HAL
open science

# Expressions for forces and torques in molecular simulations using rigid bodies

Michael Allen, Guido Germano

## To cite this version:

Michael Allen, Guido Germano. Expressions for forces and torques in molecular simulations using rigid bodies. Molecular Physics, 2007, 104 (20-21), pp.3225-3235. 10.1080/00268970601075238 . hal-00513057

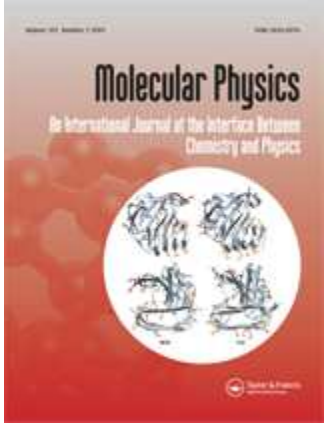
**HAL Id: hal-00513057**

**https://hal.science/hal-00513057v1**

Submitted on 1 Sep 2010

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.




# Expressions for forces and torques in molecular simulations using rigid bodies

| | |
|---|---|
| Journal: | *Molecular Physics* |
| Manuscript ID: | TMPH-2006-0002 |
| Manuscript Type: | Full Paper |
| Date Submitted by the Author: | 22-Aug-2006 |
| Complete List of Authors: | Allen, Michael; University of Warwick, Department of Physics<br>Germano, Guido; Philipps-Universitaet Marburg, Fachbereich Chemie |
| Keywords: | Molecular simulation, Gay-Berne, coarse graining, anisotropic potentials, rigid body potentials |
| | |

scholarONE™
Manuscript Central

*Molecular Physics*, Vol. 00, No. 00, DD Month 200x, 1–18

# Expressions for forces and torques in molecular simulations using rigid bodies

Michael P. Allen *

Department of Physics and Centre for Scientific Computing

University of Warwick, Coventry CV4 7AL, United Kingdom

Guido Germano

Fachbereich Chemie, Philipps-Universität Marburg, 35032 Marburg, Germany

(*Received 00 Month 200x; In final form 00 Month 200x*)

Expressions for intermolecular forces and torques, derived from pair potentials between rigid non-spherical units, are presented. The aim is to give compact and clear expressions, which are easily generalised, and which minimise the risk of error in writing molecular dynamics simulation programs. It is anticipated that these expressions will be useful in the simulation of liquid crystalline systems, and in coarse-grained modelling of macromolecules.

*Keywords:* Molecular simulation; Gay-Berne; coarse graining; anisotropic potentials; angular-dependent potentials; rigid body potentials.

## 1 Introduction

This paper is intended to clarify the way in which forces and torques may be computed from an expression for the pair potential between two, generally nonlinear, molecules. These forces and torques are then typically incorporated into molecular dynamics simulation programs [1–3]. The particular focus is on pair potentials which are expressed directly as functions of the molecular centre-centre vector and orientational variables such as Euler angles, quaternion (Euler) parameters, or rotation matrix elements. Some examples, based on potentials used in the simulation of liquid crystals and macromolecules, are given, but the intention is also to provide a formalism that is easily generalised. The more common case of atomic site-site potentials is not considered here. Several schemes exist for systematically "coarse-graining" such atomistically-detailed interaction potentials, often by performing simulations over relatively short times and fitting either coarse-grained pair distribution functions or aggregated forces [4–8], but this is also not the focus of the present paper. The aim is to streamline, and make more robust, the process of analytically deriving forces and torques, once the coarse-grained potentials have been determined, and parametrised

*Corresponding author. E-mail: m.p.allen@warwick.ac.uk

For Peer Review Only

in a standard way. Even with the help of symbolic algebra packages, performing this task is prone to error and may result in molecular dynamics code which is inefficient, hard to understand, and difficult to adapt. By the use of some examples, based on spheroidal geometry, it is shown here that standard vector and matrix notation helps to simplify the formulae, leading to an improved insight into the machinery of the potentials as well as giving a more reliable route to the simulation code.

Consider two nonlinear molecules A and B, position vectors $\boldsymbol{r}_A$, $\boldsymbol{r}_B$. Define the intermolecular vector $\boldsymbol{r} = \boldsymbol{r}_{AB} = \boldsymbol{r}_A - \boldsymbol{r}_B$, distance $r = |\boldsymbol{r}|$, and unit vector $\hat{\boldsymbol{r}} = \boldsymbol{r}/r$. Specify the orientations by the orthogonal rotation matrices $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$, which convert from space-fixed $(xyz)$ to molecule-fixed (123) coordinates [9]:

$$\hat{\mathbf{a}} = \begin{pmatrix} \hat{\boldsymbol{a}}_1 \\ \hat{\boldsymbol{a}}_2 \\ \hat{\boldsymbol{a}}_3 \end{pmatrix} = \begin{pmatrix} \hat{a}_{1x} & \hat{a}_{1y} & \hat{a}_{1z} \\ \hat{a}_{2x} & \hat{a}_{2y} & \hat{a}_{2z} \\ \hat{a}_{3x} & \hat{a}_{3y} & \hat{a}_{3z} \end{pmatrix} , \qquad \hat{\mathbf{b}} = \begin{pmatrix} \hat{\boldsymbol{b}}_1 \\ \hat{\boldsymbol{b}}_2 \\ \hat{\boldsymbol{b}}_3 \end{pmatrix} = \begin{pmatrix} \hat{b}_{1x} & \hat{b}_{1y} & \hat{b}_{1z} \\ \hat{b}_{2x} & \hat{b}_{2y} & \hat{b}_{2z} \\ \hat{b}_{3x} & \hat{b}_{3y} & \hat{b}_{3z} \end{pmatrix} .$$

The rows of these matrices are the three molecule-fixed orthonormal principal axis vectors $\hat{\boldsymbol{a}}_m$, $\hat{\boldsymbol{b}}_m$, $m = 1, 2, 3$. Note that it is possible to write $[\hat{\mathbf{a}}]_{m\mu} = [\hat{\boldsymbol{a}}_m]_\mu = \hat{a}_{m\mu}$, $\mu = x, y, z$, without ambiguity.

It is assumed that the pair potential may be written as a function $U = U(\boldsymbol{r}, \hat{\mathbf{a}}, \hat{\mathbf{b}})$ and that it is invariant to a global rotation of the coordinates. Quite generally the force $\boldsymbol{f}_A$ on A due to B will be the negative of the force $\boldsymbol{f}_B$ on B due to A, so

$$\boldsymbol{f}_A = -\boldsymbol{f}_B \equiv \boldsymbol{f} = -\frac{\partial U}{\partial \boldsymbol{r}} .$$

Depending on the form of the potential it may be possible to evaluate this derivative directly, or it may be more convenient to separate the components along, and perpendicular to, the line of centres:

$$\boldsymbol{f} = -\frac{\partial U}{\partial r}\frac{\partial r}{\partial \boldsymbol{r}} - \frac{\partial U}{\partial \hat{\boldsymbol{r}}} \cdot \left(\frac{\partial \hat{\boldsymbol{r}}}{\partial \boldsymbol{r}}\right) = -\frac{\partial U}{\partial r}\hat{\boldsymbol{r}} - r^{-1}\frac{\partial U}{\partial \hat{\boldsymbol{r}}} \cdot \left(\mathbf{1} - \hat{\boldsymbol{r}} \otimes \hat{\boldsymbol{r}}\right) . \tag{1}$$

On the right, $\otimes$ constructs a dyadic matrix from two vectors, and $\mathbf{1}$ is the unit $3 \times 3$ matrix. The torque calculation follows Price et al. [10], with minor variations. Consider the negative of the derivative of $U$ with respect to rotation of molecule A through an angle $\psi$ about any axis represented by a unit vector $\hat{\boldsymbol{\psi}}$. By definition, this gives the corresponding component of the torque $\boldsymbol{\tau}_A$, and the chain rule may be used to express this in terms of the body-fixed unit vectors

$$\hat{\boldsymbol{\psi}} \cdot \boldsymbol{\tau}_A = -\frac{\partial U}{\partial \psi} = -\sum_m \frac{\partial U}{\partial \hat{\boldsymbol{a}}_m} \cdot \frac{\partial \hat{\boldsymbol{a}}_m}{\partial \psi} = -\sum_m \frac{\partial U}{\partial \hat{\boldsymbol{a}}_m} \cdot \hat{\boldsymbol{\psi}} \times \hat{\boldsymbol{a}}_m .$$

The last equation follows from the rotation formula [9] for any vector $\partial \boldsymbol{e}/\partial \psi = \hat{\boldsymbol{\psi}} \times \boldsymbol{e}$. Cyclic permutation of the vectors in the scalar triple product then gives

$$\hat{\boldsymbol{\psi}} \cdot \boldsymbol{\tau}_A = -\hat{\boldsymbol{\psi}} \cdot \sum_m \hat{\boldsymbol{a}}_m \times \frac{\partial U}{\partial \hat{\boldsymbol{a}}_m} .$$

For Peer Review Only

Choosing $\hat{\boldsymbol{\psi}}$ to be each of the coordinate directions in turn allows the identification of every component of the torque, and the expression for $\boldsymbol{\tau}_B$ is similar

$$\boldsymbol{\tau}_A = -\sum_m \hat{\boldsymbol{a}}_m \times \frac{\partial U}{\partial \hat{\boldsymbol{a}}_m}\,, \qquad \boldsymbol{\tau}_B = -\sum_m \hat{\boldsymbol{b}}_m \times \frac{\partial U}{\partial \hat{\boldsymbol{b}}_m}\,. \tag{2}$$

In the succeeding sections, more specific examples of the above formulae will be given for particular choices of pair potential $U$.

## 2 Scalar Product Potentials

A very common case, and a useful preamble for what follows, is when the pair potential between A and B may be written in the form [10]

$$U = U(\boldsymbol{r}, \hat{\mathbf{a}}, \hat{\mathbf{b}}) = U(r, \{\hat{\boldsymbol{a}}_m \cdot \hat{\boldsymbol{r}}\}, \{\hat{\boldsymbol{b}}_n \cdot \hat{\boldsymbol{r}}\}, \{\hat{\boldsymbol{a}}_m \cdot \hat{\boldsymbol{b}}_n\})\,. \tag{3}$$

This is a function of the centre-centre separation $r$, and all possible scalar products of the unit vectors $\hat{\boldsymbol{r}}$, $\hat{\boldsymbol{a}}_m$ and $\hat{\boldsymbol{b}}_n$. It is manifestly invariant to a global rotation of coordinates. The force may be written

$$\begin{aligned}\boldsymbol{f} = -\frac{\partial U}{\partial \boldsymbol{r}} &= -\frac{\partial U}{\partial r}\frac{\partial r}{\partial \boldsymbol{r}} - \sum_m \left( \frac{\partial U}{\partial(\hat{\boldsymbol{a}}_m \cdot \hat{\boldsymbol{r}})}\frac{\partial(\hat{\boldsymbol{a}}_m \cdot \hat{\boldsymbol{r}})}{\partial \boldsymbol{r}} + \frac{\partial U}{\partial(\hat{\boldsymbol{b}}_m \cdot \hat{\boldsymbol{r}})}\frac{\partial(\hat{\boldsymbol{b}}_m \cdot \hat{\boldsymbol{r}})}{\partial \boldsymbol{r}} \right) \\ &= -\frac{\partial U}{\partial r}\hat{\boldsymbol{r}} - r^{-1}\sum_m \left( \frac{\partial U}{\partial(\hat{\boldsymbol{a}}_m \cdot \hat{\boldsymbol{r}})}\hat{\boldsymbol{a}}_m^{\perp} + \frac{\partial U}{\partial(\hat{\boldsymbol{b}}_m \cdot \hat{\boldsymbol{r}})}\hat{\boldsymbol{b}}_m^{\perp} \right)\,.\end{aligned} \tag{4}$$

The sum ranges over all the orientation vectors on both molecules, $\{\hat{\boldsymbol{a}}_m, \hat{\boldsymbol{b}}_m\}$. The notation

$$\boldsymbol{v}^{\perp} \equiv \boldsymbol{v} - (\boldsymbol{v} \cdot \hat{\boldsymbol{r}})\hat{\boldsymbol{r}} = -\hat{\boldsymbol{r}} \times \left(\hat{\boldsymbol{r}} \times \boldsymbol{v}\right)$$

is short for the component of a vector $\boldsymbol{v}$ perpendicular to $\hat{\boldsymbol{r}}$. The derivatives of the potential appearing in eqn (4) are easily evaluated, assuming that it has the general form of eqn (3). The torque calculation once more follows Price et al. [10]. The derivative of $U$ with respect to rotation of molecule A through an angle $\psi$ about an axis $\hat{\boldsymbol{\psi}}$ takes the form

$$\hat{\boldsymbol{\psi}} \cdot \boldsymbol{\tau}_A = -\frac{\partial U}{\partial \psi} = -\sum_m \frac{\partial U}{\partial(\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{a}}_m)}\frac{\partial(\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{a}}_m)}{\partial \psi} - \sum_{mn} \frac{\partial U}{\partial(\hat{\boldsymbol{b}}_n \cdot \hat{\boldsymbol{a}}_m)}\frac{\partial(\hat{\boldsymbol{b}}_n \cdot \hat{\boldsymbol{a}}_m)}{\partial \psi}\,.$$

All combinations of unit vectors for which one, $\hat{\boldsymbol{a}}_m$, rotates with the molecule while the other, $\hat{\boldsymbol{r}}$ or $\hat{\boldsymbol{b}}_n$, remains stationary, appear on the right. The rotation formula in this case gives $\partial(\hat{\boldsymbol{v}} \cdot \hat{\boldsymbol{a}}_m)/\partial\psi = \hat{\boldsymbol{v}} \cdot \hat{\boldsymbol{\psi}} \times \hat{\boldsymbol{a}}_m =$

For Peer Review Only

$-\hat{\boldsymbol{\psi}} \cdot \hat{\boldsymbol{v}} \times \hat{\boldsymbol{a}}_m$ and once again $\hat{\boldsymbol{\psi}}$ may be chosen arbitrarily. The explicit result for molecules A and B is

$$\boldsymbol{\tau}_A = \sum_m \frac{\partial U}{\partial(\hat{\boldsymbol{a}}_m \cdot \hat{\boldsymbol{r}})} \left(\hat{\boldsymbol{r}} \times \hat{\boldsymbol{a}}_m\right) - \sum_{mn} \frac{\partial U}{\partial(\hat{\boldsymbol{a}}_m \cdot \hat{\boldsymbol{b}}_n)} \left(\hat{\boldsymbol{a}}_m \times \hat{\boldsymbol{b}}_n\right) , \tag{5a}$$

$$\boldsymbol{\tau}_B = \sum_n \frac{\partial U}{\partial(\hat{\boldsymbol{b}}_n \cdot \hat{\boldsymbol{r}})} \left(\hat{\boldsymbol{r}} \times \hat{\boldsymbol{b}}_n\right) + \sum_{mn} \frac{\partial U}{\partial(\hat{\boldsymbol{a}}_m \cdot \hat{\boldsymbol{b}}_n)} \left(\hat{\boldsymbol{a}}_m \times \hat{\boldsymbol{b}}_n\right) . \tag{5b}$$

Note that the combination of eqns (4), (5a) and (5b) gives

$$\boldsymbol{\tau}_A + \boldsymbol{\tau}_B + \boldsymbol{r} \times \boldsymbol{f} = 0 . \tag{6}$$

This is the expression of local angular momentum conservation, which follows directly from the invariance of the potential energy, eqn (3), to a rotation of all the vectors $\hat{\boldsymbol{r}}$, $\hat{\boldsymbol{a}}_m$ and $\hat{\boldsymbol{b}}_n$ together.

## 3 Biaxial Gay-Berne, and Related, Potentials

The original Gay-Berne family of potentials [11–14] was developed for molecules having the symmetry, and approximate shape, of uniaxial ellipsoids. They have now been generalised to include biaxiality [15–18]. The general form is [17]

$$U_{\mathrm{GB}} = \varepsilon_1^{\nu}(\hat{\mathbf{a}}, \hat{\mathbf{b}})\, \varepsilon_2^{\mu}(\hat{\mathbf{a}}, \hat{\mathbf{b}}, \hat{\boldsymbol{r}})\, U_{\mathrm{shape}}\big(r, \sigma(\hat{\boldsymbol{r}}, \hat{\mathbf{a}}, \hat{\mathbf{b}})\big)$$

Here the two $\varepsilon$ terms represent orientation-dependent strength factors, raised to powers $\mu$, $\nu$ which characterise different variants of the model. The last term roughly defines the molecular shape, via an orientation-dependent distance function $\sigma$ which will be discussed in more detail below. $U_{\mathrm{shape}}$ typically is based on a Lennard-Jones 12-6 potential

$$U_{\mathrm{shape}}(r, \sigma) = 4\varepsilon_0 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{7}$$

although, as shall be seen, this has been refined somewhat. The Gay-Berne potentials have been extensively used to model small organic molecules [19–21] and liquid crystalline systems [22,23]; linked Gay-Berne units may also be used in the coarse-grained modelling of polymer chains including biological macromolecules [4, 24].

For illustrative purposes here, attention will focus on the "shape" term above, and the energy-dependent $\varepsilon$ terms will be taken to be constants. (Their contributions to forces and torques may be straightforwardly included using similar methods). It is therefore assumed that the potential may be written

$$U = U\big(r, \sigma(\hat{\boldsymbol{r}}, \hat{\mathbf{a}}, \hat{\mathbf{b}})\big) . \tag{8}$$

The relation between the Gay-Berne distance function $\sigma$ and the geometry of ellipsoids has been clarified

For Peer Review Only

by Perram et al. [25–27]. Define the matrices

$$\mathbf{A} = \sum_m a_m^2 \hat{\boldsymbol{a}}_m \otimes \hat{\boldsymbol{a}}_m = \sum_m \boldsymbol{a}_m \otimes \boldsymbol{a}_m \,, \qquad \mathbf{B} = \sum_m b_m^2 \hat{\boldsymbol{b}}_m \otimes \hat{\boldsymbol{b}}_m = \sum_m \boldsymbol{b}_m \otimes \boldsymbol{b}_m \tag{9}$$

(but note that our $\mathbf{A}$ is $\mathbf{A}^{-1}$ in Ref. [27]). Here the $a_m$ and $b_m$ are semi-axis lengths of the ellipsoidal particles, and these have been used to define the un-normalised semi-axis vectors $\boldsymbol{a}_m = a_m \hat{\boldsymbol{a}}_m$ etc. These matrices may also be written in terms of the rotation matrices defined earlier [15]

$$A_{\mu\nu} = \sum_m a_m^2 \hat{a}_{m\mu} \hat{a}_{m\nu} = \sum_{mn} a_m a_n \delta_{mn} \hat{a}_{m\mu} \hat{a}_{n\nu} = \sum_{mn} \left[\hat{\mathbf{a}}^{\mathsf{T}}\right]_{\mu m} a_m \delta_{mn} a_n \left[\hat{\mathbf{a}}\right]_{n\nu} . \tag{10}$$

Defining the diagonal shape matrix $\mathbf{S} = \mathrm{diag}(a_1, a_2, a_3)$, and the matrix $\mathbf{a}$ whose rows are the un-normalised semi-axis vectors $\mathbf{a} = \mathbf{S}\hat{\mathbf{a}}$, i.e. $[\mathbf{a}]_{m\mu} = [\boldsymbol{a}_m]_\mu = a_{m\mu} = a_m \hat{a}_{m\mu}$, gives

$$\mathbf{A} = \hat{\mathbf{a}}^{\mathsf{T}} \mathbf{S}^2 \hat{\mathbf{a}} = \mathbf{a}^{\mathsf{T}} \mathbf{a} \,. \tag{11}$$

Recall that the rotation matrix is orthogonal, $\hat{\mathbf{a}}^{\mathsf{T}} \hat{\mathbf{a}} = \hat{\mathbf{a}} \hat{\mathbf{a}}^{\mathsf{T}} = \mathbf{1}$, whereas this is not true for $\mathbf{a}$.

The diameter $\sigma$ is defined through the following equations [15, 16, 27]

$$\sigma = 1/\sqrt{\varphi} \,, \tag{12a}$$

$$\varphi = \sigma^{-2} = \tfrac{1}{2}\, \hat{\boldsymbol{r}} \cdot \left(\mathbf{A} + \mathbf{B}\right)^{-1} \cdot \hat{\boldsymbol{r}} \equiv \tfrac{1}{2}\, \hat{\boldsymbol{r}} \cdot \mathbf{H}^{-1} \cdot \hat{\boldsymbol{r}} \,, \tag{12b}$$

$$\text{where} \quad \mathbf{H} = \mathbf{A} + \mathbf{B} \,. \tag{12c}$$

All of the $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ dependence lies within the matrix inverse $\mathbf{H}^{-1}$ while all the $\hat{\boldsymbol{r}}$ dependence lies outside it. It is comparatively easy, though cumbersome, to evaluate the matrix inverse in a suitable form, perform the scalar products with $\hat{\boldsymbol{r}}$ explicitly, and use eqns (4), (5) for the forces and torques [15, 16, 28]. The following alternative approach was suggested by Perram et al. [27], and leads to more compact expressions based on eqns (1), (2).

### 3.1 *Scaled Potential*

First consider the special class of potentials for which [27]

$$U = U\big(r^2/\sigma^2(\hat{\boldsymbol{r}}, \hat{\mathbf{a}}, \hat{\mathbf{b}})\big) = U(\Phi) \tag{13}$$

$$\text{where} \quad \Phi = r^2 \varphi = r^2/\sigma^2 = \tfrac{1}{2}\, \boldsymbol{r} \cdot \left(\mathbf{A} + \mathbf{B}\right)^{-1} \cdot \boldsymbol{r} \equiv \tfrac{1}{2}\, \boldsymbol{r} \cdot \mathbf{H}^{-1} \cdot \boldsymbol{r} \,. \tag{14}$$

The simple form (7) is an example. This form of potential is simple to implement, but it does have the disadvantage that the length scale is entirely determined by $\sigma$; hence, a Lennard-Jones form will have an attractive range which is proportional to the repulsive diameter at any given orientation of molecules,

For Peer Review Only

which may be unphysical. The shifted form of the potential (see sec 3.2) was introduced by Gay and Berne [14] to address this fault. On the other hand, in certain cases, e.g. for rapidly-varying, completely repulsive potentials, this may not be so much a problem.

Following [27], define an auxiliary vector $\boldsymbol{\kappa}$ by solving the equations

$$\mathbf{H} \cdot \boldsymbol{\kappa} = \boldsymbol{r} \qquad \Leftrightarrow \qquad \boldsymbol{\kappa} = \mathbf{H}^{-1} \cdot \boldsymbol{r} \,. \tag{15}$$

In what follows, there is no need to fully evaluate $\mathbf{H}^{-1}$. In terms of $\boldsymbol{\kappa}$

$$\Phi = \tfrac{1}{2} \boldsymbol{r} \cdot \boldsymbol{\kappa} \,, \qquad \frac{\partial \Phi}{\partial \boldsymbol{r}} = \mathbf{H}^{-1} \cdot \boldsymbol{r} = \boldsymbol{\kappa} \,.$$

This last formula gives the interparticle force from

$$\boldsymbol{f} = -\frac{\mathrm{d}U}{\mathrm{d}\Phi} \frac{\partial \Phi}{\partial \boldsymbol{r}} = -\frac{\mathrm{d}U}{\mathrm{d}\Phi} \boldsymbol{\kappa} \,. \tag{16}$$

To obtain the torque, write

$$\boldsymbol{\tau}_A = -\sum_m \hat{\boldsymbol{a}}_m \times \frac{\partial U}{\partial \hat{\boldsymbol{a}}_m} = -\sum_m \boldsymbol{a}_m \times \frac{\partial U}{\partial \boldsymbol{a}_m} = -\frac{\mathrm{d}U}{\mathrm{d}\Phi} \sum_m \boldsymbol{a}_m \times \frac{\partial \Phi}{\partial \boldsymbol{a}_m} \,. \tag{17}$$

The evaluation of $\partial \Phi / \partial \boldsymbol{a}_m$ proceeds as follows.

$$\frac{\partial \Phi}{\partial a_{m\mu}} = \tfrac{1}{2} \, \boldsymbol{r} \cdot \frac{\partial \mathbf{H}^{-1}}{\partial a_{m\mu}} \cdot \boldsymbol{r} = -\tfrac{1}{2} \, \boldsymbol{r} \cdot \mathbf{H}^{-1} \frac{\partial \mathbf{H}}{\partial a_{m\mu}} \mathbf{H}^{-1} \cdot \boldsymbol{r} = -\tfrac{1}{2} \, \boldsymbol{\kappa} \cdot \frac{\partial \mathbf{A}}{\partial a_{m\mu}} \cdot \boldsymbol{\kappa} \,.$$

The definition of $\mathbf{A}$ implies $\partial \mathbf{A} / \partial a_{m\mu} = \hat{\boldsymbol{e}}_\mu \otimes \boldsymbol{a}_m + \boldsymbol{a}_m \otimes \hat{\boldsymbol{e}}_\mu$, where $\hat{\boldsymbol{e}}_\mu$, $\mu = x, y, z$ is the appropriate unit vector in the space-fixed Cartesian coordinate system. Therefore

$$\partial \Phi / \partial a_{m\mu} = -(\boldsymbol{\kappa} \cdot \boldsymbol{a}_m) \kappa_\mu \qquad \Rightarrow \qquad \partial \Phi / \partial \boldsymbol{a}_m = -(\boldsymbol{\kappa} \cdot \boldsymbol{a}_m) \boldsymbol{\kappa} \,.$$

Combining with eqn (17), and applying a similar formula to molecule B, gives the torques

$$\boldsymbol{\tau}_A = \frac{\mathrm{d}U}{\mathrm{d}\Phi} \sum_m (\boldsymbol{\kappa} \cdot \boldsymbol{a}_m)(\boldsymbol{a}_m \times \boldsymbol{\kappa}) = \frac{\mathrm{d}U}{\mathrm{d}\Phi} (\boldsymbol{\kappa} \cdot \mathbf{A} \times \boldsymbol{\kappa}) \,, \tag{18a}$$

$$\boldsymbol{\tau}_B = \frac{\mathrm{d}U}{\mathrm{d}\Phi} \sum_m (\boldsymbol{\kappa} \cdot \boldsymbol{b}_m)(\boldsymbol{b}_m \times \boldsymbol{\kappa}) = \frac{\mathrm{d}U}{\mathrm{d}\Phi} (\boldsymbol{\kappa} \cdot \mathbf{B} \times \boldsymbol{\kappa}) \,. \tag{18b}$$

These equations are essentially those of Perram et al. [27]. Using eqn (16), it is possible to write them in the form

$$\boldsymbol{\tau}_A = -\boldsymbol{\kappa} \cdot \mathbf{A} \times \boldsymbol{f} = \boldsymbol{r}_{CA} \times \boldsymbol{f} \qquad = (\boldsymbol{r}_C - \boldsymbol{r}_A) \times \boldsymbol{f} \,, \tag{19a}$$

$$\boldsymbol{\tau}_B = -\boldsymbol{\kappa} \cdot \mathbf{B} \times \boldsymbol{f} = \boldsymbol{r}_{CB} \times (-\boldsymbol{f}) = (\boldsymbol{r}_C - \boldsymbol{r}_B) \times (-\boldsymbol{f}) \tag{19b}$$

For Peer Review Only

where $\boldsymbol{r}_C$ is defined by

$$\boldsymbol{r}_C = \boldsymbol{r}_A - \mathbf{A}\cdot\boldsymbol{\kappa} = \boldsymbol{r}_A + \boldsymbol{r}_{CA} \tag{20a}$$

$$= \boldsymbol{r}_B + \mathbf{B}\cdot\boldsymbol{\kappa} = \boldsymbol{r}_B + \boldsymbol{r}_{CB} \tag{20b}$$

(see Appendix A). The physical interpretation of this is that the intermolecular force may be taken to act at the "contact point" $\boldsymbol{r}_C$, and the torques about the molecular centres are then given by the usual moment formulae. Conservation of angular momentum follows immediately since $\boldsymbol{\tau}_A + \boldsymbol{\tau}_B = (\boldsymbol{r}_{CA} - \boldsymbol{r}_{CB}) \times \boldsymbol{f} = -\boldsymbol{r}_{AB} \times \boldsymbol{f} = -\boldsymbol{r} \times \boldsymbol{f}$.

It is illuminating to consider the case of identical uniaxial particles. Suppose the orientation of both particles is defined by unit vectors $\hat{\boldsymbol{a}}_3$, $\hat{\boldsymbol{b}}_3$ along the 3-direction, and that the semiaxes are given by $a_1 = b_1 = a_2 = b_2 = \ell_\perp$, $a_3 = b_3 = \ell_\parallel$. Then, the orthonormality relation $\sum_m \hat{\boldsymbol{a}}_m \otimes \hat{\boldsymbol{a}}_m = \mathbf{1}$ allows the orientation matrices to be written in terms of $\hat{\boldsymbol{a}}_3$ and $\hat{\boldsymbol{b}}_3$ alone:

$$\mathbf{A} = \ell_\perp^2\mathbf{1} + \big(\ell_\parallel^2 - \ell_\perp^2\big)\hat{\boldsymbol{a}}_3 \otimes \hat{\boldsymbol{a}}_3 \,, \qquad \mathbf{B} = \ell_\perp^2\mathbf{1} + \big(\ell_\parallel^2 - \ell_\perp^2\big)\hat{\boldsymbol{b}}_3 \otimes \hat{\boldsymbol{b}}_3 \,,$$
$$\mathbf{H} = \mathbf{A} + \mathbf{B} = 2\ell_\perp^2\mathbf{1} + \big(\ell_\parallel^2 - \ell_\perp^2\big)\big(\hat{\boldsymbol{a}}_3 \otimes \hat{\boldsymbol{a}}_3 + \hat{\boldsymbol{b}}_3 \otimes \hat{\boldsymbol{b}}_3\big) \,.$$

Inverting such a matrix is a standard exercise. One route is to observe that the orthonormal eigenvectors and eigenvalues are [16]

$$\hat{\boldsymbol{e}}_\pm = \frac{\hat{\boldsymbol{a}}_3 \pm \hat{\boldsymbol{b}}_3}{\sqrt{2(1 \pm \hat{\boldsymbol{a}}_3\cdot\hat{\boldsymbol{b}}_3)}} \,, \qquad \lambda_\pm = (\ell_\parallel^2 + \ell_\perp^2) \pm (\ell_\parallel^2 - \ell_\perp^2)\hat{\boldsymbol{a}}_3\cdot\hat{\boldsymbol{b}}_3 \,,$$
$$\hat{\boldsymbol{e}}_0 = \hat{\boldsymbol{e}}_+ \times \hat{\boldsymbol{e}}_- \,, \qquad \lambda_0 = 2\ell_\perp^2 \,.$$

Then both $\mathbf{H}$ and its inverse may be expressed as sums:

$$\mathbf{H} = \sum_m \lambda_m \hat{\boldsymbol{e}}_m \otimes \hat{\boldsymbol{e}}_m = \lambda_0\mathbf{1} + (\lambda_+ - \lambda_0)\hat{\boldsymbol{e}}_+ \otimes \hat{\boldsymbol{e}}_+ + (\lambda_- - \lambda_0)\hat{\boldsymbol{e}}_- \otimes \hat{\boldsymbol{e}}_- \,,$$
$$\mathbf{H}^{-1} = \sum_m \lambda_m^{-1} \hat{\boldsymbol{e}}_m \otimes \hat{\boldsymbol{e}}_m = \lambda_0^{-1}\mathbf{1} + \big(\lambda_+^{-1} - \lambda_0^{-1}\big)\hat{\boldsymbol{e}}_+ \otimes \hat{\boldsymbol{e}}_+ + \big(\lambda_-^{-1} - \lambda_0^{-1}\big)\hat{\boldsymbol{e}}_- \otimes \hat{\boldsymbol{e}}_- \,,$$

where the orthonormality property $\sum_m \hat{\boldsymbol{e}}_m \otimes \hat{\boldsymbol{e}}_m = \mathbf{1}$ has been used.

It is convenient to define the elongation parameter $\chi = (\ell_\parallel^2 - \ell_\perp^2)/(\ell_\parallel^2 + \ell_\perp^2)$, so that $1 - \chi = 2\ell_\perp^2/(\ell_\parallel^2 + \ell_\perp^2)$; also scalar products of the relevant unit vectors: $c_a = \hat{\boldsymbol{a}}_3\cdot\hat{\boldsymbol{r}}$, $c_b = \hat{\boldsymbol{b}}_3\cdot\hat{\boldsymbol{r}}$, $c_{ab} = \hat{\boldsymbol{a}}_3\cdot\hat{\boldsymbol{b}}_3$; and to set $\chi_c = \chi c_{ab}$.

For Peer Review Only

Then

$$\mathsf{H}^{-1} = \frac{1}{2\ell_\perp^2}\left\{\mathbf{1} - \frac{\chi}{1-\chi_c^2}\left[\hat{\boldsymbol{a}}_3\otimes\hat{\boldsymbol{a}}_3 + \hat{\boldsymbol{b}}_3\otimes\hat{\boldsymbol{b}}_3 - \chi_c(\hat{\boldsymbol{a}}_3\otimes\hat{\boldsymbol{b}}_3 + \hat{\boldsymbol{b}}_3\otimes\hat{\boldsymbol{a}}_3)\right]\right\}$$
$$= \frac{1}{2\ell_\perp^2}\left\{\mathbf{1} - \frac{\chi}{2}\left[\frac{(\hat{\boldsymbol{a}}_3+\hat{\boldsymbol{b}}_3)\otimes(\hat{\boldsymbol{a}}_3+\hat{\boldsymbol{b}}_3)}{1+\chi_c} + \frac{(\hat{\boldsymbol{a}}_3-\hat{\boldsymbol{b}}_3)\otimes(\hat{\boldsymbol{a}}_3-\hat{\boldsymbol{b}}_3)}{1-\chi_c}\right]\right\} ,$$

which gives the standard form [12] for identical uniaxial particles

$$\sigma^{-2} = \tfrac{1}{2}\,\hat{\boldsymbol{r}}\cdot\mathsf{H}^{-1}\cdot\hat{\boldsymbol{r}} = \sigma_0^{-2}\left\{1 - \frac{\chi}{2}\left[\frac{(c_a+c_b)^2}{1+\chi_c} + \frac{(c_a-c_b)^2}{1-\chi_c}\right]\right\} ,$$

with a width parameter $\sigma_0 = 2\ell_\perp$. The auxiliary vector is

$$\boldsymbol{\kappa} = \mathsf{H}^{-1}\cdot\boldsymbol{r} = \frac{r}{2\ell_\perp^2}\left\{\hat{\boldsymbol{r}} - \frac{\chi}{1-\chi_c^2}\left[(c_a-\chi_c c_b)\hat{\boldsymbol{a}}_3 + (c_b-\chi_c c_a)\hat{\boldsymbol{b}}_3\right]\right\} .$$

The position vector of the "contact point" $\boldsymbol{r}_C$ may be written

$$\boldsymbol{r}_C = \tfrac{1}{2}(\boldsymbol{r}_A+\boldsymbol{r}_B) - \tfrac{1}{2}r\frac{\chi}{1-\chi_c^2}\left[(c_a-\chi_c c_b)\hat{\boldsymbol{a}}_3 - (c_b-\chi_c c_a)\hat{\boldsymbol{b}}_3\right] .$$

Having chosen the form of $U(\Phi)$, these last two equations make it easy to calculate forces and torques through eqns (16) and (19).

### 3.2 *Shifted Potential*

The shape-dependent part of the Gay-Berne potential [14] does not have the simple form of eqn (13), but uses the more general eqn (8), with the definition of $\sigma$ given in eqn (12b). This means that the potential is *not* a function of the single variable $\Phi = r^2/\sigma^2$, but instead depends on both $r$ and $\sigma$ (or $\varphi = \sigma^{-2}$) separately, typically through the shifted form

$$\varrho = \frac{r-\sigma+\sigma_{\min}}{\sigma_{\min}} , \tag{21}$$

where $\sigma_{\min}$ is a constant. Define as before $\boldsymbol{\kappa} = \mathsf{H}^{-1}\cdot\boldsymbol{r}$, $\varphi = \frac{1}{2}\hat{\boldsymbol{r}}\cdot\mathsf{H}^{-1}\cdot\hat{\boldsymbol{r}} = \frac{1}{2}r^{-1}\hat{\boldsymbol{r}}\cdot\boldsymbol{\kappa}$, so

$$\frac{\partial\varphi}{\partial\hat{\boldsymbol{r}}} = \mathsf{H}^{-1}\cdot\hat{\boldsymbol{r}} = r^{-1}\boldsymbol{\kappa} .$$

This gives the interparticle force

$$\boldsymbol{f} = -\frac{\partial U}{\partial r}\hat{\boldsymbol{r}} - r^{-1}\frac{\partial U}{\partial\varphi}\frac{\partial\varphi}{\partial\hat{\boldsymbol{r}}}\cdot\left(\mathbf{1}-\hat{\boldsymbol{r}}\otimes\hat{\boldsymbol{r}}\right) = -\frac{\partial U}{\partial r}\hat{\boldsymbol{r}} - r^{-2}\frac{\partial U}{\partial\varphi}\left[\boldsymbol{\kappa}-(\boldsymbol{\kappa}\cdot\hat{\boldsymbol{r}})\hat{\boldsymbol{r}}\right] . \tag{22}$$

The torque derivation proceeds exactly as before, and the results are

$$\boldsymbol{\tau}_A = r^{-2}\frac{\partial U}{\partial\varphi}(\boldsymbol{\kappa}\cdot\mathsf{A}\times\boldsymbol{\kappa}) , \qquad \boldsymbol{\tau}_B = r^{-2}\frac{\partial U}{\partial\varphi}(\boldsymbol{\kappa}\cdot\mathsf{B}\times\boldsymbol{\kappa}) . \tag{23}$$

For Peer Review Only

Identifying part of the force $\boldsymbol{f}_\kappa = -r^{-2}(\partial U/\partial\varphi)\boldsymbol{\kappa}$ these equations may be written

$$\boldsymbol{\tau}_A = -\boldsymbol{\kappa}\cdot\mathbf{A}\times\boldsymbol{f}_\kappa = \boldsymbol{r}_{CA}\times\boldsymbol{f}_\kappa\,, \qquad \boldsymbol{\tau}_B = -\boldsymbol{\kappa}\cdot\mathbf{B}\times\boldsymbol{f}_\kappa = \boldsymbol{r}_{CB}\times(-\boldsymbol{f}_\kappa)\,, \tag{24}$$

where $\boldsymbol{r}_C$ is given by eqn (20) as before. Angular momentum conservation follows directly, since $\boldsymbol{f}-\boldsymbol{f}_\kappa$ is parallel to $\hat{\boldsymbol{r}}$, so $\boldsymbol{r}\times\boldsymbol{f} = \boldsymbol{r}\times\boldsymbol{f}_\kappa$.

As an example, consider the repulsive potential

$$U = \begin{cases} 4\varepsilon_0\left(\varrho^{-12}-\varrho^{-6}\right)+\varepsilon_0\,, & \varrho^6<2 \\ 0\,, & \varrho^6>2 \end{cases} \tag{25}$$

with $\varrho$ given by eqn (21) and $\sigma$ given by eqn (12b). It is sensible to set $\sigma_{\min}$ to be the minimum value of $\sigma$ over all relative orientations. The potential then takes a constant value $U=+\varepsilon_0$ when $r\to\sigma$, for any orientation, and diverges as $r\to\sigma-\sigma_{\min}$. For example, for the identical uniaxial particles of the previous section, $\sigma_{\min}=\sigma_0=2\ell_\perp$ for the prolate case $\ell_\parallel>\ell_\perp$, corresponding to side-by-side arrangements of the particles; but $\sigma_{\min}=2\ell_\parallel$ for oblate, disk-like, shapes, corresponding to the face-to-face orientation [29]. In the general case, eqn (12b) shows that if the minimum particle dimensions are $a_{\min}=\min(a_1,a_2,a_3)$, $b_{\min}=\min(b_1,b_2,b_3)$, then

$$\sigma_{\min}^2 = 2H_{\min} = 2(a_{\min}^2+b_{\min}^2)\,.$$

The geometrically correct value for spheroids would be $\sigma_{\min}=a_{\min}+b_{\min}$ but this distance function does not faithfully represent the geometry of spheroids [27]. Then

$$-\frac{\partial U}{\partial\varphi} = -\frac{\partial U}{\partial\varrho}\frac{\partial\varrho}{\partial\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}\varphi} = 24\varepsilon_0\left(2\varrho^{-13}-\varrho^{-7}\right)\sigma^3/2\sigma_{\min}\,.$$

Also

$$-\frac{\partial U}{\partial r} = -\frac{\partial U}{\partial\varrho}\frac{\partial\varrho}{\partial r} = 24\varepsilon_0\left(2\varrho^{-13}-\varrho^{-7}\right)/\sigma_{\min}\,.$$

From these two expressions, together with eqns (22)–(24), the forces and torques may be easily calculated.

The above equations generalise simply to the case of the full Gay-Berne potential, where the orientation-dependent energy functions $\varepsilon_1$ and $\varepsilon_2$ are included [17]. When the Lennard-Jones form (25) is not truncated, the limiting long-range form is proportional to $r^{-6}$, as might be expected. However, a well-known criticism of the potential is that the full orientation-dependence is preserved at long range, whereas the van der Waals attractions in real molecules become isotropic at long range. It should be noted that Everaers and Ejtehadi [30] have derived a coarse-grained biaxial potential, called the RE-squared model, using Hamaker theory from colloid science. The result has features in common with the biaxial Gay-Berne potential, but also has the correct long-distance form. Babadi et al. [31] have shown how to parametrise the RE-squared

For Peer Review Only

model using atomistic representations of small molecules. Forces and torques may be derived from this potential in a way analogous to that described above.

## 4 Gaussian Potential

Some years ago, Smith and Singer [32] proposed an extension of the approach of Berne and Pechukas [12], which they incorporated into the CCP5 Library program MDZOID. Each molecule is represented by a normalised Gaussian distribution of particle density, centred at $\boldsymbol{r}_A$ and $\boldsymbol{r}_B$, characterised by matrices $\mathbf{A}$ and $\mathbf{B}$:

$$\rho_A(\boldsymbol{r}) = \frac{1}{\sqrt{8\pi^3|\mathbf{A}|}} \exp\left[-\tfrac{1}{2}(\boldsymbol{r}-\boldsymbol{r}_A)\cdot\mathbf{A}^{-1}\cdot(\boldsymbol{r}-\boldsymbol{r}_A)\right] , \tag{26a}$$

$$\rho_B(\boldsymbol{r}) = \frac{1}{\sqrt{8\pi^3|\mathbf{B}|}} \exp\left[-\tfrac{1}{2}(\boldsymbol{r}-\boldsymbol{r}_B)\cdot\mathbf{B}^{-1}\cdot(\boldsymbol{r}-\boldsymbol{r}_B)\right] , \tag{26b}$$

where $|\cdots|$ is the determinant of a matrix. The interaction between volume elements $\mathrm{d}\boldsymbol{r}_a$, $\mathrm{d}\boldsymbol{r}_b$ at $\boldsymbol{r}_a$ and $\boldsymbol{r}_b$, respectively, is represented as a Gaussian function of their separation

$$u(\boldsymbol{r}_a-\boldsymbol{r}_b)\mathrm{d}\boldsymbol{r}_a\mathrm{d}\boldsymbol{r}_b = C\ell^{-3}\exp\left(-\tfrac{1}{2}\left|\boldsymbol{r}_a-\boldsymbol{r}_b\right|^2/\ell^2\right)\,\mathrm{d}\boldsymbol{r}_a\mathrm{d}\boldsymbol{r}_b , \tag{27}$$

characterised by a range parameter $\ell$ and a strength parameter $C$ (with units of energy multiplied by volume). (More generally, Smith and Singer [32] suggested fitting a desired atom-atom potential with a sum of such Gaussians, with positive or negative coefficients). The potential energy between molecules A and B is obtained by integrating $u(\boldsymbol{r}_a-\boldsymbol{r}_b)$ over the density distributions $\rho_A(\boldsymbol{r}_a)$ and $\rho_B(\boldsymbol{r}_b)$; the integrals may be performed analytically (see Appendix B) and the result is, with $\boldsymbol{r}=\boldsymbol{r}_{AB}$,

$$U = C|\mathbf{H}|^{-1/2}\exp(-\Phi) , \tag{28a}$$

$$\text{with}\quad \mathbf{H} = \ell^2\mathbf{1}+\mathbf{A}+\mathbf{B} , \tag{28b}$$

$$\text{and}\quad \Phi = \tfrac{1}{2}\boldsymbol{r}\cdot\left(\ell^2\mathbf{1}+\mathbf{A}+\mathbf{B}\right)^{-1}\cdot\boldsymbol{r} = \tfrac{1}{2}\boldsymbol{r}\cdot\mathbf{H}^{-1}\cdot\boldsymbol{r} . \tag{28c}$$

In the limit $\ell\to 0$, $\mathbf{H}$ and $\Phi$ reduce to the definitions (12c), (14) seen before. This potential belongs to the class of "core-softened" potentials, which have recently attracted attention in condensed matter physics. The interaction between polymer coils at low concentration, for instance, is well represented by a (spherically symmetric) Gaussian potential [33].

The forces are derived exactly as for the scaled potential, sec. 3.1:

$$\boldsymbol{f} = -\frac{\partial U}{\partial\Phi}\frac{\partial\Phi}{\partial\boldsymbol{r}} = -\frac{\partial U}{\partial\Phi}\mathbf{H}^{-1}\cdot\boldsymbol{r} = U\mathbf{H}^{-1}\cdot\boldsymbol{r} = U\boldsymbol{\kappa} , \tag{29}$$

with $\boldsymbol{\kappa}=\mathbf{H}^{-1}\cdot\boldsymbol{r}$ as before. The torques have contributions from the dependence of $U$ on both $\Phi$ and $|\mathbf{H}|$.

For Peer Review Only

The $\Phi$ contributions are given by

$$\boldsymbol{\tau}_A^\Phi = -\boldsymbol{\kappa}\cdot\mathbf{A}\times\boldsymbol{f} = \boldsymbol{q}_A\times\boldsymbol{f}\ ,$$
$$\boldsymbol{\tau}_B^\Phi = -\boldsymbol{\kappa}\cdot\mathbf{B}\times\boldsymbol{f} = \boldsymbol{q}_B\times(-\boldsymbol{f})\ ,$$

which are eqns (19), with $\boldsymbol{r}_{CA}\to\boldsymbol{q}_A = -\mathbf{A}\cdot\boldsymbol{\kappa}$, $\boldsymbol{r}_{CB}\to\boldsymbol{q}_B = \mathbf{B}\cdot\boldsymbol{\kappa}$. The reason for the change in notation is that these equations do not define a contact point $\boldsymbol{r}_C$ as before in eqns (20), because the new definition of $\mathbf{H}$ gives

$$\boldsymbol{r}+\boldsymbol{q}_A-\boldsymbol{q}_B = \ell^2\boldsymbol{\kappa}\ , \tag{30}$$

rather than zero. Using the expression $\frac{1}{2}|\mathbf{H}|^{-1}(\partial|\mathbf{H}|/\partial\boldsymbol{a}_m) = \mathbf{H}^{-1}\cdot\boldsymbol{a}_m$ (see appendix B), the $|\mathbf{H}|$-dependent terms in $\boldsymbol{\tau}_A$ give

$$-\frac{\partial U}{\partial|\mathbf{H}|}\sum_m \boldsymbol{a}_m\times\frac{\partial|\mathbf{H}|}{\partial\boldsymbol{a}_m} = \tfrac{1}{2}|\mathbf{H}|^{-1}U\sum_m\boldsymbol{a}_m\times\frac{\partial|\mathbf{H}|}{\partial\boldsymbol{a}_m} = U\sum_m\boldsymbol{a}_m\times\mathbf{H}^{-1}\cdot\boldsymbol{a}_m\ . \tag{31}$$

With the use of the Levi-Civita tensor $\boldsymbol{\epsilon}$ the final results may be expressed

$$\boldsymbol{\tau}_A = U\sum_m\boldsymbol{a}_m\times\mathbf{H}^{-1}\cdot\boldsymbol{a}_m+\boldsymbol{q}_A\times\boldsymbol{f} = U\boldsymbol{\epsilon}:\mathbf{H}^{-1}\mathbf{A}+\boldsymbol{q}_A\times\boldsymbol{f}\ , \tag{32a}$$

$$\boldsymbol{\tau}_B = U\sum_m\boldsymbol{b}_m\times\mathbf{H}^{-1}\cdot\boldsymbol{b}_m-\boldsymbol{q}_B\times\boldsymbol{f} = U\boldsymbol{\epsilon}:\mathbf{H}^{-1}\mathbf{B}+\boldsymbol{q}_B\times(-\boldsymbol{f})\ . \tag{32b}$$

Smith and Singer [32] obtained the same result, by a different method and written in a different form (see Appendix B). Once more, angular momentum conservation follows straightforwardly:

$$\begin{aligned}\boldsymbol{\tau}_A+\boldsymbol{\tau}_B+\boldsymbol{r}\times\boldsymbol{f} &= U\boldsymbol{\epsilon}:\mathbf{H}^{-1}\big(\mathbf{A}+\mathbf{B}\big)+(\boldsymbol{r}+\boldsymbol{q}_A-\boldsymbol{q}_B)\times\boldsymbol{f}\\ &= U\boldsymbol{\epsilon}:\big(\mathbf{1}-\ell^2\mathbf{H}^{-1}\big)+\ell^2\boldsymbol{\kappa}\times\boldsymbol{f}\ ,\end{aligned}$$

using eqn (30). The tensor $\mathbf{1}-\ell^2\mathbf{H}^{-1}$ is symmetric, so the double contraction with $\boldsymbol{\epsilon}$ gives zero, and $\boldsymbol{f} = U\boldsymbol{\kappa}$, so the last cross product also gives zero.

## 5 Ellipsoid Contact Potential

As mentioned in section 3.2, the distance function appearing in the Gay-Berne and related potentials does not correctly represent the geometry of ellipsoidal particles. Formulae reflecting the true ellipsoid geometry were set out by Perram et al. [27]. The distance function takes the more general form

$$\varphi = \sigma^{-2} = \alpha\beta\,\hat{\boldsymbol{r}}\cdot\big(\alpha\mathbf{A}+\beta\mathbf{B}\big)^{-1}\cdot\hat{\boldsymbol{r}} \equiv \alpha\beta\,\hat{\boldsymbol{r}}\cdot\mathbf{G}^{-1}\cdot\hat{\boldsymbol{r}}\ , \tag{33}$$

For Peer Review Only

where $\alpha + \beta = 1$. The matrix

$$\mathbf{G} = \alpha \mathbf{A} + \beta \mathbf{B} \tag{34}$$

plays a similar role to $\mathbf{H}$ in the previous sections; the case $\alpha = \beta = \frac{1}{2}$ corresponds to the standard Gay-Berne, or Gaussian overlap, definition of diameter seen earlier, and in this case $\mathbf{G} = \frac{1}{2}\mathbf{H}$. The 'true' ellipsoid geometry corresponds to the case where $\alpha = (1 - \beta)$ has been chosen to maximise $\varphi$, i.e. minimise $\sigma$. This procedure is carried out numerically in the simulation.

The "scaled potential" analogous to eqn (13)

$$U = U\big(r^2/\sigma^2(\hat{\boldsymbol{r}}, \hat{\mathbf{a}}, \hat{\mathbf{b}})\big) = U(\Phi) \,,$$
$$\text{where} \quad \Phi = r^2\varphi = r^2/\sigma^2 = \alpha\beta\, \boldsymbol{r} \cdot \big(\alpha \mathbf{A} + \beta \mathbf{B}\big)^{-1} \cdot \boldsymbol{r} \equiv \alpha\beta\, \boldsymbol{r} \cdot \mathbf{G}^{-1} \cdot \boldsymbol{r} \,, \tag{35}$$

is termed an *ellipsoid contact potential* [27]. The forces and torques are derived in a manner analogous to that of Section 3.1. Define an auxiliary vector $\boldsymbol{k}$ by solving the equations

$$\mathbf{G} \cdot \boldsymbol{k} = \boldsymbol{r} \qquad \Leftrightarrow \qquad \boldsymbol{k} = \mathbf{G}^{-1} \cdot \boldsymbol{r} \,. \tag{36}$$

In terms of $\boldsymbol{k}$

$$\Phi = \alpha\beta \boldsymbol{r} \cdot \boldsymbol{k} \,, \tag{37}$$

$$\frac{\partial \Phi}{\partial \boldsymbol{r}} = 2\alpha\beta \mathbf{G}^{-1} \cdot \boldsymbol{r} = 2\alpha\beta \boldsymbol{k} \,. \tag{38}$$

This last formula will give the interparticle force from

$$\boldsymbol{f} = -\frac{\mathrm{d}U}{\mathrm{d}\Phi}\frac{\partial \Phi}{\partial \boldsymbol{r}} = -\frac{\mathrm{d}U}{\mathrm{d}\Phi} 2\alpha\beta \boldsymbol{k} \,. \tag{39}$$

The derivation of torques follows the pattern of previous sections. The results are

$$\boldsymbol{\tau}_A = \frac{\mathrm{d}U}{\mathrm{d}\Phi} 2\alpha^2\beta \sum_m (\boldsymbol{k} \cdot \boldsymbol{a}_m)(\boldsymbol{a}_m \times \boldsymbol{k}) = \frac{\mathrm{d}U}{\mathrm{d}\Phi} 2\alpha^2\beta (\boldsymbol{k} \cdot \mathbf{A} \times \boldsymbol{k}) \,, \tag{40a}$$

$$\boldsymbol{\tau}_B = \frac{\mathrm{d}U}{\mathrm{d}\Phi} 2\alpha\beta^2 \sum_m (\boldsymbol{k} \cdot \boldsymbol{b}_m)(\boldsymbol{b}_m \times \boldsymbol{k}) = \frac{\mathrm{d}U}{\mathrm{d}\Phi} 2\alpha\beta^2 (\boldsymbol{k} \cdot \mathbf{B} \times \boldsymbol{k}) \,. \tag{40b}$$

Once again these may be written

$$\boldsymbol{\tau}_A = -\alpha \boldsymbol{k} \cdot \mathbf{A} \times \boldsymbol{f} = \boldsymbol{r}_{CA} \times \boldsymbol{f} \,, \tag{41a}$$

$$\boldsymbol{\tau}_B = -\beta \boldsymbol{k} \cdot \mathbf{B} \times \boldsymbol{f} = \boldsymbol{r}_{CB} \times (-\boldsymbol{f}) \,, \tag{41b}$$

For Peer Review Only

where $\boldsymbol{r}_C$ is now defined by

$$\boldsymbol{r}_C = \boldsymbol{r}_A - \alpha \mathbf{A} \cdot \boldsymbol{k} = \boldsymbol{r}_B + \beta \mathbf{B} \cdot \boldsymbol{k} \tag{42}$$

(see Appendix A). Conservation of angular momentum follows immediately. One final point [27]: the above derivatives take no account of the variation of $\alpha, \beta$ as the particles are moved; but these extra terms vanish because the relevant functions have been minimised/maximised with respect to variations of these parameters.

The corresponding formulae for more general (for example, shifted) potentials based on true ellipsoid geometry are

$$\varphi = \alpha\beta \hat{\boldsymbol{r}} \cdot \mathbf{G}^{-1} \cdot \hat{\boldsymbol{r}} = \alpha\beta r^{-1} \hat{\boldsymbol{r}} \cdot \boldsymbol{k} \,, \tag{43}$$

$$\frac{\partial \varphi}{\partial \hat{\boldsymbol{r}}} = 2\alpha\beta \mathbf{G}^{-1} \cdot \hat{\boldsymbol{r}} = 2\alpha\beta r^{-1} \boldsymbol{k} \,. \tag{44}$$

The forces and torques are

$$\boldsymbol{f} = -\frac{\partial U}{\partial r}\hat{\boldsymbol{r}} - \frac{\partial U}{\partial \varphi} r^{-1} \frac{\partial \varphi}{\partial \hat{\boldsymbol{r}}} \cdot \big(\mathbf{1} - \hat{\boldsymbol{r}} \otimes \hat{\boldsymbol{r}}\big) = -\frac{\partial U}{\partial r}\hat{\boldsymbol{r}} - \frac{\partial U}{\partial \varphi}\frac{2\alpha\beta}{r^2}\big(\boldsymbol{k} - (\boldsymbol{k}\cdot\hat{\boldsymbol{r}})\hat{\boldsymbol{r}}\big) \,, \tag{45a}$$

$$\boldsymbol{\tau}_A = \frac{\partial U}{\partial \varphi}\frac{2\alpha^2\beta}{r^2}\sum_m (\boldsymbol{k}\cdot\boldsymbol{a}_m)(\boldsymbol{a}_m \times \boldsymbol{k}) = \frac{\partial U}{\partial \varphi}\frac{2\alpha^2\beta}{r^2}(\boldsymbol{k}\cdot\mathbf{A}\times\boldsymbol{k}) \,, \tag{45b}$$

$$\boldsymbol{\tau}_B = \frac{\partial U}{\partial \varphi}\frac{2\alpha\beta^2}{r^2}\sum_m (\boldsymbol{k}\cdot\boldsymbol{b}_m)(\boldsymbol{b}_m \times \boldsymbol{k}) = \frac{\partial U}{\partial \varphi}\frac{2\alpha\beta^2}{r^2}(\boldsymbol{k}\cdot\mathbf{B}\times\boldsymbol{k}) \,. \tag{45c}$$

Identifying part of the force $\boldsymbol{f}_k = -(\partial U/\partial\varphi)(2\alpha\beta/r^2)\boldsymbol{k}$ the torques become

$$\boldsymbol{\tau}_A = -\alpha \boldsymbol{k}\cdot\mathbf{A}\times\boldsymbol{f}_k = \boldsymbol{r}_{CA}\times\boldsymbol{f}_k \,, \tag{46a}$$

$$\boldsymbol{\tau}_B = -\beta \boldsymbol{k}\cdot\mathbf{B}\times\boldsymbol{f}_k = \boldsymbol{r}_{CB}\times(-\boldsymbol{f}_k) \,, \tag{46b}$$

and, since $\boldsymbol{f} - \boldsymbol{f}_k$ is parallel to $\hat{\boldsymbol{r}}$, angular momentum conservation follows as before.

A modification of the ellipsoid contact potential, based on the surface-surface distance calculated along a vector parallel to the line of centres, has recently been proposed [34]. Analytical formulae for the forces and torques are given in that paper.

## 6 Conclusions

In the preceding sections it has been shown how compact expressions for forces and torques may be derived for pairwise intermolecular potentials which are written as functions of the molecular orientation matrices and the centre-centre vector. Illustrations have been given for various members of the "extended Gay-Berne

For Peer Review Only

family"; in particular, for the Gaussian potential of Smith and Singer [32], much simpler expressions for the torques may be obtained in this way.

The above expressions for forces and torques may be used in molecular dynamics simulations, as well as hybrid Monte Carlo simulations or other applications. They may be straightforwardly combined with symplectic and reversible integration algorithms based either on quaternion parameter representations of the rigid-body orientations, or on the rotation matrix itself [35–37].

## Appendix A: The Contact Function

This appendix recalls the relations leading to the definition of the "contact point" of eqn (42), and the link with the Berne-Pechukas distance parameter. The following function has a unique minimum as $\boldsymbol{r}$ varies for fixed $\alpha$ and $\beta = 1 - \alpha$ [25, 26]:

$$\Psi(\boldsymbol{r}; \alpha, \beta) = \beta(\boldsymbol{r} - \boldsymbol{r}_A) \cdot \mathbf{A}^{-1} \cdot (\boldsymbol{r} - \boldsymbol{r}_A) + \alpha(\boldsymbol{r} - \boldsymbol{r}_B) \cdot \mathbf{B}^{-1} \cdot (\boldsymbol{r} - \boldsymbol{r}_B) \,. \tag{A1}$$

The location of this minimum, $\boldsymbol{r} = \boldsymbol{r}_C$, satisfies

$$\frac{1}{2} \left. \frac{\partial \Psi}{\partial \boldsymbol{r}} \right|_{\boldsymbol{r}=\boldsymbol{r}_C} = \beta \mathbf{A}^{-1} \cdot (\boldsymbol{r}_C - \boldsymbol{r}_A) + \alpha \mathbf{B}^{-1} \cdot (\boldsymbol{r}_C - \boldsymbol{r}_B) = \mathbf{0} \,. \tag{A2}$$

The definition $\mathbf{G} \cdot \boldsymbol{k} = \boldsymbol{r}_{AB} = \boldsymbol{r}$, eqn (36), with $\mathbf{G} = \alpha \mathbf{A} + \beta \mathbf{B}$, eqn (34), leads to an expression for $\boldsymbol{r}_C$

$$\boldsymbol{r} = \mathbf{G} \cdot \boldsymbol{k} = \alpha \mathbf{A} \cdot \boldsymbol{k} + \beta \mathbf{B} \cdot \boldsymbol{k} = (\boldsymbol{r}_A - \boldsymbol{r}_C) + (\boldsymbol{r}_C - \boldsymbol{r}_B) \,,$$
$$\text{where} \quad \boldsymbol{r}_C = \boldsymbol{r}_A - \alpha \mathbf{A} \cdot \boldsymbol{k} = \boldsymbol{r}_B + \beta \mathbf{B} \cdot \boldsymbol{k} \,,$$

which satisfies eqn (A2). The value at the minimum is

$$\begin{aligned} \Psi|_{\boldsymbol{r}=\boldsymbol{r}_C} &= \beta(\boldsymbol{r}_C - \boldsymbol{r}_A) \cdot (-\alpha \boldsymbol{k}) + \alpha(\boldsymbol{r}_C - \boldsymbol{r}_B) \cdot (\beta \boldsymbol{k}) \\ &= \alpha\beta \boldsymbol{r} \cdot \boldsymbol{k} = \alpha\beta \boldsymbol{r} \cdot \mathbf{G}^{-1} \cdot \boldsymbol{r} \equiv \Phi \,, \end{aligned}$$

as defined in eqn (37). Having identified $\boldsymbol{r}_C$ and $\Phi$, the function $\Psi$ may be re-written

$$\Psi(\boldsymbol{r}; \alpha, \beta) = (\boldsymbol{r} - \boldsymbol{r}_C) \cdot \left(\beta \mathbf{A}^{-1} + \alpha \mathbf{B}^{-1}\right) \cdot (\boldsymbol{r} - \boldsymbol{r}_C) + \Phi \,, \tag{A3}$$

as may be checked by expanding and comparing coefficients.

The corresponding equations for the case $\alpha = \beta = \frac{1}{2}$ are conveniently written with the definitions

For Peer Review Only

$\mathbf{H}\cdot\boldsymbol{\kappa} = \boldsymbol{r}_{AB} = \boldsymbol{r}$, eqn (15), $\mathbf{H} = \mathbf{A} + \mathbf{B}$, eqn (12c),

$$\Psi(\boldsymbol{r}) = \tfrac{1}{2}(\boldsymbol{r}-\boldsymbol{r}_A)\cdot\mathbf{A}^{-1}\cdot(\boldsymbol{r}-\boldsymbol{r}_A) + \tfrac{1}{2}(\boldsymbol{r}-\boldsymbol{r}_B)\cdot\mathbf{B}^{-1}\cdot(\boldsymbol{r}-\boldsymbol{r}_B)\ , \tag{A4}$$

$$\boldsymbol{r} = \mathbf{H}\cdot\boldsymbol{\kappa} = \mathbf{A}\cdot\boldsymbol{\kappa} + \mathbf{B}\cdot\boldsymbol{\kappa} = (\boldsymbol{r}_A - \boldsymbol{r}_C) + (\boldsymbol{r}_C - \boldsymbol{r}_B)\ , \tag{A5}$$

$$\boldsymbol{r}_C = \boldsymbol{r}_A - \mathbf{A}\cdot\boldsymbol{\kappa} = \boldsymbol{r}_B + \mathbf{B}\cdot\boldsymbol{\kappa}\ , \tag{A6}$$

$$\Psi|_{\boldsymbol{r}=\boldsymbol{r}_C} = \tfrac{1}{2}\boldsymbol{r}\cdot\boldsymbol{\kappa} = \tfrac{1}{2}\boldsymbol{r}\cdot\mathbf{H}^{-1}\cdot\boldsymbol{r} \equiv \Phi\ , \tag{A7}$$

$$\Psi(\boldsymbol{r}) = \tfrac{1}{2}(\boldsymbol{r}-\boldsymbol{r}_C)\cdot\left(\mathbf{A}^{-1}+\mathbf{B}^{-1}\right)\cdot(\boldsymbol{r}-\boldsymbol{r}_C) + \Phi\ . \tag{A8}$$

The generalised Berne-Pechukas overlap function is computed in terms of the two-centre Gaussian overlap integral

$$\begin{aligned} I &= \int \mathrm{d}\boldsymbol{r}\ \rho_A(\boldsymbol{r}-\boldsymbol{r}_A)\rho_B(\boldsymbol{r}-\boldsymbol{r}_B) \\ &= \frac{1}{8\pi^3\sqrt{|\mathbf{A}||\mathbf{B}|}}\int \mathrm{d}\boldsymbol{r}\ \exp\bigl(-\Psi(\boldsymbol{r})\bigr) = \frac{\exp(-\Phi)}{\sqrt{8\pi^3}\sqrt{|\mathbf{A}+\mathbf{B}|}}\ , \end{aligned} \tag{A9}$$

where the densities $\rho_A$, $\rho_B$, are defined in eqns (26) and the function $\Psi(\boldsymbol{r})$ is defined in eqn (A4). The last step is carried out either by using Fourier transforms [15] or by re-writing $\Psi(\boldsymbol{r})$ in the form of eqn (A8) and shifting origin to $\boldsymbol{r}_C$ [27]; $\Phi$ is defined in eqn (A7). In practice, the Gaussian form of eqn (A9) is not commonly used as a potential in simulations; instead, the function $\Phi$ is extracted from it, used to define a range parameter $\sigma$, through $\varphi = \Phi/r^2$ and $\sigma = 1/\sqrt{\varphi}$, eqns (12) of the text; and this range parameter is used in a variety of potentials.

## Appendix B: The Gaussian Potential

The Gaussian potential of Smith and Singer [32] is computed in terms of the double integral

$$U = \iint \mathrm{d}\boldsymbol{r}_a\mathrm{d}\boldsymbol{r}_b\ \rho_A(\boldsymbol{r}_a-\boldsymbol{r}_A)\rho_B(\boldsymbol{r}_b-\boldsymbol{r}_B)u(\boldsymbol{r}_a-\boldsymbol{r}_b)\ ,$$

where $u(\boldsymbol{r}_a-\boldsymbol{r}_b)$ is defined by eqn (27). The two integrals are carried out successively: each has the same two-centre form as eqn (A9), so they are straightforward. The result is

$$U = C|\mathbf{H}|^{-1/2}\ \exp\bigl(-\tfrac{1}{2}\boldsymbol{r}\cdot\mathbf{H}^{-1}\cdot\boldsymbol{r}\bigr)\ , \quad \text{where } \boldsymbol{r} = \boldsymbol{r}_A - \boldsymbol{r}_B \text{ and } \mathbf{H} = \ell^2\mathbf{1} + \mathbf{A} + \mathbf{B}\ ,$$

and this is eqn (28) of the main text. Smith and Singer derived an expression for the torque arising from the Gaussian potential, from first principles, treating $u(\boldsymbol{r}_a-\boldsymbol{r}_b)$ as a site-site potential and integrating

For Peer Review Only

$\boldsymbol{r}_{ab} \times \boldsymbol{f}_{ab}$ over the density distributions. In the notation of sec 4, their result for the torque on $A$ is

$$\begin{aligned}\boldsymbol{\tau}_A &= -\left(\ell^2\mathbf{1} + \mathbf{B}\right)^{-1} * \left(\boldsymbol{q}_A \otimes \boldsymbol{r} + \boldsymbol{q}_A \otimes \boldsymbol{q}_A + \mathbf{A} - \mathbf{A}\mathbf{H}^{-1}\mathbf{A}\right)U \\ &= -\left(\mathbf{H} - \mathbf{A}\right)^{-1} * \left[\boldsymbol{q}_A \otimes (\mathbf{1} - \mathbf{A}\mathbf{H}^{-1}) \cdot \boldsymbol{r} + (\mathbf{1} - \mathbf{A}\mathbf{H}^{-1})\mathbf{A}\right] U \,, \end{aligned} \tag{B1}$$

where the definition $\boldsymbol{q}_A = -\mathbf{A} \cdot \boldsymbol{\kappa} = -\mathbf{A}\mathbf{H}^{-1} \cdot \boldsymbol{r}$ is used to simplify. Smith and Singer define the operation $*$ to give a vector from two matrices $(\mathbf{A} * \mathbf{B})_k = \epsilon_{ijk} A_{il} B_{jl}$ (note the conventional summation over all three repeated indices $i$, $j$ and $l$). This may be recognised as a double contraction of the Levi-Civita tensor $\boldsymbol{\epsilon}$ with a matrix product:

$$\mathbf{A} * \mathbf{B} = -\boldsymbol{\epsilon} : \mathbf{A}\mathbf{B}^{\mathsf{T}} = \boldsymbol{\epsilon} : \mathbf{B}\mathbf{A}^{\mathsf{T}} \,.$$

Using this, and noting that

$$(\mathbf{H} - \mathbf{A})^{-1}(\mathbf{1} - \mathbf{A}\mathbf{H}^{-1}) = (\mathbf{H} - \mathbf{A})^{-1}(\mathbf{H} - \mathbf{A})\mathbf{H}^{-1} = \mathbf{H}^{-1} \,,$$

eqn (B1) simplifies considerably:

$$\begin{aligned}\boldsymbol{\tau}_A &= \boldsymbol{\epsilon} : \left(\mathbf{H}^{-1} \cdot \boldsymbol{r} \otimes \boldsymbol{q}_A + \mathbf{H}^{-1}\mathbf{A}\right)U = \boldsymbol{\epsilon} : \left(\boldsymbol{\kappa} \otimes \boldsymbol{q}_A + \mathbf{H}^{-1}\mathbf{A}\right)U \\ &= \left(\boldsymbol{q}_A \times \boldsymbol{\kappa} + \boldsymbol{\epsilon} : \mathbf{H}^{-1}\mathbf{A}\right)U \,.\end{aligned}$$

This is eqn (32a) of the main text.

In the derivation of eqn (31), it is necessary to obtain the derivative of $|\mathbf{H}|$ with respect to a component of one of the rotation matrices. Use

$$|\mathbf{H}|' = \begin{vmatrix} H'_{xx} & H'_{xy} & H'_{xz} \\ H_{yx} & H_{yy} & H_{yz} \\ H_{zx} & H_{zy} & H_{zz} \end{vmatrix} + \begin{vmatrix} H_{xx} & H_{xy} & H_{xz} \\ H'_{yx} & H'_{yy} & H'_{yz} \\ H_{zx} & H_{zy} & H_{zz} \end{vmatrix} + \begin{vmatrix} H_{xx} & H_{xy} & H_{xz} \\ H_{yx} & H_{yy} & H_{yz} \\ H'_{zx} & H'_{zy} & H'_{zz} \end{vmatrix} \,.$$

Here, $H_{\mu\nu} = \ell^2\delta_{\mu\nu} + \sum_m a_{m\mu}a_{m\nu} + \sum_n b_{n\mu}b_{n\nu}$, so $\partial H_{\mu\nu}/\partial a_{mx} = \delta_{\mu x}a_{m\nu} + \delta_{\nu x}a_{m\mu}$. Hence

$$\begin{aligned}\frac{\partial|\mathbf{H}|}{\partial a_{mx}} &= \begin{vmatrix} 2a_{mx} & a_{my} & a_{mz} \\ H_{yx} & H_{yy} & H_{yz} \\ H_{zx} & H_{zy} & H_{zz} \end{vmatrix} + \begin{vmatrix} H_{xx} & H_{xy} & H_{xz} \\ a_{my} & 0 & 0 \\ H_{zx} & H_{zy} & H_{zz} \end{vmatrix} + \begin{vmatrix} H_{xx} & H_{xy} & H_{xz} \\ H_{yx} & H_{yy} & H_{yz} \\ a_{mz} & 0 & 0 \end{vmatrix} \\ &= 2a_{mx}\begin{vmatrix} H_{yy} & H_{yz} \\ H_{zy} & H_{zz} \end{vmatrix} - 2a_{my}\begin{vmatrix} H_{xy} & H_{xz} \\ H_{zy} & H_{zz} \end{vmatrix} + 2a_{mz}\begin{vmatrix} H_{xy} & H_{xz} \\ H_{yy} & H_{yz} \end{vmatrix} \,,\end{aligned}$$

using the fact that $\mathbf{H}$ is symmetric. Moreover, each (signed) $2 \times 2$ determinant here is an element of the (signed) cofactor matrix, the transpose of which is $\mathbf{H}^{-1}$ multiplied by $|\mathbf{H}|$. This allows the desired derivative

For Peer Review Only

to be written

$$\frac{\partial|\mathbf{H}|}{\partial a_{mx}} = 2|\mathbf{H}|\left(a_{mx}\left[\mathbf{H}^{-1}\right]_{xx} + a_{my}\left[\mathbf{H}^{-1}\right]_{yx} + a_{mz}\left[\mathbf{H}^{-1}\right]_{zx}\right) .$$

Collecting together results for all the components gives

$$\frac{1}{2}|\mathbf{H}|^{-1}\frac{\partial|\mathbf{H}|}{\partial \boldsymbol{a}_m} = \boldsymbol{a}_m \cdot \mathbf{H}^{-1} = \mathbf{H}^{-1} \cdot \boldsymbol{a}_m .$$

This is used in the derivation of eqn (31).

For Peer Review Only

## References

[1] M. P. Allen, D. J. Tildesley. *Computer simulation of liquids*. Clarendon Press, Oxford, paperback edition (1989). ISBN 0-19-855645-4.
[2] R. J. Sadus. *Molecular Simulation of Fluids: Theory, Algorithms and Object-Orientation*. Elsevier, Amsterdam, paperback edition (2002). ISBN 0444510826.
[3] D. C. Rapaport. *The art of molecular dynamics simulation*. Cambridge University Press, 2nd edition (2004). ISBN 0521825687.
[4] O. Hahn, L. Delle Site, K. Kremer. *Macrom. Theor. Simul.*, **10**, 288 (2001).
[5] K. Kremer, F. Müller-Plathe. *Molec. Simul.*, **28**, 729 (2002).
[6] S. O. Nielsen, C. F. Lopez, G. Srinivas, M. L. Klein. *J. Phys. Cond. Mat.*, **16**, R481 (2004).
[7] S. Izvekov, G. A. Voth. *J. Chem. Phys.*, **123**, 134105 (2005).
[8] M. Praprotnik, L. Delle Site, K. Kremer. *J. Chem. Phys.*, **123**, 224106 (2005).
[9] H. Goldstein, C. P. Poole, J. L. Safko. *Classical Mechanics*. Addison Wesley, San Francisco, third edition (2002). ISBN 0201657023.
[10] S. L. Price, A. J. Stone, M. Alderton. *Molec. Phys.*, **52**, 987 (1984).
[11] J. Corner. *Proc. Roy. Soc. Lond. A*, **192**, 275 (1948).
[12] B. J. Berne, P. Pechukas. *J. Chem. Phys.*, **56**, 4213 (1972).
[13] J. Kushick, B. J. Berne. *J. Chem. Phys.*, **64**, 1362 (1976).
[14] J. G. Gay, B. J. Berne. *J. Chem. Phys.*, **74**, 3316 (1981).
[15] R. Berardi, C. Fava, C. Zannoni. *Chem. Phys. Lett.*, **236**, 462 (1995).
[16] D. J. Cleaver, C. M. Care, M. P. Allen, M. P. Neal. *Phys. Rev. E*, **54**, 559 (1996).
[17] R. Berardi, C. Fava, C. Zannoni. *Chem. Phys. Lett.*, **297**, 8 (1998).
[18] R. Berardi, C. Zannoni. *J. Chem. Phys.*, **113**, 5971 (2000).
[19] S. Gupta, W. B. Sediawan, E. McLaughlin. *Molec. Phys.*, **65**, 961 (1988).
[20] T. R. Walsh. *Molec. Phys.*, **100**, 2867 (2002).
[21] I. Cacelli, G. Cinacchi, G. Prampolini, A. Tani. *J. Chem. Phys.*, **120**, 3648 (2004).
[22] C. Zannoni. *J. Mater. Chem.*, **11**, 2637 (2001).
[23] C. M. Care, D. J. Cleaver. *Rep. Prog. Phys.*, **68**, 2665 (2005).
[24] M. R. Ejtehadi, R. Everaers. *Comput. Phys. Commun.*, **147**, 339 (2002).
[25] J. W. Perram, M. S. Wertheim, J. L. Lebowitz, G. O. Williams. *Chem. Phys. Lett.*, **105**, 277 (1984).
[26] J. W. Perram, M. S. Wertheim. *J. Comput. Phys.*, **58**, 409 (1985).
[27] J. W. Perram, J. Rasmussen, E. Praestgaard, J. L. Lebowitz. *Phys. Rev. E*, **54**, 6565 (1996).
[28] M. P. Allen, G. T. Evans, D. Frenkel, B. Mulder. *Adv. Chem. Phys.*, **86**, 1 (1993).
[29] M. A. Bates, G. R. Luckhurst. *J. Chem. Phys.*, **104**, 6696 (1996).
[30] R. Everaers, M. R. Ejtehadi. *Phys. Rev. E*, **67**, 041710 (2003).
[31] M. Babadi, R. Everaers, M. R. Ejtehadi. *J. Chem. Phys.*, **124**, 174708 (2006).
[32] W. Smith, K. Singer. *CCP5 Quarterly*, **17**, 53 (1985).
[33] V. Krakoviack, J.-P. Hansen, A. A. Louis. *Phys. Rev. E*, **67**, 041801/1 (2003).
[34] L. Paramonov, S. N. Yaliraki. *J. Chem. Phys.*, **123**, 194111 (2005).
[35] A. Dullweber, B. Leimkuhler, R. McLachlan. *J. Chem. Phys.*, **107**, 5840 (1997).
[36] T. F. Miller, M. Eleftheriou, P. Pattnaik, A. Ndirango, D. Newns, G. J. Martyna. *J. Chem. Phys.*, **116**, 8649 (2002).
[37] H. Kamberaj, R. J. Low, M. P. Neal. *J. Chem. Phys.*, **122**, 224114 (2005).

For Peer Review Only