

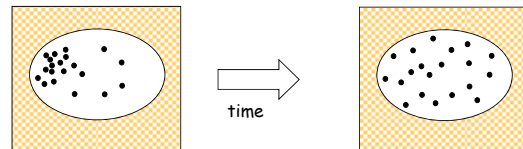
## Lecture 42

### Entropy

## Energy dispersal

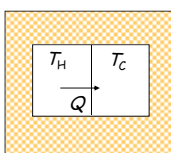
All spontaneous happenings in physical systems produce an **increase in energy dispersal**

Over time, differences in temperature, pressure, and density tend to even out in a physical system which is isolated from the outside world.



Microscopic explanation: random collisions  
Macroscopic challenge: how to describe this with state variables?

## A simple system to begin with...

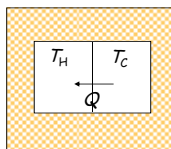


Two systems in thermal contact

- Thermally conducting wall
- Systems isolated from rest of the world

Heat transfer from hot to cold

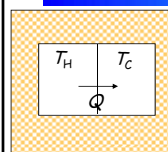
- $(Q_H < 0), (Q_C > 0)$  : same magnitude  $Q$
- energy dispersal, towards equal  $T$



Heat transfer **not** from cold to hot

- Even though 1<sup>st</sup> law of thermodynamics says this could happen
- Does not violate energy conservation

## New state variable: entropy



$$Q_C + Q_H = 0 \quad (Q_C > 0), (Q_H < 0) : \text{same magnitude } Q$$

$$\left| \frac{Q_C}{T_C} \right| > \left| \frac{Q_H}{T_H} \right| \quad \text{since } T_C < T_H$$

$$\frac{Q_C}{T_C} + \frac{Q_H}{T_H} > 0$$

(positive large)      (negative small)

This is positive ( $> 0$ ) for all types of interacting systems.

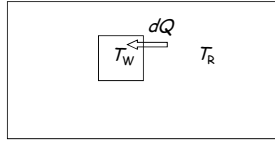
Define new state variable **entropy**:  $\Delta S = \frac{Q}{T}$

The change of entropy gives the direction of the process (direction of energy dispersion): entropy must increase  $\Delta S = \Delta S_C + \Delta S_H > 0$

## ACT: Glass of cold water

A glass of cold water is placed in a hot room. Consider a small heat transfer  $dQ$ . Which of the following statements is a true?

- A.  $\Delta S_W > 0, \Delta S_R > 0$
- B.  $\Delta S_W < 0, \Delta S_R > 0$
- C.  $\Delta S_W > 0, \Delta S_R < 0$



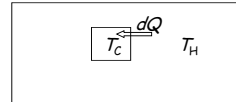
$$dS_{\text{water}} = \frac{dQ_{\text{water}}}{T_C} \quad dQ_{\text{water}} > 0 \quad \text{Entropy of water increased}$$

$$dS_{\text{water}} > 0$$

$$dS_{\text{room}} = \frac{dQ_{\text{room}}}{T_H} \quad dQ_{\text{room}} < 0 \quad \text{Entropy of room decreased}$$

$$dS_{\text{room}} < 0$$

## Terminology



Glass of cold water (system) in hot room (environment)

Interacting components naturally exchange energy: real, spontaneous processes. Often there are two interacting parts labeled as **system** and **environment**

$$dS_{\text{interacting parts}} = (dS_{\text{system}} + dS_{\text{environment}}) > 0$$

These two are isolated from the **rest-of-the-world**,  $dS_{\text{rest}}=0$

Universe = {system + environment + rest-of-the-world}

$$dS_{\text{universe}} > 0 \quad \text{Second law of thermodynamics in terms of entropy}$$

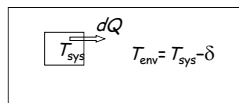
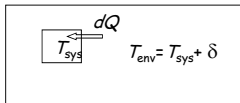
## Reversibility

The processes we have analyzed are **irreversible**:

- spontaneous dispersion of energy (in one direction)
- the entropy of the universe increases

If a system and its environment are almost at the same temperature:

- a small change in any temperature can reverse the direction of the heat flow  $\rightarrow$  **reversible** process
- the entropy of the **universe** (not of each part) remains constant



## Change of entropy in an adiabatic process

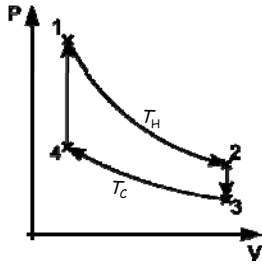
That's the easiest case: since  $Q=0, \Delta S=0$

We can now re-write our list:

- Isobaric: Constant  $p$
- Isochoric: Constant  $V$
- Isothermal: Constant  $T$
- **Adiabatic: Constant  $S$**

### Example: Entropy change in a Stirling cycle

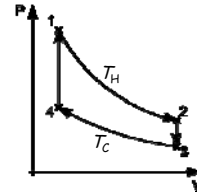
Entropy change in an isothermal is "easy" because heat exchange happens at a fixed temperature:



$$\Delta S_{1 \rightarrow 2} = \frac{Q_{1 \rightarrow 2}}{T_H} = \frac{nRT_H \ln \frac{V_2}{V_1}}{T_H} = nR \ln \frac{V_2}{V_1} > 0$$

$$Q_{1 \rightarrow 2} = \Delta U_{1 \rightarrow 2} + W_{1 \rightarrow 2} = 0 + \int_{V_1}^{V_2} p dV = nRT_H \ln \frac{V_2}{V_1}$$

$$\Delta S_{3 \rightarrow 4} = nR \ln \frac{V_4}{V_3} = nR \ln \frac{V_1}{V_2} = -\Delta S_{1 \rightarrow 2} < 0$$



Isochoric processes require an integration.

$$\Delta S_{2 \rightarrow 3} = \int_{T_H}^{T_C} \frac{dQ_{2 \rightarrow 3}}{T} = \int_{T_H}^{T_C} \frac{nC_V dT}{T} = nC_V \ln \frac{T_C}{T_H} < 0$$

$$\Delta S_{4 \rightarrow 1} = \int_{T_C}^{T_H} \frac{dQ_{4 \rightarrow 1}}{T} = \int_{T_C}^{T_H} \frac{nC_V dT}{T} = nC_V \ln \frac{T_H}{T_C} = -\Delta S_{2 \rightarrow 3} > 0$$

#### ACT: Stirling

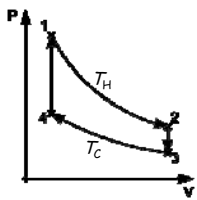
Since we obtained  $\Delta S_{\text{cycle}} = 0$ , we conclude that:

- A. The cycle is reversible.
- B. The cycle is irreversible.
- C. There is nothing to conclude.

A process is reversible (irreversible) if the entropy of the universe remains the same (increases).

Entropy is state variable, so the change in entropy in a cycle is *always* zero. Duh.

How much does the entropy of the environment change?



Our environment is a cold source and a hot source. Heat exchange happens at these constant temperatures for them.

Isochoric is irreversible:  
 $\Delta S_{2 \rightarrow 3}(\text{environment}) + \Delta S_{2 \rightarrow 3}(\text{gas}) > 0$

$$\neq -\Delta S_{2 \rightarrow 3}(\text{gas})$$

$$\Delta S_{\text{hot source}} = \frac{-(Q_{4 \rightarrow 1} + Q_{1 \rightarrow 2})}{T_H} = -\frac{\Delta U_{4 \rightarrow 1} + W_{1 \rightarrow 2}}{T_H} = -\frac{nC_V(T_H - T_C)}{T_H} - \frac{nRT_H \ln \frac{V_2}{V_1}}{T_H}$$

$$= -\Delta S_{1 \rightarrow 2}(\text{gas})$$

Isothermal is reversible:  
 $\Delta S_{1 \rightarrow 2}(\text{environment}) + \Delta S_{1 \rightarrow 2}(\text{gas}) = 0$

Signs from the point of view of the environment

+ something similar for the cold source.

Overall,  $\Delta S_{\text{all}} > 0 \Rightarrow$  this cycle is an irreversible process

Any process involving exchange of heat between bodies at different temperature is irreversible.

Only ideal isothermal and adiabatic processes can be reversible.

And this is why the Carnot cycle is reversible...

Exercise: Prove that  $\Delta S_{\text{all}} = 0$  for a Carnot cycle.

## In-class example: Second law

Which of the following is NOT an accurate statement of the second law of thermodynamics?

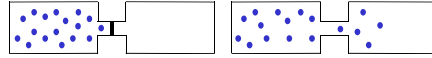
- A. The change of entropy in an object can never be less than zero.
- B. A perfect heat engine ( $e = 1$ ) cannot exist.
- C. A perfect refrigerator ( $K = \infty$ ) cannot exist.
- D.  $\Delta S_{\text{total (isolated system)}} > 0$
- E. All of the above are accurate statements of the second law of thermodynamics.

Entropy of a part can decrease. Entropy of the total (universe) cannot decrease.

## The Meaning of Equilibrium

Introduction to Statistical Mechanics

In the free expansion process, why do the particles tend towards equal numbers in each equal-size box?



Macroscopic point of view:

Spontaneous process  $\Leftrightarrow$  Entropy increase

Let's try to understand it from the microscopic point of view.

## Probability: 4-particle gas

A chamber contains 4 particles labeled A, B, C and D. What is the probability of finding all four particles in the left half of the chamber?



1 configuration ("microstate") with 4 particles on the left



4 microstates with 3 particles on the left



6 microstates with 2 particles on the left



# particles on the left	0	1	2	3	4	total
# of microstates (w)	1	4	6	4	1	16

Probability of finding all 4 particles on the left  $p(4 \text{ left}) = \frac{1}{16}$

Probability of finding 3 particles on the left  $p(3 \text{ left}) = \frac{4}{16}$

Probability of finding 2 particles on the left  $p(2 \text{ left}) = \frac{6}{16}$

**States with more "disorder" are more likely to happen.**

...especially when there are  $10^{23}$  particles instead of 4...

## Entropy is disorder

A system evolves spontaneously toward the state with

- most microstates  $w$
- greatest disorder
- largest entropy

All these must be  
the same thing

$$S = k \ln w$$

Microscopic expression of entropy

Example:

Go back to the Stirling example and note:

- Entropy of the gas increases in expansion and heating (increase of disorder)
- Entropy decreases in compression and cooling (decrease of disorder)