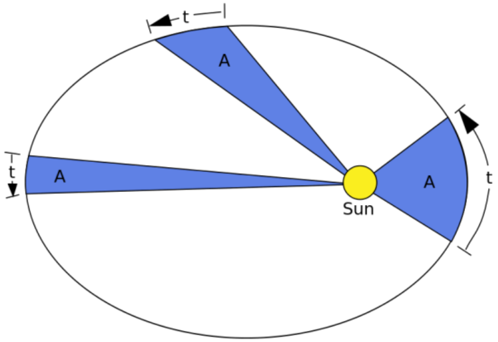
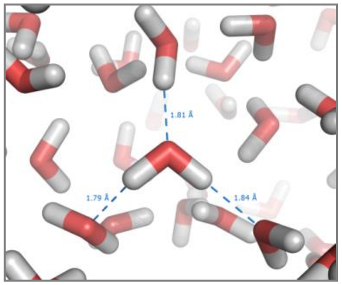
A disconnect between microscopic and macroscopic descriptions?





Mechanical / microscopic description based on atomic / molecular motions

- Molecules obey the laws of mechanics (classical or quantum);
- Based on evidence of molecular sizes, many variables O(10^{23}) are needed to characterize the system: $\mathbf{r}_i$, $\mathbf{v}_i = d\mathbf{r}/dt$;
- Motions occur on nm length scales and ps time scales;
- Time is a critical variable in the analysis

Thermodynamic / macroscopic or 'bulk' description

- Macroscopic systems obey the laws of thermodynamics, temperature?, entropy?
- The system is characterized by a few variables: P, T, V
- Processes occur on large length scales
- No reference is made to time and atomic structure
- Cannot determine quantities like equilibrium constants

Statistical mechanics starts with the microscopic picture and provides a framework for determining macroscopic properties.

Why do we need statistical mechanics?

Statistical mechanics was developed in the mid 19th century as an effort to link the two major, seemingly disparate, branches of physics, i.e., classical mechanics and thermodynamics.

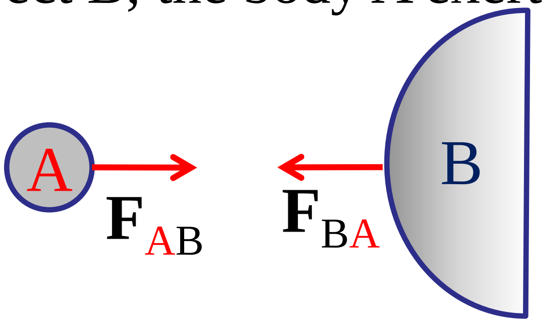
Atomic theory was not universally accepted at that time (by physicists) and the kinetic theory of gases and statistical mechanics were attempts to use mechanics of atomic and molecular motions to explain macroscopic properties of bulk materials and thermodynamic laws.

- Statistical mechanics provides systematic methods for determining the probability distribution based on the microscopic properties of system and provides a route to determine macroscopic behavior.

Classical Mechanics: Newton's laws of motion

The empirical knowledge was given a mathematical foundation by Newton, summarized in the three laws:

1. Particles move in linear motion with fixed speed (constant velocity) unless acted on by a force
2. The acceleration (change in velocity with time) of the particle is proportional to the force: $\mathbf{F} = m\mathbf{a} = d^2\mathbf{x}/dt^2$
   - Forces are determined by the nature of the interactions (gravitational, electrostatic, magnetic, "van der Waals", …)
3. For each force on an object A by an object B, the body A exerts an equal and opposing force on body B



The theory was very successful in predicting:

- All macroscopic mechanical motions up to the nineteenth century
- Extended into molecular scale using the kinetic theory of gases

The Laws of Thermodynamics

By the mid 1800's and early 1900's empirical knowledge of macroscopic systems was formulated into the laws of thermodynamics:

1. First Law: Heat and work are equivalent forms of energy and their total amount is conserved in any process in an isolated system: $dU = q + w$

2. Second Law: Entropy increases in spontaneous processes;
   $dA = -SdT - PdV$
   $dG = -SdT + VdP$
   (which lead to equilibrium constants and chemical thermodynamics)

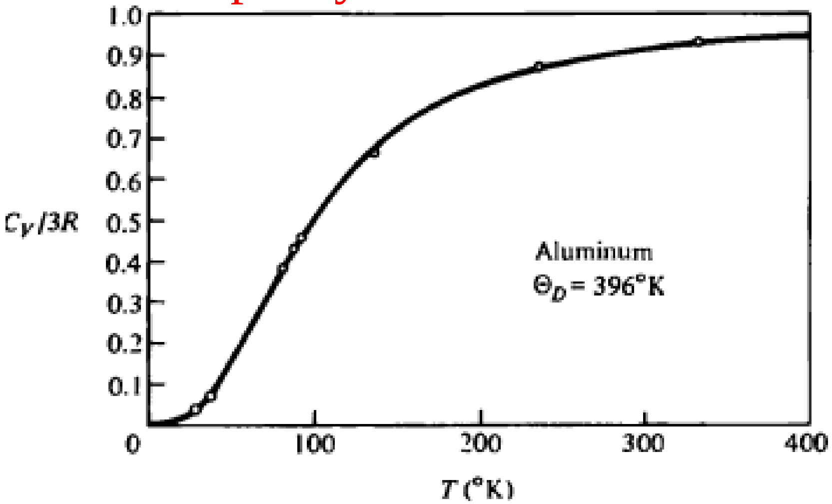
3. Third Law: The entropy change of a reversible isothermal process approaches zero as the temperature approaches 0 K.

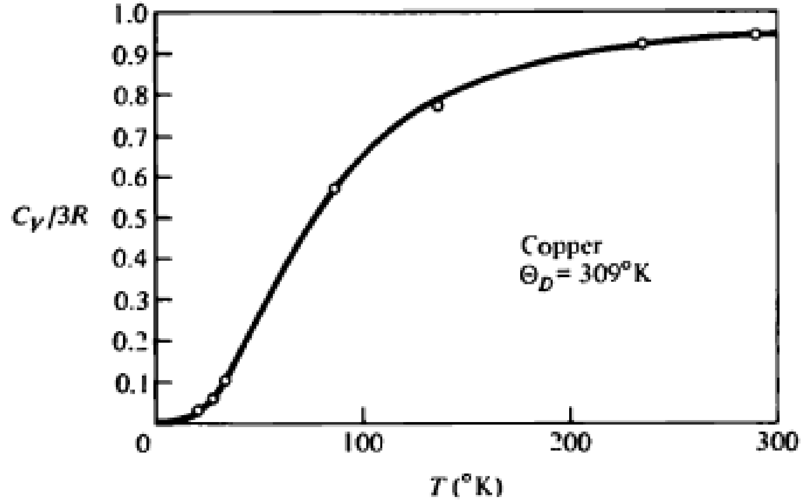
The laws of equilibrium thermodynamics do not explicitly include time!
They also include non-mechanical quantities of T, S, μ, A, and G.

Applications of statistical mechanics

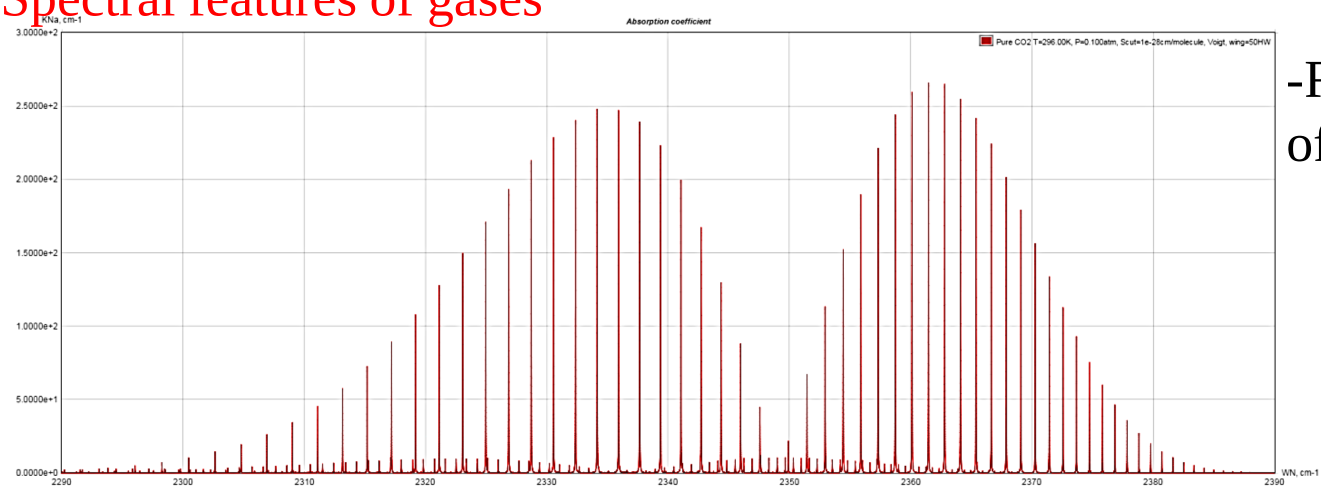
Statistical mechanics relates macroscopic thermodynamic behaviour and parameters of materials and their underlying molecular structure.

Heat capacity of metals





Spectral features of gases



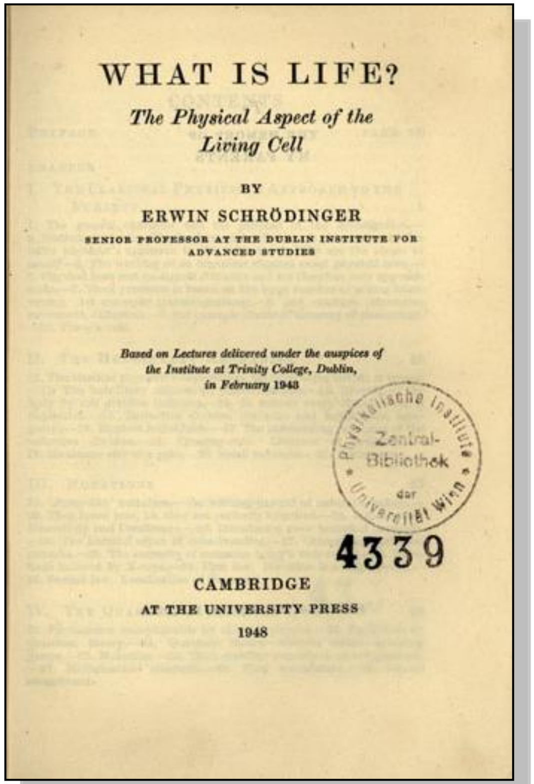
-Ro-vibrational spectrum of CO_2 gas

Thermodynamics relations are the consequences of probability!

A hint towards this direction is given by a question relating fundamental properties of life itself.

E. Schrödinger poses the question:

Why are atoms so small?



WHAT IS LIFE?

The Physical Aspect of the Living Cell

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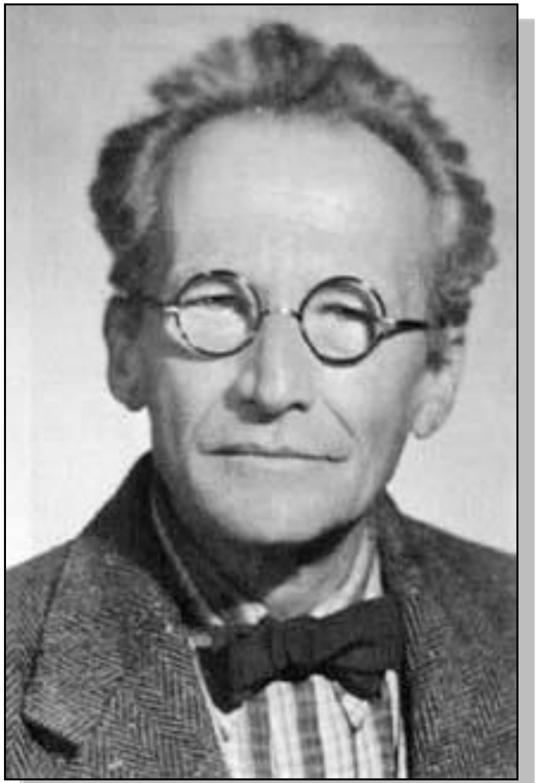

- Size of atoms and molecules: 0.1 to 1 nm
- Typical samples of matter contain in the order of 10^{23} atoms / molecules
- Time scales of molecular level events take place on 10^{-12} s

Why are atoms so fast?

Large numbers of molecules are needed to form stable environments

- Before complexity can even develop, macroscopic numbers of atoms and molecules are needed to lead to the emergence of stable and predictable environments suitable for the development of complex structures and processes.
- For large collections of molecules, the random, fluctuating behavior of individual atoms and molecules are averaged out.
- This is where the arguments of statistical mechanics come into play!

- For the complexity of life to develop, even for simple unicellular organisms, large collections of atoms are required (10^{23})