal{Z} = -\beta\Sigma$

or $\boxed{\Sigma = -k_B T \ln \mathcal{Z}}$

~~Thus~~ Analogous to what we did for the canonical ensemble, one can show that in the thermodynamic limit, $N \to \infty$, computing in the <u>grand canonical</u> ensemble, with a fixed μ determining an <u>average</u> $\langle N \rangle$, 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 <u>not</u> in contact with a reservoir. Just choose a T and a μ to give the desired E and N via eqns (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 microcanonical 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 $\langle E \rangle$ and $\langle N \rangle$

Particle Number

We had $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} (\ln \mathcal{Z})$

$$\Rightarrow \quad \frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \frac{1}{\beta^2} \frac{\partial^2 (\ln \mathcal{Z})}{\partial \mu^2}$$

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

Now $\frac{1}{\beta \mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \langle N \rangle$

and $$\frac{1}{\beta^2 \mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} = \frac{1}{\beta^2} \frac{\frac{\partial^2}{\partial \mu^2} \sum_i e^{-\beta E_i} e^{\beta \mu N_i}}{\mathcal{Z}} = \langle N^2 \rangle$$

So $$\frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \frac{1}{\beta^2} \frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} = \langle N^2 \rangle - \langle N \rangle^2$$

$$\sigma_N^2 \equiv \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} \sim N \quad \text{as } \mu, \beta \text{ intensive}$$

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

fluctuations in N vanish as $N \to \infty$