

Origin of the attractive part of Lennard-Jones potential

Masahiro Yamamoto

*Department of Energy and Hydrocarbon Chemistry,
Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan*

(Dated: March 4, 2008)

Now we consider two hydrogen atoms. If the two atoms are located far away, the Hamiltonian H_0 and the wavefunction Ψ of the system is given by two independent H atoms,

$$H_0 = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} \quad (1)$$

$$\Psi = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) = R_{nl}(r_1)Y_{lm}(\hat{\mathbf{r}}_1)R_{nl}(r_2)Y_{lm}(\hat{\mathbf{r}}_2) = |nlm\rangle|nlm\rangle \quad (2)$$

The ground state Ψ_0 is given by $|100\rangle|100\rangle$. If the two H atoms get closer, they interact each other and the potential

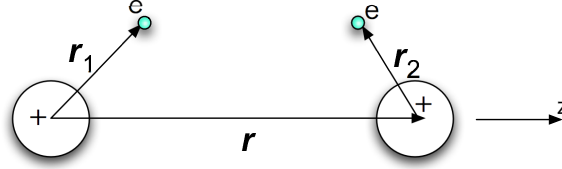


FIG. 1: van der Waals interaction between two hydrogen atom

V (perturbation) is given by

$$V = \frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 + \mathbf{r}|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} + \mathbf{r}_2|} + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 + \mathbf{r} + \mathbf{r}_2|} \quad (3)$$

If we assume $r \gg r_1, r_2$, and vector \mathbf{r} is in the z direction. $\mathbf{r} = (0, 0, z)$. If we consider the order up to $r^{-1}(x_1^2/r^2)$ because the $(1/r)(z_1/r)$ order terms are cancelled out. If we use $(1+x)^{-1/2} \simeq 1 - x/2 + 3x^2/8 \dots$

$$\begin{aligned} |\mathbf{r} - \mathbf{r}_1|^{-1} &= [(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2]^{-1/2} = r^{-1} \left[\frac{z^2 - 2zz_1 + x_1^2 + y_1^2 + z_1^2}{r^2} \right]^{-1/2} \\ &= r^{-1} \left[1 + \frac{-2zz_1 + x_1^2 + y_1^2 + z_1^2}{r^2} \right]^{-1/2} \simeq r^{-1} \left(1 - \frac{-2zz_1 + x_1^2 + y_1^2 + z_1^2}{2r^2} + \frac{3z_1^2}{2r^2} \right) \\ |\mathbf{r} + \mathbf{r}_2|^{-1} &\simeq r^{-1} \left(1 - \frac{2zz_2 + x_2^2 + y_2^2 + z_2^2}{2r^2} + \frac{3z_2^2}{2r^2} \right) \\ |\mathbf{r} - \mathbf{r}_1 + \mathbf{r}_2|^{-1} &\simeq r^{-1} \left[1 - \frac{-2zz_1 + 2zz_2 + x_1^2 - 2x_1x_2 + x_2^2 + y_1^2 - 2y_1y_2 + y_2^2 + z_1^2 - 2z_1z_2 + z_2^2}{2r^2} + \frac{3(z_2 - z_1)^2}{2r^2} \right] \\ V &\simeq \frac{e^2}{4\pi\epsilon_0 r} \left(1 - 1 + \frac{-2zz_1 + x_1^2 + y_1^2 + z_1^2}{2r^2} - \frac{3z_1^2}{2} - 1 + \frac{2zz_2 + x_2^2 + y_2^2 + z_2^2}{2r^2} - \frac{3z_2^2}{2} \right. \\ &\quad \left. + 1 - \frac{-2zz_1 + 2zz_2 + x_1^2 - 2x_1x_2 + x_2^2 + y_1^2 - 2y_1y_2 + y_2^2 + z_1^2 - 2z_1z_2 + z_2^2}{2r^2} + \frac{3(z_1^2 + z_2^2 - 2z_1z_2)}{2r^2} \right) \\ &= \frac{e^2}{4\pi\epsilon_0 r^3} (x_1x_2 + y_1y_2 + z_1z_2 - 3z_1z_2) = \frac{e^2}{4\pi\epsilon_0 r^3} (x_1x_2 + y_1y_2 - 2z_1z_2) \end{aligned} \quad (4)$$

This is the instantaneous dipole-dipole interaction $1/(4\pi\epsilon_0 r^3)[\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{\mathbf{r}})(\vec{\mu}_2 \cdot \hat{\mathbf{r}})]$. Here $\vec{\mu}_1 = e(-\mathbf{r}_1)$, $\vec{\mu}_2 = e(-\mathbf{r}_2)$. Using perturbation theory the energy change is given by

$$E_n = E_n^{(0)} + \Delta_n^{(1)} + \Delta_n^{(2)} + \dots \quad (5)$$

$$\Delta_n^{(1)} = \langle n|V|n\rangle = V_{nn} \quad (6)$$

$$\Delta_n^{(2)} = \sum_{k \neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} \quad (7)$$

For ground state $n = 0$, $E_0^{(0)} = \epsilon_0(\text{atom1}) + \epsilon_0(\text{atom2})$ and

$$\begin{aligned}\Delta_n^{(1)} &= \langle 0 | \frac{e^2}{4\pi\epsilon_0 r^3} (x_1 x_2 + y_1 y_2 - 2z_1 z_2) | 0 \rangle \\ &= \frac{e^2}{4\pi\epsilon_0 r^3} \langle 1, 0, 0(\text{atom1}) | \langle 1, 0, 0(\text{atom2}) | (x_1 x_2 + y_1 y_2 - 2z_1 z_2) | 1, 0, 0(\text{atom1}) \rangle | 1, 0, 0(\text{atom2}) \rangle \\ &= \frac{e^2}{4\pi\epsilon_0 r^3} \langle 1, 0, 0(\text{atom1}) | x_1 | 1, 0, 0(\text{atom1}) \rangle \langle 1, 0, 0(\text{atom2}) | x_2 | 1, 0, 0(\text{atom2}) \rangle + \dots \\ &= 0\end{aligned}\tag{8}$$

In the last equation the integral of the product of even, odd, even functions becomes zero. and the second order

$$\begin{aligned}\Delta_0^{(2)} &= \sum_{k \neq 0} \frac{|V_{0k}|^2}{\epsilon_0(\text{atom1}) + \epsilon_0(\text{atom2}) - \epsilon_k(\text{atom1}) + \epsilon_k(\text{atom2})} \\ &= \frac{e^4}{(4\pi\epsilon_0)^2 r^6} \sum_{k \neq 0} \frac{\langle 0 | x_1 x_2 + y_1 y_2 - 2z_1 z_2 | k \rangle \langle k | x_1 x_2 + y_1 y_2 - 2z_1 z_2 | 0 \rangle}{\epsilon_0(\text{atom1}) + \epsilon_0(\text{atom2}) - \epsilon_k(\text{atom1}) + \epsilon_k(\text{atom2})}\end{aligned}\tag{9}$$

Using the relation $\sum_k |k\rangle \langle k| = 1 = |0\rangle \langle 0| + \sum_{k \neq 0} |k\rangle \langle k|$, and we assume that the denominator is constant and $\epsilon_0(\text{atom1}) + \epsilon_0(\text{atom2}) - \epsilon_k(\text{atom1}) + \epsilon_k(\text{atom2}) \simeq -(I_1 + I_2)$, here I_1, I_2 is the ionization energy of atom1 and 2.

$$\begin{aligned}\Delta_0^{(2)} &= -\frac{e^4}{(4\pi\epsilon_0)^2 r^6} \frac{1}{I_1 + I_2} \langle 0 | (x_1 x_2 + y_1 y_2 - 2z_1 z_2)^2 | 0 \rangle \\ &= -\frac{e^4}{(4\pi\epsilon_0)^2 r^6} \frac{1}{I_1 + I_2} [\langle 0(\text{atom1}) | x_1^2 | 0(\text{atom1}) \rangle \langle 0(\text{atom2}) | x_2^2 | 0(\text{atom2}) \rangle \\ &\quad + \langle 0(\text{atom1}) | y_1^2 | 0(\text{atom1}) \rangle \langle 0(\text{atom2}) | y_2^2 | 0(\text{atom2}) \rangle + 4 \langle 0(\text{atom1}) | z_1^2 | 0(\text{atom1}) \rangle \langle 0(\text{atom2}) | z_2^2 | 0(\text{atom2}) \rangle]\end{aligned}$$

In the same perturbation theory the atomic polarizability is given by

$$\alpha = -2e^2 \sum_{k \neq 0} \frac{\langle 0 | z | k \rangle \langle k | z | 0 \rangle}{E_0^{(0)} - E_k^{(0)}} \simeq -\frac{2e^2}{I} \langle 0 | z^2 | 0 \rangle\tag{10}$$

Here the electric field is in z -direction. Then we can get $\langle 0 | z^2 | 0 \rangle = \langle 0 | x^2 | 0 \rangle = \langle 0 | y^2 | 0 \rangle = -(\alpha I)/(2e^2)$ With this relation

$$\begin{aligned}\Delta_0^{(2)} &= -\frac{e^4}{(4\pi\epsilon_0)^2 r^6} \frac{1}{I_1 + I_2} \left[\frac{\alpha_1 I_1}{2e^2} \frac{\alpha_2 I_2}{2e^2} + \frac{\alpha_1 I_1}{2e^2} \frac{\alpha_2 I_2}{2e^2} + 4 \frac{\alpha_1 I_1}{2e^2} \frac{\alpha_2 I_2}{2e^2} \right] \\ &= -\frac{3}{2} \frac{\alpha_1 \alpha_2}{(4\pi\epsilon_0)^2 r^6} \frac{I_1 I_2}{I_1 + I_2}\end{aligned}\tag{11}$$

This equation was derived by F. London (Z. Phys. 63, 245-279, 1930). Since the vdW interaction can not be estimated from usual density functional theory(because we should consider excitation and dynamical dipole-dipole interaction), some semiempirical correction based on Eq.(11) is reported. (e.g. F. Ortmann et al. PRB, 73, 205101, 2006)

The final result give the attractive part of the Lennard-Jones potential, $\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. In the mixed system one can use the following convention(Lorentz-Berthelot mixing rule)

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}\tag{12}$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}\tag{13}$$

In the case of σ_{ij} we can understand the rule from the view point of hard-sphere. In the case of ϵ_{ij} we should consider Eq.(11)

$$\begin{aligned}-4\epsilon_i \sigma_i^6 &= -\frac{3}{2} \frac{\alpha_i^2}{(4\pi\epsilon_0)^2} \frac{I_i}{2}, \quad -4\epsilon_j \sigma_j^6 = -\frac{3}{2} \frac{\alpha_j^2}{(4\pi\epsilon_0)^2} \frac{I_j}{2} \\ \epsilon_{ij} &= \sqrt{\epsilon_i \epsilon_j} = \frac{3}{16} \frac{\alpha_i \alpha_j}{(4\pi\epsilon_0)^2} \frac{\sqrt{I_i I_j}}{\sigma_i^3 \sigma_j^3}\end{aligned}\tag{14}$$

From the final equation the approximation of Eq.(13) may be not bad. If one consider the deviation form the standard mixing rule, the modified Lorentz-Berthelot mixing rule can be used. ξ is the deviation parameter.

$$\epsilon_{ij} = \xi \sqrt{\epsilon_i \epsilon_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (15)$$

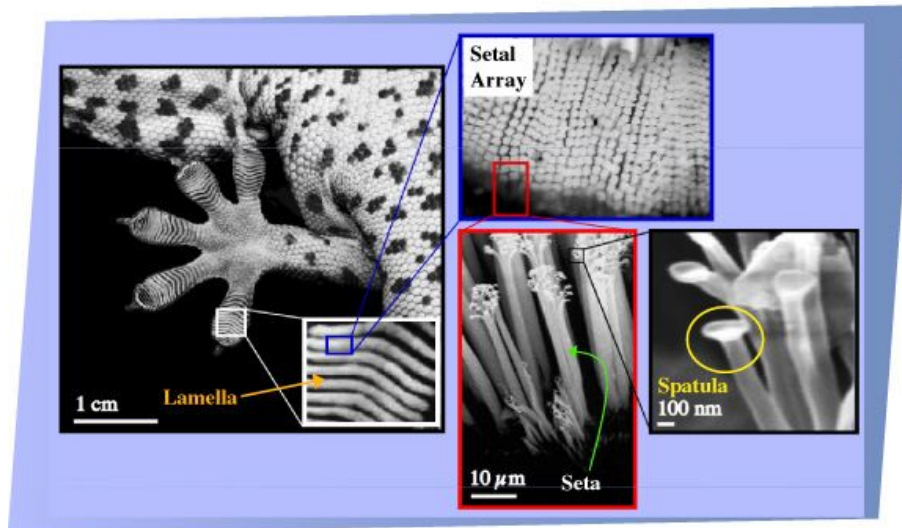


FIG. 2: from http://socrates.berkeley.edu/~peattiea/research_main.html

The Gecko (やもり) can stick to the wall. (both on the hydrophilic and hydrophobic surace and even dead gacko can stick!!) They have 1 billion contacting point per foot and **interact via van der Waals force!!**. The total adhesive stress from Autumn's force measurements is 576 kPa (5.68 atm).

[Kellar Autumn, Yiching A. Liang, S. Tonia Hsieh, Wolfgang Zesch, Wai Pang Chan, Thomas W. Lenny, Ronald Fearing and Robert J. Full (2000) "Adhesive force of a single gecko foot-hair", Nature, 405(6787). 681-685, and Proc Natl Acad Sci U S A. 2002 99, 12252-6. "Evidence for van der Waals adhesion in gecko setae." Autumn K, Sitti M, Liang YA, Peattie AM, Hansen WR, Sponberg S, Kenny TW, Fearing R, Israelachvili JN, Full RJ.]

Recently Huber et al. showed that the evidence for **capillary force contribution** to gecko adhesion from single spatula AFM force measurement. (PNAS, 102, 16293-16296, 2005) The pull-off force is increased lineary (from 7 nN to 12 nN) with the humidity for hydrophilic flat surface and the the increase is not so much (from 6 nN to 9 nN) for hydrophobic surface. At the humidity around 90 % the monolayer of water is adsorbed on the hydrophilic surface.

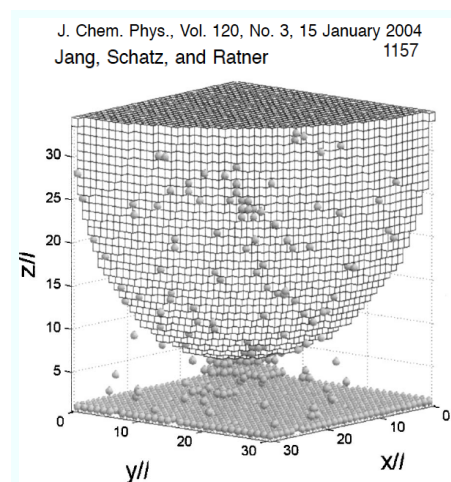


FIG. 3: capillary force