

# Statistical thermodynamics

## Lectures 7, 8

Quantum  $\longleftrightarrow$  Classical

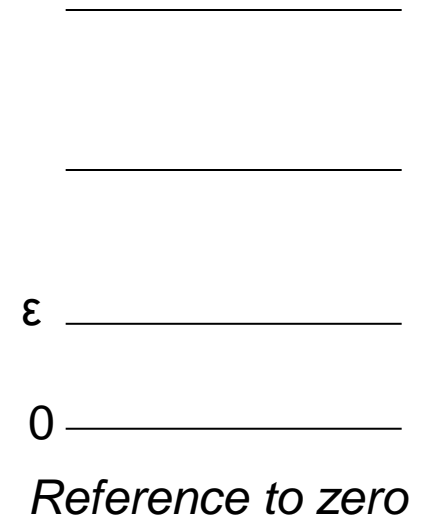
*Energy levels*

*Bulk properties*

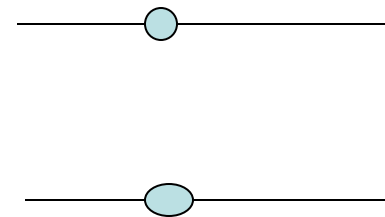
Various forms of energies.

Everything turns out to be controlled by temperature

Need for statistical thermodynamics  
 Microscopic and macroscopic world  
 Energy states  
 Distribution of energy - **population**  
 Principle of equal *a priori* probabilities



Configuration - instantaneous  
 $n_1, n_2, \dots$  molecules exist in states with energies  $\epsilon_0, \epsilon_1, \dots$   
 $N$  is the total number of molecules  
 $\{N, 0, 0, \dots\}$  and  $\{N-2, 2, 0, \dots\}$  are configurations  
 Second is more likely than the first



*Fluctuations occur*

$\{1, 1\}, \{2, 0\}, \{0, 2\}$   
 Weight of a configuration = how many times  
 the configuration can be reached.

Energy

# Generalized picture of weight

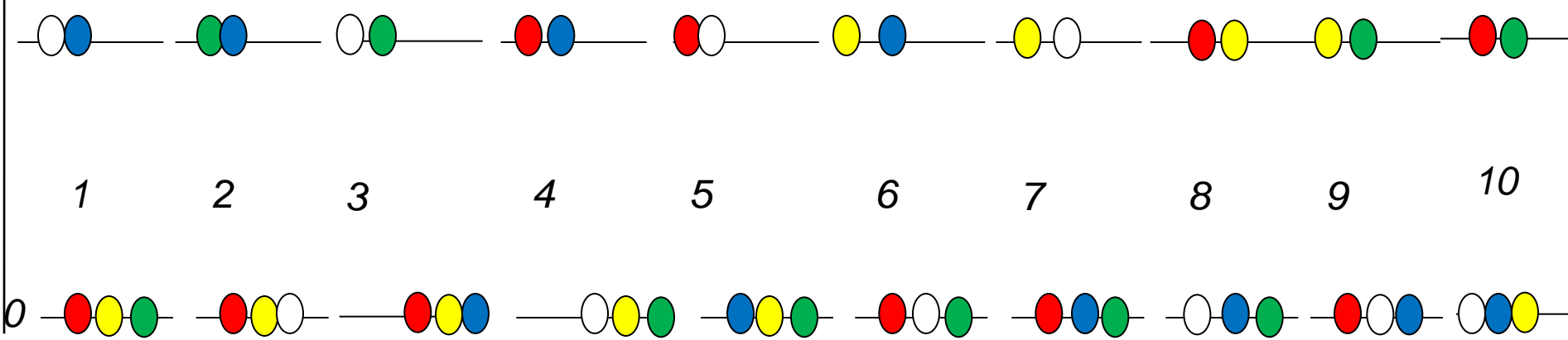
A configuration  $\{N-2, 2, 0, 0, \dots\}$

First ball of the higher state can be chosen in  $N$  ways, because there are  $N$  balls

Second ball can be chosen in  $N-1$  ways as there are  $N-1$  balls

But we need to avoid  $A, B$  from  $B, A$ .

Thus total number of distinguishable configurations is,  $\frac{1}{2} [N(N-1)]$



A configuration  $\{3, 2, 0, 0, \dots\}$  is chosen in 10 different ways - weight of a configuration

How about a general case of  $N$  particles?  $\{n_0, n_1, \dots\}$  configuration of  $N$  particles.

Distinct ways,

$$W = \frac{N!}{n_0! n_1! n_2! \dots}$$

$N!$  ways of selecting balls (first ball  $N$ , second  $(N-1)$ , etc.)

$n_0!$  ways of choosing balls in the first level.  $n_1!$  for the second, etc.

**$W$  is the weight of the configuration.**  
**How many ways a configuration can be achieved.**

*Better to use natural logarithm*

$$\ln W = \ln \frac{N!}{n_0! n_1! n_2! \dots}$$

$$= \ln N! - \ln(n_0! n_1! n_2! \dots)$$

$$= \ln N! - (\ln n_0! + \ln n_1! + \ln n_2! + \dots)$$

$$= \ln N! - \sum_i \ln n_i!$$

$\ln x! \approx x \ln x - x$  Stirling's approximation

$$\ln W = (N \ln N - N) - \sum_i (n_i \ln n_i - n_i) = N \ln N - \sum_i n_i \ln n_i$$

We have used,  $\sum_i n_i = N$

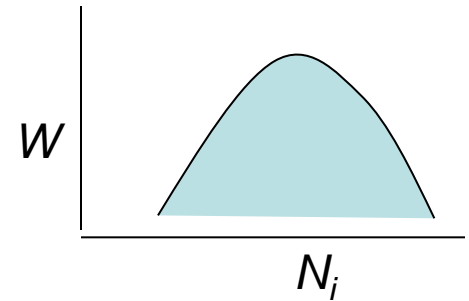
# Which is the dominating configuration having maximum weight?

Generalized approach is to set  $dW = 0$

There are problems as any configuration is not valid.

1. Energy is constant.  $\sum_i N_i \epsilon_i = E$

2. Constant number of molecules.  $\sum_i N_i = N$



*Populations in the configuration of greatest weight depends on the energy of the state.*

$$\frac{N_i}{N} = \frac{e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}}$$

Boltzmann distribution

$\sum_i$  is a sum over available states

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

*Temperature gives the most probable populations*

Boltzmann distribution – population,  $p_i = \frac{e^{-\beta \epsilon_i}}{q}$  ← Molecular partition function

$q = \sum_i e^{-\beta \epsilon_i}$  There are several ways of looking at i

Another form of q:  $q = \sum_{\text{levels } l} g_l e^{-\beta \epsilon_l}$

How to look at partition functions?

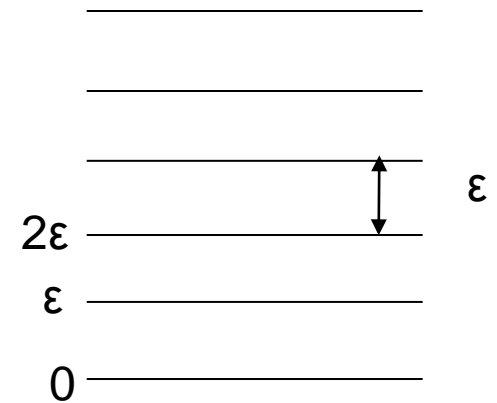
Look at limiting cases  $\lim_{T \rightarrow 0} q = g_0$  Because,  $\epsilon_0 = 0$   
 For all higher levels  $\epsilon$  is finite.  
 $e^{-\beta \epsilon} = 1$ . Because,  $e^{-x}$  is 0 when  $x$  is  $\infty$ .

*When number of states is finite, we will not get  $\infty$ .*  $\lim_{T \rightarrow \infty} = \infty$  All terms will reduce to 1.  
 $e^{-x}$  is 1 when  $x$  is 0

1. Partition function is the number of available states.
2. Partition function is the number of thermally accessible states.
3. How molecules are 'partitioned' into available states.

How to look at thermodynamic properties?

# Evaluation of molecular partition function



$$1 + x + x^2 + x^3 + \dots = 1/(1-x)$$

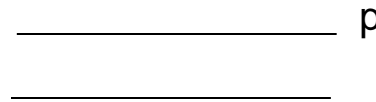
$$q = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + \dots = 1 + e^{-\beta\epsilon} + (e^{-\beta\epsilon})^2 + (e^{-\beta\epsilon})^2 + \dots = 1/(1 - e^{-\beta\epsilon})$$

Fraction of molecules in energy levels is,

$$p_i = e^{-\beta\epsilon_i}/q = (1 - e^{-\beta\epsilon}) e^{-\beta\epsilon_i}$$

Discussion of figure, next slide

For a two level system,

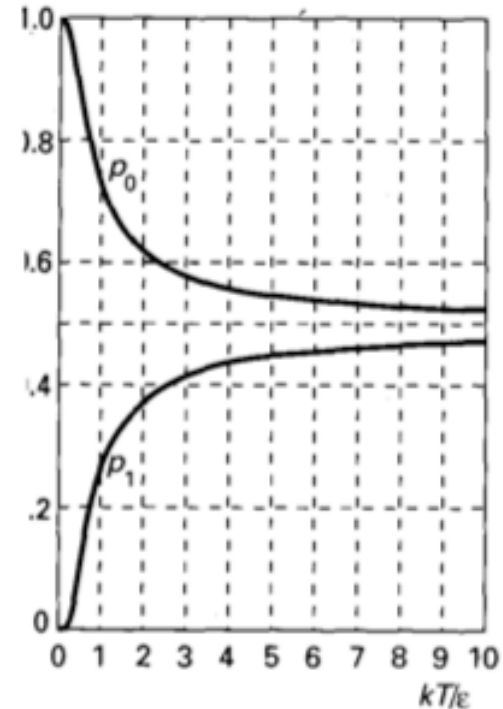


$$p_0 = 1/(1 + e^{-\beta\epsilon})$$

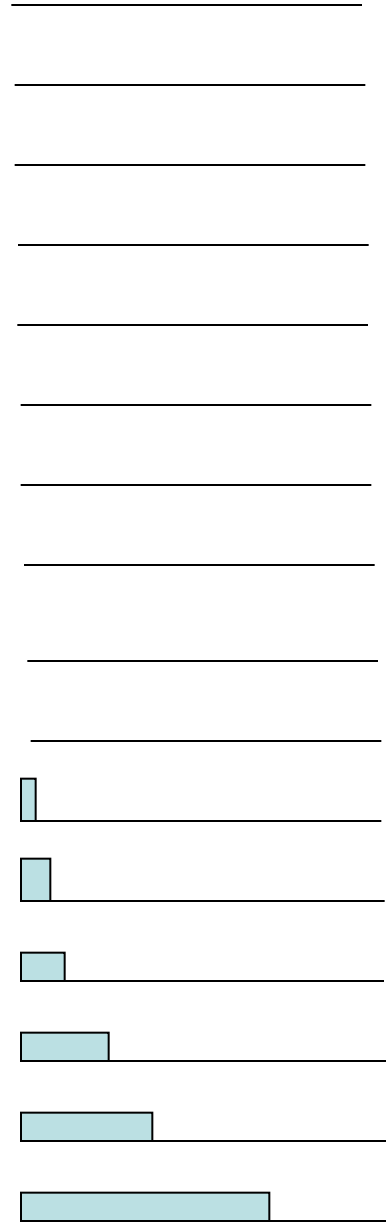
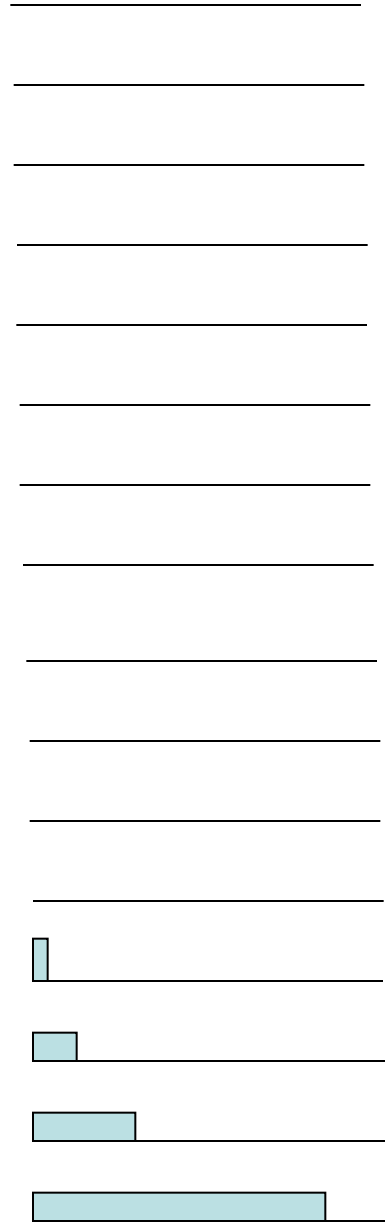
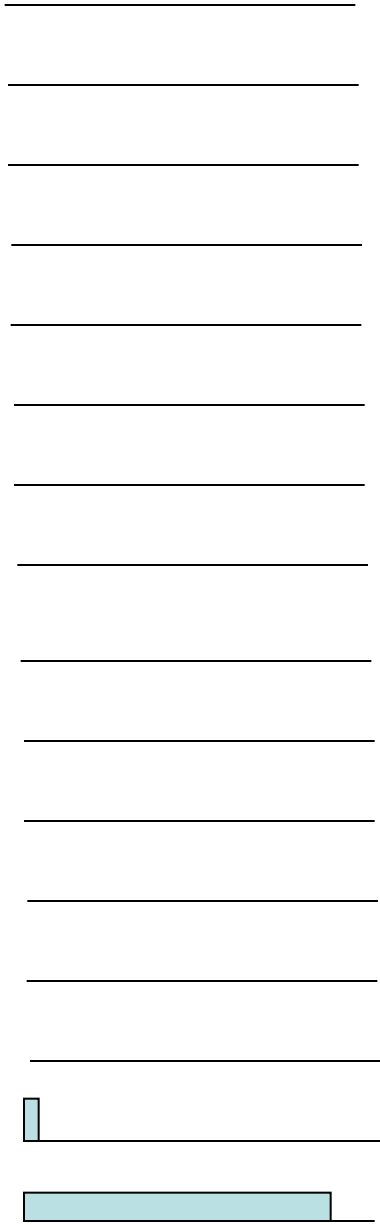
$$p_1 = e^{-\beta\epsilon}/q = e^{-\beta\epsilon}/(1 + e^{-\beta\epsilon})$$

As  $T \rightarrow \infty$ , both  $p_0$  and  $p_1$  go to  $1/2$ .

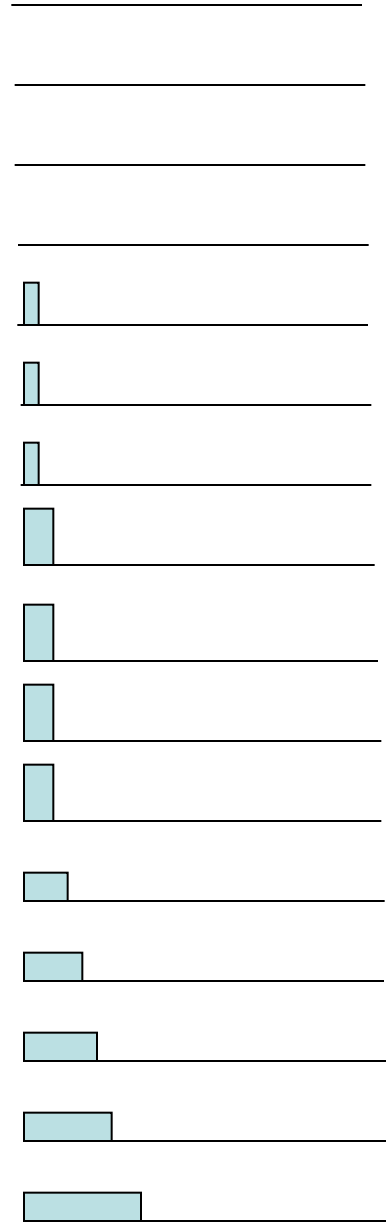
Consequences?



# Low temperature



# High temperature





Approximations: Partition functions are often complex. Analytical expressions cannot be obtained in several cases. Approximations become very useful.

**For example, partition function for one dimensional motion**

$$E_n = \frac{n^2 h^2}{8mX^2} \quad n = 1, 2, \dots$$

$$\epsilon_n = (n^2 - 1)\epsilon \quad \epsilon = \frac{h^2}{8mX^2}$$

$$q_x = \sum_{n=1}^{\infty} e^{-(n^2-1)\beta\epsilon}$$

$$q_x = \int_1^{\infty} e^{-(n^2-1)\beta\epsilon} dn \quad \text{energy levels are close, sum becomes an integral}$$

Lowest energy level has an energy of  $\frac{h^2}{8mX^2}$   
Energy with respect to this level is,

*No big difference, if we take the lower limit to 0 and replace  $n^2-1$  to  $n^2$ .*

$$q_x = \left[ \frac{1}{\beta\epsilon} \right]^{1/2} \int_0^{\infty} e^{-x^2} dx = \left[ \frac{1}{\beta\epsilon} \right]^{1/2} \left[ \frac{\pi}{2} \right]^{1/2} = \left[ \frac{2\pi m}{h^2\beta} \right]^{1/2} X$$

Substitute,  $x^2 = n^2\beta\epsilon$ , meaning  $dn = dx/(\beta\epsilon)^{1/2}$

$$q_x = \left[ \frac{2\pi m}{h^2\beta} \right]^{1/2} X$$

Substitute for  $\epsilon$

## Independent motion in three dimensions

$$\epsilon_{n_1 n_2 n_3} = \epsilon_{n_1}^{(X)} + \epsilon_{n_2}^{(Y)} + \epsilon_{n_3}^{(Z)} \quad \text{Energy is a sum of independent terms}$$

$$\begin{aligned} q &= \sum_{\text{all } n} e^{-\beta \epsilon_{n_1}^{(X)}} e^{-\beta \epsilon_{n_2}^{(Y)}} e^{-\beta \epsilon_{n_3}^{(Z)}} \\ &= \left[ \sum_{n_1} e^{-\beta \epsilon_{n_1}^{(X)}} \right] \left[ \sum_{n_2} e^{-\beta \epsilon_{n_2}^{(Y)}} \right] \left[ \sum_{n_3} e^{-\beta \epsilon_{n_3}^{(Z)}} \right] \\ &= q_x q_y q_z \end{aligned}$$

$$q = \left[ \frac{2\pi m}{h^2 \beta} \right]^{3/2} XYZ$$

$$q = \frac{V}{\Lambda^3} \quad \Lambda = h \left[ \frac{\beta}{2\pi m} \right]^{1/2} = \frac{h}{(2\pi m k T)^{1/2}}$$

$\Lambda$  has dimensions of length,  
thermal wavelength

$$J = \text{kg m}^{-2} \text{s}^{-2}$$

*Question: How many more quantum states will be accessible for  $^{18}\text{O}_2$  compared to  $^{16}\text{O}_2$ , if it were to be confined in a box of  $1 \text{ cm}^3$ ?*

# How to get thermodynamics?

All information about the thermodynamic properties of the system is contained in the partition function. Thermal wavefunction.

Total energy

$$E = \sum_i n_i \epsilon_i$$

$$E = \frac{N}{q} \sum_i \epsilon_i e^{-\beta \epsilon_i}$$

Most probable configuration is dominating.  
We use Boltzmann distribution.

We know,  $\epsilon_i e^{-\beta \epsilon_i} = - \frac{d}{d\beta} e^{-\beta \epsilon_i}$

$$E = - \frac{N}{q} \sum_i \frac{d}{d\beta} e^{-\beta \epsilon_i} = - \frac{N}{q} \frac{d}{d\beta} \sum_i e^{-\beta \epsilon_i} = - \frac{N}{q} \frac{dq}{d\beta}$$

$U = U(0) + E$  → 1. All E's are relative  
E is the value of U relative to T = 0.

$$U = U(0) - \frac{N}{q} \left[ \frac{\partial q}{\partial \beta} \right]_v$$

$$U = U(0) - N \left[ \frac{\partial \ln q}{\partial \beta} \right]_v$$

2. Derivative w.r.t.  $\beta$  is partial as there are other parameters (such as V) on which energy depends on.

**Partition function gives internal energy of the system.**

# How to get entropy?

For a process, change in internal energy,  $U = U(0) + E$

$$U = U(0) + \sum_i n_i \epsilon_i$$

*Internal energy changes occur due to change in populations ( $N_i + dN_i$ ) or energy states ( $\epsilon_i + d\epsilon_i$ ). Consider a general case:*

$$dU = dU(0) + \sum_i N_i d\epsilon_i + \sum_i \epsilon_i dN_i$$

*For constant volume changes,  $dU = \sum_i \epsilon_i dN_i$*

$$dU = dq_{rev} = TdS \quad dS = dU/T = k \beta \sum_i \epsilon_i dN_i$$

$$dS = k \sum_i (\partial \ln W / \partial N_i) dN_i + k \alpha \sum_i dN_i$$

$$\beta \epsilon_i = (\partial \ln W / \partial N_i) + \alpha$$

*Number of molecules do not change. Second term is zero.*

$$dS = k \sum_i (\partial \ln W / \partial N_i) dN_i = k (d \ln W)$$

$$S = k \ln W$$

*From the derivation of Boltzmann distribution  $\alpha$  and  $\beta$  are constants*