

Introduction to Statistical Mechanics and Ensembles

PHAS0076:

TYC Materials Modelling

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Thermodynamic Description of Systems

- Consider a thermodynamic system, e.g. water at the triple point in a box...
- “Macroscopic” description in terms of:

Intensive variables:

Temperature (T)

Pressure (p)

Chemical potential (μ)

Extensive variables:

Number of moles/molecules (N) Volume (V)

Entropy (S)

Thermodynamic potentials:

Internal/Thermal Energy (U)

Enthalpy (H)

Helmholtz free energy (A)

Gibbs free energy (G)



$T = 273.16 \text{ K}$

$p = 6.11657 \text{ mbar}$

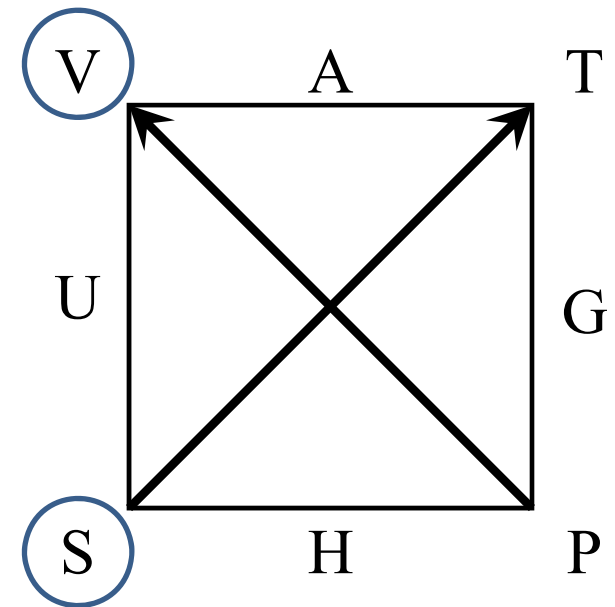
Interrelations between Thermodynamic Potentials

2

- Interrelations between these thermodynamic variables:

$$dU = T dS - p dV + \sum_{i=1}^m \mu_i dN_i$$

Natural variables



$$\left. \frac{\partial U}{\partial S} \right|_{V, \{N_i\}} = T \qquad \left. \frac{\partial U}{\partial V} \right|_{S, \{N_i\}} = -p$$

- Similar relations hold for the other variables...

Interrelations between Thermodynamic Potentials

3

- Interrelations between these thermodynamic variables:

$$dU = T dS - p dV + \sum_{i=1}^m \mu_i dN_i$$

$$dH = T dS + V dp + \sum_{i=1}^m \mu_i dN_i$$

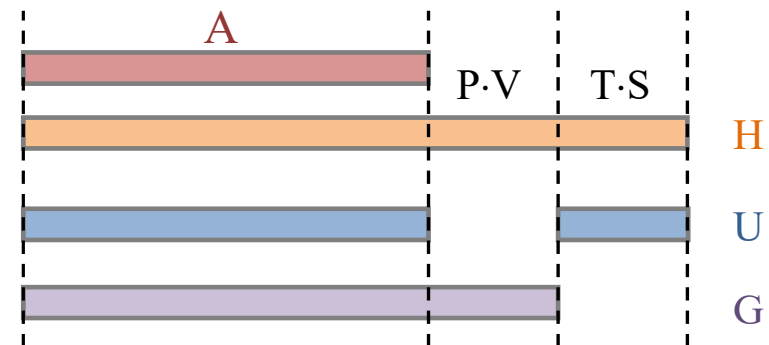
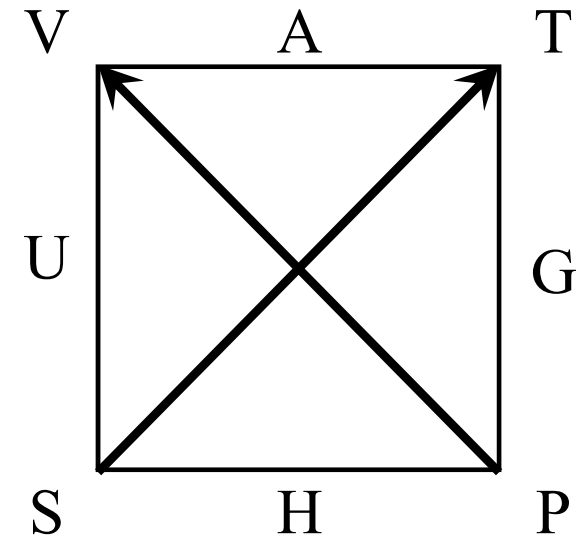
$$dG = -S dT + V dp + \sum_{i=1}^m \mu_i dN_i$$

$$dA = -S dT - p dV + \sum_{i=1}^m \mu_i dN_i$$

$$H = U + P V$$

$$G = H - T S$$

$$A = U - T S = G - P V = H - P V - T S$$



Euler's Theorem for Extensive Variables

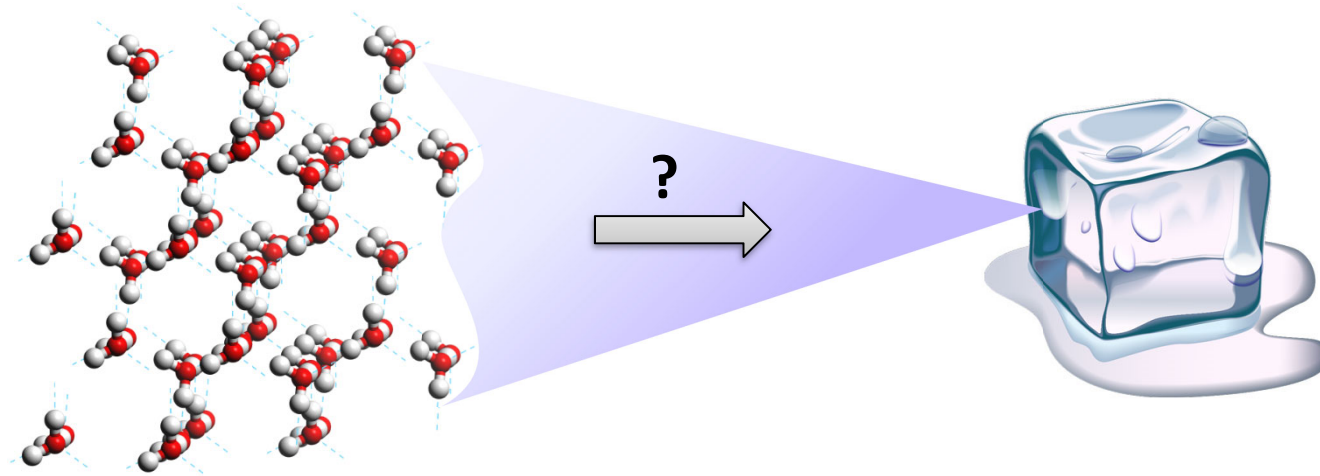
- Euler's theorem for first-order homogeneous functions:
 - If function f satisfies: $f(\lambda x_1, \lambda x_2, \dots, \lambda x_n) = \lambda f(x_1, x_2, \dots, x_n)$
 - Then:
$$f(x_1, x_2, \dots, x_n) = \sum_i \left. \frac{\partial f}{\partial x_i} \right|_{x_{j \neq i}} x_i$$
- This can be used for the thermodynamic potentials as they are indeed first-order homogeneous functions, e.g.:

$$U = \left. \frac{\partial U}{\partial V} \right|_{S, \{N_i\}} V + \left. \frac{\partial U}{\partial S} \right|_{V, \{N_i\}} S + \sum_i \left. \frac{\partial U}{\partial N_i} \right|_{S, V} N_i$$

$$U = -pV + TS + \sum_i \mu_i N_i$$

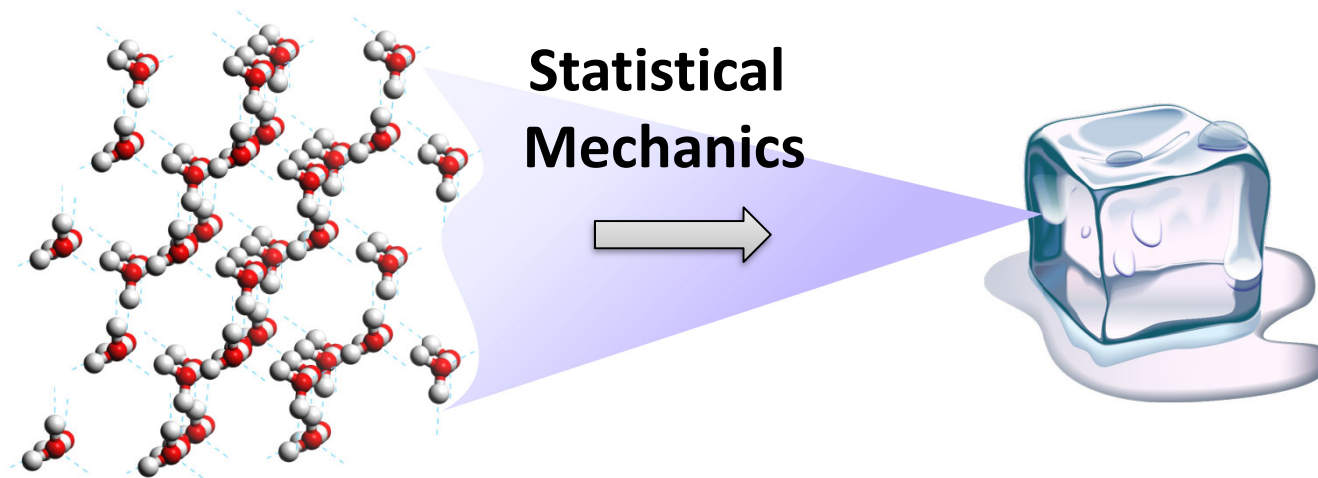
Bridging with the Microscopic World

- Within the framework of Chemical Thermodynamics we can study the interrelation of **heat** and **work** with **chemical reactions** or with **physical changes** of state...
- But how are these macroscopic processes, properties or quantities related to the “molecular world”?



The Challenge

- **Particles** (atoms, molecules) **obey known laws** (Schrodinger equation, Newton's laws of motion) with specified inter-particle interactions...
- What are the observable properties of a system consisting of a (very) large number of such particles?
- Solving the microscopic equations for $\mathcal{O}(10^{23})$ is impossible, but we can invoke statistical arguments...



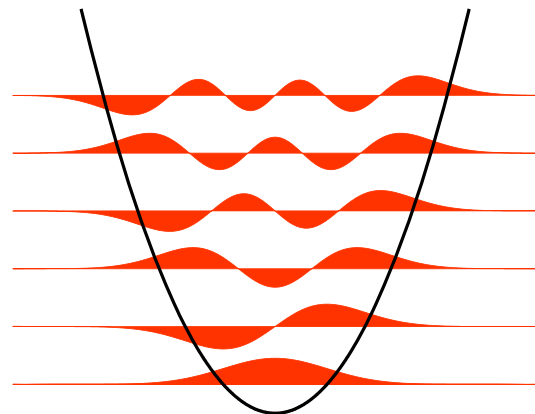
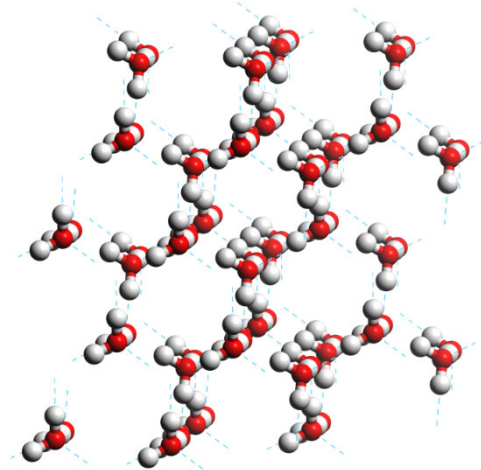
Microstates

- Key to these statistical arguments: how frequently a microstate is visited... **but what is a microstate?**
- Classical description of an ice-cube:
 - A *microstate* s contains all information about the position and momentum of each atom:

$$s \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$$

- Quantal description of non-interacting particles in a (known) potential:
 - A *microstate* s contains all information about the quantum state of each particle:

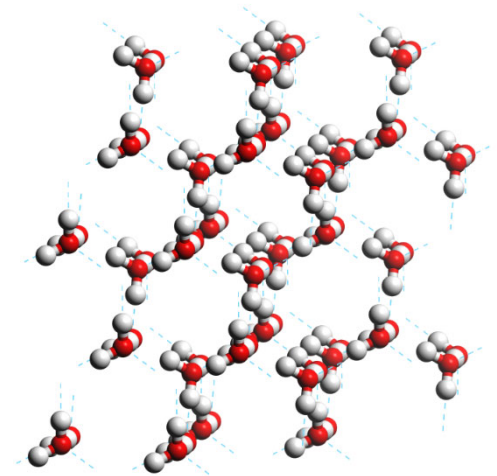
$$s \equiv (\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_N)$$



Hamiltonian

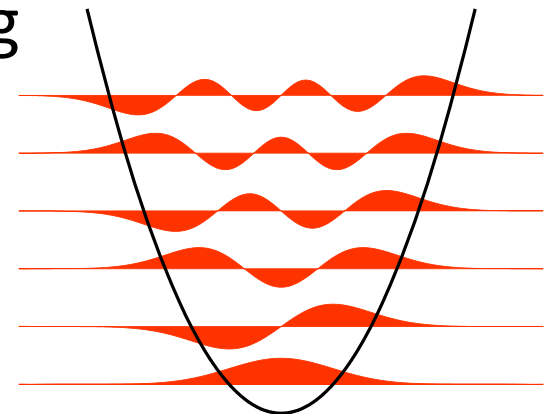
- The Hamiltonian of a system gives the energy of a microstate
- Classical Hamiltonian of an ice-cube:

$$\mathcal{H}(\mathbf{s}) = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2 m_i} + \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

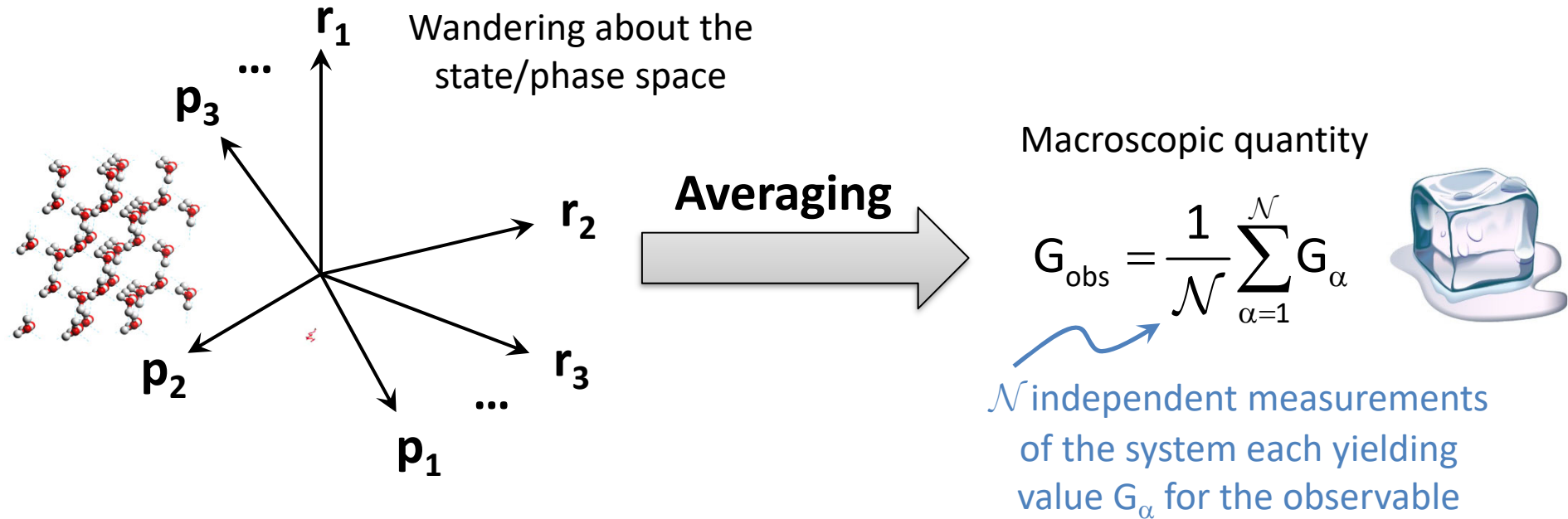


- Quantal Hamiltonian of non-interacting particles in a (known) potential:

$$\mathcal{H} = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_i} \nabla^2 + \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$



From Micro to Macro via Averaging



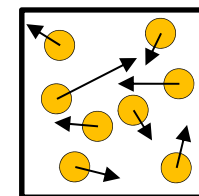
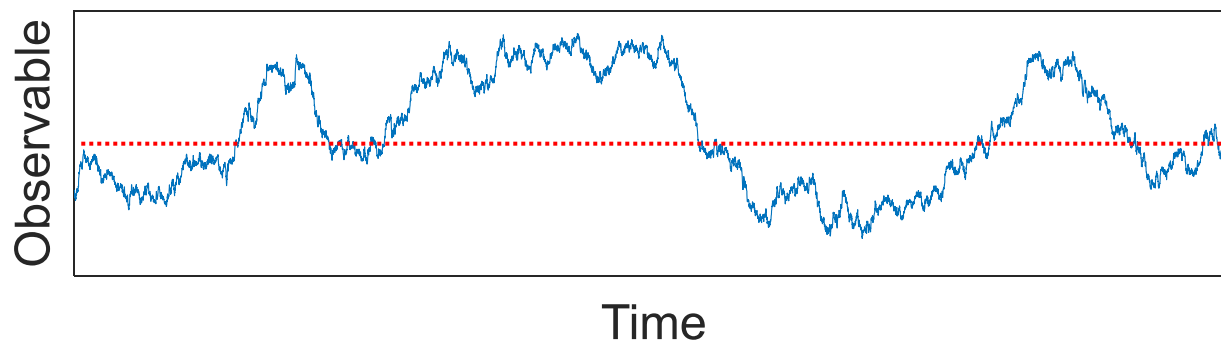
- Fundamental postulates in Statistical Mechanics:
 - **Principle of equal weights:** microstates with equal energy are visited with the same frequency
 - **Ergodic hypothesis:** averages over time are equal with *ensemble* averages...

Averaging Operations and Ensembles

- Let us consider the time average of an observable...
and try to partition the sum as follows:

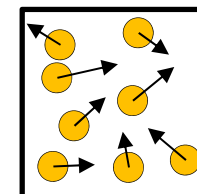
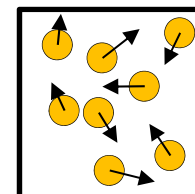
$$G_{\text{obs}} = \frac{1}{\mathcal{N}} \sum_{\alpha=1}^{\mathcal{N}} G_{\alpha} = \sum_{\chi} \frac{1}{\mathcal{N}} \left(\begin{array}{l} \text{Number of times state } \mathbf{s}_{\chi} \text{ is} \\ \text{observed in the } \mathcal{N} \text{ samples} \end{array} \right) G_{\chi}$$

Time average...

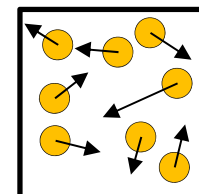


$$\Rightarrow G_{\text{obs}} = \sum_{\chi} P_{\chi} G_{\chi} = \langle G \rangle$$

Ensemble average...



...

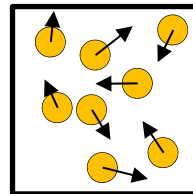


“Copies” of a system each in a different micro-state...

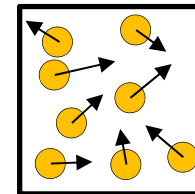
Ensembles

$$G_{\text{obs}} = \sum_{\chi} P_{\chi} G_{\chi} = \langle G \rangle$$

Ensemble average...

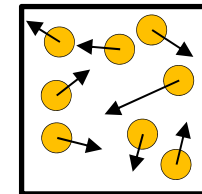


State s_1
Probability P_1



State s_2
Probability P_2

...



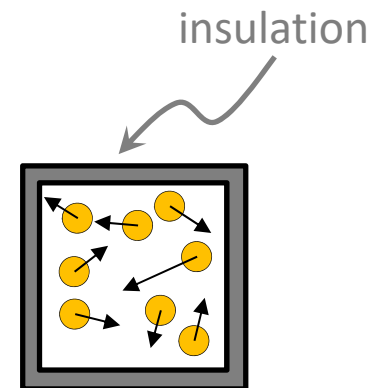
State s_{χ}
Probability P_{χ}

- An **ensemble** is the collection/assembly of all possible microstates, which the system can visit given some macroscopic constraints, for example:
 - **MICROCANONICAL ENSEMBLE**: all states with fixed number of molecules, volume and energy (N, V, E)
 - **CANONICAL ENSEMBLE**: all states with fixed number of molecules, volume and temperature (N, V, T)
 - **GRAND CANONICAL ENSEMBLE**: all states with fixed chemical potential, volume and temperature (μ, V, T)

Microcanonical Ensemble (N, V, E)

- All microstates have the same energy \Rightarrow they are visited with equal probability
- For discrete systems, define the **degeneracy** as:

$$\Omega(N, V, E) = \left(\begin{array}{l} \text{Number of microstates} \\ \text{with } N, V \text{ and energy } E \end{array} \right)$$



No matter exchange
No heat exchange

- Analogously, for continuous systems one can define the **density of states** as:

$$\bar{\Omega}(N, V, E) dE = \left(\begin{array}{l} \text{Number of microstates with} \\ N, V \text{ and energy between } E, E + dE \end{array} \right)$$

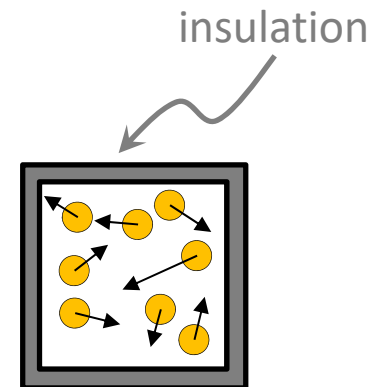
Microcanonical Ensemble

- The probability of each microstate is:

$$P_{\chi} = \frac{1}{\Omega(N, V, E)}$$

Notes:

- States that are not in the ensemble have probability of zero.
- For continuous systems P_{χ} is replaced with a probability density, but similar equations hold. To keep the discussion simple we will focus on the discrete case.



No matter exchange
No heat exchange

*How does this help us
understand the macroscopic world ?*

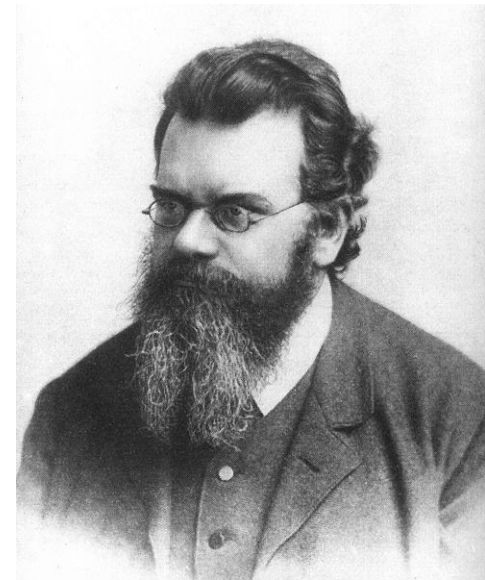
Definition of Entropy

- The microcanonical ensemble allows us to define entropy as:

$$S = k_B \log(\Omega(N, V, E))$$

where k_B is Boltzmann's constant:

$$\begin{aligned} k_B &= 1.38064852 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \\ &= 8.6173303 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1} \end{aligned}$$

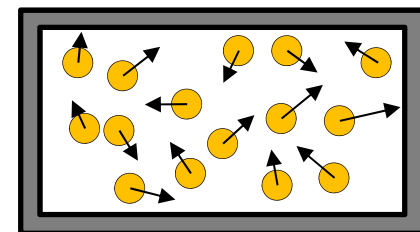
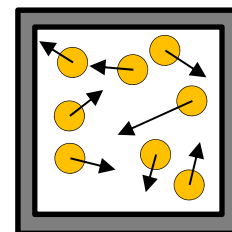


Ludwig Eduard Boltzmann

- By the above definition entropy is **extensive**: if a system is composed of two independent subsystems A and B:

$$\Omega_{AB} = \Omega_A \cdot \Omega_B \Rightarrow$$

$$S_{AB} = k_B \log(\Omega_A \cdot \Omega_B) = S_A + S_B$$



Temperature in the Microcanonical Ensemble ¹⁵

- Since all microstates have the same energy in the microcanonical ensemble, the thermal energy is: $U = E$

- Recall that: $T = \left. \frac{\partial U}{\partial S} \right|_{V,N}$

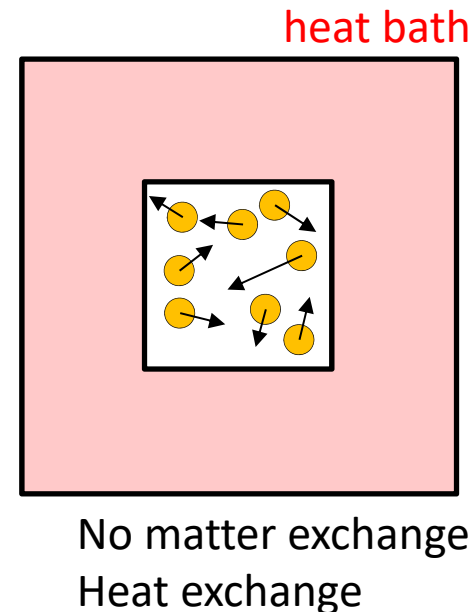
- Therefore the temperature can be calculated from:

$$\beta = (k_B \cdot T)^{-1} = \left. \frac{\partial \log(\Omega)}{\partial E} \right|_{V,N}$$

- For macroscopic systems encountered in nature $\beta > 0$
- Now that we have S , U and T we can calculate any other thermodynamic quantity (see equations of slides 2, 3)

Canonical Ensemble (N, V, T)

- This ensemble comprises microstates with fixed volume and number of molecules
- Energy can fluctuate and the system is at thermal equilibrium with a heat bath kept at temperature T
- Heat bath \gg system

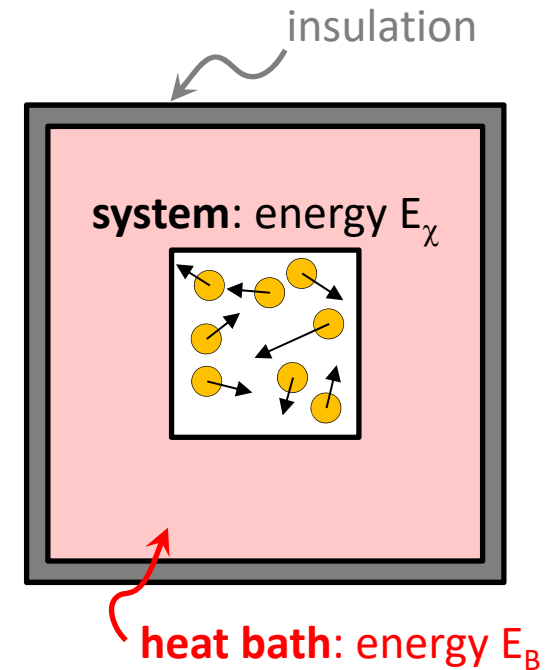
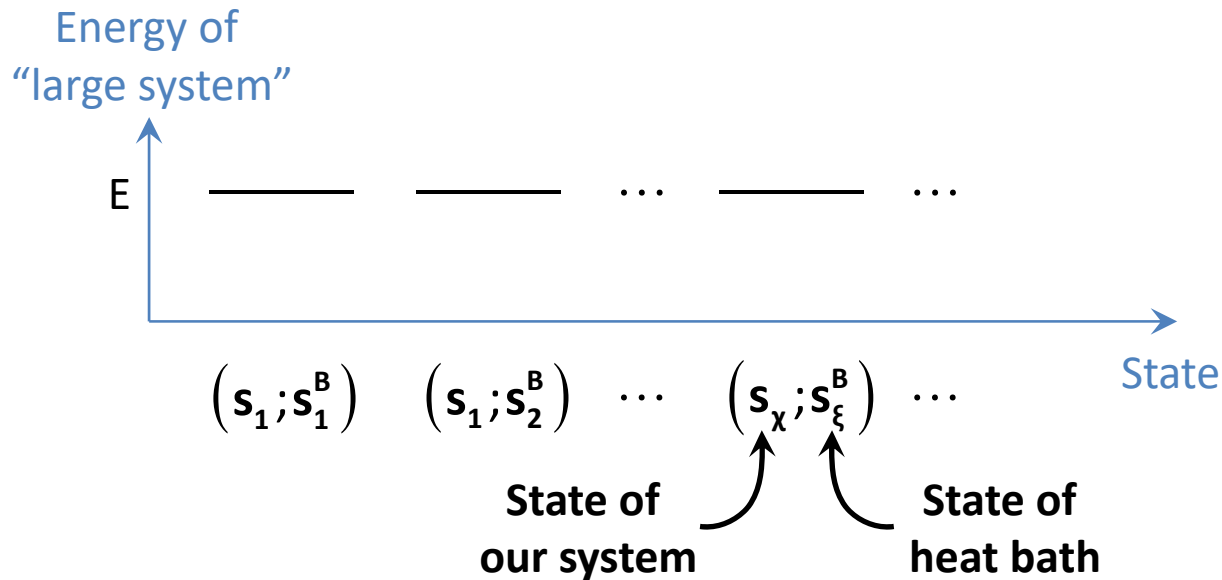


What is the probability that each microstate is visited in this ensemble ?

Probability Distribution in Canonical Ensemble¹⁷

- Consider the system in the canonical ensemble as a subsystem of a “large system” in the microcanonical

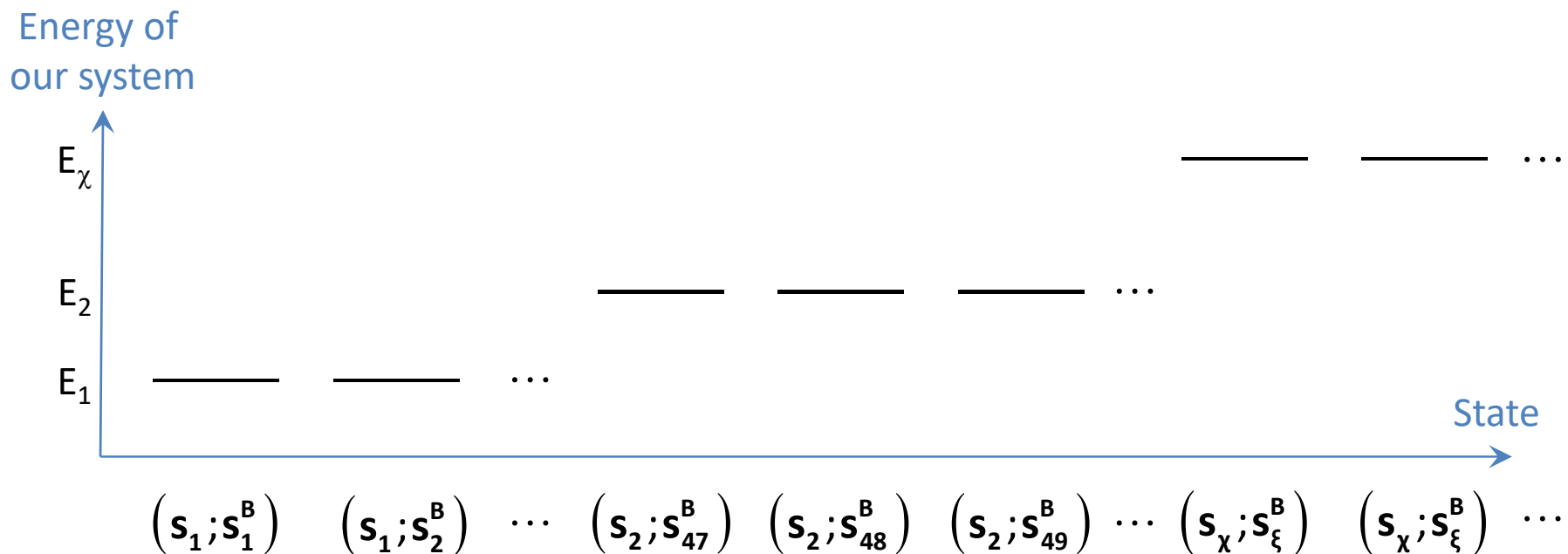
Total energy of “large system”: $E = E_\chi + E_B$



- Proper combinations of these microstates (i.e. with energies summing up to E) are indeed valid (accessible) states of the large system in the microcanonical ensemble...

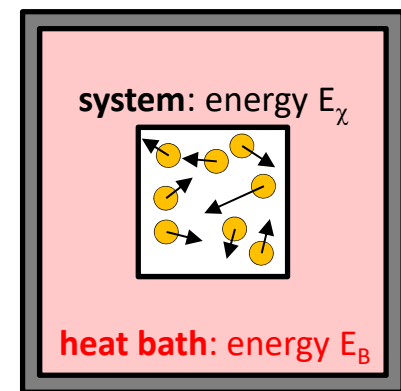
Probability Distribution in Canonical Ensemble ¹⁸

- Consider now a different partitioning of these states:



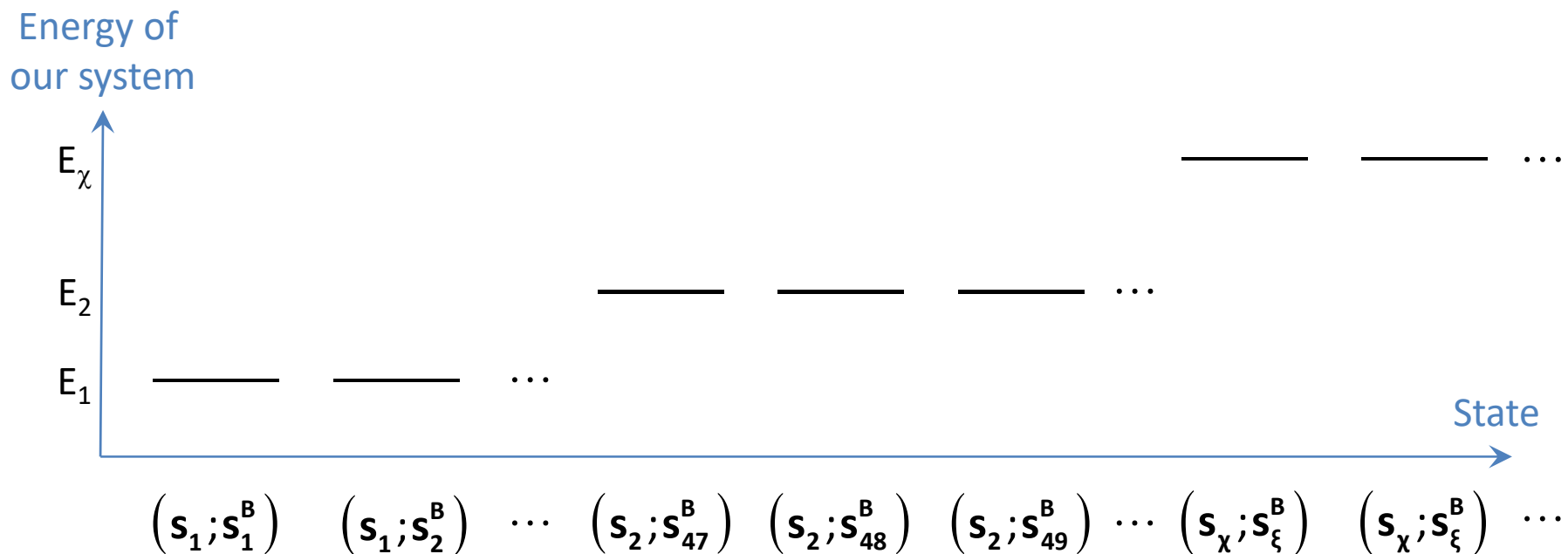
- For a moment, fix the system in state χ . Then the accessible states for the large system are those of the bath, hence:

$$\Omega(E_B) = \Omega(E - E_\chi) \quad \text{since} \quad E = E_\chi + E_B$$



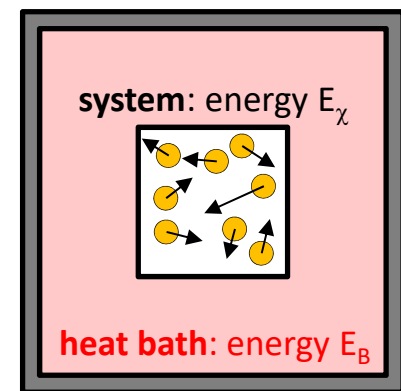
Probability Distribution in Canonical Ensemble¹⁹

- Consider now a different partitioning of these states:



- By the *principle of equal weights* the probability of state χ of the system is:

$$P_\chi \propto \Omega(E_B) = \Omega(E - E_\chi)$$



Probability Distribution in Canonical Ensemble ²⁰

- So, the probability of state s_χ in the canonical ensemble:

Degeneracy of bath energy level

A more “well-behaved” function...

$$P_\chi \propto \Omega(E - E_\chi) = \exp\left[\log(\Omega(E - E_\chi))\right]$$

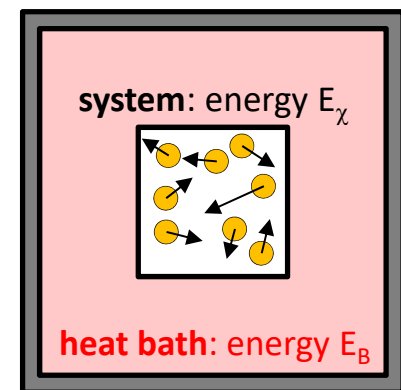
Energy of “large system”
in microcanonical ensemble

Energy of state χ of system
in canonical ensemble

- The presence of Ω and E in this equation is inconvenient!
- Since E_χ is small, introduce a Taylor expansion for $\log(\Omega)$:

$$\log(\Omega(E - E_\chi)) = \log(\Omega(E)) - E_\chi \frac{d\log(\Omega)}{dE} + \dots$$

$$\text{but } \left. \frac{\partial \log(\Omega)}{\partial E} \right|_{V,N} = \beta$$

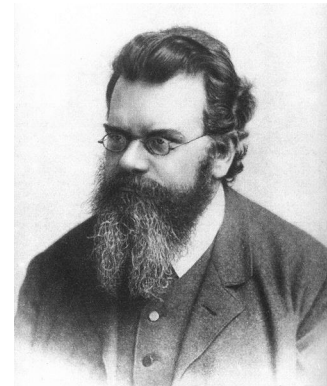


Canonical Partition Function

- Therefore: $P_{\chi} \propto \exp(-\beta E_{\chi})$

Canonical (or Boltzmann) distribution law

- Proportionality constant determined by normalisation condition: $\sum_{\chi} P_{\chi} = 1$
- Hence: $P_{\chi} = \frac{1}{Q} \exp(-\beta E_{\chi})$ with $Q = \sum_{\chi} \exp(-\beta E_{\chi})$
 - Q is referred to as the “**canonical partition function**”
 - It is a function of N, V, T (or equivalently N, V, β)
 - If the partition function of a system is known, one can derive any thermodynamic quantity!



Thermal Energy in the Canonical Ensemble

- Consider for example the internal/thermal energy:

$$U = \langle E \rangle = \sum_{\chi} E_{\chi} P_{\chi}$$

Quantity being averaged

$$\langle E \rangle = \frac{\sum_{\chi} E_{\chi} \exp(-\beta E_{\chi})}{\sum_{\zeta} \exp(-\beta E_{\zeta})}$$

Probability of microstate χ

Canonical partition function, Q

\Rightarrow

$$\langle E \rangle = \frac{1}{Q} \sum_{\chi} \frac{\partial \exp(-\beta E_{\chi})}{\partial(-\beta)} = -\frac{1}{Q} \frac{\partial}{\partial \beta} \sum_{\chi} \exp(-\beta E_{\chi}) \Rightarrow$$

$$\langle E \rangle = - \left. \frac{\partial \log Q}{\partial \beta} \right|_{N,V}$$

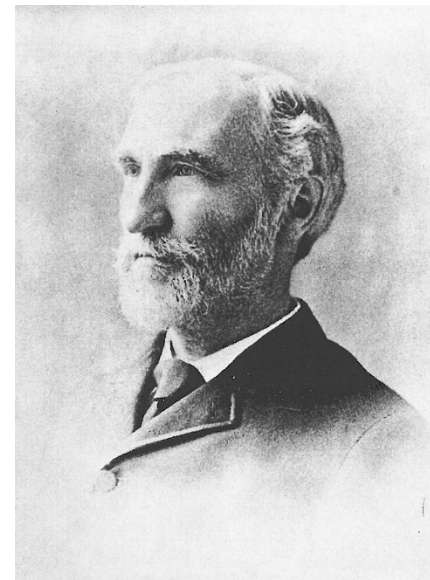
Calculation of Entropy

- Gibbs provided a general equation for **entropy**, valid in fact for *any ensemble*:

$$S = -k_B \sum_{\chi} P_{\chi} \log(P_{\chi})$$

- In the microcanonical ensemble, this simplifies to Boltzmann's formula! (slide 14)

Prove this as homework... 



Josiah Willard Gibbs

- In the canonical ensemble: $P_{\chi} = \frac{1}{Q} \exp(-\beta E_{\chi})$

$$S = -k_B \frac{1}{Q} \sum_{\chi} \exp(-\beta E_{\chi}) [-\beta E_{\chi} - \log(Q)]$$

Entropy and Helmholtz Free Energy

- Continuing with entropy in the canonical ensemble...

$$S = -k_B \frac{1}{Q} \sum_{\chi} \exp(-\beta E_{\chi}) [-\beta E_{\chi} - \log(Q)] \Rightarrow$$

$$S = -k_B \frac{1}{Q} \left[-\beta \sum_{\chi} E_{\chi} \exp(-\beta E_{\chi}) - Q \log(Q) \right] \Rightarrow$$

$$S = -k_B \left[-\frac{1}{k_B T} U - \log(Q) \right] = \frac{U}{T} + k_B \log(Q) \Rightarrow$$

$$T S = U + k_B T \log(Q)$$

- But from thermodynamics we know: $A = U - T S$ (slide 3)

... therefore: $A = -k_B T \log(Q)$

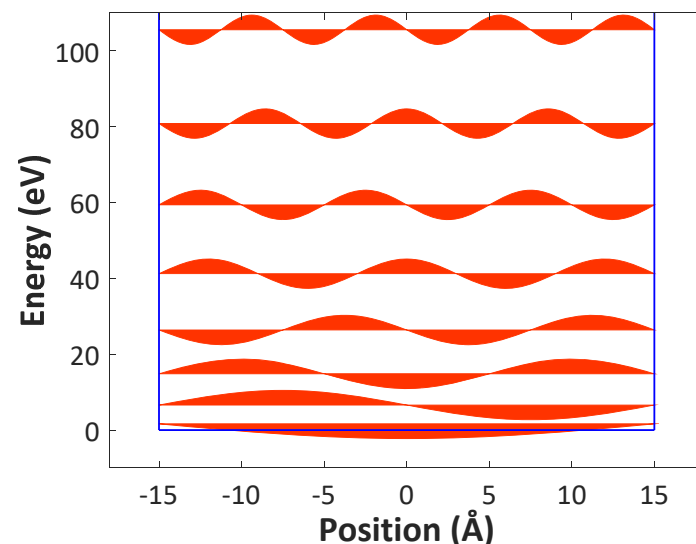
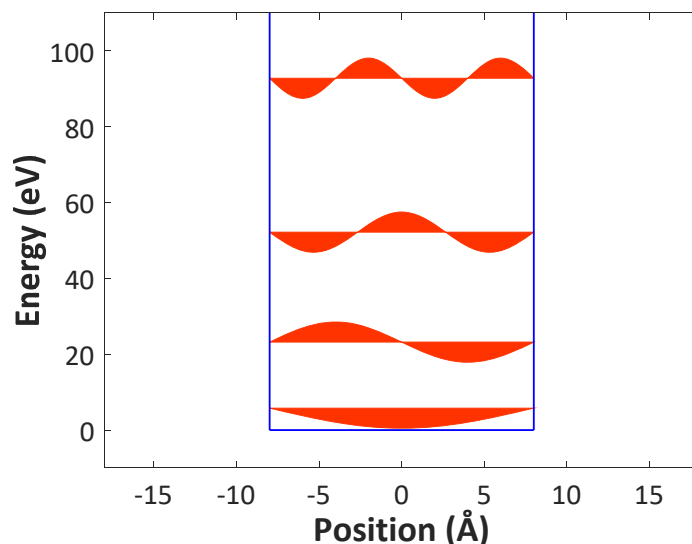
Pressure in the Canonical Ensemble

- Pressure is now easy to calculate, since: $\left. \frac{\partial A}{\partial V} \right|_{N,T} = -p$

$$\Rightarrow p = k_B T \frac{\partial \log(Q)}{\partial V}$$

- The volume doesn't appear explicitly in Q , but it's there... It affects the energy levels!

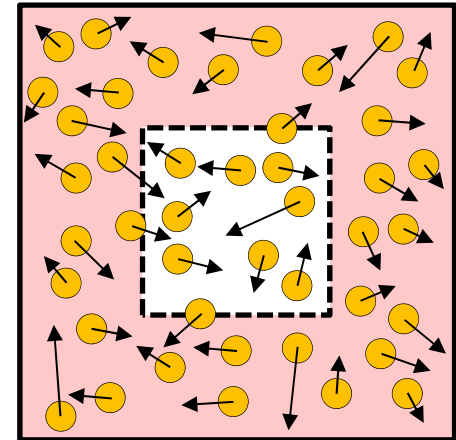
– e.g. for a quantum particle in a 1D box: $E_n = \frac{n^2 h^2}{8 m L^2}$



Grand Canonical Ensemble (μ, V, T)

- This ensemble comprises microstates with fixed volume
- Energy and number of molecules can fluctuate and the system is at thermodynamic equilibrium with
 - a heat bath kept at temperature T
 - a matter reservoir kept at chemical potential μ
- Heat bath & matter reservoir \gg system

heat bath, matter reservoir



Matter exchange
Heat exchange

One can apply a similar reasoning as that for the canonical ensemble to prove that...

Probability Distribution in Grand Canonical Ensemble²⁷

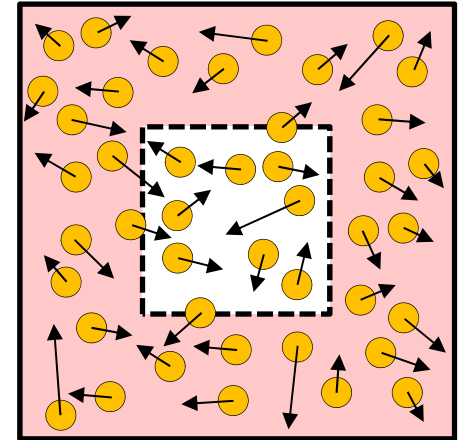
- The probability in the Grand Canonical Ensemble is:

$$P_{\chi} = \frac{1}{\Xi} \exp(-\beta E_{\chi} + \beta \mu N_{\chi})$$

$$\text{with } \Xi = \sum_{\chi} \exp(-\beta E_{\chi} + \beta \mu N_{\chi})$$

- Ξ is referred to as the “**grand canonical partition function**”
- It is a function of μ , V , T (or equivalently μ , V , β)

heat bath, matter reservoir



Matter exchange
Heat exchange

Number of Particles in Grand Canonical Ensemble

- In the microcanonical and canonical ensembles, the number of particles (molecules) was fixed.
- Not the case in grand canonical! How can we find the **average number of particles**?

$$\langle N \rangle = \frac{1}{\Xi} \sum_{\chi} N_{\chi} \exp(-\beta E_{\chi} + \beta \mu N_{\chi}) \quad \Rightarrow$$

$$\langle N \rangle = \frac{1}{\Xi} \sum_{\chi} \frac{\partial \exp(-\beta E_{\chi} + \beta \mu N_{\chi})}{\partial(\beta \mu)} \quad \Rightarrow$$

$$\langle N \rangle = \frac{1}{\Xi} \frac{\partial}{\partial(\beta \mu)} \sum_{\chi} \exp(-\beta E_{\chi} + \beta \mu N_{\chi}) = \frac{\partial \log(\Xi)}{\partial(\beta \mu)}$$

Entropy and Pressure in Grand Canonical Ensemble ²⁹

- Let us calculate the entropy from Gibbs' formula:

$$S = -k_B \sum_{\chi} P_{\chi} \log(P_{\chi}) \Rightarrow$$

$$S = -k_B \sum_{\chi} P_{\chi} \left[-\log(\Xi) - \beta E_{\chi} + \beta \mu N_{\chi} \right] \Rightarrow$$

$$S = -k_B \left[-\log(\Xi) - \beta \langle E \rangle + \beta \mu \langle N \rangle \right] \Rightarrow$$

Recall:
 $\beta = (k_B T)^{-1}$

$$TS = k_B T \log(\Xi) + U - \mu N$$

↖ The macroscopic number of molecules

Recalling Euler's
theorem (slide 4):

$$pV = k_B T \log(\Xi)$$

Take Home Messages

- Statistical Mechanics is all about deriving expressions for familiar macroscopic thermodynamic variables from microscopic laws (e.g. Schrödinger's equation or Newton's law of motion)
- Two fundamental postulates:
 - **Principle of equal weights...**
 - **Ergodic hypothesis...**
- Averaging makes use of **ensembles**. Commonly used:
 - Microcanonical (N, V, E)
 - Canonical (N, V, T)
 - Grand canonical (μ, V, T)
- **Macroscopically, all ensembles give “same answers” ...**