Review on Complex Atoms

Physics 390 Fall 2004

Wolfgang Lorenzon

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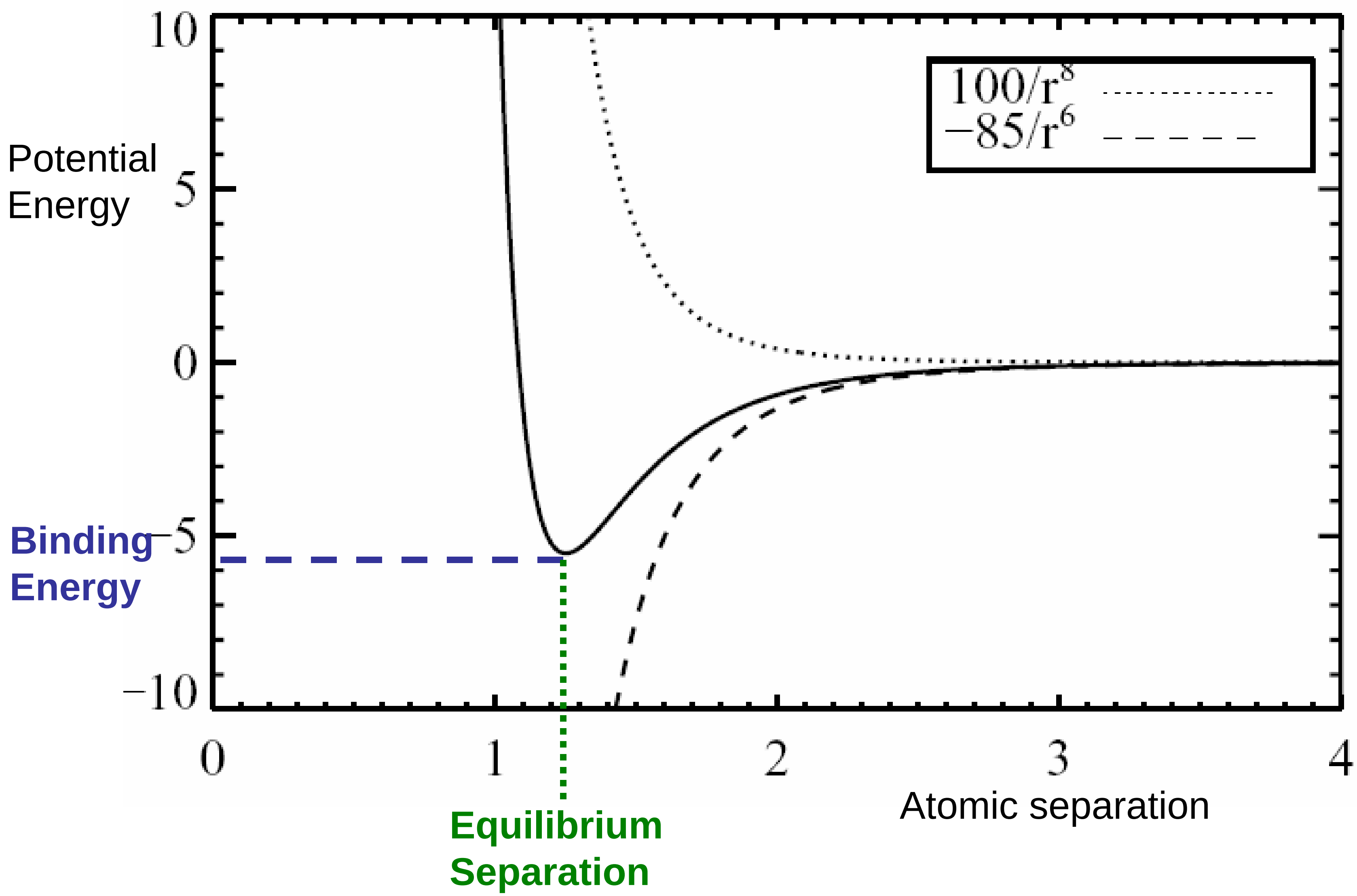
Molecules

- Atoms bind together when the combination has a lower total energy (is more tightly bound
- Binding is mostly born of asymmetry in electron orbitals
- Ultimately all electromagnetic effects

- Types of bonds:

1. Ionic: Coulomb attraction between charged atoms (one atom ‘wants’ an electron the other is willing to surrender: NaCl)
2. Covalent: Bonding by electron sharing (both atoms really want an electron: H_2, F_2, CO, etc.)

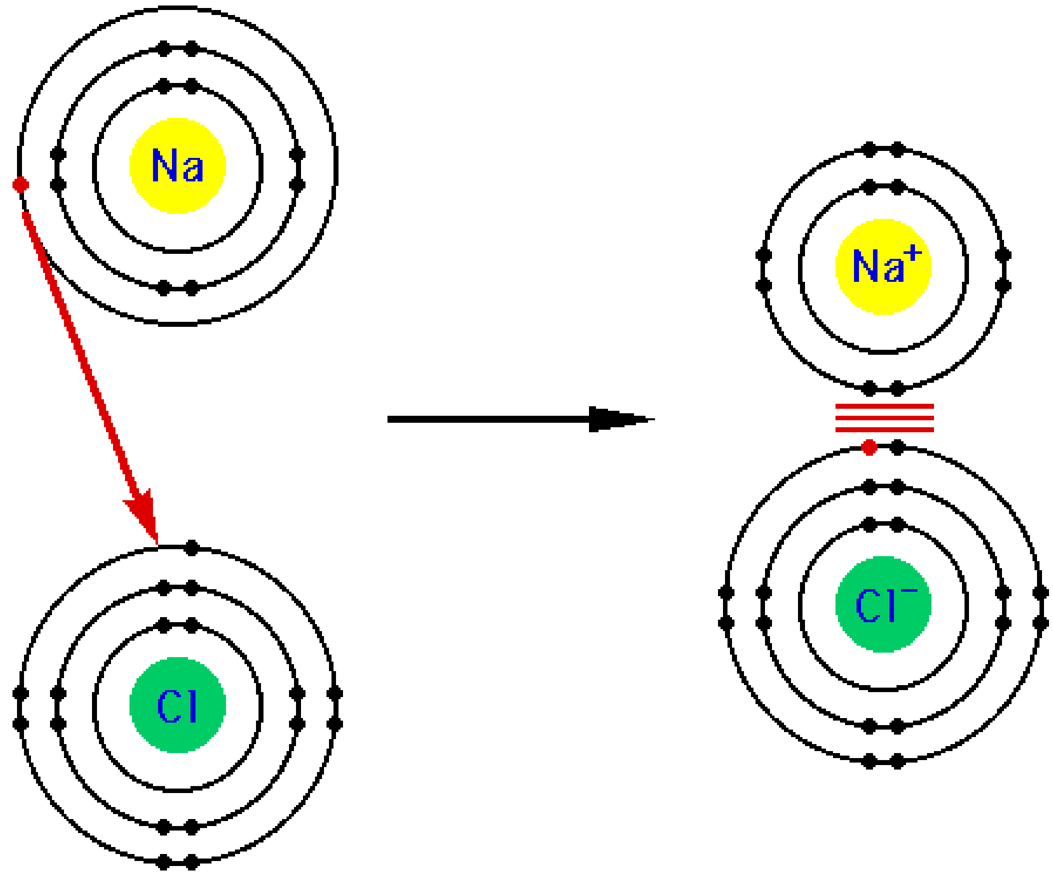
Typical interatomic potential



Ionic Bond: Electron is transferred, then charged atoms attract one another….

“Extra” electron
=> low ionization
energy

Short one electron
=> high electron
affinity

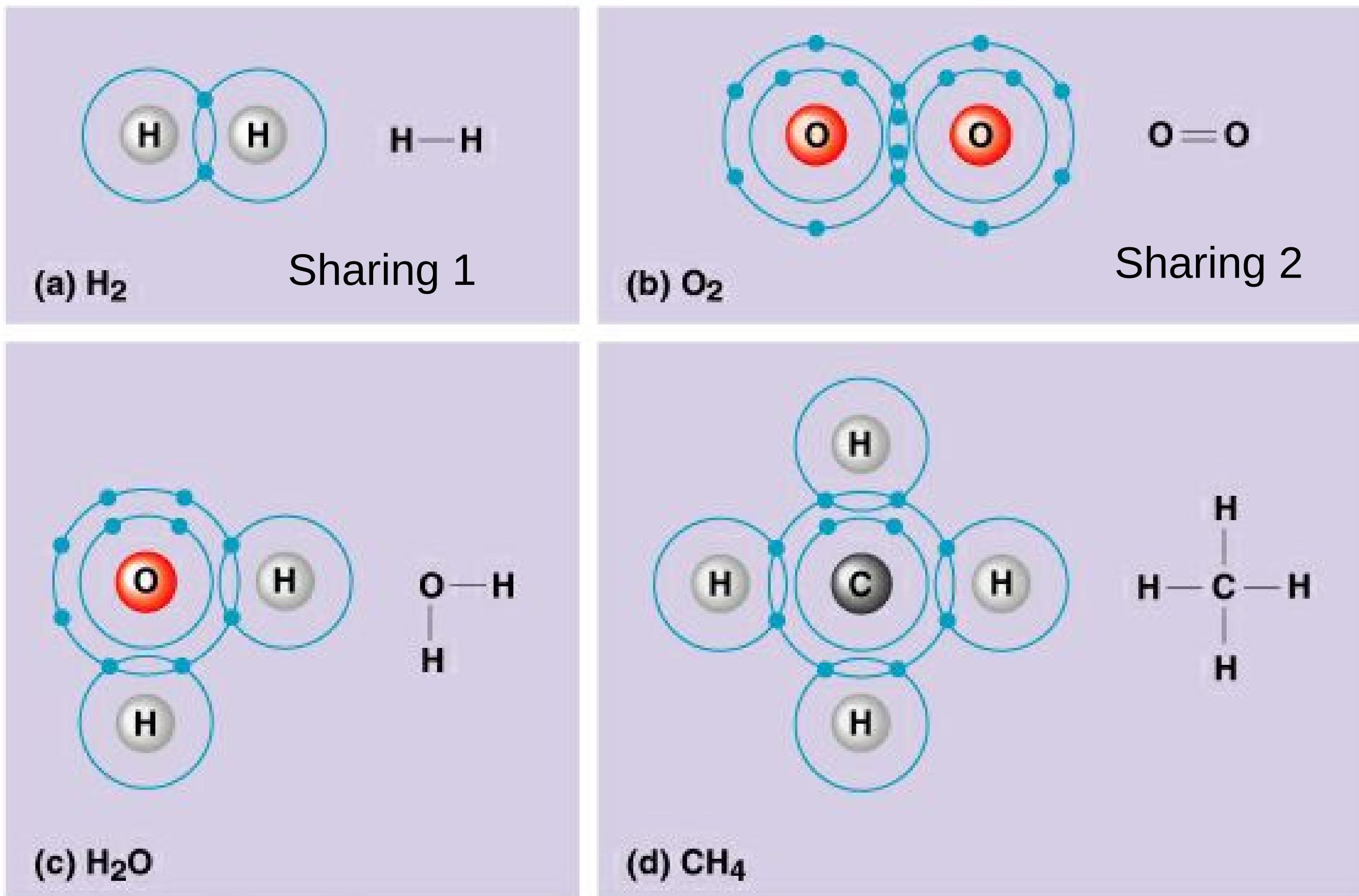


Binding energy from (electron affinity – ionization energy + Coulomb attraction)

Covalent bond: sharing of a valence electron. This happens when both atoms 'want' an electron about equally badly.

Identical atoms

Covalent bonds are dominant in organic chemistry



Which bond will occur?

- Whichever one lowers the energy the most!
- Ionic vs. Covalent can be determined by “electronegativity” calculated for *each atom*

  Electronegativity = Ionization energy + electron affinity

- If atoms have *different* electronegativities an ionic bond will form
- If atoms have similar electronegativities, a covalent bond will form
- **In reality all bonds are partly both!**

Intermolecular bonds

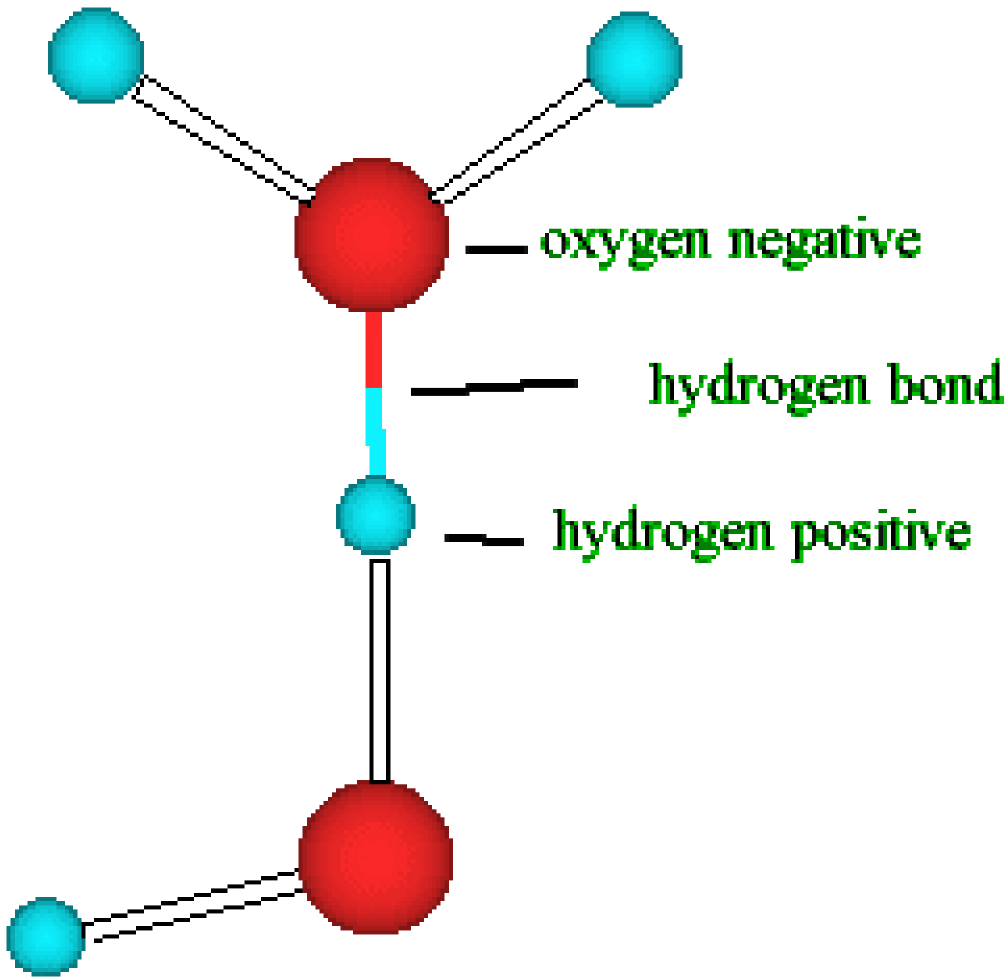
- Once an atom has joined a molecule and satisfied its chemical desires, why bond further?
- Why are there solids and liquids?
- What remains to bond them together?

- Weak attractions collectively called “van der Waal’s forces”
- + and – charge in molecules is not uniformly distributed

One more type: Hydrogen bonds

- Bonds only atoms which include N, O, or F
- Connects the above through a hydrogen as in A – H – B in a straight line
- 10 times as strong as van der Waals when it can occur
- Responsible for many organic compounds
- Also affects solvent capability of water
- H-bonds are key to protein structure: basic to the functioning of life
- Others (Li bonds for example) don't happen. H is very small

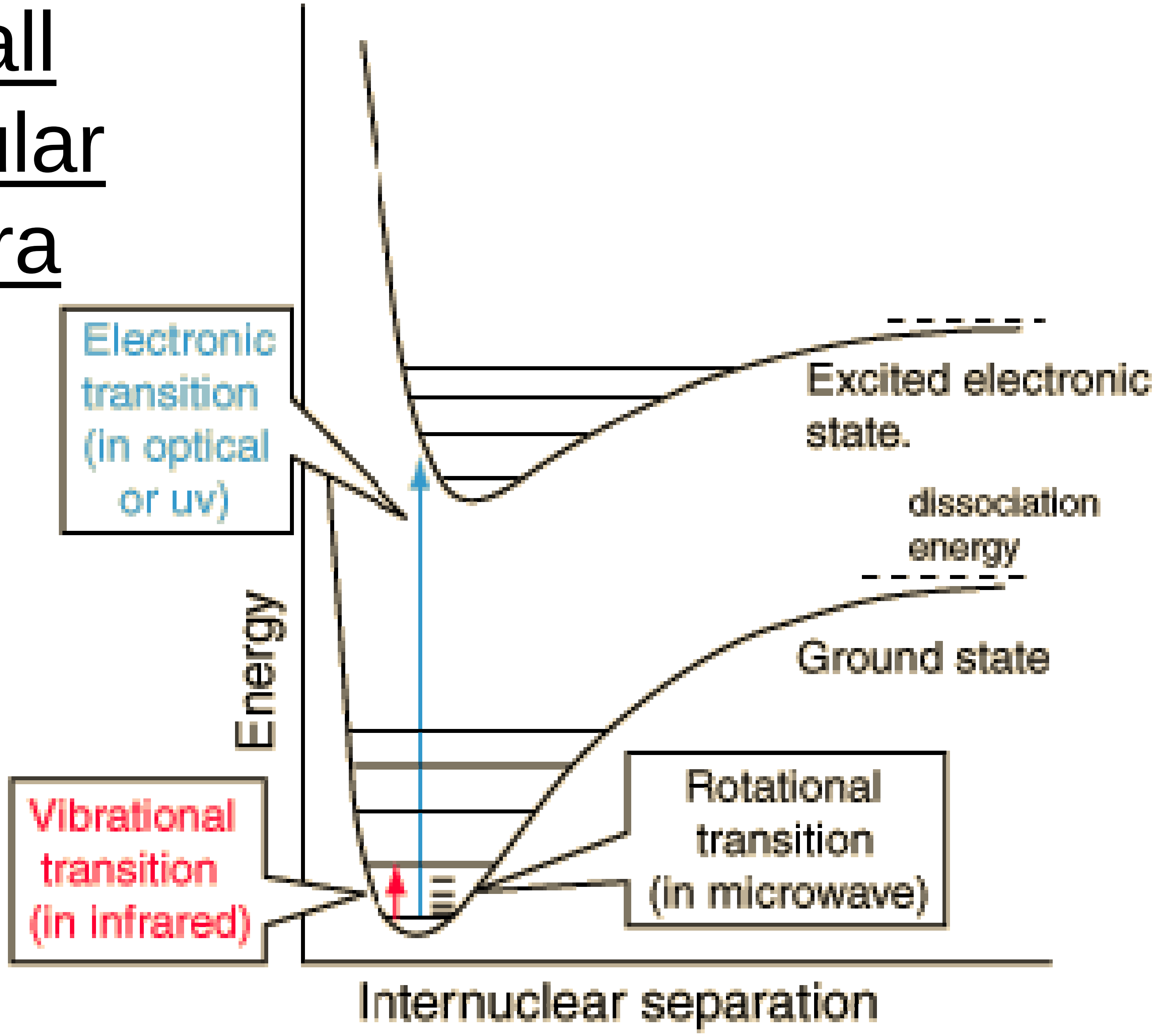
This ‘stickiness’ of water keeps it liquid at quite high temperature, much higher than N_2 for example….



Energy stored in molecules

- Energy can be stored in molecules in many ways
  - Energy of translation
  - Energy of electron states
  - Energy of vibration
  - Energy of rotation
- We discussed rotation and vibration, the energies associated with locations of the atoms in the molecule…

Overall molecular spectra



Molecular spectroscopy

- Most transitions are in the infrared (longer wavelength than optical)
- Infrared spectroscopy pioneered by David Dennison here at Michigan
- Used to reveal the presence of molecules in the atmosphere (pollutants, ozone…) and in space
- Interstellar clouds contain water, ammonia, etc.

Classical Statistical Mechanics

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Classical Statistical Mechanics

- Turn from the study of individual objects (atoms, molecules) to something more practical: statistical study of really *enormous* groups of objects
- Atoms are tiny. Everything is made of enormous numbers…
- Following the detailed behavior of each is impossible
- Instead we measure 'macroscopic' properties, like temperature and density
- Today we will revisit Classical statistical mechanics and discuss Quantum statistical mechanics.

Physics and change

- Laws of physics: forces and fields
  - Gravity
  - Electromagnetism
  - Strong and Weak nuclear
- All have time symmetry! Basic processes can all be reversed.
- Conservation laws, things which *never* change
  - Energy
  - Momentum
  - Angular momentum
- Change reduced to ***ex***change, flow of permanent quantities

Energy flow

- Energy takes many related forms
  - Kinetic
  - Gravitational
  - Elastic
  - Electric
  - Heat
  - Mass
- Energy is a convertible quantity
- Total energy content is fixed
- Laws tell us what conversions *can* happen, they don't tell us which *will* happen…
- Something more is needed to determine what *will* happen

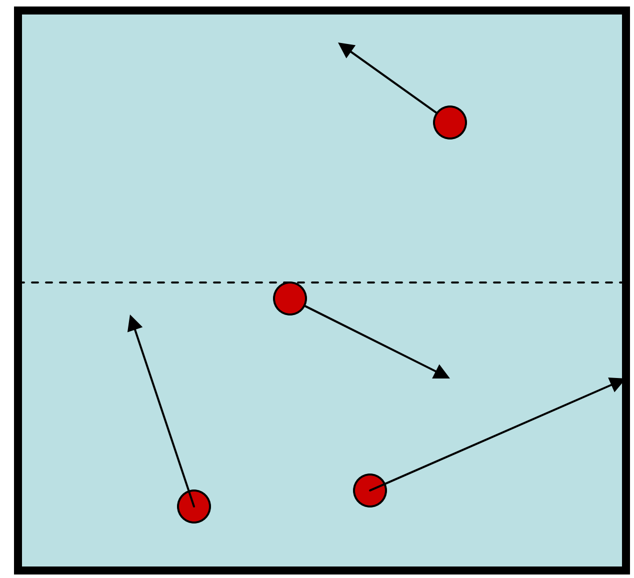
Irreversibility

- In the world, energy flow constraints *allow* some transformations which never occur
- How do we determine which among the possible outcomes will occur?
- Make the simplest assumption:

  $\Rightarrow$ All possible outcomes are equally probable

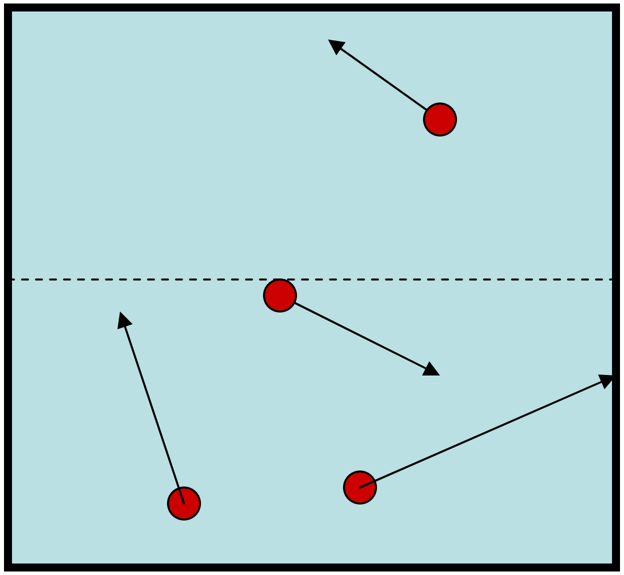
A model system

- Gas atoms in a box
  - Initial positions and velocities
  - Every collision conserves energy and momentum
  - Use laws to predict motion
- Computers can do a 'Monte Carlo simulation' of this
- Prediction here is simple and secure



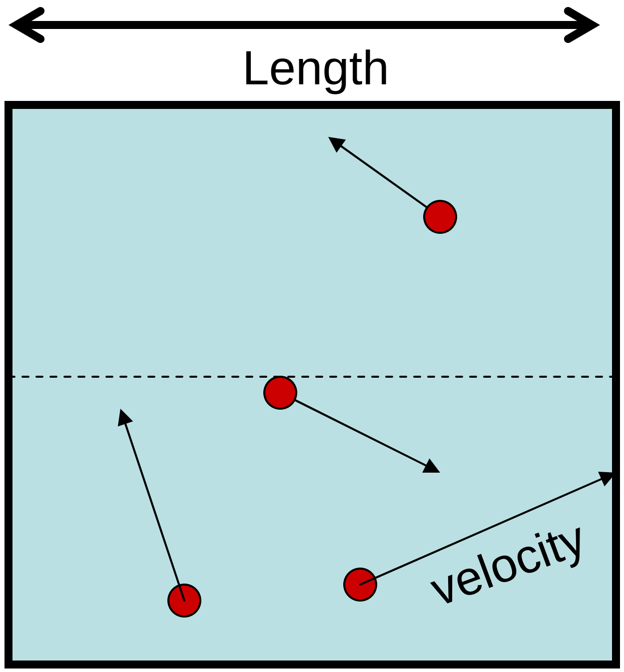
Micro & macrostates

- Microstate: details for each atom
  - Position and velocity
- Macrostate: some feature of positions and velocities of all atoms
  - Average position?
  - Average velocity?
  - Are they all on top?



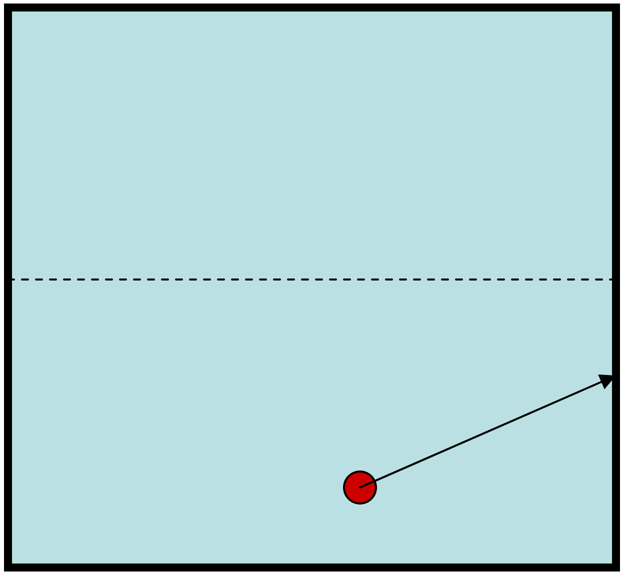
Timescales

- This system rearranges itself on some timescale
  - ~ length / velocity
- Ask too soon, microstate cannot change
- Wait a few characteristic times before asking, the microstate will be rearranged
- All allowed arrangements *will* occur.



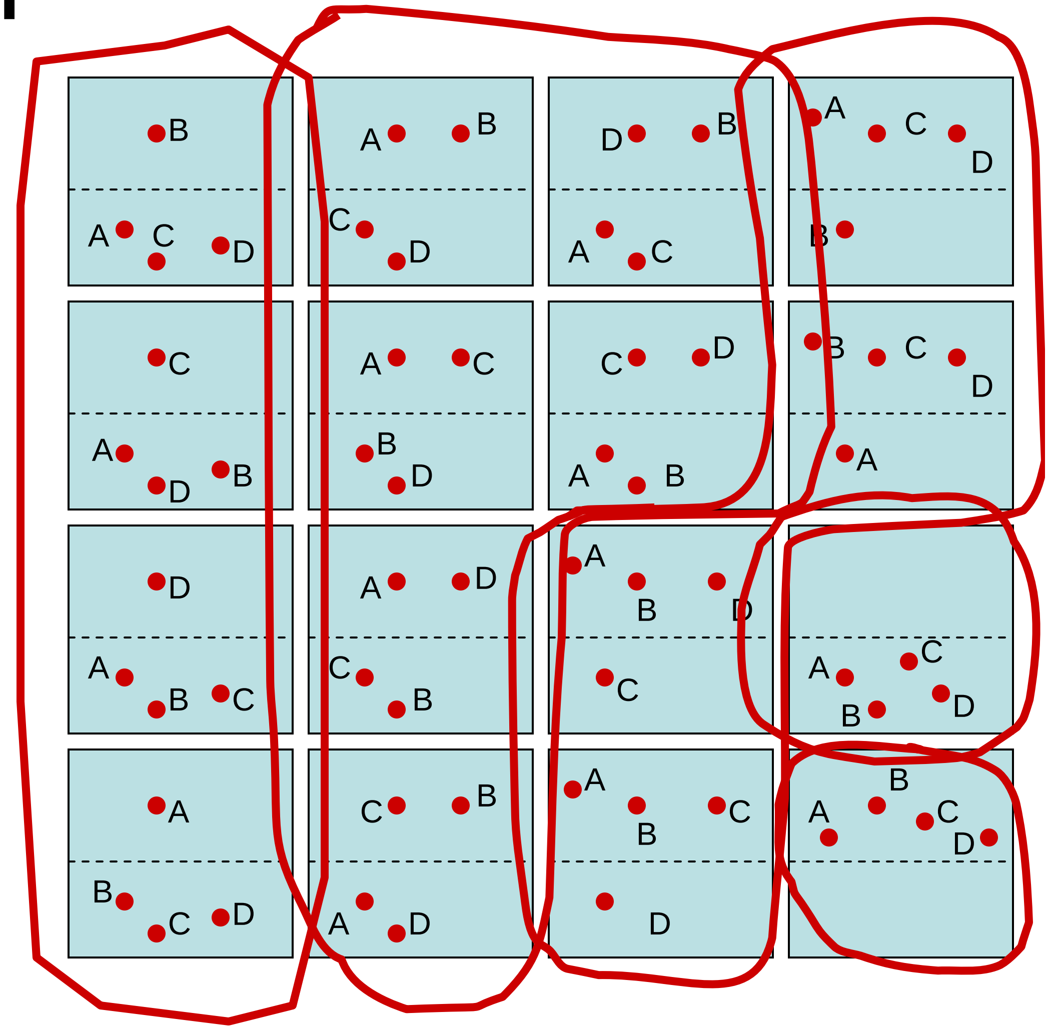
An example: 1 atom

- How often are all the particles on top?
- One atom: can be on top or bottom
  - (# top arrangements / total # arrangements)
  - 50%



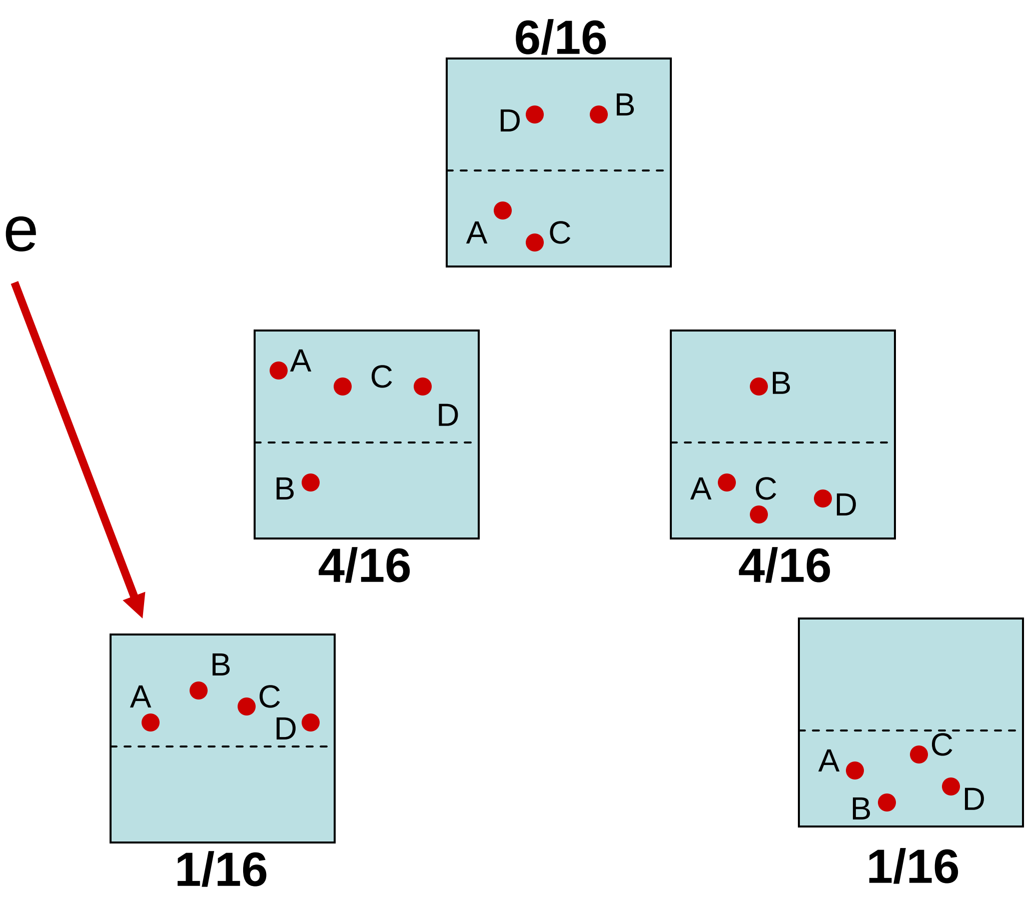
An example: 4 atoms

- How often are all the particles on top?
- Four particles, each on top or bottom
- 16 microstates here
- Each microstate is equally likely
- 1 microstate has them all on top



Macrostates

- Example macrostate, all the atoms on top
- All are on top 1/16th of the time
- Other probabilities from counting microstates
- This is a question about what happens. All are allowed, which ones actually occur?



The point

- Some macrostates are made by many microstates (1/2 the atoms on each side)
- Some macrostates are made by very few microstates (all on one side)
- If all microstates are all equally probable, some macrostates will happen a *lot* more often.
- All on one side happens $1/2^N$ of the time (N = # of atoms)

Is this irreversibility?

- 1 atom: 1/2
- 4 atoms: 1/16
- 10 atoms: 1/1024
- 20 atoms: 1/10 million
- 40 atoms: 1/trillion
- 80 atoms: 1/1200000000000000000000000000

- Consider an 80 atom system:
  - Assume rearrangement happens a million times a second
  - How long before we see them all on top?
  - 10^{18} seconds
  - 30 billion years……

A realistic example

- 1 cm^3 of air
- ~$2x10^{19}$ atoms
  - Assume rearrangement a million times a second
- All on one side every

$$10^{7.5x10^{18}}$$

seconds

- This is an irreversible process:
  - Start with all on one side
  - Release them
  - They could all come back, but never do…