Second Law of Thermodynamics and Entropy

Alexei Tkachenko

Perpetual motion

- **First kind: No energy source.**
Impossible because of energy conservation (The First Law of Thermodynamics) .

- **Second kind: converting the heat of an environment to work?**

Perpetual motion

• **First kind: No energy source.**
Impossible because of energy conservation
(The First Law of Thermodynamics) .

• **Second kind: converting the heat of an environment to work?**

NOPE!

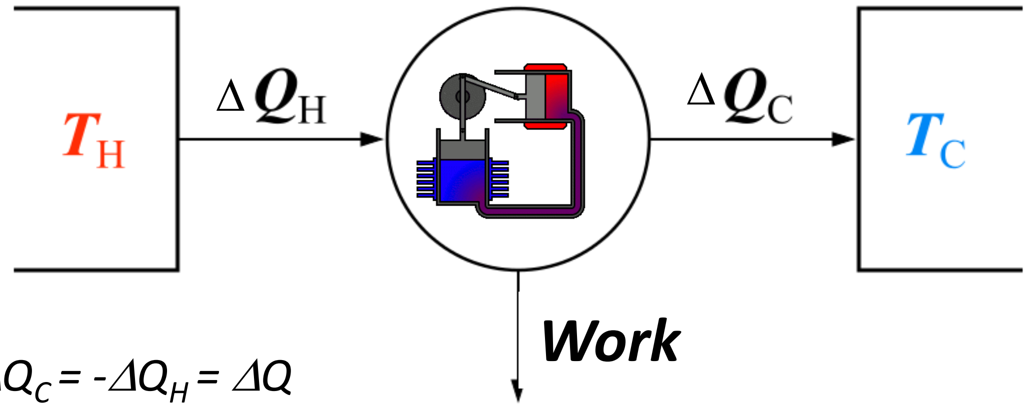
"It is impossible to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."

Kelvin's version of the Second Law

Entropy

Change in entropy (Clausius definition):

$$\boxed{\Delta S = \frac{\Delta Q}{T}}$$



If *Work=0* , $\Delta Q_C = -\Delta Q_H = \Delta Q$

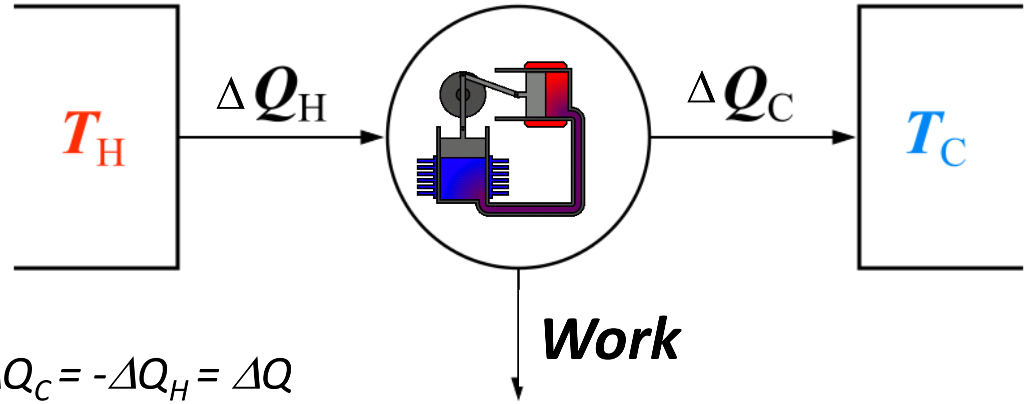
$$\Delta S_{total} = \frac{\Delta Q_C}{T_C} - \frac{\Delta Q_H}{T_H} = \Delta Q\left(\frac{1}{T_C} - \frac{1}{T_H}\right) \geq 0$$

The total **entropy** can only increase over time for an isolated system.

Entropy

Change in entropy (Clausius definition):

$$\Delta S = \frac{\Delta Q}{T}$$



If *Work=0* , $\Delta Q_C = -\Delta Q_H = \Delta Q$

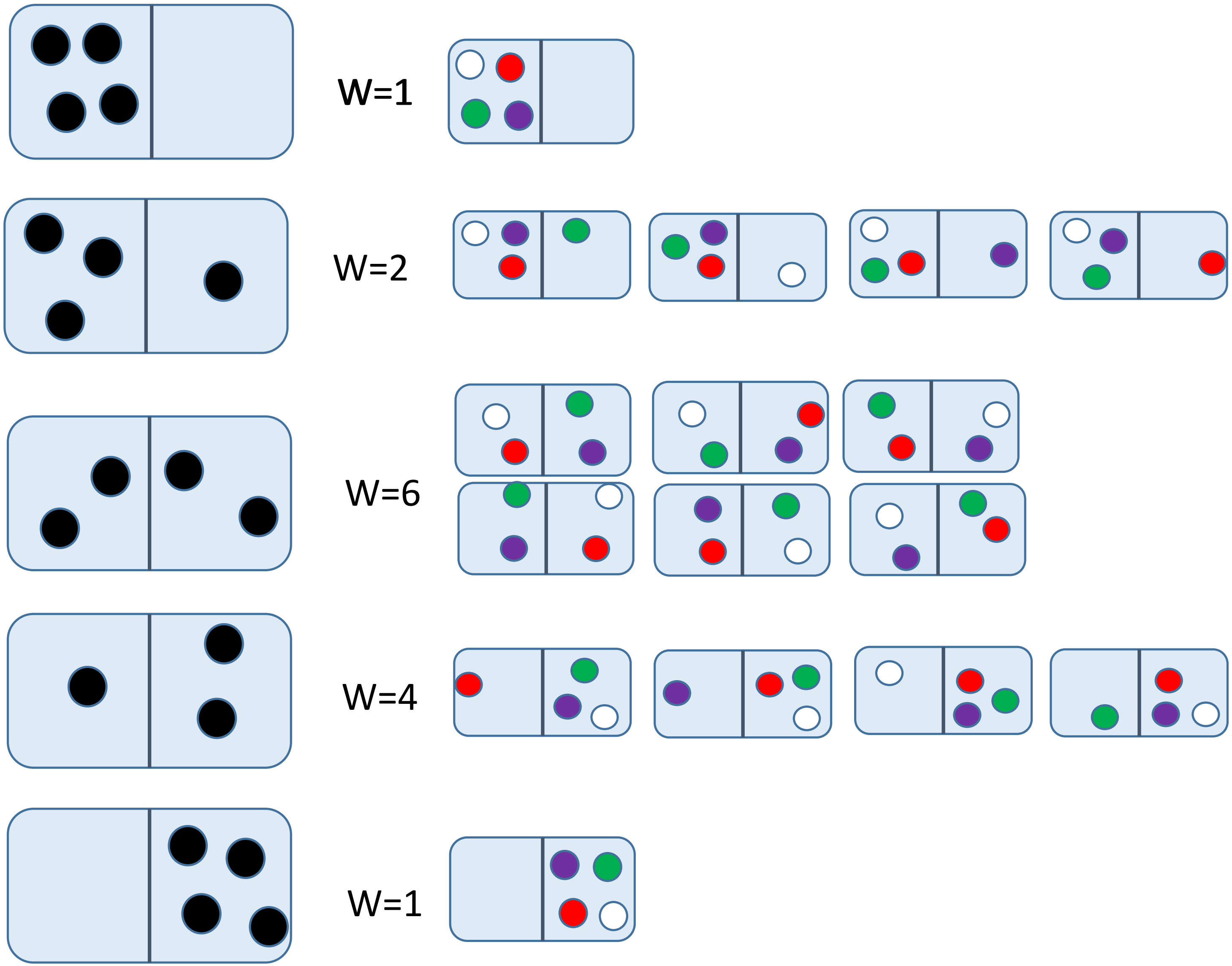
$$\Delta S_{total} = \frac{\Delta Q_C}{T_C} - \frac{\Delta Q_H}{T_H} = \Delta Q\left(\frac{1}{T_C} - \frac{1}{T_H}\right) \geq 0$$

The total **entropy** can only increase over time for an isolated system.

$$\Delta S_{total} = \Delta Q_H\left(\frac{1}{T_C} - \frac{1}{T_H}\right) - \frac{Work}{T_C} \geq 0$$

$$Work \leq \Delta Q_H\left(1 - \frac{T_C}{T_H}\right)$$

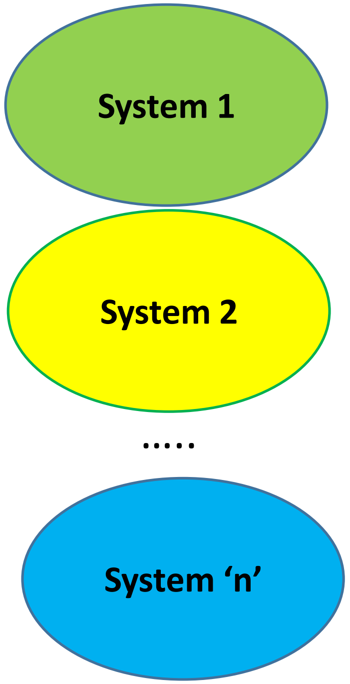
Let’s count “microstates”



Can *W* be the entropy?
No. Entropy must be <u>*additive*</u>

- Volume: $V_{total} = V_1 + V_2 + \ldots + V_n$
- Energy: $E_{total} = E_1 + E_2 + \cdots + E_n$
- Number of molecules: $N_{total} = N_1 + N_2 + \cdots + N_n$
- Entropy: $S_{total} = S_1 + S_2 + \cdots + S_n$

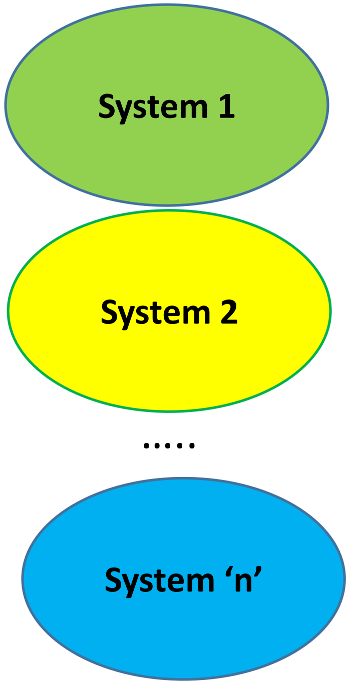
- Number of “microstates”: $W_{total} = W_1 \times W_2 \times \cdots \times W_n$



Can W be the entropy?
No. Entropy must be *additive*

- Volume: $V_{total} = V_1 + V_2 + \ldots + V_n$
- Energy: $E_{total} = E_1 + E_2 + \cdots + E_n$
- Number of molecules: $N_{total} = N_1 + N_2 + \cdots + N_n$
- Entropy: $S_{total} = S_1 + S_2 + \cdots + S_n$

- Number of “microstates”: $W_{total} = W_1 \times W_2 \times \cdots \times W_n$



Let us use magic of **logarithm**: $y = a^x \rightarrow \quad x = \log_a y$

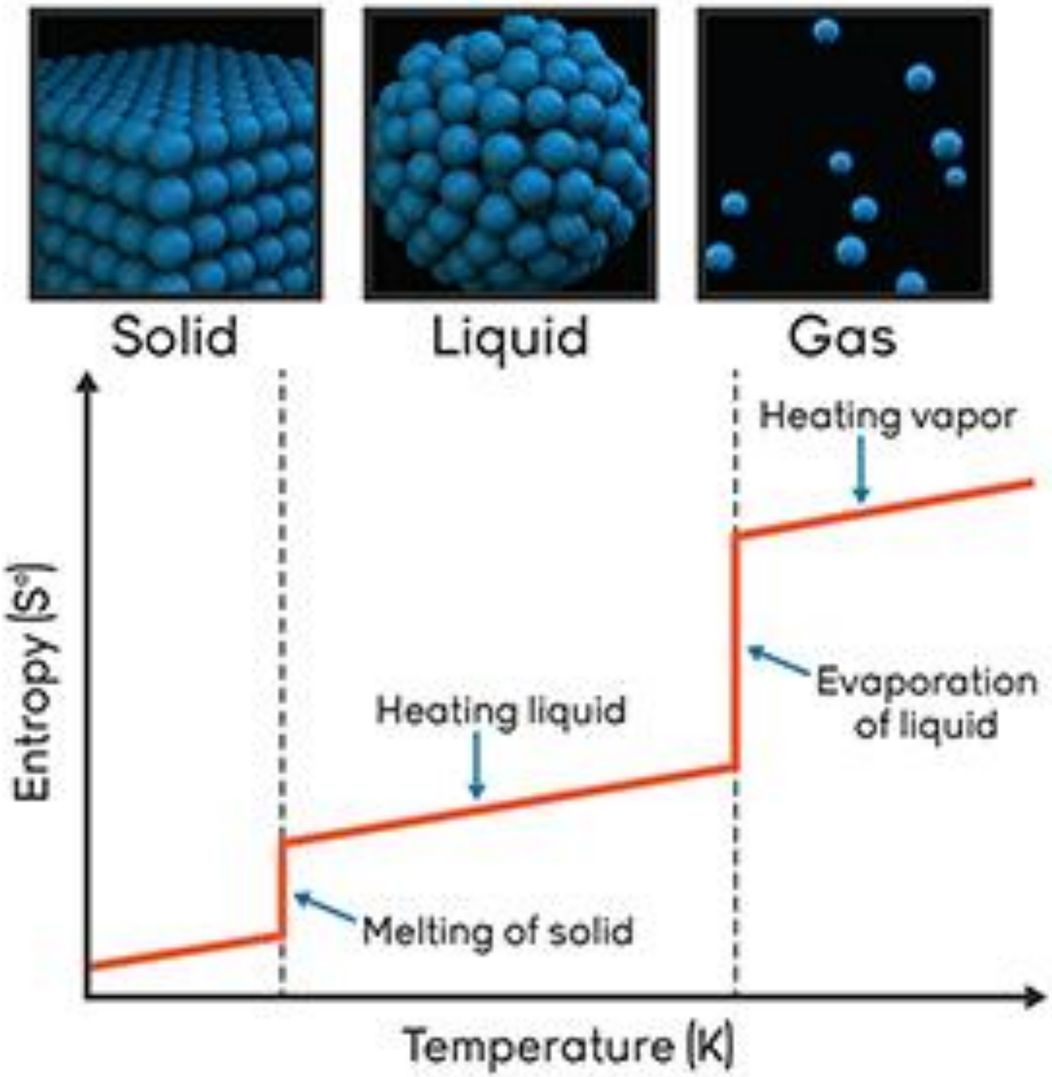
$$y_1 \times y_2 \rightarrow x_1 + x_2$$

$$\boxed{S = k \log W}$$

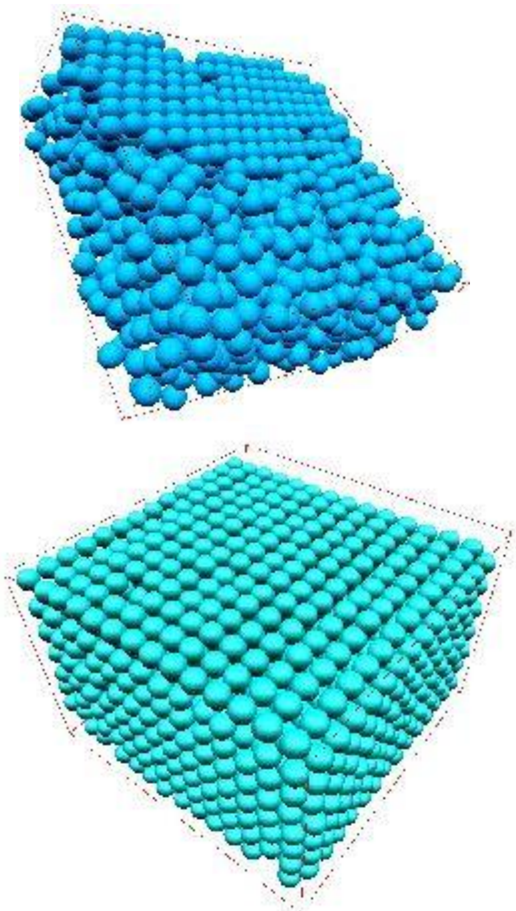
Ludwig Boltzmann: father of statistical physics

Problem: Mechanics is reversible but thermodynamics is not.

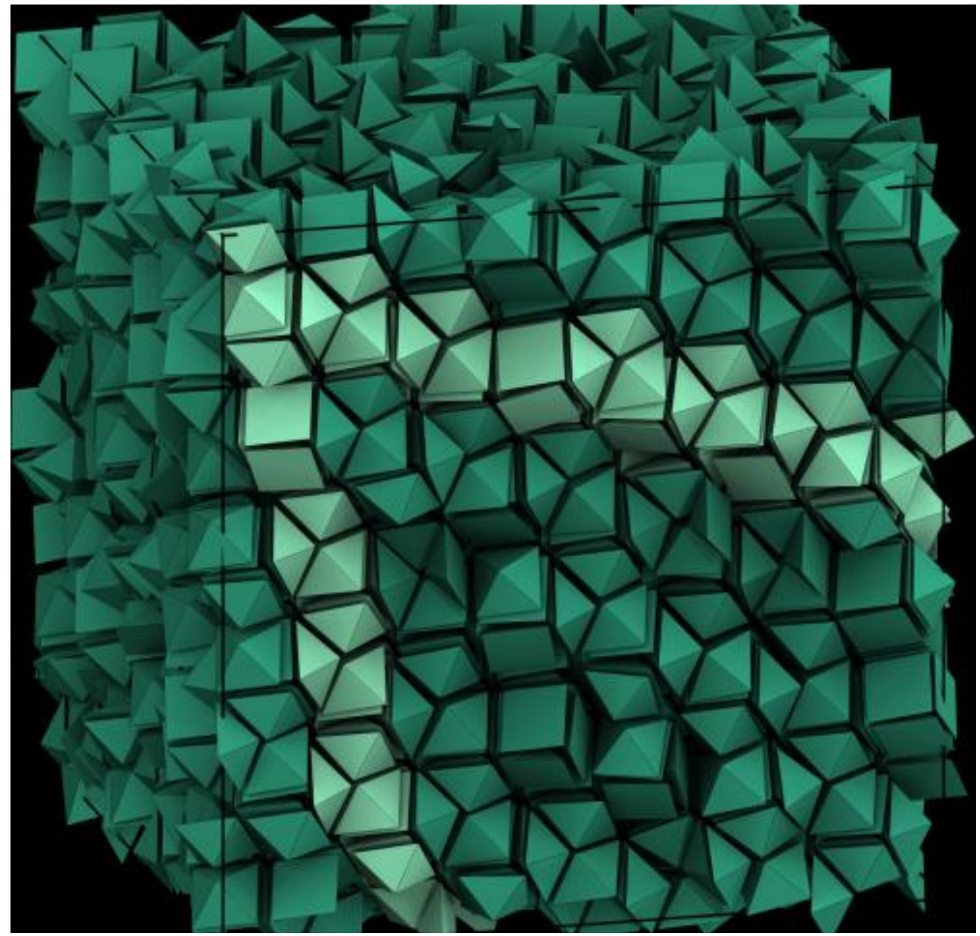
Entropy is the “Measure of Disorder”



But… Entropy also can lead to Order!



Hard Spheres



Hard Polyhedra

Homework

In class I discussed a simple example of 4 particles (say, molecules) that have to be distributed between two identical volumes, and calculated statistical weight of various configurations.

Now imagine that you have N=100 such particles. What is the statistical weight of finding a fraction f of them in one half of the system (say, left)? In order words, you want 100f particles to be in one half and 100(1-f) – in the other. Obtain the formula for statistical weight W (f), and for the entropy S(f). Use your favorite plotting software to plot the function S(f). I suggest this one: https://www.desmos.com/calculator

Note that

1) Natural log (base e) used in Bolzmann definition, is typically called “ln”;

2) There will be factorials in the formula. We only know how to work with factorials of integers. There is a way of actually define a factorial for an arbitrary number (don’t tell anyone, it’s a very-very fancy thing called Gamma function). Anyway, some software, including the calculator above will be able to plot a function that has factorials in it.