

Intermolecular Potentials

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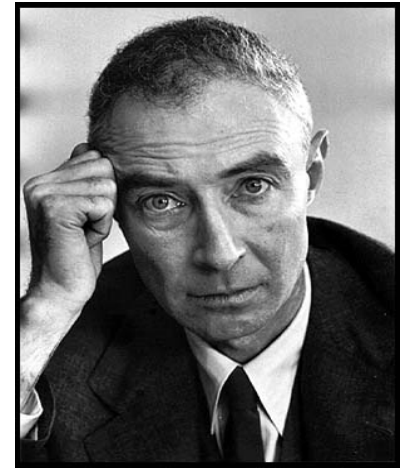
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<http://www.jncasr.ac.in/bala>



Born-Oppenheimer approximation



N nuclei, N_e electrons

$\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{P}_1, \dots, \mathbf{P}_N, M_1, \dots, M_N$

$\mathbf{r}_1, \dots, \mathbf{r}_{N_e}, \mathbf{p}_1, \dots, \mathbf{p}_{N_e}$

$$H = \sum_{I=1}^N \frac{\mathbf{P}_I^2}{2M_I} + \sum_{i=1}^{N_e} \frac{\mathbf{p}_i^2}{2m} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|}$$

$$\equiv T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})$$

Find out the solution of the time-independent Schroedinger equation:

$$[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})] \Psi(\mathbf{x}, \mathbf{R}) = E \Psi(\mathbf{x}, \mathbf{R})$$

Separation of time scales of electronic & nuclear motion

$$M_p / M_e = 1836$$

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi(\mathbf{x}, \mathbf{R}) \chi(\mathbf{R})$$

$$\mathbf{X} \equiv (\mathbf{r}, \mathbf{s})$$

BO continued...

Electrons can be treated as particles which follow the nuclear motion, adiabatically

As the nuclei move, the electrons are dragged along, with *no* lag

Assume classical dynamics for the nuclei. The nuclei are considerably more localized than the electrons, i.e., nuclear wave functions are much steeper than the electronic ones.

$$\nabla_I \chi(\mathbf{R}) \gg \nabla_I \phi(\mathbf{x}, \mathbf{R})$$

So,

$$\begin{aligned} T_N \phi(\mathbf{x}, \mathbf{R}) \chi(\mathbf{R}) &= -\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \left[\phi(\mathbf{x}, \mathbf{R}) \nabla_I^2 \chi(\mathbf{R}) \right. \\ &+ \left. \chi(\mathbf{R}) \nabla_I^2 \phi(\mathbf{x}, \mathbf{R}) + 2 \nabla_I \phi(\mathbf{x}, \mathbf{R}) \nabla_I \chi(\mathbf{R}) \right] \\ &\approx -\frac{\hbar^2}{2} \sum_I \frac{1}{M_I} \left[\phi(\mathbf{x}, \mathbf{R}) \nabla_I^2 \chi(\mathbf{R}) \right] \end{aligned}$$

$$[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})] \Psi(\mathbf{x}, \mathbf{R}) = E \Psi(\mathbf{x}, \mathbf{R})$$

With this approximation, the eigenvalue equation becomes

$$\frac{[T_e + V_{ee}(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R})] \phi(\mathbf{x}, \mathbf{R})}{\phi(\mathbf{x}, \mathbf{R})} = E - \frac{[T_N + V_{NN}(\mathbf{R})] \chi(\mathbf{R})}{\chi(\mathbf{R})}$$

LHS can be a function of only \mathbf{R} . Let it be $\varepsilon(\mathbf{R})$

$$[T_e + V_{ee}(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R})] \phi(\mathbf{x}, \mathbf{R}) = \varepsilon(\mathbf{R}) \phi(\mathbf{x}, \mathbf{R})$$

This is an eigenvalue equation for the electronic Hamiltonian,

$$H_e(\mathbf{R}) = T_e + V_{ee}(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R})$$

The eigenvalues and eigenfunctions are $\varepsilon_n(\mathbf{R})$ and $\phi_n(\mathbf{x}, \mathbf{R})$

For each solution of the electronic problem, there is a nuclear eigenvalue equation:

$$[T_N + V_{NN}(\mathbf{R}) + \varepsilon_n(\mathbf{R})] \chi(\mathbf{R}) = E \chi(\mathbf{R})$$

Born-Oppenheimer surface

$$[T_N + V_{NN}(\mathbf{R}) + \varepsilon_n(\mathbf{R})] \chi(\mathbf{R}) = E \chi(\mathbf{R})$$

Inter-nuclear potential

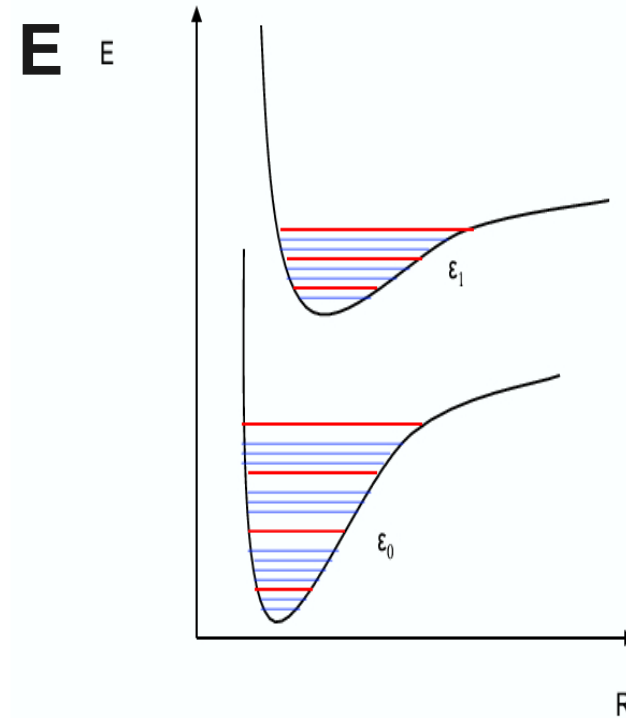
Each electronic eigenvalue $\varepsilon_n(\mathbf{R})$ is an electronic surface

Such surfaces are called BO surfaces

When we solve the nuclear eigenvalue equation in each surface, we obtain rotational and vibrational levels

Excitations across surfaces are non-adiabatic and are not considered here

$$|\varepsilon_1(\mathbf{R}) - \varepsilon_0(\mathbf{R})| \gg kT$$



Potential: Expansion

$$U_{tot}(\{\mathbf{r}\}) = U_0 + U_1(\mathbf{r}_i) + U_2(\mathbf{r}_i, \mathbf{r}_j) \\ + U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + U_4(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_\ell) + \dots$$

U_0 : Some constant potential energy

U_1 : External potential depending on coordinate (gravitation)

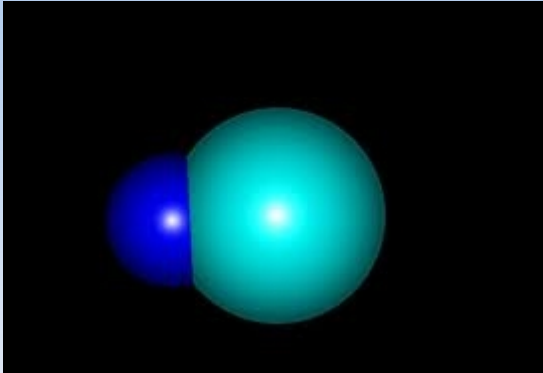
U_2 : Two body

U_3 : Three body

Configuration Integral

$$\begin{aligned} Z(N, V, T) &= \frac{h^{-3N}}{N!} \int d\mathbf{p}^N \int_V d\mathbf{r}^N \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] \\ &= \frac{h^{-3N}}{N!} \int d\mathbf{p}^N \exp[-\beta K_N(\mathbf{p}^N)] \int_V d\mathbf{r}^N \exp[-\beta U_N(\mathbf{r}^N)] \\ &= \frac{\Lambda^{-3N}}{N!} \int_V d\mathbf{r}^N \exp[-\beta U_N(\mathbf{r}^N)] \\ &= Z^{id}(N, V, T) V^{-N} \int_V d\mathbf{r}^N \exp[-\beta U_N(\mathbf{r}^N)] \end{aligned}$$

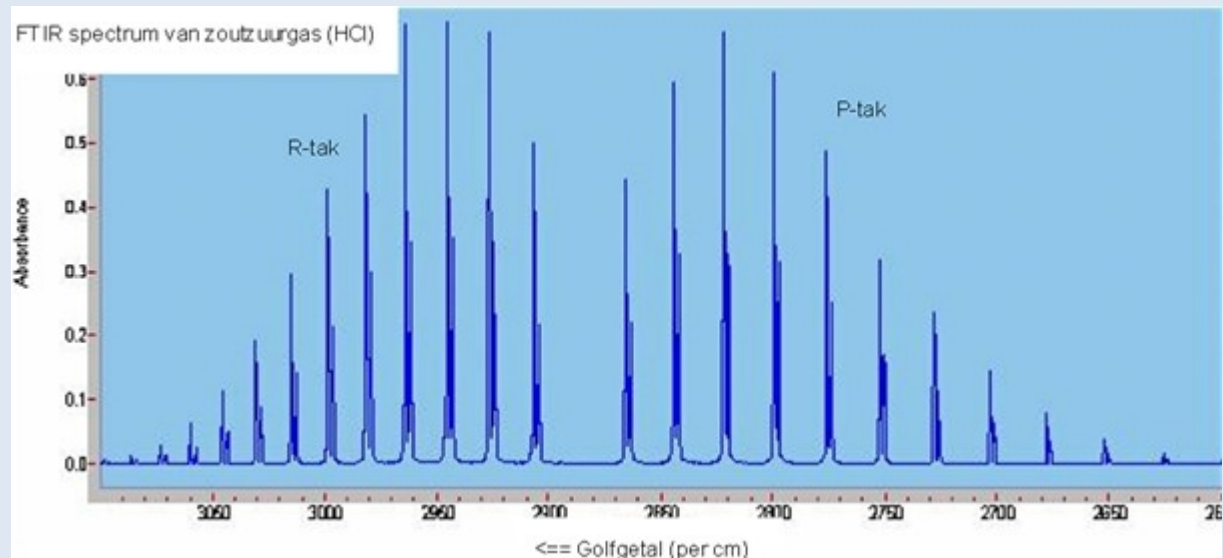
Infrared spectrum



HCl

Equilibrium bond length = 0.1274 nm

$$1/\lambda = 2886 \text{ cm}^{-1}$$



1-d harmonic oscillator

$$U(x) = \frac{1}{2}kx^2$$

$$F(x) = -\frac{\partial U}{\partial x} = -kx$$

$$\omega = \sqrt{\left(\frac{k}{m}\right)}$$

$$T = \frac{1}{\nu} = 2\pi/\omega = 2\pi\sqrt{\left(\frac{m}{k}\right)}$$

Time step

Let $k=1$, $m=1$. So, $T = 2\pi = 6.28$

Time step has to be much smaller than the time period

Given $\{x(0), v(0)\}$, how do we obtain $\{x(t), v(t)\}$

Get $F(0)$

$$v = v + dt * F / 2m$$

$$x = x + v * dt$$

$$v = v + dt * F / 2m$$

velocity Verlet

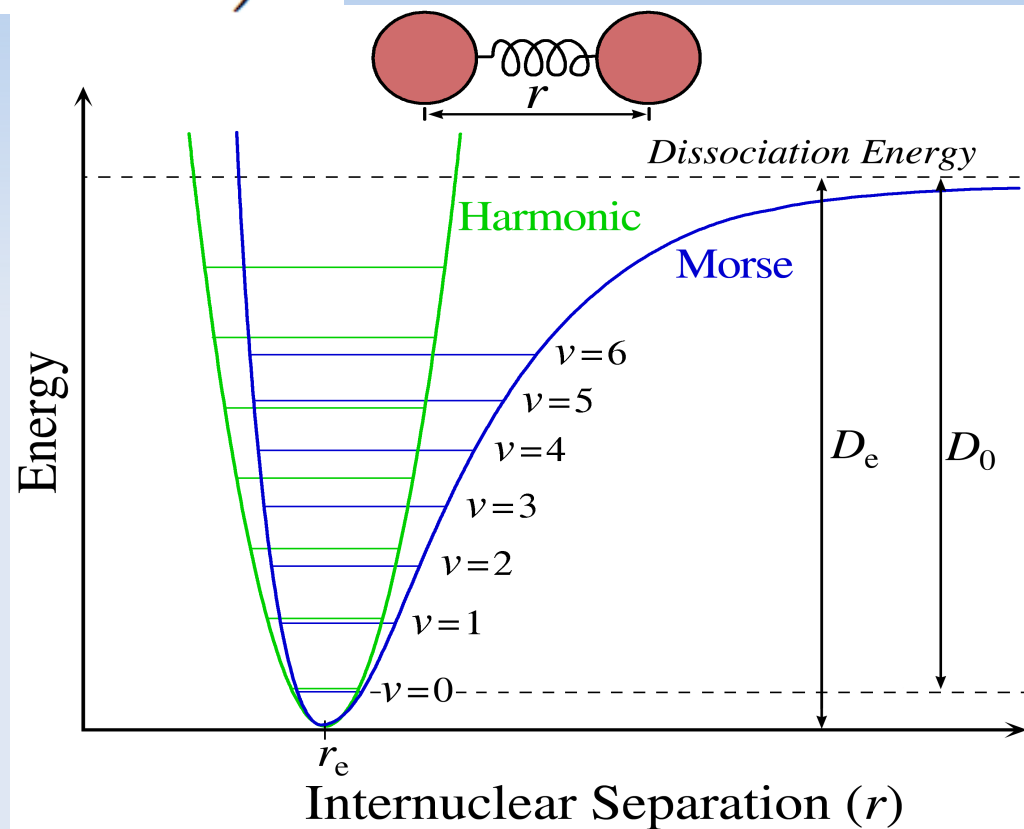
Morse oscillator



$$U(r) = D_e \left(1 - e^{-a(r-r_e)} \right)^2$$

$$a = \sqrt{\frac{k_e}{2D_e}}$$

$$\nu_0 = \frac{a}{2\pi} \sqrt{\frac{2D_e}{m}}$$

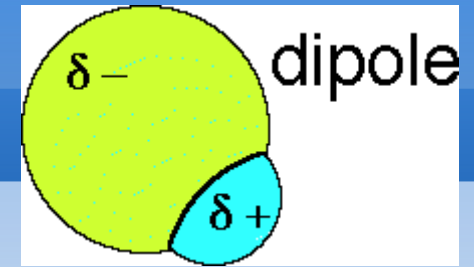


$$E(v+1) - E(v) = h\nu_0 - (v+1) \frac{(h\nu_0)^2}{2D_e}$$

Limitations

- Although "dissociation is allowed", this isn't quantum mechanics
- If the molecule gets associated (say, forms a hydrogen bond) with another molecule, the bond frequency should show a red shift. This will not happen with harmonic/Morse potentials
- Force constants, equilibrium length are temperature independent. Really?
- Rotational-vibrational coupling terms need to be added

More on HCl



- HCl has a permanent dipole moment, 1.03 D
- $1\text{D} = 0.208194\text{ eA}$ $l=0.1274\text{A}$
- Since $\mu=qd$, $q= 0.168e$. This is the magnitude of charge that should be present on hydrogen and chlorine, to yield the dipole moment of HCl
- If one modelled a bunch of HCl molecules as containing two atoms and the potential as due to harmonic bonds and point charges, it will lead to an unphysical situation.

Q: What?

Size

- The size of an atom is a parameter describing its mean spatial extent
- It captures the distance over which the atom exerts its influence
- Size is a scalar variable; hence the influence is assumed to be radial
- Since the nature of the influence can depend on the environment (what is the nature of the second atom?), the size of a given atom can change depending on the environment
- Size is captured variously as "ionic radius", "van der Waals radius", "covalent radius" etc..

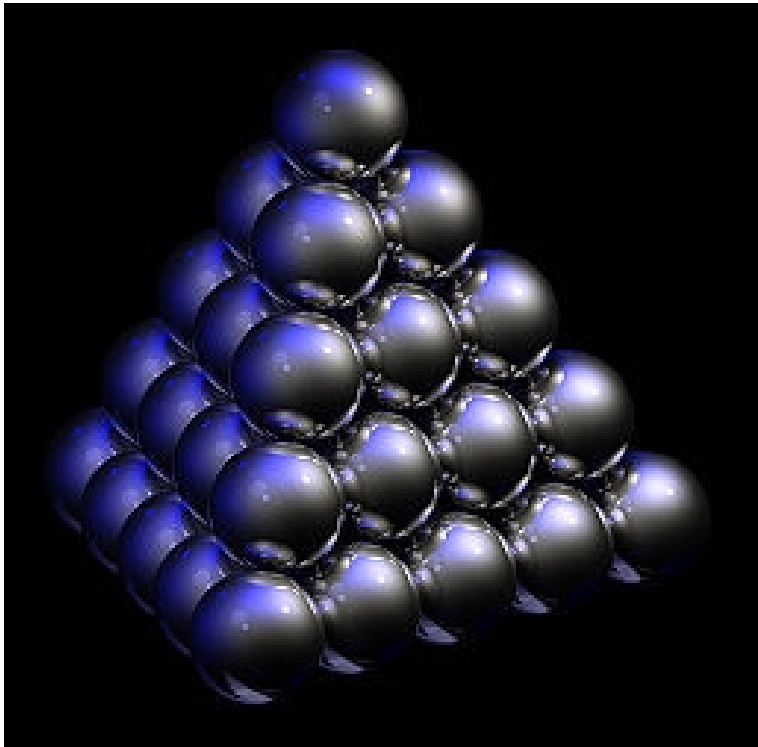
Moral: We have to somehow add size of an atom into the potential for HCl

Noble solids

Although vdW interactions are present between any atoms/molecules, it is the only one present for atoms of noble gases.



vdW is all I got

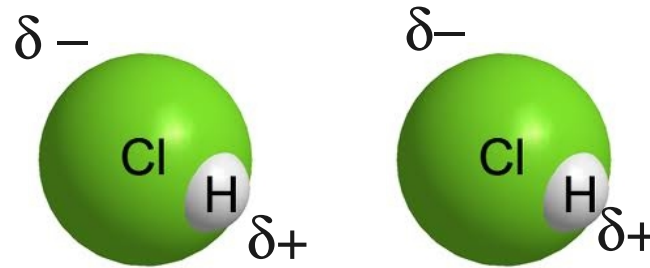


Atoms of all noble gases form solids in this arrangement only

What makes them stick together in this fashion is the van der Waals interaction between the atoms

van der Waals forces

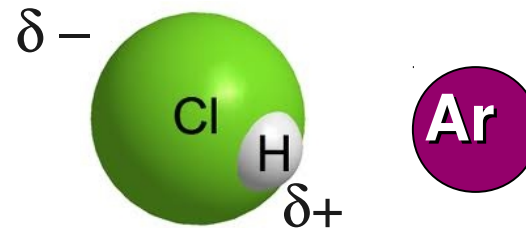
Dipole-dipole
(Keesom, 1912)



Dutch



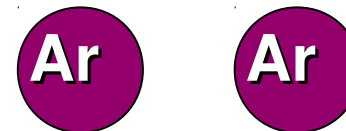
Dipole-induced dipole
(Debye, 1912)
(Nobel Chemistry 1936)



Dutch



Induced dipole-induced dipole
(London, 1927)

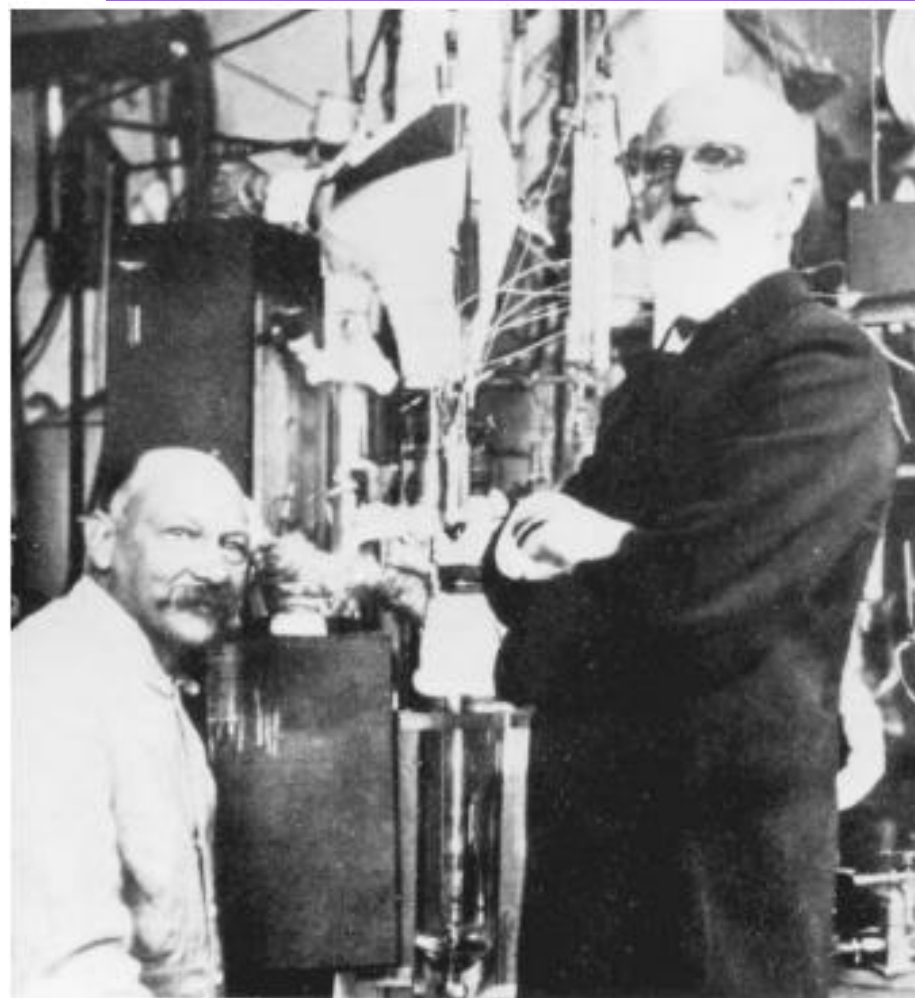


↑
Omnipresent

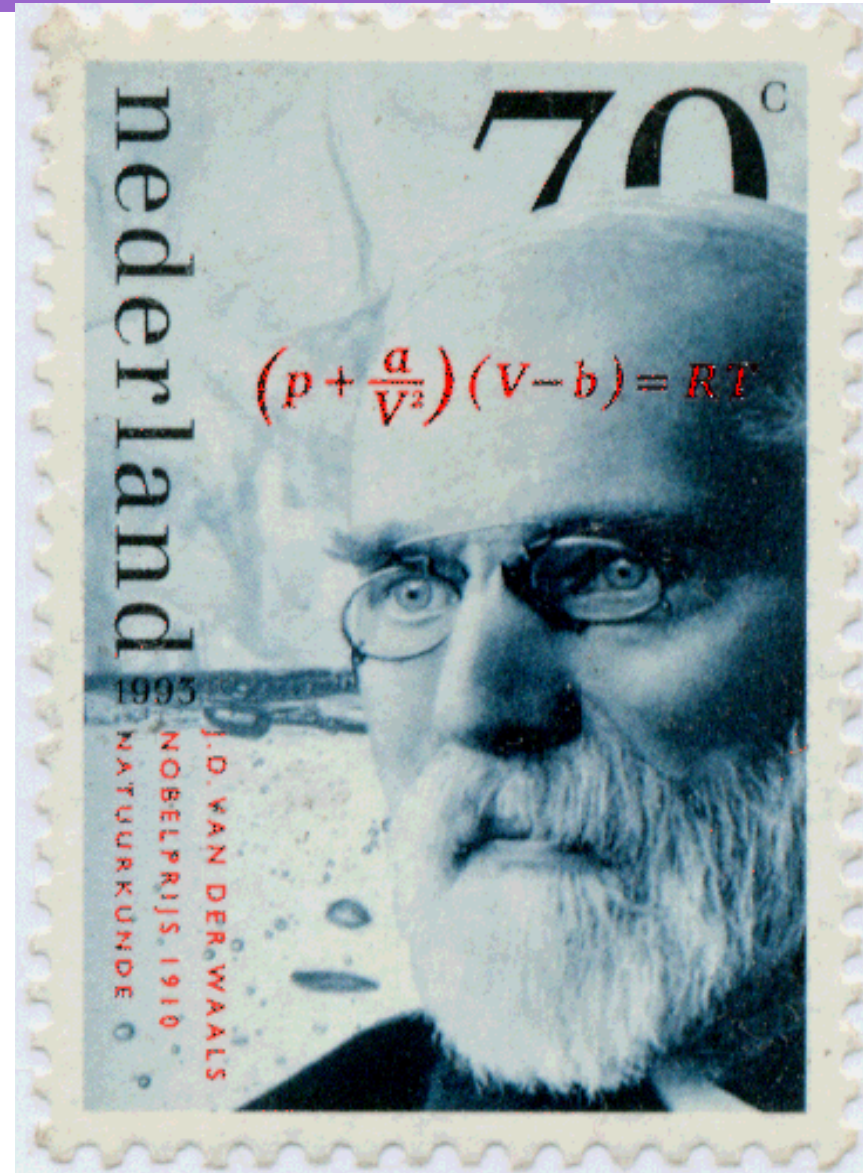
German



Johannes Diderik van der Waals



Nobel prize in Physics, 1910
Law of corresponding states



1837-1923

Who am I? Identify

van der Waals forces

The attractive or repulsive forces between molecular entities (or between groups within the same molecular entity) other than those due to bond formation or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules.

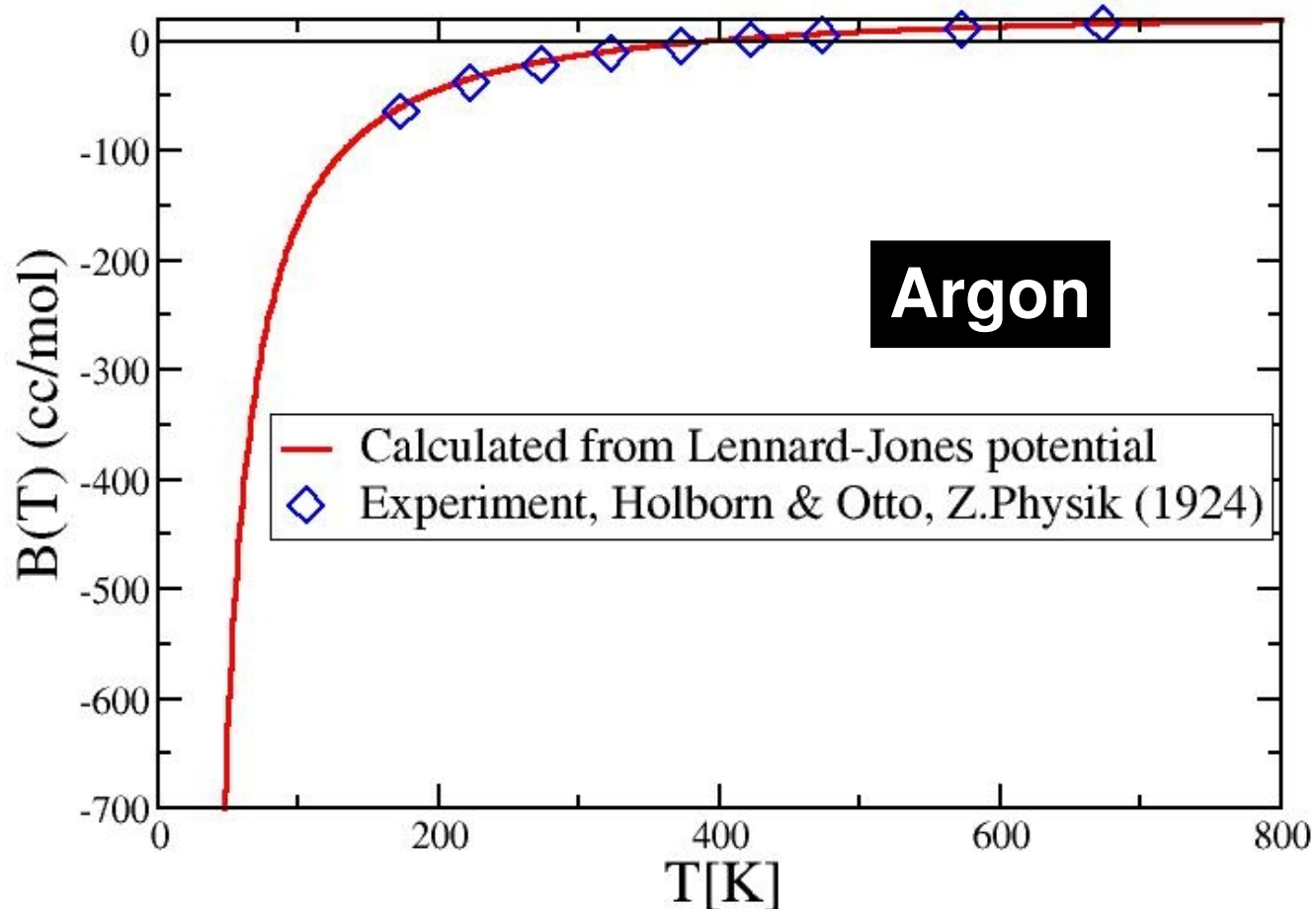
The term includes: dipole–dipole, dipole-induced dipole and London (instantaneous induced dipole-induced dipole) forces. The term is sometimes used loosely for the totality of nonspecific attractive or repulsive intermolecular forces.

Source: <http://goldbook.iupac.org/V06597.html>

Second virial coefficient

$$\frac{P}{nRT} = \rho + B(T)\rho^2 + C(T)\rho^3 + \dots$$

$$B(T) = 2\pi N_A \int_0^\infty r^2 \left[1 - e^{-U(r)/k_B T} \right] dr$$



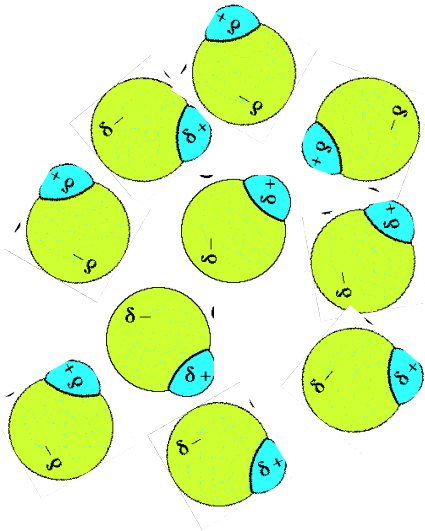
Total Potential energy

$$U_{tot}(\{\mathbf{r}\}) = \sum_{\substack{\text{bonded} \\ i}} U_{harm}(r_{ij}) + \sum_{\substack{\text{non-bonded} \\ i < j}} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

$$+ A_{ij} e^{-\frac{(r_{ij} - \sigma_{ij})}{\rho_{ij}}} - \frac{B_{ij}}{r_{ij}^6} \quad \text{Dispersion}$$

Size
Empirical form

The form has basis in
2nd order perturbation
theory



Bunch of HCl molecules

$\sigma \rightarrow$ size

$\rho \rightarrow$ range of repulsion

The molecules are assumed to be non-polarizable