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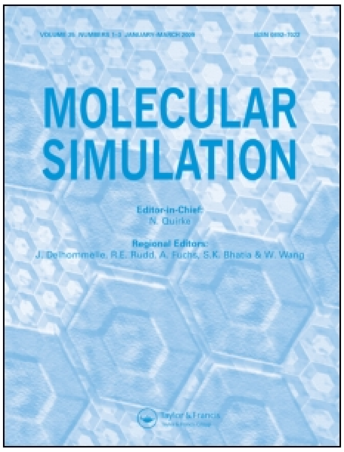

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Anisotropic Site-Site Potentials in Molecular Dynamics

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To cite this Article Rodger, P. M. , Stone, A. J. and Tildesley, D. J.(1992) 'Anisotropic Site-Site Potentials in Molecular Dynamics', Molecular Simulation, 8: 3, 145 — 164
To link to this Article: DOI: 10.1080/08927029208022473
URL: http://dx.doi.org/10.1080/08927029208022473

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Molecular Simulation, 1992, Vol. 8, pp. 145–164
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ANISOTROPIC SITE–SITE POTENTIALS IN MOLECULAR DYNAMICS

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(Received June 1991, accepted July 1991)

This paper describes techniques for calculating the forces and torques for molecular simulations that use anisotropic site–site potentials. The general techniques are illustrated for pairs of linear and tetrahedral molecules. A technique for combining anisotropic site–site potentials with constraint dynamics is described. These ideas are tested by simulating an anisotropic site–site potential model for the non-bonded interactions in liquid butane. This model is as accurate as the all-atom Williams potential from which it is derived but can be simulated using approximately half the computer time of the all-atom potential. Anisotropic site–site potentials offer a flexible and cost-effective method of simulating a range of hydrocarbon systems.

KEY WORDS: Anisotropic site–site potentials, liquid butane, molecular simulation

1 INTRODUCTION

Molecular dynamics simulations (MD) of condensed phases, where the constituent particles are molecules, are now routine [1]. If the molecule can be approximated adequately as a rigid body, e.g., CF_4, N_2, H_2O or C_6H_6, then the Newton–Euler equations for translation and rotation are solved using a quaternion algorithm [2]. If the molecules are flexible, e.g., C_4H_{10} or a decapeptide, the Newtonian equations are often supplemented by a constraint force, that fixes the bond lengths in the molecule at their equilibrium values, and the constraint dynamics is solved using the SHAKE algorithm, a direct matrix inversion or some other technique [3, 4]. Some workers prefer to use the constraint method for rigid body dynamics [5] and the quaternion method for flexible particles [6]; the algorithms are versatile and robust.

Nearly all of these studies use isotropic site–site potentials to represent the repulsion–dispersion between molecules. For example, in the study of liquid N_2, the molecular potential $V(R_{12}, \Omega_1, \Omega_2)$, which depends on the separation of the centre of mass of the molecules and the three Euler angles required to fix the relative orientation of a pair of linear molecules is written as

$$V(R_{12}, \Omega_1, \Omega_2) = \sum_{\alpha=1}^{2} \sum_{\gamma=1}^{2} V_{\alpha\gamma}(r_{\alpha\gamma})$$

where $r_{\alpha\gamma}$ is the separation of the two sites (or atoms) α and γ in different molecules, and $V_{\alpha\gamma}(r_{\alpha\gamma})$ is a Lennard-Jones site-site potential with energy and length parameter $\varepsilon/k_B = 37.31$ K, and $\sigma = 3.31$ Å [7]. Addtional electrostatic interactions are normally included in these molecules in one of two ways: (i) a number of ideal multipoles are placed at the centre of mass of the molecules and moments on different molecules interact through the appropriate terms in the multipole expansion [7], or (ii) partial charges are distributed within the repulsive core of the molecules and their position and magnitude are chosen to represent a number of the low non-zero electrostatic moments of the molecule; the partial charges on different molecules interact through a Coulomb potential [8].

These intermolecular potentials are an important input to any simulation study of condesed phases. They can only be avoided by returning to a description of the problem in terms of the positions of the nuclei and the total electronic wavefunction of the system, and although some progress is being made in this direction [9, 10], it is likely that for most problems the approximate intermolecular description will be the normal starting point. It is clear that if the intermolecular potentials which describe the system are inaccurate or incomplete, then the equilibrium averages and time correlation functions obtained in the simulation may be worthless.

Recently the use of isotropic site-site potentials to describe the repulsion-dispersion and the representation of the charge density in terms of partial charges or a limited number of multipoles at the centre of mass of the molecule, has been called into question [11]. It is now clear that the molecular charge distribution can be efficiently and accurately represented by using a distributed multipole analysis (DMA). Separate charges, dipoles, quadrupoles etc, are placed at a number of sites inside the repulsive core of the molecules. The values of these moments can be calculated by a straightforward extension of the Mulliken analysis of the wavefunctions [12]. This technique gives a simple and accurate representation of the charge distribution. The distributed multipole expansion is more rapidly convergent than the normal centre-of-mass expansion and it seldom requires a consideration of moments which are higher than the distributed quadrupole. The DMA has been used successfully to rationalize the structure of a number of van der Waals dimers [13] and the structure of solids composed of S_2 molecules [14]. Distributed multipoles have been calculated for aromatic hydrocarbons [15] and small peptides [16]. The need for an anisotropic repulsion-dispersion interaction has been demonstrated in the studies of solid and liquid chlorine [17, 18]. Price [19] has discussed the potential savings of representing methylene groups in hydrocarbons using anisotropic site-site potentials. In a molecule such as stearic acid, the methylene, methyl and carboxylic acid groups could be represented as single united atoms. In this case there would be 324 site-site interactions per pair of molecules. However at the close intermolecular separations in stearic acid crystals the isotropic united atom site-site model is inadequate. A switch to a full atom representation of the carboxylic acid molecule would require the evaluation of 3249 interactions per pair and would entail an order of magnitude increase in computing time. An anisotropic site-site represention of the interaction between methylene groups is a compromise which is likely to increase the computing time over the united atom model by a factor of only 3 and yet retain much of the accuracy and flexibility of the full site–site approach. This saving may be even more pronounced for dense polymer systems such as crystalline polyethylene. The development of more realistic anisotropic site–site potentials, which may be transferable within functional groups from molecule to molecule, requires more theoretical guidance on the functional form of the anisotropy and some progress is being made in the *ab-initio* predictions of these potentials [18]. Anisotropic site–site potentials with distributed multipoles will continue to develop as an important part of the armoury of the molecular modeller.

In this paper, we will give some technical details about the use of anisotropic site–site potentials in MD. In Section 2 we discuss the detailed calculation of the forces and torques arising from the anisotropic site–site model of a linear molecule such as chlorine. In section 3 we discuss the extension of these ideas to a simple non-linear molecule such as benzene, or methane. In Section 4 we address the problem of using anisotropic site–site potentials in a simulation of a flexible molecule such as butane.

2 FORCES AND TORQUES FOR A LINEAR MOLECULE

The principles of calculating forces and torques for a linear molecule can be illustrated by considering a pair of chlorine molecules [17]. The model for Cl_2 consisted of two anisotropic sites (atoms) fixed rigidly at a bond-length of $2l$. There are four site–site interactions per pair of molecules. Each of the interactions is a function of the inter-site separation $r_{\alpha\gamma}$ and the Euler angles Ω_α and Ω_γ which describe the relative orientation of the molecular axes with respect to $r_{\alpha\gamma}$. The form of these interactions is

$$\begin{aligned} V = V_{\alpha\gamma}(r_{\alpha\gamma}, \Omega_\alpha, \Omega_\gamma) &= \mathrm{K}\exp\{-A(r_{\alpha\gamma} - \sigma_0 - \sigma(r_{\alpha\gamma}, \Omega_\alpha, \Omega_\gamma))\} \\ &\quad -\mathrm{C}(r_{\alpha\gamma} - \xi_0 - \sigma(r_{\alpha\gamma}, \Omega_\alpha, \Omega_\gamma))^{-6} + E_{es} \end{aligned} \tag{1}$$

where

$$\alpha(r_{\alpha\gamma}, \Omega_\alpha, \Omega_\gamma) = \sigma_{110}S_{110} + \sigma_2(S_{202} + S_{022}) + \sigma_3(S_{303} + S_{033}). \tag{2}$$

The first term in Equation (1) represents the anisotropic repulsion between the two atoms, the second term represents the anisotropic dispersion interaction between the atoms, and E_{es} represents the electrostatic interaction arising from the dipole and quadruopole on each atom. $\mathrm{K} = 1\,\mathrm{kJmol}^{-1}$ is a purely dimensional constant. A, σ_0, ξ_0, σ_{110}, σ_2, and σ_3 are parameters which have been found to reproduce the thermodynamic properties and structure of the three phases of chlorine. somewhat different models were used by the present authors for Br_2 and I_2 [17], and there is a later model for Cl_2 which appears rather better [20], but the function given above will serve for illustrative purposes.

In fact, in the rest of this section, we will consider only the first term in V, which provides a representative example of the calculation of the forces and torques for the complete anisotropic site-site potential. From now on

$$V = \mathrm{K}\exp\{-A(r_{\alpha\gamma} - \sigma_0 - \sigma(r_{\alpha\gamma}, \Omega_\alpha, \Omega_\gamma))\}. \tag{3}$$

The anisotropy in the repulsion is described in terms of the spherical harmonic functions, which form a complete set of expansion functions for any scalar property of the relative orientation of a pair of molecules [21]. The particular functions required

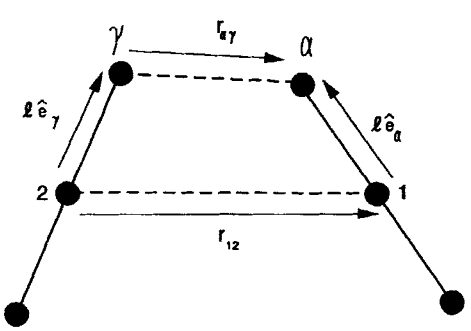

Figure 1 The geometry of a pair of linear molecules. 1 and 2 are the centres of mass of the molecules and α and γ are the positions of anisotropic sites in each molecule.

in this section are

$$
\begin{aligned}
S_{110} &= \hat{\mathbf{e}}_\alpha \cdot \hat{\mathbf{e}}_\gamma \\
S_{202} &= \tfrac{1}{2}[3(\hat{\mathbf{e}}_\alpha \cdot \hat{\mathbf{r}}_{\alpha\gamma})^2 - 1] \\
S_{022} &= \tfrac{1}{2}[3(\hat{\mathbf{e}}_\gamma \cdot \hat{\mathbf{r}}_{\alpha\gamma})^2 - 1] \\
S_{303} &= \tfrac{1}{2}[5(\hat{\mathbf{e}}_\alpha \cdot \hat{\mathbf{r}}_{\alpha\gamma})^3 - 3(\hat{\mathbf{e}}_\alpha \cdot \hat{\mathbf{r}}_{\alpha\gamma})] \\
S_{033} &= -\tfrac{1}{2}[5(\hat{\mathbf{e}}_\gamma \cdot \hat{\mathbf{r}}_{\alpha\gamma})^3 - 3(\hat{\mathbf{e}}_\gamma \cdot \hat{\mathbf{r}}_{\alpha\gamma})]
\end{aligned}
\tag{4}
$$

where $\hat{\mathbf{r}}_{\alpha\gamma} = (\boldsymbol{r}_\alpha - \boldsymbol{r}_\gamma)/r_{\alpha\gamma}$ is a unit vector in the space-fixed frame which points from site γ on molecule 2 to site α on molecule 1. $\hat{\mathbf{e}}_\alpha$ is a unit vector from the centre of mass of molecule 1 to a site α in that molecule, and $\hat{\mathbf{e}}_\gamma$ is a unit vector from the centre of mass of molecule 2 to a site γ in that molecule. Both these vectors are in the space-fixed frame. This geometry is shown in Figure 1. Expressions and generating functions for other S functions are given in [21]. We note that S_{jlm} is obtained from S_{ljm} by interchanging the subscripts α and γ in Equation (4), and recognising that $\hat{\mathbf{r}}_{\gamma\alpha} = -\hat{\mathbf{r}}_{\alpha\gamma}$.

2.1 *The Force*

The force acting on molecule 1 from the site–site potential V is

$$f_1 = -\nabla_1 V \tag{5}$$

where the gradient is with respect to the centre of mass of molecule 1, r_1. Following the ideas developed in [21] we use the chain rule to express this derivative in terms of the three dot products containing the site–site vector: $D = \boldsymbol{r}_{\alpha\gamma} \cdot \boldsymbol{r}_{\alpha\gamma}$, $D_\alpha = \boldsymbol{e}_\alpha \cdot \boldsymbol{r}_{\alpha\gamma}$ and $D_\gamma = \boldsymbol{e}_\gamma \cdot \boldsymbol{r}_{\gamma\alpha}$ where $\boldsymbol{e}_\alpha = l\hat{\mathbf{e}}_\alpha$ and $\boldsymbol{e}_\gamma = l\hat{\mathbf{e}}_\gamma$. The direction $\boldsymbol{r}_{\gamma\alpha}$ instead of $\boldsymbol{r}_{\alpha\gamma}$ is chosen for the dot product D_γ to simplify the notation throughout the paper. In this notation

$$
\begin{aligned}
V = \mathrm{K}\exp\{&-A(D^{1/2} - \sigma_0 - \sigma_{110}l^{-2}D_{\alpha\gamma} - \tfrac{1}{2}\sigma_2[3l^{-2}D^{-1}D_\alpha^2 + 3l^{-2}D^{-1}D_\gamma^2 - 2] \\
&- \tfrac{1}{2}\sigma_3[5l^{-3}D^{-3/2}D_\alpha^3 + 5l^{-3}D^{-3/2}D_\gamma^3 - 3l^{-1}D^{-1/2}D_\alpha - 3l^{-1}D^{-1/2}D_\gamma])\}
\end{aligned}
\tag{6}
$$

where $D_{\alpha\gamma} = \boldsymbol{e}_\alpha \cdot \boldsymbol{e}_\gamma$. The force is

$$f_1 = \left[\frac{\partial V}{\partial D}\right]\boldsymbol{F}_1 D + \left[\frac{\partial V}{\partial D_\alpha}\right]\boldsymbol{F}_1 D_\alpha + \left[\frac{\partial V}{\partial D_\gamma}\right]\boldsymbol{F}_1 D_\gamma \tag{7}$$

where $\boldsymbol{F}_1$ is the force operator $-\nabla_1$. The differentials with respect to the dot products can be obtained routinely from equation (6).

$$\begin{aligned}
\partial V/\partial D &= -\tfrac{1}{2}AVD^{-1/2}\{1 + 3\sigma_2 l^{-2}D^{-3/2}[D_\alpha^2 + D_\gamma^2] \\
&\quad + (3/2)\sigma_3 l^{-3}D^{-2}[5D_\alpha^3 - l^2DD_\alpha + 5D_\gamma^3 - l^2DD_\gamma]\} \\
\partial V/\partial D_\alpha &= AVD^{-1}l^{-2}\{3\sigma_2 D_\alpha + (3/2)\sigma_3 lD^{1/2}(5l^{-2}D^{-1}D_\alpha^2 - 1)\} \\
\partial V/\partial D_\gamma &= AVD^{-1}l^{-2}\{3\sigma_2 D_\gamma + (3/2)\sigma_3 lD^{1/2}(5l^{-2}D^{-1}D_\gamma^2 - 1)\}. \qquad (8)
\end{aligned}$$

The gradients of the dot products can be obtained by substituting $\boldsymbol{r}_{12} = (\boldsymbol{r}_1 - \boldsymbol{r}_2)$ for $\boldsymbol{r}_{\alpha\gamma}$ using

$$\boldsymbol{r}_{\alpha\gamma} = \boldsymbol{r}_{12} + \boldsymbol{e}_\alpha - \boldsymbol{e}_\gamma .$$

Then

$$\begin{aligned}
\mathbf{F}_1\{D\} &= -\boldsymbol{\nabla}_1\{D\} = -\boldsymbol{\nabla}_1\{(\boldsymbol{r}_{12} + \boldsymbol{e}_\alpha - \boldsymbol{e}_\gamma)\cdot(\boldsymbol{r}_{12} + \boldsymbol{e}_\alpha - \boldsymbol{e}_\gamma)\} \\
&= -2(\boldsymbol{r}_{12} + \boldsymbol{e}_\alpha - \boldsymbol{e}_\gamma) \\
&= -2\boldsymbol{r}_{\alpha\gamma} \\
\mathbf{F}_1\{D_\alpha\} &= -\boldsymbol{\nabla}_1\{D_\alpha\} = -\boldsymbol{\nabla}_1\{(\boldsymbol{r}_{12} + \boldsymbol{e}_\alpha - \boldsymbol{e}_\gamma)\cdot\boldsymbol{e}_\alpha\} \\
&= -\boldsymbol{e}_\alpha \\
\mathbf{F}_1\{D_\gamma\} &= -\boldsymbol{\nabla}_1\{D_\gamma\} = -\boldsymbol{\nabla}_1\{-(\boldsymbol{r}_{12} + \boldsymbol{e}_\alpha - \boldsymbol{e}_\gamma)\cdot\boldsymbol{e}_\gamma\} \\
&= \boldsymbol{e}_\gamma . \qquad (9)
\end{aligned}$$

Equations (8) and (9) can be substituted into Equation (7) to obtain a formula for the force on the centre of mass of molecule 1 in terms of the gradients of the three dot products. The force on molecule 2, from this particular site–site interaction, is $\boldsymbol{f}_2 = -\boldsymbol{f}_1$.

2.2 *The Torque*

The torque on the molecule can also be written as a sum over four dot products

$$\boldsymbol{t}_1 = \left[\frac{\partial V}{\partial D}\right]\boldsymbol{T}_1\{D\} + \left[\frac{\partial V}{\partial D_\alpha}\right]\boldsymbol{T}_1\{D_\alpha\} + \left[\frac{\partial V}{\partial D_\gamma}\right]\boldsymbol{T}_1\{D_\gamma\} + \left[\frac{\partial V}{\partial D_{\alpha\gamma}}\right]\boldsymbol{T}_1\{D_{\alpha\gamma}\} \qquad (10)$$

where $\boldsymbol{T}_1$ is the torque operator acting on molecule 1 and $\boldsymbol{t}_1$ is the torque acting at the centre of mass of molecule 1 due to the site–site interaction. In general [21]

$$\boldsymbol{T}_1(\boldsymbol{a}\cdot\boldsymbol{b}_1) = \boldsymbol{a}\times\boldsymbol{b}_1 \qquad (11)$$

where $\boldsymbol{b}_1$ is a vector which rotates with molecule 1 and $\boldsymbol{a}$ is a vector which is fixed with respect to the rotation of molecule 1. If $\boldsymbol{a}$ and $\boldsymbol{b}_1$ were both fixed in space or both rotated with the molecule then the torque operator produces zero. Using equation (11), we can readily calculate the four operators in Equation (10). For example

$$\begin{aligned} \boldsymbol{T}_1\{D\} &= \boldsymbol{T}_1\{(\boldsymbol{r}_{12} + \boldsymbol{e}_\alpha - \boldsymbol{e}_\gamma)\cdot(\boldsymbol{r}_{12} + \boldsymbol{e}_\alpha - \boldsymbol{e}_\gamma)\} \\ &= \boldsymbol{T}_1\{\boldsymbol{r}_{12}\cdot\boldsymbol{r}_{12} + 2\boldsymbol{r}_{12}\cdot\boldsymbol{e}_\alpha - 2\boldsymbol{r}_{12}\cdot\boldsymbol{e}_\gamma - 2\boldsymbol{e}_\alpha\cdot\boldsymbol{e}_\gamma \\ &\quad + \boldsymbol{e}_\alpha\cdot\boldsymbol{e}_\alpha + \boldsymbol{e}_\gamma\cdot\boldsymbol{e}_\gamma\} \\ &= 2\boldsymbol{T}_1\{(\boldsymbol{r}_{12} - \boldsymbol{e}_\gamma)\cdot\boldsymbol{e}_\alpha\}. \end{aligned} \tag{12}$$

Note the terms $\boldsymbol{T}_1(\boldsymbol{r}_{12}\cdot\boldsymbol{r}_{12})$, $\boldsymbol{T}_1(\boldsymbol{r}_{12}\cdot\boldsymbol{e}_\gamma)$ and $\boldsymbol{T}_1(\boldsymbol{e}_\gamma\cdot\boldsymbol{e}_\gamma)$ are zero since both vectors in the dot products are stationary as molecule 1 rotates, and the term $\boldsymbol{T}_1(\boldsymbol{e}_\alpha\cdot\boldsymbol{e}_\alpha)$ is zero because both vectors rotate with molecule 1. Finally, using Equation (11),

$$\begin{aligned} \boldsymbol{T}_1(D\} &= 2((\boldsymbol{r}_{12} - \boldsymbol{e}_\gamma) \times \boldsymbol{e}_\alpha) \\ &= 2((\boldsymbol{r}_{\alpha\gamma} - \boldsymbol{e}_\alpha) \times \boldsymbol{e}_\alpha) \\ &= 2\boldsymbol{r}_{\alpha\gamma} \times \boldsymbol{e}_\alpha \end{aligned} \tag{13}$$

Similar manipulations give the following results for $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$ acting on the four dot products

$$\begin{array}{lll} & \boldsymbol{T}_1 & \boldsymbol{T}_2 \\ \frac{1}{2}D & \boldsymbol{r}_{\alpha\gamma} \times \boldsymbol{e}_\alpha & -(\boldsymbol{r}_{\alpha\gamma} \times \boldsymbol{e}_\gamma) \\ D_\alpha & \boldsymbol{r}_{\alpha\gamma} \times \boldsymbol{e}_\alpha & -(\boldsymbol{e}_\alpha \times \boldsymbol{e}_\gamma) \\ D_\gamma & \boldsymbol{e}_\alpha \times \boldsymbol{e}_\gamma & -(\boldsymbol{r}_{\alpha\gamma} \times \boldsymbol{e}_\gamma) \\ D_{\alpha\gamma} & -(\boldsymbol{e}_\alpha \times \boldsymbol{e}_\gamma) & (\boldsymbol{e}_\alpha \times \boldsymbol{e}_\gamma) \end{array} \tag{14}$$

where the torque operator $\boldsymbol{T}_2(\boldsymbol{a}\cdot\boldsymbol{b}_2) = \boldsymbol{a} \times \boldsymbol{b}_2$, if the vector $\boldsymbol{b}_2$ rotates with molecule 2 while the vector $\boldsymbol{a}$ is stationary.

Since the torque operators acting on $D_{\alpha\gamma} = (\boldsymbol{e}_\alpha\cdot\boldsymbol{e}_\gamma)$ gives a non-zero result, we need to add another derivative to the results of Equation (8)

$$\partial V/\partial D_{\alpha\gamma} = AV\sigma_{110}l^{-2}. \tag{15}$$

Now the substitution of Equations (8), (14), and (15) into (10), and the corresponding equation for $\boldsymbol{t}_2$ gives the torques on the centre of mass of molecules 1 and 2, in terms of the four dot products. For an isolated pair of molecules the torques $\boldsymbol{t}_1$ and $\boldsymbol{t}_2$ are not equal and opposite, unlike the forces $\boldsymbol{f}_1$ and $\boldsymbol{f}_2$, but the relationship $\boldsymbol{t}_1 + \boldsymbol{t}_2 + \boldsymbol{r}_1 \times \boldsymbol{f}_1 + \boldsymbol{r}_2 \times \boldsymbol{f}_2 = 0$ is a useful check on the algebraic manipulation and coding. Once the total force and torque on the molecules has been calculated one of the standard algorithms for rigid body dynamics of linear molecules can be used to solve the equations of motion [1].

3 NON-LINEAR MOLECULES

The use of an anisotropic site–site model for simulating non-linear molecules is best considered in two separate stages; the first step being to develop a suitable functional form for the intermolecular potential, and the second, to implement this within a simulation scheme such as MD. Although this paper is mainly concerned with the second step, some general comments on the first step will be helpful.

3.1 *Development of a Potential – Local Symmetry*

Clearly the choice of orientational dependence is an important part of developing an anisotropic site–site potential. While the description can be achieved by expressing various parameters as linear expansions of S functions, one still has to ask which of the infinite number of S functions to use in this expansion. If all possible combinations are to be considered then the problem rapidly becomes too complex to be useful, as can be seen from the general expression for the quadrupole–quadrupole interaction energy [21]. However, the choice of S functions also defines the resulting shape of the molecule, and so can be simplified by utilising the molecular symmetry. For example, the cylindrical symmetry of the linear molecules considered in the last section ensures that only the Q_{20} component of the atomic quadrupole can contribute to the quadrupolar interactions between atoms on different molecules, and that the other four possible components (and 24 extra terms in the energy) are identically zero.

Symmetry can also be used to limit the possible combinations of S functions in non-linear molecules. In this case the general approach to modelling the anisotropic sites will be to identify the combinations of S functions that are consistent with the site symmetry, and then to incorporate one or two of the lowest order combinations into the intermolecular potential; various projection operator techniques exist for identifying these symmetry adapted functions [22]. In order to do this, however, it is first necessary to ask what is meant by the symmetry of a site within a molecule. As we shall show, the best answer to this question requires the judicious use of chemical intuition.

Strictly speaking, the symmetry of a site within a molecule can not exceed that of the molecule itself: the local symmetry must be a subgroup of the molecular symmetry. This is because the site interacts with the rest of the molecule and thus exists within an intramolecular field that has the molecular symmetry. The electron distribution around the chosen site will be perturbed by these influences, so that ultimately the symmetry of the site will be limited by that of the molecule. However, such a precise application of symmetry is not always the most appropriate way of proceeding. One must remember that symmetry is best used to say what effects cannot exist, and while this does imply what other effects might be possible, it gives no indication of their magnitude. If this magnitude is small enough, it may be possible to use an "approximate" site symmetry that is higher than it should be without adversely affecting the quality of the description that results. Such an approach will result in a series of intermolecular potentials analogous to successive steps in a perturbation theory, with the simplest models using sites of the highest symmetry, and added sophistication being introduced by reducing the local symmetry of the sites; the level of sophistication needed will depend on both the molecule and the property being studied, and may even be different for different types of interaction.

As a corollary to this discussion, we note that is is also important to identify just what each site is meant to model. The use of anisotropic sites makes it possible to model chemical groups rather than just atoms, and there is no requirement for these groups to be roughly spherical. Thus it is possible to reproduce the shape of a methylene group using a single site of C_{2v} symmetry, rather than having to use 3 isotropic sites. Increasing the sophistication of a potential will therefore be a balance between increasing the number of sites, and lowering the symmetry of each site, but the inclusion of the latter option results in a much more flexible approach to developing intermolecular potentials.

To make these ideas a bit more concrete we shall discuss several specific examples beginning with the archetypical asymmetric molecule: CHBrClF. As a first step, one might imagine that the atoms involved should be roughly spherical, so that the molecule could be modelled with 5 isotropic sites. However, for very dense systems, or for some of the more subtle electrostatic interactions, it might be important to recognise that the intramolecular interactions will distort the electron distribution about the various nuclei, resulting in anisotropic atoms. The major distortion is likely to be along the bonds, and so an improved description could be achieved by using 4 sites with $C_{\infty v}$ symmetry (the rotation axis being along the bond in each case) and one site (the C) with tetrahedral symmetry. If needed, further refinements could be made by using a distorted tetrahedron for the central site, or by recognising that each of the four outer sites will be distorted by the presence of the other three and so should be completely asymmetric (e.g. the Br atom will be polarized by the presence of the Cl and F atoms).

A second example is provided by the 6-anisotropic-site model of benzene proposed by Yashonath *et al.* [15]. This is a particularly informative example, as it is a system in which the main repulsive and electrostatic interactions arise from different aspects of the electronic distribution, and so are modelled with different symmetries. The electrostatic interactions in benzene are dominated by its π electron system, which arises from the electron density in the 6 carbon p_z orbitals (where z is perpendicular to the plane of the benzene molecule). Since the electron density depends on the square of the wave function, this effect may be modelled by 6 sites with $D_{\infty h}$ symmetry, which means that the first non-vanishing multipole at each site is the quadrupole, and that only the Q_{00} component (which is analogous to a d_z^2 orbital) need be considered. On the other hand, the hard core repulsive interactions arise mainly from the σ-bonding framework. As a first approximation, one might expect this to be dominated by the sp_2 hybridisation of the carbon sites, which would result in a local symmetry of D_{3h}; however the difference between the bond to the H atom and bonds to the two C atoms will perturb the central carbon site, thus reducing its local symmetry to C_{2v}. Therefore, Yashonath *et al.* modelled benzene with 6 sites, each having $D_{\infty h}$ symmetry (oriented perpendicular to the plane) with respect to the electrostatic interactions, but C_{2v} symmetry (oriented in the plane) with respect to the repulsive forces. The repulsive interactions have been reduced further to the sum of a D_{3h} term and a perturbation with cylindrical symmetry along the C–H bond which reduces the overall symmetry to C_{2v}.

3.2 *Evaluation of the Forces and Torques*

As a final example of an anisotropic model of a non-linear molecule, we consider Price's potential for methane [19], and in this case we shall give explicit expressions for the evalution of the forces and torques. Since this potential uses isotropic dispersion forces and restricts the anisotropy to the hard core repulsive forces, we shall confine our attention to the repulsive part of the potential.

This potential uses a single anisotropic site to model methane. Note that since the site is coincident with the centre of mass, there is no difference between $\boldsymbol{r}_{\alpha\gamma}$ (the site–site vector) and $\boldsymbol{r}_{12}$ (the vector between the centres of mass). As with the other examples, the orientational dependence is expressed as shifted exponential, $\exp\{-A(r_{12} - \sigma(\Omega_1, \Omega_2))\}$. Price has shown how the tetrahedral symmetry of methane can be used to specify a linear exapansion for $\sigma(\Omega_1, \Omega_2)$. The resulting potential is

$$V = \exp\{-A(r_{12} - \sigma_0 - \sigma_3 z_3 - \sigma_4 z_4)\} \qquad (16)$$

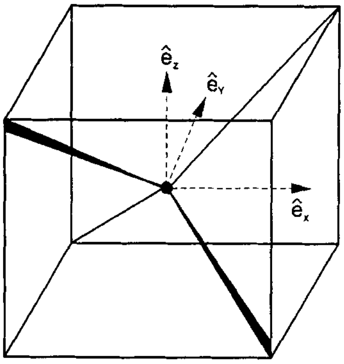

Figure 2 The body-fixed axis system of a tetrahedral molecule such as methane used to define the anisotropic site potential of equations (16) and (17) [19]. The axes point to the centre of the faces of the cube.

where A, σ_0, σ_3 and σ_4 are constants, and

$$\begin{aligned} z_3 &= -(3\sqrt{3})\{D_{1x}D_{1y}D_{1z} + D_{2x}D_{2y}D_{2z}\}/r_{12}^3 \\ z_4 &= \tfrac{1}{2}\left\{5\sum_a [(D_{1a})^4 + (D_{2a})^4]/r_{12}^4 - 6\right\}. \end{aligned} \tag{17}$$

In writing Equation (16) we have used the notation D_{1a} for the dot product between $\boldsymbol{r}_{12}(=\boldsymbol{r}_{\alpha\gamma})$ and $\hat{\mathbf{e}}_{1a}$, where the $\hat{\mathbf{e}}_{1a}$, $a = x, y, z$, are the space-fixed unit vectors defining the body-fixed axis system on molecule 1. Following the notation of the previous section, $D_{2a} = \boldsymbol{r}_{21} \cdot \hat{\mathbf{e}}_{2a}$. The body-fixed basis vectors are shown in Figure 2. For methane we need three such unit vectors, whereas for linear molecules only one was required. In contrast to the linear case, it is more natural to use the unit vectors $\hat{\mathbf{e}}_{1a}$ in the dot products since there is not natural site-centre length in the potential. Once again, explicit formulae for the forces and the torques are obtained by using the chain rule to differentiate (16) with respect to the seven scalar products ($\boldsymbol{r}_{12} \cdot \boldsymbol{r}_{12} = D$ and the D_{ia}, $i = 1, 2$) and then calculating the force or torque arising from these scalar products. The net result of this procedure will be expressions of the form

$$\begin{aligned} \boldsymbol{f}_1 &= \frac{1}{2r_{12}}\frac{\partial V}{\partial r_{12}}\boldsymbol{F}_1(D) + \sum_{\substack{a=x,y,z \\ j=1,2}} \left\{\frac{\partial V}{\partial D_{ja}}\right\} \boldsymbol{F}_1(D_{ja}) \\ \boldsymbol{t}_1 &= \frac{1}{2r_{12}}\frac{\partial V}{\partial r_{12}}\boldsymbol{T}_1(D) + \sum_{\substack{a=x,y,z \\ j=1,2}} \left\{\frac{\partial V}{\partial D_{ja}}\right\} \boldsymbol{T}_1(D_{ja}) \end{aligned} \tag{18}$$

where as before, $\boldsymbol{f}_1$ and $\boldsymbol{t}_1$ are the forces and torques acting on molecule 1, and $\boldsymbol{F}_1$ and $\boldsymbol{T}_1$ are the corresponding operators. The explicit forms for the deriviatives with respect to the scalar products are

$$\begin{aligned} \frac{\partial V}{\partial r_{12}} &= -AV\left[1 + \frac{3\sigma_3 z_3}{r_{12}} + \frac{4\sigma_4(z_4 + 3)}{r_{12}}\right] \\ \frac{\partial V}{\partial D_{ja}} &= -AV\left[\frac{3\sqrt{3}\sigma_3 D_{jb}D_{jc}}{r_{12}^3} - \frac{10\sigma_4(D_{ja})^3}{r_{12}^4}\right] \end{aligned} \tag{19}$$

where a, b, and c are cyclic in order x, y and z. For the forces, the second step is straightforward, and yields

$$\begin{aligned} \mathbf{F}_1\{D\} &= -\nabla_1\{\boldsymbol{r}_{12}\cdot\boldsymbol{r}_{12}\} = -2\boldsymbol{r}_{12} \\ \mathbf{F}_1\{D_{1a}\} &= -\nabla_1\{\boldsymbol{r}_{12}\cdot\hat{\mathbf{e}}_{1a}\} = -\hat{\mathbf{e}}_{1a} \\ \mathbf{F}_1\{D_{2a}\} &= -\nabla_1\{\boldsymbol{r}_{21}\cdot\hat{\mathbf{e}}_{2a}\} = +\hat{\mathbf{e}}_{2a}. \end{aligned} \tag{20}$$

The force on molecules 1 and 2 is given by

$$\begin{aligned} \boldsymbol{f}_1 &= -AV\left[1 + \frac{3\sigma_3 z_3 + 4\sigma_4(z_4+3)}{r_{12}}\right]\hat{\mathbf{r}}_{12} \\ &\quad + \sum_a \left\{-\frac{\partial V}{\partial D_{1a}}\hat{\mathbf{e}}_{1a} + \frac{\partial V}{\partial D_{2a}}\hat{\mathbf{e}}_{2a}\right\} \\ \boldsymbol{f}_2 &= -\boldsymbol{f}_1. \end{aligned} \tag{21}$$

The torques arising from the various scalar products may be evaluated in a fashion analogous to that discussed in Section 2.2. Once again, the torque arising from the scalar product will vanish unless one vector contains some component that rotates with the molecule, while the other contains some component that is unaltered by rotations of the molecule. Since the site is coincident with the centre of mass in this model, the site–site vector will be unaltered by rotations of either molecule, and so terms of the form $\boldsymbol{T}_1(D)$ and $\boldsymbol{T}_1(D_{2a})$, must vanish. The remaining scalar products can be seen from (11) to give

$$\begin{aligned} \boldsymbol{T}_1(D_{1a}) &= \boldsymbol{r}_{12}\times\hat{\mathbf{e}}_{1a} \\ \boldsymbol{T}_2(D_{2a}) &= -\boldsymbol{r}_{12}\times\hat{\mathbf{e}}_{2a} = \boldsymbol{r}_{21}\times\hat{\mathbf{e}}_{2a} \end{aligned} \tag{22}$$

and so the torques are simply

$$\begin{aligned} \boldsymbol{t}_1 &= \sum_a \frac{\partial V}{\partial D_{1a}}\{\boldsymbol{r}_{12}\times\hat{\mathbf{e}}_{1a}\} \\ \boldsymbol{t}_2 &= -\sum_a \frac{\partial V}{\partial D_{2a}}\{\boldsymbol{r}_{12}\times\hat{\mathbf{e}}_{2a}\}. \end{aligned} \tag{23}$$

To anticipate the next section, we note that if the centre of mass does not coincide with the interaction site, as is the case for the anisotropic site on a carbon atom which is used to model a methyl or methylene group, then the site–site vector will contain a component that rotates with the molecule, and the terms $\boldsymbol{T}_1(D_{2a})$ or $\boldsymbol{T}_1(D)$ will no longer vanish. The torques arising for this case have been listed in Appendix 1.

4 MD OF HYDROCARBON CHAINS

4.1 *The problem*

MD simulations of flexible hydrocarbon chains have played an important rôle in understanding the properties of hydrocarbon fluids [23], mesophases [24], Langmuir Blodgett films [25], alkane crystals [26], lipid bilayers [27], and amorphous polymers [28]. Most studies have used a united atom (UA) representation of the hydrocarbon chain in which a methylene group is treated as an isotropic force site. Recently, the importance of explicitly including the hydrogen atoms in studies where the chains can be close-packed has been recognised [26, 29]. For long chain molecules, this is an expensive enhancement of the potential model which can increase the computer time for a calculation by an order of magnitude. This increase in computer time is particularly significant since the intramolecular degrees of freedom require the use of a small time step, 2–3 fs, and yet conformational equilibrium in these systems is typically established on a timescale of 200–500 ps. Accurate results on conformational distributions in butane can only be obtained with runs of a million timesteps [30].

Recent work has suggested that the UA model can be improved significantly by shifting the interaction sites away from the carbon atoms and towards the centre of the CH_2 or CH_3 groups [31, 32, 33]. Toxvaerd has suggested that this be referred to as the Anisotropic United Atom model (AUA), since this shift of the interaction sites makes the overall molecule more anisotropic. However, in the context of existing work on anisotropic site–site potentials we feel this name is misleading: the AUA still uses isotropic sites, and as such the potential energy does not give rise to an intrinsic torque about the interaction site (as will occur with anisotropic sites). The AUA model does much better than the UA model at reproducing the liquid state properties of hydrocarbons [32, 33]; however simulations of very dense phases such as solid hydrocarbons and Langmuir Blodgett films, suggest that the precise shape of the methyl and methylene groups becomes important at high densities, with an interlocking of the hydrogens allowing more efficient packing of the molecules. Since the AUA retains spherical CH_2 and CH_3 groups, it is likely that a more sophisticated treatment of the intermolecular potentials will still be needed if a unified treatment of all the condensed phase properties is to be found.

In the case where the inclusion of the hydrogen atoms is thought to be important, a possible way to save time would be to model the methylene groups of the hydrocarbon chain as single anisotropic sites. Indeed, Price [19] has parametrized a suitable model which recognises the approximate tetrahedral symmetry of the methylene group about the carbon site.

A problem with this approach has been that the anisotropic site potentials and the constraint techniques used to perform the MD simulation of flexible molecules are difficult to combine. Normally, in the constraint method, the total force on a UA methylene group is calculated. This force will consist of a part from the bond-angle potential, which maintains the valence angles, a part from the dihedral or torsional potential which controls the conformation of the backbone, and a part from the so-called 1–5 interaction which prevents distant atoms in the same chain from overlapping. In addition to these additive intramolecular potentials, there are intermolecular forces from UA's on different chains in the system. Once these forces have been calculated, the atoms are moved through space for one timestep as if they are independent of one another i.e. by ignoring the bond length constraints. At the end of this free motion the constraint forces are applied to pull the molecule back into the correct geometry. The Verlet algorithm is a convenient method of performing the free atom dynamics and this can be combined with the iterative SHAKE technique for imposing the constraints [1, 3, 5]. The normal practice in these calculations is to constrain all bond lengths, but to control bond-angle distortions using harmonic potentials.

One of the difficulties of extending this technique to the anisotropic site–site potentials is that the non-bonded intermolecular interactions and the 1–5 intramolecular interaction create both a force and a torque at the anisotropic methylene site. The free motion of the anisotropic site involves the displacement of its centre of mass, and a rotation about that centre. The bond length constraint forces would act on the centres of mass of the methylene fragments, as before, to fix the bond lengths, but now we would require an additional torque of constraint which would reorient the methylene fragments. The constraint torque would ensure that two local vectors in the fragment (those pointing along the original directions of the carbon–carbon bonds) were colinear with the corresponding vectors in neighbouring fragments. However, a simple extension of the Verlet/SHAKE scheme to the orientational equations of the methylene sites would not be easy. There is no simple analogue of the Verlet equation for orientational motion. The orientational equations for the body-fixed vectors are usually solved using a quaternion technique and a leap-frog algorithm with additional equations used to estimate the orientations at the half-time step, $t + \frac{1}{2}\delta t$ [34]. This algorithm is easy to use and stable, but it does not fit readily into the framework of constraint dynamics.

A straightforward solution to this problem, which avoids the use of the rotational equations of motion, is to convert the torque on the centre of mass of the methylene fragment into three forces located on the two hydrogen atoms and the carbon atom of the methylene group. It is important to stress that these three atoms play no part in the calculation of the total torque and force on the anisotropic methylene; they are simply devices for resolving the torque into forces and ensuring that the mass distribution of the fragment is appropriate for the dynamics. Once the forces on all the "atoms" are calculated they are then moved independently using the Verlet algorithm and the SHAKE technique is used to implement the scalar and vector constraints necessary to reconstruct the tetrahedral structure of the chain. Each of these steps is outlined in Section 4.2 and some timings for the proposed technique are presented in Section 4.3.

4.2 *Anisotropic Methylene Sites*

4.2.1 *Calculation of the forces and torques*

The hydrocarbon is modeled as a chain of anisotropic methylene sites. The potential between two such methylene units, in different chains, is precisely that given in Equations (16) and (17) and is described in terms of the body-fixed axes $\hat{\mathbf{e}}_x$, $\hat{\mathbf{e}}_y$, $\hat{\mathbf{e}}_z$ shown in Figure 2. The centre of mass of the methylene unit is not coincident with the carbon atom, which is at $-l\hat{\mathbf{e}}_z$. If the centre of mass does not coincide with the interaction site, then the site–site vector will contain a component that rotates with the molecule, and the terms $\boldsymbol{T}_1(D_{2a})$ or $\boldsymbol{T}_1(D)$ will no longer vanish. In this case it is possible to calculate the force and torque and the centre of mass directly using the ideas developed in this paper. The details of the calculation are given in Appendix A.

4.2.2. *Distribution of the force and torque*

To distribute the force and torque at the centre of mass of the methylene unit it is convenient to switch them from the space-fixed axis system into the principal axis system of the methylene unit. This axis system, which is unfortunately different from the body-fixed system used to define the potential [19], is shown in figure 3. The basis vectors are defined as

$$\begin{aligned}
\hat{\mathbf{e}}_{px} &= (\boldsymbol{r}_{\mathrm{H1}} - \boldsymbol{r}_{\mathrm{H2}})/|\boldsymbol{r}_{\mathrm{H1}} - \boldsymbol{r}_{\mathrm{H2}}| \\
\hat{\mathbf{e}}_{py} &= \hat{\mathbf{e}}_{pz} \times \hat{\mathbf{e}}_{px} \\
\hat{\mathbf{e}}_{pz} &= (\boldsymbol{r}_{\mathrm{CH1}} + \boldsymbol{r}_{\mathrm{CH2}})/|\boldsymbol{r}_{\mathrm{CH1}} + \boldsymbol{r}_{\mathrm{CH2}}|. \qquad (24)
\end{aligned}$$

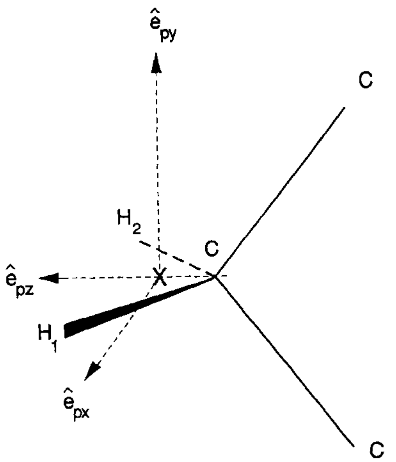

Figure 3 The principal-axis system of a methylene fragment defined in equation (23). The local axis system is used in the distribution of the torque and force on the anisotropic site as forces on the constituent atoms. X is the centre of mass of the methylene fragment.

Using this basis we can construct a unitary transformation matrix, $\boldsymbol{R}$, whose columns are the vectors $\hat{\boldsymbol{e}}_{px}$, $\hat{\boldsymbol{e}}_{py}$ and $\hat{\boldsymbol{e}}_{pz}$. Then the forces and torques in the principal frame are

$$\begin{aligned} \boldsymbol{f}_p &= \boldsymbol{R}^{-1}\boldsymbol{f} \\ \boldsymbol{t}_p &= \boldsymbol{R}^{-1}\boldsymbol{t}. \end{aligned} \tag{25}$$

The force and torque on the methylene unit in the principal frame can be used to determine six of the nine components of the three forces on the atoms of the group. There is some freedom in choosing the other three components. We have used the following scheme

	C	H1	H2
X	f_{Cx}	f_{Hx}	f_{Hx}
Y	f_{Cy}	$f_{Hy} + f'_{Hy}$	$f_{Hy} - f'_{Hy}$
Z	f_{Cz}	f_{Hz}	f_{Hz}

The three additional degrees of freedom are fixed by setting the x and z components of the forces on the two hydrogen atoms to be equal, and by ensuring that the acceleration on the three atoms in the z direction is the same. It is also convenient to divide the y component of the force on the hydrogen atoms into two parts. This ensures the $f_{Hy}{}'$ determines the z component of the principle torque. The following seven equations for the components are readily derived

$$\begin{aligned} f_{Hz} &= f_{pz}/14 \\ f_{Cz} &= 12f_{pz}/14 \\ f_{Hy}{}' &= t_{pz}/2x_H \\ f_{Hy} &= (z_C f_{py} + t_{px})/(2(z_C - z_H)) \\ f_{Cy} &= -(2z_H f_{Hy} + t_{px})/z_C \end{aligned}$$

$$f_{Hx} = (z_C f_{px} - t_{py})/(2(z_C - z_H))$$
$$f_{Cx} = (t_{py} - 2z_H f_{Hx})/z_C \qquad (26)$$

where $(0, 0, z_C)$, $(x_H, 0, z_H)$ and $(-x_H, 0, z_H)$ are the coordinates of C, H1 and H2 respectively in the principal axis system; note that $z_C = -l$. The factors 14 and 12 in Equation (26) come from the relative masses of the methylene unit and the carbon atom. Once the three forces have been determined in the principal axis system they can be transformed to the space-fixed axis system by applying the transformation matrix $\boldsymbol{R}$. A copy of the Fortran code to calculate and distribute the forces and torques on the methylene groups is available from the authors by electronic mail.

4.2.3 *Constraints*

The forces on the carbon and hydrogen atoms are used in the Verlet algorithm to move the atoms without constraints for one time-step. At the end of that step, the following constraints are applied using the SHAKE algorithm [35]:

(a) the carbon–carbon bonds between the methylene groups are constrained to the equilibrium bond length, d_{CC};

(b) the two carbon–hydrogen bonds in each methylene group are constrained to the equilibrium bond-length, d_{CH};

(c) the plane $H_1C_iH_2$ is constrained to be perpendicular to the plane $C_{i-1}C_iC_{i+1}$;

(d) the vector from the mid-point of $C_{i-1}C_{i+1}$ to C_i is constrained to bisect the vector H_1H_2 at a distance $d_{CH}\cos(\alpha/2)$ from C_i, where α is the angle $H_1C_iH_2$.

The four constraints (c) and (d) freeze out the CH stretches, the HCH scissoring, and the CH_2 rocking and wagging vibrations, but do not affect the CCC bending vibration which is comparable with the torsional frequency and which should be included using a harmonic potential. Details of this technique are given in [32], a copy of this SHAKE routine is available from the authors by electronic mail.

4.3 *An example*

We have performed simulations of liquid butane close to the boiling point using systems of 64 and 108 molecules in normal periodic boundary conditions. We have used four potential models:

(1) the united atom model (UA) of Rykaert and Bellemans [23] where each methylene and methyl group is represented as a single Lennard-Jones atom;

(2) a united atom model with a Williams type exponential-6 potential in place of the Lennard-Jones interaction (UA-W);

(3) Price's anisotropic site potential for each methyl and methylene group [19] (ASS), this potential includes an exponential repulsion and a dispersion interaction;

(4) an all-atom potential model with 14 isotropic Williams potentials [36] (ISS).

In Table 1, we show the average times for a single pass through the non-bonded force/energy subroutine for the molecular dynamics program running on the CRAY X-MP. t_f is the ratio of the time for a single pass through this subroutine for a particular model to the time for the UA-W model. We also report

Table 1 The average time t for a single pass through the non-bonded force/energy subroutine on the CRAY X/MP. t_f is the ratio of this time to that for the UA-W model. P is the % of time that program spends in the force subroutine.

64 Molecules

	t/ms	t_f	*P*/% *of total runtime*
UA	25.6	0.68	85
UA-W	37.6	1.0	90
ASS	150.0	4.0	55
ISS	366.0	9.7	75

108 Molecules

	t/ms	t_f	*P*/% *of total runtime*
UA	57.5	0.64	89
UA-W	90.0	1.0	93
ASS	387.0	4.3	66
ISS	941.0	10.5	82

the percentage of the total run time spent in the force routine during the simulation.

In the UA simulation 85% of the computer time is spent in the force subroutine for 64 molecules. As the system size increases to 108 molecules, the percentage of time in the force routine increases to 89%. The UA-W model requires the evaluation of the more complicated intrinsic exponential function and this slows the force routine by a factor of about 1.6 and increases the percentage of the total time spent in it. A change from the UA-W model to the all-atom ISS model increases the time for an evaluation of the forces by an order of magnitude. This reflects the increase in the number of site–site potentials per pair from 16 to 196 in changing from the UA-W to the ISS model. The change from the UA-W to the ASS model increases the time for the force evaluation by a factor of 4.3. This reflects the increase in complexity of the site–site potential, the need to calculate forces and torques and to distribute them onto the mass sites of the methylene groups. The force/energy subroutine in the ASS calculation is evaluated 2.5 times faster than in the ISS simulation because there are fewer sites. Both these models give very similar results for the structural properties of the butane fluid and these will be reported elsewhere [37].

As expected, the percentage of computer time spent in the force/energy subroutine is much smaller for the ASS model than for the other models discussed in this section. Considering the percentage P in Table 1 for 108 molecules, we note that the fall from 90% to 75% in changing from the UA-W to the ISS model reflects the greater complexity of the vector constraints implemented in the ISS simulation. The fall from 75% to 55% in changing from the ISS to the ASS model is due to the increase in speed of the force subroutine in the ASS simulation. This is confirmed in Table 2 which contains the average time, t, for one complete pass through the constraint routine and the percentage of the total run time that this subroutine requires. The constraint algorithm is the same for the ASS and ISS simulations, so the times are almost identical.

Table 3 shows the average time for one complete timestep of the molecular dynamics program for 27, 64, 108 and 256 butane molecules. The ASS potential runs 2.2 times faster than the ISS model for 256 butane molecules. For a longer-chain molecule such

Table 2 The average time *t* for a single pass through the constraint subroutine on the CRAY X/MP. P is the % of time that program spends in the constraint subroutine.

	64 Molecules	
	t/ms	*P/% of total runtime*
UA	2.7	10
UA-W	2.6	7
ASS	109.0	44
ISS	110.0	24
	108 Molecules	
	t/ms	*P/% of total runtime*
UA	4.4	7
UA-W	4.5	5
ASS	179.0	33
ISS	184.0	18

Table 3 The computing time per molecular dynamics timestep for butane containing N = 27, 64, 108 and 256 molecules and for decane with N = 64 molecules. In each case we report the time in milliseconds, to the nearest millisecond, for the four potential models and the ratio of time per timestep for the ISS and ASS models.

	Butane				*Decane*
N	27	64	108	256	64
model			cpu time per timestep/ms		
UA	11	30	65	272	165
UA-W	14	42	97	438	246
ASS	107	273	586	2339	1183
ISS	166	488	1148	5178	2147
ISS/ASS	1.55	1.79	1.96	2.21	1.81

as decane, the ratio of the speeds of the ASS to the ISS simultion for 64 molecules is 1.82. This ratio will decrease with increasing chain length due to the increase in the number of methylene units with respect to the two end methyl units, but will also increase with chain length due to the smaller percentage of time spent in the constraint routine for the longer molecule.

The importance of the constraint routine diminishes slightly with increasing system size, but for the simulation of 256 butane molecules it still consumes 12% of the total time. Significant improvements to the timings reported in this paper will only be achieved by detailed consideration of both the force and constraint routines and the balance between them.

These simple tests indicated that an anisotropic site-site representation of a methylene group is cost-effective and versatile. We believe that this model will play a central role in this simulation of a wide range of hydrocarbon systems at high density.

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APPENDIX 1

Forces and Torques on a Methylene Group

As indicated in the text, the expressions for the torque induced by an anisotropic site become somewhat more complicated when the interaction site does not coincide with the centre of mass of the relevant rigid unit. In this appendix we consider the difference between a rigid methylene group (with the site coincident with the carbon atom) and the methane molecule treated in Section 3. Following the suggestion of Price [19], the methylene group will be modelled by a tetrahedral site on the carbon atom, with the form of the potential being given by Equation (15); once again we will limit the discussion to the repulsive interactions since these contain all the essential features of anisotropic site–site interactions.

Expressions for the derivative of the potential with respect to the various scalar products and for the force on each methylene group are exactly the same as for the methane case [Equations (18) and (20)], but with $\boldsymbol{r}_{12}$ being replaced by $\boldsymbol{r}_{\alpha\gamma}$ (and hence $D_{\alpha a} = \boldsymbol{r}_{\alpha\gamma} \cdot \hat{e}_{\alpha a}$ for D_{1a}, and $D_{\gamma a} = \boldsymbol{r}_{\gamma a} \cdot \hat{e}_{\gamma a}$ for D_{2a}, $a = x, y, z$). The only difference comes in evaluating the torque arising from each of the scalar products. These may be evaluated, as before, by expressing the vectors as the sum of a part that rotates with the molecule and a part that does not, and then using Equation (10) (noting that the expressions differ from those given in Equation (20) due to the fact that the site–site vector $\boldsymbol{r}_{\alpha\gamma}$ now contains a part that rotates with the molecule.

The form of the potential given in Equation (15) assumes that the local z-axis for a methylene group points from the carbon atom to the centre of mass of the CH_2 unit. Thus, if we denote the distance between the methylene centre of mass and the carbon atom by l, the site–site vector is given by

$$\boldsymbol{r}_{\alpha\gamma} = \boldsymbol{r}_{12} - l\hat{\mathbf{e}}_{1z} + l\hat{\mathbf{e}}_{2z}.$$

This may then be broken up into a part that rotates with group 1,

$$\boldsymbol{b}_1 = -l\hat{\mathbf{e}}_{1z},$$

and a part that is independent of the orientation of group 1,

$$\boldsymbol{a} = \boldsymbol{r}_{12} + l\hat{\mathbf{e}}_{2z} = \boldsymbol{r}_{\alpha\gamma} + l\hat{\mathbf{e}}_{1z}.$$

These two expressions may be combined with Equation (11) to give the desired results. For example, the torque on group 1 arising from the scalar product $\boldsymbol{r}_{\alpha\gamma} \cdot \hat{\mathbf{e}}_{1x}$ is

$$\begin{aligned} \boldsymbol{T}_1(D_{\alpha x}) &= \boldsymbol{T}_1(\boldsymbol{r}_{\alpha\gamma}.\cdot \hat{\mathbf{e}}_{1x}) \\ &= \boldsymbol{T}_1(\boldsymbol{a} + \boldsymbol{b}_1)\cdot \hat{\mathbf{e}}_{1x}) \\ &= \boldsymbol{a} \times \hat{\mathbf{e}}_{1x} \\ &= \boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{1x} + l\hat{\mathbf{e}}_{1y} \end{aligned} \tag{A1}$$

where the last step makes use of the fact that $\{\hat{\mathbf{e}}_{1a}\}$ form a right handed orthonormal basis set, and so $\hat{\mathbf{e}}_{1x} \times \hat{\mathbf{e}}_{1y} = \hat{\mathbf{e}}_{1z}$ etc. A similar procedure results in the following expressions

$$\begin{array}{lll} & \boldsymbol{T}_1 & \boldsymbol{T}_2 \\ \frac{1}{2}D & -l\boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{1z} & l\boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{2z} \\ D_{\alpha x} & \boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{1x} + l\hat{\mathbf{e}}_{1y} & l\hat{\mathbf{e}}_{1x} \times \hat{\mathbf{e}}_{2z} \\ D_{\alpha y} & \boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{1y} - l\hat{\mathbf{e}}_{1x} & l\hat{\mathbf{e}}_{1y} \times \hat{\mathbf{e}}_{2z} \\ D_{\alpha z} & \boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{1z} & l\hat{\mathbf{e}}_{1z} \times \hat{\mathbf{e}}_{2z} \\ D_{\gamma x} & l\hat{\mathbf{e}}_{2x} \times \hat{\mathbf{e}}_{1z} & -\boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{2x} + l\hat{\mathbf{e}}_{2y} \\ D_{\gamma y} & l\hat{\mathbf{e}}_{2y} \times \hat{\mathbf{e}}_{1z} & -\boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{2y} - l\hat{\mathbf{e}}_{2x} \\ D_{\gamma z} & l\hat{\mathbf{e}}_{2z} \times \hat{\mathbf{e}}_{1z} & -\boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{2z} \end{array} \tag{A2}$$

which may be combined with Equations (17) and (18) to give the desired torques.

We note, finally, that is is possible to simplify the calculation of the cross products in Equation (A2). To do this we recall that the vectors $\{\hat{\mathbf{e}}_{1a}\}$ and $\{\hat{\mathbf{e}}_{2a}\}$ both form a suitable right handed orthonormal basis set for describing any vector. For example, the site–site vector may be expressed as

$$\begin{aligned} \boldsymbol{r}_{\alpha\gamma} &= (\boldsymbol{r}_{\alpha\gamma} \cdot \hat{\mathbf{e}}_{1x})\hat{\mathbf{e}}_{1x} + (\boldsymbol{r}_{\alpha\gamma} \cdot \hat{\mathbf{e}}_{1y})\mathbf{e}_{1y} + (\boldsymbol{r}_{\alpha\gamma} \cdot \hat{\mathbf{e}}_{1z})\hat{\mathbf{e}}_{1z} \\ &= D_{\alpha x}\hat{\mathbf{e}}_{1x} + D_{\alpha y}\hat{\mathbf{e}}_{1y} + D_{\alpha z}\hat{\mathbf{e}}_{1z} \end{aligned} \tag{A3}$$

so that the cross product $\boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{1x}$ is given by

$$\boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{1x} = D_{\alpha y}\hat{\mathbf{e}}_{1z} + D_{\alpha y}\hat{\mathbf{e}}_{1y}. \tag{A4}$$

The advantage of this technique is that both the scalar products $D_{\alpha a}$ and the vectors $\hat{\mathbf{e}}_{1a}$ will already have been worked out in evaluating the energy from Equation (14). Similar expressions can be found for all the vector products involving $\boldsymbol{r}_{\alpha\gamma}$:

$$\begin{array}{lcc} & \boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{1a} & \boldsymbol{r}_{\alpha\gamma} \times \hat{\mathbf{e}}_{2a} \\ a = x & -D_{\alpha y}\hat{\mathbf{e}}_{1z} + D_{\alpha z}\hat{\mathbf{e}}_{1y} & D_{\gamma y}\hat{\mathbf{e}}_{2z} - D_{\gamma z}\hat{\mathbf{e}}_{2y} \\ a = y & D_{\alpha x}\hat{\mathbf{e}}_{1z} - D_{\alpha z}\hat{\mathbf{e}}_{1x} & -D_{\gamma x}\hat{\mathbf{e}}_{2z} + D_{\gamma z}\hat{\mathbf{e}}_{2x} \\ a = z & -D_{\alpha x}\hat{\mathbf{e}}_{1y} + D_{\alpha y}\hat{\mathbf{e}}_{1x} & D_{\gamma x}\hat{\mathbf{e}}_{2y} - D_{\gamma y}\hat{\mathbf{e}}_{2x} \end{array} \tag{A5}$$

A similar technique might also be useful in evaluating products of the form $\hat{\mathbf{e}}_{1a} \times \hat{\mathbf{e}}_{2b}$. By projecting one basis set, say $\hat{\mathbf{e}}_{1a}$, onto the other one, say $\hat{\mathbf{e}}_{2b}$, it is possible to express the remaining vector products in terms of scalar products $E_{ab} = \hat{\mathbf{e}}_{1a} \cdot \hat{\mathbf{e}}_{2b}$:

$$\begin{aligned}
\hat{\mathbf{e}}_{1x} \times \hat{\mathbf{e}}_{2z} &= -E_{xx}\hat{\mathbf{e}}_{2y} + E_{xy}\hat{\mathbf{e}}_{2x} \\
\hat{\mathbf{e}}_{1y} \times \hat{\mathbf{e}}_{2z} &= -E_{yx}\hat{\mathbf{e}}_{2y} + E_{yy}\hat{\mathbf{e}}_{2x} \\
\hat{\mathbf{e}}_{1z} \times \hat{\mathbf{e}}_{2z} &= -E_{zx}\hat{\mathbf{e}}_{2y} + E_{zy}\hat{\mathbf{e}}_{2x} \\
\hat{\mathbf{e}}_{2x} \times \hat{\mathbf{e}}_{1z} &= E_{zy}\hat{\mathbf{e}}_{2z} - E_{zz}\hat{\mathbf{e}}_{2y} \\
\hat{\mathbf{e}}_{2y} \times \hat{\mathbf{e}}_{1z} &= -E_{zx}\hat{\mathbf{e}}_{2z} + E_{zz}\hat{\mathbf{e}}_{2x}
\end{aligned} \tag{A6}$$