NOTE 1
Introduction to Intermolecular Interactions

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1 Intermolecular interactions

Intermolecular interactions are noncovalent interactions between molecules and they are responsible of the existence of condensed states of matter. In the absence of intermolecular interactions our world would be a uniform ideal gas. The cohesive behavior of matter is evidence of attractive interactions between molecules, but the very low compressibility of liquids and solids shows that at short range the interactions become repulsive.

The intermolecular interaction energy E between two molecules A and B is defined by

$$E = E(A \cdots B) - E(A) - E(B), \tag{1}$$

where $E(A)$ and $E(B)$ is the energy of each isolated molecule, respectively. Obviously, the interaction energy (1) is very sensitive to the distance and relative orientation of both molecules. A typical curve of the interaction energy, $E(R)$, for two spherical molecules as a function of the center-center distance R is shown in Fig. 1.1. There is a separation R_m where the energy is a minimum, and a closer distance σ where the energy of interaction goes through zero before climbing steeply. The depth of the attractive well is usually denoted as ε.
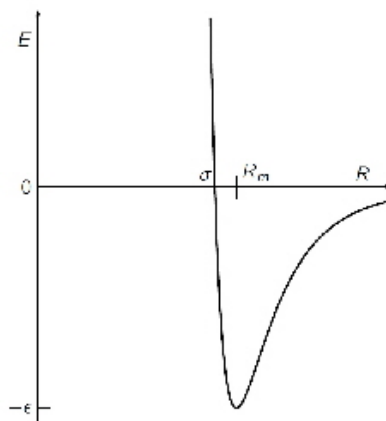

Figure 1.1. A typical intermolecular interaction energy function.

The magnitude of intermolecular interactions can be estimated from the energy of vaporization of liquids, since it is the energy required to pull the molecules from the liquid, where they are in proximity, and bring them into the gas where they are widely separated. In this way, Table 1.1 shows normal heat of vaporization (ΔH^0_{vap}, at boiling point) and bond dissociation energy (BDE, at 298K) for some representative molecules in order to compare the strength of the intramolecular covalent interactions and the intermolecular interactions.

Table 1.1 Normal heat of vaporization at boiling point and bond dissociation energy at 298K.

	ΔH^0_{vap} / kJ mol^{-1}	BDE / kJ mol^{-1}
Ar	6.44	-
H_2	0.46	436
O_2	6.74	498
N_2	5.68	945
CO	5.91	460
CH_4	8.16	439
H_2O	39.5	268

2 Real gases

Real gases are relatively simple systems which illustrate the role played by the intermolecular interactions to define the physical properties of bulk matter. An ideal gas is a system where molecules are moving freely without any interactions between them, in a volume V, at pressure P and temperature T in such a way that, under thermodynamical equilibrium conditions, the variables are related by the so-called equation of state of ideal gas:

$$P\bar{V} = RT, \tag{2}$$

where $\bar{V} = V/n$ is the molar volume. The intermolecular interactions introduce deviations from equation (2) which can be displayed graphically by plotting the *compressibility factor* Z, defined as

$$Z = \frac{\bar{V}}{\bar{V}_{ideal}} = \frac{P\bar{V}}{RT}, \tag{3}$$

as a function of pressure. If the repulsive intermolecular interactions are dominant then $\bar{V} > \bar{V}_{ideal}$ and $Z > 1$. On contrary, $Z < 1$ if attractive intermolecular interactions are dominant. Figure 1.2 shows the behavior of Z for some gases.
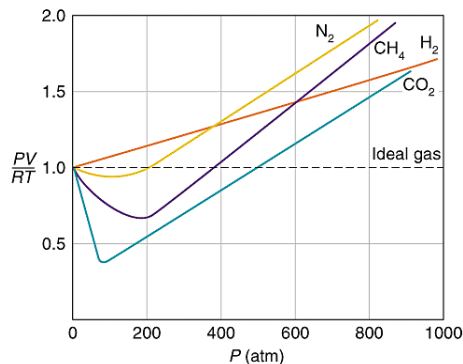

Figure 1.2: Compressibility factor for some gases at 300K.

Compressibility factor can be expanded as a power series in the reciprocal molar volume:

$$Z = 1 + B(T)\frac{1}{\overline{V}} + C(T)\frac{1}{\overline{V}^2} + \cdots , \tag{4}$$

where $B(T)$, $C(T)$, ... is the second virial coefficient, third virial coefficient, and so on. That coefficient are functions of temperature only. The second virial coefficient is the most important virial coefficient because it reflects the first deviation from ideality as the volume of the gas is decreased (or the pressure is increased). It is the most easily measured virial coefficient and is well tabulated for many gases. Finally, statistical thermodynamics provides us the following simple formula

$$B(T) = -2\pi N_A \int_0^\infty \left[e^{-u(r)/kT} - 1 \right] r^2 dr \tag{5}$$

that connects the second virial coefficient with the intermolecular interaction energy $u(r)$. For instance, for spherical molecules with impenetrable hard core of diameter σ and attractive term r^{-6}, the interaction energy reads

$$u(r) = \begin{cases} \infty & , r < \sigma, \\ -\frac{c_6}{r^6} & , r > \sigma. \end{cases} \tag{6}$$

Substituting (6) in (5),

$$B(T) = -2\pi N_A \int_0^\sigma (-1) r^2 dr - -2\pi N_A \int_\sigma^\infty \left[e^{c_6/kTr^6} - 1 \right] r^2 dr. \tag{7}$$

But, assuming $c_6/kTr^6 \ll 1$ and using the series expansion for e^x, and keep only the first two terms, the second virial coefficient is given by the following simple formula

$$B(T) = \frac{2}{3}\pi\sigma^3 N_A - \frac{2\pi N_A c_6}{3\sigma^3 kT}, \tag{8}$$

which includes the dependence on temperature as reciprocal powers of it.

3   Electric nature of molecules

Consider a paralell-plate charged capacitor in a vacuum with charge density $+\sigma$ (in C m^{-2}) on one plate and $-\sigma$ on the other plate. The electric field, E_0, due to these charges is perpendicular to the plates and is given by

$$E_0 = \frac{\sigma}{\epsilon_0}, \tag{9}$$

where ϵ_0 is the permitivity of vacuum. The *capacitance*, C, is defined as the ratio of the charge on one of the plates to the potential difference, $E_0 d$, where d is the separation of the plates in meters. So, if S is the surface area of the plate then

$$C_0 = \frac{\sigma S}{E_0 d} = \frac{\epsilon_0 S}{d} \tag{10}$$

is the capacity of the paralell-plate charged capacitor in a vacuum. Now, when the vacuum is replaced with some dielectric (i.e., nonconducting) material the capacitance is always observed to increase and may be written

$$C = C_0 D, \tag{11}$$

where $D > 1$ is the *relative permitivity* of the dielectric, more commonly called the *dielectric constant* of the medium. This increase occurs because the field E polarizes the dielectric, that is, causes dipoles

in the dielectric to rotate preferentially, such that their negative ends toward the negatively charged plate, and hence induce a surface charge density of magnitude $\mp P$ on the surface of the dielectric at the positive and negative plates, respectively. P is called the polarization of the dielectric, and for electrically isotropic media it is also the dipole moment per unit volume of the dielectric (see Figure 1.3). This follows because the dielectric will have a charge of $+PS$ separated by distance d from a charge of $-PS$ in a volume Sd such that

$$\frac{\text{dipole moment}}{\text{volume}} = \frac{PSd}{Sd} = P. \tag{12}$$
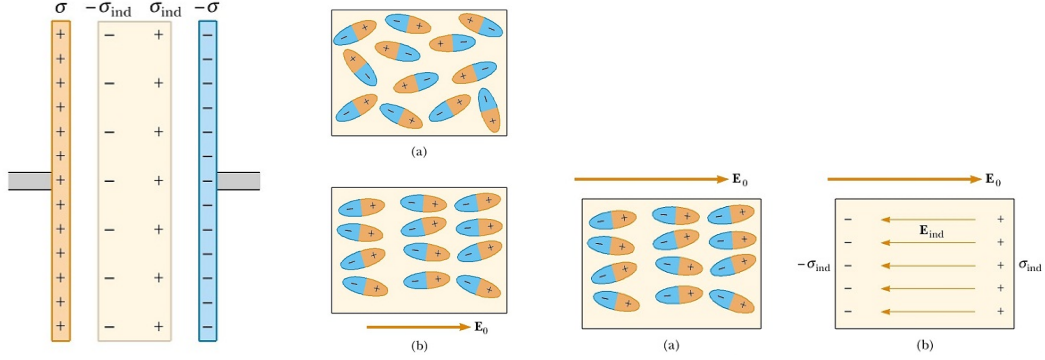

Figure 1.3: Paralell-plate charged capacitor with a dielectric material.

For Eq.(11) to hold with the same charge on the plates, the macroscopic electric field E inside the dielectric must be E_0/D, but we may also consider that the effect of the dielectric is to change density from σ to $\sigma - P$; thus

$$E = \frac{E_0}{D} = \frac{\sigma}{\epsilon_0 D} = \frac{\sigma - P}{\epsilon_0} \tag{13}$$

and eliminating σ gives

$$P = \epsilon_0 (D - 1)E. \tag{14}$$

A molecule inside the dielectric feels, in addition to the macroscopic net field on the plates by Eq.(13), a further contribution generated by the polarization of its neighbors. Assuming the molecules to be in a spherical cavity in a homogeneous medium, this contribution can be shown to be $(4\pi/3)(P/(4\pi\epsilon_0))$. Therefore the total field, E^*, at the molecule in this approximation becomes

$$E^* = E + \frac{1}{3}\frac{P}{\epsilon_0}. \tag{15}$$

This field will distort the electron cloud of the molecule, assumed here to have no permanent dipole moment ($\mu = 0$), and induce a dipole moment m_i that is proportional to and in the direction of E^*:

$$m_i = \alpha E^*, \tag{16}$$

where α (units of Cm^2V^{-1}) is called the polarizability of the molecule. Since P is the dipole moment per unit volume we have

$$P = m_i \rho \tag{17}$$

where $\rho = N/V$ is the number density of molecules in the dielectric. Then using Eqs. (14) and (15) we may solve for m_i:

$$m_i = \frac{3\epsilon_0 (D - 1)E^*}{\rho(D - 2)} = \alpha E^*. \tag{18}$$

4

Since according to classical electrostatics the polarizability α of a perfectly conducting sphere in a vacuum may be shown to be equal to $4\pi\epsilon_0 r^3$, where r is the radius of the sphere, it has become customary to call $\alpha/(3\epsilon_0) = 4/3\pi r^3$ the polarizability volume of a molecule and to call $N_A\alpha/(3\epsilon_0)$ the molar polarization P_m (units of volume per mole). We find from Eq. (18), using ρ' as the mass density $(\rho M/N_A)$ with M the molar mass of the molecules

$$P_m = \frac{N_A\alpha}{3\epsilon_0} = \left(\frac{M}{\rho'}\right)\left(\frac{D-1}{D+2}\right). \tag{19}$$

This is the Clausius-Mossotti equation and holds for nonpolar molecules. For such molecules P_m is independent of temperature (α, being a molecular property, is always independent of temperature) and Eq. (19) may be solved for D:

$$D = \frac{1+2s}{1-s}, \tag{20}$$

where $s = P_m\rho'/M$ is temperature dependent and less than unity. For gases s is very tiny and D is close to unity.

For molecules that possess a permanent dipole μ, their mean dipole moment in the absence of an applied field must be zero if the dielectric is a gas or liquid because their rotational motion averages the net effect to zero. In the presence of a field, orientation of their dipoles along the field direction will be energetically preferred. We shall use a classical staristical calculation to determine the average orientational dipole moment $\bar{m}_o$ along the field direction. Taking the z axis of spherical coordinates along the field direction, we may show from electrostatic that the estra separable energy of a dipole that makes an angle θ with the field of strength E^* is

$$\varepsilon = -\mu E^* \cos\theta$$

and of course the component of μ along the E^* direction will be $\mu\cos\theta$. Therefore,

$$\bar{m}_o = \frac{\int_0^{2\pi} d\phi \int_0^\pi \mu\cos\theta \exp(-\varepsilon/kT)\sin\theta d\theta}{\int_0^{2\pi} d\phi \int_0^\pi \exp(-\varepsilon/kT)\sin\theta d\theta} \tag{21}$$

$$= \mu\frac{\int_0^{2\pi} d\phi \int_0^\pi \cos\theta \exp(\mu E^*\cos\theta/kT)\sin\theta d\theta}{\int_0^{2\pi} d\phi \int_0^\pi \exp(\mu E^*\cos\theta/kT)\sin\theta d\theta}. \tag{22}$$

Introduce $y = \mu E^*/kT$ and note that the numerator is the derivative of the denominator, that is,

$$\bar{m}_o = \mu L(y), \tag{23}$$

where $L(y)$, known as the Langevin function, is

$$L(y) = \frac{\frac{d}{dy}\int_0^\pi \exp(y\cos\theta)\sin\theta d\theta}{\int_0^\pi \exp(y\cos\theta)\sin\theta d\theta} = \frac{\frac{d}{dy}\int_{-1}^{+1}\exp(yp)dp}{\int_{-1}^{+1}\exp(yp)dp} \tag{24}$$

$$= \frac{\frac{d}{dy}\left[(e^y - e^{-y})/y\right]}{(e^y - e^{-y})/y} = \frac{(e^y + e^{-y})}{(e^y - e^{-y})} - \frac{1}{y} \tag{25}$$

For small y we may expand $L(y)$ to obtain

$$L(y) = \frac{y}{3} - \frac{y^3}{45} + \dots \tag{26}$$

Under practical experimental conditions y is very small and only the leading term in Eq. (26) need be retained. Therefore, for a polar molecule in the dielectric the net dipole moment along the field direction is a sum of the induced and orientational contributions:

$$m = m_i + m_o = \alpha E^* + \frac{\mu^2 E^*}{3kT}.$$ (27)

The polarization is now Eq. (17) with m in place of m_i:

$$P = m\rho = \rho E^* \left(\alpha + \frac{\mu^2}{3kT} \right)$$ (28)

and the molar polarization remains defined by the right-hand side of Eq.(19) but now consists of two terms:

$$P_m = \left(\frac{M}{\rho'} \right) \left(\frac{D-1}{D+2} \right) = \frac{N_A \alpha}{3\epsilon_0} + \frac{N_A \mu^2}{9\epsilon_0 kT}.$$ (29)

Equation (29) is called the *Debye equation*, and it shows that P_m is temperature dependent.

The term $(N_A \alpha)/(3\epsilon_0)$ can be written as a sum

$$\frac{N_A \alpha}{3\epsilon_0} = P_a + P_{el}$$ (30)

of atomic polarization P_a due to motions of the atomic nuclei (generally a very small term) and electronic polarization P_{el} due to electron response to the alternating electric field. As Maxwell derived, $D(\nu)$, the dielectric constant at frequency ν, is given by

$$D(\nu) = n_r^2,$$ (31)

where n_r is the index of refraction. At such high frequencies (visible radiation), with orientation effect washed out the $D(\nu)$ values will not be large and Eq.(29) in the form

$$\left(\frac{M}{\rho'} \right) \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right) = \frac{N_A \alpha}{3\epsilon_0} = P_a + P_{el}$$ (32)

will be accurate for condensed phases as well as gaseous phases of any type of molecule. The index of refraction id the ratio of speed of light in vacuum to that in the dielectric medium. The speed in the medium is slower as the wavelenght is shorter (the frequency is higher) because higher frequency induces a higher frequancy of oscillation among the electrons of the dielectric. The quantity R_m, the molar refractivity,

$$R_m = \left(\frac{M}{\rho'} \right) \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right)$$ (33)

using a fixed wavelenght is nearly independent of temperature, pressure, and state of aggregation of the molecules. Using visible radiation (the only kind for which n_r can be conveniently measured), R_m is strictly equal to P_{el}.

Problems

1.1 Use Trouton's rule to show that normal boiling point is directly related to the strenght of the intermolecular interaction energy.

1.2 Lennard-Jones potential

$$E(R) = 4\varepsilon \left[(R_0/R)^{12} - (R_0/R)^6 \right],$$

where $R_m = 2^{1/6}R_0$, is widely used to model intermolecular interactions of spherical molecules. Plot the Lennard-Jones potential for the argon with parameters $\varepsilon/k = 111.84\,\mathrm{K}$ and $R_0 = 362.3\,\mathrm{pm}$. Calculate numerically the second virial coefficient as function of temperature. Compare your result with the following experimental fit [Dymond et al, *Virial Coefficients of Pure Gases and Mixture*, Volume A, Landolt-Börnstein, 2001], within the range 76K to 1000K:

$$B/\,\mathrm{cm}^3\,\mathrm{mol}^{-1} = 3.4162 \times 10^1 - 1.2087 \times 10^4/(T/\,\mathrm{K}) - 7.6702 \times 10^5/(T/\,\mathrm{K})^2 - 1.9600 \times 10^7/(T/\,\mathrm{K})^3$$

1.3 Calculate the second virial coefficient as a function of temperature for rare gas from He to Rn using the model reported by Tang and Toennies in J. Chem. Phys. 118 (2003) 4976-4983 [DOI: 10.1063/1.1543944]

$$V(R) = Ae^{-bR} - \sum_{n=3}^{N} f_{2n}(bR) \frac{C_{2n}}{R^{2n}},$$

where

$$f_{2n}(x) = 1 - e^{-x} \sum_{k=0}^{2n} \frac{x^k}{k!}$$

and

System	R_m	$\varepsilon \times 10^4$	C_6	C_8	C_{10}	A	b
$He \cdots He$	5.62	0.348	1.461	14.11	183.6	41.96	2.523
$Ne \cdots Ne$	5.84	1.34	6.383	90.34	1536	199.5	2.458
$Ar \cdots Ar$	7.10	4.54	64.30	1623	49060	748.3	2.031
$Kr \cdots Kr$	7.58	6.38	129.6	4187	155500	832.4	1.865
$Xe \cdots XE$	8.25	8.96	285.9	12810	619800	951.8	1.681
$Rn \cdots Rn$	8.46	12.6	420.6	19260	1067000	5565	1.824

Compare with the experimental fits reported by Dymond et al. in *Virial Coefficients of Pure Gases and Mixture*, Volume A, Landolt-Börnstein, 2001:

$$B/\,\mathrm{cm}^3\,\mathrm{mol}^{-1} = B_0 + B_1/(T/\,\mathrm{K}) + B_2/(T/\,\mathrm{K})^2 + B_3/(T/\,\mathrm{K})^3 + B_4/(T/\,\mathrm{K})^4$$

Gas	Range	B_0	B_1	B_2	B_3	B_4
He	35.1K to 1470K	9.2479	1.0876×10^3	-1.0880×10^5	2.3869×10^6	0
Ne	50.0K to 870K	15.894	-9.9406×10^2	-1.2641×10^5	2.2721×10^6	0
Ar	76.0K to 1000K	34.162	-1.2087×10^4	-7.6702×10^5	-1.9600×10^7	0
Kr	110K to 870K	38.030	-1.9985×10^4	-1.4767×10^6	-1.3450×10^8	0
Xe	160K to 970K	67.836	-5.3169×10^4	2.2239×10^6	-1.3905×10^9	5.8510×10^{10}

1.4 The following values have been reported for the dielectric constant of BrF_5 vapor at 1.00 atm presure [M. Rogers et al., J. Am. Chem. Soc. 78 (1956) 44]:

T / K	D
345.6	1.006320
362.6	1.005824
374.9	1.005525
388.9	1.005180
402.4	1.004910
417.2	1.004603
430.8	1.004378

Assuming ideal gas behavior for density values, determine the molecular polarizability α and dipole moment μ of BrF_5.