

Origin of the attractive part of Lennard-Jones potential

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A. Origin of the attractive part of L-J potential

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

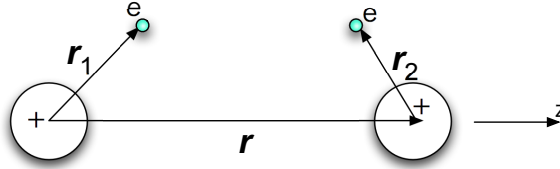


FIG. 1: van der Waals interaction between two hydrogen atom

V (perturbation) is given by

$$V = \frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 + \mathbf{r}|} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} + \mathbf{r}_2|} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 + \mathbf{r} + \mathbf{r}_2|} \quad (3)$$

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 $(1+x)^{-1/2} \simeq 1 - x/2 + 3x^2/8 \dots$

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

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

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

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

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

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

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

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

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

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)

B. LJ potential

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)

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (12)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (13)$$

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)

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

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.

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

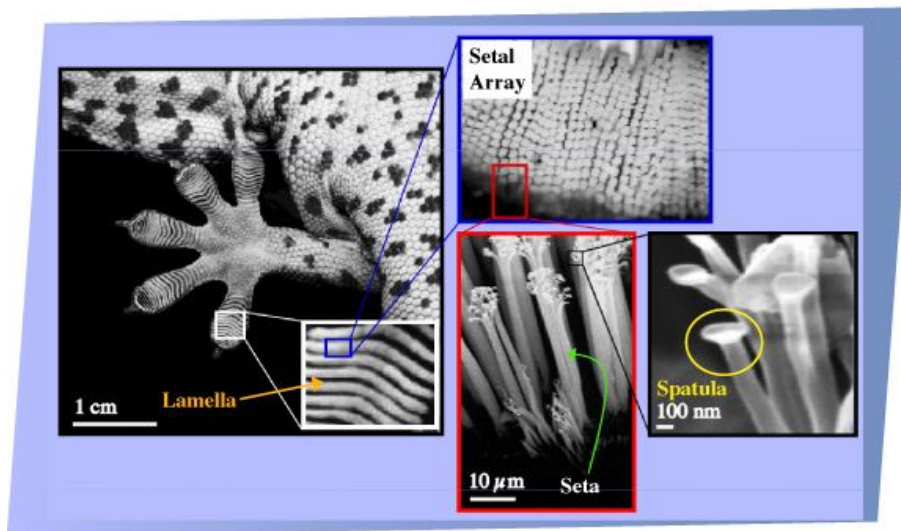


FIG. 2: from http://socrates.berkeley.edu/~peattiea/research_main.html

The Gecko (→√ϕ →?√† →?√?→ Å jcan 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 measurment. (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.

C. Kittel's derivation of the attractive part of LJ potential: dynamical effect

Now we consider the two neutral atom is separated by R . At a certain moment the atoms induce dipole moment in each other and the induced dipole moments cause an attractive interaction between the atoms.

We assume the two atoms are identical linear harmonic oscillators and only electrons move in the x -direction. When the displacement of electrons are x_1 and x_2 , the force constants are K , and the momenta of the oscillators are p_1 and p_2 The hamiltonian of the system without the interaction between the induced dipole moments is

$$H_0 = \frac{1}{2m}p_1^2 + \frac{1}{2}Kx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}Kx_2^2 \quad (16)$$

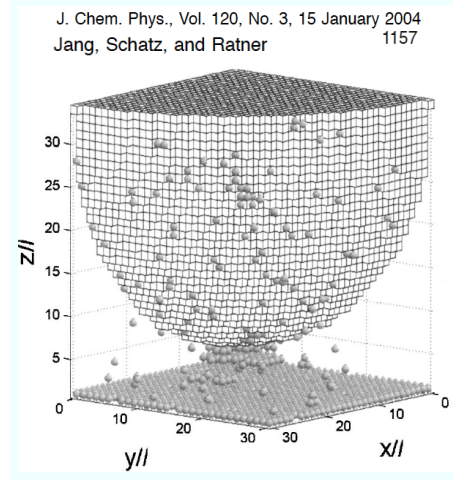


FIG. 3: capillary force

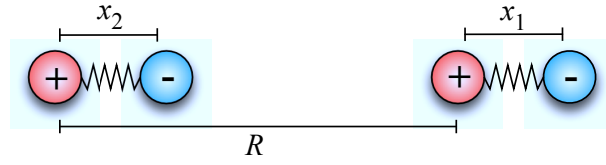


FIG. 4: Kittel's explanation on the vdW attractive potential (ISSP book)

Here m is the mass of electron and $K = m\omega_0^2$. The energy of the ground state is the double of the zero point energy

$$E_0 = 2\frac{1}{2}\hbar\omega_0 = \hbar\omega_0 \quad (17)$$

The interaction H_1 between the dipoles becomes

$$H_1 = \underbrace{\frac{e^2}{4\pi\epsilon_0 R}}_{++} - \underbrace{\frac{e^2}{4\pi\epsilon_0(R+x_1)}}_{+-} + \underbrace{\frac{e^2}{4\pi\epsilon_0(R+x_1-x_2)}}_{--} - \underbrace{\frac{e^2}{4\pi\epsilon_0(R-x_2)}}_{-+} \quad (18)$$

Here e is the elementary charge and ϵ_0 is the permittivity of free space. If we assume that $R \gg |x_1|, |x_2|$.

$$\frac{4\pi\epsilon_0 H_1}{e^2} \simeq \frac{1}{R} - \frac{1}{R} \left(1 - \frac{x_1}{R} + \frac{x_1^2}{2R^2}\right) + \frac{1}{R} \left[1 - \frac{x_1 - x_2}{R} + \frac{(x_1 - x_2)^2}{2R^2}\right] - \frac{1}{R} \left(1 + \frac{x_2}{R} + \frac{x_2^2}{2R^2}\right) \quad (19)$$

$$= \frac{1}{2R^2}[-x_1^2 + (x_1 - x_2)^2 - x_2^2] = -\frac{2x_1x_2}{R^3} \quad (20)$$

Here we used the approximation $1/(1 \pm x) \simeq 1 \mp x + (1/2)x^2 + \dots$. The total hamiltonian becomes

$$H = H_0 + H_1 = \frac{1}{2m}p_1^2 + \frac{1}{2}Kx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}Kx_2^2 - \frac{2x_1x_2}{R^3} \quad (21)$$

If we use the symmetric and anti-symmetric coordinate

$$x_s \equiv \frac{1}{\sqrt{2}}(x_1 + x_2), \quad x_a \equiv \frac{1}{\sqrt{2}}(x_1 - x_2) \quad (22)$$

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a), \quad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) \quad (23)$$

and also use the symmetric and anti-symmetric momenta

$$p_s \equiv \frac{1}{\sqrt{2}}(p_1 + p_2), \quad p_a \equiv \frac{1}{\sqrt{2}}(p_1 - p_2) \quad (24)$$

$$p_1 = \frac{1}{\sqrt{2}}(p_s + p_a), \quad p_2 = \frac{1}{\sqrt{2}}(p_s - p_a) \quad (25)$$

The total hamiltonian becomes

$$H = \left[\frac{1}{2m} p_s^2 + \frac{1}{2} \left(K - \frac{2e^2}{4\pi\epsilon_0 R^3} \right) x_s^2 \right] + \left[\frac{1}{2m} p_a^2 + \frac{1}{2} \left(K + \frac{2e^2}{4\pi\epsilon_0 R^3} \right) x_a^2 \right] \quad (26)$$

The two vibrational frequencies are found for this interacting system

$$\omega = \left[\left(K \pm \frac{2e^2}{4\pi\epsilon_0 R^3} \right) / m \right]^{1/2} = \left[\frac{K}{m} \left(1 \pm \frac{2e^2}{4\pi\epsilon_0 K R^3} \right) \right]^{1/2} \quad (27)$$

$$= \omega_0 \left(1 \pm \frac{2e^2}{4\pi\epsilon_0 K R^3} \right)^{1/2} \quad (28)$$

If assume that $1 \gg (2e^2)/(4\pi\epsilon_0 K R^3)$, we can use $(1 \pm x)^{1/2} \simeq 1 \pm (1/2)x - (1/8)x^2 + \dots$

$$\omega = \omega_0 \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{4\pi\epsilon_0 K R^3} \right) - \frac{1}{8} \left(\frac{2e^2}{4\pi\epsilon_0 K R^3} \right)^2 + \dots \right] \quad (29)$$

The zero point energy change is

$$\begin{aligned} \Delta E &= \frac{1}{2} \hbar \omega_0 \left[1 + \frac{1}{2} \left(\frac{2e^2}{4\pi\epsilon_0 K R^3} \right) - \frac{1}{8} \left(\frac{2e^2}{4\pi\epsilon_0 K R^3} \right)^2 \right] + \frac{1}{2} \hbar \omega_0 \left[1 - \frac{1}{2} \left(\frac{2e^2}{4\pi\epsilon_0 K R^3} \right) - \frac{1}{8} \left(\frac{2e^2}{4\pi\epsilon_0 K R^3} \right)^2 \right] - 2 \frac{1}{2} \hbar \omega_0 \\ &= \hbar \omega_0 \frac{1}{8} \left(\frac{2e^2}{4\pi\epsilon_0 K R^3} \right)^2 = -\frac{\hbar \omega_0 e^4}{32\pi^2 \epsilon_0^2 K^2 R^6} = -\frac{A}{R^6} \end{aligned} \quad (30)$$

The attractive interaction is proportional to R^{-6} and A include the dynamics of the oscillator through ω_0