# Lennard-Jones Energy Parameter for Pure Fluids from Scaled Particle Theory

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**ABSTACT:** *By considering the fact that the surface tension of a real fluid arises from a combination of both repulsive and attractive forces between molecules, a new expression for the interfacial tension has been derived from scaled particle theory (SPT) based on the work of cavity formation and the interaction energy between molecules. At the critical temperature, the interfacial tension between coexisting liquid and vapour phases vanishes and the intermolecular attractive forces must exactly counterbalance the repulsive forces associated with cavity formation. The effective Lennard-Jones energy parameter has been calculated by using a simple equation derived from SPT for a range of pure fluids including noble gases, diatomic and triatomic gases, short and medium length hydrocarbons, aromatic compounds, oxygen containing compounds. The evaluated Lennard-Jones energy parameters and Reiss's SPT theory were used to calculate the surface tension of pure compounds near critical temperature and were compared with the experimental data. The results indicated that the developed SPT in this work calculates the surface tensions much closer to the experimental data compared with those Reiss's SPT theory .*

**KEY WORDS:** *Scaled Particle Theory, Lennard-Jones energy parameter, Surface tension.*

## INTRODUCTION

Interaction energy between solute and solvent is responsible in some phenomena like solubility, viscosity and surface tension. The interaction energy between solute and solvent can be adequetely approximated by a (6-12) *Lennard-Jones* (LJ) potential, therefore estimation of LJ potential parameters is very important. LJ potential parameters can be estimated by various methods. Many authors [1,2] used viscosity data, some researchers used second virial coefficient [3-5] or gas solubility data [6-15] for evaluation of LJ energy parameters. As an

instance of research work which includes the application of SPT to determine the LJ energy parameter, the work of *Pardo et al.* [6,7,16,17] can be mentioned in which by measuring the solubility of gases in various solvents they determined LJ potential parameters for the solvents.

SPT is a simple statistical mechanical treatment for hard sphere fluids [18], and has been applied with considerable success to various studies, i.e., surface tension of pure fluids [19], partition coefficient in phase equilibria [20], volotality in extractive distillation [21],

solubility of gases in liquids [9,22], micellization of surfactants [23-25], glass transition of liquids [26], and estimation thermodynamic properties [27,28].

In this paper we extended the SPT to obtain an equation for surface tension of pure fluids. This equation was derived for solubility of a solute in a solvent to form a binary solution. According to the SPT concepts the prime step in the process of solubility is the formation of a cavity of molecular size in the solvent for accomodating the solute molecule. This cavity is formed by molecular interactins of attractive and repulsive type between solute and solvent molecules. Reducing the obtained equation for surface tension of binary mixture to a pure fluid and imposing the critical condition of pure fluid on the resulting equation, a simple equation was derived and used to determine the LJ energy parameters. This equation was applied to various types of pure fluids and the calculated LJ energy parameters were compared with those obtained by the other methods.

The essence of the theory used in this work is explained in the following section.

**THEORY**

Hard sphere assumption has provided a successful tool for treating the molecular behaviour of fluids by using the concepts of statistical mechanics. In statistical mechanical theory of hard spheres the solubility of a solute in a solvent is explained by the reversible work of cavity formation in solvent to accommodate the solute. SPT [29-32] is a statistical mechanical theory of hard spheres fluids which is based on the reversible work of cavity formation in a fluid. *Reiss* [30] derived an equation for the work required to open a cavity in a solvent composed of hard-sphere molecules. *Mayer* [19] used this expression for the surface tension of a hard sphere fluid and found that the predicted results for real fluids are compared remarkably well with experimental data for a wide range of pure liquids including simple diatomic molecules, short chain alkanes and polar organic compounds. This showed that the approach has a wider applicability than just for hard sphere fluids.

By considering the interaction energy, $\varepsilon_i(r)$, of solute molecule with a given solvent molecule, the partial molar Gibbs free energy for this interaction can be approximated in the following manner [22]:

$$\overline{G}_i = N_\circ \int_{vol} \varepsilon_i(r) 4\pi r_2 \rho g(\sigma_2, r) dr \tag{1}$$

where $\rho$ is the number density of fluid, $N_o$ is Avogadro's number, and $g(\sigma_2, r)$ is a radial distribution function (RDF) and measures the probability of finding a solvent molecular center at the distance *r* from the center of a solute molecule of hard sphere radius $\sigma_2$. The consistent approach here would be to obtain the RDF directly from the SPT. To our knowledge, so far RDF has not been derived from SPT. Generally in previous works on the SPT it is assumed that the solvent is uniformly distributed in the solution and then the RDF, $g(\sigma_2, r)$, is taken as unity outside the radius $\sigma_2$ [22]. On the otherhand, according to the concepts of SPT, the partial molar *Gibbs* free energy is considered as the work of cavity formation ($W_i$) in a given solvent to accommodate the solute molecules.

The interaction energy, $\varepsilon_i(r)$, of a polarizable polar solute molecule with a polarizable polar solvent molecule can be expressed as [22]:

$$\varepsilon_i(r) = -C_{dis}\left[\left(\frac{1}{r}\right)^6 - \left(\frac{\sigma_{12}}{r}\right)^{12}\left(\frac{1}{\sigma_{12}}\right)^6\right] - \tag{2}$$
$$(C_{ind} + C_{dip})\sigma\left(\frac{1}{r}\right)^6$$

where $C_{dis}$ is the dispersion (or London) energy constant, $C_{ind}$ is the inductive energy constant, $C_{dip}$ is the dipole-dipole energy constant, r is the separation distance between the centers of the cavity and a solvent molecule and $\sigma_{12}$ is the distance at which the dispersion and repulsive interactions are equal in magnitude, i.e. $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ where $\sigma_1$ and $\sigma_2$ are the hard sphere diameters of the solvent and solute respectively.

By substituting for $\varepsilon_i(r)$ from Eq. (2) in Eq. (1)

$$\overline{G}_i = -N_\circ \int_\circ^{\sigma_{12}} C_{dis.}\left[(1/r)^6 - (\sigma_{12}/r)^{12}(1/\sigma_{12})^6\right] 4\pi r^2 \rho dr \tag{3}$$
$$- N_\circ \int_\circ^{\sigma_{12}} (C_{ind} + C_{dip})(1/r)^6 4\pi r^2 \rho dr$$

and upon integration yields the following equation [22]:

$$\overline{G}_i = N_\circ\left[-\frac{8\pi\rho C_{dis.}}{9\sigma_{12}^3} - \frac{4\pi\rho C_{ind.}}{3\sigma_{12}^3} - \frac{4\pi\rho C_{dip.}}{3\sigma_{12}^3}\right] \tag{4}$$

which can be rearranged as:

$$\frac{\overline{G}_i}{kT} = \frac{W_i}{kT} = -\frac{16}{3}\left(\frac{\varepsilon^*_{dis}}{kT}\right) - 8\left(\frac{\varepsilon^*_{ind} + \varepsilon^*_{dip}}{kT}\right) \quad (5)$$

where T and k are absolute temperature and Boltzmann constant and $\varepsilon^*_i$ is defined as:

$$\varepsilon^*_i = \frac{\pi\rho C_i N_\circ}{6\sigma^3_{12}} \quad (6)$$

The dispersion energy, $C_{dis}$, for a (6-12) LJ potential is given by [22,33]:

$$C_{dis} = 4\varepsilon_{12}\sigma^6_{12} = 4(\varepsilon_1\varepsilon_2)^{1/2}\left(\frac{\sigma_1 + \sigma_2}{2}\right)^6 \quad (7)$$

where the cross-terms, $\varepsilon_{12}$ and $\sigma_{12}$, are given by the *Lorentz-Bertholet* mixing rules [33] defined in the right hand side of the equation. $C_{ind}$, the inductive energy constant, is given by [34]:

$$C_{ind} = \mu^2_1\alpha_2 + \mu^2_2\alpha_1 \quad (8)$$

where $\mu_1$ and $\mu_2$ are the dipole moments of the solvent and solute and $\alpha_1$ and $\alpha_2$ are the corresponding polarizabilities. Finally, the dipole-dipole interaction constant is given by [34]:

$$C_{dip} = \frac{2}{3}\frac{\mu^2_1\mu^2_2}{kT} \quad (9)$$

Substitution of Eq. (7), (8) and (9) into Eq. (5) gives the work of interaction per cavity between each molecule of solute and the solvent:

$$W_i = -y\left[\frac{64}{3}\varepsilon_{12} + \frac{8}{\sigma^6_{12}}\left(\alpha_1\mu^2_2 + \alpha_2\mu^2_1 + \frac{2\mu^2_1\mu^2_2}{3kT}\right)\right] \quad (10)$$

where $y = \pi\rho\sigma^6_{12}/6$ is the reduced number density or packing fraction. The surface tension of a real fluid arises from a combination of both attractive and repulsive forces between molecules. Also the surface tension is the energy per unit area and within the concept of SPT this can be defined as:

$$\gamma = \frac{W^s_{cav} + W^s_i}{A_{cav}} = \gamma_{cav} + \gamma_i \quad (11)$$

where s is the surface contribution to the work, W, for both the cavity (cav) and the interaction (i) terms and the denominator is the surface area of the cavity. *Reiss et al.* [30] by separating the pV work from surface work, have

shown that the contribution to the work of cavity formation arising from the surface tension is given by:

$$\gamma_{cav} = \frac{kT}{4\pi\sigma^2_{12}}\left(12\left(\frac{y_1}{1-y_1}\right) + 18\left(\frac{y_1}{1-y_1}\right)^2\right) - \frac{\rho\sigma_{12}}{2} \quad (12)$$

where p is the external confining pressure, $y_1 = \pi\rho^3_1/6$ is the reduced number density or packing fraction of the solvent and the other terms are as defined previously. The second term containing the pressure is generally negligible in comparison to the first and can be ignored unless the pressure is very high.

The surface tension due to solute-solvent interaction per cavity, $\gamma_i$, is obtained by dividing the work of interaction by the area of the cavity $\gamma_i = W^s_i/A_{cav}$ where $A_{cav} = 4\pi\sigma^2_{12}$ and then Eq. (10) will be presented as :

$$\gamma_i = -\frac{y}{4\pi\sigma^2_{12}} \times \quad (13)$$

$$\left[\frac{64}{3}\varepsilon_{12} + \frac{8}{\sigma^6_{12}}\left(\alpha^2_1\mu^2_2 + \alpha^2_2\mu^2_1 + \frac{2}{3}\frac{\mu^2_1\mu^2_2}{kT}\right)\right]$$

By substituting for $\gamma_{cav}$ from Eq. (12) and $\gamma_i$ from Eq. (13) the surface tension of binary mixture is derived by the following equation:

$$\gamma = \frac{KT}{4\pi\sigma^2_{12}}\left(12\left(\frac{y_1}{1-y_1}\right) + 18\left(\frac{y_1}{1-y_1}\right)^2\right) - \frac{p\sigma_{12}}{2} \quad (14)$$

$$-\frac{y}{4\pi\sigma^2_{12}}\left[\frac{64}{3}\varepsilon_{12} + \frac{8}{6^6_{12}}\right]\left(\alpha^2_1\mu^2_2 + \alpha^2_2\mu^2_1 + \frac{2}{3}\frac{\mu^2_1\mu^2_2}{KT}\right)$$

As it was mentioned, this equation clearly shows that the surface tension of real fluid is the sum of both repulsive and attractive terms. The first and the second terms in Eq. (14) are due to repulsive forces and the third term is due to attractive forces. At the critical point, these terms balance exactly and the surface tension vanishes. For a pure fluid $\sigma_1 = \sigma_2$, $\mu_1 = \mu_2$, $\alpha_1 = \alpha_2$ and $y_1 = y_2 = y_c$ and at this point T=$T_c$. By introducing these equalities into Eqs. (12), (13) and (14) and neglecting the term $\rho\sigma_{12}/2$ the following relationship is obtained:

$$\left(\frac{\varepsilon}{k}\right) = \frac{9(2 + y_c)}{32(1 - y_c)^2}T_c - \frac{3\mu^2}{4\sigma^6 k}\left(\alpha + \frac{\mu^2}{3kT_c}\right) \quad (15)$$

3

Inspection of Eq. (15) shows that for a given compound or atom there are two temperature independent contributions to the LJ energy parameter, a geometric packing density term and molecular or atomic constants ($\alpha$ and $\mu$). Eq. (15) gives a simple means of computing the LJ energy parameter of a pure component from its critical number density, the hard sphere diameter, critical temperature, polarizability and dipole moment.

For molecules with no dipole moment, we can rewrite Eq. (15) for energy parameter of the (6-12) LJ:

$$\left(\frac{\varepsilon}{k}\right) = \frac{9(2+y_c)}{32(1-y_c)^2} T_c \tag{16}$$

As is noted later on, the critical packing fraction function, $9(2+y_c)/32(1-y_c)^2$ in Eq. (16) does not vary much for different compounds and therefore, Eq. (16) can provide a good approximation to the LJ energy parameter from critical temperature and the reduced number density or packing fraction at critical point. For most compounds critical volume and temperature are known with high accuracy and Eq. (16) enables us to estimate the LJ energy parameter very accurate.

**RESULTS AND DISCUSSION**

Eqs. (15) and (16) have been used to calculate the LJ energy parameter ($\varepsilon/k$) for a range of pure fluids including noble gases, diatomic gases, short and medium length hydrocarbons, aromatic compounds and some oxygen containing compounds. The properties required for calculations as input data are $T_c$, $V_c$, $\mu$, $\alpha$ and hard sphere diameter. It is worth noting that $(\sigma)_{Meth.}^{Ref.}$ was obtained from other methods, i.e., second virial coefficient (a), isothermal compressibility (b), viscosity (c), gas solubility (d), cell theory (e), cavity theory (f) and free volume theory (g) are also collected and reported in table 1, where the fluids are ordered according to their type. It should be noted that in the reported values of $(\sigma)_{Meth.}^{Ref.}$, the subscript indicates the method and the superscript indicates the reference where the data has been taken from. The calculated effective LJ energy parameters $(\varepsilon/k)^{Calc.}$ are reported in table 1. However as mentioned by other researchers the shortcomings of the methods used in calculating of $\varepsilon/k$ should be considered [37].

Also table 1 shows the dependence of $\varepsilon/k$ on molecular size. For small molecules, $\varepsilon/k \leq 350$ K, and for large molecules; $\varepsilon/k > 350$ K. These values are quite expected since larger molecules have higher interaction energy due to larger surface of interaction.

The size parameter ($\sigma$) depends on the method used. For example ($\sigma$) values evaluated from various methods such as second virial coefficients [33], viscosity [1,2] and gas solubility [6-15] are largely different from each other. De Ligny and van der Veen [10] have argued that ($\sigma$) values obtained from solubility data and by using their correlation [10,36] can be more reliable than the other methods.

The size parameter $\sigma$ can be calculated from the *van der Waals* volume based on group contributions [35] by assuming hard sphere shape for molecules. However in the case of large molecules our calculations indicated that hard sphere assumption makes a large deviation in the calculated results, therefore the literature data of size parameter $\sigma$, as sited in table 1, have been used in the calculations of $\varepsilon/k$. It is worth mentioning that the calculated $\varepsilon/k$, as it is the case for similar calculations of $\varepsilon/k$, is in fact an effective parameter for *Lennard-Jones* potential.

Since a direct experimental method is not available to obtain a reliable values for $\varepsilon/k$ the only way left is calculating another property such as surface tension and compare the results with experimental data to judge which method gives more reliable value for effective $\varepsilon/k$.

The calculated effective $\varepsilon/k$ by SPT are presented in table 1 as $(\varepsilon/k)^{Calc.}$. The results of $(\varepsilon/k)^{Calc.}$ were used in Eq. (14) to predict the surface tension of the substances whose surface tensions near critical temperature were reported in literature. The results are reported in table 2. Also in this table the surface tensions calculated by *Reiss* SPT theory [30] are reported. The absolute deviations (*AD*) calculated as:

$$AD = \left| \gamma_{Exp.} - \gamma_{Calc.} \right| \tag{17}$$

indicate that calculated surface tensions by the SPT theory proposed in this work are in better agreement than those calculated by the SPT theory of *Reiss* [30].

The overall absolute deviation (OAD) for all pure compounds is defined as:

**Table 1: The effective Lennard-Jones energy parameters $(e/k)^{Cal.}$ calculated by SPT in this work and the input data of the substances: critical temperature $T_c$, critical molar volume $V_c$, dipole moment $m$, polarizibility $a$ and $(s)_{Meth.}^{Ref.}$.**

| Substance | $T_c$ (K) | $V_c$ (cm³/mol) | μ (Debye) | α /10⁻²⁴ (cm³/mol) | $(\sigma)_{Meth.}^{Ref.} \times 1.^\wedge$ (cm) | $(\varepsilon / k)^{Calc.}$ (K) |
|---|---|---|---|---|---|---|
| He | 5.19 | 57.4 | | 0.204[22] | 2.63 a[33] | 3.78 |
| Ne | 44.4 | 41.6 | | 0.393[22] | 2.75 a[33] | 37.96 |
| Ar | 150.8 | 74.9 | | 1.63[22] | 3.423 b[33] | 133.13 |
| Kr | 209.4 | 91.2 | | 2.46[22] | 3.59 a[33] | 180.24 |
| Xe | 289.7 | 118.4 | | 4[22] | 4.055 c[33] | 262.26 |
| $H_2$ | 33.2 | 65.1 | | 0.82[45] | 2.87 a[33] | 25.18 |
| $N_2$ | 126.2 | 89.8 | | 1.76[45] | 3.4 d[41] | 102.12 |
| $O_2$ | 154.6 | 73.4 | | 1.6[45] | 3.46 a[33] | 140.11 |
| CO | 132.9 | 93.2 | 0.112[46] | 1.94[45] | 3.763 a[33] | 120.53 |
| NO | 180 | 57.7 | 0.158[46] | 1.7[45] | 3.17 a[33] | 153.26 |
| $CS_2$ | 552 | 160 | 0.326[46] | 8.05[45] | 4.438 c[33] | 472.74 |
| $CF_4$ | 227.6 | 139.6 | | 2.89[45] | 4.15 c[42] | 196.73 |
| $CCl_4$ | 556.4 | 275.9 | | 10.24[45] | 5.35 e[38] | 499.99 |
| $CH_4$ | 190.4 | 99.2 | | 2.6[45] | 3.697 b[33] | 164.19 |
| $C_2H_6$ | 305.4 | 148.3 | | 4.4[45] | 4.384 c[33] | 277.74 |
| $C_3H_8$ | 369.8 | 203 | | 6.23[45] | 5.06 f[43] | 358.75 |
| $n$-$C_4H_{10}$ | 425.2 | 255 | | 8.02[45] | 5.52 f[43] | 420.84 |
| $i$-$C_4H_{10}$ | 408.2 | 263 | | 8.01[45] | 5.55 f[43] | 400.4 |
| $n$-$C_5H_{12}$ | 469.7 | 304 | | 9.88[45] | 5.78 f[43] | 454.4 |
| $n$-$C_6H_{14}$ | 507.5 | 370 | | 11.63[45] | 5.964 e[44] | 463.73 |
| $n$-$C_7H_{16}$ | 540.3 | 432 | | 13.37[45] | 6.24 g[8] | 488.81 |
| $n$-$C_8H_{18}$ | 568.8 | 492 | | 15.24[45] | 6.52 d[8] | 515.02 |
| $i$-$C_8H_{18}$ | 544 | 468 | 0.03[48] | 9.336[47] | 6.44 e[38] | 495.88 |
| $n$-$C_9H_{20}$ | 594.6 | 548 | | 17.37[45] | 6.83 d[49] | 547.34 |
| $n$-$C_{10}H_{22}$ | 617.7 | 603 | | 19.1[45] | 7.08 d[49] | 572.34 |
| $n$-$C_{12}H_{26}$ | 658.2 | 713 | | 22.72[45] | 7.58 d[49] | 622.51 |
| $C_8H_{18}$ [I] | 563.7 | 464 | | 15.44[45] | 6.52 d[49] | 526.55 |
| $C_8H_{18}$ [II] | 563.5 | 468 | | 15.45[50] | 6.5 d[49] | 521.29 |
| $C_8H_{18}$ [III] | 553.5 | 472 | | 15.45[50] | 6.52 d[49] | 512.23 |
| $n$-$C_7F_{16}$ | 474.8 | 664 | | 14.57[22] | 7.04 d[49] | 415.4 |
| $C_2H_4$ | 282.4 | 130.4 | | 4.09[45] | 4.066 c[33] | 244.86 |
| $C_6H_6$ | 562.2 | 259 | | 9.96[45] | 5.25 d[8] | 506.9 |
| $C_6F_6$ | 516.7 | 335 | | 9.83[45] | 5.65 d[49] | 457.37 |
| $C_7H_8$ | 591.8 | 316 | 0.37[46] | 11.86[45] | 5.64 d[49] | 530.36 |
| $m$-$C_8H_{10}$ | 617.1 | 376 | 0.34[46] | 13.69[45] | 5.97 d[49] | 556.18 |
| $c$-$C_5H_{10}$ | 511.7 | 260 | | 9.17[45] | 5.4 f[43] | 481.64 |
| $c$-$C_6H_{12}$ | 553.5 | 308 | | 10.75[45] | 5.62 g[8] | 507.14 |
| $C_7H_{14}$ [IV] | 572.2 | 368 | | 13.1[51] | 5.99 d[49] | 527.99 |

*[I] 3-Methylheptane, [II] 2,3-Dimethylhexane, [III] 2,4-Dimethylhexane, [IV] Methylcyclohexane.*

*\* All critical temperature and volume have been taken from Ref. [52].*

*\* The superscript indicates the reference to the data source. The subscript indicates the method (property or theory) used to obtain $(\sigma)_{Meth.}^{Ref.}$. The methods are, a: second virial coefficient, b: isothermal compressibility, c: viscosity, d: gas solubility, e: cell theory, f: cavity theory and g: free volume theory.*

***Table 2: The experimental density d and surface tension g_Exp. at near critical pressure P and temperature T and the surface
tensions (g_Calc.) calculated in this work by using Eq. (14) compared with the Reiss's surface tension (g_Reiss) calculated by Eq. (12).
The (AD_1) and (AD_2) are respectively the absolute deviations in surface tensions from experimental values calculated
by SPT theory in this work and calculated by SPT theory of Reiss[30] .The AD is defined as:*** $AD = \left| \gamma_{Exp.} - \gamma_{Calc.} \right|$

| Substance | T (K) | P (KPa) | d (gr/cm³) | $\gamma_{Exp.}$ (mN/m) | $\gamma_{Cal.}$ (mN/m) | (AD)$_1$ | $\gamma_{Reiss}$ (mN/m) | (AD)$_2$ |
|---|---|---|---|---|---|---|---|---|
| Ar | 143.8 | 3702 | 0.877 | 2.61 | 1.77 | 0.84 | 9.16 | 6.55 |
| Ne | 41 | 1688 | 0.859 | 0.65 | 0.86 | 0.21 | 4.14 | 3.49 |
| Ne | 43 | 2216 | 0.754 | 0.2 | 0.43 | 0.23 | 3.31 | 3.11 |
| CO | 125 | 2423 | 0.526 | 1.13 | 2.32 | 1.19 | 8.61 | 7.48 |
| CH$_4$ | 18.38 | 3288 | 0.2764 | 1.048 | 1.98 | 0.93 | 9.71 | 8.66 |
| CH$_4$ | 181.86 | 3470.2 | 0.269 | 0.865 | 1.72 | 0.86 | 9.24 | 8.38 |
| CH$_4$ | 183.15 | 3650 | 0.26 | 0.5 | 1.41 | 0.91 | 8.68 | 8.18 |
| CH$_4$ | 188.06 | 4246.63 | 0.2288 | 0.17 | 0.50 | 0.33 | 6.90 | 6.73 |
| C$_2$H$_6$ | 300 | 4365 | 0.3163 | 0.43 | 2.19 | 1.76 | 11.66 | 11.23 |
| C$_2$H$_6$ | 301 | 4474.9 | 0.2998 | 0.233 | 1.50 | 1.27 | 10.47 | 10.24 |
| C$_2$H$_6$ | 304 | 4737.7 | 0.2659 | 0.055 | 0.35 | 0.30 | 8.31 | 8.26 |
| C$_3$H$_8$ | 367.18 | 4052 | 0.3 | 0.4 | 1.32 | 0.92 | 10.45 | 10.05 |
| n- C$_4$H$_{10}$ | 405 | 2739 | 0.388 | 1.34 | 5.27 | 3.93 | 16.73 | 15.39 |
| n- C$_5$H$_{12}$ | 440 | 2103 | 0.4235 | 1.6 | 5.70 | 4.10 | 17.09 | 15.49 |
| n- C$_6$H$_{14}$ | 475 | 1859 | .432 | 1.63 | 4.79 | 3.16 | 15.03 | 13.40 |
| C$_6$H$_6$ | 553.5 | 4387 | 0.446 | 0.37 | 1.86 | 1.43 | 13.10 | 12.37 |
| c-C$_6$H$_{12}$ | 535 | 3723 | 0.445 | 0.5 | 3.12 | 2.62 | 14.26 | 13.76 |
| OAD | | | | | | 1.32 | | 8.59 |

*\* All experimental data for density and surface tension have been taken from Ref. [53].*

$$OAD = \sum_{i=1}^{N} AD_i / N \qquad (18)$$

where N is the number of pure compounds reported in table 2.

To show the effect of molecular interactions in surface tension calculations, as considered in our SPT theory, the equation derived by *Reiss* (Eq. (12)) in which the molecular interactions are neglected, was also used in the surface tension calculation. The results of these calculations are also reported in table 2. By comparing Eq. (12), in *Reiss's* SPT theory and Eq. (14) obtained in this work, it can be seen that the following term due to molecular interactions has been neglected in the

$$-\frac{y}{4\pi\sigma_{12}^2}\left[\frac{64}{3}\varepsilon_{12} + \frac{8}{\sigma_{12}^6}\left(\alpha_1^2\mu_2^2 + \alpha_2^2\mu_1^2 + \frac{2}{3}\frac{\mu_1^2\mu_2^2}{kT}\right)\right]$$

*Reiss's* SPT theory which causes a large deviation from experimental values of surface tension near critical temperature. This is indicated by comparing AD$_{(1)}$, AD$_{(2)}$ where subscripts (1) and (2) indicate this work and *Reiss's* SPT theory. The calculated OADs also confirm this conclusions.

The calculation of the LJ energy parameter (Eqs. (15) and (16)) requires the knowledge of the critical packing fraction, $y_c = \pi\rho_c\sigma_1^3/6$, and hence, the critical number density. It is instructive to determine the relative sensitivity of the input parameters in Eqs. (15) and (16), due to their functional form, to the predicted values of the LJ energy parameter. To carry this out, the value of each of the properties in turn was increased by 10 percent and the percentage change in the LJ energy parameter was determined. An increase of the critical volume by 10 % gave only a 0.99 % decrease in the predicted value of the

LJ energy parameter. By comparison a 10 % increase in the critical temperature, gave only a 4 % raise in the LJ energy parameter. It was also observed that the packing fraction function, $9(2+y_c)/32(1-y_c)^2$ in Eq. (16) is very close to a constant for the non polar compounds listed in table 1. It has an average value of 0.9264 with a standard deviation of only 0.0676. In other words, in nonpolar fluids the LJ energy parameter is principally a function of the critical temperature multiplied by a constant (0.9264). The conclusion of this analysis is that; the predicted values of the LJ energy parameter are relatively insensitive to uncertainty in the critical densities.

## CONCLUSIONS

For a range of pure fluids including noble gases, diatomic and triatomic gases, short and medium length hydrocarbons, aromatic compounds, oxygen containing compounds the effective *Lennard-Jones* energy parameters have been calculated by using a simple equation derived from SPT. The results are compared with those calculated by Reiss SPT theory. The effective *Lennard-Jones* energy parameters calculated by both SPT theories were used to calculate the surface tension of pure compounds near critical temperature and were compared with the experimental data. The results indicated that the developed SPT in this work calculates the surface tensions much closer to the experimental data compared with those of *Reiss's* SPT theory.

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