# Thermodynamics

PHY 215
Thermodynamics and
Modern Physics

Fall 2025
MSU

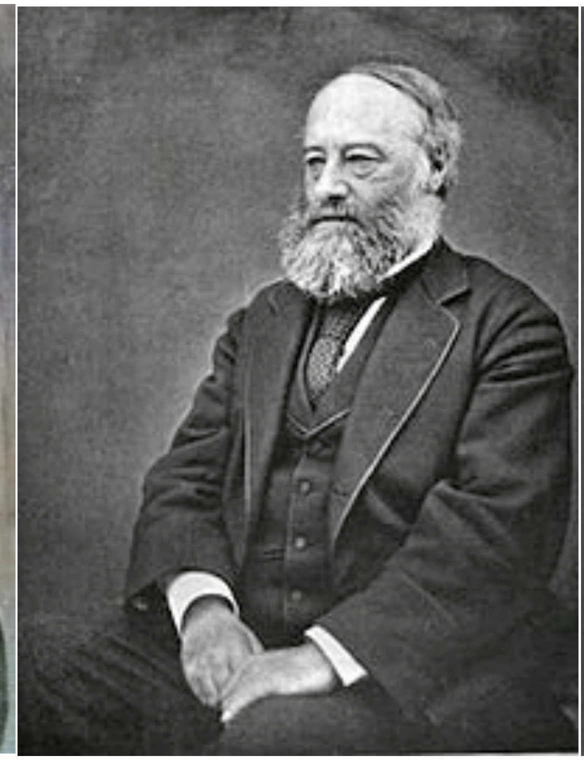
# Outline

- Thermodynamics vs. Statistical Mechanics
  - Kinetic Theory of Gases
- What is Entropy?
  - Microstates, Macrostates, & Probability
- Entropy of an Ideal Gas
  - Boltzman's Relation

# Thermodynamics

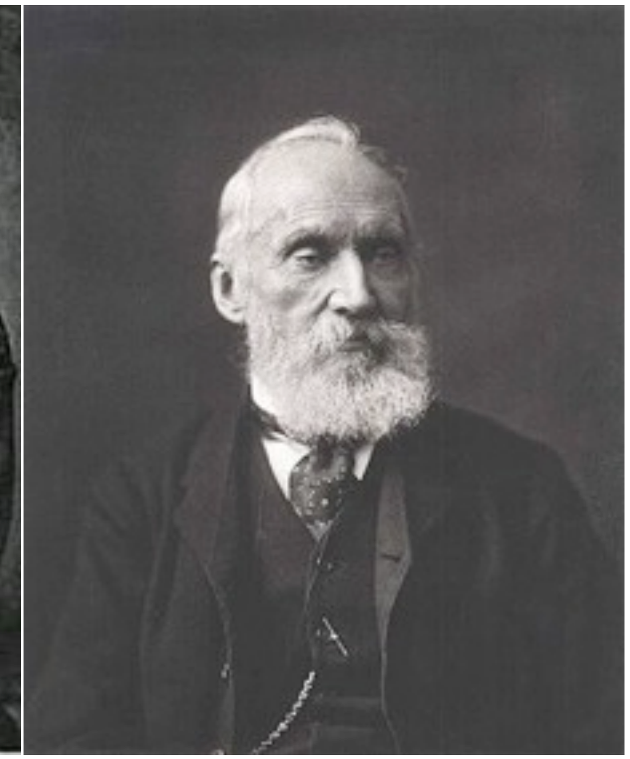
Sadi Carnot

1796 –1832



James Joule

1818 - 1889



William Thomson,
Lord Kelvin

1824 - 1907

Thermodyamics is the study of thermal properties of a system *without* reference to the *atomic* nature of matter!

Images: http://en.wikipedia.org

# But, atoms are important!

"If, in some cataclysm, all scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words?

I believe it is the *atomic hypothesis* (or atomic fact, or whatever you wish to call it) that *all things are made of atoms — little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.*

Richard Feynman

1918-1988

In that one sentence you will see an enormous amount of information about the world, if just a little imagination and thinking are applied."

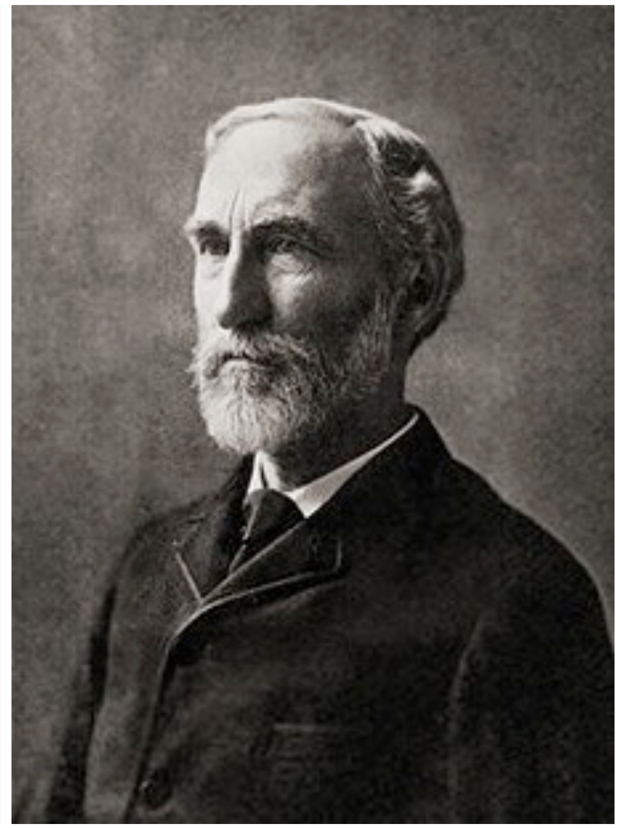
The Feynman Lectures on Physics

Image: http://en.wikipedia.org

# Statistical Mechanics

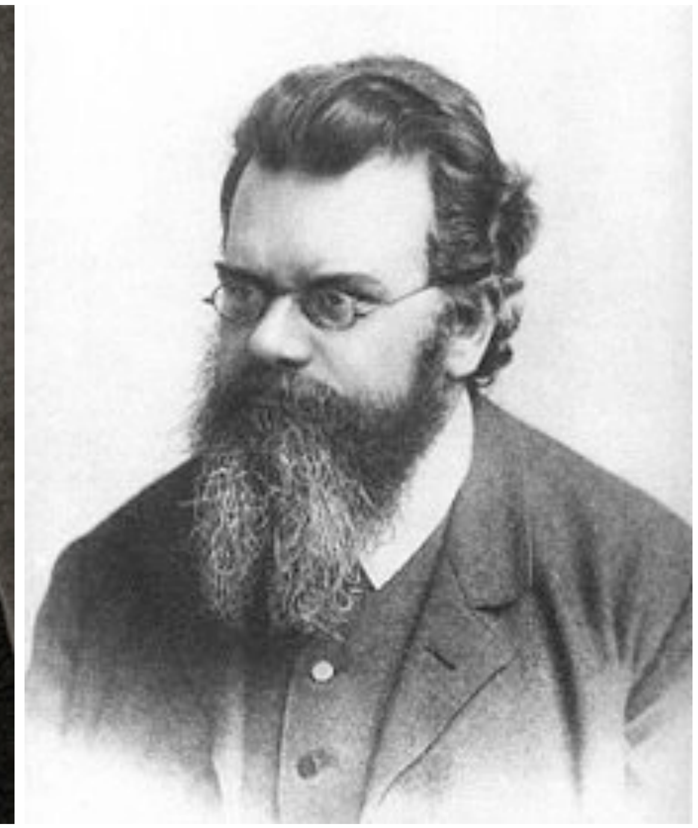
James Maxwell

1831-1879



Josiah Gibbs

1839-1903



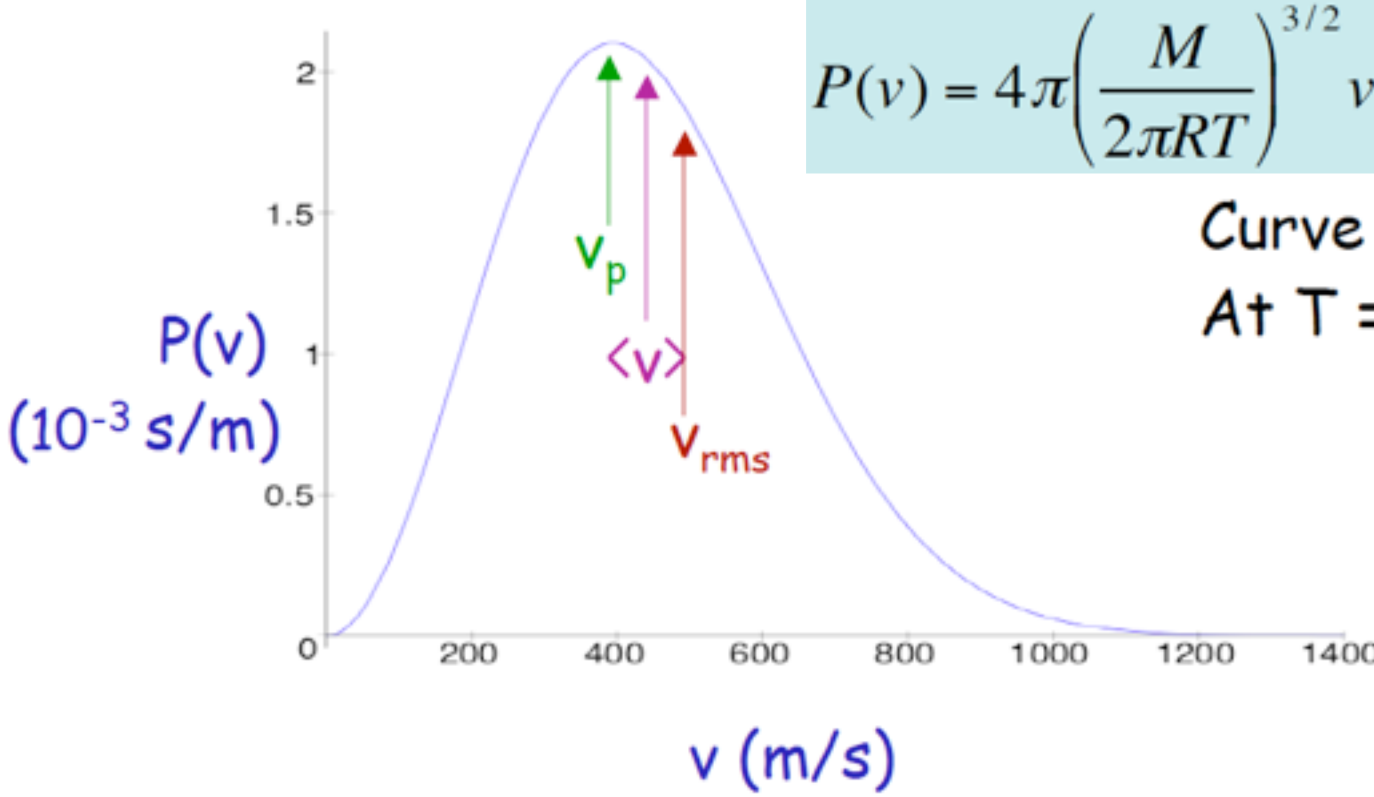
Ludwig Boltzmann

1844-1906

Statistical Mechanics is the study of thermal properties of a system in terms of *average properties* of an *ensemble* of individual particles

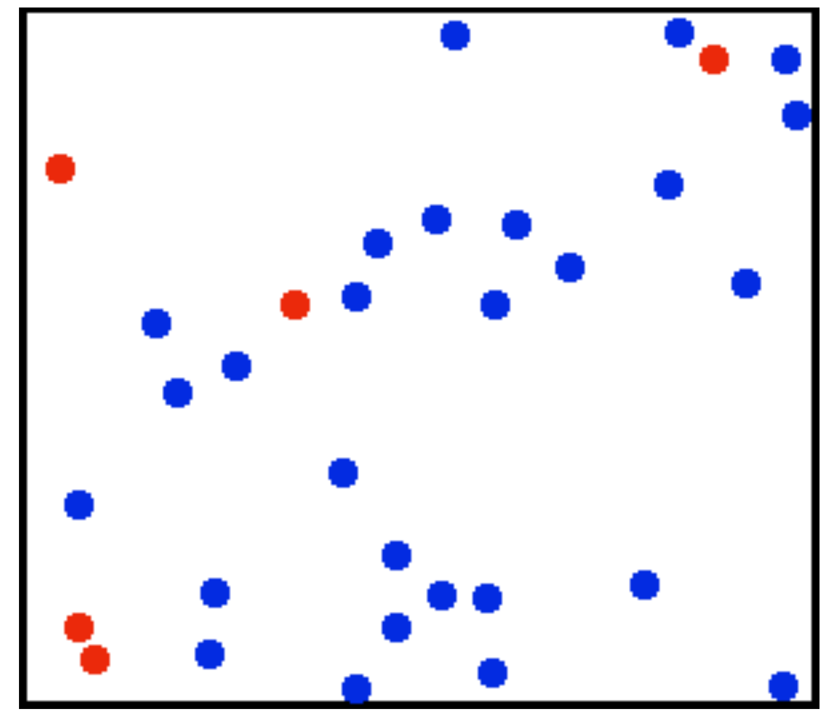
Images: http://en.wikipedia.org

# Kinetic Theory of Gases




$$P(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}}$$

Curve for $O_2$
At T = 300 K



$PV = NkT$

where N is the number of molecules in the gas
and k is the Boltzmann's constant,

$k = 1.38\times10^{-23}$ J/K

$PV = (nM/3)\, v^2_{rms}$

From ideal gas law: $PV = nRT$

$\Rightarrow \quad (nM/3)\, v^2_{rms} = nRT$

$\Rightarrow \quad v_{rms} = \sqrt{3RT/M}$

Image: http://en.wikipedia.org

# What is Entropy?

Entropy ~ a measure of the disorder of a system.

A state of high order = low probability
A state of low order = high probability

In an irreversible process, the universe moves from a state of low probability to a state of higher probability.

Can we make this more precise?

# Macro- and Micro-States

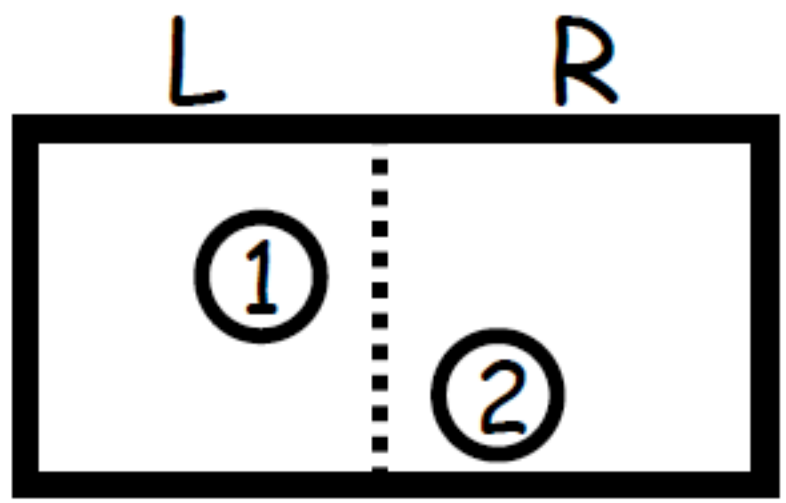
Microstate: a description of a system that specifies the properties (position and/or momentum, etc.) of each individual particle.

Averages
"State Variables"

Macrostate: a more generalized description of the system; it can be in terms of macroscopic quantities, such as P and V, or it can be in terms of the number of particles whose properties fall within a given range.

In general, each macrostate corresponds to large number of microstates.

# Example: Two Molecules in a Divided Container




(equal volumes)

There are 3 macrostates: both molecules on the left, both on the right, and one on each side.

There are 4 microstates: LL, RR, LR, RL.

# Concept Test

- How many macrostates and microstates are there for <u>three</u> molecules in a divided container?

  A. 2 macrostates & 2 microstates

  B. 3 macrostates & 6 microstates

  C. 4 macrostates & 8 microstates

  D. 4 macrostates & 16 microstates

# 3 & 4 Molecules

How about 3 molecules? Now we have:

LLL, (LLR, LRL, RLL), (LRR, RLR, RRL), RRR

(all L) (2 L, 1 R) (2 R, 1 L) (all R)

i.e. 8 microstates, 4 macrostates

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How about 4 molecules? Now there are 16 microstates and 5 macrostates

| (all L) | (3L, 1R) | (2L, 2R) | (1L, 3R) | (all R) |
|---|---|---|---|---|
| 1 | 4 | 6 | 4 | 1 |

number of microstates

# More Molecules

In general:

1 1

1 2 1

1 3 3 1

1 4 6 4 1

1 5 10 10 5 1

1 6 15 20 15 6 1

1 7 21 35 35 21 7 1

1 8 28 56 70 56 28 8 1

| particle number N | micro-states W | macro-states M |
|---|---|---|
| 1 | 2 | 2 |
| 2 | 4 | 3 |
| 3 | 8 | 4 |
| 4 | 16 | 5 |
| 5 | 32 | 6 |
| 6 | 64 | 7 |
| 7 | 128 | 8 |
| 8 | 256 | 9 |
| | $2^N$ | $N+1$ |

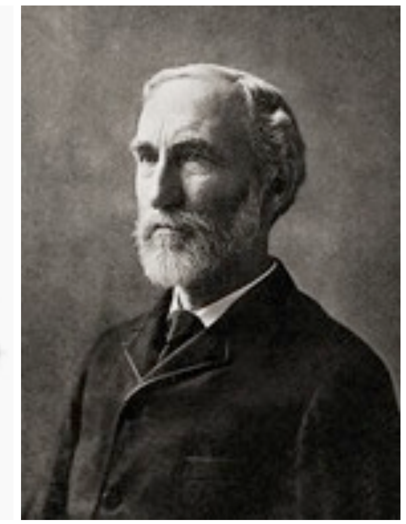
$$W_{N,n} = \frac{N!}{N!\,(N-n)!}$$

"multiplicity"

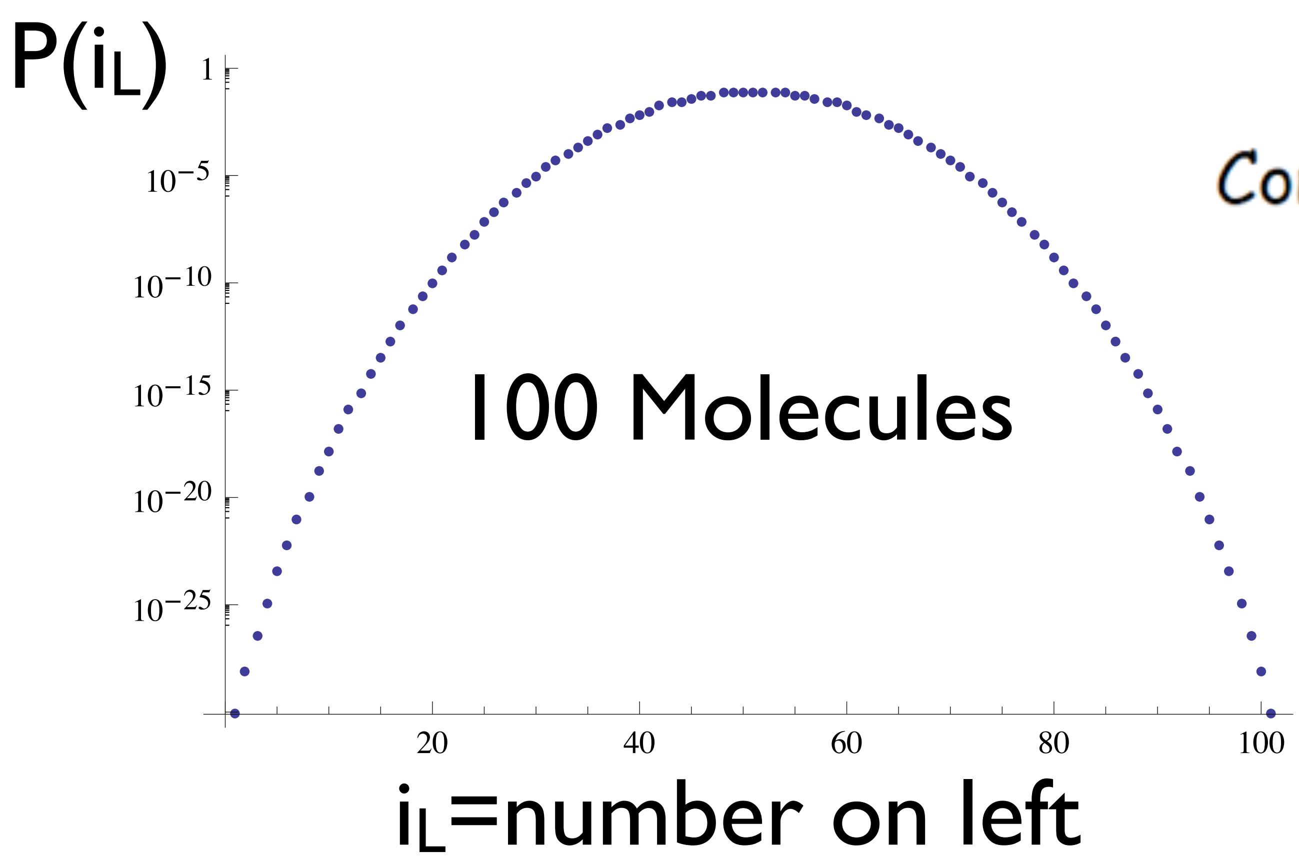
i.e. $W_{6,2} = \frac{6!}{2!\,4!} = 15$

# Statistical Mechanics

Fundamental Assumption of Statistical Mechanics: All microstates are equally probable. (subject to the applied constraints)

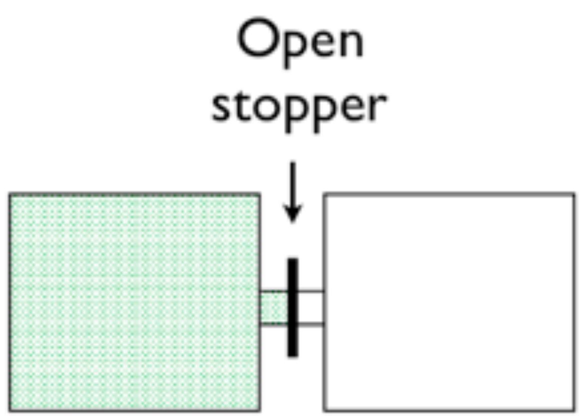

Thus, we can calculate the likelihood of finding a given arrangement of molecules in the container.

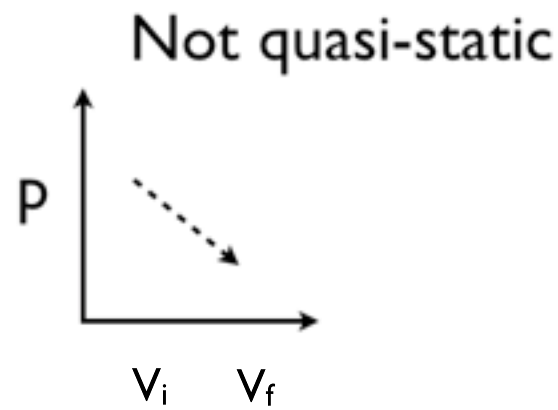



Conclusion: Events such as the spontaneous compression of a gas (or spontaneous conduction of heat from a cold body to a hot body) are not impossible, but they are so improbable that they never occur.

Images: http://en.wikipedia.org

# Ideal Gas Free Expansion




$\Delta Q = 0$ (adiabatic)
$\Delta W = 0$ (nothing to work against)
$\Rightarrow \Delta U = 0$

Thus, we arrive at an equation, first deduced by Ludwig Boltzmann, relating the entropy of a system to the number of microstates:

# microstates for macrostate

$$S = k \ln(W)$$

He was so pleased with this relation that he asked for it to be engraved on his tombstone.

If the final volume is $V_f$ then the probability of finding N molecules in a smaller volume $V_i$ is

Probability = $W_f/W_i = (V_f/V_i)^N$

- $\ln(W_f/W_i) = N \ln(V_f/V_i) = n N_A \ln(V_f/V_i)$

We have seen for a free expansion that

$\Delta S = n R \ln(V_f/V_i)$ ,

so

$\Delta S = (R/N_A) \ln(W_f/W_i) = k \ln(W_f/W_i)$

or

$$S_f - S_i = k \ln(W_f) - k \ln(W_i)$$

# Concept Test

- Some have argued that evolution is inconsistent with the 2nd law of thermodynamics, since "higher" life forms are more complex and organized. The resolution of this conundrum is:

A. Thermodynamics doesn't apply to biology

B. The earth is not an isolated system ←

C. "Higher" life forms are not more organized

Erwin Schrödinger

Images: http://spacefellowship.com
http://en.wikipedia.org

# Summary

- Statistical Mechanics relates microscopic behavior of matter to Thermodynamics.
- Fundamental Assumption: all microstates consistent with a given macrostate are equally probable.
- Entropy counts the number of microstates corresponding to a given macrostate.