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Effective Intermolecular Pair Potentials for Sulphur Dioxide

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New effective intermolecular pair potentials for sulphur dioxide, obtained by molecular dynamics simulation, are proposed. Potentials found in the literature, fitted to the gas and crystal properties, are also described. Their comparison points to the conclusion that the new ones are more realistic.

1. INTRODUCTION

The effective intermolecular pair potential is the basic microscopic property from which macroscopic quantities may be calculated. Unfortunately, this connection is very intricate and there is no direct method for obtaining the potential. Theoretical considerations can given only its general dependence on intermolecular coordinates. What is usually done is to presuppose some analytical form of the potential and to determine the free parameters by fitting some macroscopic property.

One can give a long list of publications presenting such calculations for simpler systems. These are monoatomic, i. e. rare-gas systems, homonuclear diatomics: N_2 [1], F_2, Cl_2, Br_2 [2], heteronuclear diatomics: HCl[3,4], linear triatomics: CS_2 [5], and nonlinear triatomics: H_2O [6]. These references are quoted and given only as an illustration.

Our main aim is to represent the interaction of SO_2 molecules in a liquid, and for this reason we have chosen the thermodynamic properties of a liquid, energy and pressure, as properties to be fitted. These properties are given in Section 2. Several increasingly sophisticated forms of the pair potential are considered: one site Lennard-Jones (LJ) (Section 3), three-site LJ (Section 4), three site LJ with fractional charges (Section 5) and three-site LJ with dipole and quadrupole moments (Section 6).

2. PHYSICO-CHEMICAL PROPERTIES OF SULPHUR DIOXIDE

In the gas phase sulphur dioxide has the structure of an isosceles triangle (C_{2v} symmetry) with an apex angle of $\angle OSO = (119.5 \pm 0.3)°$ and a bond length of $r(S - O) = (1.4343 \pm 0.0003)$ Å[7,8]. It is assumed, in what follows, that these structural parameters do not change appreciably in the liquid state.

The boiling and freezing point temperatures are equal to (see ref. 9):

$$T_b = 263.07 \text{ K}$$
$$T_f = 197.63 \text{ K}$$

and the critical point (see ref. 10) is

$$T_c = 430.75 \text{ K} \qquad P_c = 78.1 \ 10^5 \text{ Pa} \qquad V_c = 122 \ 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

Liquid densities along the liquid-gas coexistence curve are given by the following interpolation equation (see ref. 9)

$$\varrho = 1.434 - 2.486 \ 10^{-3} \ t - 2.62 \ 10^{-6} \ t^2 - 5.59 \ 10^{-8} \ t^3 + 8.1 \text{-} 10^{-11} \ t^4 \qquad (1)$$

where ϱ is given in gcm^{-3} and t is the temperature in °C.

On the liquid-gas coexistence curve, the internal energy of 1 mole of liquid is equal to

$$E_{liq} = H_{vap} - l - P V_{liq} \qquad (2)$$

where H_{vap} is the enthalpy of the vapour, and l the heat of vaporization.

The contribution of vibrational energy to the total energy of the liquid and gas is the same at the same temperature. Therefore, we exclude vibrational energy from further discussion and whenever we speak of energy we mean the total energy from which the vibrational energy is substracted. The enthalpy of the vapour is calculated from the virial coefficient

$$H_{vap} = 4 RT + P \left[B(T) - T \ \frac{dB(T)}{dT} \right] \qquad (3)$$

where $B(T)$ is the second virial coefficient given by the Berthelot equation of state for nonideal gas

$$B(T) = \frac{R}{8} \ \frac{T_c}{P_c} \left(1 - \frac{27}{8} \ \frac{T_c^2}{T^2} \right) \qquad (4)$$

The contribution of the rotational energy to the total energy of 1 mole of matter is equal to $3/2 \ RT$ at temperature T (in K). In the case when there are no rotational degrees of freedom (potential of spherical symmetry) we have to compare the results of our simulation for total energy with those experimentally obtained values from which the rotational contribution is substracted. In that case the expression for the enthalpy of vapour is given by

$$H_{vap} = \frac{5}{2} \ RT + P \left[B(T) - T \ \frac{dB(T)}{dT} \right] \qquad (5)$$

We have chosen four points on the liquid-gas coexistence curve to compare experimental and numerical results.

In Table I the values are given of the coresponding thermodynamical variables. The molar volume is obtained from (1) knowing that the molecular mass is $M_w = 64.066 \ g \ mol^{-1}$. The heat of vaporization (l) is deduced from Figure 2—2 of ref. 10, and the vapour pressure from Figure 2—1 of the same reference.
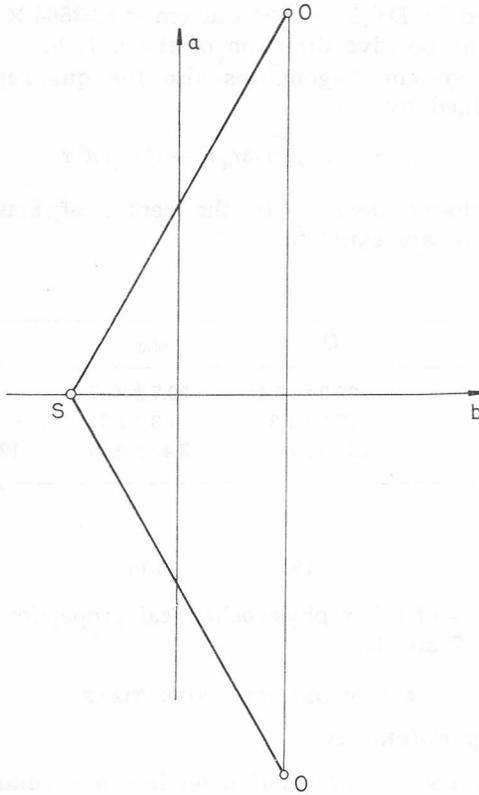
Figure 1. Inertial system of coordinates for SO₂ molecule

In the inertial system of coordinates for SO₂ molecule, Figure 1, the moments of inertia equal

I_{aa}	I_{bb}	I_{cc}
13.82	81.04	94.86

in 10^{-47} kg m²

TABLE I

Experimental Thermodynamic Properties along the Liquid-Vapour
Coexistence Line of SO₂

Thermo. state	T/K	$V_M/10^{-6}$ m³	$l/\dfrac{kJ}{mol}$	P/MPa	$E_{liq}/\dfrac{kJ}{mol}$ with rotation	without rotation
1	220	40.863	27.35 ± 0.15	0.0125	-20.06 ± 0.15	-22.80 ± 0.15
2	250	42.94	25.88 ± 0.15	0.05	-17.70 ± 0.15	-20.82 ± 0.15
3	323.16	49.395	21.05 ± 0.15	0.86	-11.19 ± 0.25	-15.22 ± 0.25
4	350	53.21	18.77 ± 0.15	1.58	-8.52 ± 0.25	-12.89 ± 0.25

In this coordinate system the dipole moment equals (see ref. 9).

$$\vec{\mu} = -1.62 \ \vec{j}$$

where $\vec{\mu}$ is expressed in D $(1D = 10^{-18}$ esu cm $= 3.33564 \times 10^{-30}$ Cm) and $\vec{j}$ is the unit vector in the positive direction of the axis b.

This coordinate system diagonalizes also the quadrupole tensor, whose components are defined by

$$Q_{\alpha\beta} = {}^{1}\!/_{2} \int \varrho_e (\vec{r}) (3r_\alpha r_\beta - r^2 \delta_{\alpha\beta}) \, d^3 r \tag{6}$$

Here $\rho_e (\vec{r})$ is the charge density. In the centre of mass the components expressed in 10^{-40} Cm² are equal to

Experimental:

	Q_{aa}	Q_{bb}	Q_{cc}
Ref. 11	-22.0 ± 25.4	29.7 ± 27.7	-7.7 ± 25.4
Ref. 12	-17.7 ± 1.3	4.3 ± 1.3	13.3 ± 2.0
Ref. 13	-16.45 ± 0.33	3.42 ± 0.10	12.93 ± 0.20

Theoretical:

Ref. 14	-22.95	5.70	17.25

Extensive analysis of other physicochemical properties of sulphur dioxide can be found in ref. 7 and 9.

3. THE ONE-SITE POTENTIALS

a) *Already Existing Potentials*

Experimental sources of information on intermolecular potential are the gas phase virial coefficient and the viscosity data. The usual procedure is to postulate some two-body potential involving two or more parameters and then to determine them by fitting the experimental data. In fact, this was the way taken by Hirschfelder, Curtiss and Bird in their classical work »Molecular Theory of Gases and Liquids«[15]. In the case of sulphur dioxide they give only potential parameters obtained by fitting the viscosity data. For the Lennard-Jones potential of the form

$$U(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\} \tag{7}$$

they give, on page 1111, the following values for the parameters

$$\frac{\varepsilon}{k_B} = 252 \text{ K} \qquad\qquad \sigma = 4.290 \text{ Å}$$

where k_B is the Boltzman constant.

The interaction of polar molecules is better represented by adding to (7) the dipole-dipole interaction, which gives the angle-dependent Stockmayer potential

$$U(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\} - \frac{1}{4\pi\varepsilon_0} \frac{\mu^2}{r^3} g(\Theta_1, \Theta_2, \Phi_2 - \Phi_1) \tag{8}$$

where the function g is given by

$$g(\Theta_1, \Theta_2, \Phi_2 - \Phi_1) = 2 \cos \Theta_1 \cos \Theta_2 - \sin \Theta_1 \sin \Theta_2 \cos (\Phi_2 - \Phi_1) \tag{9}$$

The angles are defined in Figure 2:
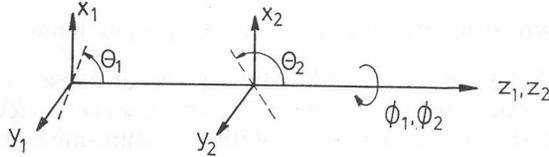
Figure 2. Definition of angles determining the relative orientation of two dipolar particles.

For very high energy collisions, where the repulsive forces are more important than the attractive forces, it is a fairly good approximation to replace this angle-dependent contribution by the expression which corresponds to the interaction of two point dipoles that are perfectly aligned

$$U(r) = 4 \varepsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right\} - \frac{1}{4 \pi \varepsilon_0} \frac{2 \mu^2}{r^3} \tag{10}$$

For such a potential, by using the data on viscosity and thermal conductivity, the following parameters are given on page 599 of ref. 15

$$\frac{\varepsilon}{k_B} = 191.4 \text{ K} \qquad \sigma = 4.341 \text{ Å} \qquad \mu = 1.611 \text{ D}$$

The parameters of the angle-dependent Stockmayer potential obtained by fitting the viscosity data are given in[16].

$$\frac{\varepsilon}{k_B} = 328.5 \text{ K} \qquad \sigma = 4.102 \text{ Å} \qquad \mu^* = \frac{\mu}{\sqrt{4 \pi \varepsilon_0 \varepsilon \sigma^3}} = 0.85$$

The Stockmayer potential parameters, not specified whether they refer to an angle-dependent or angle-independent case, can be deduced from the following quantities obtained by fitting the second virial coefficient data given in[17]

$$\frac{\varepsilon}{k_B} = 455 \text{ K} \qquad b_0 = \frac{2}{3} \pi \tilde{N} \sigma^3 = 30.29 \text{ cm}^3 \text{ mol}^{-1} \qquad t^* = \frac{1}{\sqrt{8}} \frac{\mu^2}{\varepsilon \sigma^3} = 0.6$$

where $\tilde{N}$ is the Avogadro number. One obtains

$$\frac{\varepsilon}{k_B} = 455 \text{ K} \qquad \sigma = 2.885 \text{ Å} \qquad \mu = 1.60 \text{ D}$$

Another one-site intermolecular potential fitted to the second virial coefficient data is the Barker-Bobetic (BB) potential (see ref. 18). The BB potential describes the nonpolar interaction between the particles by

$$U(R) = \varepsilon \left\{ [\exp \alpha (1 - r)] \sum_{i=0}^{5} A_i (r - 1)^i - \sum_{i=0}^{z} \frac{C_{2i+6}}{\delta + r^{2i+6}} \right\} \tag{11}$$

where r is $\dfrac{R}{R_m}$, with R_m being the separation at the minimum of the poten-
tial, and ε the depth at the minimum. The second summation in (11) ensures
that the potential has the correct form at large distances where the asymptotic
behaviour is known to involve (negative) terms proportional to $\dfrac{1}{R^6}$, $\dfrac{1}{R^8}$ etc. The
constant δ is included to supress the divergence of these terms at small R.
The first summation, intended to describe the overlap effects important at
small distances, has a form consistent with quantum-mechanical calculations
which suggest an exponentially decreasing function multiplied by a rela-
tively slowly varying polynomial. The non-polarizable dipole interaction is
described by the second summand in (8). The obtained parameters for SO_2
equal

$$\mu = 1.61 \text{ D} \qquad \frac{\varepsilon}{k_B} = 501.8 \text{ K} \qquad R_m = 3.374 \text{ Å} \qquad t^* = 0.3360$$

(see ref. 19).

b) Potentials Obtained From MD Calculations (Model A)

The first and the most unrealistic potential by which we tried to repre-
sent the intermolecular interaction between two SO_2 molecules in pure liquid
is given by the one-site Lennard-Jones (LJ) potential (7). We noticed that
it was impossible to reproduce liquid-state properties (P and E_{liq}) for dif-
ferent temperatures with only one set of parameters (ε and σ). The main
interest of this model is to notice the difference between models with and
without rotational degrees of freedom. Another interesting point of this
model is that there is a systematic way of finding the ε and σ parameters
for each temperature, which, however, do not exist for the more sophisticated
potentials we used. We describe briefly this method: For a given density
we obtain T, E_{liq} (in what follows it will be indicated simply by E) and P
as a result of the MD calculations for several values of ε and σ. We define
the reduced values

$$T^* = \frac{k_B T}{\varepsilon} \qquad E^* = \frac{E}{\bar N \, \varepsilon} \qquad p^* = \frac{P \, \sigma^3}{\varepsilon} \qquad (12)$$

We plot E^* as a function of T^* for different ε and T and fixed σ. In this
way we obtain one curve for each σ. On the same graph we represent also
the experimental dependence of E^* on T^* and we look for the intersection
of the two curves. These intersections form a curve in the (ε, σ) diagram,
where ε is obtained from the relation

$$\varepsilon = \frac{K_B T}{T^*} \qquad (13)$$

We do the same for P^* as a function of T^*, where for the experimental
dependence of P^* on T^* we take $P^* = 0$, which expresses the fact that the
experimental values of pressure at the liquid-gas coexistence line are quite
negligible in comparison with the calculated ones. The two curves in the

(ε, σ) diagram intersect at the point whose coordinates are the right ε, σ values for the given density.

Here are some details about the MD simulation on CRAY 1S computer

N	108	256	500
t/s	0.006	0.028	0.097

where N is the number of particles, and t is the time needed to perform one step in seconds. The time step is $10fs = 10^{-14}$ s.

The results for ε and σ for the thermodynamic points given in Table I are given in the following table:

TABLE II

Best Sets of (ε, σ) for the One-Site LJ Potential (Model A)

Thermo. state	$\dfrac{\varepsilon}{k_B}/K$	$\sigma/\text{Å}$
1	418.1	4.040
2	405.8	4.078
3	402.2	4.033
4	389.9	4.046

Several thousands of steps were usually performed to obtain the equilibrium configuration, and then averages were taken over the additional two to three thousand steps.

4. THE THREE-SITE LENNARD-JONES POTENTIAL

a) *Already Existing Potentials*

The potential which takes correctly into account the geometry of the molecule is the three-site LJ model where sites have been chosen to coincide with the equilibrium positions of the atoms. We do not allow intermolecular distances to change, which means that we are working in the approximation of a rigid molecule. The intermolecular pair potential is given as the sum of atom-atom contributions

$$U (r, \Theta, \Phi, \alpha, \beta, \gamma) = \sum_{ij} u_{ij} (r_{ij}) \tag{14}$$

This potential is written for one molecule being fixed at the origin and the position and orientation of the second being determined by polar coordinates and Euler angles, respectively. Atom-atom potentials are of the LJ type

$$u_{ij} (r_{ij}) = 4\,\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right\} \tag{15}$$

Interactions between unlike atoms are usually supposed to follow the Lorentz-Berthelot mixing rules

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{16}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\,\varepsilon_{jj}} \tag{17}$$

The sulphur-sulphur and oxygen-oxygen LJ parameters used in the literature are given in the Table III.

TABLE III

LJ Parameters from the Literature

	$\dfrac{\varepsilon_{ss}}{k_B}$/K	σ_{ss}/Å	$\dfrac{\varepsilon_{oo}}{k_B}$/K	σ_{oo}/Å
(a)	183.0	3.52		
(b)	190.7	3.37		
(c)	387.6	3.3		
(d)			61.6	2.95
(e)			83.1	3.383
(f)			83.1	3.014
			75.2	3.026

The origin of the data are listed in the following:
(a) study of liquid CS_2, ref. 5
(b) second virial coefficient of CS_2, ref. 20
(c) solid state properties of CS_2, ref. 21
(d) work on solid O_2, ref. 22
(e) work on gas, liquid and solid CO_2, ref. 23
(f) work on solid CO_2, ref. 24

Values (a) and (d) for ε_{ss}, σ_{ss} and ε_{oo}, σ_{oo}, respectively, are proposed by D. J. Tildesley[25] as a good first guess in constructing a new core model, although, as he notes, these parameters were not originally designed to be transferable.

As far as we know, there is only one set of LJ parameters in the literature for the three-site model of SO_2, (see ref. 26). They were used to calculate the solid-state properties. They are equal to

$$\frac{\varepsilon_{ss}}{k_B} = 17.12 \text{ K} \qquad \sigma_{ss} = 4.92 \text{ Å} \qquad \frac{\varepsilon_{oo}}{k_B} = 199.9 \text{ K} \qquad \sigma_{oo} = 2.97 \text{ Å}$$

$$\frac{\varepsilon_{so}}{k_B} = 314.0 \text{ K} \qquad \sigma_{so} = 2.82 \text{ Å}$$

One should note the following facts

(*i*) These parameters do not follow the Lorentz-Berthelot mixing rule

(*ii*) They are very different from the corresponding atom-atom parameters used for other molecules.

For comparison we present in Figure 3 and 4 the atom-atom potential dependence on distance obtained by Rastogi et al.[26] and by us (the latter is given in Table IV).

One notices that the potentials of Rastogi et al. are very deep and with a short equilibrium distance, except for the S—S interaction. This S—S interaction is very different from all the others found in the literature.

b) Potentials Obtained from the MD Calculations (Model B)

As in the case of one-site LJ potential, see Table II. It was impossible to find a set of LJ parameters that would reproduce the liquid-state properties for different points on the liquid-gas coexistence line. The fitting of the paramteers was executed by trial and error as to obtain the relevant energies and pressures. A rather important adjustment (as high as 10 per cent) of the parameter ε is necessary to follow the coexistence line with accuracy. This suggests that it may be possible to reduce the deviation substantially by taking into account the charge distribution of SO_2 explicitly. The results of the MD calculations are given in the Table IV.
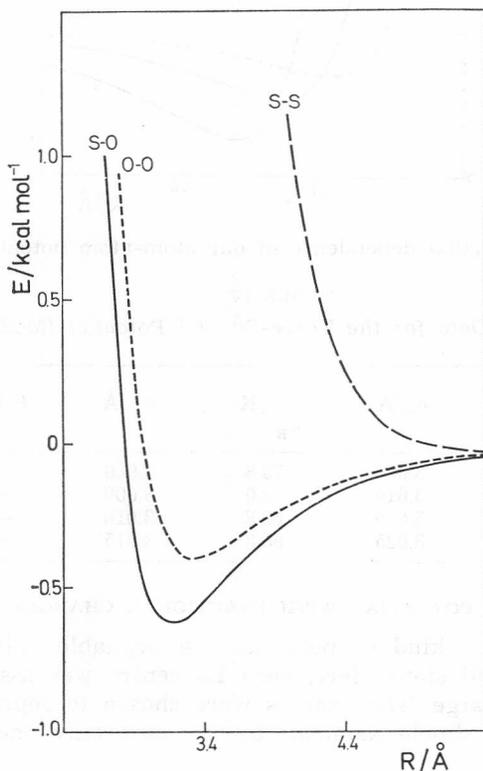
Figure 3. Radial dependence of Rastogi et al. atom-atom potentials.
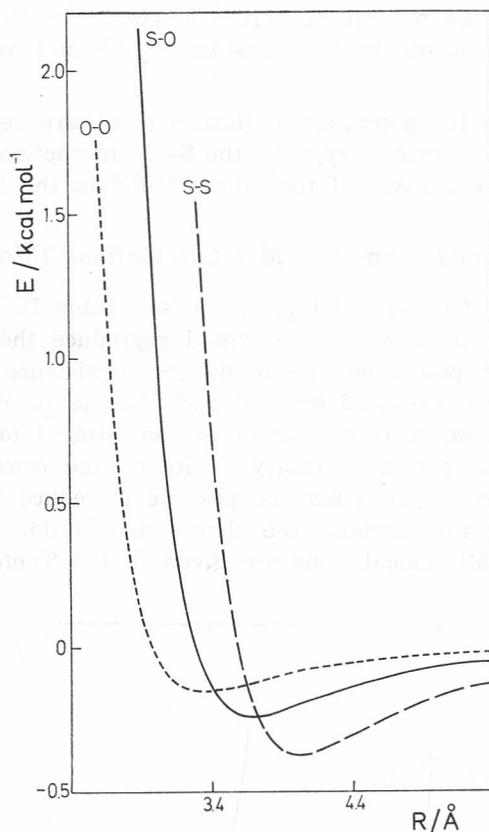
Figure 4. Radial dependence of our atom-atom potentials.

TABLE IV

Simulation Data for the Three-Site LJ Potential (Model B)

Thermo. state	$\dfrac{\varepsilon_{ss}}{k_B}$/K	σ_{ss}/Å	$\dfrac{\varepsilon_{oo}}{k_B}$/K	σ_{oo}/Å	P/MPa	$E/\dfrac{kJ}{mol}$
1	186.5	3.580	73.8	2.980	— 7	— 20.13
2	182.0	3.610	72.0	3.000	+ 1	— 17.75
3	172.5	3.610	69.8	3.010	— 2	— 11.22
4	167.5	3.625	66.8	3.015	— 1	— 8.41

5. THREE-SITE LJ POTENTIAL WITH FRACTIONAL CHARGES (MODEL C)

Parameters for this kind of potential are available only from the MD simulation of the liquid state. Here, each LJ centre was assumed to be the site of a fractional charge. The charges were chosen to reproduce the experimental value of the dipole moment. In this case only one set of charges was possible.

$$q_s = 7.53 \times 10^{-20}\,C, \qquad q_o = -\frac{1}{2}\,q_s$$

The quadrupole tensor components which correspond to this distribution of charges are

Q_{aa}	Q_{bb}	Q_{cc}
-11.44×10^{-40} Cm²	5.72×10^{-40} Cm²	5.72×10^{-40} Cm²

The axes are defined in Figure 1. It must be pointed out that these quadrupole tensor components differ from those obtained by experiment (see Section 2).

Also in this case, no acceptable agreement between the calculated and experimental thermodynamic properties can be reached with only one set of LJ parameters for different thermodynamic points; see Table V.

TABLE V

Simulation Data for the Three-Site LJ Potential with Fractional Charges (Model C)

Thermo. state	$\dfrac{\varepsilon_{ss}}{k_B}$/K	σ_{ss}/Å	$\dfrac{\varepsilon_{oo}}{k_B}$/K	σ_{oo}/Å	P/MPa	$E/\dfrac{kJ}{mol}$
1	155.5	3.575	63.2	2.988	+ 5	— 20.04
2	154.5	3.585	62.3	2.993	+ 1	— 17.60
3	148.0	3.605	58.6	2.998	+ 1	— 11.00
4	146.0	3.615	57.5	3.005	+ 1	— 8.54

However, the values of the parameters are less dispersed than previously. In particular, a slight shift of $\dfrac{\varepsilon_{ii}}{k_B}$ and σ_{ii} by 2 K and 0.01 Å, respectively, is sufficient to obtain a good agreement for two adjacent thermodynamic points (1, 2) and (3, 4).

6. THREE-SITE LJ WITH DIPOLE AND QUADRUPOLE MOMENT AT THE CENTRE OF MASS (MODEL D)

The potential energy of interaction of two distributions of charges equals

$$U(r_{12}, \Omega_{12}) = \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{q_i q_j}{r_{ij}} \qquad (18)$$

where i goes over all charges in the first ensemble of charges, and j goes over the second. If the distances between the charges in one group are much smaller than those between any two charges, from which one is of the first and the other of the second group, then we can develop both charge distributions in multipole expansion. By keeping the terms to the second order we get

$$U(\vec{r}) = \frac{1}{4\pi\varepsilon_0}(q_a - \vec{\mu}_a \cdot \nabla + \frac{1}{3}\overset{\leftrightarrow}{Q} : \nabla\nabla)(q_b + \vec{\mu}_b \cdot \nabla + \frac{1}{3}\overset{\leftrightarrow}{Q} : \nabla\nabla)\frac{1}{r} \qquad (19)$$

where r is the distance between two centres around which we have performed multipolar expansion (this is usually the centre of mass or the centre of charge). Indexes a and b correspond to two groups of charges (for instance, molecules). Dipole-dipole energy equals

$$U_{dd}(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\sum_{\alpha\beta}\left(\frac{1}{r^3}\mu_a^\alpha\mu_b^\beta\delta_{\alpha\beta} - \frac{3}{r^5}\mu_a^\alpha\mu_b^\beta r_\alpha r_\beta\right) \tag{20}$$

$$U_{dd}(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\left\{\frac{\vec{\mu}_a\cdot\vec{\mu}_b}{r^3} - \frac{3(\vec{\mu}_a\cdot\vec{r})(\vec{\mu}_b\cdot\vec{r})}{r^5}\right\} \tag{21}$$

For dipole-quadrupole energy we have

$$U_{dq}(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\sum_\alpha\sum_\mu\sum_\nu\left\{\frac{1}{r^5}\mu_a^\alpha Q_b^{\mu\nu}(r_\alpha\delta_{\mu\nu} + r_\mu\delta_{\nu\alpha} + r_\nu\delta_{\mu\alpha}) - \frac{5}{r^7}\mu_a^\alpha Q_b^{\mu\nu} r_\alpha r_\mu r_\nu\right\} \tag{22}$$

or

$$U_{dq}(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\left\{\frac{1}{r^5}[(\vec{\mu}_a\cdot\vec{r})\,\text{tr}\,\overset{\leftrightarrow}{Q}_b + \vec{\mu}_a\cdot\overset{\leftrightarrow}{Q}_b\cdot\vec{r} + \vec{r}\cdot\overset{\leftrightarrow}{Q}_b\cdot\vec{\mu}_a] - \frac{5}{r^7}(\vec{\mu}_a\cdot\vec{r})(\vec{r}\vec{r}:\overset{\leftrightarrow}{Q}_b)\right\} \tag{23}$$

where tr is the trace.

Quadrupole-quadrupole energy is equal to

$$U_{qq}(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\sum_\alpha\sum_\beta\sum_\mu\sum_\nu\left[\frac{1}{3r^5}Q_a^{\alpha\beta}Q_b^{\mu\nu}(\delta_{\alpha\beta}\delta_{\mu\nu} + \delta_{\mu\beta}\delta_{\nu\alpha} + \delta_{\mu\alpha}\delta_{\nu\beta}) - \right.$$

$$-\frac{5}{3r^7}Q_a^{\alpha\beta}Q_b^{\mu\nu}(r_\alpha r_\beta\delta_{\mu\nu} + r_\mu r_\alpha\delta_{\nu\beta} + r_\nu r_\beta\delta_{\mu\alpha} + r_\nu r_\alpha\delta_{\mu\beta} + r_\mu r_\beta\delta_{\nu\alpha} + r_\mu r_\nu\delta_{\alpha\beta}) +$$

$$\left. +\frac{35}{3r^9}Q_a^{\alpha\beta}Q_b^{\mu\nu} r_\mu r_\nu r_\alpha r_\beta\right] \tag{24}$$

or

$$U_{qq}(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\left\{\frac{1}{3r^5}[(\text{tr}\,\overset{\leftrightarrow}{Q}_a)(\text{tr}\,\overset{\leftrightarrow}{Q}_b) + Q_a^{\alpha\beta}Q_b^{\mu\nu} + Q_a^{\alpha\beta}Q_b^{\mu\nu}] - \right.$$

$$-\frac{5}{3r^7}[(\vec{r}\vec{r}:\overset{\leftrightarrow}{Q}_a)(\text{tr}\,\overset{\leftrightarrow}{Q}_b) + (\text{tr}\,\overset{\leftrightarrow}{Q}_a)(\vec{r}\vec{r}:\overset{\leftrightarrow}{Q}_b) + (\vec{r}\cdot\overset{\leftrightarrow}{Q}_a)(\vec{r}\cdot\overset{\leftrightarrow}{Q}_b) +$$

$$\left. + (\overset{\leftrightarrow}{Q}_a\cdot\vec{r})\cdot(\overset{\leftrightarrow}{Q}_b\cdot\vec{r}) + (\vec{r}\cdot\overset{\leftrightarrow}{Q}_a)\cdot(\overset{\leftrightarrow}{Q}_b\cdot\vec{r}) + (\overset{\leftrightarrow}{Q}_a\cdot\vec{r})\cdot(\vec{r}\cdot\overset{\leftrightarrow}{Q}_b)] + \frac{35}{3r^9}(\overset{\leftrightarrow}{Q}_a:\vec{r}\vec{r})(\overset{\leftrightarrow}{Q}_b:\vec{r}\vec{r})\right\} \tag{25}$$

The meaning of the contractions is obvious from a comparison of (24) and (25). The scalar product of the vector and tensor is still a vector, and can be written

$$(\overset{\leftrightarrow}{Q}\cdot\vec{r})_\alpha = Q^{\alpha\beta} r_\beta = \sum_\beta Q^{\alpha\beta} r_\beta \tag{26}$$

The model potential is in the form of a three-site LJ potential including a point dipole and a point quadrupole at the centre of mass. The dipole and quadrupole can then be chosen independently. The experimental values given in Section 2 ref. 13 are used for computations.

In this case a reasonable agreement was obtained between the computed thermodynamic properties and the experimental data for all thermodynamic points by one set of parameters. This fact emphasizes the role played by the quadrupole interactions in polar liquid, which is to blur the angular correlations. At 350 K a better agreement is found by using a slightly different set of parameters. The results are summarized in the Table VI

TABLE VI

Simulation Data for the Three-Site LJ Potential with a Point Dipole and a Point Quadrupole Moment (Model D)

Thermo. state	$\dfrac{\varepsilon_{ss}}{k_B}$ /K	σ_{ss}/Å	$\dfrac{\varepsilon_{oo}}{k_B}$ /K	σ_{oo}/Å	P/MPa	$E/\dfrac{kJ}{mol}$
1	129	3.61	46	3.01	—7	—20.04
2					—3	—17.50
3					—1	—11.42
4					—4	—9.08
4	125	3.595	44	2.998	+3	—8.43

7. THREE-SITE LJ WITH ATOMIC DIPOLES

Another model for sulphur dioxide intermolecular interaction was used by Rastogi et al.[26] to reproduce solid-state properties. They used the same LJ parameters as those given earlier for the three-site LJ model, and they added a dipole onto each atom. Dipole magnitudes were fitted to solid-state properties in such a way as to satisfy the condition

$$\sum_i \vec{\mu}_i = \vec{\mu} \tag{27}$$

where i denotes the atomic sites and $\vec{\mu}$ is the dipole moment of the molecule. In the inertial coordinate system presented in Figure 1, the atom coordinates (in Å) and dipole moment components (in 10^{-30} Cm) equal (see ref. 26*).

$$\vec{r}_s = (0, -0.3577, 0) \qquad \vec{\mu}_s = 15.34\,(0, -1, 0)$$

$$\vec{r}_{o_1} = (1.237, 0.3673, 0) \qquad \vec{\mu}_{o_1} = 9.87\,(0.863, 0.506, 0)$$

$$\vec{r}_{o_2} = (-1.237, 0.3673, 0) \qquad \vec{\mu}_{o_2} = 9.87\,(-0.863, 0.506, 0)$$

* As it was pointed to us by one of the authors[27] the directions of atomic dipoles given above are just the opposite of what they supposed[26]. This is not clear from their article, and even more, their orientation gives a molecular dipole for which a positive effective charge on the oxygen atom is assumed. This is contrary to the well konwn fact that the oxygen is more electronegative than the sulphur.

To compare this potential with the others we can calculate the quadru-pole moment components corresponding to this distribution of atomic dipoles.

Starting from the standard definition of the traceless quadrupole moment components (6) we want to deduce the form of these components for a distri-bution of point dipoles. Point dipoles are defined so that charges forming the dipole, q_i, are increased while the distance between them, l_i, is decreased, in such a way that the value of dipole moment

$$\vec{\mu}_i = q_i \vec{l}_i \tag{28}$$

remains constant. Let us denote the negative charge of the i-th dipole by q_i', then

$$q_i' = -q_i \tag{29}$$

and its radius vector by $\vec{r}_i'$

$$\vec{r}_i' = \vec{r}_i - \vec{l}_i \tag{30}$$

For all charges, by using (29), from (6) we obtain:

$$Q_{\alpha\beta} = \tfrac{1}{2} \sum_i q_i (3r_{i\alpha} r_{i\beta} - \vec{r}_i \vec{r}_i \delta_{\alpha\beta}) - \tfrac{1}{2} \sum_i q_i (3r_{i\alpha}' r_{i\beta}' - \vec{r}_i' \cdot \vec{r}_i' \delta_{\alpha\beta}) \tag{31}$$

Now we use (30) to obtain:

$$Q_{\alpha\beta} = \tfrac{1}{2} \sum_i q_i [3 (r_{i\alpha} l_{i\beta} + l_{i\alpha} r_{i\beta} - l_{i\alpha} l_{i\beta}) - 2\vec{r}_i \cdot \vec{l}_i \delta_{\alpha\beta} + \vec{l}_i \cdot \vec{l}_i \delta_{\alpha\beta}] \tag{32}$$

Since we are dealing with point dipoles, we may neglect all the members where l_i occurs twice. So, by using (19) we finally get:

$$Q_{\alpha\beta} = \tfrac{1}{2} \sum_i [3 (r_{i\alpha} \mu_{i\beta} + \mu_{i\alpha} r_{i\beta}) - 2\vec{r}_i \cdot \vec{\mu}_i \delta_{\alpha\beta}] \tag{33}$$

This gives the expression for quadrupole moment components for the distri-bution of dipoles.

By using this expression we obtain for the quadrupole moment com-ponents in the centre of mass of the molecule

$Q_{aa} = 33.077 \times 10^{-40}$ Cm² $Q_{bb} = -2.769 \times 10^{-40}$ Cm² $Q_{cc} = -30.307 \times 10^{-40}$ Cm²

The values given by the authors[26] are different

$Q_{aa} = -16.381 \times 10^{-40}$ Cm² $Q_{bb} = 1.270 \times 10^{-40}$ Cm² $Q_{cc} = 15.111 \times 10^{-40}$ Cm²

With our formula (33) we obtain the quadrupole moment which is quite different from the experimental value in gas (see Section 2). Factor 2 is missing in their expression.[27]

This potential has a too strong attractive part at small distances because of the strong dipole-dipole (DD) interaction for parallel orientation of mole-cules. This can be seen from the following figure which represents the angular dependence of LJ energy and total dipole-dipole energy for the centre of mass distance $r = 4$ Å. The variable Θ is defined in Section 4.a.

The MD results for the potential with quadrupole moment given by Rastogi et al.[26] are given in the following table

We see that this potential gives values of pressure and energy which are very far from the experimental ones. This is due to the too strong attractive part of potential for some orientation. This unphysical situation

TABLE VII

Simulation Data for Three-Site LJ with a Point Dipole and a Point Quadrupole Moment from Rastogi et al.

Thermo. state	P/MPa	$E/\dfrac{kJ}{mol}$
1	—331	—39.00
4	—142	—24.26

does not occur in the crystal because the neighbours are in a fixed relative orientation which does not represent a problem.

Recently we were told by one of the authors[27] that there was an error in their calculation[26]. It resulted in using effectively the dipolar moments which are 0.263 times those quoted in their work. This may explain the discrepancy existing between their and our LJ parameters.

8. CONCLUSION

To describe the intermolecular interaction of sulphur dioxide molecules in the liquid state, an extensive molecular dynamics simulation study was performed. The free parameters of four different forms of potential were fitted to the energy and pressure values of a liquid along the liquid-gas coexistence curve. These potentials were compared with those found in the literature and obtained by fitting other properties of a gas or liquid SO₂, such as the second virial coefficient and viscosity. These potentials from the literature are very simple and are not expected to be of particular predictive value. The only sophisticated potential for SO₂ interaction, found in the literature was that of Rastogi et al.[26], fitted to solid state properties. When comparing its LJ parameters with those for similar molecular systems, a large difference in their values may be noted. The calculation of quadrupole moment components for the distribution of atomic dipoles is not correctly done. Finally, as expected, the Rastogi et al.[26] potential gave a too low energy and pressure in the liquid phase (see Table VII), which is a consequence of a too strong electrostatic-interaction at small distances (see Figure 5).
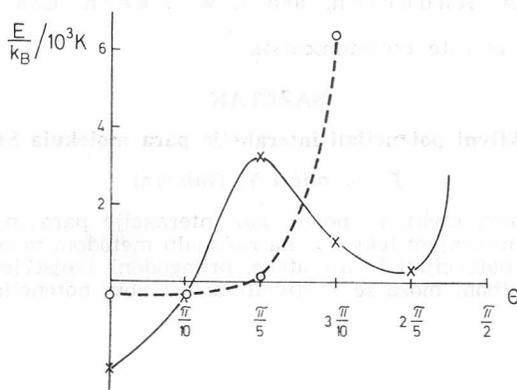
Figure 5. Dipole-dipole (———) and LJ (— — —) interaction energy for Rastogi et al.[26] model.

The proposed potentials should be further investigated. These simple considerations already show that they are by far superior to those found in the literature.

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SAŽETAK

Efektivni potencijali interakcije para molekula SO₂

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Predloženi su novi efektivni potencijali interakcije para molekula sumpornog dioksiđa dobiveni simulacijom tekućine na računalu metodom molekularne dinamike. Također su opisani potencijali iz literature, prilagođeni svojstvima plina i kristala. Međusobnom usporedbom može se zaključiti da su novi potencijali bliži stvarnosti.