

# **Lesson 5- Grand Canonical**

# Statement

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So far, we have focused on the study of closed systems (N,V,E). Now we are going to learn to study parts of our system.

If we ignore most of our system—agreeing not to ask questions about certain degrees of freedom—the statistical mechanical predictions about the remaining parts of our system are embodied in a new statistical ensemble and its associated free energy.

What do we ignore? We ignore the external world. If the coupling to the external world is weak, we can remove it from consideration.

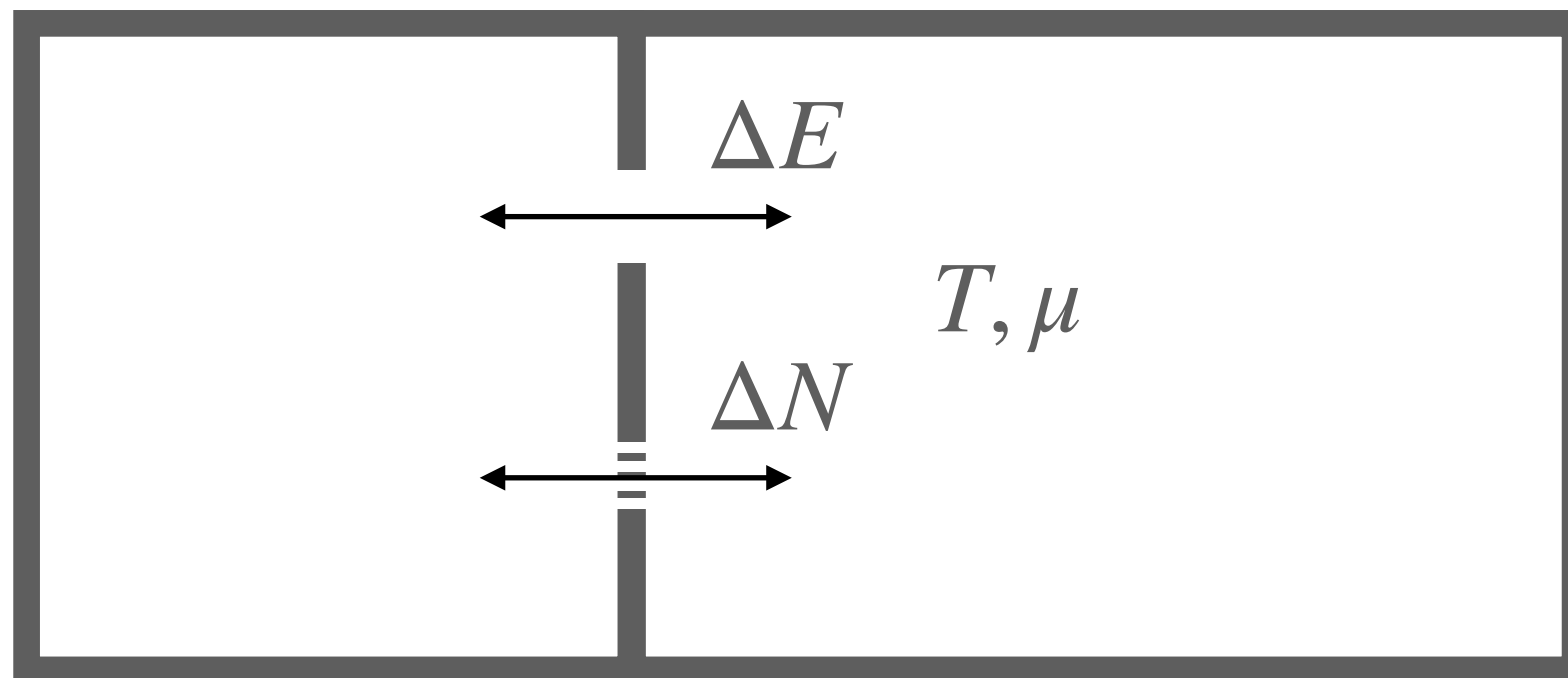
Why? Most systems are typically not isolated (they can exchange energy, volume and particles with its environment)

- If the system exchanges energy with the ‘outside world’ (or heat bath at fixed temperature) then we have the **canonical ensemble** and the **Hemholtz free energy** to describe the system
- If the system exchanges energy and particles with the heat bath (with fixed temperature and chemical potential), then we have the **grand canonical ensemble** and the **grand free energy**.

# Grand Canonical Ensemble

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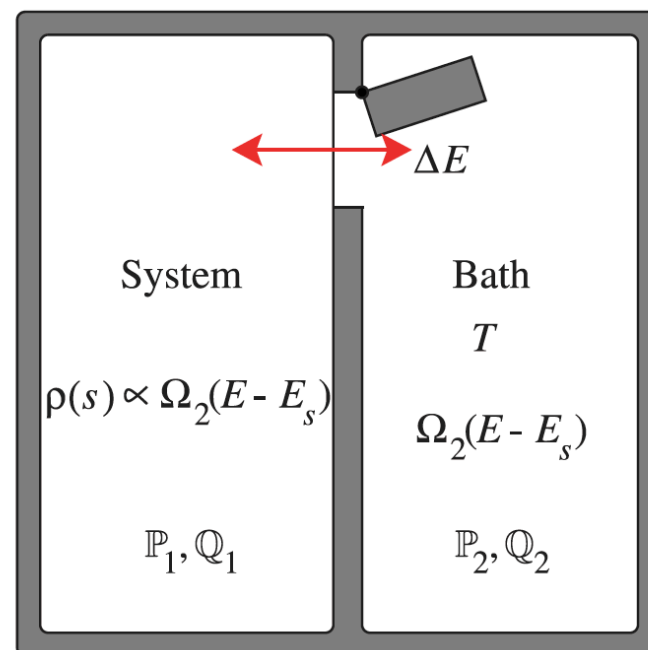
The grand canonical ensemble describes a system of particles in a box of volume  $V$  **weakly coupled to an infinitely large particle reservoir at temperature  $T$  and chemical potential  $\mu$** . To maintain equilibrium ( $T$  and  $\mu$ ), both heat and particles are exchanged with the environment.



## Reminder micro-canonical and canonical ensemble

How does the probability that our system is in a state  $s$  depend upon its energy  $E_s$ ? Note that the full system is a microcanonical ensemble. Remember slides micro canonical definition of temperature (slides 15-16). the probability density that our system will be in the particular state  $s$  is proportional to the volume of the energy shell for our heat bath at bath energy  $E_b = E - E_s$ . Using the definition of entropy  $\Omega(E_2) = e^{S_2(E_2)/K_B}$  we obtained

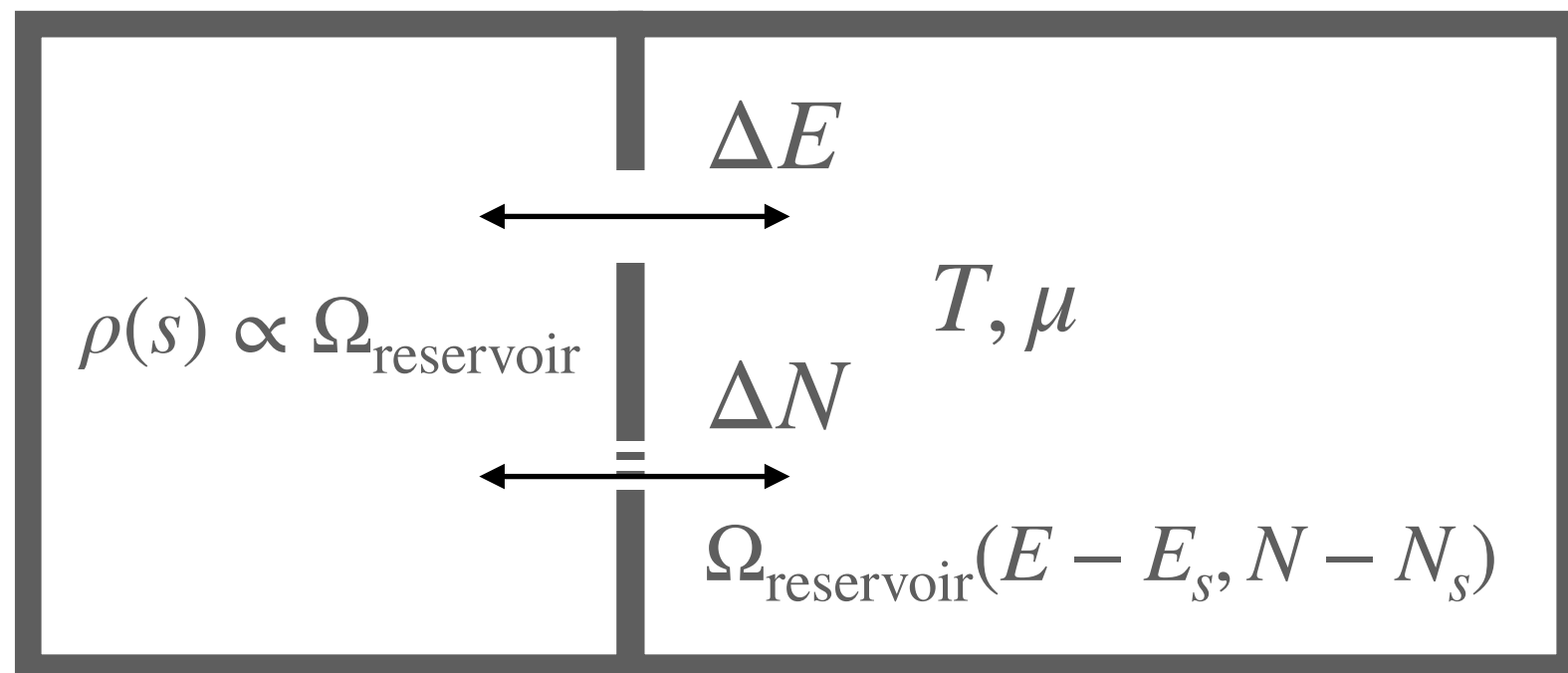
$$\rho(s) \propto \Omega_2(E - E_s) = e^{\frac{S_2(E - E_s)}{k_B}}$$



# Grand canonical ensemble

How does the probability that our system is in a state  $s$  depend upon its energy  $E_s$  and number of particles  $N_s$ ? Note that the full system is a still microcanonical ensemble. The probability density that our system will be in the particular state  $s$  is proportional to the volume of the energy shell for the reservoir with energy  $E_r = E - E_s$  and number of particles  $N_r = N - N_s$ . Using again the definition of entropy in the micro canonical  $\Omega(E_r) = e^{S_r(E_r)/k_B}$  we obtain that

$$\rho(s) \propto \Omega_r(E - E_s, N - N_s) = e^{\frac{S_r(E - E_s, N - N_s)}{k_B}}$$



# Grand Canonical Ensemble

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Let us compare the probability of two typical states A and B of our equilibrium system with energy and number of particles  $(E_A, N_A)$  and  $(E_B, N_B)$ , respectively. We know that the energy fluctuations are small, and we assume that the reservoir is large so that the fluctuations in the number of particles are small. We can therefore assume that the inverse temperature  $1/T = \partial S_r / \partial E_r$  and the chemical potential  $\mu = -T \partial S_r / \partial N_r$  of the reservoir are constant in the range  $E_r \in [E - E_A, E - E_B]$  and  $N_r \in [N - N_A, N - N_B]$  hence

$$\begin{aligned} \frac{\rho(s_B)}{\rho(s_A)} &\propto \frac{\Omega_r(E - E_B, N - N_B)}{\Omega_r(E - E_A, N - N_A)} = e^{(S_2(E-E_B, N-N_B) - S_2(E-E_A, N-N_A))/k_B} \\ &= e^{((E_A - E_B) \partial S_r / \partial E + (N_A - N_B) \partial S_r / \partial N) / k_B} = e^{((E_A - E_B) - \mu(N_A - N_B)) / (k_B T)} \\ &\rightarrow \frac{\rho(s_B)}{\rho(s_A)} \propto \frac{e^{-(E_B - \mu N_B) / k_B T}}{e^{-(E_A - \mu N_A) / k_B T}} \end{aligned}$$

Then, in the gran canonical ensemble, the probability of a particular system state of energy  $E_s$  and number of particles  $N_s$  is:

$$\rho(s) \propto \exp \left( -(E_s - \mu N_s) / k_B T \right)$$

# Chemical potential

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$$\rho(s) \propto \exp \left( -(E_s - \mu N_s)/k_B T \right)$$

Note that from the expression above  $\mu N$  has units of energy, therefore the chemical potential is an 'energy per particle'.

In particular, the chemical potential is for a system at equilibrium with the reservoir is the energy change needed to add one more particle to the system adiabatically and keep the system at equilibrium with  $N + 1$

particles  $\frac{\partial E}{\partial N} = \mu$ .

At fixed  $T$ , the system will keep adding particles from the reservoir until the energy change associated to adding one more particle equals  $\mu$  (so equal chemical potentials is another condition for equilibrium when the number of particles can change - sometimes this equilibrium is called diffusive equilibrium!).

## Partition Function Grand Canonical Ensemble

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Given that the probability has to be normalized, for every state with energy  $E_s$  and number of particles  $N_s$  we have that:

$$\rho(s) = \frac{\exp \left( -(E_s - \mu N_s)/k_B T \right)}{\mathcal{Z}}$$

$$\mathcal{Z} = \sum_n \exp \left( -(E_n - \mu N_n)/k_B T \right)$$

The grandpartition function  $\mathcal{Z}$  is just the normalization factor that keeps the total probability summing to one.

The term  $e^{\beta\mu N}$  is often expressed in terms of the fugacity  $z = e^{\beta\mu}$ , so that  $\mathcal{Z}(\mu, T, V) = \sum_n z^{N_n} e^{-\beta E_n}$



# Partition Function Grand Canonical Ensemble and Grand Free Energy

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As in the canonical ensemble this partition function is related to a thermodynamic potential - the grand free-energy (analogous to the Helmholtz free energy in the canonical ensemble:

$$\begin{aligned}\Phi(T, V, \mu) &= -k_B T \log \mathcal{Z} \\ &= \langle E \rangle - TS - \mu \langle N \rangle\end{aligned}$$

To obtain this expression we have to start from the Gibbs definition of entropy

$$S = -k_B \sum_s p_s \log p_s$$

Also note that using the relationship  $E = TS - PV + \mu N$ , we obtain that  $\Phi(T, V, \mu) = TS - PV + \mu N - TS - \mu N = -PV$  which is constant for the ensemble (for  $T, V, \mu$  fixed).

## Partial traces and the relationship with the Hemholtz free energy

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We can write  $\mathcal{Z}$  in terms of two partial sums:

a sum over the number of particles

a sum over the energy states with fixed number of particles

$$\begin{aligned}\mathcal{Z} &= \sum_N e^{\beta\mu N} \sum_{E_N} e^{-\beta E_N} g(E_N) \\ &= \sum_N e^{\beta\mu N} Z \\ &= \sum_N e^{\beta\mu N} e^{-\beta F(N,V,T)}\end{aligned}$$

Where  $F(N, V, T)$  is the Hemholtz free energy (from which thermodynamic quantities can be derived in the canonical ensemble)

## Fluctuations in the number of particles

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$$\begin{aligned}\langle N \rangle &= \sum_n N_n P_n = \frac{\sum_n N_n e^{-\beta(E_n - \mu N_n)}}{\mathcal{Z}} \\ &= \frac{\frac{1}{\beta} \frac{\partial \mathcal{Z}}{\partial \mu}}{\mathcal{Z}} = \frac{1}{\beta} \frac{\partial \log \mathcal{Z}}{\partial \mu} = - \frac{\partial (\Phi(T, V, \mu))}{\partial \mu}\end{aligned}$$

So that  $\langle N \rangle$  can be directly obtained as a derivative of the grand free energy.

$$\begin{aligned}\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} &= - \frac{\partial^2 \Phi(T, V, \mu)}{\partial \mu^2} = \frac{1}{\beta} \left( \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \left( \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \right) \\ &= \frac{1}{\beta} \left( \sum_n N_n^2 P_n - \left( \sum_n N_n P_n \right)^2 \right) = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\beta} = \frac{\sigma_N^2}{\beta}\end{aligned}$$

so that  $\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = \frac{\sigma_N^2}{\beta} = - \frac{\partial^2 (\Phi(T, V, \mu))}{\partial \mu^2}$  is another

fluctuation-response relationship like in the case of the energy fluctuations and the specific heat.

## Computation of average energy

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$$\begin{aligned}\langle E \rangle &= \sum_n E_n P_n = \frac{\sum_n E_n e^{-\beta(E_n - \mu N_n)}}{\mathcal{Z}} \\ &= -\frac{1}{\mathcal{Z}} \left( \frac{\partial \mathcal{Z}}{\partial \beta} \right)_{\beta\mu} = - \left( \frac{\partial \log \mathcal{Z}}{\partial \beta} \right)_{\beta\mu} = \left( \frac{\partial \beta \Phi(T, V, N)}{\partial \beta} \right)_{\beta\mu}\end{aligned}$$

Note that if we take just the derivative with respect to  $\beta$  keeping  $\mu$  constant then we get that:

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

so it is necessary to fix  $\beta\mu$  when taking the partial derivative (this is equivalent to fixing the fugacity  $z = e^{\beta\mu}$ ).

## Other thermodynamical properties and scaling of fluctuations

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We can compute other thermodynamic quantities by taking derivatives with respect to  $T$  and  $V$ .

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

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

## Other thermodynamical properties

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Note that this yields that the partial derivative of the pressure is related to the expected number of particles:

$$\left(\frac{\partial P}{\partial \mu}\right)_{T,V} = -\frac{1}{V} \left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = \frac{\langle N \rangle}{V} \text{ and therefore}$$

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

Note that, since  $P$  and  $\mu$  are intensive quantities we have that  $\sigma_N^2 \sim V$  (which scales a  $N$ ) so that the relative fluctuations in  $N$  decay as

$$\frac{\sigma_N}{\langle N \rangle} \sim \frac{1}{\sqrt{N}}.$$

# Comparison of ensembles

**Table 1.1.** Expressions for some useful thermodynamic quantities in terms of the microcanonical, canonical and grand canonical partition functions

	Microcanonical $\Omega(E, V, N)$	Canonical $Z(T, V, N)$	Grand canonical $\mathcal{Z}(T, V, \mu)$
$\frac{S}{k}$	$\ln \Omega$	$\left( \frac{\partial(T \ln Z)}{\partial T} \right)_{V, N}$	$\left( \frac{\partial(T \ln \mathcal{Z})}{\partial T} \right)_{V, \mu}$
$F$	$E - kT \ln \Omega$	$-kT \ln Z$	$kT \mu^2 \left( \frac{\partial(\mu^{-1} \ln \mathcal{Z})}{\partial \mu} \right)_{T, V}$
$U$	Fixed ( $=E$ )	$kT^2 \left( \frac{\partial(\ln Z)}{\partial T} \right)_{V, N}$	$-\left( \frac{\partial(\ln \mathcal{Z})}{\partial \beta} \right)_{\beta \mu, V}$
$N$	Fixed	Fixed	$kT \left( \frac{\partial(\ln \mathcal{Z})}{\partial \mu} \right)_{T, V}$
$kT$	$\left( \frac{\partial(\ln \Omega)}{\partial E} \right)_{V, N}^{-1}$	Fixed	Fixed
$\frac{\mu}{kT}$	$-\left( \frac{\partial(\ln \Omega)}{\partial N} \right)_{E, V}$	$-\left( \frac{\partial(\ln Z)}{\partial N} \right)_{T, V}$	Fixed
$P$	$kT \left( \frac{\partial(\ln \Omega)}{\partial V} \right)_{E, N}$	$kT \left( \frac{\partial(\ln Z)}{\partial V} \right)_{T, N}$	$\frac{kT}{V} \ln \mathcal{Z}$
$\frac{C_V}{k}$	$-\beta^2 \left( \frac{\partial^2(\ln \Omega)}{\partial E^2} \right)_{V, N}^{-1}$	$\beta^2 \left( \frac{\partial^2(\ln Z)}{\partial \beta^2} \right)_{V, N}$	$T \left( \frac{\partial^2(T \ln \mathcal{Z})}{\partial T^2} \right)_{V, \mu}$
$(\Delta N)^2$	0	0	$\left( \frac{\partial^2(\ln \mathcal{Z})}{\partial(\beta \mu)^2} \right)_{\beta, V}$
$(\Delta E)^2$	0	$\left( \frac{\partial^2(\ln Z)}{\partial \beta^2} \right)_{V, N}$	$\left( \frac{\partial^2(\ln \mathcal{Z})}{\partial \beta^2} \right)_{\beta \mu, V}$