

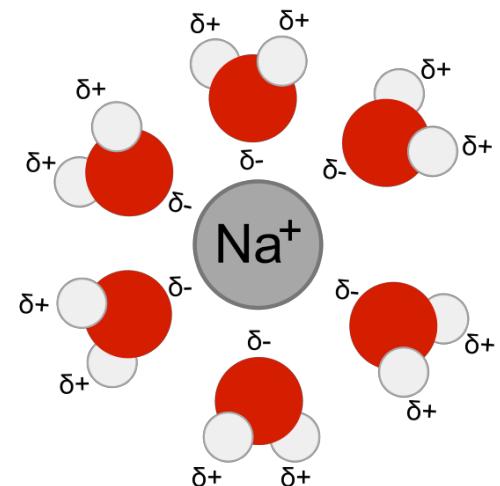
Ch 1b Lecture 11

January 31st, 2013

Next few lectures – Moving toward chemical reactivity, we'll start with the gaseous state.

Today: (Not so) Ideal gases & intermolecular forces.

Reading: OGC Chapter 9, esp. section 9.7;
Chapter 10, esp. sections 10.2, 10.3



Last time, we used Newtonian mechanics and the Maxwell-Boltzmann velocity distribution to derive the

IDEAL GAS LAW: $PV = nRT$

P = Pressure

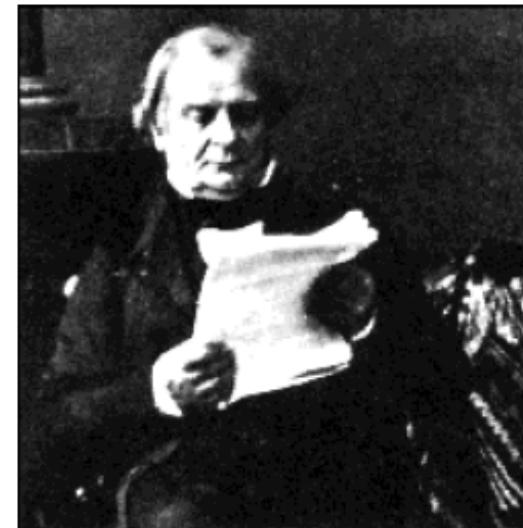
V = Volume

n = # moles

R = ideal gas constant

$= 8.314 \text{ Joules Kelvin}^{-1} \text{ Mol}^{-1}$

T = Temperature



The Ideal Gas Law - first written in 1834 by Emil Clapeyron (shown here relaxing at home)

Today we'll look at how closely actual gases conform to the Ideal Gas Law and the fundamental intermolecular interactions that drive the observed deviations.

Even the Noble Gases are not Perfect!

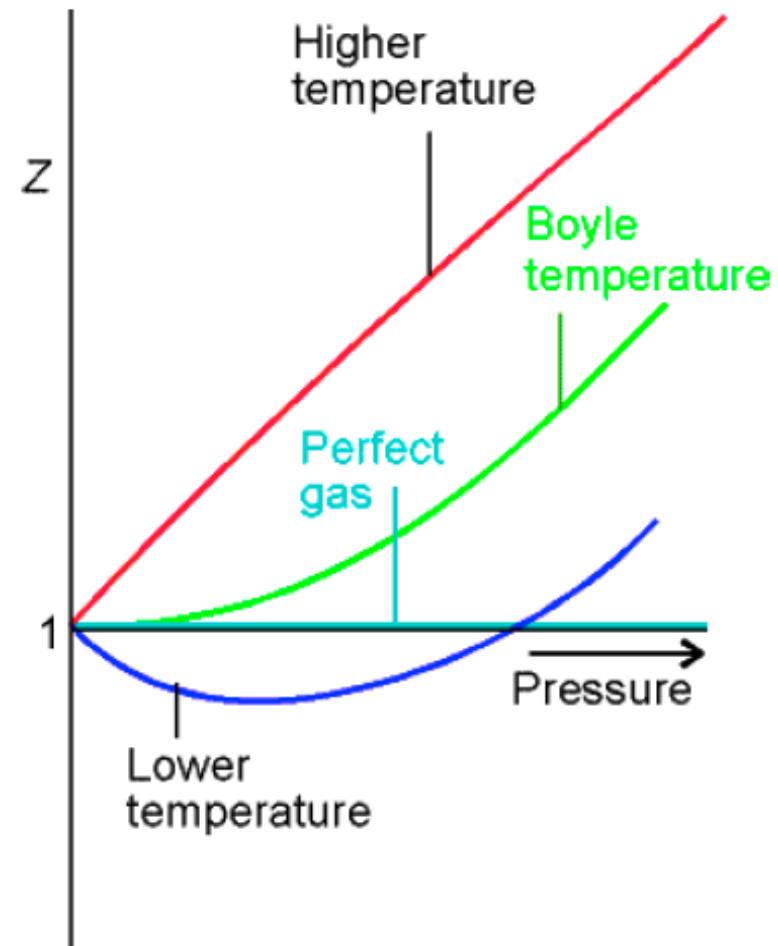
Perfect Gas:

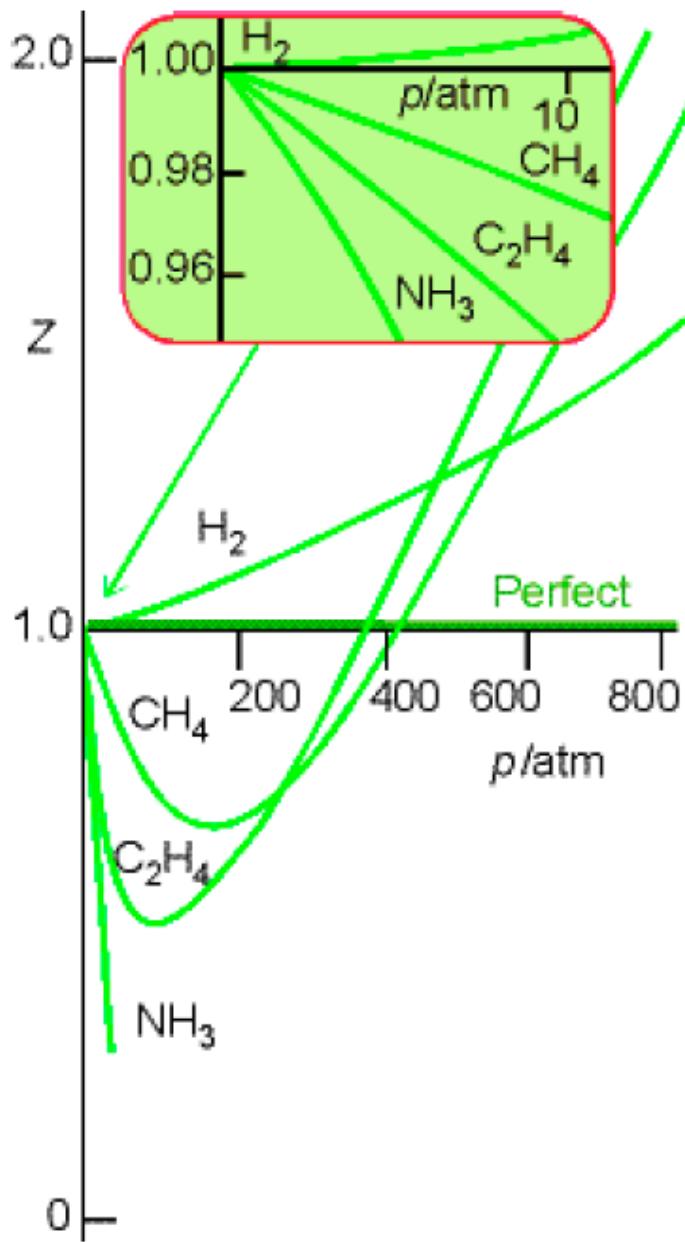
$$PV = nRT$$

Define a compression factor:

$$z = PV/nRT$$

(not to be confused with the isothermal compressibility, κ).





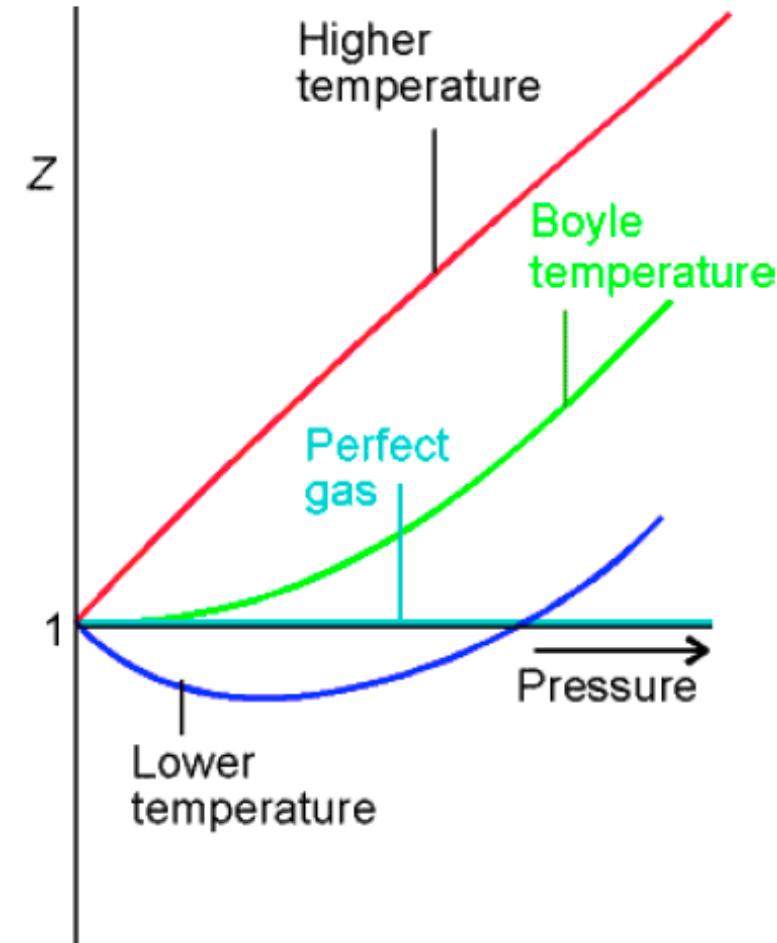
The variation of the compression factor $Z = pV/nRT$ with pressure for several gases at 0°C . A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

Virial Equation of State:

$$pV_m = RT \{1 + B'(T)p + C'(T)p^2 + D'(T)p^3 + \dots\}$$

where V_m is the molar volume, etc. The Boyle temperature is that at which $B'(T)=0$.

Physically, it is the temperature at which the gas conforms to ~Ideal Gas law behavior over the widest range of pressures.



Convenient mathematically, but does not provide much insight.

From Lecture #10:

Which Assumptions are the worst?

Worst assumptions highlighted in red

1. An ideal gas consists of discrete particles (*could be molecules or atoms*).
- 2. The particles are far apart and occupy zero volume**
3. The particles are in constant motion – *Newtonian type physics describes those motions*
- 4. The particles couldn't care less about each other or the container that holds them**
5. The particles do collide with one another and the sides of the container.
6. Energy is conserved. *A particle may gain energy if another loses an equal amount.*

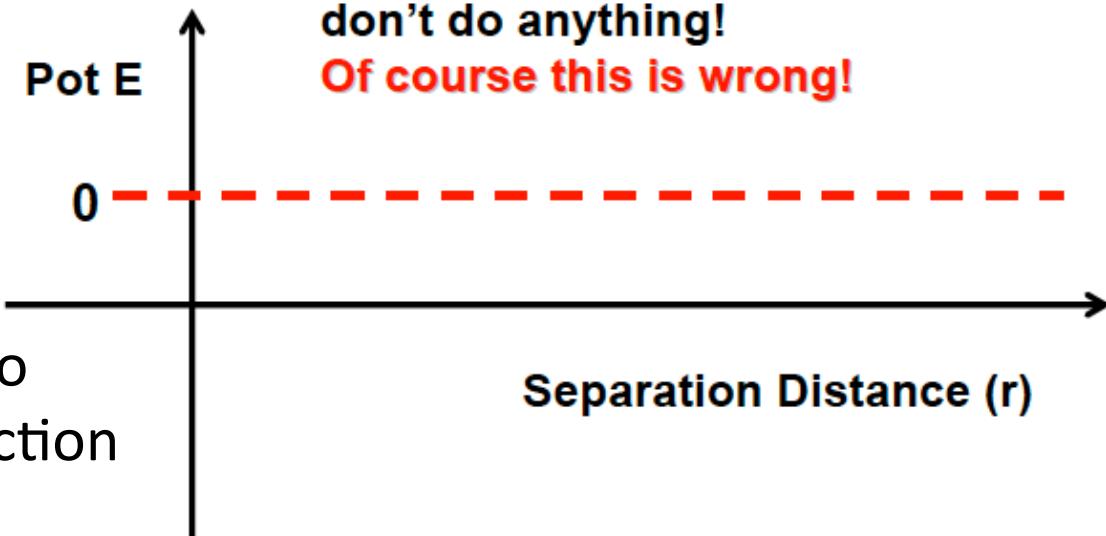
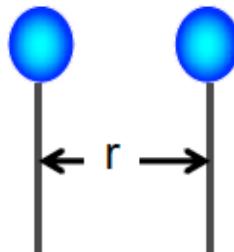
How might we correct for these bad assumptions?

1. The particles are far apart and occupy zero volume
(implies no repulsive interactions)

2. The particles couldn't care less about each other or the container that holds them *(no attractive forces)*.

What does this mean in terms of how 'ideal' gas particles will interact?

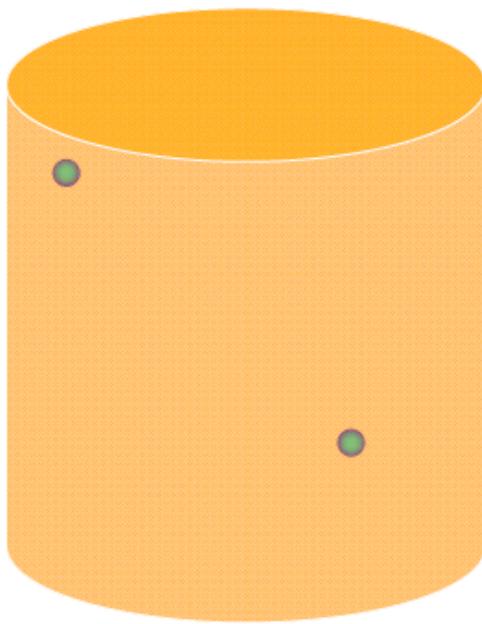
1. The particles are far apart and occupy zero volume (*implies no repulsive interactions*)
2. The particles couldn't care less about each other or the container that holds them (*no attractive forces*).



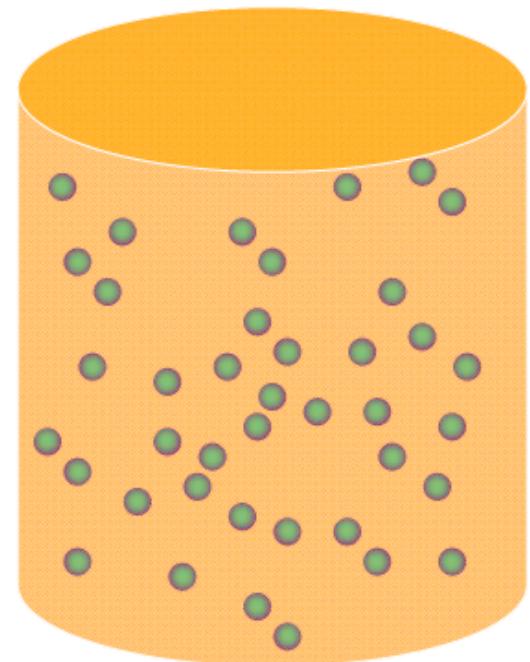
We will come back to what realistic interaction potentials look like.

Bad Assumption #1

1. The particles are far apart and occupy zero volume
(implies no repulsive interactions)



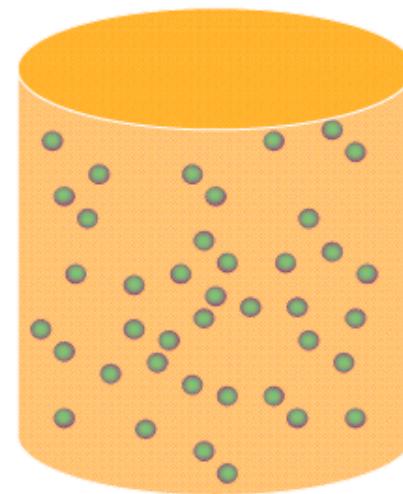
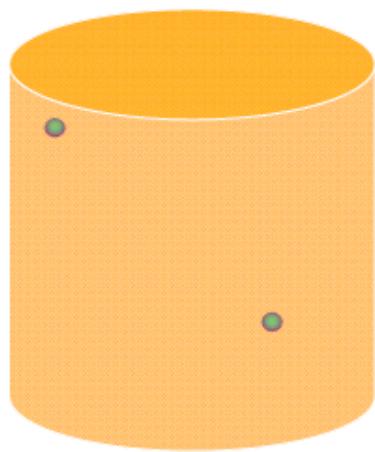
Here the particles are pretty far apart and they occupy very little of the total volume – probably assumption is ok



Here the particles are closer together and occupy a significant fraction of the total volume – they can't occupy same volume because they repel each other like billiard balls – our assumption is likely to be poor

How might we correct for these bad assumptions?

1. The particles are far apart and occupy zero volume
(implies no repulsive interactions)



Prediction: Gases at low Pressure will be more ideal

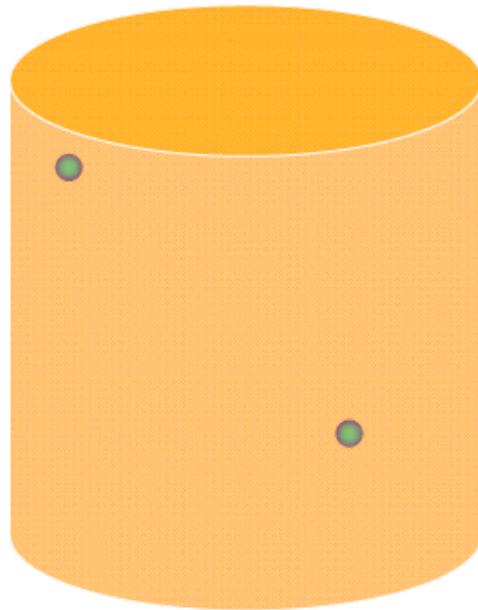
At high P: hypothesize a volume correction to the ideal gas law

$$P(V-x) \approx nRT$$

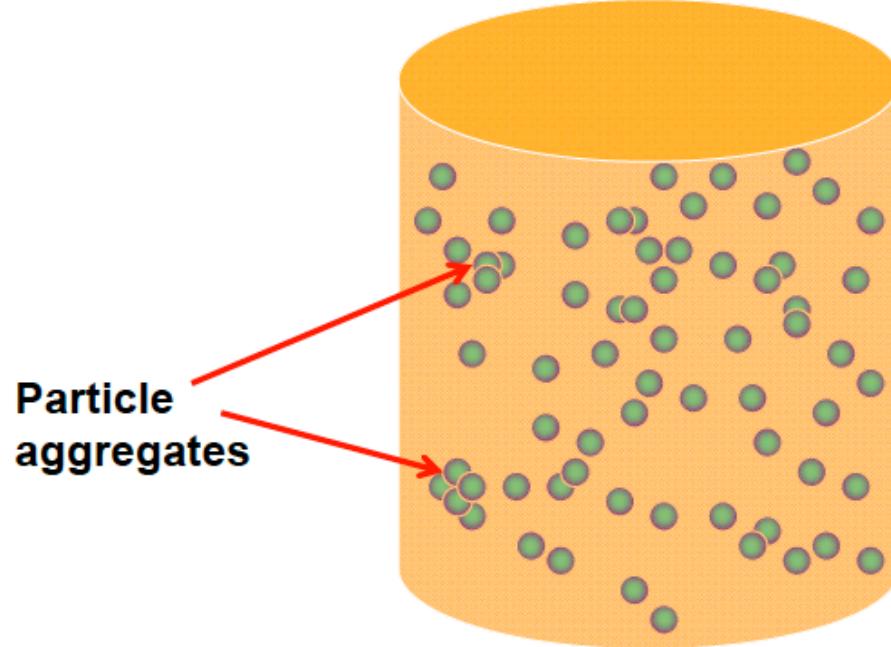
Note: $PV-Px \approx nRT$ (when P is large, correction is large)

Bad assumption #2

2. The particles couldn't care less about each other or the container that holds them (*no attractive forces*).



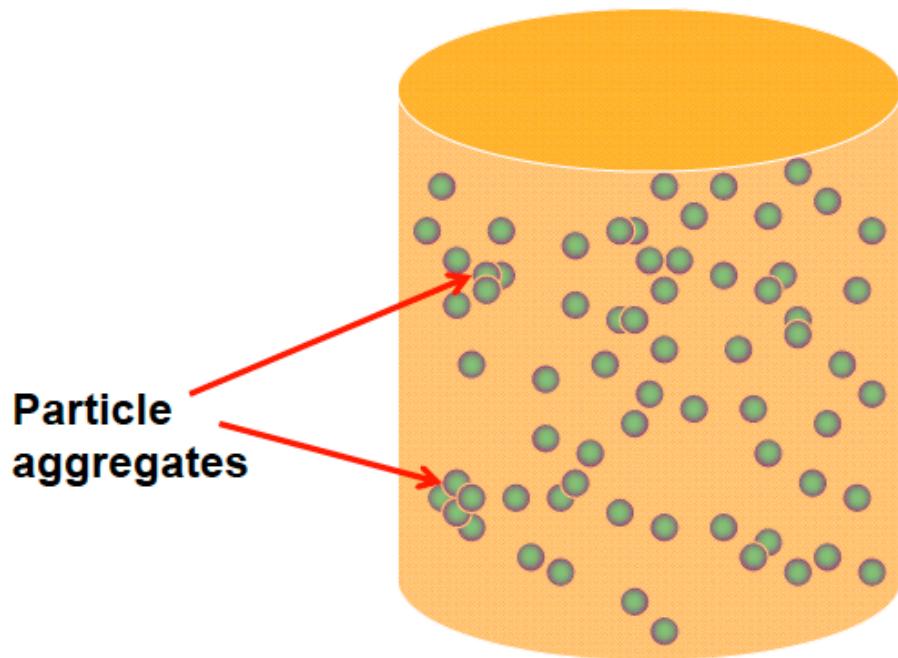
Here the particles are pretty far apart and, if they are atoms, they behave as isolated particles



At sufficiently high pressures (and/or low temperatures) particles will begin to aggregate – i.e. they attract one another (via van-der Waals attractions)
Again, at high P (or low T), assumption 2 is likely to be poor.

Bad assumption #2

2. The particles couldn't care less about each other or the container that holds them (*no attractive forces*).



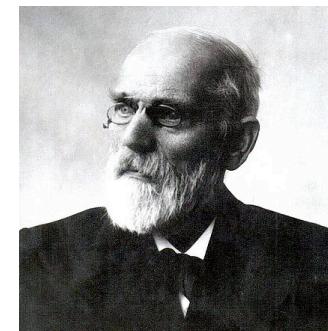
This implies that the gas is more compressible than it otherwise would be – i.e. the real Pressure is really a 'reduced' ideal gas Pressure

Johannes Diderik van der Waals
(1873)

$$(P+y) \cdot (V-x) \approx nRT$$

Correction to account for attractions

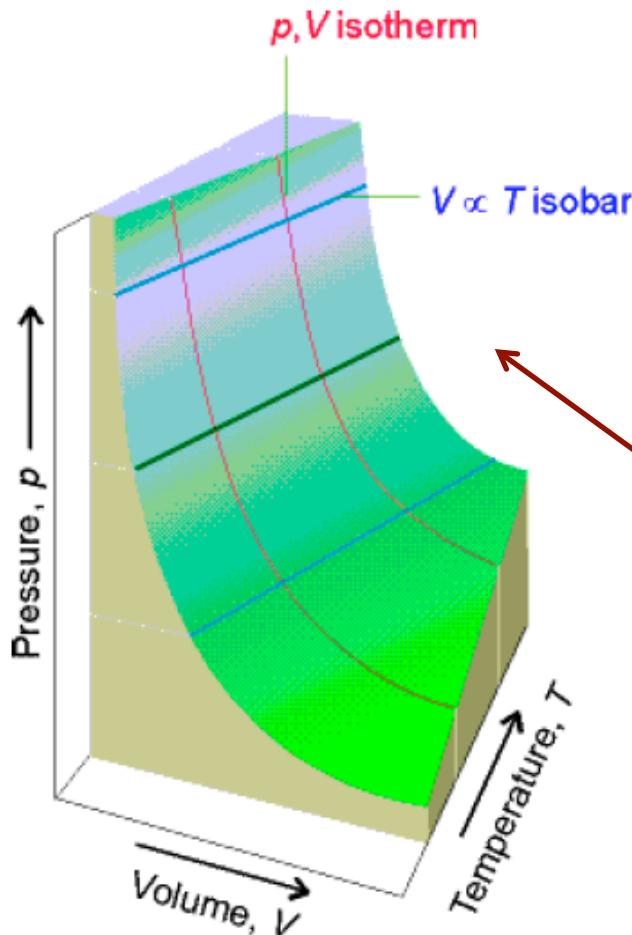
Corrections to account for repulsions



Isotherms & van der Waals Gases:

Our guess

$$(P+y) \cdot (V-x) \approx nRT$$

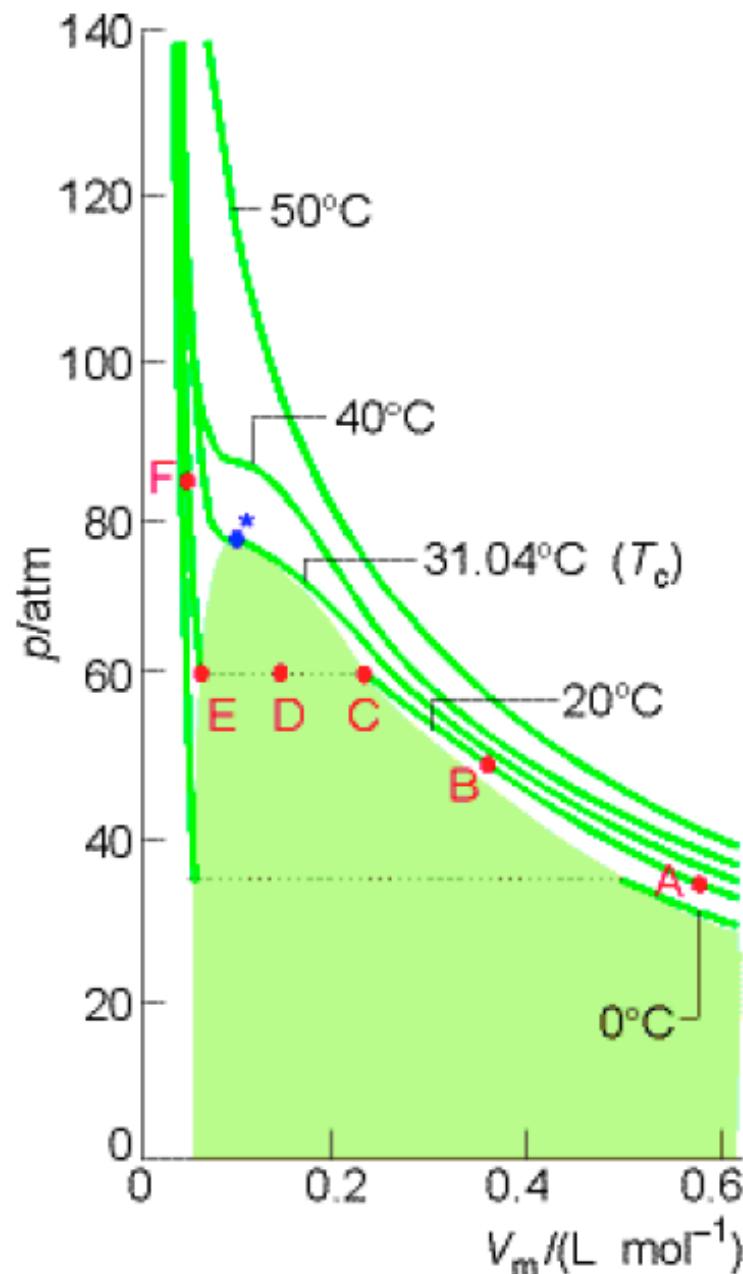


Before the advent of quantum mechanics, scientists sought to estimate corrections to the ideal gas law by fitting the deviations between Pressure/Volume/Temperature plots of real gases and those predicted by $PV=nRT$.

Called an isotherm because it represents a measurement of how Volume varies with Pressure at constant Temperature.

Isotherms of CO₂

Experimental isotherms of carbon dioxide at several temperatures. These are very different from those predicted by a perfect gas.



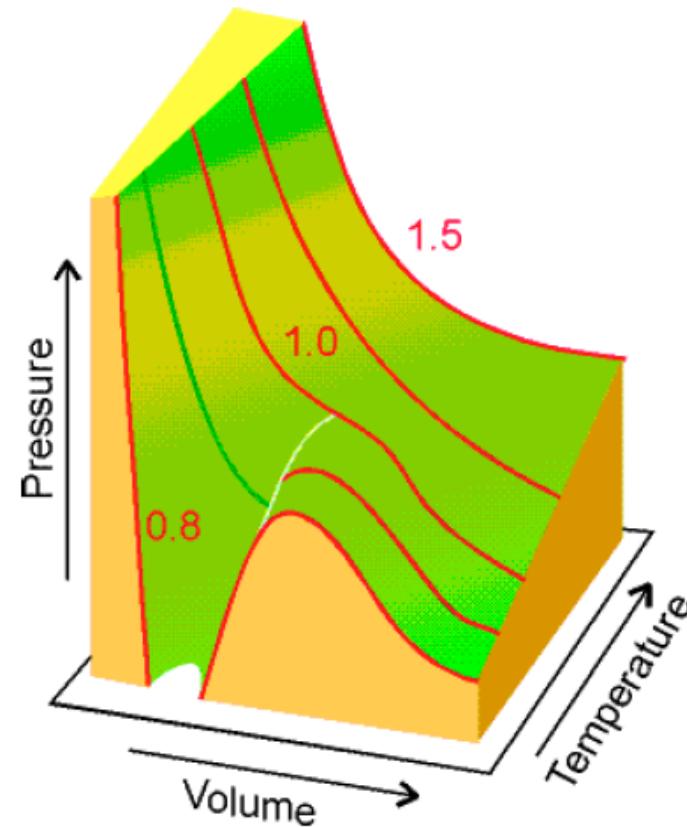
Van der Waals Equation of State

(a , b constants)

$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

Accounts for reduced pressure due to attraction of molecules (clustering)

Accounts for excluded volume due to finite size of molecules



The surface of possible states allowed by the van der Waals equation.

Fairly good match to experiment, at least under compressible (i.e. gas phase) conditions.

Van der Waals Constants

$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

Table KT.1. Van der Waals Constants

Name	Formula	a (atm L ² mol ⁻²)	b (L mol ⁻¹)
Ammonia	NH ₃	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO ₂	3.592	0.04267
Hydrogen	H ₂	0.2444	0.02661
Hydrogen chloride	HCl	3.667	0.04081
Methane	CH ₄	2.253	0.04278
Nitrogen	N ₂	1.390	0.03913
Nitrogen dioxide	NO ₂	5.284	0.04424
Oxygen	O ₂	1.360	0.03183
Sulfur dioxide	SO ₂	6.714	0.05636
Water	H ₂ O	5.464	0.03049

How do we make sense of this?

Intermolecular Potentials

At long range, molecules exert an attractive force on each other. Repulsive forces become dominant as the molecules approach and their electron clouds begin to overlap.

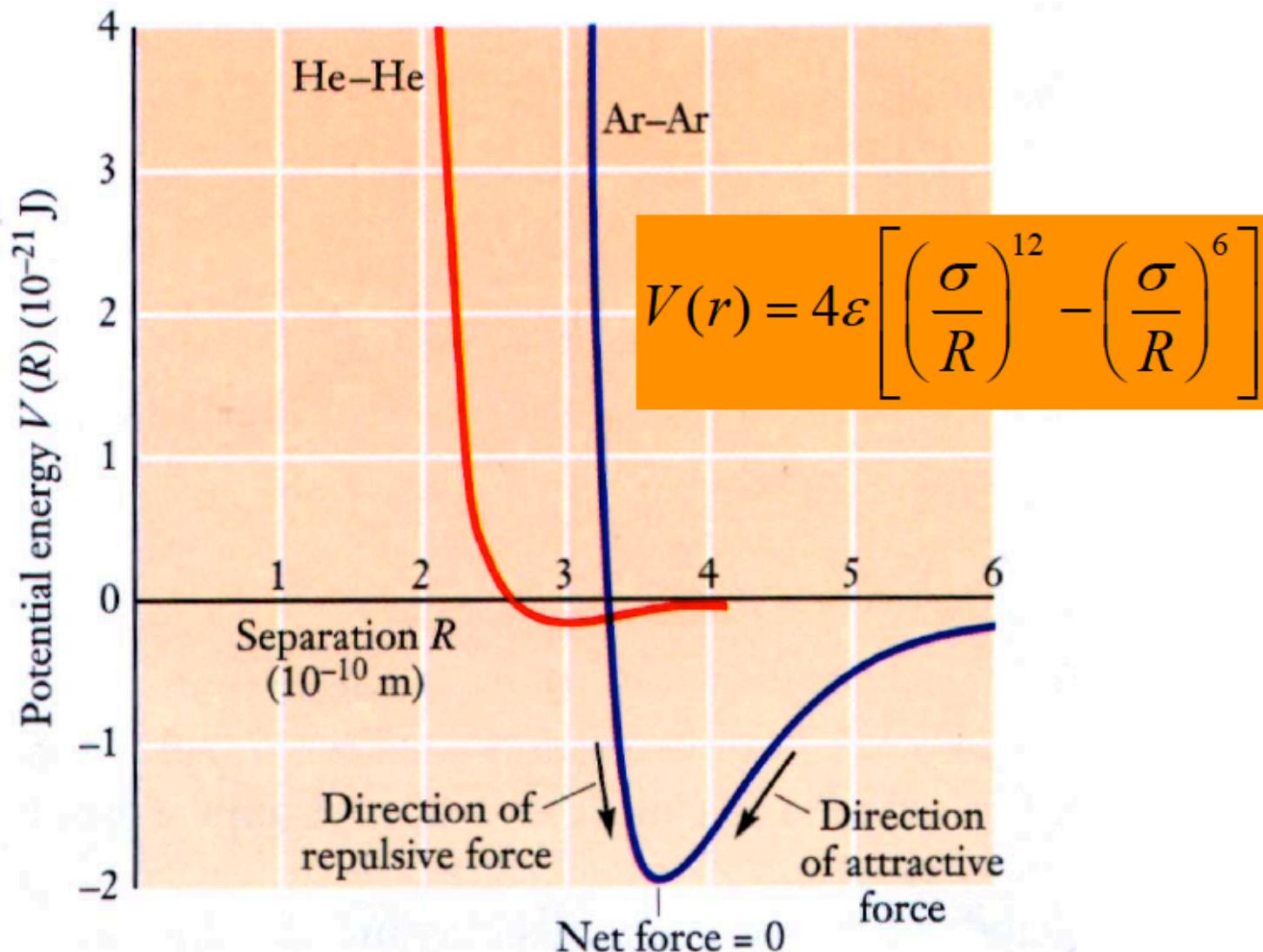
The most commonly used model is the **Lennard-Jones Potential** which has the form:

$$V(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

ϵ = well depth

σ = R at which $V(R) = 0$

Lennard Jones Potential



Atomic/Molecular Lennard-Jones Potential Parameters

Substance	$\sigma(m)$	$\epsilon(J)$
He	2.56×10^{-10}	1.41×10^{-22}
Ne	2.75×10^{-10}	4.92×10^{-22}
Ar	3.40×10^{-10}	1.654×10^{-21}
Kr	3.60×10^{-10}	2.36×10^{-21}
Xe	4.10×10^{-10}	3.06×10^{-21}
H ₂	2.93×10^{-10}	5.11×10^{-22}
O ₂	3.58×10^{-10}	1.622×10^{-21}
CO	3.76×10^{-10}	1.383×10^{-21}
N ₂	3.70×10^{-10}	1.312×10^{-21}
CH ₄	3.82×10^{-10}	2.045×10^{-21}

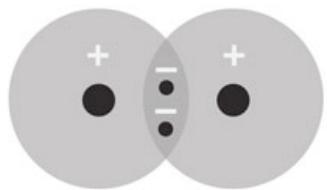
*Repulsions
(all sort of
similar)*

attractions

Nicely correlated with vdW E.o.S. parameters.

Where does the large variation in attractive forces come from?

Attractive Atomic/Molecular Forces:



Hydrogen Molecule (H_2)

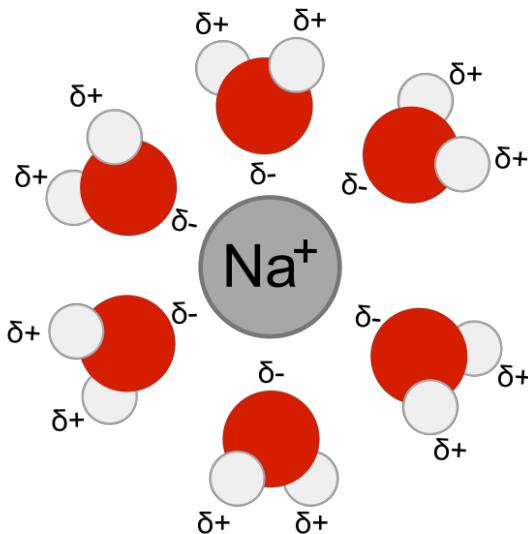


For open shell atoms, you've already learned about the *short range* forces in chemical bonds. Strength of order $\sim 200 \text{ kJ/mole}$.

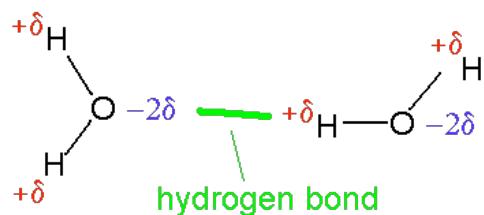


Closed shell? Strongest and longest range would be the Coulomb force between two charged ions. $V(R)$ goes like R^{-1} .

Attractive Atomic/Molecular Forces:

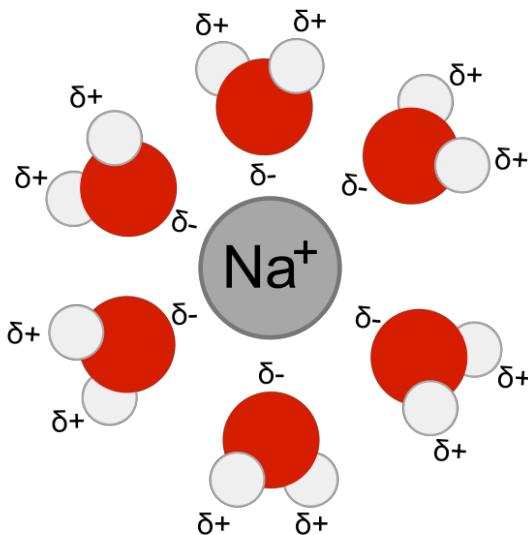


Closed shell? Next comes charge-dipole interactions. Here $V(R)$ goes like R^{-2} (but also depends on the dipole orientation).



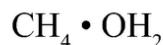
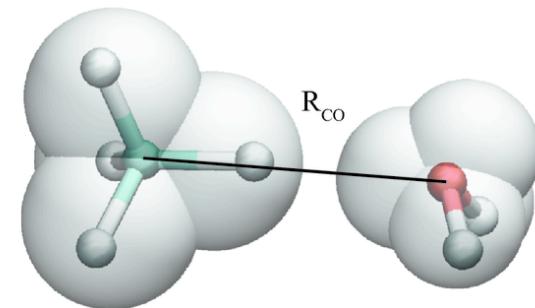
Closed shell? There are also dipole-dipole interactions (similar to where NMR spin-spin splittings come from, mathematically). Here $V(R)$ goes like R^{-3} (but also depends on the dipole orientation).

Attractive Atomic/Molecular Forces:

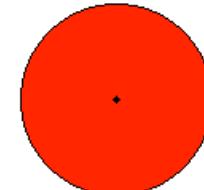


Polarizability

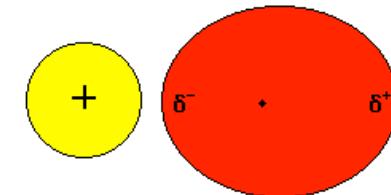
$$\mu_{\text{ind}} = \alpha \cdot E (\text{V/cm})$$



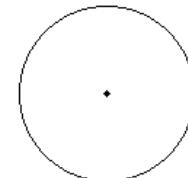
$$\begin{aligned} E &= -3.9 \text{ (-0.9 kcal/mol)} \\ R_{\text{oc}} &= 3.18 \text{ (3.51 Å)} \end{aligned}$$



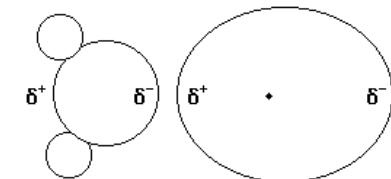
Spherical atom with no dipole. The dot indicates the location of the nucleus.



Upon approach of a charged ion, electrons in the atom respond and the atom develops a dipole.

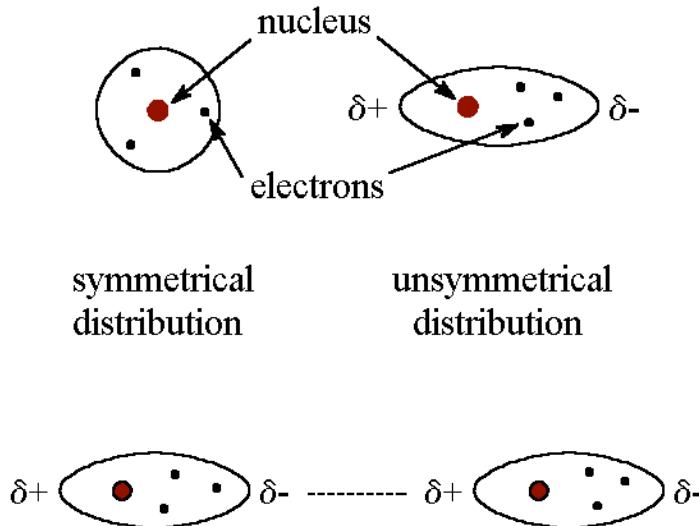


Spherical atom with no dipole. The dot indicates the location of the nucleus.



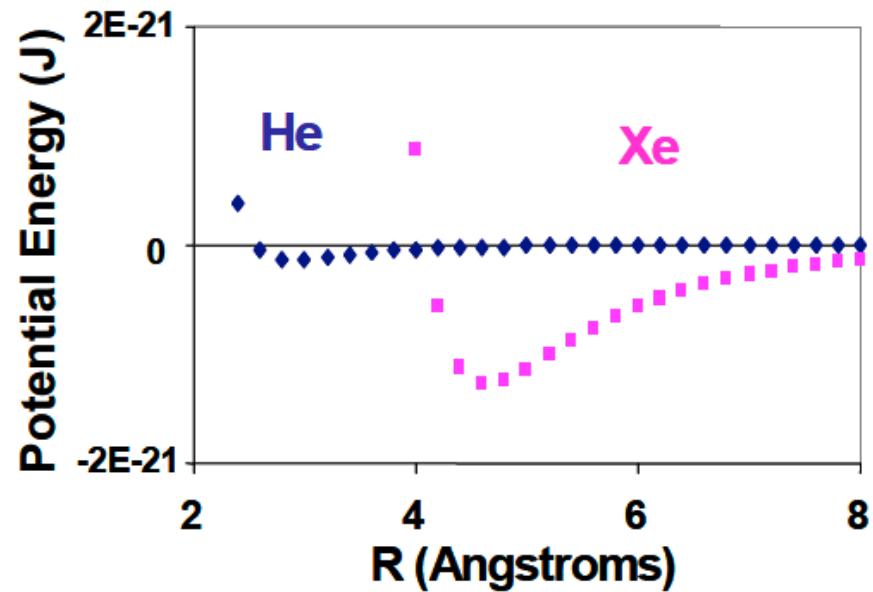
Upon approach of a molecule with a dipole, electrons in the atom respond and the atom develops a dipole.

Attractive Atomic/Molecular Forces:

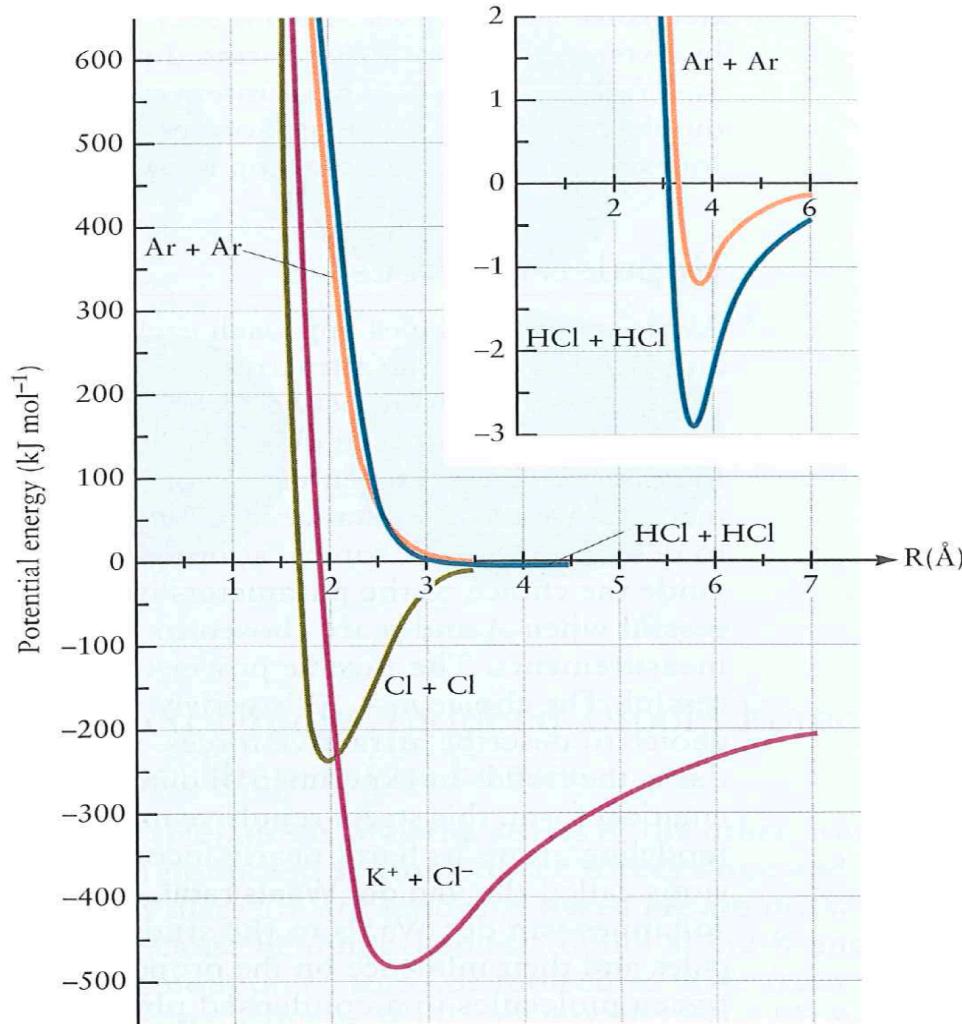


Dispersion forces involve the instantaneous fluctuations of electrons on adjacent atoms or molecules. $V(R)$ goes like R^{-6} .

Highly polarizability dependent, basis of L-J attractive term
fluctuations of electrons on adjacent atoms or molecules.
 $V(R)$ goes like (R^{-6} part, R^{-12} chosen for convenience).

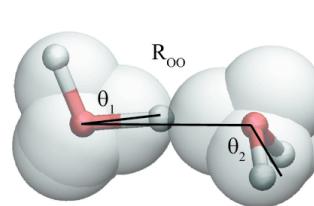


Attractive Atomic/Molecular Forces:

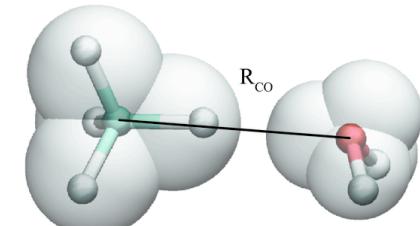


Putting it all together:

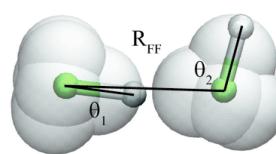
Large variation in attractive forces tied to molecular structure, charge distributions.



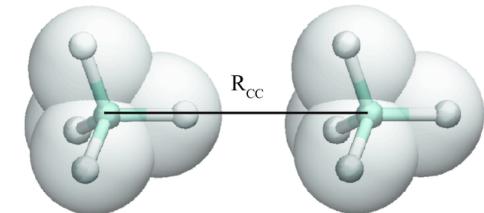
$(\text{H}_2\text{O})_2$ $E = -35.5$ (-5.44 kcal/mol)
 $R_{\text{OO}} = 2.29$ (2.92 Å),
 $\theta_1 = 4.6^\circ$ (6°), $\theta_2 = 112.4^\circ$ (123°)



$\text{CH}_4 \cdot \text{OH}_2$ $E = -3.9$ (-0.9 kcal/mol)
 $R_{\text{OC}} = 3.18$ (3.51 Å)



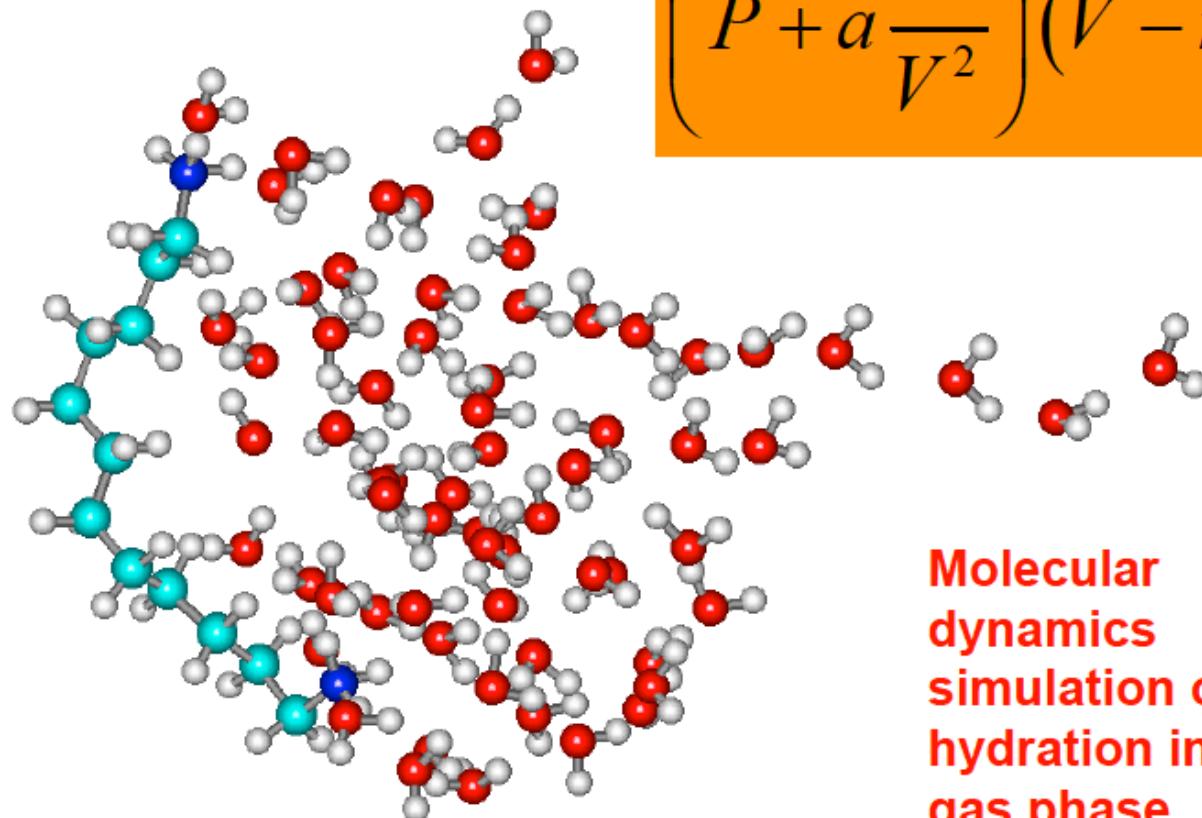
$(\text{HF})_2$ $E = -53.7$ (-4.56 kcal/mol)
 $R_{\text{FF}} = 2.13$ (2.73 Å),
 $\theta_1 = 5.8^\circ$ (7°), $\theta_2 = 103.5^\circ$ (112°)



$(\text{CH}_4)_2$ $E = -0.5$ (-0.3 kcal/mol)
 $R_{\text{CC}} = 3.91$ (4.13 Å)

Water has an unusually large value for **a** in the van der Waals equation due to hydrogen bond formation

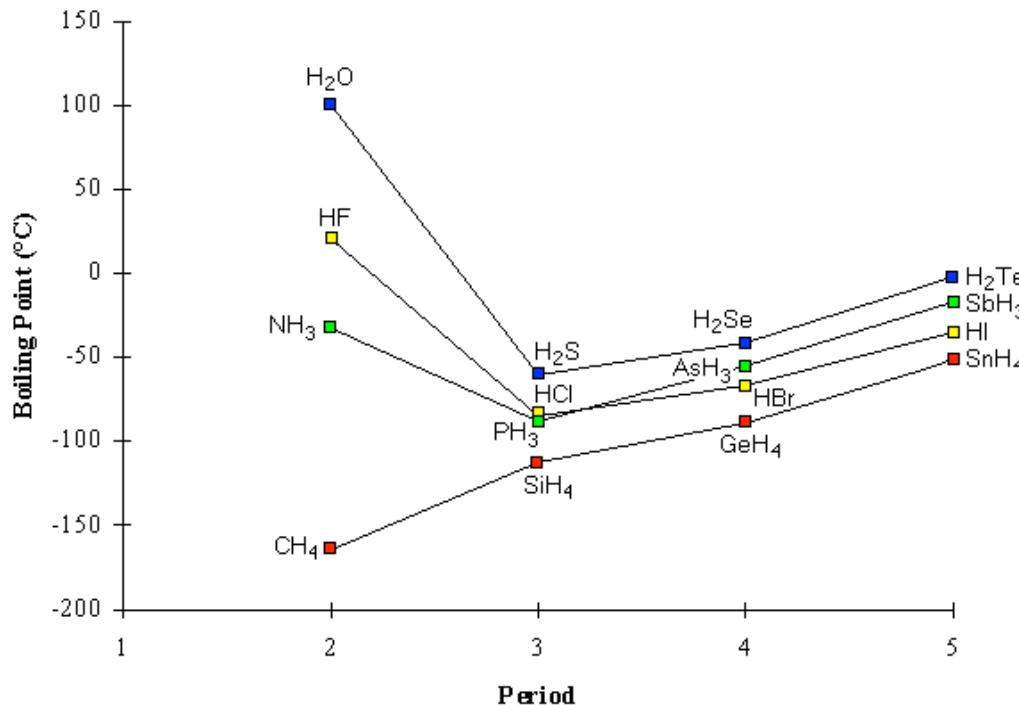
$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$



Molecular
dynamics
simulation of ion
hydration in the
gas phase

HYDROGEN BONDING!!

Hydrogen Bonding:



Critical to the unusual properties of liquid and solid water, and thus for life.

We will talk more about phase changes and diagrams once we have some thermodynamics under our belts!

