AN APPROACH TO THE INTERMOLECULAR ENERGY
IN PURE LIQUIDS

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RESUMEN

Se propone un método para: estimar la energía potencial de repulsión de cualquier molécula central como una función de las densidades ortobáricas en líquidos puros no auto asociados; estimar los parámetros necesarios para calcular la energía de dispersión de London; calcular los números de coordinación promedio, distancias intermoleculares de interacción, diámetros moleculares y de grupos; en moléculas globulares, moléculas planas y parafinas normales.

ABSTRACT

A method is proposed to estimate: the repulsion potential energy of any central molecule as a function of the orthobaric densities in pure non-auto-associated liquids, the parameters for London's dispersion energy, average coordination numbers, interaction distances and molecular or group diameters. Globular molecules, plane molecules and normal paraffins are considered.

INTRODUCTION

The Model.

With relation to a pure crystalline substance at zero absolute temperature where its own perfect order is defined, the molecules of a liquid have absorbed enough energy to overcome the cohesive forces in the solid and to settle the liquid–vapor equilibrium at a given temperature. At any instant each molecule in the liquid is surrounded by an average number C of nearest but always changing neighbors, with different intermolecular distances among molecular centers whose average value is r_e; these average equilibrium positions are themselves free to wander. The condensed phase can be treated on the basis of an Einstein model in which every molecule is assumed to have a set of possible energy values which is essentially unaffected by the energy states of neighboring molecules. Inside this defined cell the translational energy levels are very closely spaced and it is possible to replace summation by integration in the kinetic Boltzmann factors to obtain the translational partition function of a molecule restricted to its own cell, but the molecules are able to interchange sites with its neighbors to have access to all the liquid phase giving rise to an higher disorder (number e in the translational partition function).

With

$$q = \frac{(2\pi mKT)^{3/2}}{h^3} \qquad (1)$$

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and $v_L = V_L/N_L$ the mean molecular volume, the translational partition function is

$$(f_{tr})_L = qev_L \qquad (2)$$

Where m is the molecular mass, K the Boltzmann constant, T the absolute temperature, h the Planck constant, v_L the volume and N_L the number of molecules in the liquid phase. If $(f_{rve})_L$ represents the product of rotational, vibrational (nuclei and atomic groups in the molecule) and electronic partition functions, the molecular partition function is expressed by

$$f_L = (f_{tr})_L (f_{rve})_L e^{-C(u_a+u_r)/KT} \qquad (3)$$

where u_a and u_r are the attraction and repulsion potentials respectively; these potentials depend for any molecule on the average distance r_e only and so the exponential form appears as a factor. The pair molecular potential energy is

$$\varepsilon_p = u_a + u_r \qquad (4)$$

For the vapor in equilibrium with the liquid, let N_v the number of molecules in the volume V_v, the vapor molecular partition function is, in analogous way

$$f_V = (f_{tr})_V (f_{rve})_V e^{-(\overline{\varepsilon_p})_V/KT} \qquad (5)$$

where $(\overline{\varepsilon_p})_V$ is the average potential energy of a molecule in the vapor phase and

$$(f_{tr})_V = qe\frac{V_V}{N_V} \qquad (6)$$

Interaction energy between two similar molecules.

According to the arguments presented by London (1), the interaction energy between two three-dimensional isotropic harmonic oscillators with no permanent moment in their rest position and separated by a distance r between centers is given by

$$E_o = \frac{h}{2}\left[v_x^+ + v_y^+ + v_z^+ \right.$$
$$\left. + v_x^- + v_y^- + v_z^- \right]$$

where the frequencies are:

$$v_x^+ = v\left[1 + \frac{\alpha_o}{r^3}\right]^{1/2}$$

$$v_y^+ = v\left[1 + \frac{\alpha_o}{r^3}\right]^{1/2}$$

$$v_z^+ = v\left[1 - 2\frac{\alpha_o}{r^3}\right]^{1/2}$$

$$v_x^- = v\left[1 - \frac{\alpha_o}{r^3}\right]^{1/2}$$

$$v_y^- = v\left[1 - \frac{\alpha_o}{r^3}\right]^{1/2}$$

$$v_z^- = v\left[1 + 2\frac{\alpha_o}{r^3}\right]^{1/2}$$

with v the fundamental frequency of the two elastic systems and α_o the polarizability in static field. The internal zero point energy of the two isolated systems is $6(1/2hv)$, then the interaction energy is

$$u_d = E_o - 3hv$$

These equations allow to write

$$u_d = hv\left[\left[1 + \frac{\alpha_o}{r^3}\right]^{1/2} + \left[1 - \frac{\alpha_o}{r^3}\right]^{1/2}\right.$$
$$\left. + \frac{1}{2}\left[1 + 2\frac{\alpha_o}{r^3}\right]^{1/2} + \frac{1}{2}\left[1 - 2\frac{\alpha_o}{r^3}\right]^{1/2} - 3\right]$$

If the molecules are separated by a distance $r(r>>A_1, A_2$ the amplitudes of each oscillator in molecules 1 and 2 respectively; $\vec{A}_1 = (x_1, y_1, z_1), \vec{A}_2 = (x_2, y_2, z_2)$) the interaction of s oscillators of a molecule with s oscillators in the other one, gives rise to a total of s^2 interactions, and the potential energy is given by

$$V = \frac{1}{2}K_f A_1^{\ 2} + \frac{1}{2}K_f A_2^{\ 2}$$

$$+ \frac{s^2 e^2}{r^3}\left[x_1 x_2 + y_1 y_2 - 2z_1 z_2\right] \quad (7)$$

The first and second terms in this equation represent the elastic energy of a set of s oscillators in each molecule; the force constant $K_f = 4\pi^2 v^2 sm$ is taken as the sum of s individual force constants. The elastic energy of the set of s identical three dimensional oscillators may be taken as that of one oscillator of mass m, amplitude A and charge e vibrating with an equivalent frequency $v_e = v\sqrt{s}$. The third term is the interaction energy of the oscillating dipoles.

The molecular polarizability in static field is expressed by (see eq. (17) in this paper)

$$\alpha_o = \frac{se^2}{4\pi^2 v^2 m} = \frac{(se)^2}{4\pi^2 v^2 sm} = \frac{(se)^2}{K_f}$$

and the potential energy may be written as

$$V = \frac{1}{2}K_f\left[x_1^{\ 2} + y_1^{\ 2} + z_1^{\ 2}\right]$$

$$+ \frac{1}{2}K_f\left[x_2^{\ 2} + y_2^{\ 2} + z_2^{\ 2}\right]$$

$$+ \frac{K_f \alpha_o}{r^3}\left[x_1 x_2 + y_1 y_2 - 2z_1 z_2\right] \quad (8)$$

By the same mathematical procedure given in ref. (1) the following equation for the interaction energy of a pair of identical molecules due to the coupling of s electronic oscillators in each is obtained:

$$u_d = hv\sqrt{s}\left[\left[1 + \frac{\alpha_o}{r^3}\right]^{\frac{1}{2}} + \left[1 - \frac{\alpha_o}{r^3}\right]^{\frac{1}{2}}\right.$$

$$\left. + \frac{1}{2}\left[1 + 2\frac{\alpha_o}{r^3}\right]^{\frac{1}{2}} + \frac{1}{2}\left[1 - 2\frac{\alpha_o}{r^3}\right]^{\frac{1}{2}} - 3\right] \quad (9)$$

If the expansion of the square roots by means of the binomial theorem is made, and powers of α_o/r^3 greater than the second are neglected,

$$u_d \cong -\frac{3}{4}hv\frac{\sqrt{s}\alpha_o^{\ 2}}{r^6} \quad (10)$$

that is, the approximation found by Slater and Kirkwood (2).

Estimation of parameters α_o, v, s.

The molar refraction (Lorentz – Lorenz) determined with a refractive index n measured with light of any appropriate frequency is

$$R = \frac{n^2 - 1}{n^2 + 2}\varphi \quad (11)$$

where φ is the molar volume. The molar refraction is also related with the average polarizability (α) by the equation (electronic polarization, Clausius – Mosotti)

$$\frac{4}{3}\pi N\alpha = R \quad (12)$$

In the classical theory of normal dispersion of light (3a), a small displacement x of one electron respect to its equilibrium position due to the action of the electric field E of light of frequency v_L is given by

$$x = \frac{eE}{4\pi^2 m}\left[\frac{1}{v^2 - v_L^{\ 2}}\right] \quad (13)$$

where e and m are the charge and mass of the electron, and v is the fundamental frequency of the electronic oscilla-

tor. It is here interpreted that the magnitude of the induced dipole moment (μ_i) in the molecule, with s oscillators displaced a distance x each (in the same direction due to the action of the electric field of light) is $\mu_i = s(ex)$ (sum of oscillator strengths). Besides, the induced dipole moment is proportional to the electric field acting on the molecule, $\mu_i = \alpha E$. These considerations allow to deduce that

$$\alpha = \frac{se^2}{4\pi^2 m}\left[\frac{1}{v^2 - v_L^2}\right] \quad (14)$$

and

$$R = \frac{Nse^2}{3\pi m}\left[\frac{1}{v^2 - v_L^2}\right] \quad (15)$$

In static field $v_L = 0$, $R = R_o$ the internal refraction, and $\alpha = \alpha_o$.

$$R_o = \frac{Nse^2}{3\pi m v^2} \quad (16)$$

$$\alpha_o = \frac{se^2}{4\pi^2 v^2 m} \quad (17)$$

As a function of R_o, eq. (15) may be written as

$$R = R_o\left[\frac{v^2}{v^2 - v_L^2}\right] \quad (18)$$

and rearranged in the form

$$\frac{1}{R} = \frac{1}{R_o} - \frac{v_L^2}{R_o v^2} \quad (19)$$

This equations shows that a graphic of $1/R$ vs v_L^2 must be a straight line with $1/R_o$ as intercept and $-1/R_o v^2$ as slope. In this way the internal molar refraction is

Table 1. Dispersion energy parameters. Globular and plane molecules (25°C).

Substance	R_o $(cm^3/mole)$	v $10^{-15}sec^{-1}$	α_o $10^{23}cm^3$	s	n_o
CCl_4	25.771821	3.167334	1.021343	15.9788	1.44371
$CHCl_3$[a]	20.805969	3.194160	0.824545	13.1194	1.43543
Cyclohexane	27.102173	3.396913	1.074065	19.3279	1.41271
Me-cyclohexane	31.791579	3.369792	1.259907	22.3116	1.40968
CH_4[b]	6.855	3.4200	0.2699	4.83	————
Benzene	25.141721	2.525127	0.996372	9.9077	1.47433
Toluene	29.879993	2.558837	1.184151	12.0914	1.47136
o-Xylene	34.459089	2.597392	1.365621	14.3678	1.48038
m-Xylene[a]	34.567261	2.597619	1.369908	14.4155	1.47198
p-Xylene[a]	34.617703	2.593481	1.371907	14.3904	1.47064
C_2Cl_4[a]	29.277724	2.799878	1.160282	14.1850	1.48196

[a]15°C. [b]Gas [3b].

determined, and by the slope the frequency v of the oscillators. By means of eq. (16) the number of oscillators is calculated, the polarizability in static field α_o determined by eq (12) at $R=R_o$, and the internal refractive index n_o by eq. (11) at $R=R_o$ (table 1 for globular and plane molecules).

For n-alkanes, the group refraction, here defined by

$$R_g = \frac{R}{n_g} \qquad (20)$$

where n_g is the number of groups in the molecule (equal to the number of carbon atoms) is used in eq. (19); by the same procedure, the internal group refraction R_{og}, group polarizability in static field α_{og}, number of oscillators per group s_g and the oscillators frequency n are obtained (table 2).

Several decimal places are given to avoid round cut off errors in dispersion energy, eq. (9).

For eq. 19 the following light frequencies have been used, (velocity of light = $2.997925 \cdot 10^{10}$ cm/sec, CRC Handbook of Chemistry and Physics). Wave lengths in references (4) and (5).

$$v_L = \frac{c}{\lambda} \qquad (21)$$

Light	$v_L \cdot 10^{-14} sec^{-1}$
He.r	4.489155
He(Hα)	4.568441
Na_D(D)	5.087610
He. Y	5.102313
Hg. e	5.490001
He. blue	5.977082
He. g	6.090954
H_F(β)	6.166882
Hg. g	6.878657

Table 2. Dispersion energy parameters. Lineal molecules n-alkanes (25°C).

Substance	R_{og} $(cm^3/mole)$	v $10^{-15}sec^{-1}$	α_o $10^{23}cm^3$	Sg	n_o
C_5	4.944158	3.356732	0.195938	3.4430	1.34588
C_6	4.874313	3.374584	0.193170	3.4306	1.36283
C_7	4.826830	3.392007	0.191288	3.4323	1.37540
C_8	4.792059	3.406542	0.189910	3.4369	1.38530
C_9	4.764354	3.402137	0.188812	3.4082	1.39294
C_{11}	4.723738	3.395060	0.187203	3.3651	1.40449
C_{13}	4.693895	3.393770	0.186020	3.3413	1.41262
C_{14}	4.683414	3.395367	0.185605	3.3369	1.41593
C_{15}	4.672729	3.395598	0.185181	3.3298	1.41879
C_{16}	4.667296	3.401875	0.184966	3.3382	1.42145

In what follows, the light used for refractive index (in reference (6)) to calculate the molar refraction and the correlation coefficient (written as cc.) for eq. (19) are given:

CCl$_4$: Hα, D, Hβ, (cc. -1)
CHCl$_3$: Hα, Hey, Hβ (cc. -0.99991)
Cyclohexane: Hα, D, Hβ, (cc. -0.99990)
Me-cyclohexane: Hα, D, Hβ (cc. -0.99992)
m-Xylene: Hα, Hey, Hβ (cc. -1)
p-Xilene: Hα, Hey, Hβ (cc. -0.99997)
n-Pentane: Hα, D, Hβ (cc. -0.99993)
n-Hexane: Hα, D, Hβ (cc. -0.99998)
n-Octane: Hα, D, Hβ (cc. -0.99998)
C$_2$Cl$_4$: He.r, Hα, Hey, Hβ (cc. -0.99999)

For the following substances, light used: He.r, He, Na$_D$, Hg.e, He blue, H$_F$, Hg .g, in reference (4). Benzene (cc. -099993). Toluene (cc.-0.99992). O-xylene (cc.-0.99991). Normal paraffins C$_7$ and C$_9$ to C$_{16}$ all with cc.-1.

Orientation and induction energies in similar polar molecules.

For the polar molecules here studied (CHC1$_3$, Me- cyclohexane, toluene, o-xylene and m-xylene) a good enough approximation to the orientation energy is (Keesom (3c))

$$u_o = -\frac{2}{3}\frac{\mu_p^4}{r^6 KT}$$

valid for $\qquad \dfrac{\mu_p^2}{r^3} < KT \qquad$ (22)

The induction energy (Debye (3a)) is given by

$$u_i = -\frac{2\mu_p^2 \alpha_o}{r^6} \qquad (23)$$

where μ_p is the permanent dipole moment.

The total attraction energy is then

$$u_a = u_d + u_o + u_i \qquad (24)$$

The permanent dipole moment of a molecule in the liquid phase can be estimate by the Onsager-Fröhlich equation:

$$\mu_p^2 = \frac{9KT}{4\pi N}\varphi \frac{\left[D_e - n_o^2\right]\left[2D_e + n_o^2\right]}{D_e\left[n_o^2 + 2\right]^2} \qquad (25)$$

where n_o is the internal refractive, D_e the dielectric constant, N the Avogadro's number and φ the molar volume. This equation is valid for polar non-autoassociated liquids.

Many of the basic theories of liquids and solutions (ref (7) to (17)) are connected with the parameters a) Average intermolecular distance; b) Attraction and repulsion potential energy; c) Coordination number.

In this work the following liquids have been selected to study:

1. Globular or approximately globular molecules: carbon tetrachloride, chloroform, cyclohexane, methyl-cyclohexane and methane.

2. The normal paraffins from C$_5$H$_{12}$ to C$_{16}$H$_{34}$.

3. Plane molecules: benzene, toluene, o-m-p-xylene and tetrachloroethylene.

Intermolecular distance in pure liquids.

Evidently the distance between the centers of two molecules is a function of the molecular geometry.

1. If the molecules are globular of approximately globular, the middle point of distance r_e between centers defines a radius such that

$$\frac{4}{3}\pi\left[\frac{r_e}{2}\right]^3 = \frac{\varphi}{N} \qquad (26)$$

and

$$r_e = \left[\frac{6\varphi}{\pi N}\right]^{1/3} \qquad (27)$$

2. For n-alkanes, depending on the length chain, the molecules may have different flexible and coexisting forms as cylinders, toroids, spirals , etc. and respecting the tetrahedral geometry (angle 109.47°) it is possible to assume that in any of these forms the change in the diameter of the cross section of the molecule is not very important and as an approximation the cylindrical model may be adopted. If ρ_{cL} is the radius of the cylinder, L its length, n_g the number of groups (equal to the number of carbon atoms in the molecule) and r_g the mean radius of a group

$$\pi\rho_{cL}^2 L = \frac{\varphi}{N} \qquad (28a)$$

$$L = \left[n_g - 1\right]r_{cc}\cos\beta + 2r_g \qquad (28b)$$

$$\rho_{cL} = \frac{r_{cc}}{2}\sin\beta + r_g \qquad (28c)$$

where β is the angle between the carbon-carbon distance ($r_{CC} = 1.541$ Å) and the cylinder axis ($\beta = 35.265°$). By these equations we have

$$\rho_{cL}^3 + \frac{r_{CC}}{2}\left[\left(n_g - 1\right)\cos\beta - \sin\beta\right]\rho_{cL}^2 - \frac{\varphi}{2\pi N} = 0 \qquad (29)$$

Once ρ_{cL} is obtained by eq. (29), r_g is calculated by eq. (28c). The interaction between two groups belonging the neighbor molecules is realized at a distance

$$r = 2r_g = r_{gg} \qquad (30)$$

Distance r_e (eq. (27)) and molecular parameters for globular molecules (table 1) are used in connection with eqs. (9), (22) and (23) to estimate the attraction energy (eq. (24)). Distance r_{gg} (eq.(30)) and group parameters for n-alkanes (table 2) are used in connection with eq. (9) to estimate the group-group attraction energy.

3. For molecules whose constituent atoms are in a plane, a spheroid oblate may be adequate to average their volumes. This is the case with benzene, toluene and the xylenes. The volume is generated by rotation of an ellipse of major semi-axis a around its minor semi-axis b

$$v = \frac{4}{3}\pi a^2 b = \frac{\varphi}{N} \qquad (31)$$

The relation b/a depends on the excentricity $\varepsilon = c/a$ of the ellipse, where c is the focal distance; $b/a = g = (1-\varepsilon^2)^{1/2}$*

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* Structure of benzene: b is perpendicular to the ring plane at its center. Focal distance chosen at $c=r_{cc}=1.39$Å, where r_{cc} is the carbon-carbon distance; distance carbon-hydrogen $r_{CH}=1.084$ Å, and major semi-axis $a=c+r_{CH}=2.474$ Å; excentricity $\varepsilon=0.56184$; $b/a=g=0.82725$, this relation is assumed to hold at any temperature.

Structure of toluene: b is perpendicular to the ring plane at its center. The same excentricity is assumed $\varepsilon=0.56184$. We have five distances $a_1=2.474$Å as in benzene and one distance a_2 in the methyl position. $a_2 = (r_{CC})_{ar} + (r_{CC})_{pa} + (r_{CH})_{pa}$; $(r_{CH})_{ar}=1.39$Å, $(r_{CC})_{paraf}=1.541$Å, $(r_{CH})_{paraf}=1.070$ Å; $a_2=4.001$ Å. Major semi-axis $a=5/6\,a_1+1/6a_2=2.7285$ Å, $b/a=0.82725$.

Structure of xylenes: b is perpendicular to the ring plane at its center. The same excentricity is assumed $\varepsilon=0.56184$. We have four distances $a_1=2.474$ Å as in benzene and two distances $a_2=4.001$ Å as in toluene. Major semi-axis $a=4/6a_1+2/6a_2=2.9830$ Å; $b/a=g=0.82725$.

$$a = \left[\frac{3\varphi}{4\pi g N}\right]^{1/3} \quad (32)$$

For this kind of molecules three principal average interaction distances between centers can be distinguished: $r_\alpha = 2a$, $r_\beta = 2b$, $r_\gamma = a + b$, and three main energies u_α, u_β and u_γ consequently (calculated with eq (9) at r_α, r_β and r_γ) this implicates the existence of preferred orientations in the contacts, that is those of lower energy. If N_α, N_β and N_γ are number of contacts at distances indicated and $N_\alpha + N_\beta + N_\gamma = N_T$ the total, the fractions or probabilities for interaction can be established:

$$X_\alpha = \frac{1}{1 + \dfrac{N_\beta}{N_\alpha} + \dfrac{N_\gamma}{N_\alpha}}$$

$$X_\beta = \frac{1}{1 + \dfrac{N_\alpha}{N_\beta} + \dfrac{N_\gamma}{N_\beta}}$$

$$X_\gamma = \frac{1}{1 + \dfrac{N_\alpha}{N_\gamma} + \dfrac{N_\beta}{N_\gamma}} \quad (33)$$

As the system is at equilibrium, the Boltzmann's exponential law can be used to calculate the relation among contacts

$$\frac{N_\alpha}{N_\beta} = e^{-(u_\alpha - u_\beta)/KT}$$

$$\frac{N_\alpha}{N_\gamma} = e^{-(u_\alpha - u_\gamma)/KT}$$

$$\frac{N_\beta}{N_\gamma} = e^{-(u_\beta - u_\gamma)/KT} \quad (34)$$

Once the contact probabilities been calculated, the average interaction distance may be estimated by

$$r = r_\alpha X_\alpha + r_\beta X_\beta + r_\gamma X_\gamma \quad (35)$$

This distance and the parameters α_o, v, s (table 1) are used in connection with eq. (9), (22) and (23) to calculate the attraction energy (see table 5).

Coordination number in pure liquids.

If one mole of a liquid is completely vaporized at pressure p, evidently the absorbed energy is the heat of vaporization ΔH_v and the change in the internal energy is $\Delta E_v = \Delta H_v - p\Delta V$ for one molecule the energy $\Delta \varepsilon = \Delta E/N$ is enough to overcome the attractive energy originated by its C nearest neighbors, $\Delta \varepsilon = C(-u_a)$ and

$$C = \frac{\Delta \varepsilon}{-u_a} \quad (36)$$

for n-alkanes

$$C_g = \frac{\Delta \varepsilon}{n_g (-u_a)_{gg}}$$

where $(u_a)_{gg}$ is the group-group attraction energy.

By means of the Clapeyron equation for the liquid-vapor equilibrium (saturation, subscript σ)

$$\Delta \varepsilon = \frac{\Delta E}{N} = \frac{(T\gamma_\sigma - p)}{N}(\varphi_V - \varphi_L) \quad (37)$$

with p the vapor pressure, $\gamma_\sigma = (dp/dT)_\sigma$, φ_V and φ_L the molar volume of vapor and liquid respectively.

Repulsion potential energy. Numerical estimation.

The quantum mechanics ab-initio method to establish the interaction energy between a pair of molecules ((20) to (24)) is very difficult, yet for relatively complex molecules, and is still necessary to resort to empirical methods to establish the intermolecular potential.

In this work a method is proposed to estimate numerically the repulsion potential and to interpret these results.

By means of the relations among Helmholtz free energy (A), chemical potential (μ) and partition function (f):

$$A = -NKT \ln f \qquad (38)$$

$$\mu = \left[\frac{dA}{dN}\right]_{T,V} \qquad (39)$$

the corresponding expressions for the liquid and vapor are obtained (eqs. (3) and (5)):

1. Liquid:

$$A_L = -N_L KT \ln\left[qeV_L / N_L\right]$$

$$- N_L KT \ln\left[f_{rve}\right]_L + N_L C\left[u_a + u_r\right] \quad (40)$$

$$\mu_L = -KT \ln\left[qeV_L / N_L\right] + KT$$

$$- KT \ln\left[f_{rve}\right]_L + C\left[u_a + u_r\right] \qquad (41)$$

2. Vapor:

$$A_V = -N_V KT \ln\left[qeV_V / N_V\right]$$

$$- N_V KT \ln\left[f_{rve}\right]_V + N_V(\varepsilon_p)_V \quad (42)$$

$$\mu_V = -KT \ln\left[qeV_V / N_V\right] + KT$$

$$- KT \ln\left[f_{rve}\right]_V + (\varepsilon_p)_V \qquad (43)$$

By the equilibrium condition $\mu_L = \mu_V$ and considering that the vibrational and electronic partition functions are equal in the liquid and vapor, and assuming free rotation in both phases:

$$C\left[u_a + u_r\right] = KT \ln\left[\frac{V_L / N_L}{V_V / N_V}\right] + (\bar{\varepsilon}_p)_V \quad (44)$$

With M the molar mass, d_L and d_V the orthobaric densities respectively,

$$\frac{V_L}{N_L} = \frac{\varphi_L}{N} = \frac{M}{Nd_L}$$

$$\frac{V_V}{N_V} = \frac{\varphi_V}{N} = \frac{M}{Nd_V} \qquad (45)$$

and

$$\frac{V_L / N_L}{V_V / N_V} = \frac{d_V}{d_L}$$

For those zones of the equilibrium where the intermolecular distances in the vapor are so great that $(\varepsilon_p)_V << C(u_a + u_r)$, the state equation for the vapor is close to that of ideal gas, eq. (44) becomes

$$C\left[u_a + u_r\right] = KT \ln\left[\frac{d_V}{d_L}\right] \qquad (46)$$

or with eq (4)

$$C\varepsilon_p = KT \ln\left[\frac{d_V}{d_L}\right] \qquad (47)$$

This is the potential energy of any central molecule as a function of the orthobaric densities.

By means of eq. (36) for C and eq. (46), the numerical value of the repulsion potential can be obtained:

$$u_r = (-u_a)\left[1 + \frac{KT}{\Delta\varepsilon} \ln(d_V / d_L)\right] \quad (48)$$

This equation is valid only when the vapor behaves ideally.

RESULTS AND DISCUSSION

Repulsion potential energy. Numerical estimation.

The examples selected to be presented here are: globular molecule CCl_4 (table 3); n-alkane, n-heptane (table 4); plane molecule, benzene (table 5); for all the substances studied: vapor pressures and γ_0 coefficient with Antoine's equation (4) except:

CCl_4: $A_0 = 15.384676$, $B_0 = 2406.2521$, $C_0 = 229284.52$ for $\ln p = A_0 - B_0/T - C_0/T^2$ (I).

$CHCl_3$: $A_0 = 15.954502$, $B_0 = 2535.6369$, $C_0 = 191139.51$ for eq. (I) above.

C_2Cl_4: $A_a = 15.366760$, $B_a = 2900.2563$, $C_a = 208.201$ for Antoine's equation from data in CRC Handbook of Chemistry and Physics (1987).

For CH_4: $A_0 = 15.478955$, $B_0 = 943.0703$, $C_0 = 4940.67$ for eq. (I) above, from data in Rowlinson, S. J., "Liquids and Liquids Mixtures", Butterworth, London, 2nd ed., 1969, p. 51. Densities in ref. (4), except CCl_4, cyclohexane, $CHCl_3$, C_2Cl_4 (6). Vapor densities: ideal except CH_4, $d_V = -3.645392 \cdot 10^{-5} + 2.74342 \cdot 10^{-4}$ (P/T); $d_L = 0.58085 - 1.40439 T \cdot 10^{-3}$; p_{mm}, TK (Chemical Engineer's Handbook, J. H. Perry, McGraw Hill, 3rd ed. (1950), p. 285). Dipole moments (eq. (25)) with data in (6) and table 1: $CHCl_3$: $\mu_p = 1.255$, Me-cyclohexane: $\mu_p = 0.313$, toluene: $\mu_p = 0.422$, o-xylene: $\mu_p = 0.594$, m-xylene: $\mu_p = 0.449$ in Debye units.

The average number of nearest neighbors (eq.(36)), that has been called the coordination number C, has the tendency to be greater as temperature raises, the intermolecular distances are also greater and more molecules may take place around any central molecule. For n-alkanes this number is rather low because each CH_2 group is chemically bonded with two groups (ex-

cept the CH_3 terminal groups). For all the globular and plane molecules here studied $6 < C < 9$ and for normal paraffins $4 < C_g < 5$. Similar numerical values are found for the repulsion potential, as those given in tables 3, 4 and 5.

In plane molecules (for example benzene, table 5), the contacts in the position with the molecular planes parallel (distance $r_\beta = 2b$) predominate (X_β) at any temperature (lower energy u_β); when the temperature increases the proportion of these contacts decreases and the proportion (X_α, X_γ) of the other two main positions (consecutive planes: distance $r_\alpha = 2a$; perpendicular planes: $r_\gamma = a + b$) is increased .

The repulsion potential.

The numerical values of the repulsion potential obtained by the proposed method can be interpreted in two ways:

a. According to wave mechanics the repulsive potential at great distances can be represented by

$$u_r = P(r)e^{-r/b_o} \qquad (49)$$

Where $P(r)$ is a polynomial containing positive and negative powers of r and b_o is a constant. Replacement of $P(r)$ by a constant (B), as an approximation, yields a simpler expression (great distances)

$$u_r = Be^{-r/b_o} \qquad (50a)$$

or

$$\ln u_r = \ln B - r / b_o \qquad (50b)$$

The overlap energy in general can lead either to strong attractions or strong repulsions at short distances. If all the possible chemical bonds have been formed, the overlap energy gives repulsions. At short distances the electron fields of molecules interact strongly, the electronic sheaths deformed and they

Table 3. Repulsion potential energy. Numerical estimation. Globular molecule. CCl_4: M = 153.82 g/mol.

t °C	d_L g/cm³	r_e 10⁸ cm	p mm	γ_σ dyne/cm²K	d_V 10⁴g/cm³	$\Delta\varepsilon$ 10¹³ erg	u_a 10¹⁴ erg	C	u_r 10¹⁴ erg
10	1.6132	6.711408	56.10	3755.347	4.886441	5.164292	-7.187443	7.1852	2.780771
25	1.58452	6.751659	113.89	6736.874	9.421019	5.029704	-6.933889	7.2538	2.719735
40	1.5557	6.793067	213.34	11225.950	16.80226	4.905004	-6.683874	7.3386	2.660437
60	1.5163	6.851432	444.28	20186.331	32.89013	4.751038	-6.349125	7.4830	2.577867

Table 4. Repulsion potential energy. Numerical estimation. Lineal molecule. n-Heptane: M = 100.205 g/mol.

t °C	d_L g/cm³	p mm	d_V 10⁴g/cm³	ρ_{CL} 10⁸ cm	r_{ee} 10⁸ cm	γ_σ dyne/cm²K	$\Delta\varepsilon$ 10¹³ erg	$(u_a)_{ee}$ 10¹⁴ erg	C_e	$(u_r)_{ee}$ 10¹⁴ erg
10	0.6920	29.584	1.167982	2.550668	4.211627	1556.476	5.885023	-2.056862	4.1046	0.866540
25	0.67955	45.718	2.463633	2.569760	4.249809	3041.565	5.709529	-1.940185	4.2040	0.832232
40	0.6669	92.508	4.746257	2.589654	4.289599	5456.733	5.552761	-1.834618	4.3238	0.799507
60	0.6493	210.239	10.15779	2.618210	4.346710	10674.536	5.356401	-1.694585	4.5156	0.754721

Table 5. Repulsion potential energy. Numerical estimation. Plane molecule. Benzene: M = 78.114 g/mol.

t °C	d_L g/cm³	p mm	γ_σ dyne/cm²K	d_V 10⁴g/cm³	$\Delta\varepsilon$ 10¹³ erg	a 10⁸ cm	b 10⁸ cm	u_α 10¹⁴ erg	u_β 10¹⁴ erg
10	0.8895	45.432	3171.077	2.013996	5.390068	3.477957	2.877140	-3.463589	-10.82595
25	0.87368	45.180	5857.284	3.998288	5.249945	3.498824	2.894402	-3.341384	-10.44334
40	0.8577	182.785	9991.660	7.310585	5.113418	3.520419	2.912267	-3.220181	-10.06390
60	0.8359	391.472	18459.350	14.71722	4.950013	3.550761	2.937367	-3.058448	-9.557664

t °C	U_γ 10¹⁴ erg	X_α	X_β	X_γ	$\bar{r}$ 10⁸ cm	u_a 10¹⁴ erg	C	u_r 10¹⁴ erg
10	-5.959037	0.105581	0.694492	0.199927	6.001269	-8.408212	6.4105	3.290941
25	-5.748666	0.118891	0.667717	0.213393	6.061503	-7.918257	6.6302	3.145251
40	-5.540026	0.131906	0.642491	0.225603	6.122173	-7.458138	6.8562	3.002338
60	-5.261635	0.140389	0.611158	0.240124	6.20447	-6.882980	7.1917	2.827634

are no longer so effective in screening the nuclei in that part where the molecules collide and a net charge may be generated during collisions. In the liquid state the molecules collide each other constantly and the average situation for repulsion in a molecular pair can be considered as the product D of these net charges when the distance between molecular centers is r, and if ρ is the own molecular radius, then a Coulomb potential can be established for this effect (interchange of virtual photons):

$$u_r = \frac{D}{r - 2\rho} \qquad (51a)$$

or

$$r = \frac{D}{u_r} + 2\rho \qquad (51b)$$

A graphic at $r = r_e$ vs $1/u_r$ must be a straight line with the molecular diameter (2ρ) as intercept and D as slope. The same ideas are also applicable to the repulsion between molecular groups, as in the molecules of the n-alkanes.

In table 6 for globular and plane molecules and in table 7 for n-alkanes, the results obtained with eq. (51b) and eq. (50b) are presented.

Least squares with points at the following temperatures and correlation coefficients written as cc.; first value of cc. eq. (51b), second value of cc. eq. (50b) respectively.

CCl$_4$: 0, 20, 25, 30, 40, 50, 60, 70°C, (cc 0.99999), (cc.- 0.9999).

CHCl$_3$: -40, -30, -20, -10, 10, 20, 25, 30°C (cc.0.9999), (cc. - 0.9997).

Cyclohexane: 15, 20, 25, 30, 40, 60, 70, 80°C, (cc. 0.99996), (cc. - 0.9999).

Me-cyclohexane: 10, 20, 30, 40, 50, 60, 70°C (cc. 0.9996), (cc. - 0.9992).

CH$_4$: 95, 100, 110K, (cc. 09980), (cc. - 0.9957).

Benzene: 25, 30, 40, 50, 60°C, (cc. 1), (cc. - 0.9999).

Table 6. Potential repulsion energy parameters. Globular and plane molecules.

Substance	D 10^{22} (esu)^2	2ρ 10^8 cm	B 10^{12} erg	b_o 10^8 cm
CCl$_4$	4.994176	4.915440	1.006969	1.869646
CHCl$_3$	5.043282	4.272297	0.585020	1.995186
Cyclohexane	5.682413	5.040157	0.895394	2.040602
Me-cyclohexane	6.350949	5.307721	0.953294	2.146822
CH$_4$	0.567104	3.948380	1.085209	0.941594
Benzene	4.003498	4.788688	2.873018	1.342460
Toluene	4.872995	5.04090	3.456215	1.400955
o-Xylene	5.708501	5.307397	5.565769	1.364574
m-Xylene	5.649633	5.326901	5.743531	1.356937
p-Xylene	5.699693	5.306132	3.694514	1.487467

Toluene: 10, 20, 25, 30, 40, 50, 60°C, (c.c. 0.99998), (cc. - 0.9996).

o-Xylene: 10, 20, 40, 50, 60°C, (cc. 0.99998), (cc.- 0.9997).

m-Xylene: 0,10, 20, 30, 40, 50°C (cc. 0.99995), (cc.- 0.9995).

p-Xylene: 20, 30, 40, 60, 70, 80°C, (cc. 0.99998), (cc. - 0.9996).

C_5: -30, -20, -10, 0, 10, 20°C (cc.1), (cc. - 0.9999).

C_6: 0, 10, 20, 25, 30, 40, 50°C, (c.c. 0.99996), (cc. - 0.9999).

C_7: 0, 10, 20, 25, 30, 40, 50, 60, 70, 80°C, (c.c. 0.99995), (cc. - 0.9996).

C_8: 0, 10, 20, 30, 40, 50, 60, 70, 80°C, (c.c. 0.99998), (cc. - 0.9993).

C_9: 0, 10, 20, 30, 40, 50, 60, 70, 80°C, (c.c. 0.99991).

C_{11}: 0, 10, 20, 25, 30, 40, 50, 60, 70, 80°C, (c.c. 0.9994), (cc. -0.999).

C_{13}: 25, 30, 40, 50, 60, 70, 80, 90°C, (c.c. 0.99997), (cc. -0.9996).

C_{14}: 30, 40, 50, 60, 70,80, 90, 100, 110°C, (c.c. 0.99999), (cc. -0.9996)

The analysis of the correlation coefficients obtained with eqs (51b) and (50b) shows that at intermolecular distances prevailing in liquids both forms for the repulsion potential are adequate, the correlation coefficients are somewhat better for eq. (51b), which may be due to the approximation involved with eq. (50b) ; the average situation described by eq. (51a) has however a simpler and direct physical sense. Besides $u_r \to \infty$, as $r \to 2\rho$ (short distances), what is not obtained with eq. (50a) which is valid for longer distances.

In a liquid each molecule is always surrounded by C nearest and always changing neighbors, with an average potential energy $C\varepsilon_p$ (eq.47) which is not easy to visualize, however a scheme in one direction can be obtained if we imagine a central mobile molecule limited by two fixed molecules at a distance $2r_e$ apart ; in this case the potential energy for the central mobile molecule becomes

$$\varepsilon_p = \varepsilon_p(r) + \varepsilon_p(R); \quad r + R = 2r_e \quad (52)$$

Table 7. Potential repulsion energy parameters. Lineal molecules n-alkanes.

Substance	D_g 10^{22} (esu)^2	ρ_g 10^8 cm	B_g 10^{12} erg	b_{og} 10^8 cm
C_5	0.998443	1.546882	0.465921	1.069487
C_6	0.867568	1.608076	0.516976	1.034408
C_7	0.790044	1.650266	0.594689	0.995807
C_8	0.741829	1.680151	0.791295	0.933733
C_9	0.680224	1.717414	1.166604	0.861435
C_{11}	0.616166	1.760225	1.576175	0.812138
C_{13}	0.555645	1.810410	2.394720	0.755201
C_{14}	0.542909	1.819356	2.028099	0.778866

where $\varepsilon_p(r)$ and $\varepsilon_p(R)$ are eq. (24) + eq. (51a) at r variable and $R = 2r_e - r$ respectively.

A w shape graphic is obtained with two minima and a maximum at $r=r_e$. For an isolated molecular pair (gas phase) the potential energy is given by eq. (9)+eq. (51a) (apolar molecules) ; taking CH_4 as an example, and with the parameters given in tables 1 and 6 (D and ρ), the potential energy at the minimum is $(\varepsilon_p)_m = -2.7424.10^{-14} erg$, with $r_m = 4.2408$ Å, and $\varepsilon_p = 0$ at $r_o = 4.0387$ Å; $(\varepsilon_p)_m/K = -199 Kelvin$. These values may be compared with those obtained by Reid, V. M., O'Loughin N. J. and Sparks R. K., using D. C. S. method (J. Chem Phys. 83 (11) 5656 (1985)): $(\varepsilon_p)_m/K = -200$ Kelvin, $r_m = 4.02$ Å and $r_o = 3.62$ Å.

Summary

In table 8 for globular molecules , in table 9 for plane molecules at 25°C, and in table 10 for n-alkanes at 20°C, the results obtained with the proposed methods for distances, potential energies and coordination numbers are presented. The u_r values were calculated with data of D and 2ρ given in tables 6 and 7.

Table 8. Distances, potential energies and coordination numbers. Globular molecules, 25°C.

Substance	r_e 10^8 cm	u_a 10^{14} erg	u_r 10^{14} erg	ε_p 10^{14} erg	C
CCl_4	6.751659	-6.933889	2.719815	-4.210474	7.2538
$CHCl_3$	6.347948	-6.078810	2.429735	-3.649075	7.9840
Cyclohexane	7.012322	-7.205166	2.881306	-4.323860	7.1075
Me-cyclohexane	7.411361	-7.582651	3.019027	-4.563624	7.2543

Table 9. Distances, potential energies and coordination numbers. Plane molecules, 25°C.

Substance	$X_\alpha = X_{2a}$	$X_\beta = X_{2b}$	$X_\gamma = X_{(a+b)}$	$\bar{r}$ 10^8 cm	u_a 10^{14} erg	u_r 10^{14} erg	ε_p 10^{14} erg	C
Benzene	0.118890	0.667717	0.213393	6.061503	-7.918257	3.145389	-4.772868	6.6305
Toluene	0.103276	0.699231	0.197493	6.401870	-9.028137	3.578927	-5.449210	6.5845
o-Xylene	0.083511	0.741205	0.175284	6.635991	-10.71730	4.296648	-6.420648	6.4398
m-Xylene	0.087530	0.732622	0.179848	6.684940	-10.33046	4.159624	-6.170835	6.5386
p-Xylene	0.088723	0.730020	0.181257	6.696177	-10.22452	4.100366	-6.124157	6.5523

Table 10. Distances, potential energies and coordination numbers. n-Alkanes, 20°C.

Substance	r_{gg} 10^8 cm	$(u_a)_{gg}$ 10^{14} erg	$(u_r)_{gg}$ 10^{14} erg	$(\varepsilon_p)_{gg}$ 10^{14} erg	C_g
C_5	4.236095	-2.057220	0.874040	-1.183180	4.0516
C_6	4.233426	-2.014089	0.852836	-1.161253	4.0961
C_7	4.236668	-1.976525	0.843941	-1.132584	4.1671
C_8	4.242242	-1.942469	0.841133	-1.101336	4.2609
C_9	4.247697	-1.894878	0.836819	-1.058059	4.4220
C_{11}	4.258503	-1.819078	0.834853	-0.984225	4.7581

(subscrit gg denotes group-group interaction)

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