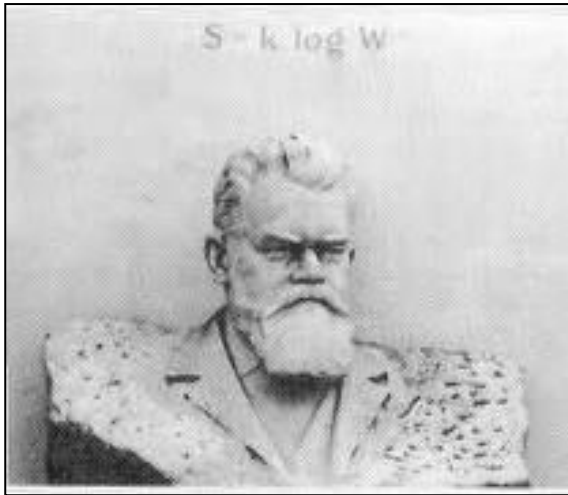
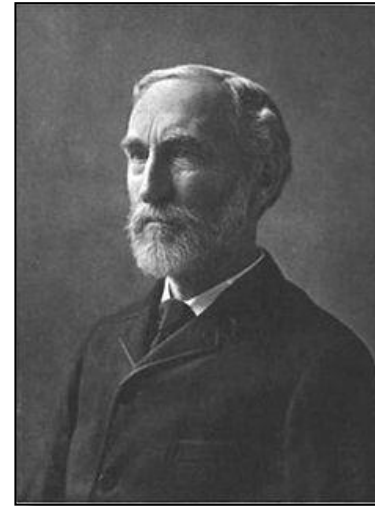


# Statistical Mechanics - Ensembles

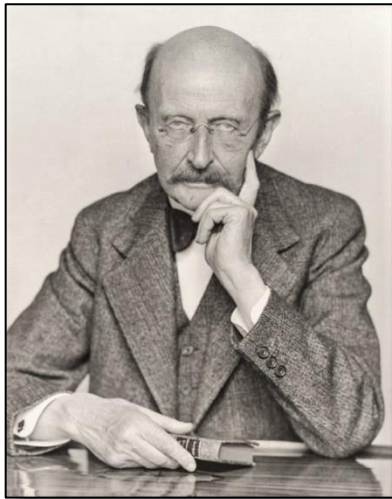
Boltzmann and Gibbs ensemble methods for systems with interacting particles



Ludwig Boltzmann  
(1844 – 1906)



J. Willard Gibbs  
(1839-1903)



Max Planck  
(1858 – 1947)



Sir C. G. Darwin  
(1887 – 1962)



Sir R. H. Fowler  
(1889-1944)

## Energy distribution of systems with interacting molecules or systems interacting with the environment

**Non-interacting systems:** Total energy is subdivided into a sum of one molecule energies.

$$E_{tot} = E_1 + E_2 + \cdots + E_N$$

The probability distribution for  $E_{tot}$  is the product of independent single molecule energy probabilities

$$P_N(E_{tot}) = P_1(E_1)P_1(E_2)P_1(E_3)\cdots P_1(E_N)$$

**Interacting systems:** Total energy cannot be subdivided into a sum of one molecule energies. Interactions between molecules also contribute to the energy

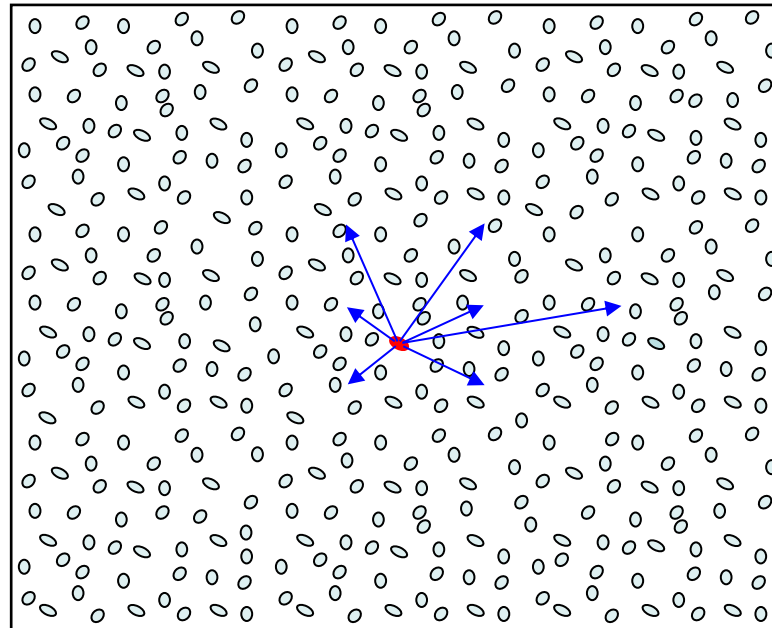
$$\begin{aligned} E_{tot} &= K_1 + K_2 + \cdots + K_N + U_{12} + U_{13} + \cdots + U_{ij} + \cdots \\ &\neq E_1 + E_2 + \cdots + E_N \end{aligned}$$

The probability distribution for  $E_{tot}$  is not the product of independent single molecule energy probabilities

$$P_N(E_{tot}) \neq P_1(E_1)P_1(E_2)P_1(E_3)\cdots P_1(E_N)$$

# Energy distribution of systems with interacting molecules or systems interacting with the environment

- How do we find the distribution of velocity and positions for systems with interactions?
- Do attractive forces increase the probability of finding molecules closer together?
- Do repulsive forces increase the probability of finding molecules farther apart?



## Distributing molecules among energy levels to give a fixed total energy

**Goal:** For interacting systems, how do we determine the distribution of molecules / systems among the states?

- 1) We know the values of a limited number of macroscopic thermodynamic variables, such as temperature, pressure, ... **(the macrostate of the system)**
- 2) We know the nature of the individual molecules (structure, energy levels, etc.) and their interactions with other molecules



How can we determine the possible microstates that are consistent with constraints related to the macrostate of the system?

How can we determine other macroscopic thermodynamic properties of the system from knowledge of the microscopic properties?

# Counting states: Ways of distributing **distinguishable** objects among bins

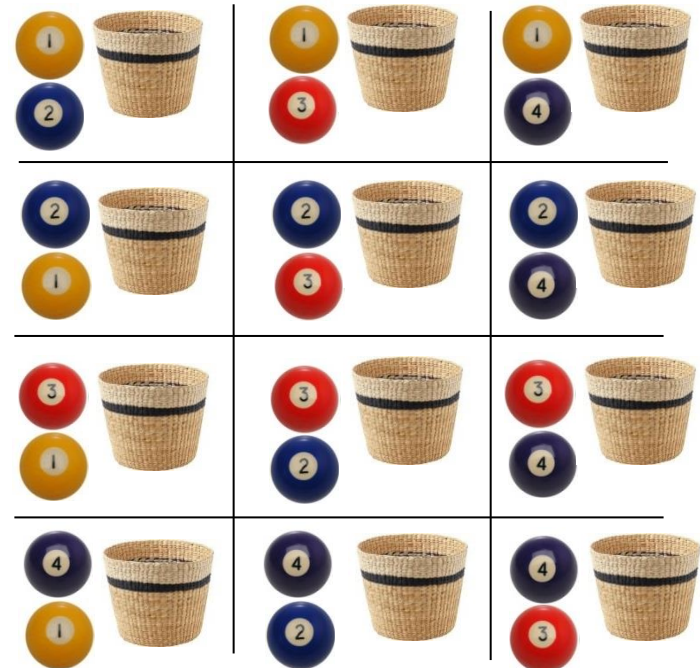


How many ways are there to place one object from a collection of four into a single bin?

How many ways are there to place two objects from a collection of four into a single bin



$W = 4$   
possible ways



$W = 4 \times 3$  possible ways

If the order of placing the objects into the bins is not important, not all ways are different

# Distributing all distinguishable objects among bins

Ways of arranging four distinguishable objects



(1234) (1243) (1324) (1342) (1423) (1432)  
 (2134) (2143) (2314) (2341) (2413) (2431)  
 (3124) (3142) (3214) (3241) (3412) (3421)  
 (4123) (4132) (4213) (4231) (4312) (4321)

$$4! = 4 \times 3 \times 2 \times 1$$

But these are all equivalent if we don't care about order!

How many ways are there to bin the four distinguishable objects into two groups?



Binning 4 distinguishable objects into two groups of 2 and 2  
 (don't care about order)

$\{(12)(34)\}$   $\{(13)(24)\}$   $\{(14)(23)\}$   
 $\{(23)(14)\}$   $\{(24)(13)\}$   $\{(34)(12)\}$

Binning 4 distinguishable objects into two groups of 3 and 1  
 (don't care about order)

$\{(123)(4)\}$   $\{(124)(3)\}$   $\{(134)(2)\}$   $\{(234)(1)\}$

# Distributing all distinguishable objects among bins

If the order of the balls in the bins is not important,

Distinct binning of 4 distinguishable objects into groups of 2 and 2

$\{(12)(34)\}$   $\{(13)(24)\}$   $\{(14)(23)\}$   
 $\{(23)(14)\}$   $\{(24)(13)\}$   $\{(34)(12)\}$

$$W = \frac{4!}{2!2!} = \frac{4 \times 3 \times 2 \times 1}{(2 \times 1) \times (2 \times 1)} = 6$$

$$a_1 = 2$$
$$a_2 = 2$$

Distinct binning of 4 distinguishable objects into groups of 3 and 1

$\{(123)(4)\}$   $\{(124)(3)\}$   $\{(134)(2)\}$   $\{(243)(1)\}$

$$W = \frac{4!}{3!1!} = \frac{4 \times 3 \times 2 \times 1}{(3 \times 2 \times 1) \times 1} = 4$$

$$a_1 = 3$$
$$a_2 = 1$$

Distinct binning of  $N$  distinguishable objects into  $k$  bins groups of  $a_1, a_2, \dots, a_k$

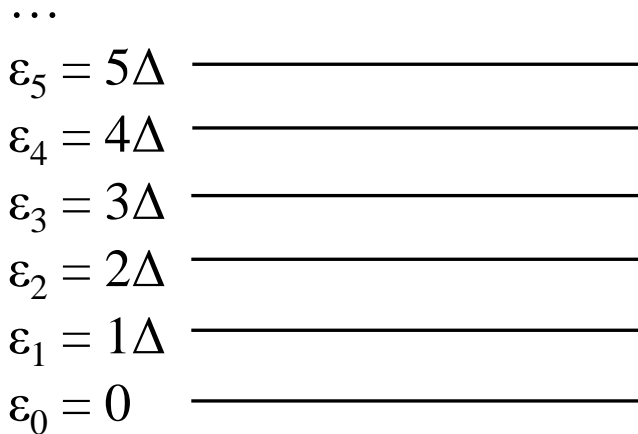
$$W = \frac{N!}{a_1! a_2! \dots a_k!} = \frac{N!}{\prod_{j=1}^k a_j!}$$

Product sign: multiplication over all bins  $j$  from 1 to  $k$

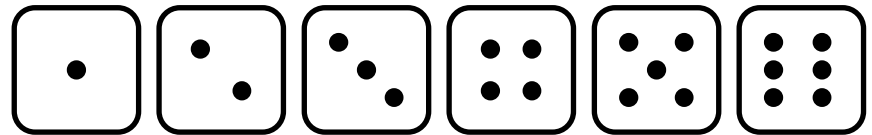
# Distributing molecules among energy levels to give a fixed total energy

**Goal:** Given the quantum states of the system, how do we determine the distribution of molecules among the states consistent with known macroscopic information on the system?

**Example:** Assume a non-interacting system with equally spaced energy levels of energy:  $0, \Delta, 2\Delta, 3\Delta, \dots$



The discrete states are analogous to the discrete outcomes of the role of a die



Find distributions of molecules among the levels (microstates) satisfying constraints:

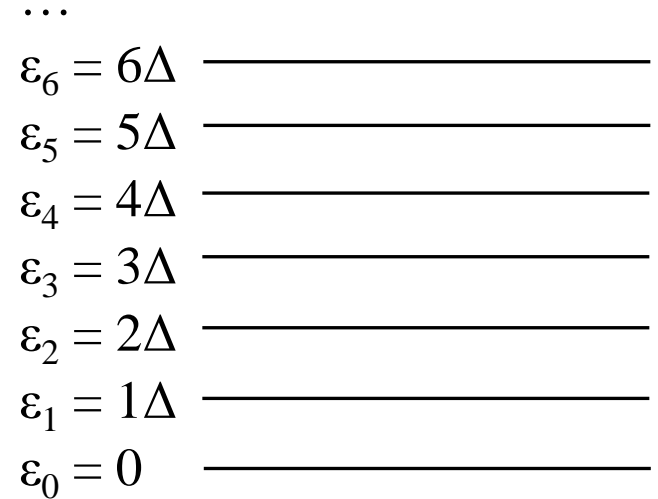
- 1) The total number of molecules in the system is constant
- 2) The total energy of the system is constant



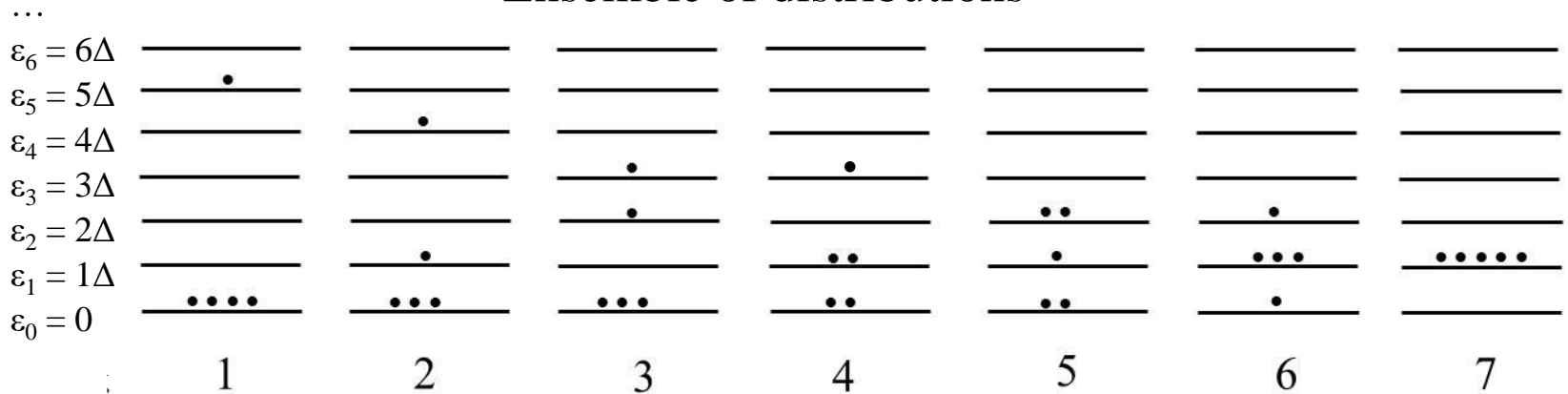
# Example: Distributing distinguishable molecules among energy levels

- A system with equally spaced energy levels;
- What are the distributions of 5 independent molecules among the energy levels satisfying the constraint:

The “macrostate”:  $E_{tot} = 5\Delta$



Ensemble of distributions



How many ways can each distribution be constructed (i.e., the degeneracy)?

$$W(\mathbf{a}) = \frac{N!}{\prod_j a_j!}$$

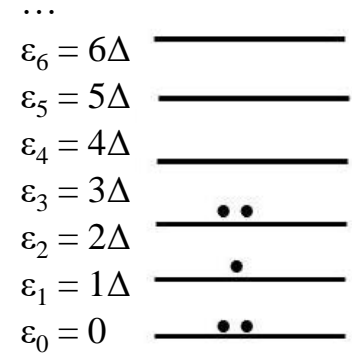
5	20	20	30	30	20	1
---	----	----	----	----	----	---

# Possible distributions satisfying the two constraints on the macrostate

Distributions ( $d_i$ ) show how molecules occupy energy levels

$a_j$  : Number of molecules that occupy energy level  $j$  in each distribution (occupancy of state  $j$ )

$a_2=2$   
 $a_1=1$   
 $a_0=2$



Distributions: $\{a_0, a_1, a_2, \dots, a_5\}$	Degeneracy (weight) $W_i = N! / \prod_j a_{j,i}!$ of each distribution	Probability of each distribution $P(d_i)$
$d_1: \{4, 0, 0, 0, 0, 1\}$	$W = 5! / [4! 0! 0! 0! 0! 1! \dots] = 5$	5/126
$d_2: \{3, 1, 0, 0, 1, 0\}$	20	20/126
$d_3: \{3, 0, 1, 1, 0, 0\}$	20	20/126
$d_4: \{2, 2, 0, 1, 0, 0\}$	30	30/126
$d_5: \{2, 1, 2, 0, 0, 0\}$	30	30/126
$d_6: \{1, 3, 1, 0, 0, 0\}$	20	20/126
$d_7: \{0, 5, 0, 0, 0, 0\}$	1 $\sum_i W_i = 126$	1/126

- A total 126 microstates of the molecules give the same macrostate
- All 126 microstates are equally probable (**law of equal *a priori* probabilities**) but different distributions,  $d_i$ , show up with different probability

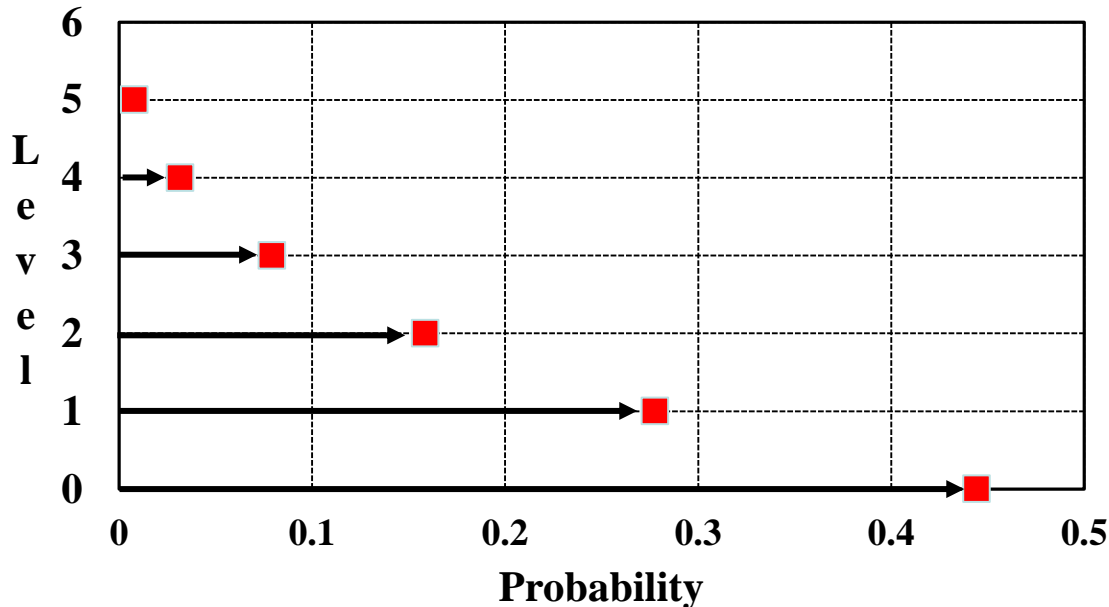
# Probability of having different levels occupied

Probability of level 0 being occupied in the collection (ensemble) of distributions

$$P(0) = \sum_{d=1}^7 p_0(d) \times P(d)$$

$$= \frac{4}{5} \times \frac{5}{126} + \frac{3}{5} \times \frac{20}{126} + \frac{3}{5} \times \frac{20}{126} + \frac{2}{5} \times \frac{30}{126} + \frac{2}{5} \times \frac{30}{126} + \frac{1}{5} \times \frac{20}{126} + \frac{0}{5} \times \frac{1}{126}$$

$$\begin{aligned} \dots \\ \varepsilon_5 &= 5\Delta \text{ —————} \\ \varepsilon_4 &= 4\Delta \text{ —————} \\ \varepsilon_3 &= 3\Delta \text{ —————} \\ \varepsilon_2 &= 2\Delta \text{ —————} \\ \varepsilon_1 &= 1\Delta \text{ —————} \\ \varepsilon_0 &= 0 \text{ —————} \end{aligned}$$



Distributions:	$P(d_i)$
$d_1: \{4,0,0,0,0,1\}$	5/126
$d_2: \{3,1,0,0,1,0\}$	20/126
$d_3: \{3,0,1,1,0,0\}$	20/126
$d_4: \{2,2,0,1,0,0\}$	30/126
$d_5: \{2,1,2,0,0,0\}$	30/126
$d_6: \{1,3,1,0,0,0\}$	20/126
$d_7: \{0,5,0,0,0,0\}$	1/126

The distribution of levels is **graded**.

- Each energy state is less populated than those below, but more populated than those above

# Systems with large numbers of molecules (Problem Set)

**Macrostate**  $N = 7$  and  $E_{\text{tot}} = 7\Delta$ ;  $\langle E \rangle = \Delta$  determine all possible distributions

Distributions: $\{a_0, a_1, a_2, \dots, a_7\}$	Degeneracy(weight) of each distribution	Probability of each distribution $P(d_i)$
{6,0,0,0,0,0,0,1}	7	7/1716
{5,1,0,0,0,0,1,0}	42	42/1716
{5,0,1,0,0,1,0,0}	42	42/1716
{5,0,0,1,1,0,0,0}	42	42/1716
{4,2,0,0,0,1,0,0}	105	105/1716
{4,1,1,0,1,0,0,0}	210	210/1716
{4,1,0,2,0,0,0,0}	105	105/1716
{4,0,2,1,0,0,0,0}	105	105/1716
{3,3,0,0,1,0,0,0}	140	140/1716
{3,2,1,1,0,0,0,0}	420	420/1716
{3,1,3,0,0,0,0,0}	140	140/1716
{2,4,0,1,0,0,0,0}	105	105/1716
{2,3,2,0,0,0,0,0}	210	210/1716
{1,5,1,0,0,0,0,0}	42	42/1716
{0,7,0,0,0,0,0,0}	1	1/1716
Total No. of microstates: 1716		

- ...
- $\epsilon_7 = 7\Delta$  \_\_\_\_\_
  - $\epsilon_6 = 6\Delta$  \_\_\_\_\_
  - $\epsilon_5 = 5\Delta$  \_\_\_\_\_
  - $\epsilon_4 = 4\Delta$  \_\_\_\_\_
  - $\epsilon_3 = 3\Delta$  \_\_\_\_\_
  - $\epsilon_2 = 2\Delta$  \_\_\_\_\_
  - $\epsilon_1 = 1\Delta$  \_\_\_\_\_
  - $\epsilon_0 = 0$  \_\_\_\_\_

Most probable  
distribution

## Systems with large numbers of molecules – Example 2

**Macrostate:**  $N = 9$  and  $E_{\text{tot}} = 9\Delta$ ;  $\langle E \rangle = \Delta$  determine all possible distributions

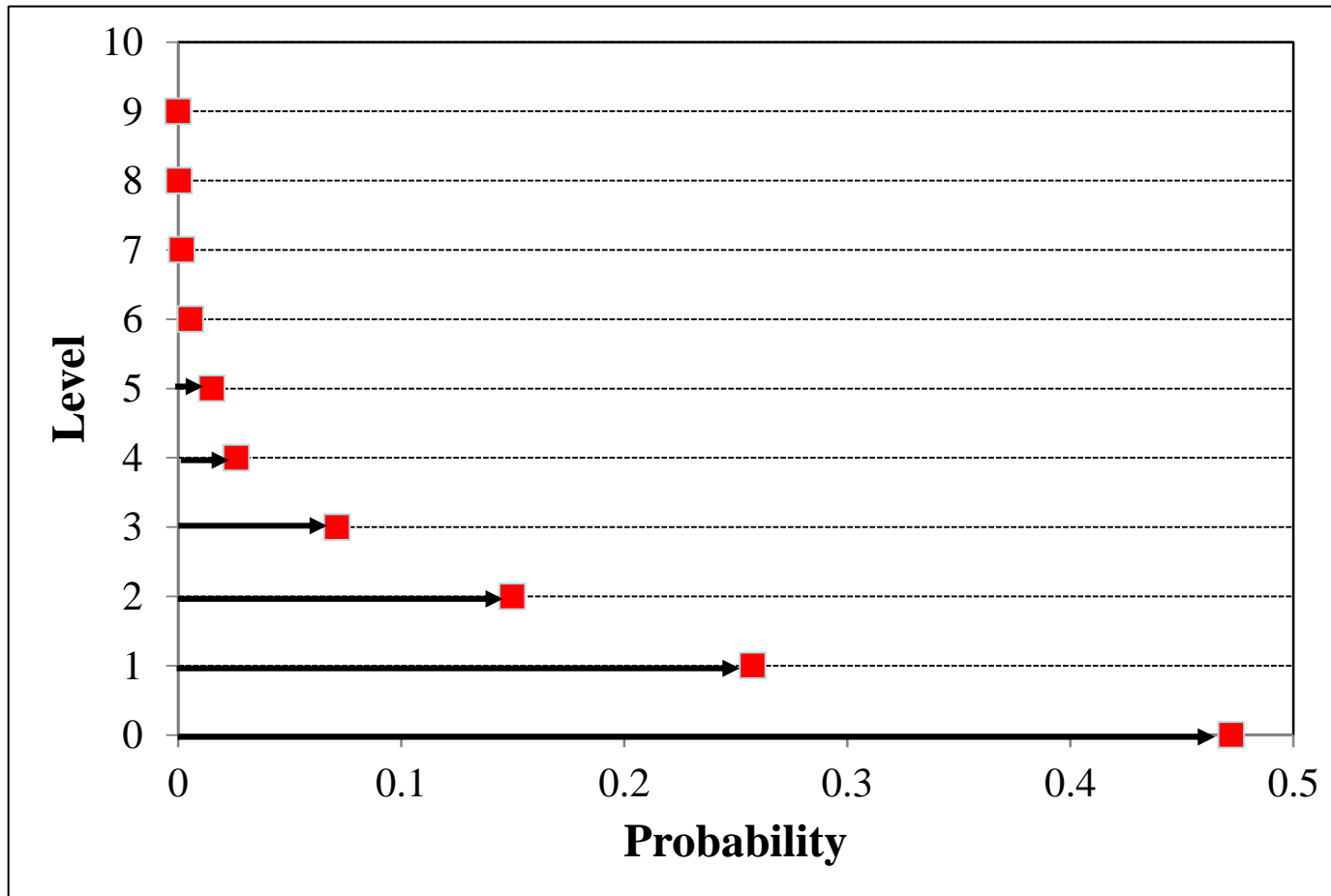
Distributions $\{a_0, a_1, a_2, \dots, a_9\}$	Degeneracy (Weight)	Distributions: $\{a_0, a_1, a_2, \dots, a_9\}$	Degeneracy (Weight)
$\{8,0,0,0,0,0,0,0,0,1\}$	9	$\{4,4,0,0,0,1,0,0,0,0\}$	630
$\{7,1,0,0,0,0,0,0,1,0\}$	72	$\{4,1,4,0,0,0,0,0,0,0\}$	630
$\{7,0,1,0,0,0,0,1,0,0\}$	72	$\{4,3,1,0,1,0,0,0,0,0\}$	2520
$\{7,0,0,1,0,0,1,0,0,0\}$	72	$\{4,3,0,2,0,0,0,0,0,0\}$	1260
$\{7,0,0,0,1,1,0,0,0,0\}$	72	$\{4,2,2,1,0,0,0,0,0,0\}$	3780
$\{6,2,0,0,0,0,0,1,0,0\}$	252	$\{3,3,3,0,0,0,0,0,0,0\}$	1680
$\{6,0,2,0,0,1,0,0,0,0\}$	252	$\{3,4,1,1,0,0,0,0,0,0\}$	2520
$\{6,1,1,0,0,0,1,0,0,0\}$	504	$\{3,5,0,0,1,0,0,0,0,0\}$	504
$\{6,1,0,1,0,1,0,0,0,0\}$	504	$\{2,6,0,1,0,0,0,0,0,0\}$	252
$\{6,0,1,1,1,0,0,0,0,0\}$	504	$\{0,9,0,0,0,0,0,0,0,0\}$	1
$\{6,0,0,3,0,0,0,0,0,0\}$	84		Sum of microstates: 21,718
$\{5,3,0,0,0,0,1,0,0,0\}$	504		
$\{5,0,3,1,0,0,0,0,0,0\}$	504		
$\{5,2,1,0,0,1,0,0,0,0\}$	1512		
$\{5,1,2,0,1,0,0,0,0,0\}$	1512		
$\{5,1,1,2,0,0,0,0,0,0\}$	1512		

As  $N$  in the system increases, there are a few distributions with larger weight and many more with smaller weights

$$W_i = N! / \prod_j a_{j,i}!$$

# Probability of having different levels occupied

$$N = 9 \text{ and } E_{\text{tot}} = 9\Delta$$



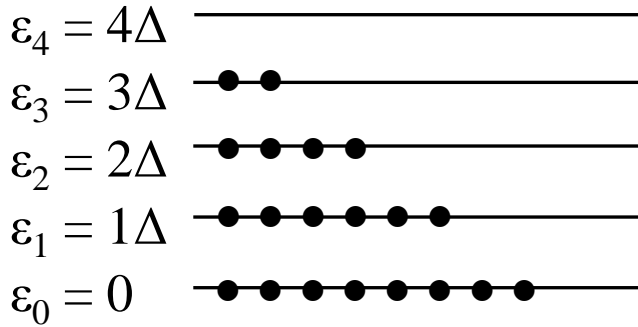
...

$\varepsilon_5 = 5\Delta$	_____
$\varepsilon_4 = 4\Delta$	_____
$\varepsilon_3 = 3\Delta$	_____
$\varepsilon_2 = 2\Delta$	_____
$\varepsilon_1 = 1\Delta$	_____
$\varepsilon_0 = 0$	_____

- Probabilities of levels being occupied are graded
- The most probable distribution of levels is also graded!  $\{4,2,2,1,0,0,0,0,0,0\}$

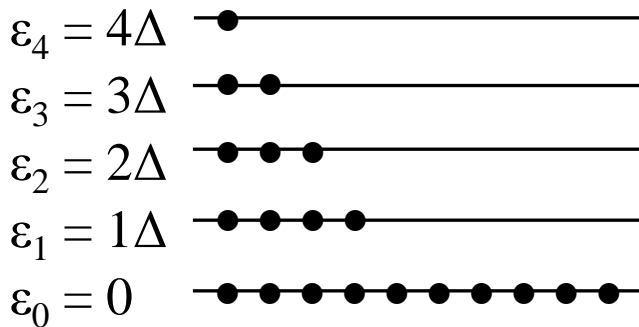
## What happens with larger numbers of molecules?

$N = 20$  and  $E_{\text{tot}} = 20\Delta$

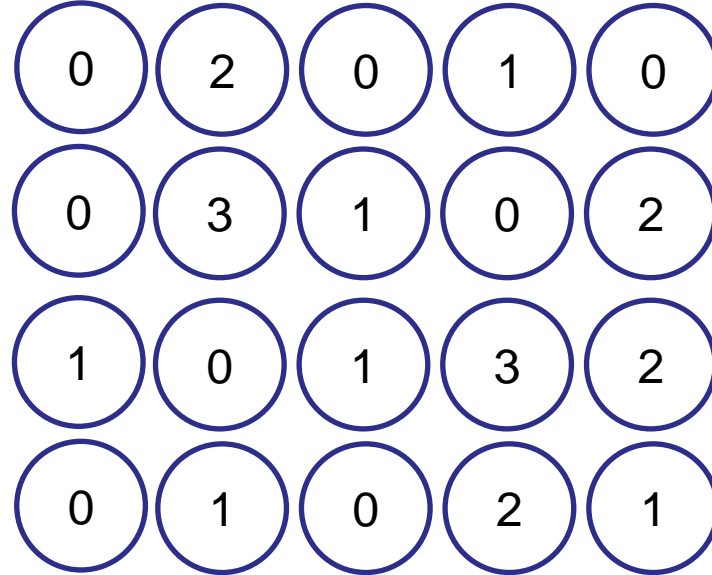


$W = 20! / \prod_j a_j! = 1.7459 \times 10^9$

Another graded distribution



Consider a specific distribution  
(energy level indicated in each circle)



$W' = 2.3279 \times 10^9$

*A limited number of graded distributions become overwhelmingly more probable and dominate the properties of the ensemble*

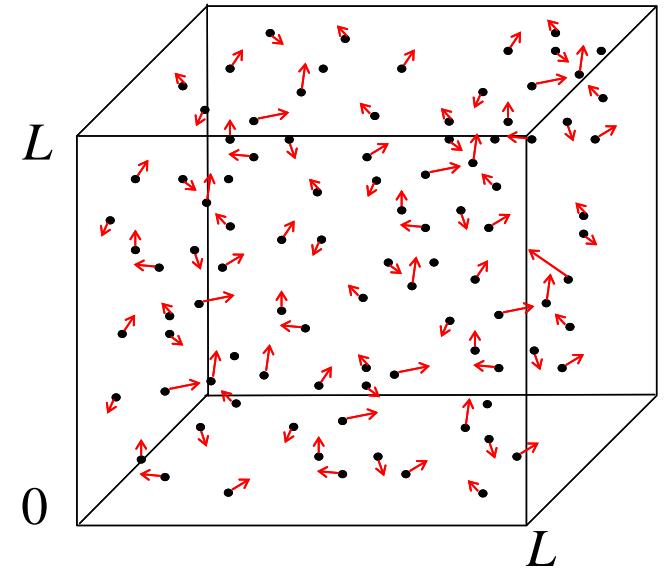
# Distribution of non-interacting molecules among discrete energy levels (states)

Take an isolated ideal gas system of  $N$  molecules with the total energy  $E_{tot}$

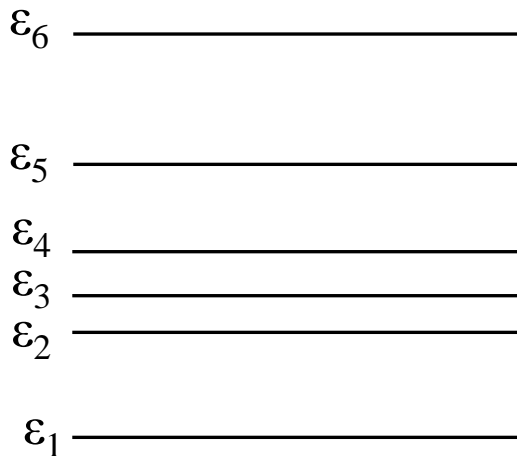
Each molecule is in a particle-in-box state

$\mathbf{n}_i = \{n_{xi}, n_{yi}, n_{zi}\}$  with energy  $\varepsilon_i$

$$\varepsilon_{\mathbf{n},i}(V) = \frac{h^2 (n_{xi}^2 + n_{yi}^2 + n_{zi}^2)}{8mV^{2/3}}$$



A set of discrete energy levels is available to each molecule:



Total energy of the  $N$ -molecule system:

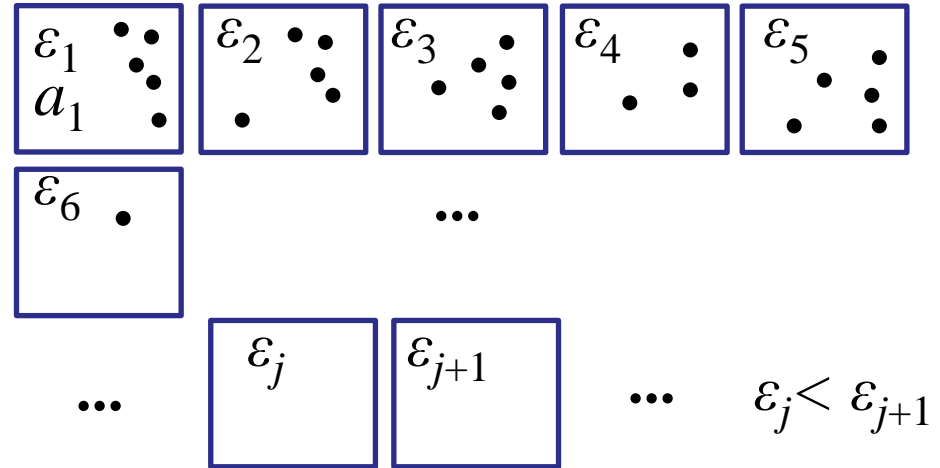
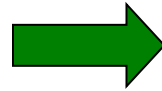
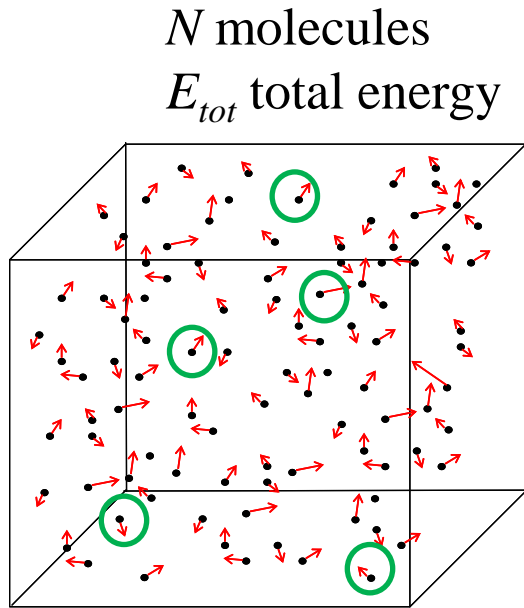
$$E_{tot}(N, V) = \frac{h^2}{8mV^{2/3}} \sum_{v=1}^N (n_{v,x}^2 + n_{v,y}^2 + n_{v,z}^2)$$



# Distribution of non-interacting molecules among state energies

All molecules are binned by placing each into a slot corresponding to its energy state

Make bins for each possible molecular energy state



$a_1$  is the occupancy (number of molecules) in energy state 1

Quantum energy level

Occupancy

$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_3$	$\varepsilon_4$	$\varepsilon_5$	...
$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	...

The distribution of molecules among levels must satisfy the constraints:

$$\begin{cases} \sum_j a_j = N \\ \sum_j a_j \varepsilon_j(V) = E_{tot} \end{cases}$$

- Total occupancies must equal the number of molecules
- Total energy of all molecules is fixed

# The most probable distribution for systems with large numbers of molecules

- The number of ways  $W(\mathbf{a})$  molecules can be distributed among energy levels increases greatly for large numbers of molecules and high energies
- The **most probable distribution**  $\{a^*\}$ , gives the greatest degeneracy  $W^*(\{\mathbf{a}\})$  and its probability dominates other macrostates as the number of molecules increases

How do we find the most probable distribution?

Maximize  $W(\mathbf{a})$  with respect to the occupancies,  $a_j$ , subject to the constraints on the system.

$$W(\mathbf{a}) = \frac{N!}{a_1! a_2! a_3! \cdots} = \frac{N!}{\prod_j a_j!} \quad \begin{cases} \sum_j a_j = N \\ \sum_j a_j \varepsilon_j(V) = E_{tot} \end{cases}$$

Volume dependence of the energy levels are shown explicitly

## Some math

A function and its logarithm have the same maxima and minima

$$\frac{d \ln f(x)}{dx} = \frac{1}{f(x)} \frac{df(x)}{dx} \quad \frac{df(x)}{dx} = 0 \Rightarrow \frac{d \ln f(x)}{dx} = 0$$

So we maximize  $\ln[W(\mathbf{a})]$  instead of  $W(\mathbf{a})$ . Why?

Finding the distribution with the maximum degeneracy (most probable distribution)

$$W(\mathbf{a}) = \frac{N!}{a_1! a_2! a_3! \cdots} = \frac{N!}{\prod_j a_j!}$$

1. The  $\ln W(\mathbf{a})$  can be evaluated using **Stirling's approximation** for large integer  $N$ ,

$$\ln N! \approx N \ln N - N$$

Giving:

$$\begin{aligned} \ln W(\mathbf{a}) &= \ln(N!) - \ln(a_1!) - \ln(a_2!) - \dots \\ &= N \ln N - N - (a_1 \ln a_1 - a_1 + a_2 \ln a_2 - a_2 + \dots) \\ &= N \ln N - \sum_j a_j \ln a_j \end{aligned}$$

2. Since the number of molecules is very ( $10^{23}$ ) occupancies are treated as continuous variables.

Can we just calculate the derivative of  $\ln W(\mathbf{a})$  with respect to the occupancy of a specific state  $i$ ,  $a_i$  to determine the most probable distribution?

$$\frac{\partial}{\partial a_i} \left\{ N \ln N - \sum_j a_j \ln a_j \right\} = 0$$

No! There are constraints on the  $a_i$ 's and they are not all independent

$$\begin{cases} \sum_j a_j = N \\ \sum_j a_j \varepsilon_j(V) = E_{tot} \end{cases}$$

## Method of Lagrange undetermined multipliers

The function for which we want to find the maximum

$$f(a_1, a_2, \dots, a_i, \dots) = \ln W(\mathbf{a}) = N \ln N - \sum_j a_j \ln a_j$$

The constraint equations

$$\begin{cases} g_1(a_1, a_2, \dots, a_i, \dots) = \sum_j a_j - N = 0 \\ g_2(a_1, a_2, \dots, a_i, \dots) = \sum_j a_j \varepsilon_j(V) - E_{tot} = 0 \end{cases}$$

The new function which includes the constraints

$$\Lambda(a_1, a_2, \dots, a_i, \dots; \lambda_1, \lambda_2) = f(a_1, a_2, \dots, a_i, \dots) - \lambda_1 g_1(a_1, a_2, \dots, a_i, \dots) - \lambda_2 g_2(a_1, a_2, \dots, a_i, \dots)$$

The maximum of the function subject to the constraints is determined by

$$\vec{\nabla} \Lambda(a_1, a_2, \dots, a_i, \dots; \lambda_1, \lambda_2) = 0$$

$$\frac{\partial}{\partial a_k} [\Lambda(a_1, a_2, \dots, a_k, \dots; \lambda_1, \lambda_2)] = 0$$

# Finding the most probable distribution subject to the constraints

## Method of Lagrange underdetermined multipliers

Add the constraint equations to the function and set derivatives to 0 to find the maximum

$$\frac{\partial}{\partial a_k} \left\{ N \ln N - \sum_j a_j \ln a_j - \alpha \left( \sum_j a_j - N \right) - \beta \left( \sum_j a_j \varepsilon_j(V) - E_{tot} \right) \right\} = 0$$



$$-\ln a_k^* - 1 - \alpha - \beta \varepsilon_k(V) = 0$$



$$a_k^* = e^{-(1+\alpha)} e^{-\beta \varepsilon_k(V)}$$

Occupancy of state  $i$  in the most probable distribution

- Constraints added with Lagrange multipliers  $\alpha$  and  $\beta$  (to be later eliminated)
- $\alpha$  is unitless and  $\beta$  has units of energy<sup>-1</sup>

The constraint on the occupancies eliminates the  $\alpha$  Lagrange multiplier:

$$\begin{aligned} N &= a_1^* + a_2^* + a_3^* + \dots = \sum_i a_i^* \\ &= e^{-(1+\alpha)} \sum_i e^{-\beta \varepsilon_i(V)} \Rightarrow e^{-(1+\alpha)} = \frac{N}{\sum_i e^{-\beta \varepsilon_i(V)}} \end{aligned}$$

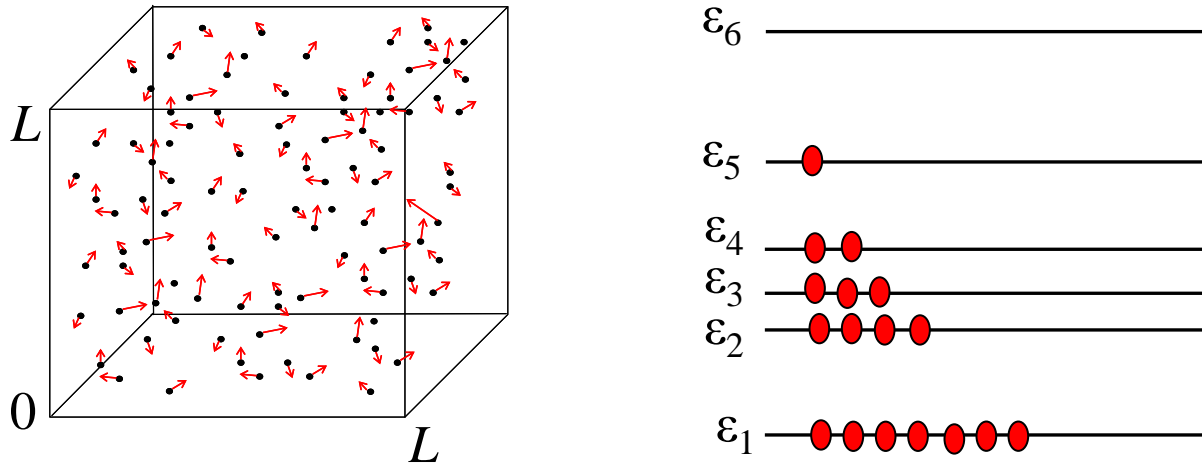
## Distribution with largest probability:

- Probability of one-molecule state  $i$  being occupied in the  $N$  molecule system in the most probable distribution

$$P_i^* = \frac{a_i^*}{N} = \frac{e^{-\beta \varepsilon_i(V)}}{\sum_j e^{-\beta \varepsilon_j(V)}} = \frac{e^{-\beta \varepsilon_i(V)}}{q(V, \beta)}$$

Partition function  
(sum-over-states) ←

- Exponential decay (grading) for the probability of occupancy based on the energy of state  $i$ .



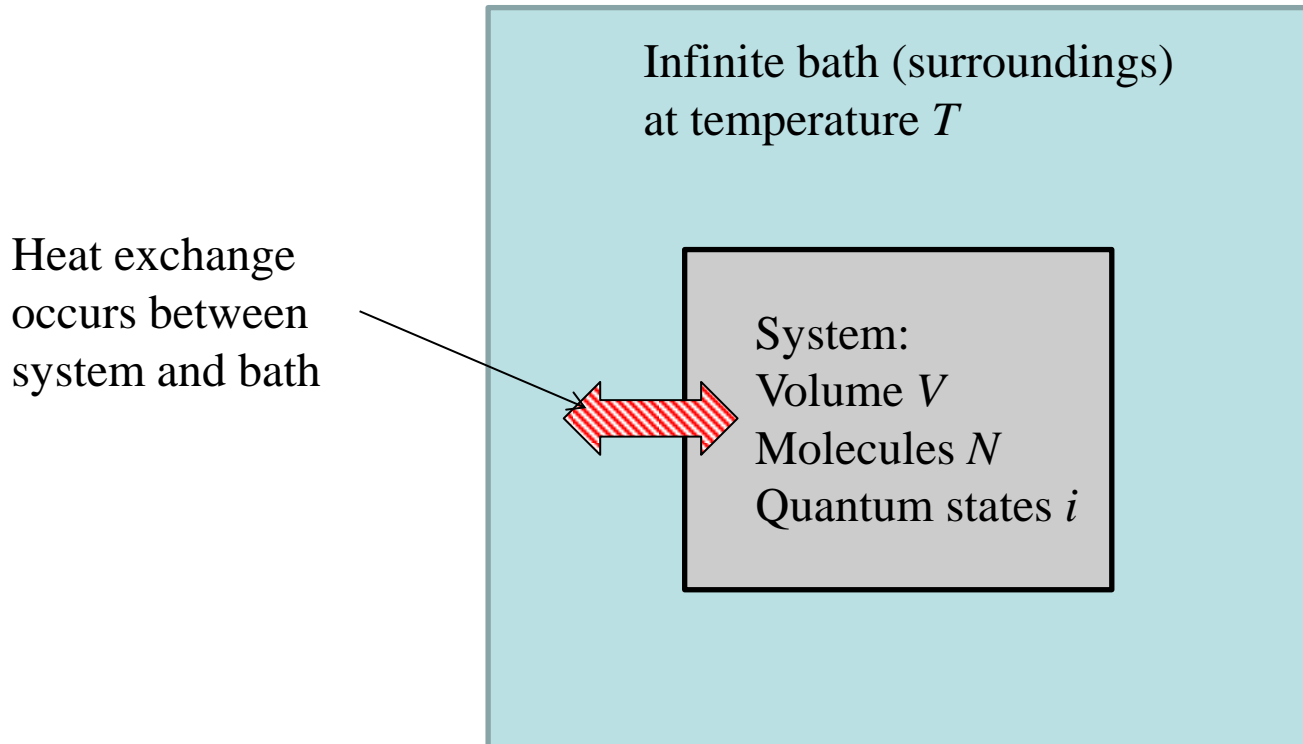
Knowing probabilities of different states, averages mechanical quantities  $M_j$  can be determined for the most probable distribution

$$\langle M \rangle = \sum_j M_j P_j^*$$

What is the role of  $\beta$ ? (see Appendix 6.A.1)

## Probabilities for systems with interacting particles: The set-up

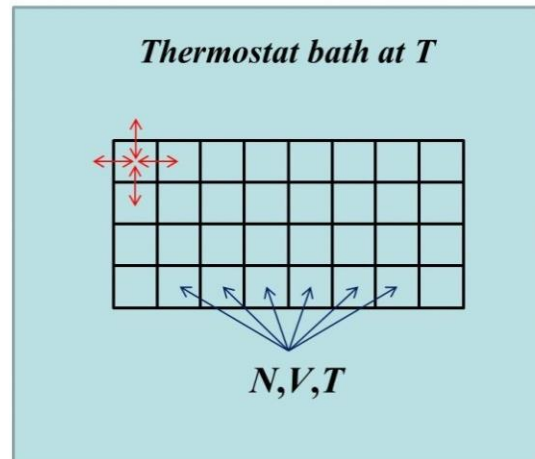
- The system has a constant volume  $V$  with  $N$  interacting molecules;
- The  $N$ -molecule interacting **system as a whole** is characterized by a quantum state  $i$  with energy  $E_i$ ;
- Interactions between molecules in the system are captured in the quantum states  $i$ ;
- The system has walls which allow it to exchange heat with its surroundings, fixing its temperature.



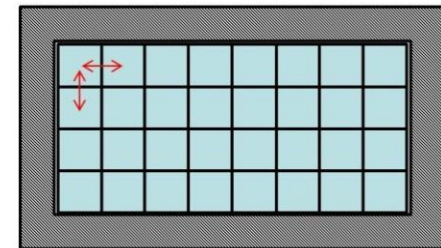
# Probabilities for systems with interacting particles: The “canonical” ensemble

- A large (infinite) number of replicas of the system (the “ensemble”) are put in contact with each other and placed in the infinite heat bath. Heat exchange is possible between systems and bath;
- The system replicas have constant volume and are maintained at constant temperature. This ensemble (collection) of systems is called the canonical ensemble;
- After the ensemble equilibrates with the bath (environment), it is removed and placed in an isolated container;
- The replicas of the system have a distribution of energies,  $E_i$ , from among possible quantum states

Ensemble of systems is equilibrated at a fixed temperature



Isolated ensemble at fixed total energy

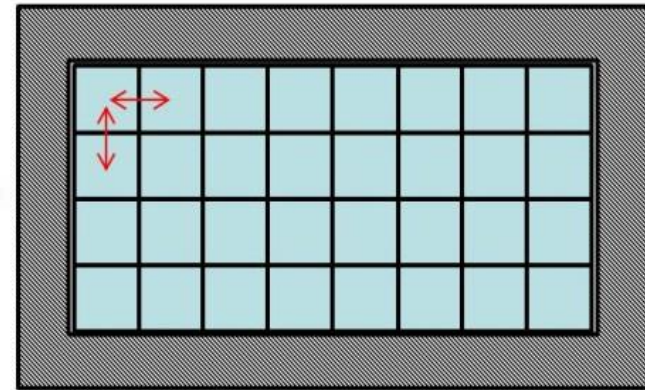




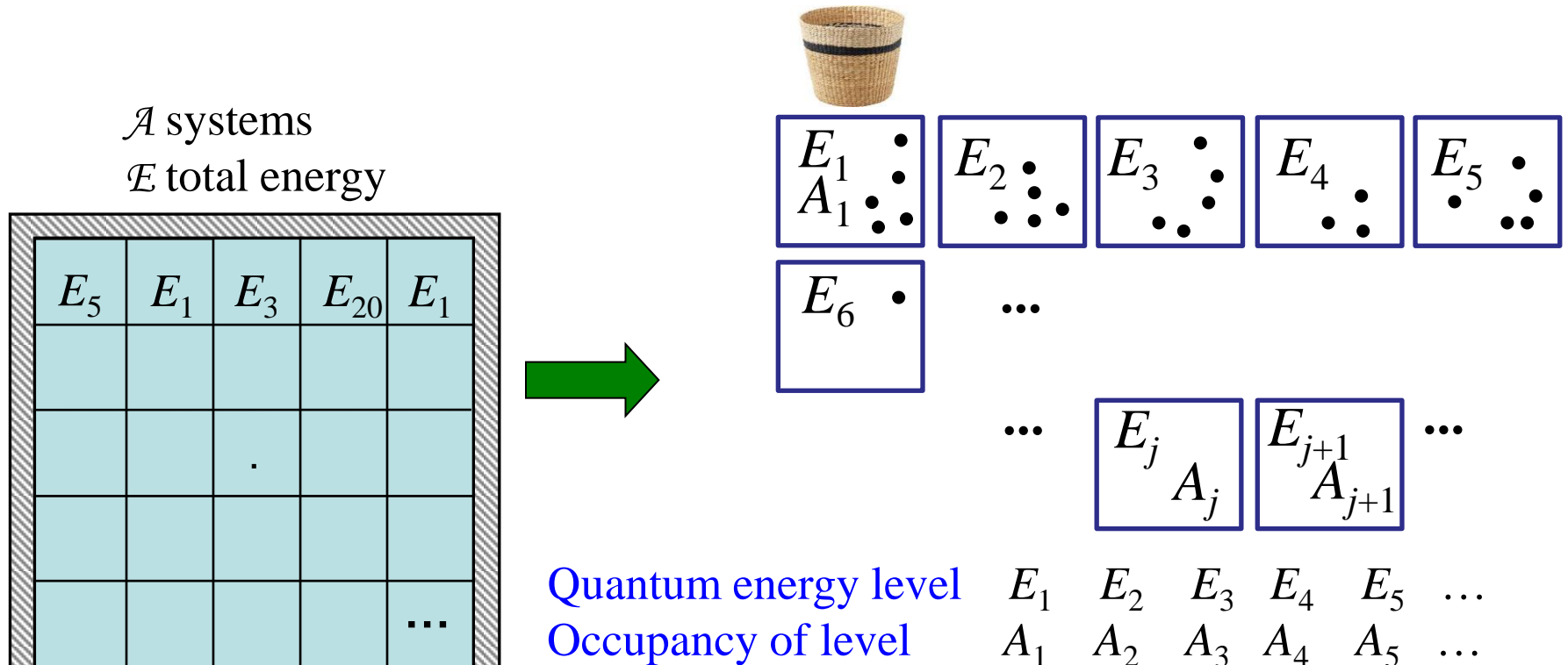
# Introducing the ensemble as a mathematical trick

- The isolated ensemble is made of  $\mathcal{A}$  copies of the original system;
- The total energy of the ensemble is  $\mathcal{E}$ ;
- $\mathcal{E}$  and  $\mathcal{A}$  are mathematical constructs and do not have physical significance.

Isolated ensemble at  $T$

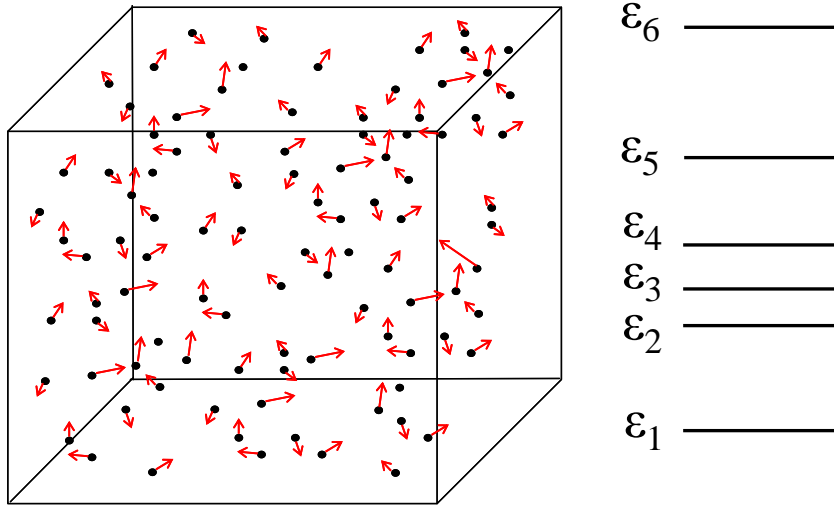


The systems in the ensemble are binned based on their energy level

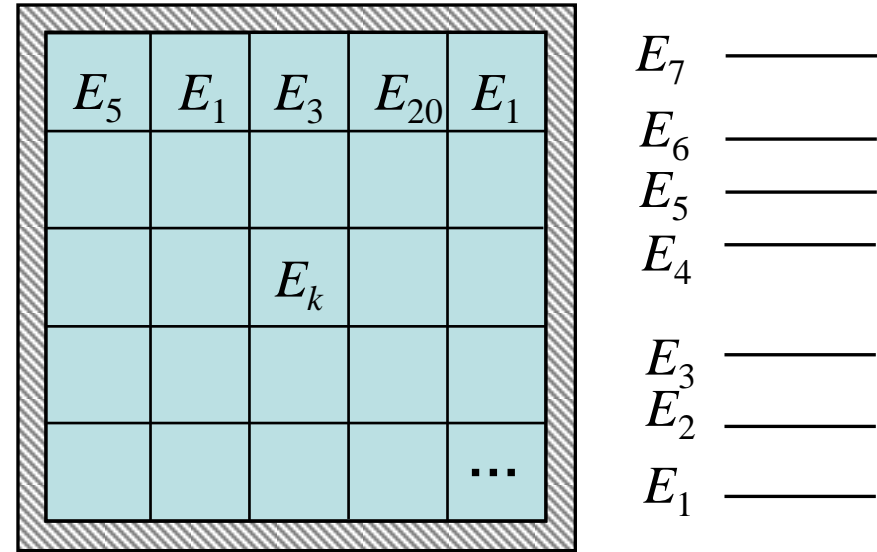


# Analogy between non-interacting system and ensemble

Molecule states  $\varepsilon_i$



Total system states  $E_i$



The total gas energy  $E$  is the sum of energies of individual molecules:

$$\begin{cases} \sum_j a_j = N \\ \sum_j a_j \varepsilon_j = E_N \end{cases}$$

The total system energy can be distributed in different ways among molecules of the gas

The ensemble energy  $\mathcal{E}$  is the sum of energies of the systems:

$$\begin{cases} \sum_j A_j = \mathcal{A} \\ \sum_j A_j E_j = \mathcal{E} \end{cases}$$

The total ensemble energy can be distributed in different ways among systems

## Finding the most probable distribution of systems in the ensemble

A particular distribution of members of the ensemble between system energy levels:

<i>N</i> -molecule quantum energy state:	$E_1$	$E_2$	$E_3$	$E_4$	$E_5$	...
Occupancy of each energy state:	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	...

Ways of assigning systems in the ensemble to different possible quantum states

$$W(\mathbf{A}) = \frac{\mathcal{A}!}{A_1!A_2!A_3!\cdots} = \frac{\mathcal{A}!}{\prod_j A_j!} \quad \text{Constraints} \quad \begin{cases} \sum_j A_j = \mathcal{A} \\ \sum_j A_j E_j = \mathcal{E} \end{cases}$$

For a large ensemble (using Stirling's approximation):  $\ln W(\mathbf{A}) = \mathcal{A} \ln \mathcal{A} - (A_1 \ln A_1 + A_2 \ln A_2 \dots)$

Maximize  $\ln W(\mathbf{A})$  with respect to the occupancy of each state  $A_i$  using Lagrange undetermined multipliers:

$$\frac{\partial}{\partial A_i} \left\{ \ln W(\mathbf{A}) - \alpha \left( \sum_j A_j - \mathcal{A} \right) - \beta \left( \sum_j A_j E_j - \mathcal{E} \right) \right\} = 0$$

## Most probable distribution of systems in the ensemble

The number of systems in the ensemble in state  $i$  in the most probable distribution, are:

$$A_i^* = e^{-(1+\alpha)} e^{-\beta E_i}$$

Using the first constraint:  $\sum_i A_i^* = \mathcal{A}$  eliminate the undetermined multiplier  $\alpha$ ,

$$\sum_i A_i^* = e^{-(1+\alpha)} \sum_i e^{-\beta E_i} = \mathcal{A} \Rightarrow e^{-(1+\alpha)} = \frac{\mathcal{A}}{\sum_i e^{-\beta E_i}}$$

Probability of observing a particular  $N$ -molecule state  $i$  in the ensemble in the most probable distribution

$$P_i = \frac{A_i^*}{\mathcal{A}} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Q(N, V, \beta)}$$

“Canonical” ensemble partition function for system states

$\langle M \rangle = \sum_j M_j P_j$  Averages of quantities can be calculated from knowledge of the probabilities

We still can't use these relations since we do not know  $\beta$

## A review of a thermodynamic relation

Changes in energy of a system:

$$dE = TdS - PdV$$

Changes in the Helmholtz free energy of a system:

$$dA = -SdT - PdV \longrightarrow \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \text{Maxwell's equations}$$

Taking the derivative of the energy equation with respect to volume:

$$\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P \left( \frac{\partial V}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

Using the chain rule:

$$\left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial 1/T}{\partial T} \right)_V \left( \frac{\partial P}{\partial 1/T} \right)_V = -\frac{1}{T^2} \left( \frac{\partial P}{\partial 1/T} \right)_V$$

“Thermodynamic equation of state”:

$$\left( \frac{\partial E}{\partial V} \right)_{T,N} = -P - \frac{1}{T} \left( \frac{\partial P}{\partial 1/T} \right)_{N,V}$$

## Determining the $\beta$ undetermined multiplier by comparing statistical mechanical and thermodynamics relations

- Statistical mechanics relation for average system energy in the ensemble:

$$\langle E(N, V, \beta) \rangle = \sum_j E_j(N, V) P_j = \frac{\sum_j E_j(N, V) e^{-\beta E_j(N, V)}}{\sum_i e^{-\beta E_i(N, V)}}$$

- Thermodynamic relation for pressure  $P = \left( \frac{\partial E}{\partial V} \right)_S$

Statistical mechanics relation for average system pressure in the ensemble:

$$\langle P(N, V, \beta) \rangle = \sum_j \left( \frac{\partial E_j(N, V)}{\partial V} \right) P_j = - \frac{\sum_j \left( \frac{\partial E_j}{\partial V} \right) e^{-\beta E_j(N, V)}}{\sum_i e^{-\beta E_i(N, V)}}$$

Ensemble  
average pressure

Pressure for state  $j$     Probability of state  $j$

- After some steps:  
(see Appendix 6.A.2 of MSFP)

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


# Comparing statistical mechanics and thermodynamics relations

Thermodynamic relation:

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = -P - \frac{1}{T} \left(\frac{\partial P}{\partial 1/T}\right)_{N,V}$$


Statistical mechanics relation for ensemble averages:

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


$$\beta = \frac{1}{kT}$$

Canonical ensemble (**isothermal-isochoric ensemble**) partition function:

$$Q(N, V, T) = \sum_j e^{-E_j(N, V) / kT}$$



Energy of  $N$ -atom interacting system  
(the **Boltzmann factor!!!**)

- Temperature is a characteristic of the ensemble, not an individual member of the ensemble.
- The connection of statistical mechanics and macroscopic thermodynamics is through the constraints which show how the mechanical system is coupled to the unknown external world / universe.

## The partition function and thermodynamic quantities

Relating thermodynamic quantities from the canonical ensemble partition function:

Instead of  $Q$ , we deal with the logarithm  $\ln Q(N, V, T) = \ln \left[ \sum_j e^{-E_j(N, V)/kT} \right]$

Recall: 
$$\frac{d \ln f(x)}{dx} = \frac{1}{f(x)} \frac{df(x)}{dx}$$

The temperature derivative of  $\ln Q$  gives:

$$\left[ \frac{\partial \ln Q(N, V, T)}{\partial T} \right]_{N, V} = \frac{1}{kT^2} \frac{\sum_j E_j(N, V) e^{-E_j(N, V)/kT}}{\sum_i e^{-E_i(N, V)/kT}}$$

The ensemble average energy is recognized in this relation:

$$\langle E \rangle = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

Similarly, the volume derivative of  $\ln Q$  gives:

$$\langle P \rangle = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N, T}$$

Note that this relation is the statistical mechanical form for the equation of state!



## Probability distribution in the ensemble

Probability of observing a system in state  $i$  in most probable distribution of the ensemble

$$P_i = \frac{A_i^*}{\mathcal{A}} = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}} = \frac{e^{-E_i/kT}}{Q(N, V, T)}$$

“Canonical” ensemble  
(isothermal-isochoric ensemble)  
partition function for system states

$\langle M(T) \rangle = \sum_j M_j P_j(T)$  Averages of quantities in the ensemble can be calculated from knowledge of the probabilities of states  $j$

Ensemble average energy in terms of the canonical ensemble probability distribution

$$\langle E(N, V, T) \rangle = \sum_j E_j(N, V, T) P_j = \sum_j E_j(N, V) \left[ \frac{e^{-E_j(N, V)/kT}}{\sum_i e^{-E_i(N, V)/kT}} \right]$$

# Ways to change the $\langle E \rangle$ of a $N$ -molecule ideal gas system

$$E_{tot}(N, V) = \frac{h^2}{8mV^{2/3}} \sum_{v=1}^N (n_{xv}^2 + n_{yv}^2 + n_{zv}^2)$$

<ul style="list-style-type: none"> <li>Change the distribution of molecules among the states</li> </ul> $\frac{h^2}{8mV^{2/3}} \sum_{v=1}^N (n_{xv}^2 + n_{yv}^2 + n_{zv}^2)$	
<ul style="list-style-type: none"> <li>Change the volume <math>V</math> (which changes energy levels) without changing the distribution</li> </ul> $\frac{h^2}{8mV^{2/3}} \sum_{v=1}^N (n_{xv}^2 + n_{yv}^2 + n_{zv}^2)$	
<ul style="list-style-type: none"> <li>Change the number of molecules in the system without changing the levels</li> </ul> $\frac{h^2}{8mV^{2/3}} \sum_{v=1}^N (n_{xv}^2 + n_{yv}^2 + n_{zv}^2)$	

$$\sum_j E_j(N, V) P_j(N, V, T)$$

$$\sum_j E_j(N, V) P_j(N, V, T)$$

Important for open systems  
(grand Canonical ensemble)

# Statistical mechanical interpretation of work and heat

Thermodynamic expression  
for energy change:

$$dE = \delta w + \delta q$$

Energy can change by performing  
work or transfer of heat:

Statistical mechanical  
expression for ensemble  
average energy change:

$$\langle E \rangle = \sum_j E_j P_j$$

$$d\langle E \rangle = \sum_j P_j dE_j + \sum_j E_j dP_j$$

The ensemble average energy can varied by:

- 1) Changing system energy levels while keeping probabilities in the ensemble (i.e., distribution of systems among the levels) fixed
  - 2) Changing the probabilities for distribution in the ensemble among the energy levels
- In the particle in a box, energy levels can be changed by varying the volume of the system:

$$E_{tot}(N, V) = \frac{h^2}{8mV^{2/3}} \sum_{v=1}^N (n_{xv}^2 + n_{yv}^2 + n_{zv}^2)$$

- Therefore  $\sum_j P_j dE_j$  corresponds to change of energy due to work  
and  $\sum_j E_j dP_j$  must correspond to transfer of heat

## Statistical mechanics and thermodynamic functions

Can be shown that:  
(see Extended Lecture Notes)

$$S = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k \ln Q = -k \sum_i P_i \ln P_i$$

From the thermodynamic relation  $A = E - TS$ , we can determine the statistical mechanical expression for the Helmholtz free energy:

$$A = E - TS = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} - kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} - kT \ln Q$$

We get the simple relation:  $A = -kT \ln Q(N, V, T)$

The canonical partition function is the “characteristic” function for the Helmholtz free energy  
 $A(N, V, T) \Leftrightarrow Q(N, V, T)$

We can use the second law of thermodynamics expression:

$$dA = -PdV - SdT$$

to relate thermodynamic quantities to the canonical ensemble partition function.

$$S = - \left( \frac{\partial A}{\partial T} \right)_{N,V} \quad P = - \left( \frac{\partial A}{\partial V} \right)_{N,T}$$

## Fluctuations in the energy distribution of systems in the ensemble

How wide is the energy distribution in the ensemble?

$$\sigma_E^2 = \langle E - \langle E \rangle \rangle^2 = \langle E^2 \rangle - \langle E \rangle^2$$

Starting from the relation for the average energy of the ensemble of systems

$$\langle E \rangle = \frac{\sum_j E_j e^{-E_j(N,V)/kT}}{\sum_i e^{-E_i(N,V)/kT}}$$

Determine the temperature derivative of the energy:

$$\frac{d\langle E \rangle}{dT} = \frac{\sum_j \frac{E_j^2}{kT^2} e^{-E_j(N,V)/kT} \sum_i e^{-E_i(N,V)/kT} - \sum_j E_j e^{-E_j(N,V)/kT} \sum_i \frac{E_i}{kT^2} e^{-E_i(N,V)/kT}}{\left( \sum_i e^{-E_i(N,V)/kT} \right)^2}$$

$$\frac{d\langle E \rangle}{dT} = \frac{\sum_j \frac{E_j^2}{kT^2} e^{-E_j(N,V)/kT}}{\sum_i e^{-E_i(N,V)/kT}} - \frac{\sum_j E_j e^{-E_j(N,V)/kT} \sum_i \frac{E_i}{kT^2} e^{-E_i(N,V)/kT}}{\sum_j e^{-E_j(N,V)/kT} \sum_i e^{-E_i(N,V)/kT}}$$

$$\therefore \frac{d\langle E \rangle}{dT} = \frac{1}{kT^2} \left( \langle E^2 \rangle - \langle E \rangle^2 \right) = \frac{1}{kT^2} \sigma_E^2$$

## Fluctuations in the energy distribution of systems in the ensemble are related to the system heat capacity

Recall that the temperature derivative of the energy is the heat capacity:

$$\therefore \frac{d\langle E \rangle}{dT} = C_V = \frac{1}{kT^2} \left( \langle E^2 \rangle - \langle E \rangle^2 \right) = \frac{1}{kT^2} \sigma_E^2$$

- Meaning: Despite having the same temperature, individual members of the ensemble can have different energies.

What are the magnitudes of the energy fluctuations in the ensemble?

For a monatomic ideal gas,  $C_V = 3Nk/2$  and so  $\sigma_E^2 = \frac{3}{2} Nk^2 T^2$



$$\therefore \frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{\frac{3}{2} NkT}}{\frac{3}{2} NkT} \propto \frac{1}{\sqrt{N}}$$

- Fluctuations are small relative to the average energy for systems with large  $N$
- If  $N = 10^{23}$ , then fluctuations in  $\sim 10^{-12}$  of the average energy

## Fluctuations in the energy distribution between members of the ensemble

The probability distribution for the energy in a canonical ensemble is:

$$P(E) = \frac{\Omega(E)e^{-E/kT}}{\sum_{E'} \Omega(E')e^{-E'(V)/kT}}$$

Expanding the probability distribution about the average energy and neglecting terms of order  $1/N^2$  or smaller, a Gaussian distribution for the energy in a canonical ensemble is derived (Central limit theorem strikes again!):

$$P(E) = P(\langle E \rangle) \exp \left[ \frac{-(E - \langle E \rangle)^2}{kT^2 C_V} \right]$$

Similarly the fluctuations in the pressure for systems in a canonical ensemble can be determined

$$\sigma_P^2 = \langle P^2 \rangle - \langle P \rangle^2 = kT \left[ \left( \frac{\partial \langle P \rangle}{\partial V} \right)_{N,T} - \left\langle \frac{\partial P}{\partial V} \right\rangle_{N,T} \right]$$

We can show (see McQuarrie):

$$\frac{\sigma_P}{\langle P \rangle} \propto \frac{1}{\sqrt{N}}$$

## Partition functions for non-interacting systems

How does the partition function behave for systems with non-interacting molecules:

$$E_{tot,i}(N) = \varepsilon_{\alpha}(1) + \varepsilon_{\beta}(2) + \dots + \varepsilon_{\zeta}(N)$$

Quantum states for individual molecules

We replace this expression for energy in the canonical ensemble partition function:

$$Q(N, V, T) = \sum_j e^{-E_j/kT} = \sum_{\alpha} \sum_{\beta} \dots \sum_{\zeta} e^{-[\varepsilon_{\alpha}(1) + \varepsilon_{\beta}(2) + \dots + \varepsilon_{\zeta}(N)]/kT}$$

Sum over states of  $N$ -molecule system

Sum over states of the entire system is written in terms of the sum of states of individual molecules

$$\begin{aligned} Q(N, V, T) &= \sum_{\alpha} \sum_{\beta} \dots \sum_{\zeta} e^{-[\varepsilon_{\alpha}(1) + \varepsilon_{\beta}(2) + \dots + \varepsilon_{\zeta}(N)]/kT} \\ &= \sum_{\alpha} e^{-\varepsilon_{\alpha}(1)/kT} \sum_{\beta} e^{-\varepsilon_{\beta}(2)/kT} \dots \sum_{\zeta} e^{-\varepsilon_{\zeta}(N)/kT} = \frac{q_1 q_2 \dots q_N}{N!} \end{aligned}$$

The  $N$ -molecule partition function is decomposed to a product of 1-molecule partition functions for indistinguishable molecules



## Partition functions for non-interacting systems

We can repeat the process for the internal degrees of freedom of each molecule:

$$\varepsilon_i = \varepsilon_{\text{translational}} + \varepsilon_{\text{rotational}} + \varepsilon_{\text{vibrational}} + \varepsilon_{\text{electronic}} + \varepsilon_{\text{nuclear spin}}$$

The 1-molecule canonical ensemble partition function decomposes to partition functions for different degrees of freedom:

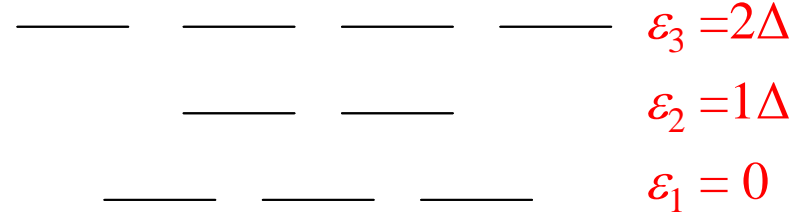
$$q(V, T) = \sum_{\alpha} e^{-\varepsilon_{\alpha}/kT} = \sum_{\text{trans}} \sum_{\text{rot}} \sum_{\text{vib}} \sum_{\text{elec}} \sum_{\text{nuc}} e^{-[\varepsilon_{i,\text{trans}} + \varepsilon_{j,\text{rot}} + \varepsilon_{k,\text{vib}} + \varepsilon_{\ell,\text{elec}} + \varepsilon_{s,\text{nuc}}]/kT}$$

$$\begin{aligned} q(V, T) &= \sum_i e^{-\varepsilon_{i,\text{trans}}/kT} \sum_j e^{-\varepsilon_{j,\text{rot}}/kT} \sum_k e^{-\varepsilon_{k,\text{vib}}/kT} \sum_{\ell} e^{-\varepsilon_{\ell,\text{elec}}/kT} \sum_s e^{-\varepsilon_{s,\text{nuc}}/kT} \\ &= q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} q_{\text{nuc}} \end{aligned}$$

Using quantum mechanical expressions for translational, rotational, vibrational, electronic, and nuclear spin energies, we can determine the partition function for each degree of freedom.

# Partition function $q(V, T)$ for one molecule as a sum over energy levels

Assume we have a system with nine states



$$q(T) = \sum_j e^{-\varepsilon_j(1)/kT} \quad \text{Sum over one-molecule states}$$

$$q(T) = e^{-0/kT} + e^{-0/kT} + e^{-0/kT} + e^{-\Delta/kT} + e^{-\Delta/kT} \\ + e^{-2\Delta/kT} + e^{-2\Delta/kT} + e^{-2\Delta/kT} + e^{-2\Delta/kT}$$



Gather similar terms

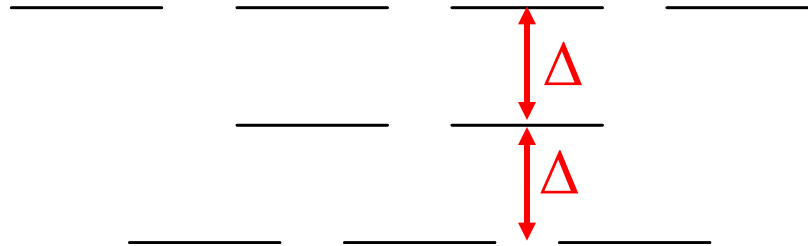
$$q(T) = 3e^{-0/kT} + 2e^{-\Delta/kT} + 4e^{-2\Delta/kT}$$

$$q(T) = \sum_E \Omega(\varepsilon) e^{-\varepsilon(N,V)/kT} \quad \text{Sum over one-molecule energy levels}$$

↖ Degeneracy of the energy state

Expressing the partition function as a sum over energy levels shows the physical content more clearly.

# Physical interpretation of the canonical partition function

$$q(V, T) = \sum_j e^{-\varepsilon_j(V)/kT}$$


$\varepsilon_3 = 2\Delta$   
 $\varepsilon_2 = 1\Delta$   
 $\varepsilon_1 = 0$

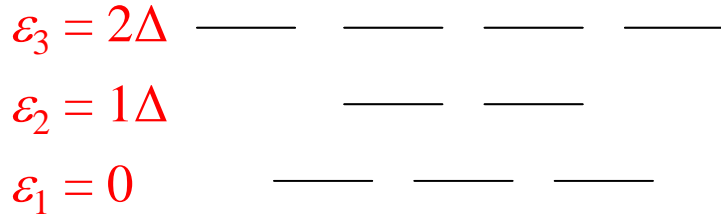
The partition function is:

$$q = 3e^{-0/kT} + 2e^{-\Delta/kT} + 4e^{-2\Delta/kT}$$

Changes in partition function and probability of energy levels with temperature

$T$ (in $\Delta/k$ units)	0	0.5	1.0	1.5	2.0	5.0	10.0	$\rightarrow \infty$
$q(T)$	3	3.34	4.28	5.08	5.68	7.32	8.08	$\rightarrow 9$
$P_1 = 3e^{-0/kT}/q$	1	0.90	0.70	0.59	0.53	0.41	0.37	$\rightarrow 0.33$
$P_2 = 2e^{-\Delta/kT}/q$	0	0.08	0.17	0.20	0.21	0.22	0.22	$\rightarrow 0.22$
$P_3 = 4e^{-2\Delta/kT}/q$	0	0.02	0.13	0.21	0.26	0.37	0.41	$\rightarrow 0.44$

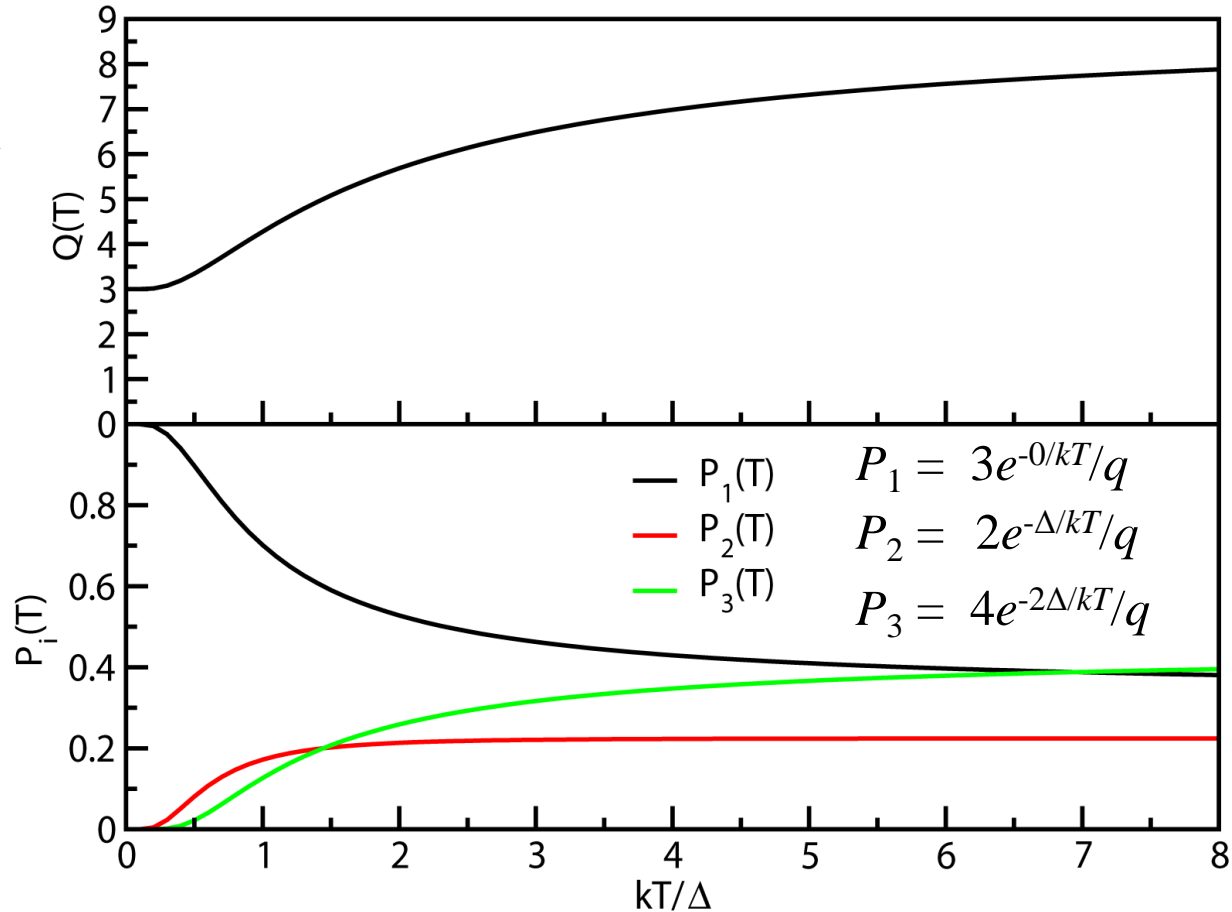
# Physical interpretation of the canonical partition function



Probability of occupancy of energy level  $E$

$$P(\varepsilon) = \frac{\Omega(\varepsilon)e^{-\varepsilon(V)/kT}}{q(V, T)}$$

Variation of partition function with temperature



Variation of probabilities with temperature

The partition function gives a measure of the number of states accessible to the system at the given temperature

## Switching from the quantum to classical description of states

The quantum description of the state of an  $N$ -atom system in terms of a discrete set of states represented by a single quantum index  $i$  is much simpler than in terms of a continuous variation of the state  $\{\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \dots, \mathbf{r}_N, \mathbf{p}_N\}$  in phase space.

It is easier to do calculations of averages with discrete states

$$\langle f(\varepsilon) \rangle = \sum_{i=1}^{\nu} f(\varepsilon_i) P_N(\varepsilon_i)$$

than with continuous states

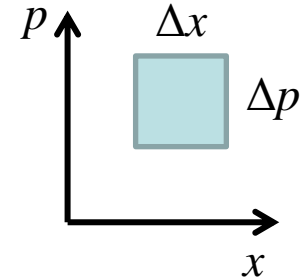
$$\langle f(\{\mathbf{r}, \mathbf{p}\}) \rangle = \int \int \cdots \int_{-\infty}^{+\infty} \left[ \int_{\mathbf{r}_{1,\min}}^{\mathbf{r}_{1,\max}} f(\{\mathbf{r}, \mathbf{p}\}) P_N(\{\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N\}) d\mathbf{r}_1 \right] d\mathbf{p}_1 \cdots d\mathbf{r}_N d\mathbf{p}_N$$

- The quantum description of the average of a function involves the sum over the discrete quantum states of an  $N$ -atom system
- The classical description of an average of a function involves an integration over the  $3N$ -dimensional phase space of the system

# The correspondence between quantum and classical states

From the Heisenberg uncertainty principle, there is minimum subdivision of phase space volume which is related to Planck's constant:

$\Delta p \Delta x = h$  is the smallest subdivision of phase space volume which is meaningful,



The correspondence between quantum states and volume in classical phase space is:

Number of quantum states  $\leftrightarrow$  Volume of phase space /  $h^{3N}$

- The phase space volume corresponds on average to a discrete quantum state

$$\sum_i \leftrightarrow \int \cdots \int \frac{d\mathbf{r}^N d\mathbf{p}^N}{h^{3N}}$$

## Semi-classical limit to the canonical partition function

- Sum over  $N$  particle quantum states

$$Q(N, V, T) = \sum_j e^{-E_j / kT}$$

Semi-classical equivalent

- Integral over **phase space** elements

$$Q = \frac{1}{N! h^{3N}} \int \cdots \int e^{-H(\mathbf{p}_1, \mathbf{q}_1, \dots, \mathbf{p}_N, \mathbf{q}_N) / kT} d\mathbf{p}_1 d\mathbf{q}_1 \cdots d\mathbf{p}_N d\mathbf{q}_N$$

$h$ : minimum volume of phase space element from quantum mechanics

Molecules are indistinguishable so many states are equivalent

$dpdq$  has units of energy·time same as the  $h$  Planck's constant  
(unit of “action” in classical mechanics)

## Semi-classical limit to the canonical partition function

Hamiltonian of the system represents the energy in a canonical ensemble

$$H = K(p_{x1}, p_{y1}, p_{z1}, \dots, p_{xN}, p_{yN}, p_{zN}) + U(x_1, y_1, z_1, \dots, x_N, y_N, z_N)$$

“Classical” (semi-classical) canonical partition function

$$Q = \frac{1}{N!h^{3N}} \int \dots \int e^{-H(\mathbf{p}_1, \mathbf{q}_1, \dots, \mathbf{p}_N, \mathbf{q}_N)/kT} d\mathbf{p}_1 d\mathbf{q}_1 \dots d\mathbf{p}_N d\mathbf{q}_N$$

We can separate the momentum and position integrals

$$Q = \frac{1}{N!h^{3N}} \int_p e^{-(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + \dots + p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2)/2mkT} d\mathbf{p}_1 \dots d\mathbf{p}_N \int_V e^{-U(q_1, \dots, q_{3N})/kT} d\mathbf{q}_1 \dots d\mathbf{q}_N$$

Momentum integrals are Gaussian!

$$I_0 = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \left(\frac{\pi}{\alpha}\right)^{1/2}$$



# Hamiltonian of the system represents the energy in a canonical ensemble

Evaluating the momentum position integrals

$$Q(N, V, T) = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} \int_V e^{-U(\mathbf{q}_1, \dots, \mathbf{q}_N)/kT} d\mathbf{q}_1 \cdots d\mathbf{q}_N = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N$$

Configurational integral 

- Regardless of the form of the potential energy function, the contribution of the kinetic energy to the partition function is always the same.
- All the complexity of the intramolecular and intermolecular forces are in the configurational integral

If there are no interactions among the molecules in the system

$$Q(N, V, T) = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} \int_V e^{-0/kT} d\mathbf{q}_1 \cdots d\mathbf{q}_N = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} V^N$$

## Classical expression for probability in the canonical ensemble

$$P(\mathbf{q}_1, \mathbf{p}_1, \dots, \mathbf{q}_N, \mathbf{p}_N) = \frac{e^{-H(\mathbf{q}_1, \mathbf{p}_1, \dots, \mathbf{q}_N, \mathbf{p}_N)/kT}}{\iint e^{-H(\mathbf{q}, \mathbf{p})/kT} d\mathbf{q}_1 d\mathbf{p}_1 \dots d\mathbf{q}_N d\mathbf{p}_N}$$

- The Hamiltonian always has the same form with respect to momentum

$$H = \frac{1}{2m} \sum_{i=1}^N (p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2) + U(x_1, y_1, z_1, \dots, x_N, y_N, z_N)$$

Substituting and separating momenta from coordinates the expression for probability :

$$\begin{aligned} \frac{e^{-H(\mathbf{q}_1, \mathbf{p}_1, \dots, \mathbf{q}_N, \mathbf{p}_N)/kT}}{\iint e^{-H(\{\mathbf{q}, \mathbf{p}\})/kT} d\mathbf{q}_1 d\mathbf{p}_1 \dots d\mathbf{q}_N d\mathbf{p}_N} &= \frac{e^{-(p_{1x}^2 + \dots + p_{Nz}^2)/2mkT}}{\int e^{-(p_{1x}^2 + \dots + p_{Nz}^2)/2mkT} d\mathbf{p}_1 \dots d\mathbf{p}_N} \frac{e^{-U(\mathbf{q}_1, \dots, \mathbf{q}_N)/kT}}{\int e^{-U(\{\mathbf{q}\})/kT} d\mathbf{q}_1 \dots d\mathbf{q}_N} \\ &= \frac{e^{-(p_{1x}^2 + \dots + p_{Nz}^2)/2mkT}}{(2\pi mkT)^{3N/2}} \frac{e^{-U(\mathbf{q}_1, \dots, \mathbf{q}_N)/kT}}{\int e^{-U(\{\mathbf{q}\})/kT} d\mathbf{q}_1 \dots d\mathbf{q}_N} \end{aligned}$$

- Classically momenta always follow the Maxwell distribution!!!
- This is true for gases, liquids, and solids!

## Classical expression for average energy in the canonical ensemble

$$\langle E(N, V, T) \rangle = \frac{\iint H(\{\mathbf{q}, \mathbf{p}\}) e^{-H(\{\mathbf{q}, \mathbf{p}\})/kT} d\mathbf{q}_1 d\mathbf{p}_1 \cdots d\mathbf{q}_N d\mathbf{p}_N}{\iint e^{-H(\{\mathbf{q}, \mathbf{p}\})/kT} d\mathbf{q}_1 d\mathbf{p}_1 \cdots d\mathbf{q}_N d\mathbf{p}_N}$$

$$H = \frac{1}{2m} (p_{1x}^2 + \cdots + p_{Nz}^2) + U(\{\mathbf{q}\})$$

- Decompose into kinetic energy and potential energy contributions:

$$\langle E(N, V, T) \rangle = \frac{\int \frac{1}{2m} (p_{1x}^2 + \cdots + p_{Nz}^2) e^{-(p_{1x}^2 + \cdots + p_{Nz}^2)/2mkT} d\mathbf{p}_1 \cdots d\mathbf{p}_N}{(2\pi mkT)^{3N/2}} + \frac{\int U(\mathbf{q}_1, \cdots, \mathbf{q}_N) e^{-U(\{\mathbf{q}\})/kT} d\mathbf{q}_1 \cdots d\mathbf{q}_N}{\int e^{-U(\{\mathbf{q}\})/kT} d\mathbf{q}_1 \cdots d\mathbf{q}_N}$$

- Each kinetic energy term gives the same contribution of  $kT/2$  to the average energy

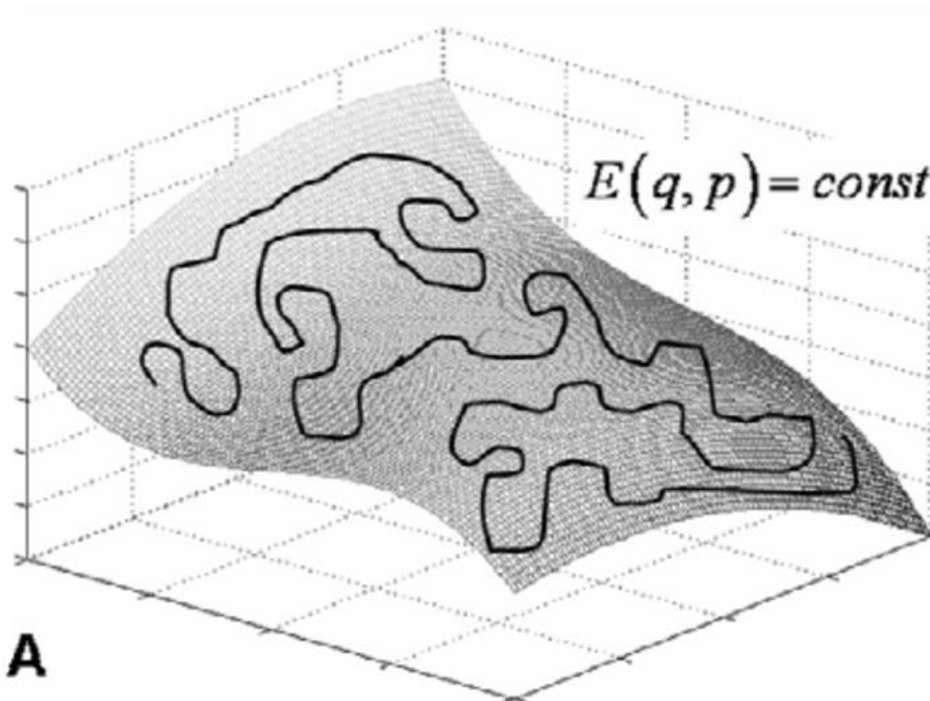
$$\langle \varepsilon_K \rangle = \frac{\int \frac{1}{2m} p_{1x}^2 e^{-p_{1x}^2/2mkT} dp_{1x}}{\int e^{-p_{1x}^2/2mkT} dp_{1x}} = \frac{1}{2} kT$$

$$I_2 = \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2\alpha} \left( \frac{\pi}{\alpha} \right)^{1/2}$$

What is relation between the ensemble average and experimental observations on a single system???

**Ergodic hypothesis:** The probability of observing a state in an ensemble of systems reflects the relative amount of time an individual system spends in that state.

$$\begin{aligned}\langle M(X) \rangle_{ensemble} &= \iint M(\{\mathbf{q}, \mathbf{p}\}) P(\{\mathbf{q}, \mathbf{p}\}; X) d\mathbf{q} d\mathbf{p} \\ &= \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} M(\{\mathbf{q}(t), \mathbf{p}(t)\}; X) dt = \langle M(X) \rangle_{time}\end{aligned}$$



B. Fresch, G. J. Moro, "Emergence of equilibrium thermodynamic properties in quantum pure states. I. Theory", J. Chem. Phys. 133, 034509 (2010)