

# **PHY101: Introduction to Physics I**

**Monsoon Semester 2024**

**Lecture 36**

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## Previous Lectures

**Entropy**

**Third Law of Thermodynamics**

## This Lecture

**Macrostates vs Microstates**



# Macrostate vs Microstate

- A macrostate of a system is its condition description from macroscopic point of view, e.g., pressure, density, temperature. In other words the conditions which can be measured without going to the microscopic details.
- A microstate, in contrast, describes the system's microscopic condition. More precisely, it refers to the microscopic configuration of a thermodynamic system that the system may occupy with a certain probability.
- Different microstates may correspond to a single macrostate.



# Macrostate vs Microstate

- For example consider a gas. We view it as built from some elementary constituents (molecules). The thermodynamic state of the gas (which characterizes the values of macroscopic observables such as energy, pressure, volume, etc. ) corresponds to many possible configurations of the constituents (the molecules). These configurations of the constituents are the microstates.
- The macroscopic, thermodynamic, state in this case would be the macrostate.

# Macrostate vs Microstate

A simple non-thermodynamic analogy:

Consider two dices being thrown. Let total value of the dice roll define our macrostate. For total value 7, microstates in would be

(First,Second):

(1,6),(2,5),(3,4),(4,3),(5,2),(6,1)

So 6 microstates.



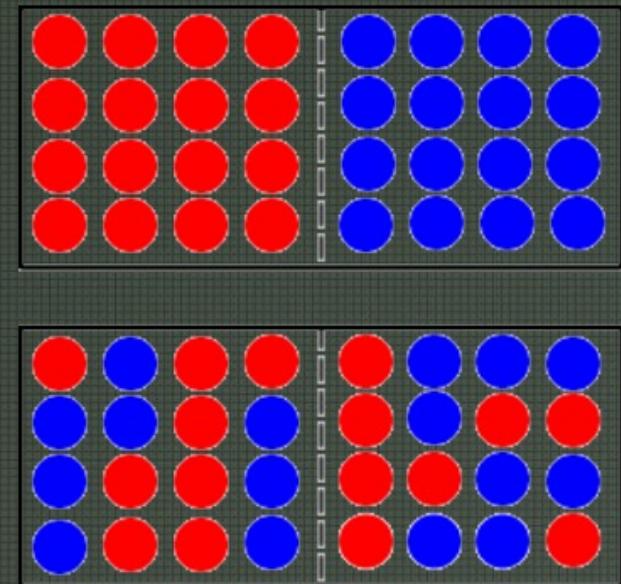
In contrast, for the macrostate 12, we just have one microstate (6,6).

Image Source:

<http://us.123rf.com/400wm/400/400/artzmey/artzmey0903/artzmey09030001/4402880-two-dices-on-a-black-background-focus-on-a-first-dice.jpg>

# Disorder

- Consider the space inside a rectangle divided into two. If we have red and blue spheres (which we may label with numbers).
- The number of ways they can be arranged with red on one side and blue on the other (**ordered**) is definitely less than the number when no restriction (**disordered**) is applied.
- Macrostate associated with **disorder** has far more possible microstates than those associated with **order** (and therefore has more entropy\*).



\*This will become clear from next slides.

# Microscopic origin of Entropy

- Consider a gas initially confined to a volume  $V_i$ . Suppose the gas molecules occupy some microscopic volume  $V_m$ .
- The total number of possible locations of a single molecule in a macroscopic initial volume  $V_i$  is the ratio

$$w_i = \frac{V_i}{V_m}.$$

- This also gives the number of ways the molecule can be placed in the initial volume, i.e., the number of microstates.
- Similarly a second molecule can also be located in  $w_i$  ways. (*We assume the probabilities of a molecule occupying any of these locations are equal.*)
- Thus total number of ways of placing the two molecules=  $w_i^2$ .

# Microscopic origin of Entropy

If there are  $N$  molecules the total number of ways would be,

$$\Omega_i = w_i^N = \left(\frac{V_i}{V_m}\right)^N.$$

If the volume of the gas increase to  $V_f$ , this number increases to

$$\Omega_f = w_f^N = \left(\frac{V_f}{V_m}\right)^N.$$

Dividing the second equation by first and taking natural log we obtain,

$$\ln\left(\frac{\Omega_f}{\Omega_i}\right) = N \ln\left(\frac{V_f}{V_i}\right)$$

# Microscopic origin of Entropy

This gives

$$\ln(\Omega_f) - \ln(\Omega_i) = N \ln\left(\frac{V_f}{V_i}\right).$$

Thermodynamically, we found that the entropy change associated with a reversible isothermal process is

$$S_f - S_i = Nk \ln\left(\frac{V_f}{V_i}\right).$$

Comparing we obtain

$$S_f - S_i = k \ln(\Omega_f) - k \ln(\Omega_i)$$

which suggests that

$$S = k \ln \Omega$$

We could have considered an additive constant in the above, but  $S$  is defined in a way that it is zero for  $\Omega = 1$  (Connection with the third law)

# Microscopic definition of Entropy

Thus if  $\Omega$  gives the number of microstates in a system leading to the same macrostate, then the entropy is given by

$$S = k \ln \Omega$$

where  $k$  is the Boltzmann constant.

The above equation is of fundamental importance in physics -- it provides a bridge between the microscopic and the macroscopic.



## Practice Problems

**Q1.** The enthalpy of fusion for water is 6.01 kJ/mol. Calculate the entropy change for 1.0 mole of ice melting to form liquid at 273 K.

The entropy change for a phase change at constant pressure is given by

$$\Delta S = \frac{q}{T} = \frac{\Delta H_{phase}}{T}$$

$$\begin{aligned}\Delta S &= \frac{(1 \text{ mol})(6010 \text{ J/mol})}{273 \text{ K}} \\ &= 22 \text{ J/K}\end{aligned}$$

**Q2.** A body at  $200^{\circ}\text{C}$  undergoes a reversible isothermal process. The heat energy removed in the process is 7875 J. Determine the change in the entropy of the body.

*System* : Closed system

*Known* :  $T_1 = T_2$

$$= 200^{\circ}\text{C}$$

$$= 473 \text{ K}$$

$$Q_{\text{rejected}} = 7875 \text{ J}$$

*Process* : Isothermal

*To find* :  $\Delta s$

*Analysis* :  $S_2 - S_1 =$  for an isothermal process

=

$$= -16.65 \text{ J/K.}$$

Entropy decreases as heat is removed from the system.

**Q3. What is the increase in entropy if one gram of ice at 0°C is melted and heated to 50°C? (Homework)**

The change in entropy is given by  $dS = \frac{dQ}{T}$ . In this case, the  $dQ$  must be calculated in two pieces. First there is the heat needed to melt the ice, and then there is the heat needed to raise the temperature of the system. Therefore,

$$\Delta Q = mL_f + mc_w\Delta T$$

where  $m = 1\text{ g}$  is the total mass of the system,  $L_f = 80\text{ cal/g}$  is the heat of fusion, and  $c_w = 1\text{ cal/(g}\cdot\text{K)}$  is the specific heat of water. Thus, the total change in entropy is

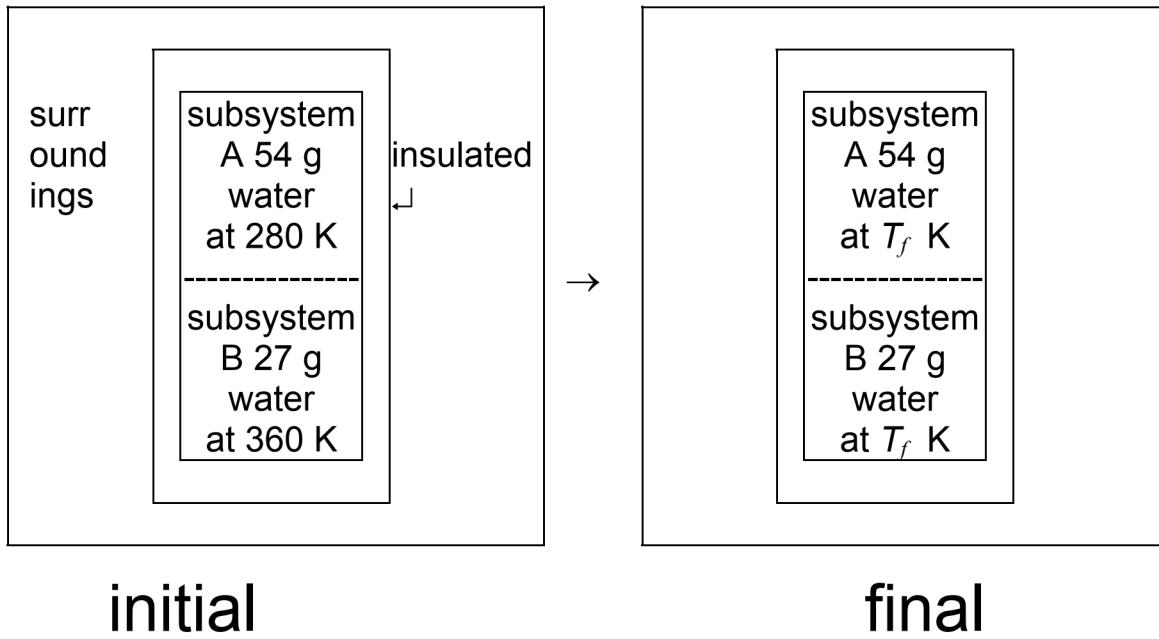
$$\Delta S = \frac{mL_f}{T_i} + \int_{T_i}^{T_f} mc_w \frac{dT}{T}$$

where  $T_i = 0^\circ\text{C} = 273\text{ K}$  and  $T_f = 50^\circ\text{C} = 323\text{ K}$ . Plugging in numbers, and remembering that we always use temperatures in Kelvin,

$$\begin{aligned}\Delta S &= \frac{(1\text{ g})(80\text{ cal/g})}{273\text{ K}} + \int_{273}^{323} (1\text{ cal/g})(1\text{ g}) \frac{dT}{T} \\ &= \frac{80}{273} \text{ cal/K} + \ln\left(\frac{323}{273}\right) \text{ cal/K} \\ \Delta S &= 0.461 \text{ cal/K}\end{aligned}$$

**Q4.** Calculate the entropy change that results from mixing 54.0 g of water at 280 K with 27.0 g of water at 360 K in a vessel whose walls are perfectly insulated from the surroundings. Is this a spontaneous process? (**Homework**)

(Consider the heat capacity of liquid water a constant over the temperature range from 280 K to 360 K and to have the value  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ ).



Look inside the system only, and imagine the system to be in two parts, separated by a thermally conducting interface, each part doing its own system accounting of  $\mathbf{q}$  (and  $\mathbf{w}$ , had there been any work). Consider each part reversibly heating or cooling the other part.

$\mathbf{q}_{\text{surr}} = 0$  since insulated, no  $\mathbf{q}$  can pass across the boundary between system and its surroundings

$\mathbf{q}_{\text{system}} = 0$  since insulated, no  $\mathbf{q}$  can pass across the boundary between system and its surroundings

Recall the definitions of concepts and terms:

Second law of thermodynamics,

$$dS = dq_{rev}/T$$

definition of heat capacity:

$$dq = C dT$$

$q_{\text{A system}}$

$$= 54.0 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (T_f - 280)$$

$q_{\text{B system}}$

$$= 27.0 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (T_f - 360)$$

$$T_f = ?$$

$$\begin{aligned}
 \mathbf{q}_{\text{system}} &= 0 = \mathbf{q}_{A \text{ system}} + \mathbf{q}_{B \text{ system}} \\
 &= 54.0 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (T_f - 280) + \\
 &\quad 27.0 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (T_f - 360) \\
 \text{Solve for } T_f : \quad T_f &= 306.67 \text{ K}
 \end{aligned}$$

$$\begin{aligned}
 d\mathbf{S} &= d\mathbf{q}_{\text{rev}} / T = C dT / T. \text{ Integrating} \\
 \text{gives } \Delta \mathbf{S}_A &= C \ln (T_f / T_i) \\
 \Delta \mathbf{S}_{A \text{ system}} &= 54.0 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \\
 &\quad \times \ln (306.67 / 280) \\
 &= +20.54 \text{ J K}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \Delta S_{B \text{ system}} &= 27.0 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \\
 &\quad \times \ln(306.67/360) \\
 &= -18.10 \text{ J K}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \Delta S_{\text{system}} &= \Delta S_{A \text{ system}} + \Delta S_{B \text{ system}} \\
 &= +20.54 - 18.10 = +2.44 \text{ J K}^{-1}
 \end{aligned}$$

$\Delta S_{\text{surr}} = 0$  since no  $q$  passed across the insulated boundary

$$\begin{aligned}
 \Delta S_{\text{universe}} &= \Delta S_{\text{system}} + \Delta S_{\text{surr}} \\
 &= +2.44 \text{ J K}^{-1}
 \end{aligned}$$

spontaneous process ? YES  
because  $\Delta S_{\text{universe}} > 0$