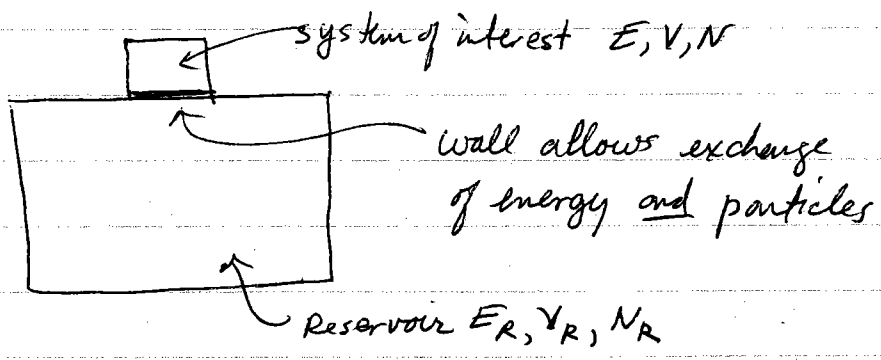
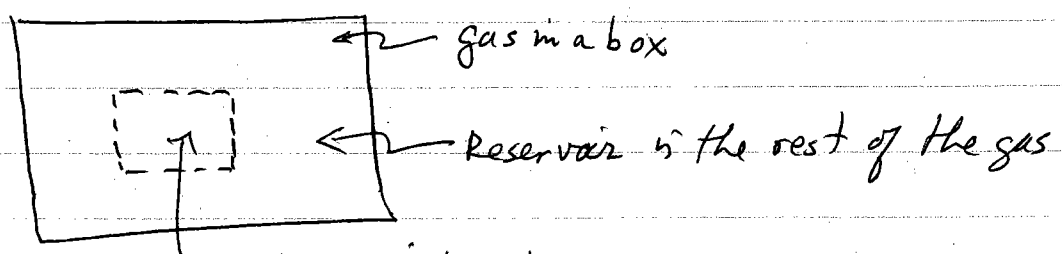


## Grand Canonical Ensemble

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  $\mu_R$  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

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

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

Similarly, if  $dN$  is transferred to the reservoir

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

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  $N + N_R = N_T$  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  $\Omega = g \Delta$  ( $\Delta$  is small energy interval as before)

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

probability density for system to have  $E$  and  $N$  is

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

expand

$$S_R(E_T - E, V_R, N_T - N) \approx S_R(E_T, V_R, N_T) + \frac{\partial S_R}{\partial E_R} (-E_R)$$

$$+ \left( \frac{\partial S_R}{\partial N_R} \right) (-N)$$

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

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

Normalize

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

probability density

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

Normalized so 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

$$\mathcal{Z}(z, V, T) = \sum_{N=0}^{\infty} z^N Q_N(V, T)$$

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

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

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

and 
$$P_i = \frac{e^{-(E_i - \mu N_i)/k_B T}}{\mathcal{Z}(z, V, T)}$$

Note: These expressions make no reference to the reservoir

Alternatively - for classical indistinguishable particles

Consider system + reservoir to be at 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

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

$H_T$  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

$$H_T = H + H_R$$

↑ system of interest      ↑ Reservoir

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

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

↑ 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 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  $\frac{N_T!}{N! N_R!}$ .

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

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

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

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

$$P(N) \propto Q_N(T, V) Q_{N_R}(T, V_R) = Q_N(T, V) e^{-A(T, V_R, N_R)/k}$$

expand

$$A(T, V_R, N_R) = A(T, V_R, N_T - N)$$

$$\approx A(T, V_R, N_T) - \left( \frac{\partial A}{\partial N} \right)_{T, V_R} N$$

$$= \text{const} - \mu N$$

↑  
indep of  $N$

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

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  $N_T \rightarrow \infty$  in upper limit of sum

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

Grand canonical partition function

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

Substitute for  $Q_N$  to get

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

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

as before

Next we want to show that  $\mathcal{Z}$  is related to the  
Grand Potential  $\Sigma(T, V, \mu) = E - TS - \mu N$

↑  
 Legendre transf of  $E$   
 with respect to  $S$  and  $N$

First note:

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

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

← regarding  $\mathcal{Z}$  as  
 a function of  
 $T, V, \mu$

$$\boxed{-\frac{\partial}{\partial \beta} (\ln \mathcal{Z})_{V, \mu} = \langle E \rangle - \mu \langle N \rangle} \quad (1)$$

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

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

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



Next from Thermodynamics

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

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

$\Rightarrow$   $E - \mu N = \frac{\partial (\beta \Sigma)}{\partial \beta}_{V, \mu}$  (see corresponding result in discussion of  $A = -k_B T \ln(Q_N)$ )

also

$$\frac{\partial \Sigma}{\partial \mu}_{T, V} = -N$$

Comparing these last two results with (1) and (2) we conclude

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

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  $E$  and  $N$ .

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

$$\Sigma = -pV \quad \text{grand potential} = -pV$$

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

~~That~~ Analogous to what we did for the canonical ensemble, one can show that in the thermodynamic limit,  $N \rightarrow \infty$ , 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 equs (1) and (2). Because, as  $N \rightarrow \infty$ , 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  $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} (\ln \mathcal{Z})$

$$\begin{aligned} \Rightarrow \frac{1}{\beta} \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} &= \frac{1}{\beta^2} \frac{\partial^2 (\ln \mathcal{Z})}{\partial \mu^2} \\ &= \frac{1}{\beta^2} \frac{\partial}{\partial \mu} \left( \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \right) = \frac{1}{\beta^2} \left[ \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \frac{1}{\mathcal{Z}^2} \left( \frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \right] \end{aligned}$$

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

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

so  $\frac{\sigma_N}{\langle N \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \rightarrow 0$  as  $N \rightarrow \infty$

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

We can write  $\sigma_N^2$  in terms of more familiar response functions as follows:

$$\sigma_N^2 = \frac{1}{\beta} \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V}$$

write  $v \equiv V/N \Rightarrow N = V/v$

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

By Gibbs-Duhem relation  $N d\mu = V dp - S dT$   
 $d\mu = v dp - (S/N) dT$

$\Rightarrow$  at constant  $T$ ,  $d\mu = v dp$

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

now, since both  $v$  and  $p$  are intensive, they are independent of

$$V, N \Rightarrow \left( \frac{\partial v}{\partial p} \right)_{T,V} = \left( \frac{\partial v}{\partial p} \right)_{T,N} = \left( \frac{\partial (V/N)}{\partial p} \right)_{T,N} = \frac{1}{N} \left( \frac{\partial V}{\partial p} \right)_{T,N}$$

$$\text{so } \frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = \frac{N}{V} \left( \frac{\partial v}{\partial p} \right)_T = \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,N} = -\kappa_T$$

$$\text{so } \frac{\sigma_N^2}{\langle N \rangle^2} = \frac{1}{\beta N^2} \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{k_B T}{N^2} \frac{N^2}{V} \kappa_T$$

$$= \frac{k_B T}{V} \kappa_T$$

$$\frac{\sigma_N}{\langle N \rangle} = \sqrt{\frac{k_B T \kappa_T}{V}}$$

$\kappa_T$  is isothermal compressibility or ~~the~~ cons except perhaps at a phase transition

## Energy

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

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

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

Now

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

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

So

$$-\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z, V} = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z, V} = \langle E^2 \rangle - \langle E \rangle^2 \equiv \sigma_E^2$$

Above expression involves derivative at constant  $\underline{z}$

We want to convert it to an expression at constant  $N$

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

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

$$E(T, N, V) = E(T, N(z, V, T), V)$$

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

$$\uparrow$$

$$= C_V$$

this term is the same  
one we had for energy  
fluctuations in the  
canonical ensemble



this term is the extra  
fluctuation in energy  
due to fluctuations in  $N$   
in the grand canonical ensemble

To ~~can~~ rewrite the ~~second~~ 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

$$\text{Then: } \left(\frac{\partial \langle E \rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V} \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V} \beta \sigma_N^2$$

last step comes from our earlier calculation of  $\sigma_N$

So finally

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

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

Note:  $C_V \sim N$ ,  $\frac{\partial \langle E \rangle}{\partial N} \sim \frac{N}{N} \sim 1$ ,  $\sigma_N^2 \sim N$

$$\text{So } \sigma_E^2 \sim N \quad \text{and} \quad \frac{\sigma_E}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$