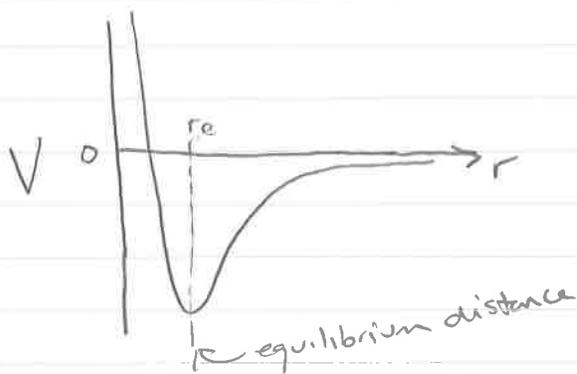


Intermolecular Forces

We've already seen how the attractive (and repulsive) forces between ions are responsible for cations and anions coming together into the ionic bonding of the crystal lattice.

The potential energy associated with this electrostatic interaction of cations and anions was

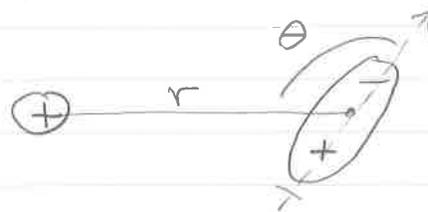
$$V = - \frac{Q_1 Q_2}{4\pi\epsilon_0 r} \left(1 - \frac{1}{n}\right) \quad \text{ion-ion interaction}$$



What about interactions between an ion and a neutral molecule?

If the neutral molecule has an electric dipole moment, then the potential energy between an ion and dipole is

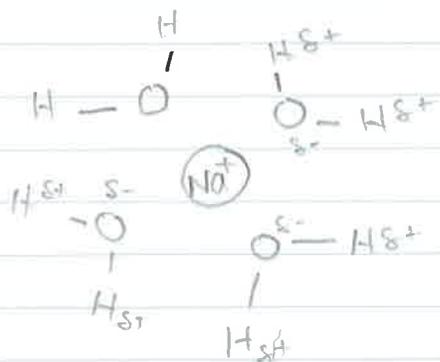
$$V(r, \theta) = - \frac{\mu Q}{4\pi\epsilon_0 r^2} \cos \theta$$



This ignores repulsions at close contact that we added to ion-ion potential, i.e., b/r^n

This interaction explains the attraction and reorientation of polar molecules around ions. The classic example is H_2O around cations and anions.

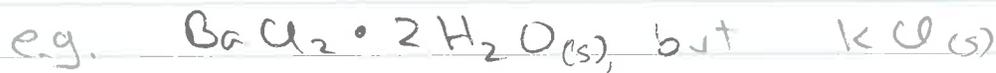
When an ionic salt dissolves in water, the water molecules surround (are attracted to) the ions in a way that minimizes this potential



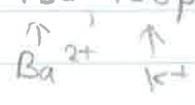
Smaller ions, usually cations attract polar molecules more strongly than larger ions. This explains why Lithium and sodium often form hydrated salts, bringing the coordinated water molecules into the crystal structure.



higher cation charge also increases likelihood of hydrated salts.

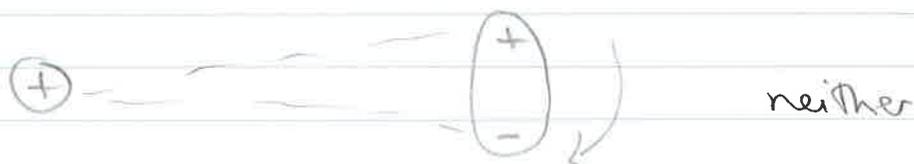
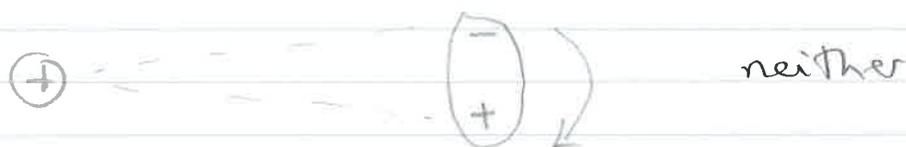


both Ba^{2+} and K^+ have similar radius 135, 138 pm
 but the higher charge $2+$ Ba^{2+} makes the H_2O molecules more strongly attracted.



Effect of Thermal Fluctuations

In the liquid phase you might expect molecule reorientation to average this ion-dipole attraction to zero.



as the temperature increases the molecules tumble faster and faster and eventually there's no attraction.

A full statistical thermodynamics calculation shows that

$$\langle V(r) \rangle = -\frac{1}{3} \frac{1}{k_B T} \left(\frac{\mu Q}{4\pi\epsilon_0} \right)^2 \frac{1}{r^4}$$

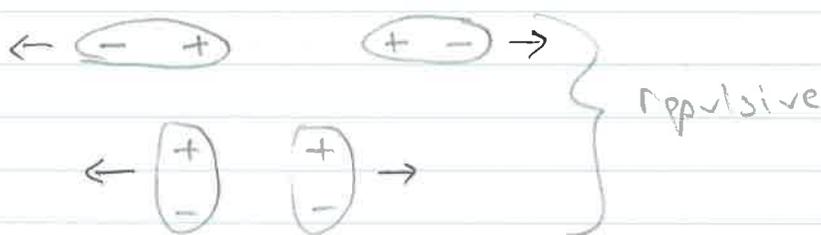
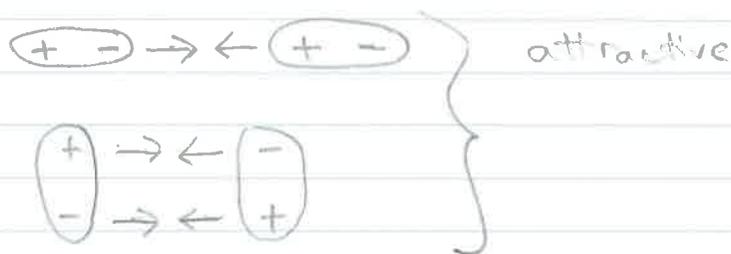
The averaged interaction is purely attractive and decreases with increasing temperature ($1/T$) and distance ($1/r^4$).

Dipole-Dipole Interactions

Next we consider two neutral molecules, both of which have an electric dipole moment,



depending on relative orientation there is attractive or repulsive forces



The potential energy has the form

$$V(r, \theta_A, \theta_B, \phi_A, \phi_B) =$$

$$\frac{\mu_A \mu_B}{4\pi\epsilon_0 r^3} \left[-2 \cos \theta_A \cos \theta_B + \sin \theta_A \sin \theta_B \cos(\phi_B - \phi_A) \right]$$

As before, in the liquid & gas phase you might expect random motion (reorientations and translations) to cause this potential to average to zero. a full statistical thermodynamic treatment gives

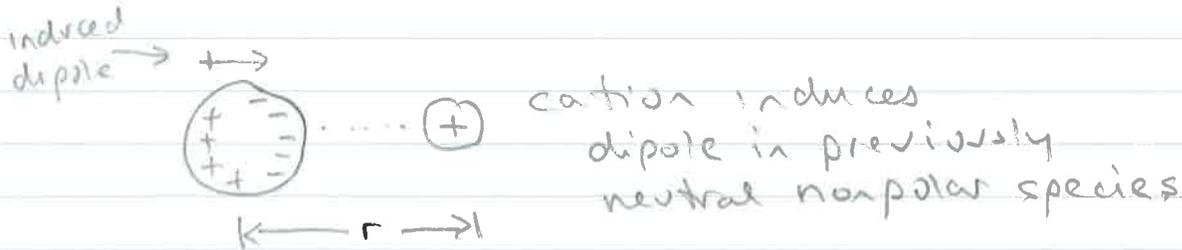
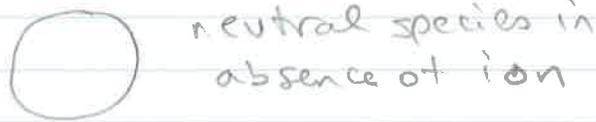
again as $T \uparrow$ the attraction decreases

$$\langle V(r) \rangle = -\frac{2}{3} \frac{1}{k_B T} \left(\frac{\mu_A \mu_B}{4\pi\epsilon_0} \right)^2 \frac{1}{r^6}$$

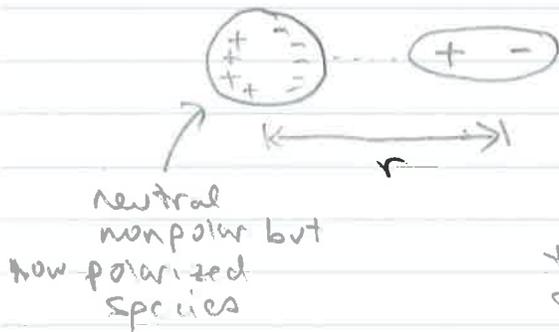
↑
Purely attractive

Even neutral & non-polar species will experience an attraction to an ion or a dipole.

This is because a nearby ion or dipole can induce a dipole in the nonpolar species



even an electric dipole can induce a dipole in a neutral nonpolar species.



The induced dipole is proportional to the electric field produced at the nonpolar species by the distant ion or dipole

$$\vec{\mu}_{\text{induced}} = \alpha' \vec{E}$$

↑ dipole moment induced in nonpolar atom or molecule

↑ Proportionality constant called Polarizability

← electric field produced at nonpolar neutral species by ion or dipole.

For the electric field of a dipole we find

$$V(r) = -\frac{\alpha \mu^2}{4\pi\epsilon_0 r^6}$$



attraction between neutral atom or molecule and an electric dipole

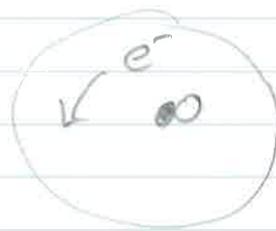
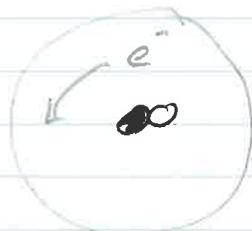
Dispersion (London) Forces

What about attractions between neutral nonpolar atoms and molecules?



Helium gas will condense into a liquid at 4K. So, there must be some attractive force, although clearly it's quite weak.

The theory is quite complicated, but a simple picture is that the motion of electrons in different helium atoms become correlated and this leads to a net attraction.



if e⁻ motion on both atoms is uncorrelated there is no attraction

Detailed Theory gives

when e⁻ motion becomes correlated atoms attract each other

$$V(r) = -\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{r^6}$$

$\alpha_A \alpha_B$ ← polarizabilities
 r^6

$I_A + I_B$
 ↑ ↑
 ionization energies

The greater the polarizability the more easily the e⁻s can be influenced by (or correlated to) e⁻s on neighboring atoms or molecules.

All the interactions between neutral species are called van der Waal forces.

These were

Dipole - Dipole

$$-\frac{2}{3} \frac{1}{k_B T} \left(\frac{\mu_A \mu_B}{4\pi\epsilon_0} \right)^2 \frac{1}{r^6}$$

induced dipole - Dipole

$$-\frac{\alpha \mu^2}{4\pi\epsilon_0} \frac{1}{r^6}$$

London forces

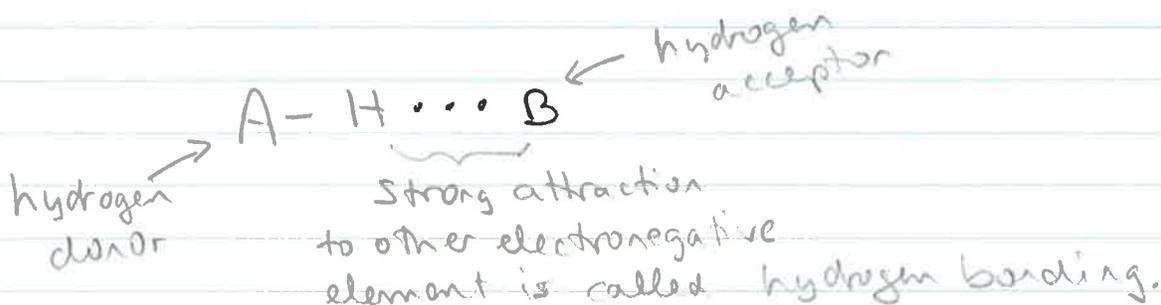
$$-\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{r^6}$$

These are the forces responsible for deviation from ideal gas behavior. Remember...?

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

$$\text{or } Z = \frac{PV}{nRT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

Hydrogen Bonding



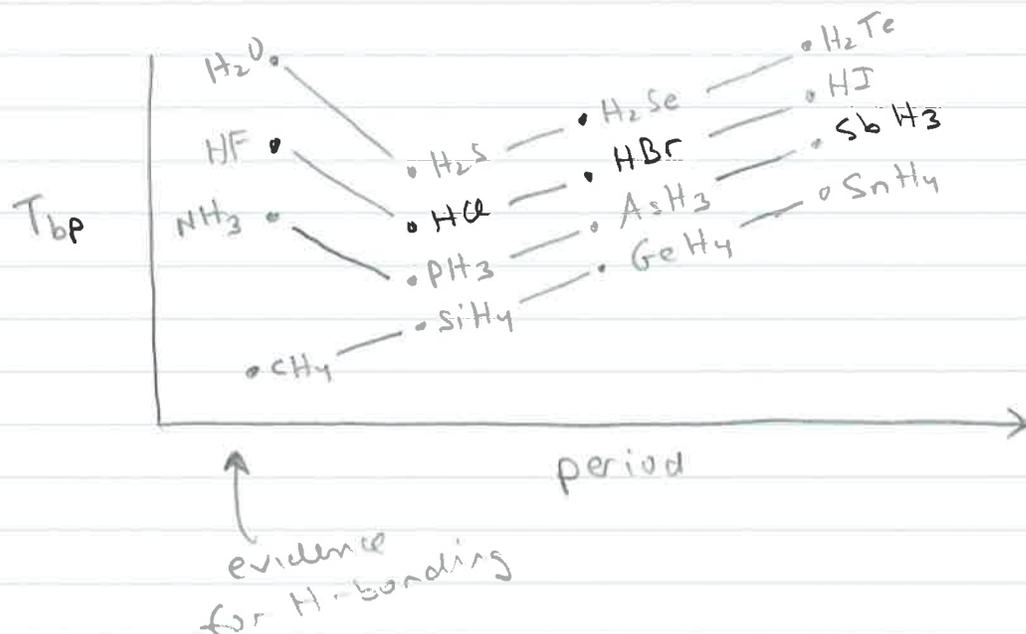
This attraction is quantum mechanical in nature, not just electrostatic.

Based on simple bonding models, H-bonding seems impossible since H has only one e^- to share.

Hydrogen is capable of sharing its one electron between certain electronegative elements in an H-bond,



How do we know H-bonds exist?



NH_3 , HF , and H_2O molecules appeared to be more strongly attracted than expected, based on van der Waals attractions.

Why only H?

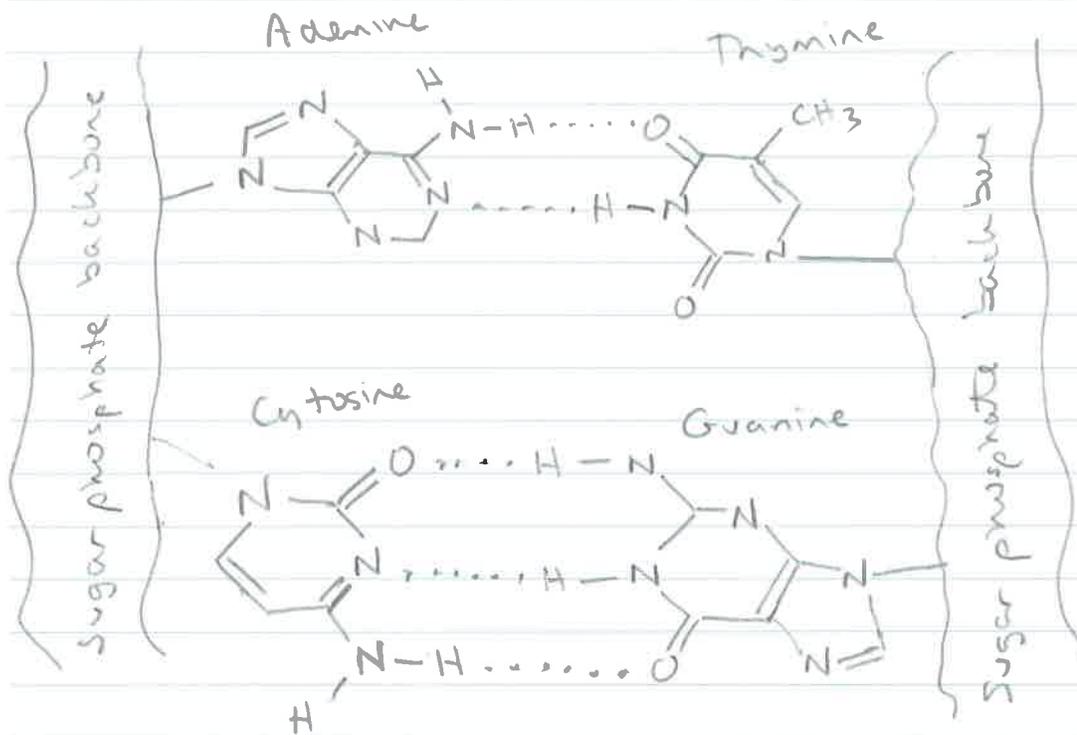
Because H nucleus becomes bare if single e^- is drawn into a sigma bond. The bare nucleus can strongly interact with nearby non-bonded electrons.

This occurs in gases, liquids, and solids

H-bonding plays an important role in H_2O 's properties.

high boiling pt, and also large heat capacity, smaller density in solid than liquid, large surface tension, ...

H-bonding plays a vital role in determining the 3D structure of proteins, DNA, and other biomolecules.



Only A-T or C-G pairings are favored because of H-bonding

