# van der Waals interaction in H₂ molecules
Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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In physical chemistry, the **van der Waals force** (or **van der Waals' interaction**), named after Dutch scientist Johannes Diderik van der Waals, is the sum of the attractive or repulsive forces between molecules (or between parts of the same molecule) other than those due to covalent bonds, or the electrostatic interaction of ions with one another, with neutral molecules, or with charged molecules.

The van der Waals forces between two neutral atoms arise from the interactions between the induced dipole moments. We wish to evaluate them in the case of two hydrogen atoms in their ground states. In order to do this we use second-order perturbation theory.

1. Origin of the van der Waals interaction
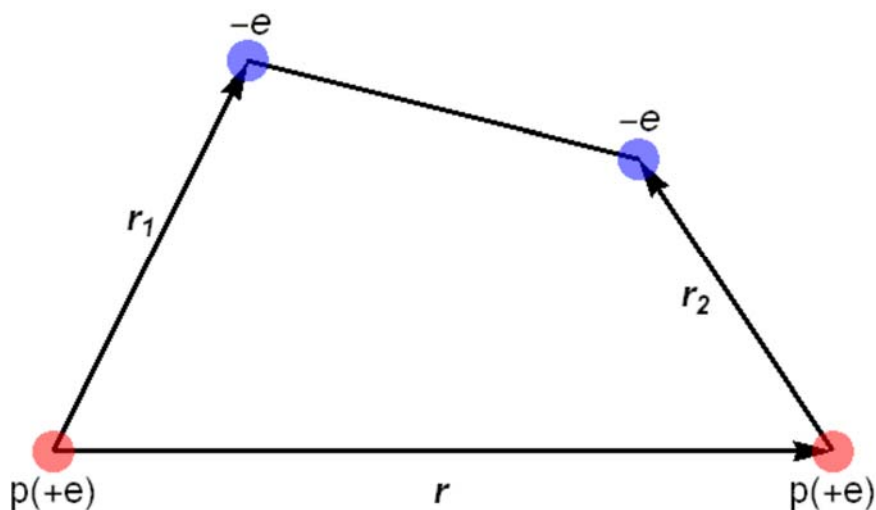
We consider the two protons of the hydrogen atoms to be fixed at a distance r (along the z axis) with r_1 the position vector from the first proton to its electron, and r_2 the position vector from the second proton to its electron.

The Hamiltonian $\hat{H}$ can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_1.$$

The unperturbed Hamiltonian:

$$\hat{H}_0 = \hat{H}_{01} + \hat{H}_{02}$$

$$\hat{H}_{01} = \frac{1}{2m}\hat{p}_1{}^2 - \frac{e^2}{|\hat{r}_1|}, \qquad\qquad \hat{H}_{02} = \frac{1}{2m}\hat{p}_2{}^2 - \frac{e^2}{|\hat{r}_2|}$$

The perturbing Hamiltonian:

$$\hat{H}_1 = \frac{e^2}{|\hat{r}|} + \frac{e^2}{|\hat{r} + \hat{r}_2 - \hat{r}_1|} - \frac{e^2}{|\hat{r} + \hat{r}_2|} - \frac{e^2}{|\hat{r} - \hat{r}_1|}.$$

The lowest-energy solution of $\hat{H}_0$ is simply the product of the ground-state wave functions of the non-interacting hydrogen atoms. For large r, we expand the perturbation in powers of $1/r$ to obtain

$$\hat{H}_1 = \frac{e^2}{|\hat{r}|^3}(\hat{x}_1\hat{x}_2 + \hat{y}_1\hat{y}_2 - 2\hat{z}_1\hat{z}_2) + O\!\left(\frac{1}{r^4}\right).$$

The lowest-order r^{-3} term corresponds to the interaction of two electric dipoles $-e r_1$ and $-e r_2$ separated by r.

((Mathematica))

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A1 = {x2 - x1, y2 - y1, z2 - z1 + r}; B1 = {x2, y2, z2 + r};
C1 = {-x1, y1, r - z1};

f1 = 1/r + 1/Sqrt[A1.A1] - 1/Sqrt[B1.B1] - 1/Sqrt[C1.C1] /. r -> 1/x;

Series[f1, {x, 0, 4}] // Simplify
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$(x1\ x2 + y1\ y2 - 2\ z1\ z2)\ x^3 + \dfrac{3}{2}$

$\left(-x2^2\ z1 + 2\ y1\ y2\ z1 - y2^2\ z1 + 2\ x1\ x2\ (z1 - z2) + x1^2\ z2 + \right.$

$\left. y1^2\ z2 - 2\ y1\ y2\ z2 - 2\ z1^2\ z2 + 2\ z1\ z2^2\right)\ x^4 + O[x]^5$

The ground state of $\hat{H}_0$ is just the product of the ground state of electrons 1 and 2,

$$\left|\Psi_0^{(0)}\right\rangle = |1s\rangle_1|1s\rangle_2,$$

with

$$\left|1s\right\rangle = \left|n = 1, l = 0, m = 0\right\rangle .$$

The first-order correction to the ground state energy:

$$E_0^{(1)} = \left\langle \Psi_0^{(0)}\left|\hat{H}_1\right|\Psi_0^{(0)}\right\rangle = 0 .$$

The second-order correction to the ground state energy:

$$\hat{H}_0\left|\Psi_0^{(0)}\right\rangle = 2E_1\left|\Psi_0^{(0)}\right\rangle ,$$

$$E_0^{(2)} = \sum_{k\neq 0}\frac{\left|\left\langle \Psi_k^{(0)}\left|\hat{H}_1\right|\Psi_0^{(0)}\right\rangle\right|^2}{E_0^{(0)} - E_k^{(0)}}$$

$$\approx \frac{1}{2E(1s)}\sum_k\left\langle \Psi_0^{(0)}\left|\hat{H}_1\right|\Psi_k^{(0)}\right\rangle\left\langle \Psi_k^{(0)}\left|\hat{H}_1\right|\Psi_0^{(0)}\right\rangle$$

$$= \frac{1}{2E(1s)}\left\langle \Psi_0^{(0)}\left|\hat{H}_1^2\right|\Psi_0^{(0)}\right\rangle$$

where we use the closure relation, and

$$\hat{H}_0\left|\Psi_0^{(0)}\right\rangle = 2E(1s)\left|\Psi_0^{(0)}\right\rangle ,$$

with

$$\left|\Psi_0^{(0)}\right\rangle = \left|1s\right\rangle_1\left|1s\right\rangle_2 ,$$

$$E_0^{(0)} = 2E(1s) = 2(-\frac{e^2}{2a_B}) = -\frac{e^2}{a_B} .$$

The use of this approximation allows one to take into no account of the detail of the form in the two-particle wave functions of the excited state $\left|\Psi_k^{(0)}\right\rangle$.

$$E_0^{(2)} = \frac{1}{2E(1s)}\frac{e^4}{r^6}\left\langle \Psi_0^{(0)}\left|(\hat{x}_1\hat{x}_2 + \hat{y}_1\hat{y}_2 - 2\hat{z}_1\hat{z}_2)^2\right|\Psi_0^{(0)}\right\rangle .$$

In the term $(\hat{x}_1\hat{x}_2 + \hat{y}_1\hat{y}_2 - 2\hat{z}_1\hat{z}_2)^2$, the cross terms will have expectation values of zero. The ground state wave function is symmetric, so all we need is

$$\langle 1s | \hat{x}^2 | 1s \rangle = a_0^2,$$

where a_0 is the Bohr radius, and

$$(\hat{x}_1 \hat{x}_2 + \hat{y}_1 \hat{y}_2 - 2\hat{z}_1 \hat{z}_2)^2 = \hat{x}_1^2 \hat{x}_2^2 + \hat{y}_1^2 \hat{y}_2^2 + 4\hat{z}_1^2 \hat{z}_2^2 + \ldots..$$

Then we have

$$E_0^{(2)} = \frac{1}{2E(1s)} \frac{e^4}{r^6} 6a_B^4 = -\frac{6e^2}{r} \left(\frac{a_B}{r} \right)^5.$$

Thus $1/r^6$ long-range attractive van der Waals' potential is a general property of the interaction between two atoms in the ground state.

2. Phase transition of van der Waals gas
2.1 van der Waals equation
The simplest model of a liquid-gas phase transition is that of van der Waals.

$$(P + \frac{N^2 a}{V^2})(V - Nb) = Nk_B T \qquad \text{(van der Waals equation of state)},$$

or more simply

$$(P + \frac{a}{v^2})(v - b) = k_B T, \qquad (1)$$

where $v = \dfrac{V}{N}$, a is a measure of the long range attractive part of the interaction between two molecules, and b is a measure of their short range repulsion. The parameters for the critical point $(T = T_c, P = P_c, \text{ and } v = v_c)$ can be determined from the conditions that

$$\left(\frac{\partial P}{\partial v} \right)_T = 0, \qquad \left(\frac{\partial^2 P}{\partial v^2} \right)_T = 0,$$

in addition to Eq,(1). From the condition $\left(\dfrac{\partial P}{\partial v} \right)_T = 0$, we get

$$\frac{2a}{v^3} - \frac{k_B T}{(v - b)^2} = 0. \qquad (2)$$

From the condition $\left(\dfrac{\partial^2 P}{\partial v^2}\right)_T = 0$, we get

$$\dfrac{-3a}{v^4} + \dfrac{k_B T}{(v-b)^3} = 0.\qquad(3)$$

From Eqs.(1) - (3), we have

$$P_c = \dfrac{a}{27b^2}, \qquad v_c = 3b, \qquad T_c = \dfrac{8a}{27k_B b}$$

Note that

$$P_c v_c = \dfrac{3}{8} k_B T_c$$

or

$$P_c (N_A v_c) = \dfrac{3}{8} k_B N_A T_c = \dfrac{3}{8} R T_c$$

$$a = \dfrac{27 k_B^2 T_c^2}{64 P_c} = \dfrac{1}{N_A^2} \dfrac{27 R^2 T_c^2}{64 P_c} \qquad\qquad b = \dfrac{k_B T_c}{8 P_c} = \dfrac{1}{N_A} \dfrac{R T_c}{8 P_c}$$

$$\dfrac{a}{b} N_A = \dfrac{\dfrac{27 R^2 T_c^2}{64 P_c}}{\dfrac{R T_c}{8 P_c}} = \dfrac{27}{8} R T_c$$

Here we define the dimensionless variables by

$$p_r = \dfrac{P}{P_c}, \qquad v_r = \dfrac{v}{v_c}, \qquad t_r = \dfrac{T}{T_c}.$$

Then the van der Waals equation can be rewritten as

$$(p_r + \dfrac{3}{v_r^2})(v_r - \dfrac{1}{3}) = \dfrac{8}{3} t_r \qquad \Rightarrow \text{Law of corresponding states.}$$

In terms of p_r, v_r, t_r, all gases look like - if they obey the van der Waals equation.
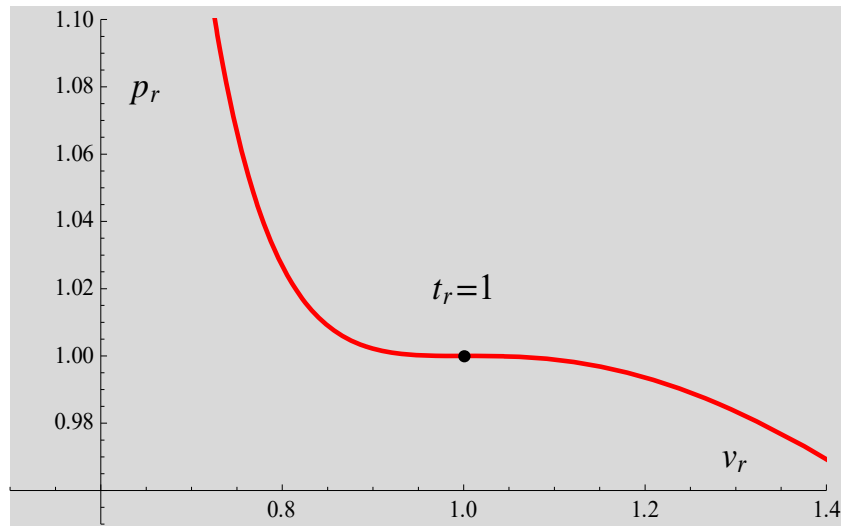

Fig. p_r vs v_r at $t_r = 1$. Critical point ($p_r = 1$ and $v_r = 1$).

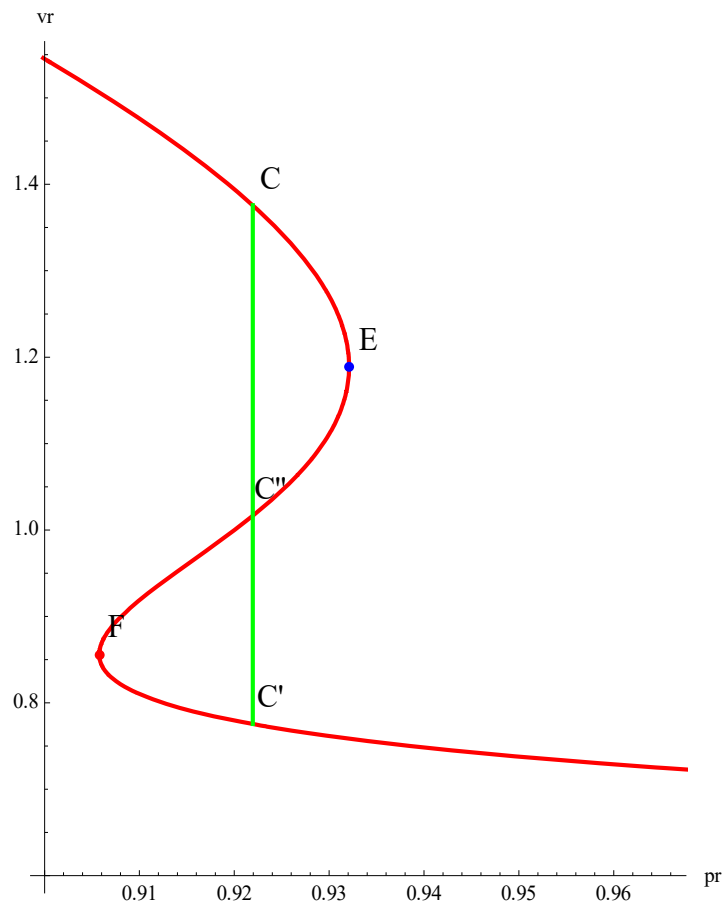## 2.2 Example: $t_r = 0.98$

Fig. p_r vs v_r for $t_r = 0.98$. The line CC'C" (the green line) is the coexistence line. The path EC"F is metastable. The path CE and the path FC' is unstable. The area enclosed by CEC" is the same as that by C"FC' (Maxwell's construction). $p_r(C) = 0.921921$. $v_r(C') = 0.775539$. $v_r(C) = 1.3761$.
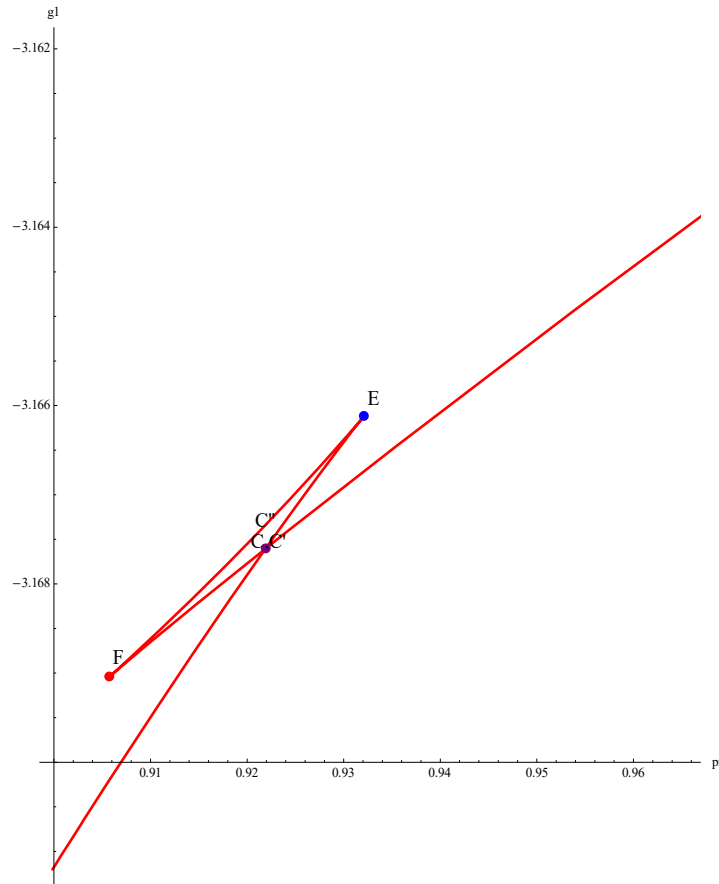

Fig. The Gibbs energy g (in the units of a/b) vs p_r for $t_r = 0.98$. The path EC"F is metastable. The shape of the EC"F is similar to spine (the spinodal decomposition). The path CE and the path FC' is unstable.
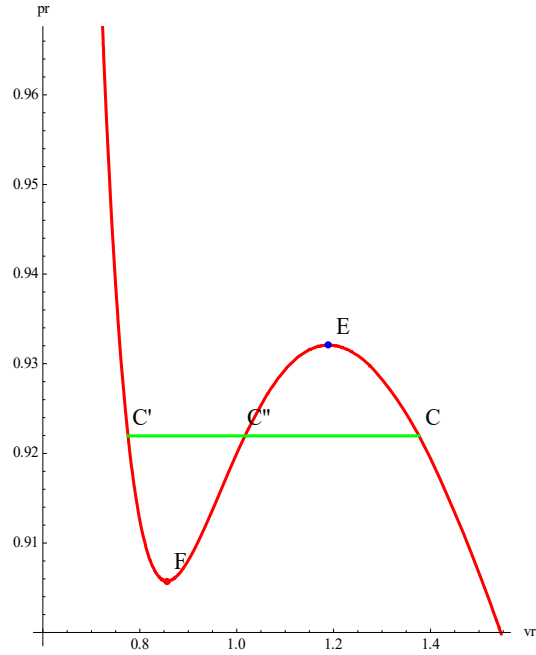
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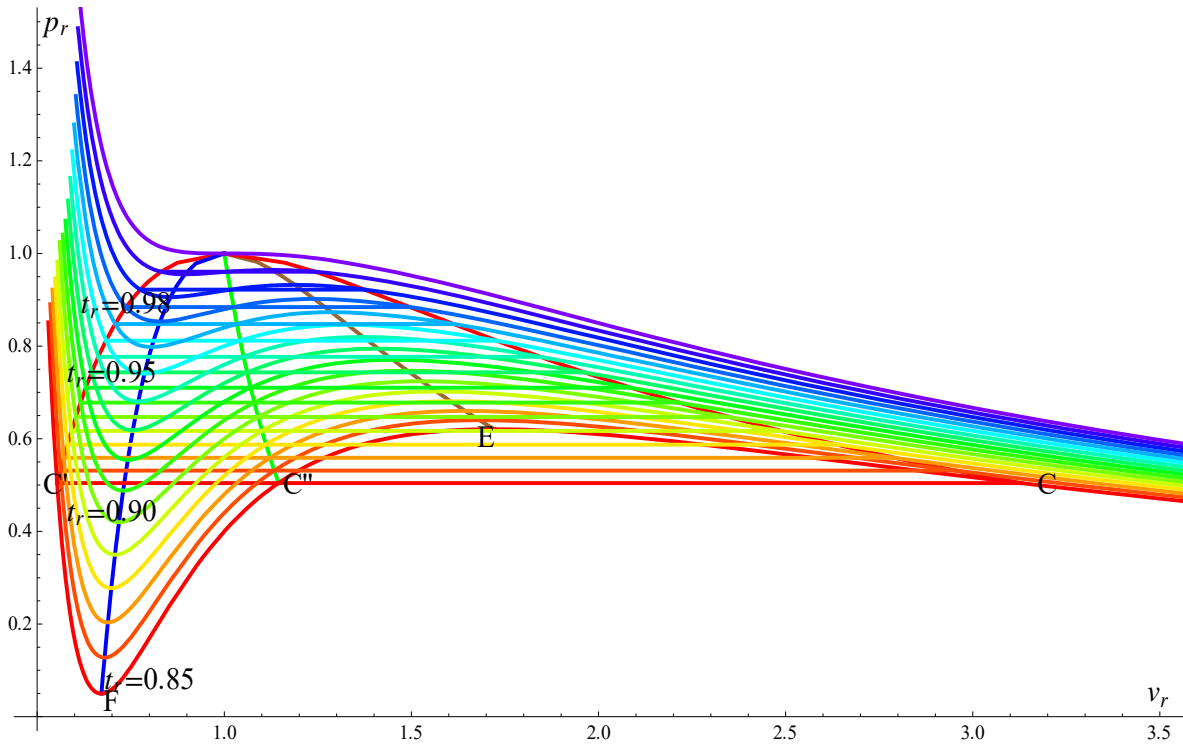
2.3. Maxwell's construction

Fig. Tthe p_r-v_r plane an isotherm of the liquid and gas. t_r(<1) is changed as a parameter.

Let us plot the p_r-v_r plane an isotherm of the liquid and gas. According to the thermodynamic inequality

$$\left(\frac{\partial p_r}{\partial v_r}\right)_{t_r} < 0,$$

p_r is a decreasing function of v_r. The segments C'F and EC of the isotherms correspond to metastable superheated liquid (C'F) and supercooled vapor (EC), in which the thermodynamic inequality is still satisfied. A complete-equilibrium isothermal change of state between the points C' and C corresponds to the horizontal segment C'C''C, on which separation into two phases occur. If we use the fact that the points C' and C have the same ordinate p_r, it is clear that the two parts of the isotherm cannot pass continuously into each other: there must be a discontinuity between them. The isotherms terminates at F and E, where

$$\left(\frac{\partial p_r}{\partial v_r}\right)_{t_r} = 0.$$

REFERENCES

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