CHAPTER - 4

THEORETICAL STUDY OF MOLECULAR INTERACTION POTENTIAL

4.1 INTRODUCTION

It is convenient to work with the pair-wise potential to deal with the statistical mechanics of liquids and solutions. The Lennard-Jones (LJ) or Kihara (K) potentials may be taken into consideration for the calculation of the effective potentials. Such effective potentials are useful to study physical association of two components or their chemical bending depending upon solvent efforts. In this chapter we have formulated expressions for interaction potentials for molecules of arbitrary and spherical shape in liquids. Also an expression for dipole dependent interaction in gas phase is given.

4.2 THEORETICAL FORMULATION OF INTERACTION POTENTIAL FOR THE LIQUID PHASE

In a solution with \( N_1 \) solvent molecules (a), and \( N_2 \) solute molecules (b) there is pairing like solvent-solvent (aa), solvent-solute (ab) and solute-solute (bb) interactions. The effective pair potential can be defined as effective potential of the pair immersed in a medium of given bulk composition (\( X_a + X_b = 1; X_a = \frac{N_1}{N_1 + N_2} \)). In a dilute solution of b in a, the situation is relatively much simpler. The environment of bb pair is essentially all a. The same is true for an ab on an aa pair. The effective potential in solution can be written as

\[
\bar{V}_{\text{eff}}^{KL} \text{(solution)} = V^{KL} + \frac{V^{KL}}{n_{\text{int}}} \left< \sum_{N_1} \frac{V^{KLM}}{V_s^{KL}} \right>
\]

where \( n_{\text{int}} = 3, K=L=M=a, r=ijk, s=ij \) for aa pair; \( n_{\text{int}} = 2, K=M=a, L=b, r=imj \) and \( s=im \)
for ab pair; and \( n_{mrl} = 1 \), \( K = L = b \), \( M = a \), \( r = ml \) and \( s = ml \) for bb pair, \( i, j, k, l, m \) indicate various sites of the molecules. The summation and average is carried out for these three cases over \( k, j, i \) respectively. All the terms which are put to see the effect of medium depend upon the solvent density \( (d_s) \). The values of \( n_{int} \) depend whether potential is considered for solvent or solute molecules. For dilute solutions one can approximately write

\[
\overline{V}_{ij, \text{eff}}^{\text{aa}} (\text{solution}) \approx \overline{V}_{ij, \text{eff}}^{\text{aa}} (\text{pure liquid})
\]

(2)

where \( i \) and \( j \) are near ab molecule and it is assumed that ab molecule, first create a cavity in the pure solvent and bb molecule is placed in it to interact with its environment, the discrepancy between LHS and RHS of eq. (2) around \( b \) appears in the microscopic, surface tension term.

Eq. (1) for non-polar interactions and quasi-spherical molecules, the main part of the effective potential in a pure liquid or dilute solution is approximately given by the following equation

\[
V_{bb'}^{\text{eff}} (R_{bb'}, d_s) \approx V_{bb'}^{\text{eff}} (R_{bb'}) + \frac{\Delta_{n_{int}}}{C_{bb'}} \left[ \frac{C_{bb'}}{R_{bb'} - \lambda_{bb'}} \right] D_{bb} L_{bb'}
\]

(3)

where \( b, b' \) molecules of solute are near to the solvent molecule \( a \). The eq. (3) discusses third order three body forces. \( R_b \) and \( R_{b'} \) are radius of solute molecule-separated by \( R_{bb'} \). \( C_{bb'} \) is the dispersion coefficient of Kihara (or LJ) potential from Kihara potential is given by following relation

\[
V_K (\rho) = C \left[ \left( \frac{\sigma^6}{\rho_12} - \frac{1}{\rho^6} \right) \right]
\]

(4)

The K-potential in eq. (4) considers the size as well as the shape of a molecule through
a core parameter $l_{bb'} \rho$ is the shortest distance between $b$ and $b'$ in fixed orientations with centres $R$-apart. In terms of minimum point parameters or lowest potential for Kihara potential, we can express the parameters in eq. (4) as

$$\rho^o = 2^{1/6} \sigma$$

(5)

$$C = 4\varepsilon \sigma^6$$

(6)

For Lennard-Jones potential $l_{bb'} = 0$ but for Kihara potential $l_{bb'} \neq 0$ because two molecules have interaction between the peripheral atoms before centre to centre $R_{bb'}$ effect.

$$R^o_{bb'} (LJ) = \rho^o + 1$$

(7)

For two component system, we can approximately write the following relations $^2$

$$\sigma_{bb'} = (\sigma_b + \sigma_{b'}) / 2$$

(8)

$$l_{bb'} = (l_b + l_{b'}) / 2$$

(9)

and

$$C_{bb'} = \frac{3}{2} \left[ \frac{\delta_b \delta_{b'}}{\delta_b + \delta_{b'}} \right] \alpha_b \alpha_{b'}$$

(10)

According to London $^3$ the proportionality constant between $\delta(i=b, b')$ and ionization potential $I_2$ is unity, therefore
\[ C_{bb'} = \frac{3}{2} \left[ \frac{I_b I_{b'}}{1 + I_b + I_{b'}} \right] \alpha_{bb'} \]  

(11)

In eq. (3) \( \Delta \) and \( L_{bb'} \) for three body forces are given by

\[ \Delta = \frac{I_a (I_b + I_{b'} + I_a)}{(I_b + I_a) (I_{b'} + I_a)} \]  

(12)

and

\[ L_{bb'} = \langle \sum_a \frac{\left( R_{ba} - 1_{ba} \right)^3 R_a^{3(1+3\cos \theta_b \cos \theta_{b'} \cos \theta_a)} \right) a \rangle \]  

(13)

\( L_{bb'} \) is a dimensionless factor which is dependent on the relative sizes of the fixed molecules, \( b \) and \( b' \) with radii \( R_b \) and \( R_{b'} \), solvent molecule \( a \) and on \( R_{ba} \). The angle \( \theta_i \) is subtended with vertex at molecule \( i \) (i.e., \( b, b', a \)). The radius \( R_a \) of solvent molecule can be obtained from the relation \( R_a = \left( (3/4) \pi \alpha_a \right)^{1/3} \), where it is assumed that sphere of radius \( R_a \) contains on average one solvent molecule \( a \).

For an ellipsoidal solute surrounded by a continuum such that continuum touches the active molecule, Buckingham has given the following relation for \( D_{bb'} \)

\[ D_{bb'} = \frac{3n^2_{bb'}}{(n^2_{bb'} + 2) \{n^2_{bb'} - (n^2_{bb'} - 1) S_p \}} \]  

(14)

where \( S_p \) is the shape factor for the principal axis \( p \) and is written as

\[ S_p = \frac{abc/2}{\int_0^\infty \frac{ds}{\sqrt{(s+a^2)^3 + (s+b^2)^3 + (s+c^2)^3}}} \]  

(15)

where \( a, b, c \) are semi axes of ellipsoid. The integral in eq. (15) can not be solved in closed form. However Osborn and Stoner have tabulated the values of \( S_p \) corresponding to the ratios of semi axes \( a, b \) and \( c \).
The calculation of effective potential in eq.(3) requires $n_{int}^{bb'}, C^{bb'}$ and $(R_{bb'} - 1)$ which can substituted for specific interaction $(n = 1, 2, 3)$ and Kihara potential parameters from eq. (5), (6) and (11). $D^{bb'}$ can be calculated either by known value of $S_p$ or by using some kind of assumption depending upon the type of the molecules fitting with the measured data of the intensity. The problem now lies in the calculation of $\Delta$ in eq.(12) and $L_{bb'}$ in eq.(13) which need exact geometry and this distribution function in addition to some reasonable approximations for the short or the large distance $R$, a function of radii of molecules $a, b$ and $b'$.

We assume an arbitrary molecular cavity and moderate distance of interaction (i.e. a distance which is neither tending to infinity nor to zero). For such interactions we assume that the product of $L_{bb'}$ and $\Delta$ is approximately unity i.e.

$$L_{bb'} \Delta \approx 1$$  \hspace{1cm} (16)

Substituting eqs. (5), (11), (14) and (16) in eq.(3). We get final expression for the effective potential as given below.

$$V_{bb'}^{eff}(R_{bb'}, d) \equiv V_{bb'}^{bb'}(R_{bb'}) + \frac{9}{2 n_{int}} \left[ \frac{1_b}{1_b} + \frac{1_b'}{1_b'} \right] \frac{\alpha_b \alpha_b'}{R_{bb'} - 1_{bb'}} \times \frac{n_{bb'}^2}{(n_{bb'}^2 + 2) \{ n_{bb'}^2 - (n_{bb'}^2 - 1) S_p \}}$$  \hspace{1cm} (17)

This is the final expression for effective interaction potential. Eq (17) has been derived in this work with an approximation in eq. (16) and $D_{bb'}$ value in eq. (14) the main part of effective potential is the second term on R.H.S. of eq. (17) which can be called as interaction potential $V$ for solute-solute interaction $(n_{int} = 1)$ or for pure liquid is (dropping suffix $bb'$).
\[ V = \frac{9 \, I \alpha^2}{4 \, R - 1 \, \left( n^2 + 2 \right) \left( n^2 - (n^2 - 1) S_p \right)} \] (18)

Yamada and Person\(^7\) defined the ratio of intensity in any medium (liquid or solid) \( I_m \), to that in gas (\( I_g \)) as given below

\[ \frac{I_m}{I_g} = n \left[ \frac{n^2}{n^2 - (n^2 - 1) S_p} \right]^2 \left( \frac{1}{1 - g \alpha_p} \right)^2 \] (19)

The data\(^7\) and the calculated interaction potential for carbon disulphide for stretching mode \( \nu_3 \) and bending mode \( \nu_2 \) are given in the Table 1. The cavity factor is defined by

\[ \text{Cavity factor} = \left[ \frac{n^2}{\{n^2 - (n^2 - 1) S_p\}} \right]^2 \] (20)

and the reaction field term by

\[ \text{Reaction field term} = (1 - \alpha_p g_p)^{-2} \] (21)

where Scholte\(^8\) has given the value of \( \alpha \) and \( g \) for a uniformly polarized ellipsoid of semi axes \( a, b, c \) in continuum of dielectric constant \( \varepsilon = n^2 \).

The ratio \( (a/b) \) in the CS\(_2\) ellipsoid is estimated\(^7\) to be 1.83 from the C-S bond distance and van der waals of radius of surface\(^9\). The molecular volume \( abc \) is calculated from the density using following relation

\[ (4/3)\pi abc = \frac{\text{Molecular Weight}}{\text{density} \times \text{Avogardo number}} \]

\[ \Rightarrow 19.4 \, \text{Å}^3 \quad \text{for CS}_2 \] (22)

Using refractive index 1.8199, \( g_a = 1.93 \times 10^{22} \, \text{cm}^{-3} \) and \( g_b = 3.61 \times 10^{22} \, \text{cm}^{-3} \) the values of
polarizability\(^{10}\), for the \(v\) mode is 15.14 Å\(^3\) and that for the \(v\) mode is 5.54 Å\(^3\). Stoner\(^{6}\) has given the shape factor 0.191 for the \(v\) mode and 0.4045 for \(v\) mode when the ratio \((a/b)\) is taken as 1.83.

The calculated values of shape factors using eq. (20) are given in Table 1. An examination of the Table 1 shows that the interaction potential for the stretching infrared fundamental vibrational mode \((v\) \(3\)) is more than six times than the bending mode \((v\) \(2\)) in both solid and liquid phases. Also the interaction potential for the liquid phase is more than that in the solid phase, due to increasing values of the cavity factor in the liquid phase.

The approximation in eq (16) has mathematical justification if one puts \(R = R = R\) \(a\) \(b\), \(l = 0\), \(\cos \theta = 1\), \((i = a, b, b')\) in eq. (13) and ionization potential for like molecules \((a = b = b')\) in eq. (12). The assumption of moderate distance corresponds to \(R = 2 R\) \(a\). Physically this approximation leads to the situation when the molecule \(a\) is placed on the line joining \(b\) and \(b'\). Therefore the approximation is realistic and simplifies the calculations.

For non-polar interaction and almost spherical molecular cavities, the main part of the effective potential in liquids is given by approximately by following equations

\[
V^{\text{eff}}(R, d) = V(R) + \Delta n_{\text{int}} \left[ \frac{C}{(R-l)} \right] \Delta L
\]  

(23)

where \(R\) is separation between two molecules of the liquids of density \(d\). The quantities \(\Lambda\) and \(L\) are given by Hirschfelder\(^{2}\), \(n\) is the index of refraction of the medium and \(d\) is defined latter, the term, \(C\) is the dispersion coefficient of Kihara, \(K\) potential same as in eq. (4)

\[
C = \frac{3}{4} \alpha^2
\]  

(24)
where I is the ionization potential $\alpha$ is the polarizability. The Lennard-Jones potential can be expressed

$$R^o (LJ) = \rho^o + L$$

We have assumed the product between L and $\Delta$ to be i.e.

$$L \Delta \approx 1.5$$

The approximation eq.(26) avoid computational difficulty and eliminates the requirement that L should be calculated. We have assumed the validity of eq.(26) for solute-solute interactions or for the pure liquids where $b=b'=a$ holds. It is also assumed that $R \geq 3r_0$ where $r_0$ is the radius of the molecule. An exact solution of eq.(13) for L can be obtained by computer simulation technique.

Eq.(23) can now be used to calculate the interaction potential

$$V = V^{\text{eff}}(R,d) - V(R)$$

For the solute-solute interaction ($n_{\text{ref}} = 1$) i.e.

$$V = \left(\frac{9}{8}\right) 1 \alpha^2 D/\rho^o$$

In Eq.(27) the reaction field term is defined as $1/D^2$ for spherical with a shape factor $1/3$ when SI Units are employed. The eq.(27) is the specialized form of eq.(17) spherical molecule with dipole moment. The eq.(27) could be transformed to eq.(27) by considering $L_{bb'} = 1.5$ instead of $L_{bb'} = 1$.

**4.3 DIPOLE DEPENDENT INTERACTION IN THE GAS PHASE**

Let us define $\Delta v_s$, as a function of molecular parameters in the following way.

$$\Delta v_s = F(\mu, b_o, RM, \nu, T, P, v)$$

where $\mu$ is dipole moment in Debye(D) units (1D is $1 \times 10^{-18}$ e.s.u. cm), $b_o$ is distance of
closest approach (in Å), $T$ is the absolute temperature (in °K) and $P = \Delta P$ is change in pressure, for the change $\Delta v_s$, $\overline{RM}$ represents reduced mass of the two molecules in collisions

$$\overline{RM} = \frac{MM_1M_2}{M_1 + M_2}$$  \hspace{1cm} (29)

Here $M_1 = M_2 = M$ for the molecules of the same kind. $M_1$, $M_2$ and $M$ are the molecular weight. The cavity resonance frequency ($\Delta v_s$) is also given by

$$\Delta v_s = (Mv / 2\pi) \sigma_s$$  \hspace{1cm} (30)

where $\sigma_s$ is the collision cross-section. The expression for the mean relative velocity ($v$) and number of dipoles per $cm^3$ are given below

$$N = 9.68 \times 10^{-18} \frac{P \text{ (mm of Hg)}}{T \text{ (°K)}}$$  \hspace{1cm} (31)

and

$$v = 2.5202 \times 10^5 \overline{(RM)}^{1/2} \{T/300\}^{1/2}$$  \hspace{1cm} (32)

from eqs. (30-32), It is clear that we can make three factors, $F$, in eq. (7). The factor $F_1 (\mu, b, \overline{RM})$ is useful to find a collision cross section or the collision rates, the factor $F_2 (v, T, P)$ can be shown using eq. (31) and (32), to have the following form

$$F_2 (v, T, P) \propto (\overline{RM} \cdot T)^{-1/2} \Delta P$$  \hspace{1cm} (33)

The effect of $F_3 (v_o)$ upon $\Delta v_s$ can be independently seen by making measurements at different frequencies. Therefore the function $F$ in eq. (28) can be factored as follows:

$$\Delta v_s = f_1 (\mu, b, \overline{RM}) \cdot f_2 (v, T, P) \cdot f_3 (v_o)$$  \hspace{1cm} (34)
Eq. (33) and (34) show that the shift in the cavity resonance frequency is directly proportional to the change in pressure as has also been pointed out. Suppressing the effect of $F(v_0)$ and considering $T=300^\circ$K as room temperature, one can write from eq. (33) and (34)

$$\frac{\Delta v}{\Delta P} = K f_1(\mu, b_0 \text{ RM})$$

(35)

or

$$f = \frac{1}{K} \left( \frac{\Delta v}{\Delta P} \right) = f_1(\mu, b_0 \text{ RM})$$

(36)

We can therefore write eq (36) as follows:

$$f = f_1(\mu, b_0 \text{ RM})$$

(37)

A linear variation between Log $f$ and Log $x$ gives

$$\log f = M \log f_1 + K$$

(38)

where

$$f_1 \propto x^{M_1} b_0^{M_2} (\text{ RM})^{M_3}$$

with $x = \mu$ and $M$ is the slope. Applying a least square fitting of experimental data of $\Delta v/\Delta P$ in eq. (38) for molecular properties of a number of molecules under studied, we get the following relation

$$\frac{\Delta v}{\Delta P} = K \frac{\mu b_0^2}{v}$$

(40)

where $K$ is parameter to be determined.
TABLE I

Interaction potential for $\nu_3$ and $\nu_2$ infrared fundamental Vibrational modes of carbon disulfide using refractive index, cavity factor and measured ratio $\frac{I_m}{I_g}$ of intensity in any dense medium ($I_m$) to that in gas ($I_g$).

<table>
<thead>
<tr>
<th>Vibrational Mode</th>
<th>Refractive Index</th>
<th>Cavity Factor</th>
<th>Measured $(I / I_g)$</th>
<th>Shape Factor $S_p$</th>
<th>Interaction Potential $(V^*) \times 10^{52}$ (erg cm$^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_3$</td>
<td>1.8199</td>
<td>1.3285</td>
<td>1.4</td>
<td>0.19</td>
<td>485.168</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1.8199</td>
<td>1.9473</td>
<td>1.5</td>
<td>0.41</td>
<td>78.650</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>1.8199</td>
<td>1.4687</td>
<td>1.3</td>
<td>0.25</td>
<td>510.136</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1.8199</td>
<td>2.0019</td>
<td>1.4</td>
<td>0.42</td>
<td>79.746</td>
</tr>
</tbody>
</table>

* Ionization potential 10.08 eV Kihara potential parameter $(R-l) = 3.72\text{Å}$, $\alpha = 15.14\text{Å}^3$. For $\nu_3$, $\alpha = 5.54\text{Å}^3$ for $\nu_2$. 

TABLE 2

<table>
<thead>
<tr>
<th>System Name</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>Impact parameter $b_0$(Å)</th>
<th>Dipole moment $\mu$(D)</th>
<th>$v_{cm^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl Sulfide</td>
<td>OCS</td>
<td>60.0</td>
<td>3.42</td>
<td>0.709</td>
<td>32535.64</td>
</tr>
<tr>
<td>Methyly Cyanide</td>
<td>$CHCN$</td>
<td>91.0</td>
<td>4.47</td>
<td>3.92</td>
<td>26418.87</td>
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<tr>
<td>Chloroform</td>
<td>CHCl$_3$</td>
<td>111.0</td>
<td>4.06</td>
<td>1.01</td>
<td>23920.68</td>
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<tr>
<td>Toluene</td>
<td>$C_7H_8$</td>
<td>92.0</td>
<td>4.37</td>
<td>0.387</td>
<td>26274.90</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>NO$_2$</td>
<td>46.0</td>
<td>2.52</td>
<td>0.31</td>
<td>37158.32</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>SO$_2$</td>
<td>64.0</td>
<td>3.10</td>
<td>1.70</td>
<td>31502.50</td>
</tr>
<tr>
<td>Water</td>
<td>HO$_2$</td>
<td>18.0</td>
<td>3.06</td>
<td>1.96</td>
<td>59401.68</td>
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<td>Formic acid</td>
<td>HCOOH</td>
<td>36.0</td>
<td>4.21</td>
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<td>Acetic Acid</td>
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<td>Methanol</td>
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<td>Acetone</td>
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<td>Aniline</td>
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<td>4.02</td>
<td>2.19</td>
<td>28354.46</td>
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TABLE 3

<table>
<thead>
<tr>
<th>Measured $(\Delta \nu / \Delta P) \times 10^4$ MHz Torr$^{-1}$</th>
<th>Calculated $(\Delta \nu / \Delta P) \times 10^4$ MHz Torr$^{-1}$</th>
<th>Present Work $(\mu (b^2) / \nu)$</th>
<th>Percent deviation $\Delta(\Delta \nu / \Delta P) \times 100 %$</th>
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<tr>
<td>185.0</td>
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<td>252.0</td>
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<td>80.3</td>
</tr>
<tr>
<td>994.4</td>
<td>30.2</td>
<td>2091.2</td>
<td>52.5</td>
</tr>
<tr>
<td>822.0</td>
<td>12.5</td>
<td>863.1</td>
<td>4.56</td>
</tr>
</tbody>
</table>
4.4 RESULTS AND DISCUSSIONS

The interaction potential computed for various bonds of carbon disulphide in gas and liquid phase are given in Table 1. There is increase in interaction potential in the liquid CS₂ in comparison to gas phase depending upon the shape factor $S_p$ & vibrational mode $v_3, v_2$.

The molecular parameters for dipolar molecules are given in the Table 2. Using these parameter we have computed velocity ($v$) of the molecules using eq.(32). The values are given in the Table 2. We have used the least square fit method between $(\Delta v / \Delta P)$ and $X = \mu b^2 / v$ to obtain the value of $K$. The averaged value of $K$ is estimated to be 69.2.

The measured values of $(\Delta v / \Delta P)$ are compared with the present calculation of $(\Delta v / \Delta P)$ in Table - 3. We have calculated $(\mu b^2 / v)$ and it has been plotted on the X-axis whereas $(\Delta v / \Delta P)$ has been plotted on the Y-axis. The slope of the straight line is found to be Table 2. and it has been used for calculated values of $(\Delta v / \Delta P)$ in the Table 904.025. We have assumed that the variation of $(\Delta v / \Delta P)$ versus $(\mu b^2 / v)$ is linear.
REFERENCES


