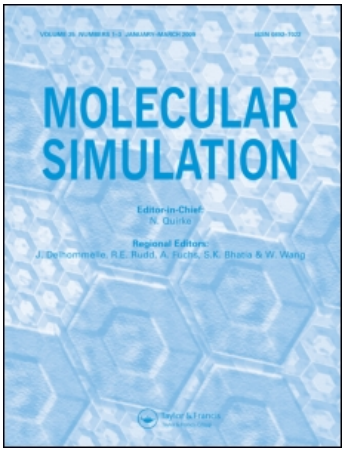

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Molecular Mechanics Studies of Molybdenum Disulphide Catalysts Parameterisation of Molybdenum and Sulphur

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MOLECULAR MECHANICS STUDIES OF MOLYBDENUM DISULPHIDE CATALYSTS PARAMETERISATION OF MOLYBDENUM AND SULPHUR

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A method for the parameterisation of molybdenum disulphide is presented which reproduces the crystal structure accurately. The method involves calculating parameters such that there is no net force contribution from any individual term of the potential on any atom. Ideal bond lengths and bond angles are taken from the X-ray crystal structure; stretching and bending force constants are calculated from a combination of spectroscopic data and quantum mechanics calculations, whereby the energy function with bond length or bond angle is calculated and fitted with an harmonic potential. For the non-bonded Lennard–Jones parameters, the dispersion coefficient C was calculated by an interpolation of existing published parameters using a multiple regression and then the crystal energy was minimised with respect to the van der Waals radius r_0 using a fixed crystal fragment.

These parameters were tested for various models of the hexagonal and rhombohedral forms of MoS_2. RMS fits between structures minimised with molecular mechanics and experimental models ranged from 0.006 Å to 0.012 Å.

KEY WORDS: Molecular mechanics, parameterisation, molybdenum disulphide, catalytic phase

1 INTRODUCTION

We are using computer modelling to investigate problems in heterogeneous catalysis. In this paper we describe the parameterisation of a molecular mechanics force field for molybdenum disulphide, the active component of hydrodesulphurisation catalysts used in the removal of sulphur compounds from crude petroleum [1]. It is now generally agreed that the active phase for hydrodesulphurisation (HDS) catalysis consists of slabs of MoS_2 dispersed over the surface of an alumina support [1]. The active sites are coordinatively unsaturated molybdenum atoms at the edges of the molybdenum disulphide slabs. In computer modelling of molybdenum disulphide and other catalysts [2], we combine molecular graphics, which enables us to represent and visualise structures accurately, and computational chemistry, which enables us to calculate a range of selected properties. A particular advantage of this method is that it enables us to investigate structures and interactions which are difficult or even impossible to study experimentally. Such a structure might be a catalytic phase: a fragment of an extended solid, distorted at edges and around defects, and undergoing reconstruction through interaction with reactant molecules. We can therefore investigate the catalytic mechanisms enabling us to quantify the activity or selectivity of a

catalyst. A good model can be used to predict how activity or selectivity may be improved. In this paper we describe how we parameterise our calculations. In subsequent papers we shall show that we are able to characterise a particular active site ensemble structure for molybdenum disulphide.

Calculations on molybdenum disulphide catalysts have been carried out at various levels of sophistication [3]. Band structure and quantum mechanics calculations have explored electronic effects in the catalysis demonstrating for example the role of a cobalt or nickel promoter in transferring charge to the molybdenum centre in the catalyst. However, much of the previous quantum mechanical work does not address the catalytic phase but regards the system as an infinite solid or a small coordinatively unsaturated molybdenum atom cluster.

In this work we have concentrated on the geometrical factor in catalysis by molybdenum disulphide. In the present paper, we investigate the geometry of the molybdenum disulphide slabs by the method of molecular mechanics. This is a conceptually simple and computationally undemanding empirical method which has been well parameterised for organic molecules [4] and has been undergoing continuing development towards the modelling of metal complexes [5, 6]. We are currently extending the use of molecular mechanics to extended inorganic solids and hence to problems in catalysis. For example, we have calculated a set of molecular mechanics parameters to use to relax fragments of the infinite crystal, the catalytic phase, to examine edge distortions and reorganisation, and the structure around the catalytic site. In a future paper we shall describe a molecular mechanics approach to calculating the relaxations about defects and active sites and the interaction energies between the active site and an adsorbed molecule.

2 COMPUTATIONAL PROCEDURES

2.1 Computer Modelling

Computer graphics visualisation was carried out on an IBM PC-AT with the PC-CHEMMOD system [7]. The atomic coordinates of molybdenum disulphide were retrieved from the S.E.R.C. crystallographic database [8] and converted into a form suitable for CHEMMOD.

2.2 Molecular Mechanics Calculations

Molecular mechanics (MM) calculates and minimises the strain energy of a structure. A substance is treated as a collection of atoms held together by elastic (harmonic) forces [4] which constitute the force field. The strain energy (E) of a structure in the force-field is the sum of energy contributions from bond stretching (E_s), bending (E_b), and torsional (E_t) motions and from non-bonded terms (E_{nb}) which include the van der Waals attraction, the core repulsions and the coulombic energy:

$$E = E_s + E_b + E_t + E_{nb} \tag{1}$$

$$E_{nb} = \sum_i \sum_j \varepsilon_{mn}\{((r_{mn})_0/r_{ij})^{12} - 2((r_{mn})_0/r_{ij})^6\} + q_i q_j/r_{ij} \tag{2}$$

This energy is summed over all pairs of atoms i, j in the structure. Subscripts m and n represent the atom types of the ith and jth atoms in the structure; atoms i and j have van der Waals radii $(r_m)_0$ and $(r_n)_0$ respectively. In Equation (2) the first two terms

represent a Lennard–Jones (6–12) potenital where $(r_{mn})_0$ is the sum of the van der Waals radii $(r_m)_0$, $(r_n)_0$ for the interacting pair of atoms which are r_{ij} apart and ε_{mn} is the potential well depth. For the two atom types, m and n, ε_{mn} is the geometric mean of values for both atoms.

$$\varepsilon_{mn} = \sqrt{\varepsilon_m \varepsilon_n} \tag{3}$$

In a molecular mechanics calculation we start with a model structure and find the optimised geometry by minimising the total steric energy, E. To parameterise the calculation for molybdenum disulphide we need to assign values for the stretching force constant and the ideal bond length for the Mo–S bond, bending force constants and ideal Mo–S–Mo and S–Mo–S angles, torsional force constants and periodicities for Mo–S–Mo–S torsions and ε and r_0 for Mo and S.

Molecular mechanics calculations were carried out using a modified version of the CHEMMIN program [9] as in our earlier work on molybdenum disulphide [2]. This program uses a standard block-diagonal Newton–Raphson minimisation scheme. The force constants for bond lengths and angles are not available directly in the program but are calculated from empirical equations involving ideal bond lengths, bond angles and electronegativities [10]. This method works well for organic compounds but, in our experience, fails for structures containing heavier elements. We modified the code to accept our own force constants, more than one angle at molybdenum and periodic angles (i.e. Θ and 2Θ). The latter modifications were necessary to deal with greater than 4-fold coordination [11]. An alternative method for treating highly coordinated atoms is to use 1–3 Lennard–Jones interactions instead of explicit angle terms as is coded in the MM2MX program [12]. We chose not to use this potential as we believe it requires different non-bonded parameters (r_0 and ε) from those used for 1–4 interactions and our investigations [13] show that it is less effective than ideal angles for coordination numbers up to and including six.

3 PARAMETERISATION

The criterion used for the parameterisation was that each term in the potential – bond stretches, angle bends, torsions and non-bonded interactions – contributes a minimum energy to the crystal structure.

3.1 Assigning Ideal Bond Lengths, Bond Angles, and Torsion Angles

Ideal bond lengths, l_0, and angles, Θ_0, are obtained directly from the X-ray crystal structure. These data represent the ideal structure: the atomic coordinates represent the centre of the thermal motion of the atom at the temperature of the structure determination and therefore refer to the structure at 0 K. This is also the structure which the molecular mechanics minimisation should attain.

To assign ideal bond lengths and angles in molybdenum disulphide, we surveyed the experimental data. There are hexagonal and rhombohedral allotropes of molybdenum disulphide. While there have been several different studies, it has proved impossible to prepare good quality single crystals for diffraction measurements. The structures have therefore been determined from poor quality single crystal X-ray diffraction data, electron diffraction and powder diffraction studies.

However it is clear that both structures contain equivalent two-dimensional polymeric slabs in the xy plane. These consist of one plane of metal atoms between two

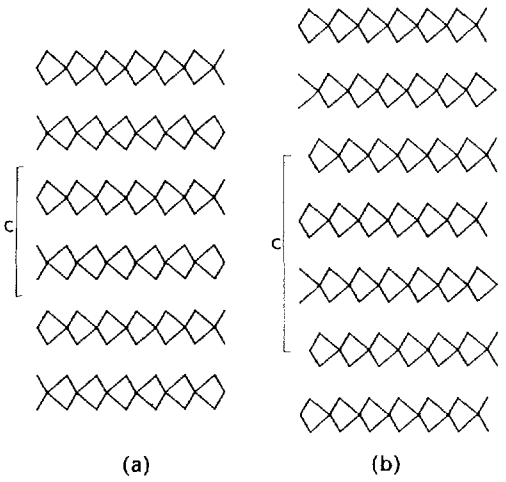

Figure 1 The crystal structures of (a) hexagonal and (b) rhombohedral forms of molybdenum disulphide, projected down the *x*-axis.

planes of sulphurs. In the slabs, the molybdenum atoms have trigonal prismatic environments. As pointed out by Bronsema *et al.* [14], there is considerable confusion in the literature concerning the structure of hexagonal MoS_2 and Strukturbericht [15] as well as the reference book by Wyckoff [16] and several recent compendia contain the wrong coordinates for the sulphur atoms. Bronsema *et al.* [14] suggest that the structure should be taken to be the average of the values obtained by electron diffraction and powder diffractometry. Thus the Mo–S bond length is estimated to be 2.42 Å, the ideal Mo–S–Mo angle 82.0 and the two S–Mo–S angles 81.8 and 135.6°. Two ideal angles are needed for angles centred on molybdenum to fit the trigonal prismatic structure. We estimate the error in these values to be approximately 2.5%. The structure of the rhombohedral form is less well determined than the hexagonal form being obtained from limited powder data [17], but it seems probable that the slabs are comparable. Fragments of the two crystal structures are shown in Figures 1 (*x*-projection) and 2 (*z*-projection).

The difference between the two structures is in the stacking of the slabs. In the hexagonal structure, spacegroup $P6_3/mmc$, there are two such slabs in the unit cell so that the stacking fits an AB pattern. The two molybdenum atoms occupy positions 1/3, 2/3, 1/4 and 2/3, 1/3, 3/4. Thus the two slabs are related via a centre of symmetry

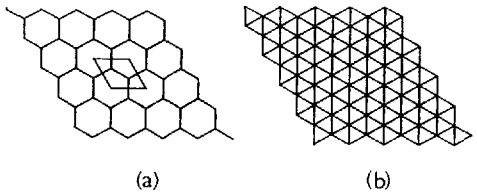

Figure 2 The crystal structues of (a) hexagonal and (b) rhombohedral forms of molybdenum disulphide, projected down the *z*-axis.

at the centre of the unitcell (Figure 1a) such that Mo and S are directly above and below S and Mo in the adjacent slabs. In the rhombohedral structure, spacegroup $R3m$, there are three such slabs in the unitcell and the c axis is larger by a factor of *ca.* 1.5 than the hexagonal form. The three slabs form an ABC pattern related by the rhombohedral operators, (0, 0, 0)+, (2/3, 1/3, 1/3)+ and (1/3, 2/3, 2/3)+; thus the packing of the layers is significantly different from the hexagonal form (Figure 1b).

We assumed that torsional forces are not necessary for molecular mechanics calculations on inorganic extended solids as the structural constraints are adequately included in the stretch and bend terms and the periodicity along the Mo–S bond is very high. Therefore in all calculations presented here, the torsional force constant was set to zero.

3.2. Bond-stretching Force Constant

We used spectroscopic data to calculate the bond-stretching force constant. For a harmonic oscillator, the force constant may be calculated from the stretching vibrational frequency:

$$k_s = \nu^2 \mu \tag{4}$$

where ν is the frequency of the vibration and μ is the reduced mass of the vibrator:

$$\mu = m_1 m_2/(m_1 + m_2) \tag{5}$$

For k_s in kcal mol^{-1} Å^{-1}, ν in cm^{-1} and m in g mol^{-1} (atomic mass units), equation (4) becomes

$$k_s = 4.1095 \times 10^{-5} \mu \nu^2 \tag{6}$$

To arrive at a reasonable force constant for a Mo–S bond we need the vibrational spectrum of a molecular or ionic species for which stretching and bending motions can be separated. We chose the $[MoS_4]^{2-}$ ion, for which the infrared spectrum is well known [18]. The frequency of the breathing mode is 460 cm^{-1}. In this vibration, the molybdenum atom is stationary, mimicking a particle of infinite mass. Thus μ is simply the atomic mass of sulphur. The calculated value of k_s for Mo–S is then 278.8 kcal mol^{-1} Å^{-1}. Using the CHEMMIN program, we calculate an unreasonably low value of 71.8 kcal mol^{-1} Å^{-1} for the Mo–S stretch force constant. This is because the empirical relationship between force constant and bond length in the program is only designed for organic systems [10] and the Mo–S bond length is outside the range within which the algorithm can be applied.

3.3. Bond-bending Force Constants

We cannot proceed in the same manner to calculate the bond-bending force constants. To do so we would need to assign bending modes to molybdenum disulphide. Data are not available and, in any case, low wave number bending modes are difficult to separate from lattice modes. We therefore developed a computational procedure in which force constants were calculated by quantum mechanics and then scaled to spectroscopic values.

Quantum mechanics calculations on MoS_2 require suitable parameters for sulphur, which are generally available, and parameters for molybdenum, which are not. Some *ab initio* programs do include molybdenum parameters but they are computationally

Table 1 Structural determinations of molybdenum disulphide.

Authors	*Cell parameters*			*Type*
	a (Å)	*b (Å)*	*c (Å)*	
Dickinson and Pauling[a]	3.150	3.150	12.300	Hexagonal
Bell and Herfert[b]	3.171	3.171	18.345	Rhombohedral
Hassel[c]	3.140	3.140	12.530	Hexagonal
Schoenfield *et al.*[d]	3.161	3.161	12.295	Hexagonal
Schoenfield *et al.*[d]	3.163	3.163	18.370	Rhombohedral
Takeuchi and Nowaki[e]	3.166	3.166	18.410	Rhombohedral
Bronsema *et al.*[f]	3.160	3.160	12.294	Hexagonal

[a] R.G. Dickinson and L. Pauling, *J. Am. Chem. Soc.*, **45**, 466 (1923).
[b] R.E. Bell and R.E. Herfert, *J. Am. Chem. Soc.*, **79**, 335 (1957).
[c] O. Hassel, *Zeit. Krist.*, **61**, 92 (1925).
[d] H. Schoenfield, J.J. Huang and S.C. Moss, *Acta. Cryst.*, **39**, 404 (1977).
[e] Y. Takeuchi and W. Nowacki, *Schweiz. Min. und Pet.*, **44**, 10 (1964).
[f] Reference 14.

demanding and in our experience yield results of dubious accuracy dependent on the selected basis set. We therefore decided to use semi-empirical methods (CNDO and INDO) that include polarisation functions (*d* orbitals) which are fast to compute. After evaluating several techniques, we found the CNDO approximation in the GEOMOS program [19] to be the most appropriate for these calculations. The parameters used are listed in Table 2.

CNDO methods do not yield accurate energies owing to the neglect of an explicit electron repulsion term [20]. To overcome this problem, a method of scaling the energies to the spectroscopic stretching force constants was used [21]. This procedure involved the following steps.

(a) Calculate the energy of the $[MoS_4]^{2-}$ ion as a function of the Mo–S bond length,

Table 2 CNDO parameters for calculation of force constants in GEOMOS.

		Slater exponent ζ *(Å)*	*Core integral* $(I + A)/2$ *(eV)*	*Beta integral* β_0 *(eV)*
Mo	5*s*	1.4000	3.93	7.50
	5*p*	1.4000	0.71	7.50
	4*d*	2.4000	4.53	11.50
Slater–Condon parameters F_0 (eV)				
	ss	0.23840	*sd* 0.23840	
	sp	0.23840	*pd* 0.23840	
	pp	0.23840	*dd* 0.52141	
		Slater exponent ζ*(Å)*	*Core integral* $(I + A)/2$ *(eV)*	*Beta integral* β_0 *(eV)*
S	3*s*	1.8167	17.65	18.15
	3*p*	1.8167	6.99	18.15
	3*d*	1.8167	0.71	18.15
Slater–Condon parameters F_0 (eV)				
	ss	0.46895	*sd* 0.46895	
	sp	0.46895	*pd* 0.46895	
	pp	0.46895	*dd* 0.46895	

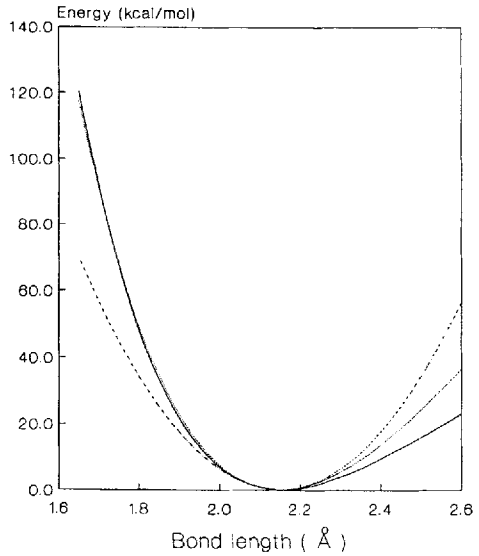

Figure 3 Calculated CNDO energy (solid) of an $[MoS_4]^{2-}$ tetrahedron as a function of one bond length is fitted by a harmonic (dashed) and Morse (dotted) type potential.

varying one bond length between $l + 0.5$ Å and $l - 0.5$ Å by moving one sulphur only along the Mo–S bond thus maintaining a threefold axis.

(b) With the minimum energy from (a) scaled to zero (i.e., energy = energy − minimum energy), plot the energy as a function of Mo–S bond length, see Figure 3.

(c) Fit a Morse potential, with an anharmonicity parameter of 1.0 and a force constant equal to the spectroscopic value, to the curve in (b) and hence obtain a scaling factor, see Figure 4. For $[MoS_4]^{2-}$ this was 2.2. The value was corroborated for a number of small molecules CO, H_2O, CS, $[SiO_2]$, $[SiS_2]$ where the scaling constant remained at 2.2. In the region of interest when the Mo–S bond distance is close to the ideal value, the Morse and harmonic potential forms with the same force constant are equivalent. The form of the Morse potential is

$$E = k_s[1 - \exp(-\alpha(l - l_0))]^2$$

If $\alpha(l - l_0)$ is small then

$$\exp[-\alpha(l - l_0)] = 1 - \alpha(l - l_0).$$

Thus

$$E = k_s[1 - (1 - \alpha(l - l_0))]^2 = k_s[\alpha(l - l_0)]^2$$

and for $\alpha = 1$, $E = k_s(l - l_0)^2$ which is the harmonic form.

(d) Calculate the energy as a function of the S–Mo–S angle of $[MoS_4]^{2-}$ and the energy of the Mo–S–Mo angle of a hypothetical $[Mo_2S]^{6+}$ species. For the $[MoS_4]^{2-}$ tetrahedron, movement was confined to one MoS_2 plane. One sulphur atom was moved towards (and away from) the other in this plane maintaining the Mo–S distance. Apart from the S–Mo–S angle in the plane, two further S–Mo–S angles were affected by this movement and we therefore scaled the final force constant by a factor of 0.5.

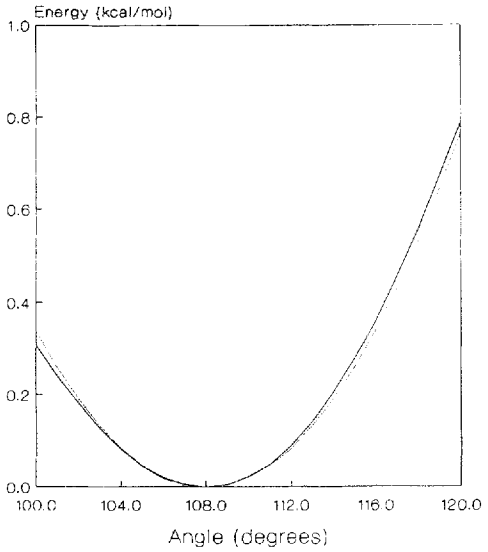

Figure 4 Calculated CNDO energy (solid) of an $[MoS_4]^{2-}$ tetrahedron as a function of one S–Mo–S bond angle is fitted with a harmonic (dotted) type potential.

For the small $[Mo_2S]^{6+}$ species only one angle varied so the final calculated force constant needed no scaling.

(e) Scale the calculated energies by the scaling factor determined in a similar manner as for the stretch force constants using the same selection of molecules. In fact this scaling factor proved to be unnecessary.

(f) Fit the energy curve to a harmonic potential and hence determine the force constant, see Figures 4 and 5.

The calculated parameters are summarised in Table 3.

This scaling procedure has proved necessary in other estimations of force-field parameters from quantum mechanical data. The quantum mechanics calculation of the potential energy curve includes all interactions (bonds, angles, torsions, non-bonded interactions) while in force-field calculations different kinds of interactions are treated individually. Thus additional contributions to the steric energy arise which should not be incorporated into the force constant [21, 22].

3.4 Non-Bonded Parameters

Having obtained the parameters for the short-range terms we next calculate values for the longer-range terms, i.e. those described by the Lennard–Jones potential and coulombic terms in Equation (2).

Two points need to be taken into consideration when dealing with the coulombic term. First, the coulombic term is only a slowly varying function with distance; thus its importance is in the calculation of energies and its effect on structural calculations is small [23]. Second, *ab initio* calculations on molybdenum–sulphur clusters show that the charges on molybdenum and sulphur are close to zero. In frozen core calculations [24] on the hypothetical MoS molecule, the charge on each atom was

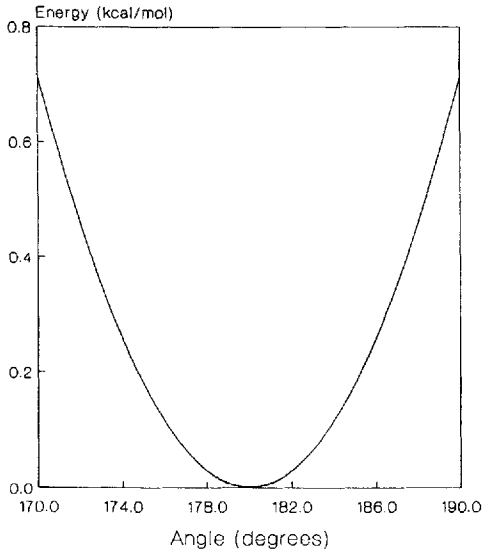

Figure 5 Calculated CNDO (solid) energy of an $[Mo_2S]^{6+}$ unit as a function of the Mo–S–Mo bond angle is fitted with a harmonic (dotted) type potential.

$\pm 0.18e$ while on $[MoS_4]^{2-}$, the charges were calculated as $0.0e$ on molybdenum and $-0.5e$ on each sulphur. Note that even if we could calculate exact charges they might not be the correct parameters to use in equation (2), as all the other energy terms, bond stretch, angle-bending, and non-bonded interactions, are derived from empirical parameters.

The most important consideration, however, is that the charge distribution be correct. For binary crystals, we assume that the coulombic term can be incorporated in the Lennard–Jones potential provided the coulombic interactions are small, because each Mo and S has characteristic non-bonded and charge parameters. We therefore decided to set the charges to zero and to parameterise the non-bonded potentials with the Lennard–Jones terms only. Lennard–Jones parameters are listed for most of the common elements in various publications and computer programs [25, 26]. They have been obtained for organic or organometallic systems which do not

Table 3 Molecular mechanics parameters for MoS_2.

Mo–S stretch	$k_s = 278.80\,\text{kcal mol}^{-1}\,\text{Å}^{-1}$	$l_0 = 2.418\,\text{Å}$
Mo–S–Mo Bend	$k_b = 0.0128\,\text{kcal mol}^{-1}\,\text{degrees}^{-2}$	$\Theta_0 = 81.64°$
S–Mo–S Bend	$k_b = 0.0095\,\text{kcal mol}^{-1}\,\text{degrees}^{-2}$	$\Theta_0 = 81.81°, 135.65°$
Mo non-bonded	$\varepsilon = 0.2020\,\text{kcal mol}^{-1}$	$r_0 = 2.694\,\text{Å}$
S non-bonded	$\varepsilon = 0.4490\,\text{kcal mol}^{-1}$	$r_0 = 1.847\,\text{Å}$
Parameters from [2]		
Mo–S stretch	$k_s = 71.754\,\text{kcal mol}^{-1}\,\text{Å}^{-1}$	$l_0 = 2.41\,\text{Å}$
Mo–S–Mo Bend	$k_b = 0.0041\,\text{kcal mol}^{-1}\,\text{degrees}^{-2}$	$\Theta_0 = 85°$
S–Mo–S Bend	$k_b = 0.0021\,\text{kcal mol}^{-1}\,\text{degrees}^{-2}$	$\Theta_0 = 80°, 135.65°$
Mo non-bonded	$\varepsilon = 0.2001\,\text{kcal mol}^{-1}$	$r_0 = 2.850\,\text{Å}$
S non-bonded	$\varepsilon = 0.2300\,\text{kcal mol}^{-1}$	$r_0 = 2.100\,\text{Å}$

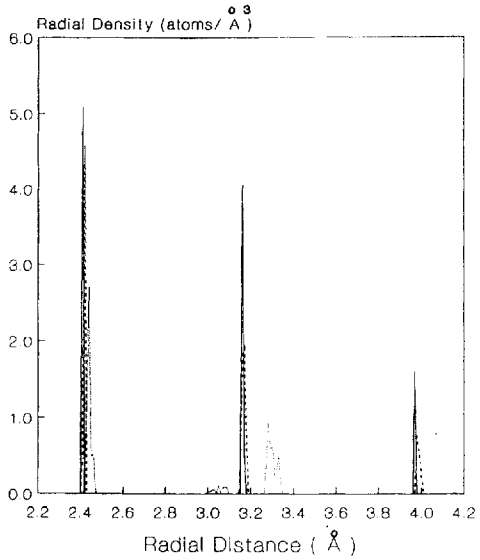

Figure 6 Radial density function of a single slab of molybdenum disulphide. The experimental crystal structure (solid) is compared with the relaxed structures using the parameters determined from the present method (dashed) and those used previously [2] (dotted).

exhibit the close packing of an extended solid. Indeed parameters for molybdenum disulphide previously used produced significant distortions in the structure due to large 1–4 repulsions as shown by the calculated radial density functions (see Figure 6). The criterion used to calculate the non-bonded parameters is that, given a particular structure, the parameters ε_{mn} and $(r_{mn})_0$ are such that the given structure is at a minimum in steric energy. To do this we altered $(r_{mn})_0$ and kept the structure fixed until the total non-bonded energy was at a minimum. ε_{mn} was calculated from the dispersion coefficient C_{mn} and the initial value of $(r_{mn})_0$ using:

$$\begin{aligned} E_{nb} &= \varepsilon_{mn}\{((r_{mn})_0/r_{ij})^{12} - 2((r_{mn})_0/r_{ij})^6\} \\ &= A_{mn}/r_{ij}^{12} - C_{mn}/r_{ij}^6 \end{aligned} \tag{7}$$

and so.

$$A_{mn} = \varepsilon_{mn}[(r_{mn})_0]^{12} \quad \text{and} \quad C_{mn} = 2\varepsilon_{mn}[(r_{mn})_0]^6$$

thus

$$\varepsilon_{mn} = C_{mn}/2[(r_{mn})_0]^6$$

Our parameterisation procedure has two steps. First values for the dispersion coefficients C_m for each element were calculated from a multiple regression of published dispersion coefficients. Second, values of the van der Waals radius were calculated which, for a particular structure, would yield the starting structure as the minimum energy structure. Values for the dispersion coefficient were plotted against various physical and chemical quantities for each atom. The quantities considered were atomic number, screening constant, first ionisation energy, electronegativity, number of valence electrons, and atomic radius. A regression analysis of the dispersion

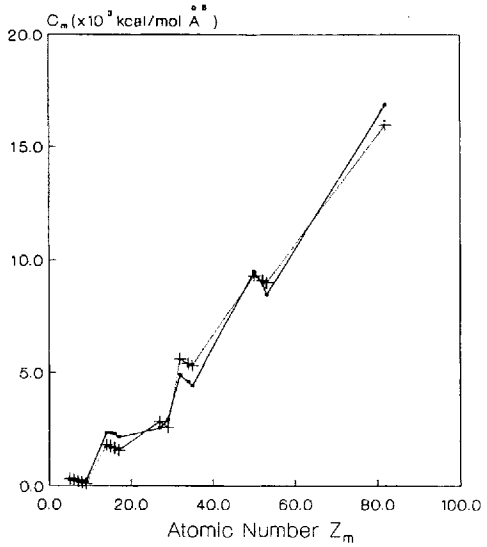

Figure 7 Multiple regression curve of the dispersion coefficient C with atomic number Z, number of valence electrons N_v and electronegativity χ showing the comparison of the input data (dots on solid line) and the regression model output (crosses on dotted line).

coefficient C_m against each of these quantities was done using the package MINITAB [27].

Initially the strongest correlation was with the atomic number Z_m. Various simple power regressions were tried (e.g. C_m vs Z_m^2, C_m vs $Z_m^{0.5}$, etc.) but the best correlation coefficient R was obtained for C_m vs Z_m. R^2 can be regarded as the percentage of the data which is represented with the regression model. The fit values of the C_m vs Z_m were then subtracted from the data and residuals fitted with other quantities. In fact only three variables were needed for the best overall fit. These were the atomic number Z_m, number of valence electrons and the electronegativity χ_m [28]. Finally a multiple regression was performed with these three variables using the powers which gave the best individual fits. The final regression equation was:

$$C_m = 208.7Z_m - 340.8(n_m)_v + 149.6\chi_m \quad (8)$$

This gave a value of R^2 of 0.968. The regression curve is shown in Figure 7 and details are given in Table 4. The fixing of the dispersion coefficient C_m was implemented by keeping ε_m fixed and allowing $(r_m)_0$ to vary until the minimum energy was obtained. With this updated value of $(r_m)_0$, a new value of ε_m was calculated from $\varepsilon_m = C_m/\{2(r_m)_0^6\}$. This process was then repeated until both $(r_m)_0$ and ε_m converged.

3.5 Truncation

To handle an infinite solid with finite computational resources we must consider methods of truncation. Commonly truncation is achieved by imposing periodic boundary conditions. As we are not including coulombic terms (and hence require the Ewald summation), this procedure is unnecessary and instead we used a 10 Å cut off. Beyond this distance non-bonded interaction is very small. The number of atoms in

Table 4 Data used for regression analysis of C_m.

Element	*Symbol*	Z_m	χ_m	n_m	C_m *data* kcal mol^{-1} Å^6	C_m *model* kcal mol^{-1} Å^6
Boron	B	5	2.01	3	262.2	321.8
Carbon	C	6	2.50	4	265.0	263.0
Nitrogen	N	7	3.07	5	255.9	216.2
Oxygen	O	8	3.50	6	206.0	148.4
Fluorine	F	9	4.10	7	201.5	106.1
Silicon	Si	14	1.74	4	2325.1	1819.2
Phosphorus	P	15	2.06	5	2308.1	1735.0
Sulphur	S	16	2.44	6	2281.6	1659.8
Chlorine	Cl	17	2.83	7	2149.8	1586.0
Cobalt	Co	27	1.70	9	2527.0	2822.7
Copper	Cu	29	1.75	11	2912.0	2566.0
Germanium	Ge	32	2.02	4	4892.2	5618.3
Selenium	Se	34	2.48	6	4584.0	5423.0
Bromine	Br	35	2.74	7	4396.4	5329.8
Tin	Sn	50	1.72	4	9502.0	9330.7
Tellurium	Te	52	2.01	6	9001.0	9109.9
Iodine	I	53	2.21	7	8462.6	9007.7
Lead	Pb	82	1.55	4	16861.0	15984.8

	Constant	*Standard deviation*	*t ratio*
k_1	208.7	6.0	34.69
k_2	−340.8	62.8	−5.42
k_3	149.6	140.0	1.07

Regression equation $C_m = k_1 Z_m + k_2 n_m + k_3 \chi_m$.

this model depends on the volume which in turn depends on r^3; but the energy at large r depends on r^{-6}. The total energy is the product of the number of atoms and their individual energies, which is proportional to r^{-3} or the density. Therefore we can calculate the non-bonded energy of a small cluster of atoms embedded in a much larger cluster the size of which defines the energy cutoff. This large cluster appears infinite to the small embedded cluster. In summary, we calculated the van der Waals radius by the following method.

(a) Generate a large structure (*ca.* 900 atoms) from the crystal unit cell (7 × 7 × 3 unit cells).

(b) Calculate the energy well depth ε_m from C_m and $(r_m)_0$.

(c) Keeping the structure fixed, calculate the non-bonded energy for the central 2 × 2 × 2 cells using the initial estimated parameters for molybdenum and sulphur. Calculate also the first and second derivative with respect to $(r_m)_0$ from

$$\frac{dE}{d(r_m)_0} = 12\varepsilon_{mn}((r_{mn})_0^{11}/r_{ij}^{12} - (r_{mn})_0^5/r_{ij}^6) \quad (9)$$

$$\frac{d^2E}{d(r_m)_0^2} = 12\varepsilon_{mn}(11(r_{mn})_0^{10}/r_{ij}^{12} - 5(r_{mn})_0^4/r_{ij}^6) \quad (10)$$

(d) Update the $(r_m)_0$ parameters from

$$(r_m)_0^{k+1} = (r_m)_0^k - \frac{dE/d(r_m)_0}{d^2E/d(r_m)_0^2} \quad (11)$$

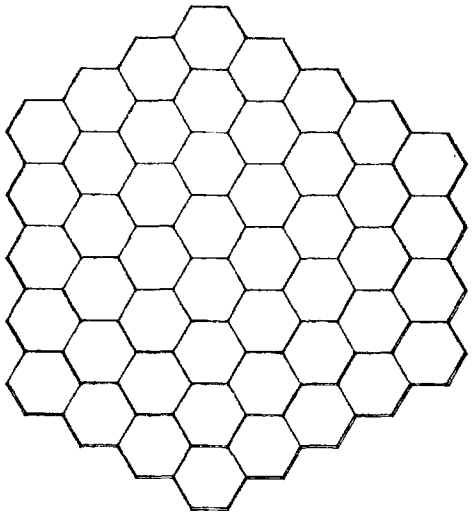

Figure 8 z projection of overlayed initial and relaxed hexagonal MoS_2 slab.

(e) Calculate ε_m from the updated value of $(r_m)_0$. Recalculate the energy and derivatives for all values of $(r_m)_0$.

(f) Continue iteratively until the energy converges (i.e. $E^{k+1} - E^k \leqslant 0.0001$ kcal mol^{-1}).

The final computed parameters are listed in Table 3. For comparison, the parameters used previously [2] are included.

4 CALCULATED STRUCTURES OF MOLYBDENUM DISULPHIDE

These new parameters (Table 3) were then evaluated from molecular mechanics calculations on both the hexagonal and rhombohedral forms of molybdenum disulphide. Because we cannot employ an infinite number of atoms, we decided to create two test models. We relaxed an hexagonal slab of 181 atoms to investigate the structure within a slab and relaxed a series of small slabs (10 slabs, 45 atoms in each) to investigate any variation in the inter-slab spacing. Figures 8 and 9 show the initial energy minimised structures overlaid for the hexagonal form with a single slab and a series of ten slabs respectively. Figures 10 and 11 show the results of calculations for the rhombohedral form. Results are summarised in Table 5.

The quality of parameters is indicated by two properties of the calculation. First, the fit values between the crystal structure and the relaxed structure should be low, and second the energy of the initial structure should be the same as that of the final structure. In both the hexagonal and rhombohedral slabs the RMS fit is 0.006 Å which is well below experimental error in the observed structures. If this displacement was incorporated betwen two bonded atoms in opposite directions along the bond, this would infer a difference of 0.012 Å in the bond length (i.e. Mo–S 2.406 Å $< l <$ 2.430 Å). Any error is enhanced by edge distortions as we are dealing with finite slabs. Figures 8 and 10 show that most of the distortion is confined to the edges and the overlay is considerably better in the centre of the slab. The difference between the

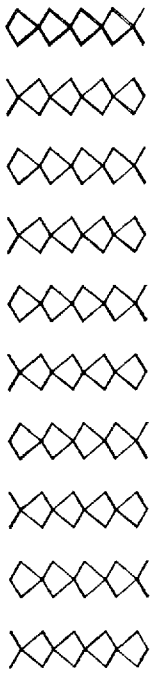

Figure 9 *x* projection of overlayed initial and relaxed hexagonal MoS_2 slabs.

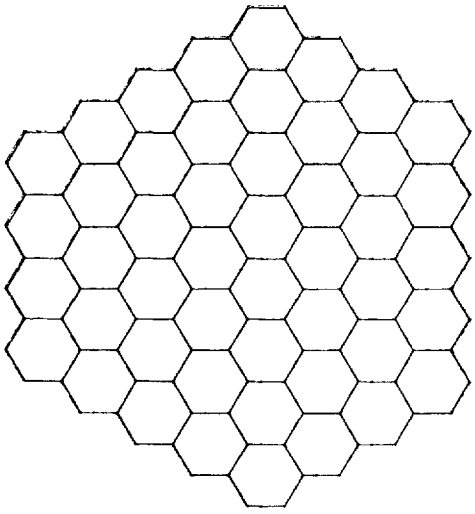

Figure 10 *z* projection of overlayed initial and relaxed rhombohedral MoS_2 slab.

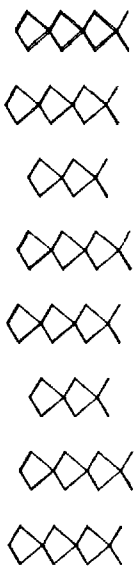

Figure 11 x projection of overlayed initial and relaxed rhombohedral MoS_2 slabs.

initial and final energies for the hexagonal form is lower than that of the rhombohedral form. The majority of this difference arises from the bonded term as we used coordinates in our experimental model of the rhombohedral form which gave rise to two different Mo–S bond lengths 2.414, 2.424 Å. However the quality of the data indicates that this difference of 0.01 Å is well below experimental error. This difference also accounts for the ca. 2.0 kcal mol^{-1} difference in the initial energies.

The fit values for the series of slabs is slightly larger for both allotropes than for the single slab case. The cause of this is the higher proportion of edge atoms for the series of slabs than for the single slabs as in these calculations, the atoms within the slabs were allowed to relax. The fit is slightly better for the hexagonal form which is not surprising as the non-bonded parameters determine the inter-slab spacing and these have been calculated for this form. However the values are very similar and the difference may be due to dissimilar edges distortions. The percentage differences in the initial and final energies are similar to those of the single slab case implying that the energy difference is mainly generated within the slabs rather than between them. A more thorough check is to test that the inter-slab separation has not changed (see Figures 9 and 11). For the hexagonal case, the series width for ten slabs decreases from

Table 5 Fit of X-ray crystal structure of MoS_2 and the molecular mechanics minimised structure.

	RMS FIT (Å)	*Initial enegy (kcal mol^{-1})*	*Final energy (kcal mol^{-1})*	*Change in energy/%*
Hexagonal slab	0.006	−235.2	−235.7	0.2
Rhombohedral slab	0.006	−233.5	−236.1	1.1
Hexagonal series	0.011	−889.2	−892.1	0.3
Rhombohedral series	0.012	−593.1	−601.3	1.4

55.35 to 55.34 Å, a change of 0.02%. For the rhombohedral structure the spacing for eight slabs decreases from 43.00 to 42.98 Å a change of 0.05%. We therefore see similar levels of good agreement for both allotropes indicating that the parameters generated are indeed transferable between the two structures. The difference between the initial and final energies also gives a measure of how much the structures have changed on relaxation. For the slabs these changes are minimal and as expected, the difference for the hexagonal form is smaller as this was the standard for the parameterisation. For the series of slabs the differences are higher, again attributable to the higher proportion of edge atoms.

5 SUMMARY

A method of parameterising molybdenum disulphide for molecular mechanics calculations has been presented which employs a combination of spectroscopic data analysis, quantum mechanics calculations and empirical fitting techniques. Parameters determined from the hexagonal form show excellent agreement between the crystal structure and the molecular mechanics relaxed structure with RMS deviations per atom of 0.006 Å within a slab and 0.011 Å for a series of slabs. In both cases, the strain energy of the fragments changed by only 0.2 to 0.3% on relaxation. The inter slab separation is maintained to within 0.02% of the crystal structure. Parameters were successfully transferred to the rhombohedral form with RMS deviations of 0.006 Å within a slab and 0.012 Å for a series of slabs. The energy difference between the crystal and relaxed structures was 1.1 to 1.4% due mainly to the bonded energy as two bond lengths are present in this form, averaging out at 2.149 Å. The inter-slab separation changes by 0.05% of the separation in the crystal structure.

This method described here can be applied to a wide range of simple crystal structures for which it is reasonable to assume that the bonded and angular energies are zero, i.e. those structures that exhibit singular bond lengths and bond angles for any particular interaction. A further method of parameterisation starting from parameters derived from the above method is being developed which does not necessarily require each individual term in the potential to exert no force on any atom.

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