

Why the Van der Waals Interaction is Determined Empirically And How it Can NOT be Determined from the Schrödinger Equation

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Abstract: Van der Waals Forces are weak electrical attractive forces that appear between any two molecules, including the electrically neutral Noble gas molecules.

It is well known that at large distance r between the molecules, these forces are proportional to $1 / r^7$

We observe here that at such large distance, the Van der Waals forces vanish.

But we show that at very short distance, say r_a , the Van der Waals force is still proportional to $1 / r_a^7$.

This explains why the empirical Lennard-Jones potential is used to estimate the Van der Waals interaction potential.

We show that the Schrödinger equation introduces many assumptions, and uncertain quantities, in order to conclude that the Van der Waals potential may depend on $1 / r^7$, for large distance r , where we have shown that the force actually vanishes. Chemistry books credit papers written by Fritz London in 1929, and in 1930, for giving the ultimate explanation to the Van der Waals interaction.

We show that London's papers are confused, get no results, do not elucidate the van der Waals forces, and were actually outdated.

In 1930, London was ignorant of the 1925 Lennard-Jones empirical potential for the Van der Waals interaction.

Keywords: Van der Waals Forces, Dispersion Forces, London Forces, Casimir Fallacy, Quantum Mechanics, Quantum Chemistry, Electric Dipole, Lennard-Jones Potential, Schrödinger Equation,

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References

0.

Van der Waals Forces

Noble gas molecules such as Helium, or Argon have closed electron shells, and are non-polar, and electrically neutral to each other.

The fact that the molecules of a noble gas can get close enough to liquefy at some temperature above the absolute zero, indicates the existence of some weak forces between the molecules.

These forces are named after van der Waals.

And they exist between polar molecules as well, although due to their weakness they are undetectable in an ionic or covalent bonds.

At any instant, the location of the electrons about the nucleus, may polarize the molecule, and make it into a dipole, that in turn will polarize a molecule in its neighborhood, and attract it with van der Waals forces.

The forces are the negative gradient of the interaction potential

$$U(R)$$

between the molecules

$$F(R) = -\text{grad}U(R)$$

1.

The Force of an Electric Dipole on a Distant Electric Dipole

We look at two molecules on a line: molecule 1, and molecule 2.

The distance between the centers of the molecules is

$$r \gg \text{radius of a molecule.}$$

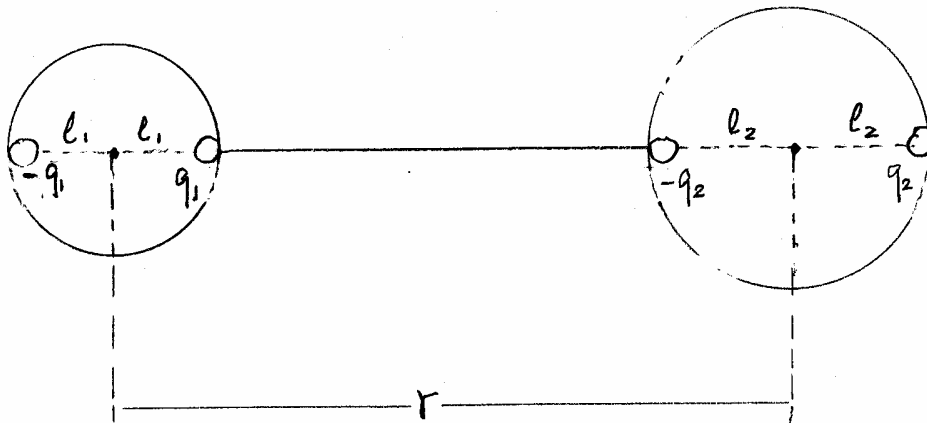
The motion of electrons around the centers of each molecule averages into zero charge on each.

But at any instant, molecule 1 may be polarized, and constitutes a dipole

$$(-q_1, q_1),$$

which polarizes molecule 2 into a dipole

$$(-q_2, q_2).$$



If the electrons' charge of molecule 1 is

$$-q_1$$

and the radius of the molecule is

$$l_1$$

The strength of that dipole is

$$\mu_1 = q_1 l_1$$

1.1 The Electric Field of Molecule 1 at Distance $R \gg l_1$ is

$$E_1(R) = \frac{1}{\pi\epsilon_0} \frac{\mu_1}{R^3}$$

Proof The field of molecule 1 at a distance R from its center is

$$\begin{aligned} E_1(R) &= \frac{1}{4\pi\epsilon_0} \frac{q_1}{R-l_1} + \frac{1}{4\pi\epsilon_0} \frac{-q_1}{R+l_1} \\ &= \frac{1}{4\pi\epsilon_0} \frac{q_1}{R^2} \left(\frac{1}{\left(1-\frac{l_1}{R}\right)^2} - \frac{1}{\left(1+\frac{l_1}{R}\right)^2} \right) \end{aligned}$$

For $l_1 \ll R$, to first order,

$$\left(1 - \frac{l_1}{R}\right)^{-2} \approx 1 + 2\frac{l_1}{R}$$

$$\left(1 + \frac{l_1}{R}\right)^{-2} \approx 1 - 2\frac{l_1}{R}$$

$$E_1(R) \approx \frac{1}{4\pi\epsilon_0} \frac{q_1}{R^2} \left(\left[1 + 2\frac{l_1}{R}\right] - \left[1 - 2\frac{l_1}{R}\right] \right)$$

$$\begin{aligned}
&= \frac{1}{\pi\epsilon_0} \frac{q_1 l_1}{R^3} \\
&= \frac{1}{\pi\epsilon_0} \frac{\mu_1}{R^3} \cdot \square
\end{aligned}$$

1.2 The Force on molecule 2 is

$$F(r) \approx -6\alpha_2 \left(\frac{\mu_1}{\pi\epsilon_0} \right)^2 \frac{1}{r^7}$$

Proof: The field of molecule 1, applied to molecule 2 at the distance r , $E_1(r)$, polarizes molecule 2 into the dipole $(-q_2, q_2)$, with strength that is proportional to $E_1(r)$, with polarizability coefficient

$$\alpha_2,$$

so that

$$\begin{aligned}
q_2 l_2 &= \alpha_2 E_1(r) \\
&\approx \alpha_2 \frac{1}{\pi\epsilon_0} \frac{\mu_1}{r^3}
\end{aligned}$$

And applies to molecule 2 the force

$$\begin{aligned}
F(r) &= q_2 E_1(r + l_2) - q_2 E_1(r - l_2) \\
&\approx q_2 \frac{1}{\pi\epsilon_0} \frac{\mu_1}{(r + l_2)^3} - q_2 \frac{1}{\pi\epsilon_0} \frac{\mu_1}{(r - l_2)^3} \\
&= q_2 \frac{\mu_1}{\pi\epsilon_0} \left(\frac{1}{(r + l_2)^3} - \frac{1}{(r - l_2)^3} \right)
\end{aligned}$$

$$= q_2 \frac{\mu_1}{\pi \epsilon_0} \frac{1}{r^3} \left(\frac{1}{\left(1 + \frac{l_2}{r}\right)^3} - \frac{1}{\left(1 - \frac{l_2}{r}\right)^3} \right)$$

For $l_2 \ll r$, to first order,

$$\left(1 + \frac{l_2}{r}\right)^{-3} \approx 1 - 3 \frac{l_2}{r}$$

$$\left(1 - \frac{l_2}{r}\right)^{-3} \approx 1 + 3 \frac{l_2}{r}$$

$$\begin{aligned} F(r) &\approx q_2 \frac{\mu_1}{\pi \epsilon_0} \frac{1}{r^3} \left(\left[1 - 3 \frac{l_2}{r}\right] - \left[1 + 3 \frac{l_2}{r}\right] \right) \\ &= -6 \frac{\mu_1}{\pi \epsilon_0} \frac{1}{r^4} \underbrace{q_2 l_2}_{\approx \alpha_2 \frac{1}{\pi \epsilon_0} \frac{\mu_1}{r^3}} \\ &\approx -6 \frac{\mu_1}{\pi \epsilon_0} \frac{1}{r^4} \alpha_2 \frac{1}{\pi \epsilon_0} \frac{\mu_1}{r^3} \\ &= -6 \alpha_2 \left(\frac{\mu_1}{\pi \epsilon_0} \right)^2 \frac{1}{r^7} \cdot \square \end{aligned}$$

1.3 The interaction Potential is

$$U(r) \approx -\alpha_2 \left(\frac{\mu_1}{\pi \epsilon_0} \right)^2 \frac{1}{r^6}$$

Proof:

$$-\frac{dU(r)}{dr} \approx \alpha_2 \left(\frac{\mu_1}{\pi \epsilon_0} \right)^2 (-6) \frac{1}{r^7}$$

And the interaction potential is

$$U(r) \approx -\alpha_2 \left(\frac{\mu_1}{\pi\epsilon_0} \right)^2 \frac{1}{r^6} \cdot \square$$

1.4 The Force, and the Energy depend on the Empirical Polarizability

Since the polarizability α_2 is specific to the molecule, the formula needs in each case the measured polarizability of the molecule.

The need for the polarizability as a parameter in the formula makes the formula empirical.

We proceed to see that the requirement of large distance between the molecules nullifies the force, and the energy.

2.

The Force, and the Energy Vanish at Large Distance

The dependence of the attractive force

$$F(r) \approx -6\alpha_2 \left(\frac{\mu_1}{\pi\epsilon_0} \right)^2 \frac{1}{r^7}$$

on the seventh power of the distance nullifies the force at the distances

$$r \gg l_1$$

to which it applies.

For instance

For *HCl*,

$$\mu_1 = q_1 l_1 = 1 \text{ Debye} = (3.33564)10^{-30} \text{ CoulombMeter}$$

For Benzene, *C₆H₆*,

$$\alpha_2 = 10^{-29} m^3$$

$$l_1 = \frac{\mu_1}{q_1} = \frac{(3.33564)10^{-30}}{(1.60217733)10^{-19}} = (2.081941828)10^{-11} \text{ meter} \approx 2 \cdot 10^{-11} m,$$

To have somewhat $r \gg l_1$, we will take

$$r = 100l_1 = 2 \cdot 10^{-9} = 2 \text{ nano meter}$$

Then,

$$F(2 \cdot 10^{-9}) \approx -6(10^{-29})4^2 \underbrace{\left(\frac{1}{4\pi\epsilon_0}\right)^2}_{(9 \cdot 10^9)^2} \underbrace{(3.33564)^2}_{\approx 11} 10^{-60} \frac{1}{(2 \cdot 10^{-9})^7} \approx -10^{-9} \text{ Newton}$$

The interaction energy $U(r) \approx -\alpha_2 \left(\frac{\mu_1}{\pi\epsilon_0}\right)^2 \frac{1}{r^6}$ is

$$U(2 \cdot 10^{-9}) \approx -(10^{-29})4^2 \underbrace{\left(\frac{1}{4\pi\epsilon_0}\right)^2}_{(9 \cdot 10^9)^2} \underbrace{(3.33564)^2}_{\approx 11} 10^{-60} \frac{1}{(2 \cdot 10^{-9})^6} \approx -3 \cdot 10^{-19} \text{ J / mole}$$

which is less than

$$2\text{eV/mole.}$$

To credibly have $r \gg l_1$, we will take

$$r = 1000l_1 = 2 \cdot 10^{-8} \text{ m}$$

Then,

$$F(2 \cdot 10^{-8}) \approx -6(10^{-29})4^2 \underbrace{\left(\frac{1}{4\pi\epsilon_0}\right)^2}_{(9 \cdot 10^9)^2} \underbrace{(3.33564)^2}_{\approx 11} 10^{-60} \frac{1}{(2 \cdot 10^{-8})^7} \approx -10^{-16} \text{ Newton}$$

The Interaction Energy is

$$U(2 \cdot 10^{-8}) \approx -(10^{-29})4^2 \underbrace{\left(\frac{1}{4\pi\epsilon_0}\right)^2}_{(9 \cdot 10^9)^2} \underbrace{(3.33564)^2}_{\approx 11} 10^{-60} \frac{1}{(2 \cdot 10^{-8})^6} \approx -3 \cdot 10^{-25} \text{ J / mole}$$

which is less than

$$2 \cdot 10^{-6} \text{ eV/mole}$$

Therefore, to have non-negligible force and energy we need to allow the molecules to be closer with r of the order of l_1 , and l_2 .

3.

The Force of an Electric Dipole on a Nearby Electric Dipole

We look at two molecules on a line: molecule 1, and molecule 2.

The distance between the centers of the molecules is of the order of the molecules radii.

Here, we will take the distance between the edges of the two molecules to be

$$l_1 + l_2$$

So the distance between their centers is

$$r_a = 2(l_1 + l_2)$$

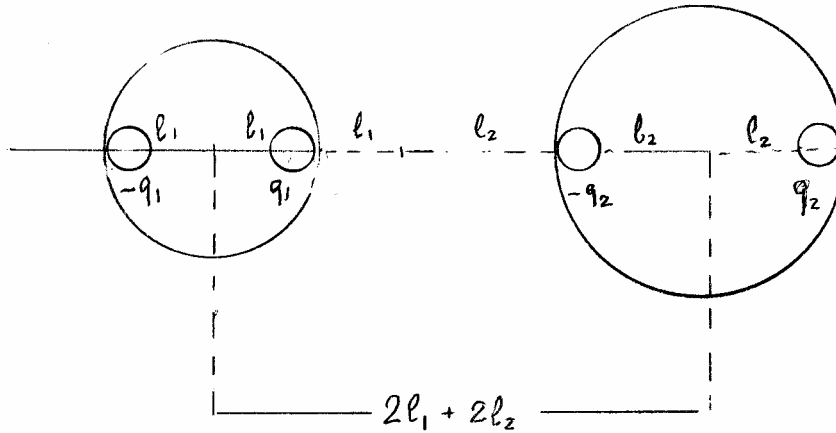
The motion of electrons around the centers of each molecule averages into zero charge on each.

But at any instant, molecule 1 may be polarized, and constitutes a dipole

$$(-q_1, q_1),$$

which polarizes molecule 2 into a dipole

$$(-q_2, q_2).$$



If the electrons' charge of molecule 1 is

$$-q_1$$

and the radius of the molecule is

$$l_1$$

The strength of that dipole is

$$\mu_1 = q_1 l_1$$

3.1 The Electric Field of Molecule 1 at Distance R is

$$E_1(R) = 4 \frac{1}{4\pi\epsilon_0} \frac{\mu_1}{R^3} \frac{1}{\left(1 - \frac{l_1^2}{R^2}\right)^2}$$

Proof The field of molecule 1 at a distance R from its center is

$$E_1(R) = \frac{1}{4\pi\epsilon_0} \frac{q_1}{R - l_1} + \frac{1}{4\pi\epsilon_0} \frac{-q_1}{R + l_1}$$

$$\begin{aligned}
&= \frac{1}{4\pi\epsilon_0} \frac{q_1}{R^2} \left(\frac{1}{\left(1 - \frac{l_1}{R}\right)^2} - \frac{1}{\left(1 + \frac{l_1}{R}\right)^2} \right) \\
&= \frac{1}{4\pi\epsilon_0} \frac{q_1}{R^2} \frac{4\frac{l_1}{R}}{\left(1 - \frac{l_1^2}{R^2}\right)^2} \\
&= 4 \frac{1}{4\pi\epsilon_0} \frac{\mu_1}{R^3} \frac{1}{\left(1 - \frac{l_1^2}{R^2}\right)^2} \cdot \square
\end{aligned}$$

3.2 $l_1 \approx l_2 \Rightarrow$ **The Force on molecule 2 is**

$$F(r_a) \approx -\alpha_2 \frac{4^6}{27} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \mu_1^2 \frac{1}{r_a^7} = -\alpha_2 \frac{1}{4 \cdot 27} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \mu_1^2 \frac{1}{l_1^7}$$

Proof: The field of molecule 1, applied to molecule 2 at the distance r_a , $E_1(r_a)$, polarizes molecule 2 into the dipole $(-q_2, q_2)$, with strength that is proportional to $E_1(r_a)$, with polarizability coefficient

$$\alpha_2,$$

so that

$$\begin{aligned}
q_2 l_2 &= \alpha_2 E_1(r_a) \\
&= \alpha_2 \frac{1}{\pi\epsilon_0} \frac{\mu_1}{r_a^3} \frac{1}{\left(1 - \frac{l_1^2}{r_a^2}\right)^2}
\end{aligned}$$

And applies to molecule 2 the force

$$\begin{aligned}
F(r_a) &= q_2 E_1(r_a + l_2) - q_2 E_1(r_a - l_2) \\
&= q_2 \frac{1}{\pi \epsilon_0} \frac{\mu_1}{(r_a + l_2)^3} \frac{1}{\left(1 - \frac{l_1^2}{(r_a + l_2)^2}\right)^2} - q_2 \frac{1}{\pi \epsilon_0} \frac{\mu_1}{(r_a - l_2)^3} \frac{1}{\left(1 - \frac{l_1^2}{(r_a - l_2)^2}\right)^2} \\
&= q_2 \frac{\mu_1}{\pi \epsilon_0} \frac{1}{(r_a - l_2)^3} \left(\frac{(r_a - l_2)^3}{(r_a + l_2)^3} \frac{1}{\left(1 - \frac{l_1^2}{(r_a + l_2)^2}\right)^2} - \frac{1}{\left(1 - \frac{l_1^2}{(r_a - l_2)^2}\right)^2} \right)
\end{aligned}$$

At $r_a = 2(l_1 + l_2)$,

$$F(2l_1 + 2l_2) = q_2 \frac{\mu_1}{\pi \epsilon_0} \frac{1}{(2l_1 + l_2)^3} \left(\frac{(2l_1 + l_2)^3}{(2l_1 + 3l_2)^3} \frac{1}{\left(1 - \frac{l_1^2}{(2l_1 + 3l_2)^2}\right)^2} - \frac{1}{\left(1 - \frac{l_1^2}{(2l_1 + l_2)^2}\right)^2} \right)$$

Assuming that

$$l_1 \approx l_2$$

$$\begin{aligned}
F(2l_1 + 2l_2) &\approx q_2 \frac{\mu_1}{\pi \epsilon_0} \frac{1}{27l_1^3} \underbrace{\left(\frac{27}{125} \frac{1}{\left(1 - \frac{1}{5^2}\right)^2} - \frac{1}{\left(1 - \frac{1}{3^2}\right)^2} \right)}_{=-1.03125} \\
&\approx -q_2 \frac{\mu_1}{\pi \epsilon_0} \frac{1}{27l_1^3} \\
&\approx -\frac{\mu_1}{4\pi \epsilon_0} \frac{4}{27} q_2 l_1 \frac{1}{l_1^4}
\end{aligned}$$

Substituting

$$\begin{aligned}
 q_2 l_1 &\approx q_2 l_2 \\
 &= \alpha_2 E(2l_1 + 2l_2) \\
 &= \alpha_2 \frac{1}{\pi \epsilon_0} \frac{\mu_1}{(2l_1 + 2l_2)^3} \frac{1}{\left(1 - \frac{l_1^2}{(2l_1 + 2l_2)^2}\right)^2} \\
 &= \alpha_2 \frac{1}{\pi \epsilon_0} \frac{\mu_1}{(2l_1 + 2l_2)^3} \frac{1}{\left(1 - \frac{l_1^2}{(2l_1 + 2l_2)^2}\right)^2} \\
 &= \alpha_2 \frac{1}{4\pi \epsilon_0} \frac{\mu_1}{4^2 l_1^3} \frac{1}{\underbrace{\left(1 - \frac{1}{4^2}\right)^2}_{\approx 1.13777}} \\
 &\approx \alpha_2 \frac{1}{4\pi \epsilon_0} \frac{\mu_1}{4^2 l_1^3}.
 \end{aligned}$$

Therefore,

$$\begin{aligned}
 F(2l_1 + 2l_2) &\approx -\frac{\mu_1}{4\pi \epsilon_0} \frac{4}{27} \frac{1}{l_1^4} \alpha_2 \frac{1}{4\pi \epsilon_0} \frac{\mu_1}{4^2 l_1^3} \\
 &= -\alpha_2 \frac{1}{4 \cdot 27} \left(\frac{1}{4\pi \epsilon_0}\right)^2 \mu_1^2 \frac{1}{l_1^7}
 \end{aligned}$$

Since we assume that $l_1 \approx \frac{1}{4} r_a$

$$F(r_a) \approx -\alpha_2 \frac{4^6}{27} \left(\frac{1}{4\pi \epsilon_0}\right)^2 \mu_1^2 \frac{1}{r_a^7} \cdot \square$$

3.3 $l_1 \approx l_2 \Rightarrow$ **The interaction Potential is**

$$\begin{aligned} U(r_a) &\approx -\alpha_2 \frac{1}{6} \frac{4^6}{27} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \mu_1^2 \frac{1}{r_a^6} \\ &= -\alpha_2 \frac{1}{6} \frac{1}{27} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \mu_1^2 \frac{1}{l_1^6} \end{aligned}$$

Proof:

$$-\frac{dU(r_a)}{dr_a} \approx \alpha_2 \frac{1}{6} \frac{4^6}{27} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \mu_1^2 (-6) \frac{1}{r_a^7}$$

And the interaction potential is

$$U(r_a) \approx -\alpha_2 \frac{1}{6} \frac{4^6}{27} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \mu_1^2 \frac{1}{r_a^6} . \square$$

4.

The Interaction between HCl Molecule, and Nearby Benzene Molecule

For *HCl*,

$$\mu_1 = q_1 l_1 = 1 \text{ Debye} = (3.33564)10^{-30} \text{ CoulombMeter}$$

For Benzene, C_6H_6 ,

$$\alpha_2 = 10^{-29} m^3$$

$$l_1 = \frac{\mu_1}{q_1} = \frac{(3.33564)10^{-30}}{(1.60217733)10^{-19}} = (2.081941828)10^{-11} \text{ meter} \approx 2 \cdot 10^{-11} m,$$

$$r_a \approx 4l_1 \approx 8 \cdot 10^{-11} \text{ meter}$$

Then,

$$F(r_a) \approx -\alpha_2 \frac{1}{4 \cdot 27} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \mu_1^2 \frac{1}{l_1^7}$$

$$F(8 \cdot 10^{-11}) \approx -(10^{-29}) \frac{1}{108} \underbrace{\left(\frac{1}{4\pi\epsilon_0} \right)^2}_{(9 \cdot 10^9)^2} \underbrace{(3.33564)^2}_{\approx 11} 10^{-60} \frac{1}{(2 \cdot 10^{-11})^7}$$

$$\approx -64,453 \text{ Newton}$$

The interaction energy $U(r) \approx -\alpha_2 \frac{1}{6} \frac{1}{27} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \mu_1^2 \frac{1}{l_1^6}$

$$U(8 \cdot 10^{-11}) \approx -(10^{-29}) \frac{1}{162} \underbrace{\left(\frac{1}{4\pi\epsilon_0} \right)^2}_{(9 \cdot 10^9)^2} \underbrace{(3.33564)^2}_{\approx 11} 10^{-60} \frac{1}{(2 \cdot 10^{-11})^6}$$

$$\approx -(8.59375)10^{-7} J / mole$$

which is

$$\approx -\frac{(8.59375)10^{-7}}{(1.60217733)10^{-19}} \text{ eV} / mole \approx (5.36)10^{12} \text{ eV} / mole .$$

5.

The Lennard-Jones Empirical Interaction Potential

Since the Van der Waals force on distant molecules vanishes, its properties are irrelevant.

But the Van der Waals force on nearby molecules applies, and depends also on $1/r^7$.

This suggests that the Van der Waals attraction potential at any distance depends on $1/r^6$.

That is, we may determine the Van der Waals attraction potential for given substance from experiment as

– constant specific to the substance times $1/r^6$.

The negative sign guarantees that the force derived from the potential

$$F = -gradU$$

has a positive sign, and is attractive

At the short range in which the Van der Waals Forces appear, electron shells of the molecules may overlap, and the molecules will be repulsed by a force with a negative sign.

That repulsive force is derived from a positive sign potential.

In 1925, Lennard-Jones suggested that the repulsion potential for a given substance is

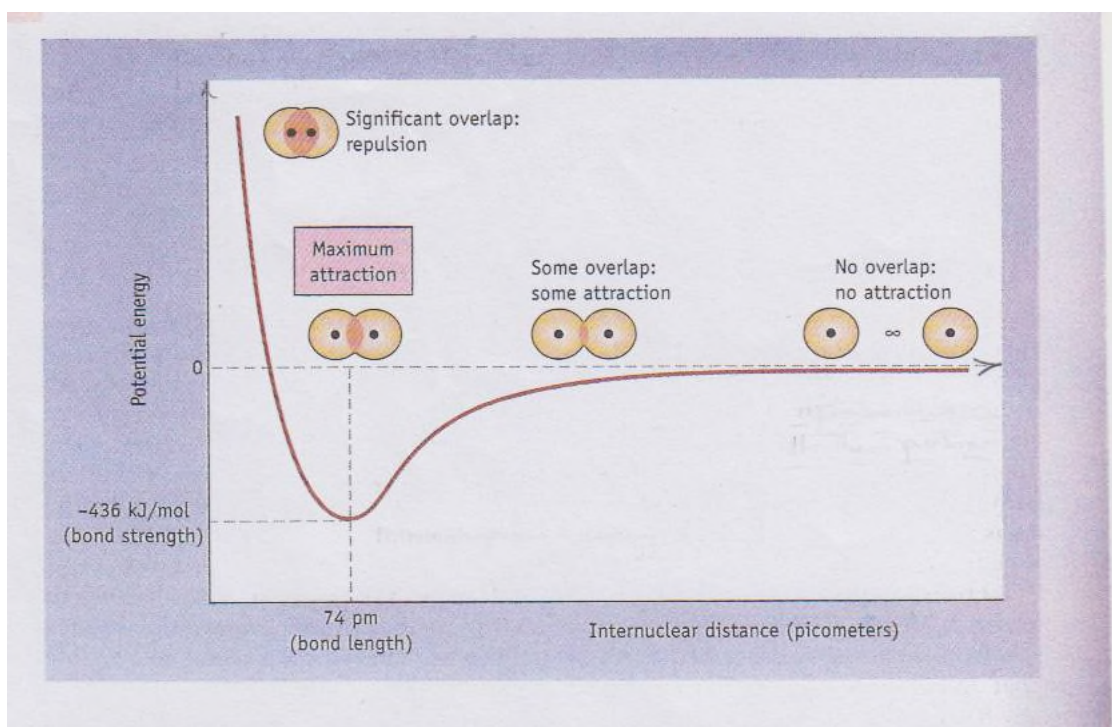
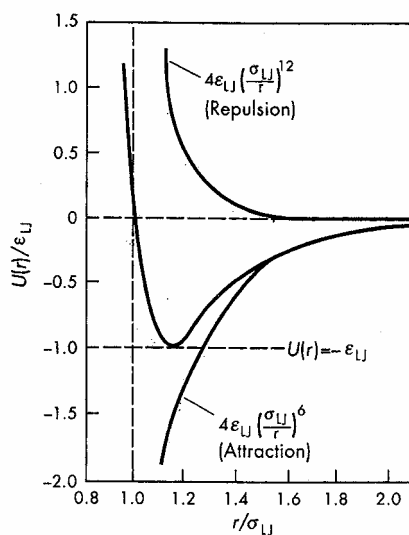
+ constant specific to the substance times $1/r^{12}$.

The total Lennard-Jones potential is the sum of

the repulsive potential depending on $1/r^{12}$

with

the attractive potential depending on $-1/r^6$.



The empirical Lennard-Jones potential that includes repulsion and attraction, depends on two parameters specific to the substance.

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

where

σ is measured in nano-meters

and

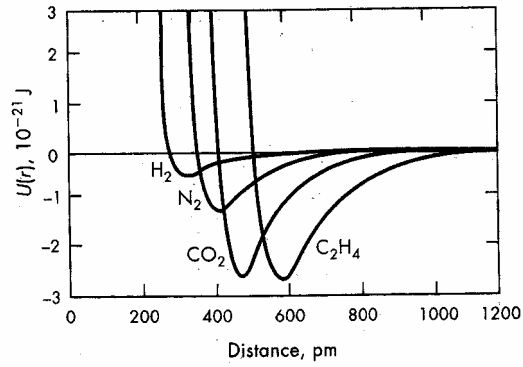
ε is measured in electron-Volts

The σ , and ε of a substance are determined in spectroscopy, and in mass spectrometry.

For molecules of Noble Gases, it was determined that

Noble Gas	σ	ε
Helium	$(0.256) 10^{-9}$ meter	$(8.79)10^{-4}$ eV
Neon	$(0.275) 10^{-9}$ meter	$(3.08)10^{-3}$ eV
Argon	$(0.340) 10^{-9}$ meter	$(1.05)10^{-2}$ eV
Krypton	$(0.368) 10^{-9}$ meter	$(1.44)10^{-2}$ eV
Xenon	$(0.407) 10^{-9}$ meter	$(1.94)10^{-2}$ eV

For different gases, the Lennard-Jones potentials keep the same shape



6.

The Unrelated Casimir Fallacy

The possible dependence of the Van der Waals attraction forces on $1/r^7$ led to the Lennard-Jones empirical potential that serves to determine the energy of the Van der Waals interaction.

That dependence on $1/r^7$ was claimed for the Casimir Force Fallacy, and supported its legitimization for shallow thinkers.

But the Casimir Fallacy is due to gross misapplication of the Euler-Maclaurin summation formula.

And makes no physical sense assuming zero point energy from nowhere violating the emptiness of the vacuum.

The unrelated van der Waals interaction follows from dipole electrodynamics, and it is the only interaction depending on $1/r^7$.

7.

How the Schrödinger Equation Fails to Supply the Energy of the Van der Waals Interaction

We look at two molecules on a line: molecule 1, and molecule 2.

The distance between the centers of the molecules is

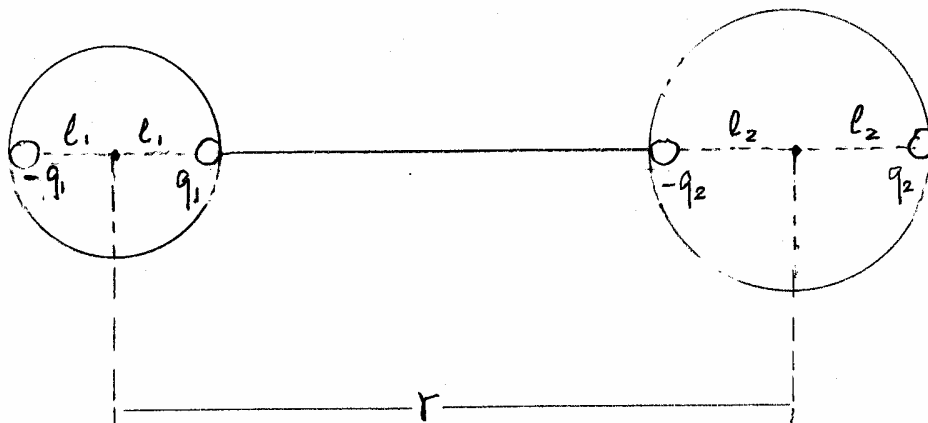
$$r.$$

The distance of electrons from the center of molecule 1 is

$$l_1$$

And the distance of electrons from the center of molecule 2 is

$$l_2.$$



The elastic restoring forces are characterized by the **unknown** spring constant

$$k,$$

which remains unknown through the proceedings.

It is crucial to the problem because the potential energy of the q_1 charge is

$$\frac{1}{2}kl_1^2$$

And the potential energy of the q_2 charge is

$$\frac{1}{2}kl_2^2$$

The dipoles mutual potential energy is another **uncertain** quantity.

It is

$$-\mu_2 E_1(r)$$

In the development that follows, it is then **assumed** that

r is much larger than the dipole sizes

so that

$$E_1(r) = 4 \frac{1}{4\pi\epsilon_0} \frac{\mu_1}{r^3}$$

This form is crucial to get dependence of the mutual dipole energy on

$$1/r^6$$

And dependence of the forces on

$$1/r^7.$$

We already seen that with such dependence the forces, and the energy vanish, cannot be distinguished from measurement errors and noise, and the treatment is irrelevant.

Under these assumptions, it is no wonder that nothing comes out of the Schrödinger equation. But to ensure that nothing saves it later, we shall proceed with that story to its end.

The potential energy is

$$\frac{1}{2}kl_1^2 + \frac{1}{2}kl_2^2 - 4\frac{1}{4\pi\epsilon_0}\frac{\mu_1\mu_2}{r^3}$$

Neglecting the motion of the nuclei, (which may be a mistake), the Schrödinger wave equation for the two molecules is

$$\frac{\partial^2\psi}{\partial l_1^2} + \frac{\partial^2\psi}{\partial l_2^2} + \frac{8\pi^2m}{h^2}\left[E - \left(\frac{1}{2}kl_1^2 + \frac{1}{2}kl_2^2 - 4\frac{1}{4\pi\epsilon_0}\frac{\mu_1\mu_2}{r^3}\right)\right] = 0.$$

We make the change of variables

$$\xi_1 = \frac{l_1 + l_2}{\sqrt{2}},$$

$$\xi_2 = \frac{l_1 - l_2}{\sqrt{2}},$$

And we define a spring parameter for molecule 1

$$k_1(r) = k - 4\frac{1}{4\pi\epsilon_0}\frac{q_1q_2}{r^3}$$

And a spring parameter for molecule 2

$$k_2(r) = k + 4\frac{1}{4\pi\epsilon_0}\frac{q_1q_2}{r^3}$$

Then, the potential energy is

$$\frac{1}{2}k_1(r)\xi_1^2 + \frac{1}{2}k_2(r)\xi_2^2$$

Indeed, $\frac{1}{2}k_1(r)\xi_1^2 + \frac{1}{2}k_2(r)\xi_2^2 =$

$$\begin{aligned} &= \frac{1}{2} \left(k - 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^3} \right) \left(\frac{l_1 + l_2}{\sqrt{2}} \right)^2 + \frac{1}{2} \left(k + 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^3} \right) \left(\frac{l_1 - l_2}{\sqrt{2}} \right)^2 \\ &= \frac{1}{2} k l_1^2 + \frac{1}{2} k l_2^2 - 4 \frac{1}{4\pi\epsilon_0} \frac{\mu_1 \mu_2}{r^3}. \end{aligned}$$

The potential energy

$$\frac{1}{2}k_1(r)\xi_1^2$$

is of oscillations with frequency

$$v_1(r) = \frac{1}{2\pi} \omega_1(r) = \frac{1}{2\pi} \sqrt{\frac{k_1(r)}{m}} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \sqrt{1 - 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}}$$

The potential energy

$$\frac{1}{2}k_2(r)\xi_2^2$$

is of oscillations with frequency

$$v_2(r) = \frac{1}{2\pi} \omega_2(r) = \frac{1}{2\pi} \sqrt{\frac{k_2(r)}{m}} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \sqrt{1 + 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}}$$

Also,

$$\frac{\partial^2 \psi}{\partial l_1^2} + \frac{\partial^2 \psi}{\partial l_2^2} = \frac{\partial^2 \psi}{\partial \xi_1^2} + \frac{\partial^2 \psi}{\partial \xi_2^2}$$

Indeed,

$$\frac{\partial \psi}{\partial l_1} = \frac{\partial \psi}{\partial \xi_1} \underbrace{\frac{\partial \xi_1}{\partial l_1}}_{1/\sqrt{2}} + \frac{\partial \psi}{\partial \xi_2} \underbrace{\frac{\partial \xi_2}{\partial l_1}}_{1/\sqrt{2}} = \frac{1}{\sqrt{2}} \left(\frac{\partial \psi}{\partial \xi_1} + \frac{\partial \psi}{\partial \xi_2} \right)$$

$$\frac{\partial}{\partial l_1} \frac{\partial \psi}{\partial l_1} = \frac{1}{\sqrt{2}} \left(\frac{\partial}{\partial l_1} \frac{\partial \psi}{\partial \xi_1} + \frac{\partial}{\partial l_1} \frac{\partial \psi}{\partial \xi_2} \right)$$

$$= \frac{1}{\sqrt{2}} \left(\frac{\partial}{\partial \xi_1} \underbrace{\frac{\partial \psi}{\partial l_1}}_{\frac{1}{\sqrt{2}} \left(\frac{\partial \psi}{\partial \xi_1} + \frac{\partial \psi}{\partial \xi_2} \right)} + \frac{\partial}{\partial \xi_2} \underbrace{\frac{\partial \psi}{\partial l_1}}_{\frac{1}{\sqrt{2}} \left(\frac{\partial \psi}{\partial \xi_1} + \frac{\partial \psi}{\partial \xi_2} \right)} \right)$$

$$= \frac{1}{2} \frac{\partial^2 \psi}{\partial \xi_1^2} + \frac{\partial^2 \psi}{\partial \xi_1 \partial \xi_2} + \frac{1}{2} \frac{\partial^2 \psi}{\partial \xi_2^2}$$

$$\frac{\partial \psi}{\partial l_2} = \frac{\partial \psi}{\partial \xi_1} \underbrace{\frac{\partial \xi_1}{\partial l_2}}_{1/\sqrt{2}} + \frac{\partial \psi}{\partial \xi_2} \underbrace{\frac{\partial \xi_2}{\partial l_2}}_{-1/\sqrt{2}} = \frac{1}{\sqrt{2}} \left(\frac{\partial \psi}{\partial \xi_1} - \frac{\partial \psi}{\partial \xi_2} \right)$$

$$\frac{\partial}{\partial l_2} \frac{\partial \psi}{\partial l_2} = \frac{1}{\sqrt{2}} \left(\frac{\partial}{\partial l_2} \frac{\partial \psi}{\partial \xi_1} + \frac{\partial}{\partial l_2} \frac{\partial \psi}{\partial \xi_2} \right)$$

$$= \frac{1}{\sqrt{2}} \left(\frac{\partial}{\partial \xi_1} \underbrace{\frac{\partial \psi}{\partial l_2}}_{\frac{1}{\sqrt{2}} \left(\frac{\partial \psi}{\partial \xi_1} - \frac{\partial \psi}{\partial \xi_2} \right)} + \frac{\partial}{\partial \xi_2} \underbrace{\frac{\partial \psi}{\partial l_2}}_{\frac{1}{\sqrt{2}} \left(\frac{\partial \psi}{\partial \xi_1} - \frac{\partial \psi}{\partial \xi_2} \right)} \right)$$

$$= \frac{1}{2} \frac{\partial^2 \psi}{\partial \xi_1^2} - \frac{\partial^2 \psi}{\partial \xi_1 \partial \xi_2} + \frac{1}{2} \frac{\partial^2 \psi}{\partial \xi_2^2}$$

Thus, the Schrödinger equation transforms into

$$\frac{\partial^2 \psi}{\partial \xi_1^2} + \frac{\partial^2 \psi}{\partial \xi_2^2} + \frac{8\pi^2 m}{h^2} \left[E - \left(\frac{1}{2} k_1(r) \xi_1^2 + \frac{1}{2} k_2(r) \xi_2^2 \right) \right] = 0$$

This equation has solution for discrete energy values

$$E_{n_1, n_2}(r) = (n_1 + \frac{1}{2})h\nu_1(r) + (n_2 + \frac{1}{2})h\nu_2(r)$$

with

$$n_1 = 0, 1, 2, 3, \dots$$

$$n_2 = 0, 1, 2, 3, \dots$$

The lowest energy is

$$E_{0,0}(r) = \frac{1}{2}h[\nu_1(r) + \nu_2(r)]$$

$$= \frac{1}{2}h \frac{1}{2\pi} \sqrt{\frac{k}{m}} \left[\left(1 - 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3} \right)^{1/2} + \left(1 + 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3} \right)^{1/2} \right]$$

To expand the square roots we need to assume that

$$1 \gg 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}$$

That is,

$$kr^3 \gg 4 \frac{1}{4\pi\epsilon_0} q_1 q_2$$

The charges q_1 , and q_2 are of the order of the electron charge which is $(1.6)10^{-19}$ *Coulomb*. Thus

$$4 \frac{1}{4\pi\epsilon_0} q_1 q_2 \approx 4 \cdot (9 \cdot 10^9) (1.6)^2 (10^{-19})^2 \approx 10^{-27}.$$

For k we have

$$k = m\omega^2 = m(2\pi\nu)^2$$

Using the electron mass which is about 10^{-30} *kg*,

and electron frequency of about $(6.57) \cdot 10^{15}$ *cycles/sec*¹,

$$k \approx 10^{-30} 4\pi^2 43 \cdot 10^{30} \approx 1700$$

¹ [Zero Point Energy, and the Charge-Radiation Equation in Bohr's Atom](#)

Therefore, we need to have

$$r^3 \gg \frac{1}{1700} 10^{-27}$$

$$r \gg \frac{1}{12} 10^{-9}$$

$$r \approx 100 \frac{1}{12} 10^{-9} \approx 10^{-8}$$

But we already seen here that the force and energy may vanish at

$$r \approx 2 \cdot 10^{-9}.$$

Nevertheless, assuming that

$$1 \gg 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}$$

$$\left(1 - 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}\right)^{1/2} \approx 1 + \frac{1}{2} \left(-4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}\right) - \frac{1}{8} \left(-4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}\right)^2$$

$$\left(1 + 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}\right)^{1/2} \approx 1 + \frac{1}{2} 4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3} - \frac{1}{8} \left(4 \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{kr^3}\right)^2$$

Hence,

$$E_{0,0}(r) = \frac{1}{2} h [v_1(r) + v_2(r)]$$

$$\approx \frac{1}{2} h \frac{1}{2\pi} \sqrt{\frac{k}{m}} \left[1 - 4 \frac{1}{(4\pi\epsilon_0)^2} \frac{(q_1 q_2)^2}{k^2} \frac{1}{r^6} \right]$$

All those assumptions to propose that the interaction energy of the attractive van der Waals forces may depend on $1/r^6$, in a range where the forces and energy vanish.

This was done first by Wang. Then, “improved” by F. London.

Chemistry books credit London for giving the ultimate explanation to the Van der Waals interaction.

We proceed to examine London's papers

8.

Eisenschitz and London (1929)

The Abstract of the paper declares

“A systematic perturbation method which brings the homopolar and the Van der Waals forces into a unified relation is developed.

The method is applied to determine the van der Waals constants”

The paper attempts to improve upon speculations by Wang who tried to obtain the interaction energy of the van der Waals forces from the Schrödinger equation for the Hydrogen molecules.

Wang (1927) speculated that the interaction potential was

$$-8.7 \frac{e^2 a_0^5}{r^6}$$

Eisenschitz and London (1929) speculated that the constant is

$$-6.47$$

As we already noted, these results apply to ranges r where the force and the energy vanish.

To get an idea about their treatment, look at page 356.

In equation (52), they **assume**

$$\frac{3}{4} < \beta < 1.$$

After equation (55), they **assume**

$$\beta = 0.925,$$

about which they say

This value is where it would be expected.

***It has been used in the numerical calculation of
(53)...***

In other words, they assume the result.

They proceed to speculate with distances of

$$2.5a_0, \text{ and } 1.5a_0$$

where a_0 is the Bohr radius of the Hydrogen Atom.

The formula applies to large distances, and does not apply to these small distances

9.

London (May 1930)

London's papers are described by Chemistry textbooks as elucidating the van der Waals forces with the help of Quantum Mechanics.

According to London, the elucidation does not happen in his May 1930 paper.

The Abstract admits that the 1929 paper that followed Wang's use of the Schrödinger equation failed to support a theory of the van der Waals forces.

Namely, the abstract states that

"...The purely theoretical determination of the molecular forces, which have to be treated as perturbational effects of second order, is hardly manageable..."

London cites measurement as the way to describe the van der Waals interaction

"Instead, the forces can be estimated from optical measurements through their theoretical relation with the f -values of the dispersion formula"

More admission of the failure of Wang-London theory to explain the empirical data follows in page 379:

“... For H Atoms, where the force field is known, ...we find that the correct value deviated by 50% from the one calculated based on these simplifications...”

At this point, it is clear that he has nothing to write about. But he concludes

“...we are therefore not too unreasonable if we assume an uncertainty of 50% in our calculations...”

And his assumptions abound. For instance look at p. 389

“...we assume that for a suitable choice of R a number of eigenvalues

$$\epsilon_{\rho_1}^{(0)}, \epsilon_{\rho_2}^{(0)}, \dots, \epsilon_{\rho_f}^{(0)}$$

lie so close to

$$\epsilon_k^{(0)} \equiv \epsilon_{\rho_0}^{(0)}$$

that

$$\epsilon_{\rho_i}^{(0)} - \epsilon_k^{(0)}$$

is of the same order of magnitude as

$$V_{\rho_i k}$$

What is the meaning of this assumption?

Overwhelmed by his very general setup, London is attempting to shift down, and get formulas a little more manageable.

It would be much preferable had London's paper never been published, enabling people who never read it to promote this 50% uncertain writings as elucidation of the van der Waals forces.

10.

London (November, 1930)

This paper promotes a phenomenological approach to intermolecular forces.

The Abstract says

“The attraction forces between molecules can ...entirely be determined from ...a dispersion curve, and so from purely optical data...”

London denies that the forces are electrical, or chemical valence relations

“The forces obtained (empirically) from the dispersion curve, in abrupt disagreement with the electrostatic, and valency type forces...”

London considers the forces to have no source, and compares them with gravitation

“...have the properties of a general cohesion, an attraction force comparable to the gravitational force, which takes place between many molecules simultaneously...”

Clearly, the comparison of the short range van der Waals forces that empirically depends on $1/r^7$, with the long range

gravitational force that depends on $1/r^2$, exhibits London incomprehension of physics.

In particular, the short range van der Waals forces are not to be treated as forces between one molecule, and clouds of molecules.

In addition, in 1930, London was unaware of the 1925 Lennard-Jones empirical potential that accounts for the repulsion between molecules.

Instead of Lennard-Jones repulsion term that depends on $1/r^{12}$, London says

*“...The precision of the agreement is always within the limits given by the uncertainty of the used data and **the lack of knowledge of the repulsive forces.**”*

The paper attempts to supply plausibility arguments for empirical data, and was outdated in 1930, after the 1925 Lennard-Jones empirical potential.

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