

Lecture #3: London Dispersion & Van der Waals Constants

- I 3 contributions to r^{-6} attractive term of LJ potential
- II. Analytical intermolecular potentials: Hard Sphere & Square Well
- III. van der Waals Constants in terms of Molecular Constants

I. 3 contributions to r^{-6} attractive term of LJ potential

LJ 6-12 potential: r^{-12} term ~ repulsion, r^{-6} term ~ attraction (well understood).
 3 contributions to r^{-6} attractive term of LJ potential

(1) dipole-dipole orientation

head-to-tail lower energy (- +) (- +)

head-to-head higher energy (- +) (+ -)

average interaction energy of dipoles accounting for energy of orientation is:

$$u_{d,d} = -\frac{2m_1^2 m_2^2}{(4\pi\epsilon_0)^2 (3k_B T)} \frac{1}{r^6} \quad (1)$$

$$4\pi\epsilon_0 = 1.113 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \quad \epsilon_0 = \text{permittivity of vacuum. } k_B =$$

$$\text{Boltzmann constant} = R/N_A = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

Example: Given $\mu(\text{NH}_3) = 5.00 \times 10^{-30} \text{ C m}$, what is $u_{d,d}$ for NH_3 at $r = 5 \text{ \AA}$, at $T = 298.15 \text{ K}$

$$\begin{aligned} u_{d,d} &= -\frac{2(5.00 \times 10^{-30} \text{ C m})^4}{(1.113 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})^2 (3 \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298.15 \text{ K})} \frac{1}{\left(5 \text{ \AA} \times \frac{1 \text{ m}}{10^{10} \text{ \AA}}\right)^6} \\ &= -\frac{2(5.00 \times 10^{-30} \text{ C m})^4}{1.529 \times 10^{-40} \text{ C}^4 \text{ J}^{-1} \text{ m}^{-2}} \frac{1}{\left(5 \text{ \AA} \times \frac{1 \text{ m}}{10^{10} \text{ \AA}}\right)^6} = -\frac{(5.00 \times 10^{-30}) \times 2 \times (5.00 \times 10^{-30})^3}{2.389 \times 10^{-96}} \text{ J} \\ &= -5.00 \times 10^{-30} \times (1.046 \times 10^8) \text{ J} = -5.23 \times 10^{-22} \text{ J} \end{aligned}$$

Note we had to partition the calculation since $(5 \times 10^{-30})^4$ is too small for most calculators, hence partitioned as $5 \times 10^{-30} \times [(5 \times 10^{-30})^3 \div \text{denominator}]$

(2) dipole-induced dipole

polarizability allows dipole to be induced by an electric field (or by another permanent dipole).

$$m_{\text{induced}} = \alpha E \quad \alpha = \text{polarizability, } E = \text{electric field strength (V m}^{-1}) \quad V = \text{J C}^{-1}$$

So what are the units of α ?

$$\alpha \sim (4\pi\epsilon_0) m^3 \quad \frac{\alpha}{4\pi\epsilon_0} = \text{polarizability vol has units of m}^3$$

polarizability $\left(\frac{a}{4\pi\epsilon_0}\right) \propto$ size and # of electrons (see Table 16.8: note $r_{Xe} > r_{Kr} > r_{Ar}$, $R_{Ne} > r_{He}$)

and same trend for $\left(\frac{a}{4\pi\epsilon_0}\right)$.

$$u_{induced}(r) = -\frac{m_1^2 a_2}{(4\pi\epsilon_0)^2 r^6} - \frac{m_2^2 a_1}{(4\pi\epsilon_0)^2 r^6} \quad (2)$$

1st term = permanent dipole of molecule #1 & induced dipole of molecule #2,
2nd term = permanent dipole of molecule #2 & induced dipole of molecule #1

(3) *London dispersion attraction*

Quantum mechanical term – electrons of one molecule attracts the nucleus of the other via distortion of electron cloud due to polarizability.

$$u_{disp}(r) = -\frac{3}{2} \left(\frac{I_1 I_2}{I_1 + I_2} \right) \frac{a_1 a_2}{(4\pi\epsilon_0)^2 r^6} \quad (3)$$

This is the dominant term more so than $u_{induced}$ and u_{dd} to r^{-6} of LJ. I_1 and I_2 are the ionization energies of molecules 1 & 2. Note u_{disp} is \propto to product of polarizability volumes of 1 & 2.

prove that u_{disp} has dimensions of energy?

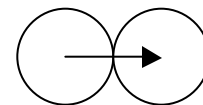
Note the sum of the equations #1, #2 and #3 are the 3 contributions to C_6 or $-C_6/r_6$

II. Analytical intermolecular potentials: Hard Sphere & Square Well

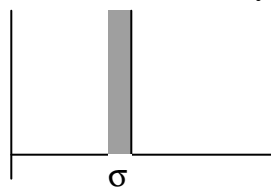
Analytical intermolecular potentials are easier to use than LJ to estimate gas properties.

Hard-Sphere potential: $u(r) = \infty$ for $r < \sigma$ & $u(r) = 0$ for $r > \sigma$ (4)

r = distance between centers, σ = hard sphere diameter
 r^{-12} term is infinitely steep, no r^{-6} term.



$\rightarrow = r$, which is equal to σ here.



At hi T ($T \gg \epsilon/k_B$) attractive forces negligible, so insert Eq. 4 above into Eq.

16.25 of text $B_{2V}(T) = -2pN_A \int_0^\infty \exp\left(\frac{-u(r)}{k_B T}\right) \frac{4\pi}{3} r^2 dr$

(integral partitioned into 2 parts $0-\sigma$, and $\sigma-\infty$: yields:

$$B_{2V}(T) = \frac{2\pi s^3 N_A}{3} \quad (5)$$

Square-well potential:

$$u(r) = \infty \text{ for } r < \sigma, \quad u(r) = -\epsilon \text{ for } \sigma < r < \lambda\sigma, \quad u(r) = 0 \text{ for } r > \lambda\sigma \quad (6)$$

well depth = ϵ , well width = $(\lambda-1)\sigma$

Substitute Eq. 6 into Eq. 16.25 of text & partition integral into 3 parts: $0-\sigma$, $\sigma-\lambda\sigma$,

$\lambda\sigma \rightarrow \infty$ to yield:

$$B_{2V}(T) = \frac{2ps^3 N_A}{3} \left[1 - (I^3 - 1) \left(\exp \left\{ \frac{e}{k_B T} \right\} - 1 \right) \right] \quad (7)$$

Pretty good fit via 3 adjustable parameters ϵ , λ , & σ

III. van Der Waals Constants expressed as Molecular Parameters

$$P = \frac{RT}{(\bar{V} - b)} - \frac{a}{\bar{V}^2} \quad (8)$$

van der Waals:

$$= \frac{RT}{\bar{V}} \frac{1}{(1 - b/\bar{V})} - \frac{a}{\bar{V}^2} \quad (9)$$

Applying geometric series Eq. 10 to Eq. 9

$$\frac{1}{1 - x} = 1 + x + x^2 + x^3 + \dots \quad \text{let } x = \frac{b}{\bar{V}} \quad (10)$$

$$P = \frac{RT}{\bar{V}} \left(1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \dots \right) - \frac{a}{\bar{V}^2} = \frac{RT}{\bar{V}} + (RTb - a) \frac{1}{\bar{V}^2} + \frac{RTb^2}{\bar{V}^3} + \dots \quad (11)$$

$$\frac{P\bar{V}}{RT} = 1 + \frac{b}{\bar{V}} - \frac{a}{RT\bar{V}} + \frac{b^2}{\bar{V}^2} + \dots \quad (12)$$

Comparison of Eq. 12 to $Z = \frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + \dots$.. (13)

$$B_{2V}(T) = b - \frac{a}{RT} \quad (14)$$

Utilizing a hybrid Lennard-Jones/Hard Sphere model in which $u(r) = \infty$ for $r < \sigma$ and $u(r) = -c_6/r^6$ $r > \sigma$

Inserting this into $B_{2V}(T) = -2pN_A \int_0^\infty \left(\exp \left\{ \frac{u(r)}{k_B T} \right\} - 1 \right) r^2 dr$ (16.25

text) and integrating from 0 to σ , and σ to ∞ , making use of e^x Taylor expansion:

$$B_{2V}(T) = \frac{2ps^3 N_A}{3} - \frac{2pN_A c_6}{3k_B T s^3} \quad (15)$$

Show that comparison of Eq. 15 to Eq. 14 yields:

$$a = \frac{2pN_A c_6}{3k_B T s^3} \quad b = \frac{2ps^3 N_A}{3} \quad (16)$$

Prove to yourself that $b = 4 \times$ volume of molecules