- ~~Because this effect arises from attractions between *pairs* of molecules, it should be proportional to the *square* of the number of molecules per unit volume $(N/V)^2$, or equivalently, to the *square* of the molar concentration $(n/V)^2$.~~
- ~~The pressure is predicted to be reduced by an amount $a(n/V)^2$, where a is a positive constant that depends on the strength of the attractive forces.~~
- ~~The potential energy describing this situation is that of long-range attraction with the form $= (1/r^6)$, where r is the distance between a pair of gas-phase molecules. This type of attraction primarily arises from *dispersion* or *London* forces (see **Topic 3F.4**).~~
- ~~The units of a are $L^2 \cdot atm \cdot mol^{-2}$.~~

~~Summary~~

- **~~Virial equation~~**
  - ~~Describes real gases~~
- **~~Van der Waal's equation~~**
  - ~~An *approximate* equation of state~~
  - ~~Takes molecular volume and intermolecular forces into account~~
- **~~Ideal gas equation~~**
  - ~~Least accurate of the gas-phase equations of state~~
  - ~~Ignores molecular volume and intermolecular forces~~
  - ~~Easiest to use~~

~~3E.3 The Liquefaction of Gases~~

- **~~Joule–Thomson effect~~**
  - ~~When attractive forces dominate, a real gas *cools* as it expands.~~
  - ~~In this case expansion requires energy that comes from the kinetic energy of the gas, lowering the temperature. (The gas to be liquefied is compressed and then allowed to expand through a small hole.) Exceptions are He and H_2, for which repulsion dominates.~~
  - ~~Expansion cooling is used in some refrigerators and to effect the condensation of gases such as oxygen, nitrogen, and argon.~~

Topic 3F: INTERMOLECULAR FORCES

3F.1 The Origin of Intermolecular Forces

- **Physical states**
  - Solid, liquid, and gas

- **Phase**
  - Form of matter uniform in both chemical composition and physical state (solid, liquid, or gas)
  - See **Table 3F.2** for melting and boiling points of substances.
- **Condensed phase**
  - Solid or liquid phase
    Examples: Ag(s); Sn/Pb(s) alloy, composition variable; $H_2O(s)$; $H_2O(l)$; 1% NaCl(s) in $H_2O(l)$
  - Molecules (or atoms or ions) are close to each other all the time, and intermolecular forces are of major importance.
- **Coulomb potential energy E_P**
  - The interaction between two charges, Q_1 and Q_2, separated by distance r is ⇒ $\boxed{E_P \propto \frac{Q_1 Q_2}{r}}$
  - See **Topic 1D.1** and **Fundamentals Topic A.**
  - Almost all intermolecular interactions can be traced back to this fundamental expression.

  Note: The term *intermolecular* is used in a general way to include atoms and ions.

3F.2 Ion-Dipole Forces

- **Hydration**
  - Attachment of water molecules to ions (cations and anions)
  - Water molecules are polar and have an electric dipole moment $\mu(H_2O)$.
  - A small positive charge on each H atom attracts anions, and a small negative charge on the O atom attracts cations.
- **Ion-dipole interaction**
  - The potential energy (interaction) between an ion with charge $|z|$ and a polar molecule with dipole moment μ at a distance r is ⇒ $\boxed{E_P \propto -\frac{|z|\mu}{r^2}}$
  - For proper *alignment* of the ion and dipole, the interaction is *attractive*: Cations attract the *partial* negative charges, and anions attract the *partial* positive charges on the polar molecule.
  - Shorter range (r^{-2}) interaction than the Coulomb potential (r^{-1})
  - Polar molecule needs to be *almost* in contact with ion for substantial ion-dipole interaction.
- **Hydrated compounds**
  - Ion-dipole interactions are much *weaker* than ion-ion interaction but are relatively strong for *small, highly charged* cations (large $|z|$, small r).
  - Accounts for the formation of salt hydrates such as $CuSO_4 \cdot 5\,H_2O$ and $CrCl_3 \cdot 6\,H_2O$
- **Size effects**
  - Li^+ and Na^+ (small) tend to form hydrated compounds.
  - K^+, Rb^+, and Cs^+ (larger) tend not to form hydrates.

- → Effective radius of NH_4^+ (143 pm) is similar in radius to Rb^+ (149 pm). NH_4^+ forms *anhydrous* compounds.

- **Charge effects**
  - → Ba^{2+} and K^+ are similar in size, yet Ba^{2+} (larger charge) forms *hydrates*.

3F.3 Dipole-Dipole Forces

- **Dipole alignment**
  - → In solids, molecules with dipole moments tend to *align* with partial positive charge on one molecule near the partial negative charge on another.
- **Dipole-dipole interaction in solids**
  - → The interaction between two polar molecules with dipole moments μ_1 and μ_2 *aligned* and separated by a distance r is ⇒

$$\boxed{E_P \propto -\frac{\mu_1 \mu_2}{r^3}}$$

  - → *Attractive* interaction in solids for head-to-tail *alignment* of dipoles
  - → Shorter range (r^{-3}) interaction than ion-dipole (r^{-2}) or Coulomb potential (r^{-1})
  - → For significant interaction, polar molecules must be *almost* in contact with each other.
- **Dipole-dipole interactions in gas-phase molecules**
  - → Dipole-dipole interactions are much *weaker* in gases than in solids. The potential energy of interaction is ⇒

$$\boxed{E_P \propto -\frac{\mu_1^2 \mu_2^2}{r^6}}$$

  - → Because gas molecules are in motion (rotating as well), they are subject to only a *weak* net attraction because of *occasional* alignment.
- **Dipole-dipole interactions in liquid-phase molecules**
  - → Same potential energy relationship as in the gas phase, but the interaction is somewhat *stronger* because the molecules are closer.
  - → The liquid *boiling point* is a measure of the *strength* of the intermolecular forces in a liquid. The boiling point of isomers is *often* related to the strength of their dipole-dipole interactions.
  - → Typically, the *larger* the dipole moment, the *higher* the boiling point (often a relatively small effect).

    Example: *cis*-dibromoethene (dipole moment ≈ 2.4 D, bp 112.5 °C) versus *trans*-dibromoethene (zero dipole moment, bp 108 °C)

3F.4 London Forces

- **Nonpolar molecules**
  - → Condensation of *nonpolar* molecules to form liquids implies the existence of a type of intermolecular interaction other than those described earlier.
- **London force**
  - → Occurs in addition to any dipole-dipole interactions
  - → Is universal; applies to all molecules

  - → Accounts for the attraction between any pair of ground-state molecules (*polar* or *nonpolar*)
  - → Arises from *instantaneous* partial charges (*instantaneous* dipole moment) in one molecule *inducing* partial charges (dipole moment) in a neighboring one
  - → Exists between atoms and *rotating* molecules as well
  - → Strength depends on polarizability and shape of molecule.

    Example: Other things equal, rod-shaped molecules tend to have stronger London forces than spherical molecules because they can approach each other more closely.
- **Polarizability, α**
  - → Of a molecule is related to the ease of deformation of its electron cloud
  - → Is proportional to the total number of electrons in the molecule
  - → Because the number of electrons correlates with molar mass (generally increases), polarizability does as well.
  - → The potential energy between two molecules (polar or nonpolar) with polarizability α_1 and α_2, separated by a distance r, is ⇒

$$\boxed{E_P \propto -\frac{\alpha_1 \alpha_2}{r^6}}$$

    Note: Same (r^{-6}) dependence as dipole-dipole (r^{-6}) with *rotating* molecules, but the London interaction is *usually* stronger at normal temperatures.
- **Liquid boiling point**
  - → A measure of the strength of intermolecular forces in a liquid
  - → In comparing the interactions discussed in **Topics 3F.3** and **3F.4**, the *major* influence on boiling point in both *polar* and *nonpolar* molecules is the London force.

    Example: We can predict the relative boiling points of the nonpolar molecules: F_2, Cl_2, Br_2, and I_2. Boiling point correlates with polarizability, which depends on the number of electrons in the molecule. The boiling points are expected to increase in the order of F_2 (18 electrons), Cl_2 (34), Br_2 (70), and I_2 (106). The experimental boiling temperatures are F_2 (−188 °C), Cl_2 (−34 °C), Br_2 (59 °C), and I_2 (184 °C).
- **Dipole-induced dipole interaction**
  - → The potential energy between a polar molecule with dipole moment μ_1 and a nonpolar molecule with polarizability α_2 at a distance r is ⇒

$$\boxed{E_P \propto -\frac{\mu_1^2 \alpha_2}{r^6}}$$

  - → Also applies to molecules that are both polar: each one can induce a dipole in the other.
  - → Weaker interaction than dipole-dipole

    Example: Carbon dioxide ($\mu = 0$) dissolved in water ($\mu > 0$)

3F.5 Hydrogen Bonding

- **Hydrogen bonds**
  - → Interaction *specific* to certain types of molecules (with strong attractive forces)
  - → Account for unusually high boiling points in ammonia (NH_3, −33 °C), water (H_2O, 100 °C), and hydrogen fluoride (HF, 20 °C)

→ Arise from an H atom, *covalently* bonded to a N, O, or F atom in *one* molecule, strongly attracted to a *lone pair* of electrons on a N, O, or F atom in *another* molecule

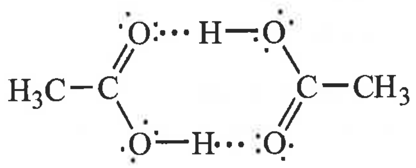
→ Are *strongest* when the three atoms are in a *straight line* and the distance between terminal atoms is within a given range

→ Common symbol for the H bond is three dots: ···

→ *Strongest* intermolecular interaction between *neutral* molecules

Examples: N–H··· :N hydrogen bonds between NH_3 molecules in pure NH_3
O–H··· :O hydrogen bonds between H_2O molecules in pure H_2O

- **Hydrogen bonding in gas-phase molecules**
  - → Aggregation of some molecules persists in the vapor phase.
  - → In HF, fragments of *zigzag* chains and $(HF)_6$ rings are formed. In CH_3COOH (acetic acid), hydrogen-bonded *dimers* are formed. The abbreviated (no C–H bonds shown) Lewis structure of the dimer $(CH_3COOH)_2$ is shown on the right.



- **Importance of hydrogen bonding**
  - → Accounts for the open structure of solid water
  - → Maintains the shape of biological molecules
  - → Binds the two strands of DNA together

3F.6 Repulsions

- **Nature of repulsions**
  - → Molecules (or atoms that do not form bonds) that are very close together repel one another.
  - → The Pauli exclusion principle forms the basis of understanding this repulsion.

Example: As two He atoms approach each other, at short separations, their $1s$ atomic orbitals overlap and form a bonding and an antibonding molecular orbital.

The bonding molecular orbital is filled with two electrons, and the remaining two electrons are required by the exclusion principle to fill the antibonding orbital.

An antibonding orbital is more antibonding in character than a bonding orbital is bonding; the result is an increase in energy as the two atoms merge into each other.

The same effect occurs for all molecules whose atoms have filled shells (e.g., H_2), even though the details of the bonding and antibonding orbitals they form may be much more complicated.

The result is that all molecules repel each other when they come into contact and their orbitals overlap.

- **Electron density**
  - → Electron density in all atomic orbitals (AOs) and the molecular orbitals (MOs) they form decreases exponentially toward zero at large distances from the nucleus.
  - → The overlap between orbitals on neighboring molecules will also depend exponentially on their separation.
  - → As a result, repulsions between molecules usually depend exponentially on separation (see text **Figure 3F.1**). Repulsions are effective only when the two molecules are very close together. Once they are close, the energy of repulsion increases rapidly as the distance between the two molecules decreases.
  - → The strong dependence of repulsion on separation is the underlying reason objects around us have definite, well-defined shapes.

~~Topic 3G: LIQUIDS~~

~~3G.1 Order in Liquids~~

- ~~**Liquid phase**~~
  - ~~→ Mobile molecules with restricted motion~~
  - ~~→ Between the extremes of gas and solid phases~~
- ~~**Long-range order**~~
  - ~~→ Characteristic of a *crystalline solid*~~
  - ~~→ Atoms or molecules are arranged in orderly patterns that are repeated over long distances.~~
- ~~**Short-range order**~~
  - ~~→ Characteristic of the *liquid phase*~~
  - ~~→ Atoms or molecules are positioned in orderly patterns at nearest-neighbor distances only.~~
  - ~~→ Local order is maintained by a continual process of forming and breaking nearest-neighbor interactions.~~

~~3G.2 Viscosity and Surface Tension~~

- ~~**Viscosity**~~
  - ~~→ Resistance of a substance to flow: *Greater* viscosity yields *slower* flow.~~
  - ~~→ Viscous liquids include those with hydrogen bonding between molecules.~~

~~**Examples of liquids with high viscosity:**~~

~~H_3PO_4 (phosphoric acid) and $C_3H_8O_3$ (glycerol) (each forms many H bonds); liquid phases of metals; and long-chain molecules that can be entangled, such as hydrocarbon oil and greases~~