

# Daresbury Laboratory

## INFORMATION NEWSLETTER FOR COMPUTER SIMULATION OF CONDENSED PHASES

An informal Newsletter associated with Collaborative Computational Project No.5  
on Molecular Dynamics, Monte Carlo & Lattice Simulations of Condensed Phases.

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## General News

### CHAIRMANSHIP OF CCP5 AND MEMBERSHIP OF EXECUTIVE COMMITTEE

Following a ballot by Email of UK members of CCP5, a new chairman was elected in February of this year. Four new executive committee members have also been elected in September. Professor M. Allen had held the post of chairman for the past two and a half years. The executive committee members who have retired are

- M. Finnis (Atomistic Simulation Group, Queen's University Belfast)
- C. Care (Materials Research Institute, Sheffield Hallam University)
- M. Stapleton (Molecular Simulations)

A table giving contact details for the current executive committee is given on the next page.

Table 1: CCP5 Executive Committee Members

Name Period of Service	Address	Email, Telephone Fax, WWW
Chairman Dr. D.M. Heyes 1996 - 1999	Department of Chemistry University of Surrey Guildford GU2 5XH	d.heyesh@surrey.ac.uk +44 (0) 1483 259580 +44 (0) 1483 259514 <a href="http://www.chem.surrey.ac.uk/~chsl dh/">http://www.chem.surrey.ac.uk/~chsl dh/</a>
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Dr. J. Anwar 1998 - 2001	Department of Pharmacy Kings College London London SW3 6LX	jamshed.anwar@kcl.ac.uk +44 (0) 171 333 4782 +44 (0) 171 351 5307 <a href="http://www.kcl.ac.uk/kis/schools/life_sciences/health/pharmacy/staff/anwar.html">http://www.kcl.ac.uk/kis/schools/life_sciences/health/pharmacy/staff/anwar.html</a>
Dr. J. Gale 1998 - 2001	Dept. of Chemistry Imperial College London SW7 2AY	j.gale@ic.ac.uk +44 (0) 171 594 5757 +44 (0) 171 594 5804 <a href="http://www.ch.ic.ac.uk/gale/.index.html">http://www.ch.ic.ac.uk/gale/.index.html</a>
Dr. J.H. Harding 1996 - 1999	Materials Research Centre University College London London WC1E 6BT	j.harding@ucl.ac.uk +44 (0) 171 419 3506 +44 (0) 171 391 1360 <a href="http://www.phys.ucl.ac.uk/~cmmp/">http://www.phys.ucl.ac.uk/~cmmp/</a>
Dr. J. Melrose 1998 - 2001	Polymer and Colloid Group, Cavendish Lab University of Cambridge Cambridge CB3 0HE	jrm23@phy.cam.ac.uk +44 (0) 1223 337263 +44 (0) 1223 337000 <a href="http://www.poco.phy.cam.ac.uk/~jrm23/">http://www.poco.phy.cam.ac.uk/~jrm23/</a>
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Prof. A.P. Sutton 1998 - 2001	Department of Materials University of Oxford Oxford OX1 3PH	adrian.sutton@materials.ox.ac.uk +44 (0) 1865 273770 +44 (0) 1865 273783 <a href="http://units.ox.ac.uk/departments/materials/MML/People/Sutton.html">http://units.ox.ac.uk/departments/materials/MML/People/Sutton.html</a>

## FUTURE MEETINGS

A summary table is given below, further details may be found on the WWW pages.

TOPIC	DATES	LOCATION	ORGANISER
URL			
Physical Chemistry in the Mesoscopic Regime	12-14 April 1999	Chester, UK	Royal Society of Chemistry
<a href="http://chemistry.rsc.org/is/journals/current/faraday/fadmeet.htm">http://chemistry.rsc.org/is/journals/current/faraday/fadmeet.htm</a>			
World Association of Theoretically Oriented Chemists	1-6 August 1999	London	WATOC
<a href="http://www.chemsoc.org/watoc99/">http://www.chemsoc.org/watoc99/</a>			
Surface Science of Metal Oxides	1-3 September 1999	Ambleside, UK	Royal Society of Chemistry
<a href="http://chemistry.rsc.org/is/journals/current/faraday/fadmeet.htm">http://chemistry.rsc.org/is/journals/current/faraday/fadmeet.htm</a>			

## CCP5 FUNDS FOR COLLABORATIONS

CCP5 can make available funds of up to £200 per annum for groups of two or more UK researchers wishing to undertake a collaborative project within the scientific area covered by CCP5. The funds are intended to cover travel and subsistence costs. Researchers who wish to apply for funds are requested to submit a brief proposal (about 1/2 a page) describing the intended work to Dr. M. Leslie at the address below.

## CCP5 VISITORS PROGRAM

CCP5 organizes a visitors program which funds the visit to the UK of overseas collaborators. We would normally expect a visitor to visit three sites in the UK and give a lecture at each site. These lectures would be open to all members of CCP5 as well as members of the host university. The visit would normally last between one or two weeks. CCP5 would pay for the cost of travel to the UK and within the UK between universities. CCP5 would expect some contribution towards accommodation expenses at the host university to be met by the university. We will also consider longer collaborations or visits just one place if this can be justified by the nature of the work to be done. If you have an overseas collaborator who you would like to invite under this program, please make a request to Dr. M. Leslie.

## ELECTRONIC DISTRIBUTION OF CCP5 NEWSLETTERS AND WORLD WIDE WEB

All newsletters starting from issue 39 (October 1993) are now available on line, together with some articles from earlier newsletters. An index of recent newsletter articles can be found on the World Wide Web server; readers can access the individual articles by this means or by anonymous ftp. (Anonymous ftp will not access the index). The URL for the CCP5 home page is <http://www.dl.ac.uk/CCP/CCP5/main.html>

Below is an index of the information held.

### HOW TO GET THIS NEWSLETTER BY FTP

- |   |                                 |
|---|---------------------------------|
| 1. move to the desired directory on YOUR machine  |                                 |
| 2. type:  | ftp ftp.dl.ac.uk                |
| or  | ftp 148.79.80.10                |
| 3. enter userid:                                  | anonymous                       |
| 4. enter passwd:                                  | <i>enter your name and site</i> |
| 5. change to ccp5.newsletters/46 directory:       | cd ccp5.newsletters/46          |
| 6. change to postscript or latex subdirectory     | cd ps                           |
| or  | cd latex                        |
| 7. to get the required files from the directory : |                                 |
| postscript from ps directory                      | get nl.ps                       |
| compressed postscript from ps directory           | get nl.ps.gz                    |
| latex from latex directory                        | get nl.tex                      |
| 8.  | quit                            |

#### INFORMATION ON WWW SERVER

History of the project.

Organisation of the project.

Current research interests .

A library of computer software maintained by the project.

An index of future meetings and workshops which CCP5 is involved in organising or has been asked to publicize.

A list of proposed visitors sponsored by CCP5 with itinerary.

An index of articles from recent issues of the newsletter.

A copy of recently published newsletters commencing with Issue 39 (October 1993).

Registration and de-registration details.

Other related information on the Web.

Readers may now **register** by filling in an on-line WWW form. Existing readers may also notify registration changes in this way.

In addition to notification of newsletters, we occasionally send other messages about meetings to the Email list. If you want us to send **notification of newsletters only**, let me know and I will place your Email address on a separate list. This will allow readers to restrict the amount of incoming Email if this will be a problem due to limited bandwidth or if readers are charged for incoming Email.

This newsletter is available by anonymous ftp either directly or by accessing the Daresbury World Wide Web server. The newsletter has been placed (in separate directories) both as postscript files and as the source latex files.

#### Distribution of Information by Email

CCP5 will distribute by Email to the members on the mailing list (about 850 world wide) information which is of interest to our members. Three lists are maintained, for UK members, members in other European countries and all other members. If you have information which you would like

sent out in this way please send it by Email to M. Leslie, indicating whether it would be appropriate to restrict its distribution. We also send out post-graduate, post-doctorate and lectureship positions notified to us. Normally the Email messages for post-graduate positions within the UK are restricted to UK members, however if the position is open to non-UK students then Email may be sent to the rest of Europe or the complete mailing list. Messages sent out may be batched together in which case there may be a short delay between the receipt of the message at Daresbury and its transmission. CCP5 no longer places the positions on the WWW or ftp servers but a link will be placed from CCP5's page to a page at a University advertising the position.

## THE CCP5 PROGRAM LIBRARY

Copies of the newsletter no longer include a complete description of the program library. If readers wish to obtain a copy of the documentation it is available by anonymous ftp or through the World Wide Web page. The program library description is in `ccp5.newsletters/library` directory (postscript and ASCII text versions).

## REQUEST FOR CONTRIBUTIONS

Contributors to the current issue

Our thanks go to:

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The deadline for contributions for the next newsletter will be **1 April 1999**. Readers are reminded that contributions are always welcome. Contributions may be sent by Email in `LaTeX`. WORD documents should preferably be sent in rtf format.

## Address

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## RATTLE Recipe For General Holonomic Constraints: Angle And Torsion Constraints

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The popular RATTLE algorithm for imposing bond-stretch constraints in molecular dynamics simulations is generalized here to handle arbitrary holonomic constraints. In particular, RATTLE expressions are given for the important angle-bend and torsional internal-coordinate constraints. This general formulation of RATTLE combines the computational advantages of the velocity Verlet integration algorithm with the flexibility and computational advantages of using general holonomic constraints.

### 1 INTRODUCTION

Ryckaert et al. [1] developed the SHAKE algorithm for applying bond-stretch constraints in molecular dynamics (MD) simulations, using the basic Verlet[2] integration algorithm. To avoid the computational drawbacks[3, 4, 5] of the basic Verlet scheme, Andersen[4] used instead the velocity Verlet algorithm[5] to impose bond-stretch constraints, and termed the resulting algorithm RATTLE. Ryckaert[6] later generalized SHAKE to handle arbitrary holonomic constraints. The possibility of imposing general holonomic constraints in MD simulations provides the ability to selectively freeze particular degrees of freedom, without having to interfere with others. As a simple example, to freeze the angle-bend in a triatomic (e.g. water model) using only bond-stretch constraints requires imposing total rigidity on the molecule by means of triangulation[7, 8]. However, freezing the angle-bend can be achieved more directly by imposing a single angle constraint, without constraining any of the bond-stretches. In addition, arbitrary holonomic constraints can offer computational advantages over equivalent pure stretch constraints, as discussed later. In Section 2, RATTLE is generalized to impose arbitrary holonomic constraints in MD simulations, and useful RATTLE expressions for angle-bend and torsional internal-coordinate constraints are given in Section 3.

### 2 RATTLE For General Holonomic Constraints

Unlike the basic Verlet scheme[2], the velocity Verlet algorithm[5, 9] involves two stages. First, the positions are determined by

$$\mathbf{r}_i(t_0 + \delta t) = \mathbf{r}_i(t_0) + [\delta t]\dot{\mathbf{r}}_i(t_0) + \frac{[\delta t]^2}{2m_i}\mathbf{f}_i(t_0) \quad (1)$$

where  $\mathbf{f}_i$  is the force on particle  $i$ , and then the velocities are computed as

$$\dot{\mathbf{r}}_i(t_0 + \delta t) = \dot{\mathbf{r}}_i(t_0) + \frac{[\delta t]}{2m_i} \{ \mathbf{f}_i(t_0) + \mathbf{f}_i(t_0 + \delta t) \} \quad (2)$$

In the first stage, the positions at time  $(t_0 + \delta t)$  are calculated from the positions and velocities at time  $t_0$ , as given by Eq. (1). With the positions at time  $(t_0 + \delta t)$  available, the forces at time

$(t_0 + \delta t)$  can be computed, for use in the second stage, to evaluate the velocities at time  $(t_0 + \delta t)$  by means of Eq. (2).

Consider a system of  $N$  interacting particles subject to  $l$  general holonomic constraints

$$\sigma_k(\{\mathbf{r}(t)\}) = 0 \quad (k = 1, \dots, l) \quad (3)$$

where  $\{\mathbf{r}(t)\}$  denotes the coordinates of the subset of  $n_k$  particles involved in  $\sigma_k$ . The constrained coordinates are given [1, 6, 10] by

$$\mathbf{r}_i(t_0 + \delta t, \{\gamma\}) = \mathbf{r}'_i(t_0 + \delta t) - \frac{[\delta t]^2}{2m_i} \sum_{k=1}^l \gamma_k [\nabla_i \sigma_k](t_0) \quad (4)$$

The unconstrained coordinates  $\mathbf{r}'_i(t_0 + \delta t)$  are given by means of Eq. (1) as

$$\mathbf{r}'_i(t_0 + \delta t) = \mathbf{r}_i(t_0) + [\delta t] \dot{\mathbf{r}}_i(t_0) + \frac{[\delta t]^2}{2m_i} \mathbf{F}_i(t_0) \quad (5)$$

where  $\mathbf{F}_i$  is the potential energy force on particle  $i$ . The parameters  $\{\gamma\}$  are chosen such that the constrained coordinates at time  $(t_0 + \delta t)$  satisfy the constraint equations (within a desired tolerance), and either the "matrix method" or the SHAKE procedure can be used [1, 6, 10] to obtain the  $\{\gamma\}$ . The constrained velocities are given by

$$\dot{\mathbf{r}}_i(t_0 + \delta t, \{\eta\}) = \dot{\mathbf{r}}'_i(t_0 + \delta t) - \frac{[\delta t]}{2m_i} \sum_{k=1}^l \eta_k [\nabla_i \sigma_k](t_0 + \delta t) \quad (6)$$

where, using Eq. (2), we have

$$\dot{\mathbf{r}}'_i(t_0 + \delta t) = \dot{\mathbf{r}}_i(t_0) + \frac{[\delta t]}{2m_i} \left\{ \mathbf{F}_i(t_0) - \sum_{k=1}^l \gamma_k [\nabla_i \sigma_k](t_0) + \mathbf{F}_i(t_0 + \delta t) \right\} \quad (7)$$

The parameters  $\{\eta\}$  are chosen such that the constrained velocities at time  $(t_0 + \delta t)$  satisfy the constraint equations, more specifically their time derivatives. Accordingly, differentiating Eq. (3) with respect to time we get

$$\frac{d}{dt} \sigma_k(\{\mathbf{r}(t_0 + \delta t)\}) = \sum_{i=1}^{n_k} \dot{\mathbf{r}}_i(t_0 + \delta t) \cdot [\nabla_i \sigma_k](\{\mathbf{r}(t_0 + \delta t)\}) = 0 \quad (8)$$

where  $\dot{\mathbf{r}}_i(t_0 + \delta t)$  is inserted from Eq. (6). Again, either numerical matrix inversion or the SHAKE procedure can be used to solve the set of  $l$  linear equations Eq. (8) for the  $\{\eta\}$ . Since solution for the  $\{\gamma\}$  and  $\{\eta\}$  by matrix techniques becomes computationally expensive for systems with large numbers of coupled constraints, we concentrate here on the solution by the SHAKE procedure, namely RATTLE.

The first of the two stages of the RATTLE formulation for general holonomic constraints, described here, is identical to the generalized SHAKE scheme [6, 10]. The SHAKE algorithm consists of an iterative loop inside which the constraints are considered individually and successively. During an iteration, the algorithm successively selects every constraint and corrects the positions of the subset of particles involved in that constraint, to satisfy it. Consider a certain iteration and a particular constraint  $\sigma_k$ . Let  $\{\mathbf{r}^{old}(t_0 + \delta t)\}$  be the subset of  $n_k$  particle positions involved in

$\sigma_k$ , with values including all changes up to this point in the iteration. The new positions of the particles  $\{\mathbf{r}^{new}(t_0 + \delta t)\}$  obtained in the current iteration are computed as

$$\mathbf{r}_i^{new}(t_0 + \delta t) = \mathbf{r}_i^{old}(t_0 + \delta t) - \frac{[\delta t]^2}{2m_i} \gamma_k^{new} [\nabla_i \sigma_k](t_0) \quad (i = 1, \dots, n_k) \quad (9)$$

where the starting value of  $\mathbf{r}_i^{old}(t_0 + \delta t)$  is given by Eq. (5). These new positions should satisfy the constraint equation for  $\sigma_k$ , leading to

$$\sigma_k(\{\mathbf{r}^{new}(t_0 + \delta t)\}) = \sigma_k\left(\{\mathbf{r}^{old}(t_0 + \delta t)\} - \left\{\frac{[\delta t]^2}{2m} \gamma_k^{new} [\nabla \sigma_k](t_0)\right\}\right) = 0 \quad (10)$$

Equation (10) is usually nonlinear in  $\gamma_k^{new}$ , even for a bond-stretch constraint. Taylor expanding  $\sigma_k(\{\mathbf{r}^{new}(t_0 + \delta t)\})$  about  $\{\mathbf{r}^{old}(t_0 + \delta t)\}$ , Eq. (10) becomes

$$\begin{aligned} & \sigma_k\left(\{\mathbf{r}^{old}(t_0 + \delta t)\} - \left\{\frac{[\delta t]^2}{2m} \gamma_k^{new} [\nabla \sigma_k](t_0)\right\}\right) = \\ & \sigma_k\left(\{\mathbf{r}^{old}(t_0 + \delta t)\}\right) - \sum_{i=1}^{n_k} \frac{[\delta t]^2}{2m_i} \gamma_k^{new} [\nabla_i \sigma_k](t_0) \cdot [\nabla_i \sigma_k]\left(\{\mathbf{r}^{old}(t_0 + \delta t)\}\right) + \dots = 0 \end{aligned} \quad (11)$$

where the nonlinear terms are not shown explicitly. For computational efficiency, all terms higher than first order in Eq. (11) are usually neglected, the iterative process over constraints ensuring the resulting solution satisfies Eq. (11). From Eq. (11) one gets

$$\gamma_k^{new} = [\delta t]^{-2} \frac{\sigma_k\left(\{\mathbf{r}^{old}(t_0 + \delta t)\}\right)}{\sum_{i=1}^{n_k} (1/2m_i) [\nabla_i \sigma_k](t_0) \cdot [\nabla_i \sigma_k]\left(\{\mathbf{r}^{old}(t_0 + \delta t)\}\right)} \quad (12)$$

Exactly as with SHAKE, iterations over the general holonomic constraints continue until all are satisfied, within some tolerance. When all constraints have been satisfied and the constrained coordinates at  $(t_0 + \delta t)$  are available, the potential energy forces  $\{\mathbf{F}(t_0 + \delta t)\}$  are computed for use in the following second stage of the generalized RATTLE.

During an iteration of this second stage, the algorithm again successively selects every constraint and corrects the velocities of the subset of particles involved in that constraint, to satisfy its time derivative. Considering again some iteration and a particular constraint  $\sigma_k$ , the new velocities of the particles  $\{\dot{\mathbf{r}}^{new}(t_0 + \delta t)\}$  obtained in the current iteration are given by

$$\dot{\mathbf{r}}_i^{new}(t_0 + \delta t) = \dot{\mathbf{r}}_i^{old}(t_0 + \delta t) - \frac{[\delta t]}{2m_i} \eta_k^{new} [\nabla_i \sigma_k](t_0 + \delta t) \quad (i = 1, \dots, n_k) \quad (13)$$

where the starting value of  $\dot{\mathbf{r}}_i^{old}(t_0 + \delta t)$  is given by Eq. (7). These new velocities should satisfy the time derivative of the constraint equation. Accordingly, inserting Eq. (13) into Eq. (8) and solving the resulting linear equation for  $\eta_k^{new}$  gives

$$\eta_k^{new} = [\delta t]^{-1} \frac{\sum_{i=1}^{n_k} \dot{\mathbf{r}}_i^{old}(t_0 + \delta t) \cdot [\nabla_i \sigma_k]\left(\{\mathbf{r}(t_0 + \delta t)\}\right)}{\sum_{i=1}^{n_k} (1/2m_i) [\nabla_i \sigma_k]\left(\{\mathbf{r}(t_0 + \delta t)\}\right) \cdot [\nabla_i \sigma_k]\left(\{\mathbf{r}(t_0 + \delta t)\}\right)} \quad (14)$$

As with the first stage of RATTLE, iteration over constraints continues until all the constraints on the velocities have been satisfied within a selected tolerance. The entire RATTLE procedure is then repeated at the next time MD step.

### 3 RATTLE With Internal-Coordinate Constraints

The above general formulation of RATTLE is specialized here to angle-bend and torsional constraints, with the bond-stretch constraints case reviewed merely for completeness. Consider the  $l$  general holonomic constraints Eq. (3) as comprising  $l_s$  bond-stretch constraints,  $l_a$  bond-angle constraints, and  $l_t$  torsional constraints. For bond-stretch constraints Eq. (3) takes the form

$$\sigma_k(\{\mathbf{r}\}) = [\mathbf{r}_j(t) - \mathbf{r}_i(t)]^2 - d_{ij}^2 = 0 \quad (k = 1, \dots, l_s) \quad (15)$$

where  $i$  and  $j$  are the two particles involved in the particular constraint  $\sigma_k$ , and  $d_{ij}$  is the constant distance between them. For the first stage of RATTLE, inserting  $\sigma_k(\{\mathbf{r}\})$  of Eq. (15) into Eq. (9) yields

$$\begin{aligned} \mathbf{r}_j^{new}(t_0 + \delta t) &= \mathbf{r}_j^{old}(t_0 + \delta t) - \frac{1}{m_j} [\delta t]^2 \gamma_k^{new} [\mathbf{r}_j(t_0) - \mathbf{r}_i(t_0)] \\ \mathbf{r}_i^{new}(t_0 + \delta t) &= \mathbf{r}_i^{old}(t_0 + \delta t) - \frac{1}{m_i} [\delta t]^2 \gamma_k^{new} [\mathbf{r}_i(t_0) - \mathbf{r}_j(t_0)] \end{aligned} \quad (16)$$

and Eq. (12) reduces to

$$\gamma_k^{new} = [\delta t]^{-2} \frac{[\mathbf{r}_j^{old}(t_0 + \delta t) - \mathbf{r}_i^{old}(t_0 + \delta t)]^2 - d_{ij}^2}{2[(1/m_i) + (1/m_j)][\mathbf{r}_j(t_0) - \mathbf{r}_i(t_0)] \cdot [\mathbf{r}_j^{old}(t_0 + \delta t) - \mathbf{r}_i^{old}(t_0 + \delta t)]} \quad (k = 1, \dots, l_s) \quad (17)$$

In the second stage Eq. (13) becomes

$$\begin{aligned} \dot{\mathbf{r}}_j^{new}(t_0 + \delta t) &= \dot{\mathbf{r}}_j^{old}(t_0 + \delta t) - \frac{1}{m_j} [\delta t] \eta_k^{new} [\mathbf{r}_j(t_0 + \delta t) - \mathbf{r}_i(t_0 + \delta t)] \\ \dot{\mathbf{r}}_i^{new}(t_0 + \delta t) &= \dot{\mathbf{r}}_i^{old}(t_0 + \delta t) - \frac{1}{m_i} [\delta t] \eta_k^{new} [\mathbf{r}_i(t_0 + \delta t) - \mathbf{r}_j(t_0 + \delta t)] \end{aligned} \quad (18)$$

and Eq. (14) reduces to

$$\eta_k^{new} = [\delta t]^{-1} \frac{[\mathbf{r}_j(t_0 + \delta t) - \mathbf{r}_i(t_0 + \delta t)][\dot{\mathbf{r}}_j^{old}(t_0 + \delta t) - \dot{\mathbf{r}}_i^{old}(t_0 + \delta t)]}{[(1/m_i) + (1/m_j)][\mathbf{r}_j(t_0 + \delta t) - \mathbf{r}_i(t_0 + \delta t)]^2} \quad (k = 1, \dots, l_s) \quad (19)$$

Because the constrained coordinates at  $(t_0 + \delta t)$ , from the first stage, satisfy (within a given tolerance) the constraint Eq. (15), Eq. (19) can be rewritten as

$$\eta_k^{new} = [\delta t]^{-1} \frac{[\mathbf{r}_j(t_0 + \delta t) - \mathbf{r}_i(t_0 + \delta t)][\dot{\mathbf{r}}_j^{old}(t_0 + \delta t) - \dot{\mathbf{r}}_i^{old}(t_0 + \delta t)]}{[(1/m_i) + (1/m_j)] d_{ij}^2} \quad (k = 1, \dots, l_s) \quad (20)$$

We have recovered in Eqs. (16), (17), (18), and (20) the usual RATTLE expressions[4]. For bond-angle constraints Eq. (3) takes the form

$$\sigma_k(\{\mathbf{r}\}) = \phi_{abc}(\{\mathbf{r}\}) - \alpha_{abc} = 0 \quad (k = 1, \dots, l_a) \quad (21)$$

where  $a$ ,  $b$  and  $c$  are the three particles involved in the particular constraint  $\sigma_k$ ,  $\phi_{abc} \equiv \arccos(\hat{\mathbf{r}}_{ab} \cdot \hat{\mathbf{r}}_{cb})$  is the angle at  $b$  formed by the  $(abc)$  triplet of particles,  $\hat{\mathbf{r}}_{ab} \equiv \mathbf{r}_{ab}/|\mathbf{r}_{ab}|$ ,  $\mathbf{r}_{ab} \equiv \mathbf{r}_a - \mathbf{r}_b$ , and  $\alpha_{abc}$  is the constant angle-bend value. For the first stage of the generalized RATTLE, inserting the constraint  $\sigma_k(\{\mathbf{r}\})$  of Eq. (21) into Eq. (9) gives

$$\mathbf{r}_i^{new}(t_0 + \delta t) = \mathbf{r}_i^{old}(t_0 + \delta t) - \frac{[\delta t]^2}{2m_i} \gamma_k^{new} [\nabla_i \phi_{abc}](t_0) \quad (i = a, b, c) \quad (22)$$

and Eq. (12) reduces to

$$\gamma_k^{new} = [\delta t]^{-2} \frac{\phi_{abc}(\{\mathbf{r}^{old}(t_0 + \delta t)\}) - \alpha_{abc}}{\sum_{i=1}^{n_k} (1/2m_i) [\nabla_i \phi_{abc}](t_0) \cdot [\nabla_i \phi_{abc}](\{\mathbf{r}^{old}(t_0 + \delta t)\})} \quad (k = 1, \dots, l_a) \quad (23)$$

For the second stage, Eq. (13) becomes

$$\dot{\mathbf{r}}_i^{new}(t_0 + \delta t) = \dot{\mathbf{r}}_i^{old}(t_0 + \delta t) - \frac{[\delta t]}{2m_i} \eta_k^{new} [\nabla_i \phi_{abc}](\{\mathbf{r}(t_0 + \delta t)\}) \quad (i = a, b, c) \quad (24)$$

and Eq. (14) reduces to

$$\eta_k^{new} = [\delta t]^{-1} \frac{\sum_{i=1}^{n_k} \dot{\mathbf{r}}_i^{old}(t_0 + \delta t) \cdot [\nabla_i \phi_{abc}](\{\mathbf{r}(t_0 + \delta t)\})}{\sum_{i=1}^{n_k} (1/2m_i) \{[\nabla_i \phi_{abc}](\{\mathbf{r}(t_0 + \delta t)\})\}^2} \quad (k = 1, \dots, l_a) \quad (25)$$

Note that the expressions for  $\nabla_i \phi_{abc}$  in Eqs. (22)-(25) are immediately available from the Wilson vectors[11] for the angle-bend internal coordinate. Finally, for torsional constraints Eq. (3) takes the form

$$\sigma_k(\{\mathbf{r}\}) = \tau_{abcd}(\{\mathbf{r}\}) - \beta_{abcd} = 0 \quad (k = 1, \dots, l_t) \quad (26)$$

where  $a, b, c,$  and  $d$  are the four particles involved in the particular constraint  $\sigma_k$ , and

$$\tau_{abcd} \equiv \arccos \left[ \frac{(\hat{\mathbf{r}}_{ab} \times \hat{\mathbf{r}}_{cb}) \cdot (\hat{\mathbf{r}}_{bc} \times \hat{\mathbf{r}}_{dc})}{\sin \phi_{abc} \sin \phi_{bcd}} \right] \quad (27)$$

is the dihedral angle formed by the  $(abcd)$  quadruplet of particles with constraint value  $\beta_{abcd}$ . For the first stage of the generalized RATTLE, inserting  $\sigma_k(\{\mathbf{r}\})$  of Eq. (26) into Eq. (9) yields

$$\mathbf{r}_i^{new}(t_0 + \delta t) = \mathbf{r}_i^{old}(t_0 + \delta t) - \frac{[\delta t]^2}{2m_i} \gamma_k^{new} [\nabla_i \tau_{abcd}](t_0) \quad (i = a, b, c, d) \quad (28)$$

and Eq. (12) reduces to

$$\gamma_k^{new} = [\delta t]^{-2} \frac{\tau_{abcd}(\{\mathbf{r}^{old}(t_0 + \delta t)\}) - \beta_{abcd}}{\sum_{i=1}^{n_k} (1/2m_i) [\nabla_i \tau_{abcd}](t_0) \cdot [\nabla_i \tau_{abcd}](\{\mathbf{r}^{old}(t_0 + \delta t)\})} \quad (k = 1, \dots, l_t) \quad (29)$$

In the second stage, Eq. (13) becomes

$$\dot{\mathbf{r}}_i^{new}(t_0 + \delta t) = \dot{\mathbf{r}}_i^{old}(t_0 + \delta t) - \frac{[\delta t]}{2m_i} \eta_k^{new} [\nabla_i \tau_{abcd}](\{\mathbf{r}(t_0 + \delta t)\}) \quad (i = a, b, c, d) \quad (30)$$

and Eq. (14) reduces to

$$\eta_k^{new} = [\delta t]^{-1} \frac{\sum_{i=1}^{n_k} \dot{\mathbf{r}}_i^{old}(t_0 + \delta t) \cdot [\nabla_i \tau_{abcd}](\{\mathbf{r}(t_0 + \delta t)\})}{\sum_{i=1}^{n_k} (1/2m_i) \{[\nabla_i \tau_{abcd}](\{\mathbf{r}(t_0 + \delta t)\})\}^2} \quad (k = 1, \dots, l_t) \quad (31)$$

Again, the expressions for  $\nabla_i \tau_{abcd}$  in Eqs. (28)-(31) are available from the Wilson vectors[11] for the torsional internal coordinate.

## CONCLUSION

A formulation of RATTLE for imposing general holonomic constraints in MD simulations was described, and expressions for angle-bend and torsional constraints were given. In MD simulations of systems involving constraints, the computation of the constraint forces typically takes far less CPU time than the computation of the forces deriving from the potential energy of the system. As larger systems with constraints are considered, or molecular models involving larger sets of constraints are simulated, the computation of constraint forces becomes increasingly CPU intensive[12, 13] and can parallel in computational cost[14, 15] the evaluation of the potential energy forces. To deal with this problem, various approaches[15, 10] have been developed for improving the efficiency of computing the constraint forces in MD simulations. One suggested strategy calls for the use of equivalent alternative constraints. A case in point is the substantial improvement in efficiency that results when angle-bend constraints are used[10] in place of the slowly converging triangulation procedure[7, 8] for imposing angle constraints. The formulation of RATTLE for general holonomic constraints, given in this article, combines these computational advantages of arbitrary forms of holonomic constraints with those of the velocity Verlet algorithm.

## References

- [1] J.P. Ryckaert, G. Ciccotti, and H.J.C. Berendsen. Numerical Integration of The Cartesian Equations of Motion of a System With Constraints: Molecular Dynamics of n-Alkanes. *J. Comput. Phys.*, **23**:327, (1977).
- [2] L. Verlet. Computer Experiments on Classical Fluids: I. Thermodynamical Properties of Lennard-Jones Molecules. *Phys. Rev.*, **159**:98, (1967).
- [3] G. Dahlquist and A. Björk. *Numerical Methods*. Prentice-Hall. Englewood Cliffs, NJ, (1974).
- [4] H.C. Andersen. RATTLE: A "Velocity" Version of The SHAKE Algorithm for Molecular Dynamics Calculations. *J. Comput. Phys.*, **52**:24, (1983).
- [5] W.C. Swope, H.C. Andersen, P.H. Berens, and K.R. Wilson. A Computer Simulation Method for The Calculation of Equilibrium Constants for The Formation of Physical Clusters of Molecules: Application to Small Water Clusters. *J. Chem. Phys.*, **76**:637, (1982).
- [6] J.P. Ryckaert. Special Geometrical Constraints in The Molecular Dynamics of Chain Molecules. *Mol. Phys.*, **55**:549, (1985).
- [7] W.F. van Gunsteren and H.J.C. Berendsen. Algorithms for Macromolecular Dynamics and Constraint Dynamics. *Mol. Phys.*, **34**:1311, (1977).
- [8] W.F. van Gunsteren. Constrained Dynamics of Flexible Molecules. *Mol. Phys.*, **40**:1015, (1980).
- [9] A.T. Allen and D.J. Tildesley. *Computer Simulation of Liquids*. Oxford University Press, New York, (1992).
- [10] R. Kutteh and T.P. Straatsma, Molecular Dynamics With General Holonomic Constraints And Application To Internal Coordinate Constraints, in *Reviews in Computational Chemistry*, edited by Kenny B. Lipkowitz and Donald B. Boyd. Wiley Publishers, Vol. 12, (1998, in press)
- [11] Jr. E.B. Wilson, J.C. Decius, and Paul C. Cross. *Molecular Vibrations*. Dover Publications, New York, (1955).
- [12] S. Miyamoto and P.A. Kollman. SETTLE: An Analytical Version of The SHAKE and RATTLE Algorithm for Rigid Water Models. *J. Comput. Chem.*, **13**:952, (1992).
- [13] J.E. Mertz, D.J. Tobias, C.L. Brooks III, and U.C. Singh. Vector and Parallel Algorithms for The Molecular Dynamics Simulation of Macromolecules on Shared-Memory Computers. *J. Comput. Chem.*, **12**:1270, (1991).
- [14] J.P. Ryckaert, I.R. McDonald, and M.L. Klein. Disorder in The Pseudohexagonal Rotator Phase of n-Alkanes: Molecular-Dynamics Calculation for Tricosane. *Mol. Phys.*, **67**:957, (1989).
- [15] K.D. Hammonds and J. P. Ryckaert. On The Convergence of The SHAKE Algorithm. *Comput. Phys. Commun.*, **62**:336, (1991).

## Point Multipoles in the Ewald Summation (Revisited)

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This article describes how to incorporate point charges, dipoles and quadrupoles (or combinations of them i.e. point multipoles) into the Ewald summation method. A full description of the multipole potential, forces and torques in a periodic system is provided.

### 1 Introduction

This article is a re-draft of a much earlier paper, which appeared in the CCP5 Newsletter as long ago as 1982! [1]. The article is now effectively out of print and, more to the point, is not accessible over the Web. However, it is apparent that the subject matter is still of interest (long range forces being an eternal problem in modelling molecular systems!), and since I still receive requests for reprints, I have therefore reproduced this draft for electronic circulation. The basic description follows that of the earlier paper, but I have added a few more points of explanation and tried to clean up the notation a little.

The purpose of this article is to outline a low level treatment of point multipoles in an Ewald summation[2]. A point multipole in this application is defined as the superposition of a point charge, point dipole and point quadrupole, with no higher terms. Such a multipole might be obtained from an arbitrary charge distribution resolved into these components. The method is capable of extension to higher order, but since it is based on a Cartesian representation, it rapidly becomes too cumbersome to be completely general. However for many systems higher orders of multipole are not necessary and the method is then worth considering. The physical properties described in this article are the potential, force and torque experienced by a point multipole in an infinite periodic system of unit cells containing irregularly spaced multipoles.

The following section describes a number of mathematical operators which are used to define the multipole and derive the multipolar Ewald summation. Section 3 derives the Ewald expression for the potential of a multipole in a periodic system. Section 4 derives the force on the multipole and Section 5 the torque, both of which are essential for molecular dynamics simulation. Some practical comments on the application of the method follow in Section 6, with conclusions in Section 7.

### 2 Multipole Operators

Taylor's expansion for a scalar function of three variables (i.e.  $F(x, y, z)$  or  $F(\underline{r})$ ) may be written as:

$$F(\underline{r} + \delta\underline{r}) = F(\underline{r}) + \sum_{\alpha} \delta r^{\alpha} \frac{\partial}{\partial r^{\alpha}} F(\underline{r}) + \frac{1}{2} \sum_{\alpha} \sum_{\beta} \delta r^{\alpha} \delta r^{\beta} \frac{\partial^2}{\partial r^{\alpha} \partial r^{\beta}} F(\underline{r}) + \dots etc, \quad (1)$$

with  $\alpha, \beta = x, y, z$  etc. It is convenient to write this expansion in the following form.

$$F(\underline{r} + \delta\underline{r}) = F(\underline{r}) + \delta\underline{r} \cdot \hat{\nabla} F(\underline{r}) + \underline{U} : \hat{\underline{\Omega}} + \dots etc. \quad (2)$$

where  $\underline{U}$  is a  $(3 \times 3)$  matrix with components

$$U^{\alpha\beta} = \frac{1}{2} \delta r^\alpha \delta r^\beta \quad \text{etc.} \quad (3)$$

$\hat{\nabla}$  is the familiar vector operator

$$\hat{\nabla} = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}, \quad (4)$$

while  $\hat{\underline{\Omega}}$  a matrix operator of dimension  $(3 \times 3)$  defined by its components:

$$\hat{\Omega}^{\alpha\beta} = \frac{\partial^2}{\partial r^\alpha \partial r^\beta} \quad \text{etc.} \quad (5)$$

The operation indicated by the colon ( $:$ ) is the dyadic scalar product of two matrices i.e.

$$\underline{A} : \underline{B} = \sum_{\alpha} \sum_{\beta} A^{\alpha\beta} B^{\alpha\beta}. \quad (6)$$

The equivalence of the forms (1) and (2) follows easily from these definitions. (The terms of the series (2) are therefore to be regarded as consecutive contractions of tensors of rank 0,1,2, ... etc. to yield a scalar result.)

Consider a cluster of  $n$  point charges ( $q_k$ ) scattered about the origin at respective positions  $\underline{r}_k$  and a *unit* point charge at a *large* distance  $r$  from the origin. The electrostatic potential of the unit point charge is then given by

$$V(\underline{r}) = \frac{1}{4\pi\epsilon_0} \sum_{k=1}^n \frac{q_k}{|\underline{r} - \underline{r}_k|}. \quad (7)$$

Seen from the location  $\underline{r}$ , the charge cluster may be regarded as a multipole located at the origin, since the vectors  $\underline{r}_k$  are assumed small in comparison with the distance  $r$  (i.e.  $r \gg r_k$ ). Thus the expansion (2) may be used with (7) to obtain the following expression for  $V(\underline{r})$  (in which contributions above quadrupole are ignored.)

$$V(\underline{r}) = \frac{1}{4\pi\epsilon_0} \left\{ C_a - \underline{D}_a \cdot \hat{\nabla} + \underline{Q}_a : \hat{\underline{\Omega}} \right\} \left\{ \frac{1}{r} \right\}, \quad (8)$$

where

$$C_a = \sum_{k=1}^n q_k \quad (9)$$

is the net multipole charge,

$$\underline{D}_a = \sum_{k=1}^n q_k \underline{r}_k \quad (10)$$

is the net multipole dipole, and

$$\underline{Q}_a = \sum_{k=1}^n q_k \underline{U}_k \quad (11)$$

is the net multipole quadrupole. In these formulae, the suffix  $a$  is to be regarded as an index of the whole cluster i.e. the multipole  $M_a$ . The multipole is to be regarded as a rigid entity (i.e. the charges  $q_k$  have a fixed displacement relative to each other.)

From (8) a multipole operator  $\hat{M}_a$  may be defined:

$$\hat{M}_a = C_a - \underline{D}_a \cdot \hat{\nabla} + \underline{Q}_a : \hat{\underline{\Omega}}, \quad (12)$$

with the aid of which (8) becomes

$$V(\underline{r}) = \frac{1}{4\pi\epsilon_0} \hat{M}_a \left\{ \frac{1}{r} \right\}. \quad (13)$$

It is therefore apparent that the potential at  $\underline{r}$ , due to a point multipole at the origin, is obtained by applying the operator  $\hat{M}_a$  to the expression describing the potential due to a unit positive charge at the origin.

By a similar reasoning it may be deduced that the potential  $\Phi(\underline{r})$  of a second point multipole ( $M_b$ ) positioned at  $\underline{r}$ , due to the potential field  $V(\underline{r})$  of the first, is given by

$$\Phi(\underline{r}) = \hat{M}_b V(\underline{r}) \quad (14)$$

or

$$\Phi(\underline{r}) = \frac{1}{4\pi\epsilon_0} \hat{M}_b \hat{M}_a \left\{ \frac{1}{r} \right\}, \quad (15)$$

where

$$\hat{M}_b = C_b + \underline{D}_b \cdot \hat{\nabla} + \underline{Q}_b : \hat{\underline{\Omega}} \quad (16)$$

The force acting on the second multipole will be given by applying the usual operator  $-\hat{\nabla}$  to the expression (15)

$$\underline{F}_b = -\frac{1}{4\pi\epsilon_0} \hat{\nabla} \hat{M}_b \hat{M}_a \left\{ \frac{1}{r} \right\}. \quad (17)$$

The torque acting on the second multipole in the potential field of the first may be written as

$$\underline{T}_b = -\sum_{k=1}^n q_k \underline{r}_k \times \hat{\nabla} V(\underline{r} + \underline{r}_k) \quad (18)$$

from which it may be deduced that

$$\underline{T}_b = -\{\underline{D}_b \times \hat{\nabla} + 2\underline{Q}_b \times \hat{\underline{\Omega}}\} V(\underline{r}), \quad (19)$$

leading to the following definition of the torque operator:

$$\hat{T}_b = -\{\underline{D}_b \times \hat{\nabla} + 2\underline{Q}_b \times \hat{\underline{\Omega}}\}. \quad (20)$$

The operation implied by  $\times$  is a vector product. The vector product of two vectors is well known, the vector product of two matrices however needs explaining. It is defined as the resultant vector  $\underline{V}$  of two matrices  $\underline{A}$  and  $\underline{B}$  according to the formula

$$V^\alpha = \sum_{\beta} \{A^{\alpha+1,\beta} B^{\alpha+2,\beta} - A^{\alpha+2,\beta} B^{\alpha+1,\beta}\}, \quad (21)$$

where indices exceeding the matrix dimension (3 in this case) are regarded as cyclic permutations. It is apparent that the vector product of two matrices is non-commutative, with

$$\underline{A} \times \underline{B} = -\underline{B} \times \underline{A} \quad (22)$$

These operators are sufficient to derive the required expressions in the Ewald summation.

### 3 The Ewald Summation

The electrostatic potential at a point  $\underline{r}$  (not a multipole site) in an infinite periodic system of unit point charges (which may be randomly distributed throughout the unit cell<sup>1</sup>) is given by the Ewald summation [2] as:

$$V_E(\underline{r}) = \frac{1}{V_o \epsilon_o} \sum_{\underline{k} \neq 0}^{\infty} A(k) \sum_j^N \exp(-i\underline{k} \cdot (\underline{r}_j - \underline{r})) + \frac{1}{4\pi \epsilon_o} \sum_j^{\infty} B_0(|\underline{r}_j - \underline{r}|) \quad (23)$$

where

$$A(k) = \left\{ \frac{1}{k^2} \right\} \exp(-k^2/4\xi^2) \quad (24)$$

$$B_0(u) = \left\{ \frac{1}{u} \right\} \operatorname{erfc}(\xi u), \quad (25)$$

$$\operatorname{erfc}(\xi u) = \frac{2}{\sqrt{\pi}} \int_{\xi u}^{\infty} \exp(-s^2) ds, \quad (26)$$

and  $N$  is the number of point charges in the unit (simulation) cell,  $\xi$  is Ewald's convergence parameter,  $V_o$  is the volume of the unit cell.  $\underline{k}$  is a reciprocal lattice vector obtained from the unit cell width ( $L$ ) for a cubic system:

$$\underline{k} = \frac{2\pi}{L} (n_a, n_b, n_c)^{\dagger}, \quad (27)$$

where  $n_a, n_b$  and  $n_c$  are integers.

According to the principles outlined in the previous section Ewald's summation may be adapted to a system of point multipoles by applying the set of operators  $\hat{M}_j$  defined by

$$\hat{M}_j = C_j - \underline{D}_j \cdot \underline{\nabla} + \underline{Q}_j : \underline{\underline{\Omega}}, \quad (28)$$

Following this prescription we obtain the following expression, which describes the potential of a unit positive charge inserted into a system of point multipoles:

$$V(\underline{r}) = \frac{1}{V_o \epsilon_o} \sum_{\underline{k} \neq 0}^{\infty} A(k) \sum_j^N (C_j - i\underline{D}_j \cdot \underline{k} - \underline{Q}_j : \underline{K}) \exp(-i\underline{k} \cdot (\underline{r}_j - \underline{r})) + \frac{1}{4\pi \epsilon_o} \sum_j^{\infty} (C_j B_0(|\underline{r}_j - \underline{r}|) - (\underline{D}_j \cdot (\underline{r}_j - \underline{r}) + \underline{Q}_j : \underline{L}) B_1(|\underline{r}_j - \underline{r}|) + \underline{Q}_j : \underline{R}_j B_2(|\underline{r}_j - \underline{r}|)) \quad (29)$$

where  $\underline{K}$  and  $\underline{R}_j$  are matrices defined as follows:

$$\underline{K}^{\alpha\beta} = k^{\alpha} k^{\beta} \quad (\text{etc.}) \quad (30)$$

$$\underline{R}_{jg}^{\alpha\beta} = r_{jg}^{\alpha} r_{jg}^{\beta} \quad (\text{etc.}) \quad (31)$$

$$(32)$$

<sup>1</sup>The unit cell in this context is, of course, the simulation cell

The functions  $B_\ell(|\underline{r}_j - \underline{r}|)$  are derived from  $B_0(|\underline{r}_j - \underline{r}|)$  according to the recurrence relation

$$B_\ell(u) = \frac{1}{u^2} \left\{ (2\ell - 1)B_{\ell-1}(u) + \frac{(2\xi^2)^\ell}{\xi\sqrt{\pi}} \exp(-\xi^2 u^2) \right\}. \quad (33)$$

Further properties of these important functions are given in the appendix.

To find the potential energy of an interstitial or 'guest' multipole inserted at the position  $\underline{r}$  within the system, (but not at an existing multipole site,) a second operator  $\hat{M}_g$  must be applied (c.f. equation 14), where

$$\hat{M}_g = C_g + \underline{D}_g \cdot \hat{\nabla} + \underline{Q}_g : \hat{\underline{\nabla}}. \quad (34)$$

The result of this operation is

$$\begin{aligned} \phi_g = & \frac{1}{V_o \epsilon_o} \sum_{\underline{k} \neq 0}^{\infty} A(\underline{k}) \sum_j^N F_{jg}(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_{jg}) + \\ & \frac{1}{4\pi \epsilon_o} \sum_{\ell}^4 \sum_j^{\infty} G_{jg}^{\ell}(r_{jg}) B_{\ell}(r_{jg}). \end{aligned} \quad (35)$$

The functions  $A(\underline{k})$  and  $B_{\ell}$  have already been described. Vector  $\underline{r}_g$  is the position adopted by the guest multipole and

$$\underline{r}_{jg} = \underline{r}_j - \underline{r}_g \quad (36)$$

is the separation vector, for which  $r_{jg}$  is the scalar separation. The *scalar* functions  $F_{jg}(\underline{k})$  and  $G_{jg}^{\ell}(r_{jg})$  are as follows:

$$F_{jg}(\underline{k}) = (C_g + i\underline{D}_g \cdot \underline{k} - \underline{Q}_g : \underline{K})(C_j - i\underline{D}_j \cdot \underline{k} - \underline{Q}_j : \underline{K}) \quad (37)$$

$$G_{jg}^0(r_{jg}) = C_g C_j \quad (38)$$

$$G_{jg}^1(r_{jg}) = \underline{D}_g \cdot \underline{D}_j + C_j(\underline{D}_g \cdot \underline{r}_{jg} - \underline{Q}_g : \underline{I}) - C_g(\underline{D}_j \cdot \underline{r}_{jg} + \underline{Q}_j : \underline{I}) \quad (39)$$

$$\begin{aligned} G_{jg}^2(r_{jg}) = & C_j \underline{Q}_g : \underline{R}_{jg} + C_g \underline{Q}_j : \underline{R}_{jg} - 2\underline{Q}_g : \underline{\Delta}_{jg} - 2\underline{Q}_j : \underline{\Delta}_{gj} + \\ & \underline{D}_j \cdot \underline{r}_{jg} \underline{Q}_g : \underline{I} - \underline{D}_g \cdot \underline{r}_{jg} \underline{Q}_j : \underline{I} - \underline{D}_g \cdot \underline{r}_{jg} \underline{D}_j \cdot \underline{r}_{jg} \\ & + 2\underline{Q}_g : \underline{Q}_j + \underline{Q}_g : \underline{I} \underline{Q}_j : \underline{I} \end{aligned} \quad (40)$$

$$\begin{aligned} G_{jg}^3(r_{jg}) = & \underline{D}_g \cdot \underline{r}_{jg} \underline{Q}_j : \underline{R}_{jg} - \underline{D}_j \cdot \underline{r}_{jg} \underline{Q}_g : \underline{R}_{jg} - \\ & \underline{Q}_g : \underline{I} \underline{Q}_j : \underline{R}_{jg} - \underline{Q}_j : \underline{I} \underline{Q}_g : \underline{R}_{jg} - 4\underline{Q}_g : \underline{\Theta}_{jg} \end{aligned} \quad (41)$$

$$G_{jg}^4(r_{jg}) = \underline{Q}_g : \underline{R}_{jg} \underline{Q}_j : \underline{R}_{jg} \quad (42)$$

where

$$\underline{\Delta}_{ij}^{\alpha\beta} = D_i^{\alpha} r_{ji}^{\beta} \quad (etc.) \quad (43)$$

$$\underline{\Theta}_{ji}^{\alpha\beta} = r_{ji}^{\alpha} \sum_{\gamma} Q_j^{\beta\gamma} r_{ji}^{\gamma} \quad (44)$$

(It is important to note that the interchange of multipole indices  $i$  and  $j$  in these formulae does not imply taking the transpose, but instead identifies a physically distinct matrix.)

Usually however it is not the potential of a guest multipole that is required, but of one of the multipoles of the system itself. Physically this means equivalencing the guest multipole to one of the multipoles of the system. The above formulae can be adapted to this circumstance in the following way.

1. The terms involving *both* the guest multipole (index  $g$ ) and the multipole of interest (index  $i$ ) must be extracted from equation (35). These terms are dealt with below.
2. In the remaining terms involving the guest multipole, the index  $g$  is changed to  $i$ . Thus as far as these terms are concerned, the guest multipole and the multipole with index  $i$  are one and the same.

Now examining the terms separated out from (35) according to (a), it is clear that if the guest multipole is to be equivalenced to the  $i$ 'th multipole, these terms represent a 'self interaction' energy in which the separation  $r_{ig}$  is zero. These terms are mathematically indeterminate and unphysical but it is not correct simply to neglect them, as the following treatment shows.

Extracting firstly the  $G_{ig}^\ell$  terms from the right of (35) gives

$$\phi^s = \frac{1}{4\pi\epsilon_0} \sum_{\ell}^4 G_{ig}^\ell(r_{ig}) B_{\ell}(r_{ig}). \quad (45)$$

Where  $\phi^s$  is used to represent the extracted self interaction terms. Putting  $\underline{u}$  to represent the vector  $\underline{r}_{ig}$ , it becomes clear from the definition of the functions  $B_{\ell}(u)$  in equations (25) and (33) that this expression becomes indeterminate when  $\underline{r}_g$  and  $\underline{r}_i$  are equivalenced (i.e. as  $u \rightarrow 0$ ). However, expanding the  $B_{\ell}(u)$  functions as polynomials in the argument  $u$  (see appendix) allows  $\phi^s$  to be rewritten as

$$\phi^s = \frac{1}{4\pi\epsilon_0} \sum_{\ell}^4 G_{ig}^\ell(\underline{u}) \left\{ \frac{(2\ell)!}{\ell! 2^{\ell} u^{2\ell+1}} - \frac{(2\xi^2)^{\ell+1}}{(2\ell+1)\xi\sqrt{\pi}} + O_{\ell}(u) \right\}, \quad (46)$$

where  $O_{\ell}(u)$  represents a sum of terms in  $u$  and higher powers of  $u$ . It is now clear that it is the first terms within the brackets on the right of this expansion that become indeterminate as  $u$  tends to zero. However on further inspection it is also clear that these terms are nothing more than the conventional (or non-Ewald) terms defining the potential energy function of two multipoles separated by the distance  $u$ . Given this identification, these terms can simply be removed, since they represent an interaction that does not physically exist. It is also apparent that the  $O_{\ell}(u)$  terms will vanish as  $u$  tends to zero, leaving the only surviving terms as

$$\phi^s = -\frac{1}{4\pi\epsilon_0} \sum_{\ell}^4 \left\{ \frac{(2\xi^2)^{\ell+1} G_{ii}^\ell(\underline{0})}{(2\ell+1)\xi\sqrt{\pi}} \right\}. \quad (47)$$

That these terms survive is of course due to the fact that the Ewald method replaces the point multipoles by a superposition of both 'Gaussian' multipoles and the original point multipoles. Removing the point multipole terms leaves the Gaussian contributions intact.

Two further comments are in order. Firstly, the identification of the first terms of (46) with the interaction potential of two multipoles, means that the expression (47) represents a *complete* correction for the self interaction term. It follows that no further correction need be made to the Fourier component of (35), other than the substitution of index  $i$  for  $g$ . Secondly, from the identities (38) to (42) it can be seen that the  $G_{ii}^\ell(\underline{0})$  terms have no distance dependent contributions, leading to the final form for the self interaction term  $\phi^s$ :

$$\phi_i^s = -\frac{2\xi}{4\epsilon_0\sqrt{\pi^3}} \left\{ G_i^2 + 2\xi^2 \left[ \frac{1}{3} (D_i^2 + 2C_i \underline{Q}_i : \underline{D}) + \frac{2\xi^2}{5} (2\underline{Q}_i : \underline{Q}_i + (\underline{Q}_i : \underline{D})^2) \right] \right\}, \quad (48)$$

where the index  $i$  has been added to  $\phi_i^s$  to express its dependence on the  $i$ 'th multipole. The final equation for the potential energy of a multipole in a periodic system of point multipoles is therefore

$$\begin{aligned} \phi_i = & \frac{1}{V_o\epsilon_o} \sum_{\underline{k} \neq 0}^{\infty} A(k) \sum_j^N F_{ji}(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_{ji}) + \\ & \frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 \sum_{j \neq i}^{\infty} G_{ji}^{\ell}(\underline{r}_{ji}) B_{\ell}(r_{ji}) + \phi_i^s. \end{aligned} \quad (49)$$

From this it is easy to obtain the total configuration energy (per simulation cell) for the system, which is

$$\begin{aligned} U_c = & \frac{1}{2V_o\epsilon_o} \sum_{\underline{k} \neq 0}^{\infty} A(k) \left| \sum_j^N f_j(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_j) \right|^2 + \\ & \frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 \sum_i^N \sum_{j > i}^{\infty} G_{ji}^{\ell}(\underline{r}_{ji}) B_{\ell}(r_{ji}) + \frac{1}{2} \sum_i^N \phi_i^s. \end{aligned} \quad (50)$$

where

$$f_j(\underline{k}) = C_j - i\underline{D}_j \cdot \underline{k} - \underline{Q}_j : \underline{K}. \quad (51)$$

It is easy to show that this formula reduces to the standard Ewald summation for point charges [2] if the dipoles and quadrupoles are set to zero. It may also be shown that setting the charges and quadrupoles to zero provides the familiar Kornfeld expression for a lattice of point dipoles [2, 3].

## 4 The Force on a Multipole

According to the prescription in equation (17), the force acting of the  $i$ 'th multipole in a lattice of multipoles is obtained by applying the operator  $-\hat{\nabla}_i$  to the potential function in equation (49). The result is

$$\begin{aligned} \underline{F}_i = & -\frac{1}{V_o\epsilon_o} \sum_{\underline{k} \neq 0}^{\infty} i\underline{k} A(k) \sum_j^N F_{ji}(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_{ji}) \\ & - \frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 \sum_{j \neq i}^{\infty} \left\{ G_{ji}^{\ell}(\underline{r}_{ji}) B_{\ell+1}(r_{ji}) \underline{r}_{ji} + B_{\ell}(r_{ji}) \hat{\nabla}_i G_{ji}^{\ell}(\underline{r}_{ji}) \right\}. \end{aligned} \quad (52)$$

Where the scalar functions  $A(k)$ ,  $B_{\ell}(u)$ ,  $F_{ji}(\underline{k})$  and  $G_{ji}^{\ell}(\underline{u})$  are defined in equations 37 to 42, and the *vector* functions  $\hat{\nabla}_i G_{ji}^{\ell}(\underline{r}_{ji})$  are as follows

$$\hat{\nabla}_i G_{ji}^0(\underline{r}_{ji}) = 0 \quad (53)$$

$$\hat{\nabla}_i G_{ji}^1(\underline{r}_{ji}) = C_i \underline{D}_j - C_j \underline{D}_i \quad (54)$$

$$\begin{aligned} \hat{\nabla}_i G_{ji}^2(\underline{r}_{ji}) = & -2C_j \underline{Q}_{ji} \cdot \underline{r}_{ji} - 2C_i \underline{Q}_{ji} \cdot \underline{r}_{ji} + 2\underline{Q}_{ji} \cdot \underline{D}_i - 2\underline{Q}_{ji} \cdot \underline{D}_j + \\ & \underline{Q}_{ji} : \underline{I} \underline{D}_i - \underline{Q}_{ji} : \underline{I} \underline{D}_j + (\underline{D}_j \cdot \underline{r}_{ji}) \underline{D}_i + (\underline{D}_i \cdot \underline{r}_{ji}) \underline{D}_j \end{aligned} \quad (55)$$

$$\begin{aligned} \hat{\nabla}_i G_{ji}^3(\underline{r}_{ji}) = & -2(\underline{D}_i \cdot \underline{r}_{ji}) \underline{Q}_{ji} \cdot \underline{r}_{ji} + 2(\underline{D}_j \cdot \underline{r}_{ji}) \underline{Q}_{ji} \cdot \underline{r}_{ji} + 2(\underline{Q}_{ji} : \underline{I}) \underline{Q}_{ji} \cdot \underline{r}_{ji} + 2(\underline{Q}_{ji} : \underline{I}) \underline{Q}_{ji} \cdot \underline{r}_{ji} \\ & + 4(\underline{Q}_{ji} \cdot \underline{Q}_{ji} + \underline{Q}_{ji} \cdot \underline{Q}_{ji}) \cdot \underline{r}_{ji} + (\underline{Q}_{ji} : \underline{R}_{ji}) \underline{D}_j - (\underline{Q}_{ji} : \underline{R}_{ji}) \underline{D}_i \end{aligned} \quad (56)$$

$$\hat{\nabla}_i G_{ji}^4(\underline{r}_{ji}) = -2(\underline{Q}_{ji} : \underline{R}_{ji}) \underline{Q}_{ji} \cdot \underline{r}_{ji} - 2(\underline{Q}_{ji} : \underline{R}_{ji}) \underline{Q}_{ji} \cdot \underline{r}_{ji} \quad (57)$$

## 5 The Torque on a Multipole

The torque acting on a point multipole in a lattice of point multipoles is obtained by applying the torque operator (20) to the potential according to the prescription given in (19).

$$\begin{aligned} \underline{T}_i = & \frac{1}{V_o \epsilon_o} \sum_{\underline{k} \neq \underline{0}}^{\infty} A(\underline{k}) \sum_j^N \underline{F}_{ji}(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_{ji}) \\ & + \frac{1}{4\pi \epsilon_o} \sum_{\ell}^4 \sum_{j \neq i}^{\infty} B_{\ell}(r_{ji}) \underline{G}_{ji}^{\ell}(\underline{r}_{ji}). \end{aligned} \quad (58)$$

Where the scalar functions  $A(\underline{k})$  and  $B_{\ell}(u)$  are as above and  $\underline{F}_{ji}(\underline{k})$  and  $\underline{G}_{ji}^{\ell}(\underline{u})$  are now vector functions with the following forms:

$$\underline{F}_{ji}(\underline{k}) = (C_j - i\underline{k} \cdot \underline{D}_j \cdot \underline{Q}_j : \underline{K})(i\underline{k} \times \underline{D}_i - 2\underline{K} \times \underline{Q}_i) \quad (59)$$

$$\underline{G}_{ji}^1(\underline{r}_{ji}) = C_j (\underline{r}_{ji} \times \underline{D}_i) + \underline{D}_j \times \underline{D}_i \quad (60)$$

$$\begin{aligned} \underline{G}_{ji}^2(\underline{r}_{ji}) = & 2C_j \underline{R}_{ji} \times \underline{Q}_i - (\underline{D}_j \cdot \underline{r}_{ji}) \underline{r}_{ji} \times \underline{D}_i + 2\underline{\Delta}_{ji} \times \underline{Q}_i + 2\underline{\Delta}_{ji}^{\dagger} \times \underline{Q}_i \\ & - 2(\underline{Q}_j \cdot \underline{r}_{ji}) \times \underline{D}_i - (\underline{Q}_j : \underline{I}) \underline{r}_{ji} \times \underline{D}_i + 4\underline{Q}_j \times \underline{Q}_i \end{aligned} \quad (61)$$

$$\begin{aligned} \underline{G}_{ji}^3(\underline{r}_{ji}) = & (\underline{Q}_j : \underline{R}_{ji}) \underline{r}_{ji} \times \underline{D}_i - 2(\underline{D}_j \cdot \underline{r}_{ji}) \underline{R}_{ji} \times \underline{Q}_i - 2(\underline{Q}_j : \underline{D}) \underline{R}_{ji} \times \underline{Q}_i \\ & - 4\underline{\Theta}_{ji} \times \underline{Q}_i - 4\underline{\Theta}_{ji}^{\dagger} \times \underline{Q}_i \end{aligned} \quad (62)$$

$$\underline{G}_{ji}^4(\underline{r}_{ji}) = 2(\underline{Q}_j : \underline{R}_{ji}) \underline{R}_{ji} \times \underline{Q}_i, \quad (63)$$

in which the superscript † indicates a matrix transpose (which of course does not mean interchanging the indices  $i$  and  $j$ ).

## 6 Comments on Application

The application of the above formulae to molecular dynamics work is not trivial (though it is easier than the formulae may suggest!). I therefore offer the following comments to guide the would-be user.

1. These formulae are available in FORTRAN source form in the CCP5 program library. The subroutines EWALD1 and EWALD2 contain the code for the reciprocal-space and real-space parts respectively. Coding of the self-interaction correction is found in EWALD1. Also available is the molecular dynamics program MDMULP, which uses these routines to simulate rigid molecules.
2. The formulae above include the calculation of the torque on each multipole. This is appropriate if the multipole sits at the molecule centre of mass, but in practice this may not be the case. It is then required to translocate the effect of this torque from the site of the multipole to the centre of mass. A method for doing this is described in a CCP5 Newsletter article [4]. Alternatively, a shift theorem may be used to redefine the multipole at the centre of mass. This is the strategy adopted by the program MDMULP.
3. Correct use of the Ewald summation requires specification of the Ewald convergence parameter  $\xi$  and an appropriate cut-off in both real and reciprocal space. A simple, practical way of optimising these parameters is to take the starting configuration and proceed as follows:

- (a) Choose the real-space cutoff ( $r_{cut}$ ) compatible with the size of simulation cell,
- (b) Set a preliminary reciprocal space cut-off ( $k_{max} = 15 * 2\pi/L$ , say),
- (c) Calculate the potential energy of the system over a range of values of  $\xi$  in steps of about  $0.1\text{\AA}^{-1}$  until the potential energy shows signs of converging. (i.e. a plateau appears in the energy *vs.*  $\xi$  plot.) A single step MD run is sufficient for this.
- (d) Use the smallest value of  $\xi$  giving a converged result for subsequent simulations.
- (e) Try reducing the value of  $k_{max}$  as far as possible, without affecting the convergence. Use the smallest safe value for subsequent simulations.

This procedure will give a reasonably optimised set of parameters for the Ewald method. Beware that the starting configuration is reasonably representative of the simulation to be undertaken e.g. if a lattice is used to as the starting configuration, make sure the multipoles are randomly orientated.

4. Users of this method should note that the definition of the quadrupole in this article is based on the form

$$Q^{\alpha\beta} = \frac{1}{2} \sum_{k=1}^n q_k r_k^\alpha r_k^\beta. \quad (64)$$

This is not the form that is commonly encountered in the literature. The matrix  $\underline{Q}$  used here is, strictly speaking, the *second moment* of the charge distribution. The standard multipole  $\underline{\underline{Q}}$  can be obtained from  $\underline{Q}$  this via the relation:

$$Q^{\alpha\beta} = 3 Q^{\alpha\beta} - \delta_{\alpha\beta} Tr \underline{Q} \quad (65)$$

where  $Tr \underline{Q}$  is the sum of the diagonal elements of  $\underline{Q}$ . Matrix  $\underline{\underline{Q}}$  is the so-called *traceless* multipole. It is not possible to convert from  $\underline{\underline{Q}}$  to  $\underline{Q}$  unless the trace of  $\underline{Q}$  is known beforehand.

5. Finally, it is important to note that this method requires that the multipoles be defined with respect to the *laboratory frame* and as a result the multipole components change as the molecules rotate in space. Recalculation of the rotated multipole is accomplished using the standard rotation matrix. i.e. if

$$\underline{r}^o = \underline{R} \underline{r} \quad (66)$$

where  $\underline{r}^o$  is a vector in the body frame of reference,  $\underline{r}$  is the corresponding vector in the laboratory frame and  $\underline{R}$  is the rotation matrix, then:

$$\underline{D} = \underline{R}^\dagger \underline{D}^o \quad (67)$$

and

$$\underline{\underline{Q}} = \underline{R}^\dagger \underline{\underline{Q}}^o \underline{R}. \quad (68)$$

In these formulae the superscript  $^o$  indicates the body frame of reference and  $^\dagger$  indicates a matrix transpose.

## 7 Conclusion

The multipole Ewald summation in Cartesian form is derived using appropriate multipole operators, which act on the corresponding expression for a lattice of unit point charges. The forces and torques acting on a multipole are calculated in a similar manner. The self interaction correction is obtained by isolating the terms in real space which correspond to the classical multipole-multipole self interaction and removing the point-multipole contributions.

## Acknowledgement

The original version of this article owed much to the advice and encouragement of Professor Konrad Singer. I am pleased to have this opportunity to restate my continuing debt to him. I recall David Heyes and David Fincham also had useful things to say.

## Appendix: Properties of the $B_\ell(u)$ Functions

The lowest order  $B_\ell(u)$  functions is

$$B_0(u) = \frac{1}{u} \operatorname{erfc}(\xi u) \quad (69)$$

where

$$\operatorname{erfc}(\xi u) = \frac{2}{\sqrt{\pi}} \int_{\xi u}^{\infty} \exp(-s^2) ds. \quad (70)$$

It is convenient also to define the recursion relation

$$B_\ell(u) = \frac{1}{u^2} \left\{ (2\ell - 1) B_{\ell-1}(u) + \frac{(2\xi^2)^\ell}{\xi\sqrt{\pi}} \exp(-\xi^2 u^2) \right\}, \quad (71)$$

which is obtained for  $\ell > 0$  by repeated differentiation of  $B_0(u)$  with respect to  $u$ , as is easily proven by induction.

If the scalar variable  $u$  is defined to be

$$u = |r_j - r_g| = [(x_j - x_g)^2 + (y_j - y_g)^2 + (z_j - z_g)^2]^{1/2} \quad (72)$$

(in keeping with the rôle of  $u$  in the equations above), then it is easily shown that for  $r^\alpha, r^\beta = x, y, z$  etc.

$$\frac{\partial}{\partial r_g^\alpha} B_\ell(r_{jg}) = (r_j^\alpha - r_g^\alpha) B_{\ell+1}(r_{jg}) \quad (73)$$

$$\frac{\partial^2}{\partial r_g^\alpha \partial r_g^\beta} B_\ell(r_{jg}) = (r_j^\alpha - r_g^\alpha)(r_j^\beta - r_g^\beta) B_{\ell+2}(r_{jg}) - \delta_{\alpha\beta} B_{\ell+1}(r_{jg}) \quad (74)$$

From these results it follows that

$$\hat{\nabla} B_\ell(r_{jg}) = (r_j - r_g) B_{\ell+1}(r_{jg}) \quad (75)$$

$$\hat{\underline{\nabla}} B_\ell(r_{jg}) = \underline{R}_{jg} B_{\ell+2}(r_{jg}) - \underline{I} B_{\ell+1}(r_{jg}). \quad (76)$$

These relationships are used throughout the derivations above.

The expansion (46) used in the derivation of the self interaction energy is obtained using the following series expansions

$$\frac{1}{u} \operatorname{erfc}(\xi u) = \frac{1}{u} - \frac{2\xi}{\sqrt{\pi}} \left\{ 1 - \frac{(\xi u)^2}{3} + \frac{(\xi u)^4}{10} - \frac{(\xi u)^6}{42} + \frac{(\xi u)^8}{216} - \dots \right\} \quad (77)$$

$$\exp(\xi^2 u^2) = 1 - (\xi u)^2 + \frac{(\xi u)^4}{2} - \frac{(\xi u)^6}{6} + \frac{(\xi u)^8}{24} - \dots \quad (78)$$

which are obtained by direct differentiation using Maclaurin's formula.

Combining these expansions in the recursion relation (71) and collecting like powers in  $u$  allows the following expansions to be produced.

$$B_0(u) = \frac{1}{u} - \frac{2\xi}{\sqrt{\pi}} + O(u) \quad (79)$$

$$B_1(u) = \frac{1}{u^3} - \frac{4\xi^3}{3\sqrt{\pi}} + O(u) \quad (80)$$

$$B_2(u) = \frac{3}{u^5} - \frac{8\xi^5}{5\sqrt{\pi}} + O(u) \quad (81)$$

$$B_3(u) = \frac{15}{u^7} - \frac{16\xi^7}{7\sqrt{\pi}} + O(u) \quad (82)$$

$$B_4(u) = \frac{105}{u^9} - \frac{32\xi^9}{9\sqrt{\pi}} + O(u) \quad (83)$$

etc. Or in general

$$B_\ell(u) = \frac{(2\ell)!}{\ell!2^\ell u^{2\ell+1}} - \frac{(2\xi^2)^{\ell+1}}{(2\ell+1)\xi\sqrt{\pi}} + O_\ell(u) \quad (84)$$

where  $O(u)$  represents terms of ascending powers of  $u$  (i.e.  $u^n$  with  $n \geq 1$ ).

## References

- [1] W. Smith, CCP5 Information Quarterly, 4 (1982) 13.
- [2] C. Kittel, "Introduction to Solid State Physics", 6th Edition, Appendix B, p. 604, John Wiley and Sons Inc. New York 1986.
- [3] D.J. Adams and I.R. McDonald, Molec. Physics 32 (1976) 931.
- [4] W. Smith, CCP5 Information Quarterly, 41 (1994)

## Recent additions to the links on the CCP5 WWW pages

M. Leslie

The CCP5 WWW pages have a page which contains a list of links to the research pages of other members of CCP5. Links are added to this list when new members register, or when a speaker is invited to give a talk at one of CCP5's meetings. Relevant links will also be added on request to the CCP5 secretary at the above address. The URL for the page is <http://www.dl.ac.uk/CCP/CCP5/links.html> I have given below a list of links I have added recently together with a line indicating the nature of the research. I have not included the URL's of the pages as these may be more easily found from the CCP5 Web page given above.

Professor David Srolovitz    Department of Materials Science and Engineering  
University of Michigan

Research studies center on defects in crystals and the formation and evolution of microstructure and morphology.

Roger Smith                    Department of Mathematical Sciences  
Loughborough University

Materials modelling, particularly of semi-conductor processing and nanotechnology; fullerenes; continuum and cellular models of surface propagation; particle ejection from ion-bombarded surfaces; modelling weld phenomena; molecular Dynamics simulations of metals, polymers and covalent materials; global optimisation of molecular structures.

Tuck Choy                      Department of Physics  
Monash University

Research Areas: Theoretical Condensed Matter Physics Worked on Superconductivity, Statistical Mechanics, Hubbard Models, Semiconductors, Porous Silicon, STM, Many - Body Theory, Positron Annihilation and Microwave Absorption.

Condensed Matter The-    Institute of Physics  
ory Group                    Johannes Gutenberg-University Mainz

Statistical thermodynamics of solids and liquids. Starting from atomistic descriptions, cooperative phenomena in thermal equilibrium are investigated, for instance phase transitions and critical phenomena. But also phenomena and/or processes out of equilibrium are studied.

Dr. Peter Gumbsch            Max-Planck Institut für Metallforschung,  
D-70174 Stuttgart, Germany.

Dislocations Faster than the Speed of Sound; Application of DDD to thin film plasticity; Finite Element - Atomistic Coupling; Lattice Trapping of Fracture Cracks; Directional Anisotropy in Cleavage Fracture ; MD Simulation of Dynamic Fracture Processes; Debye-Waller Factors of NiAl.

Professor A.D.MacKerell    Department of Pharmaceutical Science,  
University of Maryland,

Active areas of research include the development of parameters for empirical force field calculations of molecules of biological and pharmaceutical interest and the application of theoretical approaches towards the elucidation of biochemical mechanisms and the rational design of drugs.

Dr J A Anwar                    Department of Pharmacy  
King's College London

Computer simulation of molecular systems; Crystallisation and crystal engineering; Polymorphism and polymorphic phase transformations; Solid state chemistry; X-ray and Neutron diffraction.

Prof. Paul Madden            Physical and Theoretical Chemistry Laboratory,  
University of Oxford

Recent publications include

“Covalent” effects in “ionic” systems. *Chem. Soc. Reviews* 25, 339 (1997)

Polarization effects, network dynamics and the infrared spectrum of amorphous SiO<sub>2</sub> *Phys. Rev. Letters* 77, 4023 (1996).

Cluster formation in sodium-doped zeolite-Y. *J. Phys. Chem.* 99, 6697 (1995).

Peter Ahlström            Materials and surface physics group,  
Applied Physics,  
School of Physics and Engineering Physics  
Chalmers University of Technology and Göteborg University.

Computer simulations at the border between physics and chemistry, especially concerning phenomena at surfaces and interfaces. Calculation of vibrational spectra and other properties of oligomers and polymers of propylene oxide via MD simulations. Modelling of water (ice) adsorbates on platinum. Studies on pressure calculation in molecular simulations.

Grant D. Smith            Department of Materials Science & Engineering  
University of Utah  
Department of Chemical & Fuels Engineering  
University of Utah

Research in the group is concerned with elucidating property/structure relationships in soft condensed matter, with particular emphasis on polymer structure and dynamics. Modeling and experimental methods are used to study static and dynamic properties of polymer melts and glasses, polymer interfaces, and polymers in aqueous solution.

Carol K. Hall            Department of Chemical Engineering  
North Carolina State University.

Areas of interest: Molecular thermodynamics and computer simulation, equations of state, polymer modeling, bioseparations, protein folding.

Julia Yeomans            Statistical Mechanics and Soft Condensed Matter  
Oxford Theoretical Physics

The systems studied include miscible and immiscible binary and ternary fluids, amphiphilic systems, polymer solutions and colloidal suspensions.

Alexander Lyubartsev    Division of Physical Chemistry  
Arrhenius Laboratory  
Stockholm University

Computer simulations of various molecular systems and development of new methods of computer simulations.

Juan Jose Freire            Departamento de Química Física  
Facultad de Ciencias Químicas  
Universidad Complutense  
Madrid, Spain

Recent publications include

"Tricritical Behavior of an Off-lattice Flexible Polymer Model: Monte Carlo Calculations of Second Virial Coefficients" A. M. Rubio and J. J. Freire. *J. Chem Phys.* 106, 5638 (1997).

"Determination of the Potential Parameters of a Site Model from Calculations of Second Virial Coefficients of Linear and Branched Alkanes" A. Poncela, A. M. Rubio and J. J. Freire. *Molcc. Phys.* 91, 189 (1997).

"Numerical Simulation of the Scatterig Form Factor of Star Polymers" L. A. Molina, A. Rey and J. J. Freire. *Comp. and Theor. Polymer Science* 7, 243 (1997).

"Numerical Study of Scattering from Chains Composed of Two Nonsegreegated Labeled Blocks in an Athermal Solvent: Effects of Compositional Heterogeneity" L. A. Molina and J. J. Freire. *J. Chem. Phys.* 109, 2904 (1998).

Dr Peter Styring                      Lecturer in Organic Chemistry  
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Liquid Crystals: Ferroelectrics and Electroclitics; Functional Liquid Crystal Polymers; Metal-containing Liquid Crystals; Physical Effects of Chirality in Liquid Crystals

Computational Chemistry: Computer-aided Simulations; Structure-Property Effects; Force Field Development and Parameterisation; Computer-Aided Learning (CAL)

Drug Design: HIV Inhibitors; Anti-diabetics; Computer-aided Drug Design by Drug-Receptor / Active Site Simulations

Martin Dove                          Department of Earth Sciences  
Univesity of Cambridge

Research interests are in the general area of phase transitions, particularly those found in minerals and ceramics, including rigid unit mode analysis of displacive phase transitions in silicates, low-energy excitations in silicate glasses, experimental and theoretical, order/disorder phenomena in minerals.

Keith M Beardmore and      Theoretical Division.  
Niels Grønbech Jensen.      Los Alamos National Laboratory.

Homepage of the REED implant modeling code. This is a molecular dynamics based code, designed to calculate the depth concentration profile of implanted dopants in crystalline silicon.

Thomas Kraska                      Institut für Physikalische Chemie  
Universität zu Köln

Global Phase Diagrams.

## Book Review

W. Smith

### **An Introduction to Computer Simulation Methods: Applications to Physical Systems (2nd. Edition)**

Harvey Gould and Jan Tobochnik  
Addison Wesley 1996, Massachusetts USA. (ISBN 0-201-50604-1)

I reviewed the first edition of this book in 1986, when I welcomed it as a valuable addition to the teaching of computational science. I am happy to report that the second edition continues the tradition. Though there have been significant changes, the basic philosophy of the book remains the same. It manages to combine the fun of computational physics with some valuable lessons.

What has changed? Firstly, the two volumes of the first edition have been combined into one, unifying the theme somewhat. Secondly, the text has been expanded and a useful new chapter on random processes has been added. The authors continue to present code in the form of True BASIC, which is probably a sound decision given the universal availability of BASIC, though it is emphasised that the programs are designed to be read and understood, as much as to be executed. (Readers are warned that the exercises involve adaptation and modification of the programs.) For readers addicted to FORTRAN and C, detailed advice on code conversion is provided in appendices. For those not addicted to typing, the code is available over the World Wide Web.

The scope of the book is much the same as before. Starting from simple physical problems (e.g. Newton's law of cooling) the book progresses through one dimensional motion, the two body problem, harmonic motion, chaotic systems, probability distributions, molecular dynamics, wave motion, electrodynamics, Monte Carlo methods, percolation, fractals, complexity, the microcanonical and canonical ensembles, and quantum systems. This is a wide perspective, but the authors strive to unify concepts by pointing out the similarities in the underlying equations. The text is not highly mathematical. The method of choice for solving many of the differential equations appearing in the book, is Euler's algorithm, but here and there throughout the text one encounters more familiar algorithms, where their relative merits are discussed. There is more emphasis on graphical presentation than in the previous edition, though at an elementary level.

Given the broad sweep of the subject matter it is inevitable that the topics are not dealt with at great length or to a great depth. One is not likely to become an instant expert in any of the areas the book deals with. But one should not dismiss the book lightly; it is well supplied with references and would form a very valuable teaching aid to any undergraduate course. It is richly supplied with exercises that will deepen understanding and stimulate new questions for further study. Its great strength is that it is soundly based in the philosophy that physics is best learned by experimentation, and the computer is one of the best experimental tools available. Good computational practice and an understanding of the techniques employed are essential disciplines on the road of discovery. The prize is new insight into physical systems. I like the fact that one can make valuable headway into a new subject area from a standing start and I would be tempted to look first in this book if I were confronted with an unfamiliar computational challenge.

## Molecular Modelling and Neutron Scattering Workshop: Techniques for Large-scale Systems

W. Smith and B. Gabrys

This workshop sought to bring together two distinct groups of researchers with much in common but hitherto had not interacted particularly strongly. With the growing complexity of the systems in which both groups are currently interested, not least systems of increasing length scale, the time was ripe for a meeting of minds. It was hoped by the organisers that the experimentalists would leave the workshop better informed about the capabilities of molecular simulation, while the simulators would better appreciate the difficulties experimentalists face in interpreting the results of neutron scattering experiments. The meeting was sponsored by CCP5, the Institute of Physics and ISIS (the UK neutron scattering facility at Rutherford Appleton Laboratory) and took place in the pleasant surroundings of Cosener's House in Abingdon. The meeting was well attended by over fifty scientists from both academia and industry.

The first speaker was Prof. Dominic Tildesley (Imperial College), who described the molecular dynamics simulation of various air/water/oil/surfactant interfaces. Simulations of the air/water interface employed the SPC (simple point charge) model for the water molecule. A 2D periodic "slab" provided an acceptable description of the density profile, showing oscillatory behaviour near the interface at 277K (though capillary waves are dampened by the periodic boundary condition). The pressure tensor at the surface was very similar in 500 and 100 molecule simulations. The orientation of the water molecules at the surface was also investigated and attempts were made to reproduce the laser induced second harmonic generation. The results showed that water above and below the Gibbs dividing surface adopt slightly different orientations resulting in a switch of dipolar field on passing through the surface. The difficulty of interpreting the experimental result without the information gained through simulation was emphasised.

Simulations of phenol at the air-water interface showed that the orientation of phenol at the surface was unaffected by the degree of coverage, implying a dominance of the water-phenol interaction over the phenol-phenol interaction. The phenol was also observed to disrupt the structure of the water surface, changing the water dipole orientations at the surface significantly. Experimental confirmation of these observations was available from laser reflectometry.

Simulations were also undertaken to determine the microscopic origin of friction in the fabric softener dioctadecyl dimethyl ammonium chloride (DODAB). In these experiments DODAB molecules, arranged in layers attached to opposing surfaces, were slid past each other at the relatively high speed of 100 m/s (1 Å/ps) under a normal stress of 300Mpa and the friction coefficient calculated. It was observed that: the friction decreased with increasing normal force; increased with decreasing DODAB density; decreased with decreasing sliding velocity; and decreased with decreasing chain length. Some of these results were unexpected, and possible explanations were offered. For example decrease in friction with decreasing chain length may indicate the importance of the underlying surface roughness in experimental determinations of friction.

The final example of interface simulation presented was ongoing work of the DODAB/hexane interface to explore the penetration of oil into the DODAB matrix. Preliminary results showed that the hexane bulk was well accounted for and that the hexane molecules showed a tendency to align with the DODAB molecules as they penetrate the surfactant. The longer term objective was to reproduce the neutron reflectometry data for this system.

Prof. R.W. Richards (University of Durham) spoke on the subject of coarse-grain problems and asked "is there a fine grained solution?". Seeking to bridge the gap between atomistic descriptions

of polymers and the large scale, Prof. Richards described a number of experimental studies in which the current theoretical models failed to provide adequate assistance.

Beginning with small angle scattering, the assumption of a Gaussian mass distribution for polymer chains leads to the Debye equation from which the radius of gyration of the polymer may be extracted. However in the case of syndiotactic polymethyl methacrylate (PMMA or perspex) the small angle x-ray scattering (SAXS) data is inconsistent with the Debye equation. The rotational isomeric state (RIS) model, which incorporates local conformations of the chains, gives a better description, indicating the importance of local structure. However neutron scattering experiments on a related polymer (PLMA), reveal that the main chain is consistent with a Gaussian model. There are also problems with describing the proportion of cis and trans conformations in such chains. Another problem in small angle scattering work was the verification of the stretching of the "arm" chains of star polymers, which is predicted theoretically. It proves to be extremely difficult to separate out the radius of gyration of a single arm without making additional assumptions.

Moving on to discuss polymers at fluid interfaces, modelling such systems was said to be in its infancy. The example presented was PMMA, with polyethylene oxide (PEO) grafts, at the air/water interface. These systems are studied by neutron reflectometry. The simplest models are used to account for experimental results. A two layer model appears to be adequate for low and intermediate surface concentrations and a three layer model is needed for high surface concentrations; the inference being that the polymer loops out of the surface with increasing concentration. However some important questions remain. It is unclear if the grafts are stretched or if they are at the excluded volume limit. Also of interest is the "wet brush" situation, where the theoretical scaling law for the brush height with surface concentration is only weakly confirmed by experiment. With regard to the dynamics of polymers at interfaces, the phenomenology is dominated by capillary waves of the order 30 to 1000 micrometres wavelength, which strongly scatter light. The capillary waves and dilational waves of the polymers at the surface represent coupled "lossy" oscillators. Light scattering experiments yield both dielectric and visco-elastic properties of the interface. However, the interpretation of these results is fraught with difficulty. The surface tension is obtained reasonably accurately, but observed resonances do not behave in the classical manner (the characteristic signals seen in the real and imaginary parts of resonances are not seen at the same frequency.) There is no satisfactory explanation for the dilational modulus or the dilational viscosity, for example and an unknown velocity coupling seems to be responsible.

In conclusion, it was stated that while the RIS model worked for homopolymers, it was not suitable for complex systems, where the random phase approximation was more successful if lacking in fine detail. For interfaces, scaling laws and self consistent field models provide some explanation, but a deep theoretical understanding, particularly of dynamic phenomena is absent. There thus appears to be no fine grained solution as yet, but one is certainly required.

Dr G. Kneller (Aachen) sought to show how molecular dynamics (MD) simulation can be used to assist with the interpretation of neutron scattering experiments, with reference to some specific systems. The first example presented was myoglobin, which at temperatures below the glass transition shows a characteristic motion which is detectable by elastic neutron scattering experiments and is generally assigned to the "jump" rotational motion of methyl groups, since the corresponding jump distance accords with the 1.5 Å observed. However at the temperature concerned (< 200 K), there is unlikely to be sufficient thermal energy to account for the jump transition. It was shown how, in MD simulations, it is possible to isolate particular motions in a complex molecule - a video was shown of the motion of myoglobin with and without main chain motion. Computation of the elastic incoherent structure factor with these motions extracted revealed that the observed neutron scattering results could equally well be explained by liquid-like

motion of the side chains, thus avoiding the jump model.

In a second example, MD simulation of crystalline polyacetylene was able to reproduce the frequency spectrum for the molecular motion, which compared well with experiment. The characteristic motion was shown to be rigid-body-like motion of the chains. The simulations incorporated the instrument resolution function and corrections for bending of the chains. The final example showed how constant pressure MD was used to examine the internal and global chain motion of alkyl chains in a matrix of TANO molecules ( $C_9H_{16}NO_2$ ). The features of the inelastic structure factors were accounted for and shown to be due to translational motions of the chains. The angular distributions of the  $CH_2$  groups revealed the stiffness of the chains.

Dr. T. Cosgrove (Bristol) explained how statistical mechanical models of polymer chains may be used to account for the experimental properties of real polymers. Beginning with the adsorption of chains on a surface it was shown that for small chains the free energy could be determined by "counting" the possible configurations on a cubic lattice (the self avoiding walk or SAW). By such methods it was possible to determine the value of the interaction parameter (the Flory surface parameter) for which adsorption at a surface occurs. For larger systems, Monte Carlo simulation (which introduces importance sampling) is used, which avoids the need to count all the possible configurations. The self consistent field theory (Scheutjens-Fleer model) may be used to calculate the adsorption isotherms. The form of chains attached to a surface may be described by the terms "pancake", "mushroom", "block" or "parabola" according to their appearance and represent subtle differences in behaviour.

Polymers at surfaces are studied by small angle neutron scattering. In general all components of the system contribute to the resulting scattering, though the different components can be extracted by modelling. An example system shown was the PEO chain at the water surface, the volume fraction profile was adequately described by a Gaussian model. Such models work well for single polymers, but not for mixtures or block copolymers, though in these cases it may be possible to obtain a fit to experimental data by adjusting the basic parameters. However it remains difficult to deal with very large chains. Some outstanding challenges of these methods are: the effects of surface heterogeneity (the models assume perfect surfaces); surface charges and their effects; competitive adsorption; surface micellisation; the dynamics of chains; and the influence of head groups.

Dr D. Heyes (Surrey) provided an overview of molecular modelling techniques (principally MD) that have potential in modelling large scale structures. Large structures are characterised by large molecules and long relaxation times and include liquid crystals, colloids, polymers and Langmuir-Blodgett films. They can be monodisperse systems such as polystyrene latexes or polydisperse, such as colloids or clays, with a range of particle shapes as well as sizes. They may have chemical engineering interest, for example suspensions, damp powders and granular materials.

Conventional simulation methods can be extended to deal with such systems. Dr Heyes described such extensions, beginning with the smaller scale: clusters of atoms to represent colloidal particles, with a stochastic (collisional) solvent, where it is possible to examine the structure of the colloids and surrounding fluid, and dynamical properties such as velocity autocorrelation and orientational correlations. As an example of more detailed modelling, overbased detergents used in the petroleum industry to neutralise acidic combustion products were described. These are calcium carbonate nanoparticles with a surfactant "coat" to assist dissolution in oil. MD studies have addressed the nanoparticle structure and the adsorption of the surfactant.

On larger length scales the timescale becomes a limiting factor for full MD studies. The system relaxation times grow rapidly with system size. The strategy must then be to design interaction models that retain the essential physics on the length scale of interest, but abandon the microscopic

complexity. As an example, the use of a simple "dumbbell" model of a surfactant in mixtures of spherical solvent molecules is able to show both discontinuous phases and micelles with a simple change in dumbbell particle sizes. Dr Heyes concluded with a description of Brownian dynamics, which allows the effects of a solvent to be modelled, without the molecular detail. The normal deterministic motion of the particles is augmented by random forces and balanced drag forces (Ermak's algorithm). Such models have been used to model viscoelastic phenomena in colloidal systems and give the correct stretched exponential form for the correlation functions.

The final speaker was Dr D.J. Barlow (King's College, London) who spoke about structure determination and modelling of surfactant aggregates. The interest here was pharmaceutical: surfactant vesicles encapsulating the active ingredients of pharmaceutical preparations have many advantages for storage and drug delivery. It is important to be able to design surfactants with the right characteristics, but to date a purely modelling approach is not capable enough. Neutron reflectometry studies of the surfactant structure at an interface offers some evidence of the ability of the surfactant to form vesicles, though this does not rule out them forming unwanted micelles.

Dr Barlow described methods for modelling reflectometry experiments using the optical matrix method. The results may be augmented by Langmuir trough experiments to obtain a broader understanding of the surfactant behaviour. However, while these experiments may show that a monolayer of surfactant cannot form a vesicle, a vesicle may be formed from a multilayer of surfactant molecules. Small angle neutron scattering can be used to examine the surface structure of vesicles directly and it is possible to correlate vesicle thickness with surfactant molecular characteristics such as molecular weight, although no clear pattern has emerged from this. Isotopic substitution (selective deuteration) offers deeper insight into the surface structure, though the modelling of this is not particularly advanced. A program (SURFISS) has been developed to model the structure of surfactant monolayers and is yielding useful insights. Dr Barlow argued in favour of the greater availability of intelligent software to model surfactant systems, allowing greater ease in building the model system from a prescribed molecular structure.

The final event of the meeting was an open discussion chaired by Dr Jeff Penfold (RAL). In summarising the workshop he noted the great demand for reliable methods of scaling models up from atomistic to the mesoscale and larger, and the great complexity of the systems of interest. There was a strong need for more predictive capability in modelling polymers at interfaces, though the best way to feed in the chemical detail was unclear. An obvious role for simulation was to assist with the analysis of experiments, for example the detailed structure revealed by selective deuteration experiments.

In the subsequent discussion there was clear recognition that the time was ripe for closer collaboration between experimentalists and molecular modellers, particularly for mesoscale systems and small angle neutron scattering work. A role for CCP5 in developing suitable software was suggested, for which a project in modelling interfaces would be a suitable focus. With regard to computational methods, a role for reverse Monte Carlo methods was suggested as well as more conventional molecular dynamics (typified by the CCP5 simulation code DL-POLY) to assist with elastic and inelastic scattering work. A role for graphics based support software was also recommended.

## Report of the visit by Juerg Hutter

(Max-Planck-Institut fuer Festkoerperforschung Stuttgart)

### Visit of Juerg Hutter to Queen's University, Belfast

Mike Finnis. Belfast

We were interested in advances made by Juerg and the Stuttgart group led by M. Parrinello who work mainly on *ab initio* molecular dynamics. Juerg presented a talk entitled "Gaussian basis sets in large scale condensed matter simulation". This was of technical interest, representing an attempt to develop an *ab initio* code for MD which scales linearly (an "O(N)" method) with the number of atoms. It is a departure from the use of plane-waves as a basis, which has been a characteristic of the Car-Parrinello MD used in Stuttgart up to now. It seems too soon to judge if it will be successful. There are other efforts in this direction, e.g. in Mike Gillan's group at Keele, using an entirely different approach, which appear to be at least as promising. At present, however, the ("O(N<sup>3</sup>)") methods are still ahead of the game for routine applications. Juerg is also intimately acquainted with the code we use at Queen's, called FEMD, because he designed and wrote much of the CPMD package within which it now runs. His technical expertise was extremely useful in helping us to improve this code. Together with Ali Alavi, they implemented a block version of the Lanczos diagonalisation method used in FEMD. This change resulted in a greatly improved code, largely because of reducing data movement during execution. Depending on the machine and size of problem, speedups of factors of 2 to 5 have been obtained. This new code is now routinely used in our work.

### Visit of Juerg Hutter to University College London

Andrew Fisher. UCL London

The CCP5-sponsored visit of Juerg Hutter to UCL took place on 30 April 1998. He spent the day in the Condensed Matter and Materials Physics Group and gave a seminar entitled "Large-scale condensed matter calculations with Gaussian basis sets", which was attended by colleagues from the Royal Institution, Imperial College, Oxford and Keele Universities as well as members of the UCL group.

Dr Hutter described his work on applying Gaussian basis sets to *ab initio* calculations using density functional theory. This research was of great interest to the UK groups present, and after his seminar there were extended discussions with Professor M. J. Gillan and his group (Keele, now at UCL, with interests in O(N) calculations using other localized basis sets); with Dr I. Oleinik (Oxford, with interests in modelling of oxides); with Dr A. L. Shluger and his group (interests in modelling processes in oxides and in developing "embedding" codes using localized orbitals); and with Dr A. J. Fisher and his group (interests in excitations and transport theory). Dr Hutter remained at UCL until the evening, when he left for Cambridge.

This was a valuable visit which brought us up to date with work which is relevant both for fundamental developments in computational algorithms, and for many applications of interest to the UK computational physics community.

### Visit of Juerg Hutter to Cambridge

Mike Payne TCM Cambridge

Dr. Hutter's visit to Cambridge was marked by a power cut across most of Cambridge ten minutes before his seminar was supposed to begin. While this would have reduced most speakers to blithering wrecks, Dr. Hutter proceeded to give a blackboard (in blackened room, as the weather was so dull) version of his talk which amazingly managed to convey most of the ideas and methodology of his new computational scheme for performing large scale calculations using Gaussian basis sets. Dr. Hutter managed to speak to a number of people in both the Physics and Chemistry Departments in Cambridge and his 'black in black' seminar attracted a good number of people from Chemistry which is pretty unusual given the vast, in Cambridge terms, distance between the departments. Dr. Hutter's seminar finished just in time for our regular Friday afternoon drinks in the Theory of Condensed Matter Group.

### Visit of Juerg Hutter to Exeter

Bob Jones Exeter

Juerg Hutter arrived at Exeter on Monday 4 May and gave a talk to the Theoretical Physics Group on May 5 entitled "Large scale condensed matter calculations with Gaussian basis sets".

These basis sets are also used by the Exeter group of Dr. Jones but primarily in cluster calculations. Dr. Shrivastava's group, who use supercell methods, also attended the talk. He then held detailed discussions with both groups where discussion focussed on the pseudo-potentials and techniques that he uses to perform these large scale supercell calculations and the problems in implementing  $O(N)$  techniques. He left in the afternoon of May 5.

Altogether, the visit was a useful one especially in getting access to the pseudo-potentials used by the MPI group.

## Report on CCP5 Sponsored Visit to the United Kingdom (June 22 - 30 1998)

S. Melchionna, University of Rome.

My tour of UK Universities has been through Cambridge, Bristol and Daresbury Laboratory.

In Cambridge I have been in touch mostly with the group of Prof. J.-P.Hansen in the Chemistry Department. We have discussed about current issues in the classical density functional treatment of charged systems, which he has been studying for some years. Interesting insights and possibilities for collaboration on biophysical systems have emerged. In view of my permanence in Cambridge in his group starting next September, we have discussed a research project about the influence of electrostatics in structural and kinetic properties of ionic channels. Discussions with post-doctoral students of that group, namely with Dr. David Goulding and Dr. Ard Luiss, who are involved in projects concerning electrostatics and statistical properties of polymers, have been a very useful source of scientific sharings. I have discussed also with Prof. Michiel Sprik, who is working on ab-initio simulations of molecules and who is interested in efficient sampling and detection of intermediate states of chemically reactive systems. A possible collaboration is in view on some specific reactive systems. In the chemistry department I have given a talk on some recent results on the glass-like transition of proteins, as revealed by molecular dynamics studies. Subsequent feed-back with the audience has been a very useful occasion to discuss on this issue.

In Bristol I have been hosted by Prof. M. Allen of the Physics Department. Prof. Allen's main interest is in liquid crystals. Although our research fields are different he has a long experience in molecular dynamics simulation techniques. Conversations on recent developments in this field have been very interesting. Also our meeting has been the occasion to share scientific software. I have also discussed with a post-doctoral student of his group, Dr. Guido Germano, on recent advances in liquid crystals and molecular dynamics. In Bristol a very useful discussion has been with Prof. G. W. Neilson, and we have shared some results on biological systems, as he has recently performed neutron scattering experiments on polypeptides. The talk in Bristol, regarding the same subject as in Cambridge, has been an important source of discussion and insights.

In Daresbury I have been hosted by Dr. W.Smith and I had a very fruitful discussion on molecular dynamics, both as a technique and applications to complex systems. The future of the MD codes that we are developing independently (DL-POLY and DL-PROTEIN) has been discussed and loosely planned. Sharing of software of this kind has also been very important. In Daresbury I had important discussions with Dr. Nic Harrison, about ab-initio simulation of systems in the crystal phase, with Dr. Phil Lindan, on simulation of systems modeled with dynamic polarizability, and briefly with Dr. Maurice Leslie. I am very grateful to Dr. James Nicholson for an instructive tour of the Synchrotron.

The sponsorship of CCP5 is gratefully acknowledged.

## CCP5 Annual Meeting 1997

## Materials, Microstructures and Simulation

## Lecture Abstracts

**Metal oxides containing  $d$  and  $f$  electrons: a new challenge in surface science**

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Many of the transition metal oxides (i.e. oxide materials where metal ions contain  $d$ -electrons) exhibit high catalytic activity and are widely used in industrial applications. A recent discovery of the possibility of using  $U_3O_8$  for the catalytic destruction of a range of environment pollutants has stimulated research aimed at investigating the connection between the catalytic activity of transition metal and actinide oxides and the electronic structures of their surfaces. It was shown experimentally at the Department of Materials, University of Oxford, that many of the oxide materials, which are room temperature insulators, can be imaged in a scanning tunnelling microscope at an elevated temperature [1]. Theoretical study of electronic structure and STM images [2],[3] based on the LSDA+U approach have led to the conclusion that strong  $d$ - $d$  and  $f$ - $f$  electron correlations are responsible for unusual electronic properties of a number of transition metal and actinide oxides. The contents of the talk will cover both experimental and theoretical aspects of this work.

**References**

- [1] M. R. Castell, P. L. Wincott, N. G. Condon, C. Muggelberg, G. Thornton, S. L. Dudarev, A. P. Sutton and G. A. D. Briggs, *Phys. Rev.* **B55** (1997) 7859
- [2] S. L. Dudarev, D. Nguyen Manh and A. P. Sutton, *Philos. Mag.* **B75** (1997) 613
- [3] S. L. Dudarev, A. I. Liechtenstein, M. R. Castell, G. A. D. Briggs and A. P. Sutton *Phys. Rev.* **B** (1997) in press

**Temperature Dependence of Surface Energies of Oxides**

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Virtually all calculations of the surface energies of ionic crystals have been restricted to the static limit. Here we present results for the energies of different surfaces of a range of oxides over a wide range of temperature, calculated by direct minimisation of the free energy via quasiharmonic lattice dynamics. The use of lattice dynamics is particularly useful below the Debye temperature where classical Monte Carlo and molecular dynamics fail due to neglect of quantum effects.

## Molecular Dynamics Simulation of Metallic Zirconium

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Molecular dynamics simulations using a many-body potential for metallic zirconium are presented. The high temperature phase of this material is body centred cubic, which has a phase transition to hexagonal close packed via a softening of an N-point phonon coupled to a tetragonal shear. Softening of another zone boundary phonon corresponding to the  $\omega$  phase is also observed. At the transition, twins of hcp material are formed to absorb the transformation strain, their orientation corresponding to the parent bcc structure. Eventually, a laminated microstructure evolves.

## Cohesive Energies and Order-Disorder Transitions in Alloys

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This talk reports a range of Monte Carlo studies of the order-disorder transition in Cu-Au. Results for heat capacities and lattice parameters are reported. An approximate, parameterised Hamiltonian is not used. The Monte Carlo steps include both trial displacements of the atoms and trial interchanges of Cu and Au atoms. Calculations with and without interchanges allow us to determine the difference in the heat capacities of the ordered and disordered states. We are able to explain the tetragonal distortion of ordered CuAu, which is not possible using a mean-field approach.

## Self-lubrication in Scanning Force Microscope Image Formation on Ionic Surfaces

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The mechanisms of and conditions required for true atomic resolution remain the focus of Scanning Force Microscopy (SFM). We present a theoretical model of SFM using a molecular dynamics method for the calculation of the interaction between a crystalline sample and a tip nanoasperity, combined with a semiempirical treatment of the mesoscopic van der Waals attraction between tip and surface, and the macroscopic parameter of cantilever deflection. The main features of the SFM experiment were modelled, including force vs. distance curves at various tip positions on the surface, and scanning of a perfect LiF surface in contact regime with repulsive force of 1 - 2 nN. It is shown that tip contamination due to adhesion to the surface atoms may promote periodic SFM imaging, if the adsorbed surface material makes stable structures on the tip. We demonstrate that the adsorbed cluster can adjust itself to conditions of scanning by exchanging atoms with the surface and changing its structure. We believe that this dynamic "self-organisation" of the surface material on the tip during scanning could be a general effect which may explain why periodic surface images are often obtained using a variety of tips and large tip loads. We discuss the implications

of these results with respect to friction between tips and surfaces and the possibility to observe point defects at ionic surfaces with atomic resolution.

## Molecular Dynamics Simulation of the Crystalline Phases of Polyethylene

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Crystalline polyethylene is being studied at a range of temperatures and pressures using molecular dynamics (MD) and x-ray diffraction. The long term aim of the project is to study a proposed transient mobile phase of crystalline polyethylene that may occur under ambient conditions, as part of the process of crystal growth. To establish the required background for this study, the ambient orthorhombic structure and the high pressure pseudo-hexagonal (or "rotator") phase are being investigated using MD techniques, supported by data from x-ray diffraction. Preliminary simulations have been carried out for small systems, of  $2 \times 3 \times 12$  and  $2 \times 3 \times 24$  unit cells, of crystalline polyethylene using periodic boundary conditions (PBC) and infinite chains. Larger simulations, of  $3 \times 5 \times 48$  unit cells, also with PBC but with finite chains, allowing the formation of *gauche* defects and a fuller range of motion, are in progress. Data will be presented for the unit cell parameters, chain dynamics and chain conformations. This will be compared to the available experimental results for a range of temperatures at ambient pressure. Initial simulations of the high pressure mobile phases will also be discussed.

## Young's modulus for individual carbon nanotubes and a monoatomic graphite sheet: comparing theory to observations.

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A simple theory presented demonstrates how Young's modulus of an individual carbon nanotube depends on characteristics of the interatomic interaction, the external and internal radii of a tube, and on the energy expense of bending a graphitic sheet into a seamless cylinder. The theory qualitatively reproduces the first direct measurements of Young's modulus for 11 individual carbon nanotubes published recently [1]. The extreme stiffness of single walled and thick tubules relates mainly to the absence of defects in a perfect graphitic network. The Young's modulus of perfect tubules is very close to that for defectless graphitic monolayer. The theory also predicts that multilayered defectless tubes might have the Young's modulus in a range of several terapascals.

## References

- [1] Treacy, M. M. J., Ebbesen, T. W. and Gibson, J. M. *Nature*, **381**, 678-680, (1996)

## Misfit strains simulation in heterostructures: HTSC and semiconductors

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The misfit strains is one of the dislocation reasons, which leads to physical features degradation of heterostructures and, sometimes, to destruction of a film. Thus, investigation of formation of the misfit strains is a quite an important research objective.

An approach to simulation of the misfit strains is based on the information on tension module (Young modulus and Poisson ratio) and variation of crystal lattice parameter **A** in the intermediate layer.

A number of ultrasound measurements has been performed to calculate a variation of tension module in HTSC and in  $A^{2(4)}B^6$  semiconductor heterostructures. Electronic spectroscopy has been used to determine the variation of **A**. Three-dimension pictures of the misfit strains were obtained for  $A^{2(4)}B^6$  films, and isotropic approximation has been used to obtain a two-dimension plot of the misfit strains in HTSC ones. These computer simulations can be used for quality control of heterostructures.

We are comparing two reasons that cause dislocation: misfit strains and discrepancy of heat expansion coefficient. We have identified that even for films and layers which are in close agreement in the **A** parameter, the misfit strains dominate over second mechanism due to interdiffusion of the chemical elements.

Keywords: heterostructure, misfit strains, computer simulation, ultrasound, tension module.

## CVD Diamond: From Atomistics to Microstructure

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Diamond films are routinely grown via chemical vapor deposition (CVD) techniques in which a precursor gas containing a small amount of hydrocarbon (usually  $CH_4$ ) in  $H_2$  is heated by a hot filament, microwaves, or DC arc jet, dissociating some of the  $H_2$  into atomic H and creating many different hydrocarbon. Atomic H helps stabilize the diamond phase by terminating the diamond lattice with C-H bonds (i.e., passivating the surface), converting  $sp^2$ -bonded C into  $sp^3$ -bonded diamond, and etching  $sp^2$ -bonded C from the surface. We present an atomic-scale, kinetic Monte Carlo model of diamond growth that includes a wide range of surface chemical reactions and allows us to simulate in excess of  $10^9$  reaction events corresponding to reactor times of up to one hour and hundreds of  $10^4$  atom monolayers. We employ this method to predict diamond growth rate as a function of surface crystallographic orientation, gas phase composition and temperature, in excellent agreement with experiment. The resultant structures are analyzed to understand nucleation and growth on the surface, surface roughness and faceting. Using these growth rates determined from the atomistic simulations, we develop a front-tracking model of microstructural evolution on a much coarser scale. This model is used to predict the evolution of crystallographic texture, surface roughness, and grain size and to understand the growth competition between grains that leads to the development of columnar films.

## Bond Order Interatomic Potentials for Modelling of CVD Diamond Growth

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A basic understanding of surface chemical reactions which take place during CVD diamond growth can only be achieved by reliable atomistic modelling of the reaction pathways and activation barriers. Ab-initio methods are restricted to simulating very small systems, therefore, the development of semi-empirical interatomic potentials which allow us to model much larger systems for longer times is the focus of current theoretical efforts.

We develop analytical bond order potentials (BOPs) for hydrocarbon systems based on the two-center tight-binding (TB) approximation to the electronic structure. In the BOPs the electronic degrees of freedom are no longer treated explicitly but their influence is captured through the functional form of the BOP which is devised by a well-defined set of approximations to the TB Hamiltonian, thereby avoiding the many ad hoc parameters and functional forms that enter empirical potentials. We demonstrate that the first term of the BOP expansion, which corresponds to a Tersoff type potentials, is unable to account correctly for the relative stability of different structures such as graphite, diamond simple cubic and FCC. Accurate structural predictions require inclusion of the second term of the BOP expansion which guarantees that the fourth moment of density of states is included exactly. This property of the analytical BOP is of paramount importance for the covalent systems with band gaps such as silicon and carbon.

The remarkable feature of the novel BOP is that it predicts the environmentally dependent angular functions of the interatomic potentials which were recently introduced by inversion of ab-initio binding energy curves (M.Z. Bazant and E. Kaxiras, Phys Rev Let, 77, 4370 (1996)). As a result, analytical BOP gives the right ordering of different crystal structures and cohesive energies for open structures (diamond and graphite). We validate the analytical BOP against experiment and ab-initio predictions.

## Dynamic Scaling in Simulations of Island Growth and Coalescence on Substrate Steps

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Monte Carlo simulations of island growth on substrate steps have been performed, whereby monomers are randomly deposited on a bare substrate and diffuse to substrate steps where they can nucleate  $D = 2$  dimensional islands of critical size  $i = 1$ . In this work the dynamics of the cluster density during the nucleation, growth, coalescence and final percolation of the islands has been studied. It is usual to treat the growth and coalescence regimes separately, because the physical processes appear to be distinct in each. However we have found that our data display dynamic scaling for the whole evolution. In other words the density variation over time for simulations performed at different deposition rates collapse well to a universal curve under appropriately scaled time-density axes. The reason for this is that the pertinent length scale for the maximum island density is also that for the percolation regime where the clusters all join to form complete coverage of the step. In this work we show how this length scale is determined by the diffusion equation of the monomers attached to the steps, and derive explicitly the scaling exponents observed. Furthermore this treatment is generalised to the case of  $D$ -dimensional islands with critical island size  $i$ , yielding explicit predictions for the dependencies of the maximum island density and percolation regime on the deposition rate. This extension to the theory is important because  $i$  and  $D$  are accessible to experimental tests through choice of materials and control of substrate temperature.

## Comparison of Initial stages of Ni-Electrodeposition with Electroless Ni deposition on Si(100) substrate.

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Electrodeposition and electroless deposition processes provide a continuous buildup of metal coating on a substrate from suitable aqueous solutions. Both these methods are very useful for the fabrication of a high density and uniform metallisation of complementary metal oxide semiconductor devices in Ultra-Large Scale Integration. (ULSI) metallisation and in the formation of thin metal etch marks for deep ultra-violet lithography.

In this study, we have compared the electroless deposition of nickel from  $\text{NH}_4\text{F}$  solution with electrodeposition of nickel from HF solution. The initial stages of deposition by both the techniques are compared and studied using several surface analytical techniques. Each technique has been used according to its characteristics to study the parameters that can influence the metal deposition process. In both these metal deposition processes pH can be adjusted to thermodynamically facilitate the deposition (at greater pH) or a H-terminated silicon substrate (at lower pH). Evidence for (metal) deposition-induced etching of the substrate has been reported. The substrate influence (p- and n-silicon) on the deposition process has also been investigated.

Tapping mode atomic force microscopy (TMAFM) was used to characterise their main features towards atomic level deposition. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) allow us in some cases to identify the chemical nature of the observed features. The results obtained throughout this study support further demonstration on detailed mechanism.

## Modelling Non-epitaxial Growth of Metallic Clusters

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We model the growth of metallic clusters on graphite substrates using Molecular Dynamics techniques. The metal/metal interactions are modelled using the Sutton Chen potentials. The validity of these potentials for small clusters was verified by comparing the binding energies and equilibrium atomic separations with the corresponding values from density functional calculations.

The metal/graphite potentials were calculated using density functional theory. The interaction energy of an isolated metal atom with a cluster of 7 carbon rings, passivated with hydrogen, was calculated for various separations and the results fitted to a modified Lennard Jones potential. A similar calculation for an atom over a carbon bond enables the structure of the graphite substrate to be included in the model.

Using *ab initio* calculations, we have demonstrated a strong variation in the metal/substrate interaction with metal cluster size. This many body effect will have a significant influence on growth processes, therefore it is necessary to include it in the model. We have derived a many body term which has the effect of reducing the metal/substrate of a metal atom as the number of neighbours increases, similar to the many body term in the Sutton Chen potential.

The calculated potentials for Ni and Cu are used in a Molecular Dynamics simulation to model growth of these metals on a graphite substrate. We find that Ni exhibits layer-by-layer (Frank van der Merwe) growth whereas Cu exhibits island (Volmer Weber) growth. Similar growth modes are found experimentally for these metals on amorphous carbon.

## Modelling Polyethylene: Path Integral Monte Carlo, Molecular Dynamics and Lattice Monte Carlo

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When one models dense polymer systems by means of computer simulation methods, one is immediately faced with the broad range of length scales (from the bond length of  $\approx 1 \text{ \AA}$  to the radius of gyration of  $\approx 100 \text{ \AA}$ ) and time scales (from bond length vibrations of  $\approx 10^{-15}$  sec to renewal of the overall chain conformation in the ns to  $\mu$ s range for short chains) that characterize these molecules. No single simulation method or model can cover all these scales. The most promising approach is therefore to use models containing the specific level of atomistic detail required in the simulation and devise interfaces between the models on different scales.

I will present a classical and path integral monte carlo study of the orthorhombic polyethylene crystal using an all or explicit atom force field. For some quantities quantum effects will be seen to play a role even at room temperature. From there we will move on to a united atom description of a short chain polyethylene melt. This model will be validated by a comparison of molecular dynamics simulation results to various experiments at one high temperature. This will show that our model is able to reproduce the experimental findings quantitatively. Finally we will map this united atom model onto the bond fluctuation lattice model of polymers and use the monte carlo method to study large scale conformational and dynamic properties over a broad temperature range in the melt.

## A degenerate Rosenbluth Monte Carlo scheme for cluster counting and lattice animal enumeration

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We describe a new algorithm for the Monte Carlo enumeration of clusters and lattice animals. The method may be used to calculate associated properties such as moments or perimeter multiplicities of the clusters. The scheme is an adaptation of the Rosenbluth method for growing polymer chains and may be used to estimate the number of distinct lattice animals on any lattice topology. The method is validated against exact and Monte Carlo enumerations for clusters of size 30, on two and three dimensional simple cubic lattices. The method may be readily adapted to yield Boltzmann weighted averages over clusters. Work is currently being undertaken to extend the method to count clusters of chains.

## Dynamical scaling anomaly for a two-dimensional polymer chain in solution

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We report on extensive molecular dynamics simulations of a 2D polymer in solution. An analysis of the structure factor data has revealed anomalous dynamical scaling behaviour currently not

predicted by theory. Subsequently, a closer scrutiny of the Zimm model predictions has revealed a breakdown of the preaveraging approximation due to the logarithmic infinite range structure of the 2D Oseen tensor. Numerical studies of the Zimm equations upon introducing the 2D Oseen tensor have yielded results in accord with the simulations in the scaling regime. While this offers some insight into the observed anomaly, our results show that the scaling arguments in 2D are in need of a careful reexamination.

## **Modelling surface topographical development on solids subjected to bombardment by energetic particle beams**

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This paper will show how surface damage as a result of irradiation by energetic particle beams can be modelled. The techniques used in the simulation process will be classical molecular dynamics (MD) to model the effect of single particle impacts but also the effect of large doses will be considered by using continuum and Monte-Carlo models. The MD models will consider the damage on both covalent materials such as graphite and silicon and also metals such as copper or zirconium. Comparison will be made to experimental results using scanning force or scanning tunnelling microscopy. Attempts will be made to relate the development of damage on the atomic scale to micron scale structures which can develop after large doses.

## **Computer Simulation of Defect Production by Displacement Cascades in Metals**

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Molecular Dynamics (MD) techniques have been used to investigate the mechanisms and final state of defect production due to the primary cascade state of radiation damage in metals. This study includes research dealing with the effect on defect formation and clustering of primary knock-on atom (PKA) energy, irradiation temperature and the spatial overlap of cascades. The simulation has confirmed some of the early ideas based on binary-collision concepts and revealed new aspects not anticipated. The defect production efficiency in metals under cascade-producing irradiation with ions and neutrons is approximately one quarter of the NRT value, which is consistent with experimental data. Both interstitial and vacancy clusters are features of displacement cascades. Most interstitial clusters have dislocation character, but a few metastable clusters have been found and are persistent over the period of the MD simulation. Because the timescale of cascades is very short, some experimental results cannot be explained by MD simulation, for example the temperature dependence of matrix hardening, void swelling and the different mechanisms of hardening under electron and neutron irradiation. A possible way for the future development of models of the evolution of damage beyond the stage of the cascade process is discussed.

## **The Vibrational Anomalies and Polymorphism in Titanium: A Tight-Binding Approach**

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The group IV transition metals (titanium, zirconium and hafnium) possess a number of rather remarkable features in their properties attributed to strong anomalies in their phonon spectra. These include crystalline polymorphism, a high temperature saturation of the electrical conductivity, rapid increase of the constant pressure heat capacity at high temperature, and anisotropy in diffusion and thermal properties. The vibrational anomalies manifest themselves by a strong (and sometimes inverse) temperature dependence of the certain phonon frequencies even at the conditions far away from the phase transition. For example, the  $[0001]LO$  branch in the low temperature hexagonal close-packed  $\alpha$ -phase of Ti and Zr exhibits substantial softening with temperature. The frequencies of the  $[001]T_1$  zone-boundary and  $[111]L$  ( $q = \frac{1}{3}$ ) phonons in the high temperature bcc-structured  $\beta$ -phase, also decrease dramatically while approaching the  $\beta - \alpha$  transition temperature from above. The established large sensitivity of the vibrational and elastic properties of d-metals to the d-band filling, as well as to the details of d-band structure, suggests strong electron-phonon interaction effects. Thus the study of the anharmonicity in such systems requires the method accounting for at least some electron density effects and, at the same time, allowing for large scale MD simulations, so the dynamics beyond the harmonic approximation can be studied. The various  $O(N)$  implementations of the tight-binding approach seem to be adequate compromise for this purpose. Having titanium as the case study, we analyse both anharmonic and electron-phonon coupling effects in different polytypes, by means of bond order potential approximation to tight-binding approach implemented in OXON package. We apply this method for both molecular dynamics and frozen phonon calculations and compare results, were relevant, with the k-space tight-binding calculations. Based on these simulations, we discuss the static and dynamic variations of the electron chemical potential as applied to either the whole system or particular phonons, and the implications of these changes in the thermal frequency shifts and relative phase stability.

## A New Approach to Impurity Scattering in Doped Semiconductors

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There is a clear evidence that mobility data depend on the species of dopants in heavily doped semiconductors. To clarify this still unsolved problem from a physical point of view we adopt a new theoretical approach to discuss the influence of the ionized impurities on the electron mobility in doped semiconductors. We show for the first time that consideration of the charge density of the valence electrons allows not only to distinguish the majority and minority electrons, but also to differentiate between various acceptors and donors. Since the picture of the hydrogenic behavior of shallow impurities can well describe ionization and screening properties, we assume a hydrogen-like exponential electron charge distribution consisting of  $N$  electrons while retaining a point-like nucleus of total charge  $Z$  (in units of the elementary charge  $e$ ). The charge distribution of the impurities is described within the Thomas-Fermi theory in the energy functional formulation. By means of a variational principle one obtains a unique charge density for each dopant. The corresponding atomic form factor  $F(q)$  of the electron charge distribution in Fourier space is significantly different for various dopants at higher doping concentrations. Taking into account many-particle interactions the total scattering cross section within the Born approximation is derived.

We calculate the electron mobility  $\mu$  at 300 K employing the derived formulas in a single-particle Monte Carlo procedure using analytic band structure including phonon and plasmon interaction. The Pauli principle is accounted for by a rejection technique. Our results for Si, GaAs, and InP confirm experimental data indicating that ions with higher  $Z$  result in lower values of  $\mu$ .

In conclusion, the present approach to our knowledge is the first physically based model to date which explains the dependence of the majority and minority electron mobility on various species through the atomic number.

## *Ab Initio* Path Integral Molecular Dynamics of Hydrogen Diffusion

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We present here preliminary results for the simulation of hydrogen diffusion on the Si(111) surface. This is a system for which the quantum zero-point motion of the light hydrogen atom has a significant effect on observed properties. We have used an *ab initio* path integral molecular dynamics technique in order to fully simulate the zero point motion whilst at the same time calculating the electronic structure and relaxation of the surface. We highlight those features in our results that can only be explained by a proper treatment of the zero-point motion and hence demonstrate the usefulness of this technique. This is the first time that the *ab initio* path integral molecular dynamics technique has been applied to the properties of surfaces.

### Poster Abstracts

## FEOS: A Code for Lattice Dynamics and Structure Optimisation of Polar Solids

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This contribution describes FEOS, a program which uses a combination of lattice statics and quasi-harmonic lattice dynamics to calculate *analytically* the free energy of a crystal and its geometrical derivatives, at a given temperature and pressure. These quantities are used to perform efficient fully dynamic structure optimisation of unit cells containing hundreds of ions. High precision is readily obtained. Quasiharmonic lattice dynamics has proved to be a good technique for the calculation of free energies of solids, often even up to quite elevated temperatures. It is much cheaper than Monte Carlo or molecular dynamics. Recent applications include studies of the free energy of defect formation and of ceramics with large negative thermal expansion. The code is now ready for distribution to interested academic groups.

## Lattice Modelling of Fracture in Impure Metals.

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The intragranular fracture of steels has been investigated using a two dimensional lattice model. The  $D_2Q_8$  model is based on a square lattice with interactions between neighbouring and next nearest neighbour sites, bond-bending is controlled using a form of Born potential. Plastic behaviour is incorporated using a reversible two-step potential function. The model has been mapped onto the isotropic continuum to allow parameterisation from experimental data. Bonds are switched to the plastic state or broken using a stochastic technique [1], with a probability determined from the energy of the bond. We present the results of a series of simulations of metal matrices containing single and multiple particulate defects. We demonstrate that by choosing the correct parameterisation, particulates can be made to either debond from the matrix or to undergo brittle fracture.

## References

- [1] Meakin, P., *Science* ,**252** , 226, (1991)

## Thermal and Mechanical Properties of FCC metals and their binary Alloys

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The temperature dependence of thermodynamic and mechanical properties of fcc transition metals (Ni,Cu ) and their alloying behavior are studied using molecular dynamics (MD). The structures are described at elevated temperatures by the force fields developed by Sutton and co-workers within the context of tight binding approach. MD algorithms based on extended Hamiltonian formalism from the works of Andersen, Parrinello and Rahman, Nosé, Hoover and Çağın. The SIMULATOR program that we use generates information about various physical properties during the run time along with critical trajectory and stepwise information which need to be analyzed post production. The thermodynamic and mechanical properties are calculated in the temperature range between 300K to 1500K with 200K increments using the statistical fluctuation expressions over the MD trajectories.

## Excited State Dynamics in Nanodots

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Nanodots exhibit special features upon excitation, in particular broader than expected transition widths. Excitation causes a change in the volume of the dot. The consequent dilatational strain shifts the transition energy. Where the excitation does not cause a large redistribution of the charge density, the volume change is essentially independent of the volume of the nanodot. Hence the shift in transition energy is inversely proportional to the dot volume, broadening transition widths where the system consists of a distribution of dots of various sizes. However, even for single dots, there is an intrinsic broadening due to the finite time taken for the volume relaxation. The volume change takes place over a timescale determined by the radius of the dot and the velocity

of sound in the dot, leading to an electronic dephasing time of the order of several hundred fs for dots of radius 10Å. We have verified the above effects using MD simulations of NaCl nanodots. The finite size of the nanodot also affects phonon relaxation in the system. We conclude with a discussion of the nature and effect of phonon dephasing in nanodots.

## The Dynamics of the Nucleation and Coalescence Regimes in Simulations of Island Growth on Substrate Steps

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In an accompanying presentation it has been demonstrated how the dynamics of island growth and coalescence on substrate steps display dynamic scaling. In this work we focus on the detailed evolution of the cluster density in both the early stage nucleation regime and the later coalescence regime, for a simulation using island dimensionality  $D = 2$  and critical island size  $i = 1$ . We show that the inter-island gap size distribution is a scaling property of the growth, which implies a hierarchical self-similarity in the system, and derive an approximate form for this distribution from the monomer diffusion equation. In the nucleation regime we predict that the island density should grow as the fifth power of  $(\phi/r)$ , where  $\phi$  is the number of monolayers deposited on the step and  $r$  is the ratio of the monomer diffusion and deposition rates. The simulation data confirm this behaviour, and the constant of proportionality agrees reasonably well with theory given the approximations used. However this low- $\phi$  behaviour indicates that the dynamic scaling plots cannot be exact in this regime, but instead possess a residual  $1/25$  power dependence on  $r$ , an observation in agreement with the data. In the later stages we show how it is the smallest islands that coalesce first, which enables accurate calculation of the cluster density evolution in the coalescence regime based upon the gap size distribution derived above. Taken with the dynamic scaling results, this work shows how complete theoretical understanding of the detailed evolution of the simulated growth can be obtained.

## A Study of a Steric and Electric Multipole Model of Liquid Crystal Geometry

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Liquid crystals are asymmetric in varying degrees in their molecular shape, charge distribution and polarisability and the problem of relating molecular structure to phase behaviour is complex. We report results [1] from a series of molecular dynamics simulations designed to study the phase behaviour of model rod-like liquid crystal molecules interacting via the Gay Berne Potential. We also report results from a study of quadrupolar single and multi-site Gay Berne molecules.

Following classification of molecular geometry in terms of a multipole expansion of steric asymmetry, two models have been studied in detail: a zigzag model defined as a steric quadrupole and a triangle model defined as a longitudinal steric dipole, and comparison has been made with a cylindrical model. Extensive simulations in the NPT ensemble a delay in the temperature of onset of the smectic B phase, with a lower temperature of onset observed with the steric quadrupole than with the steric dipole. Local anti-parallel steric ordering within a layer was observed with the

model steric dipole in the crystal B phase but not with the model steric quadrupole. This structure is in agreement with experimental results and with the prediction of the generalised molecular asymmetry model [2]. The steric quadrupole demonstrated a rippled structure throughout the smectic B phase increasing in amplitude and wavelength sufficient to tilt molecules along a wave with respect to the system director as the system was cooled. This structure was almost absent in the final crystal structure cooled.

Results for the addition of a longitudinal and transverse electric dipole to a cylindrical Gay Berne molecule indicate that both the longitudinal and transverse electric quadrupole raise the temperature of onset of the nematic phase and destabilise the smectic phase. The effect is greater with a transverse electric quadrupole and the trend opposes that of the transverse steric quadrupole. Preliminary results for the addition of an electric quadrupole to a steric quadrupole again indicate a rise in the temperature of onset of the smectic phase compared to the steric quadrupole alone.

## References

- [1] Neal, M. P., Parker, A. J., and Care, C. M., *Molec. Phys.* , 1997, in press.
- [2] Petrov, A. G., and Derzhanski, A., *Mol. Cryst. Liq. Cryst.* ,151 , 303 (1987)

## Evolution of microstructure in the bcc-hcp martensitic phase transition in zirconium

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We report molecular dynamics simulations of the martensitic phase transition from bcc to hcp in zirconium. We show the evolution of a laminated twin microstructure, with some plastic deformation occurring to rotate the twins. This rotation is such as to alter the twinning angle from the  $60^\circ$  between the hcp variants to the  $61.5^\circ$  angle of the low energy  $(10\bar{1}1)$  twin. The proximity of a low energy twin to the twinning angle is thus identified as a cause of microscopic irreversibility in the transition.

## Ordering in Oxides and Silicates

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Cation or anion ordering is often crucial in determining phase stability and in determining thermodynamic, electrical and geochemical properties. The simulation of ionic solids with a finite impurity or defect content, or with extensive disorder, is still problematic. Such systems have largely been studied theoretically either via point defect calculations which refer only to the dilute limit, or via "supercells" in which a periodic superlattice of defects or impurities is introduced extending throughout the macroscopic crystal. These methods have clear limitations.

In this presentation we report the implementation of Monte Carlo techniques specially adapted to allow for the sampling of many configurations and to take *explicit* account of the complex relaxation accompanying the disorder, without resorting to the use of parameterised Hamiltonians.

Preliminary results for cation ordering in olivines and for the enthalpies of mixing of simple oxides are presented.

## Template-Framework Interactions in Chiral AlPO's

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Self assembly is a major tool in nanotechnologies. Intercalation of organic molecules between the layers of inorganic solids is used to construct pores and channels of controlled size on a nanometer scale.

The materials created by templating have so far been largely achiral. The fabrication of materials with chiral nano-environments will open an important field in nano-technology, where the separation of enantiomerically pure substances is desired, as in biological and medical applications.

Recently, there have been successful attempts to intercalate chiral transition metal complexes into aluminophosphates (AlPO's), forming chiral layered compounds [1]-[4].

We are undertaking Molecular Dynamics simulations to identify the key template host interactions which are the structural determinants. A Molecular Dynamics simulation has been performed to study the structural characteristics of a novel type of chiral aluminophosphate that has been recently synthesized [1]. The force fields for the Al-P-O interactions were obtained from previous work [5]-[9].

For the chiral template a rigid body scheme was used with three different approaches. A simple charged sphere model with nearly hard-sphere interactions was used first. This simple model was able to explain the mechanical stability of the structure in a constant volume simulation, but failed under constant pressure simulations. A more detailed model was then constructed by including the detailed shape of the overlap forces arising from the chiral template. This system gave a good reproduction of the experimental structure vibrational spectrum. The final model was an extension of the second model to incorporate chemical interactions such as hydrogen bonding, solid.

The aim of this study is to evaluate the different degrees of complexity needed to reproduce the features of the system. This will identify the factors needed to stabilise a chiral nanoporous material. In this work we report the optimised structures of the chiral AlPO compared with the X-ray structures, the corresponding energies, and the calculated vibrational spectra.

## References

- [1] Bruce D. A., Wilkinson A. P., White M. G., Bertrand A.; *J. Chem. Soc. Chem. Commun.* , 1995, 2059.
- [2] Morgan K., Gainsford G., Milestone N.; *J. Chem. Soc. Chem. Commun.* , 1995, 425.
- [3] D. A. Bruce, A. P. Wilkinson, M. G. White and A. Bertrand, *Journal of solid state chemistry* ,125 , 228-233 (1996)
- [4] M. J. Gray, J. D. Jasper, A. P. Wilkinson, J. C.; *Chem. mater.* ,9 , 1997, 976-980.
- [5] B. W. H. Van Beest, G. J. Kramer and R. A. van Santen, *Phys. Rev. Lett.* ,64 , 1955 (1990).
- [6] G. J. Kramer, N. P. Farragher, B. W. H. van Beest and R. A. van Santen, *Phys. Rev.* ,B 43 , 5068 (1991) and references therein.
- [7] Henson N., Cheetham A. and Gale J.; *Chem. Mater* ,8 , 1996, 664-670.

- [8] Sastre G., Lewis D. W., Catlow C. R. A.; *J. Phys. Chem* ,100 , 1996, 6722-6730.  
[9] Gale J. D., Henson N. J.; *J. Chem. Soc. Faraday Trans.* , 90(20) , 1994, 3175-3179.

## Molecular Dynamics Simulation of Homogeneous Nucleation in Vapor Phase

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Molecular dynamics computer simulation was carried out to investigate the dynamics of vapor phase homogeneous nucleation for a Lennard-Jones fluid. To control the system temperature, the 5000 target particles were mixed with 5000 soft-core carrier gas particles. The observed nucleation rate is six orders of magnitude larger than prediction of a classical nucleation theory for Lennard-Jones fluid. The kinetically-defined critical nucleus size, where the growth and decay rates are balanced, is 30–40, as large as the thermodynamically-defined value estimated with the classical theory. Using the cluster concentration expression reversely, the free energy of cluster formation  $\Delta G$  is estimated. The surface contribution term has a peculiar dependence on the cluster size  $n$  as  $\propto n^{0.88}$ . With this  $\Delta G$ , the predicted nucleation rate agrees with the simulation result. The temperature dependence of nucleation rate will be presented.

## CCP5 Annual Meeting 1998

### Making and Breaking Potentials

#### Invited Talks

##### Model interatomic potentials for covalent systems.

Jerry Tersoff.

IBM Watson Research Centre,  
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New York 10598, USA.

This talk will describe one approach to constructing model potentials for covalent systems, with sample applications. The characteristic limitations of such potentials will be discussed, along with the obstacles and opportunities for constructing new and better potentials.

##### Generalisation and augmentation of the Gay-Berne potential.

Doug. Cleaver.

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The Gay-Berne potential involves pairwise-additive anisotropic interaction sites and can be viewed as a generalisation of the Lennard-Jones potential for non-spherical particles. It is mainly used in simulations of complex fluids (liquid crystals, amphiphiles and elastomers) where its simplicity makes accessible the considerable runtimes required for free assembly of the phases/structures of interest. This talk will illustrate the strengths and weaknesses of the Gay-Berne potential, some recent developments to it that have opened up new areas in liquid crystal simulation and some ideas for more diverse future applications.

##### Atomistic aspects of cleavage fracture in crystalline materials.

Peter Gumbsch.

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The macroscopic failure of materials is ultimately determined by events on the atomic scale. This is particularly clear in the case of brittle fracture, where the crack at its tip must be atomically sharp and must break the bonds between atoms. It is therefore obvious that a detailed understanding of brittle fracture will ultimately require an understanding on the atomic scale. Atomistic modelling is a useful way to study such processes and is even more appealing if one acknowledges that it will naturally reproduce fracture by loading, whereas the widely used continuum models require explicit fracture criteria.

Similarly, the dynamics of the bond breaking, of dislocation generation and of dislocation motion in

the crack tip field, which are the underlying physical processes in the so-called semi-brittle fracture regime are all linked to the atomic length scale and can all be studied atomistically. Semi-brittle fracture is usually observed in materials which undergo a brittle-to-ductile transition (below the transition temperature) and consequently we also need to develop deeper insight into these *dynamic* processes in order eventually to understand the brittle-to-ductile transition.

The talk will be centered around three main topics. First, the requirements for the construction of atomic interaction models which can be used in the atomistic modelling of crack tip processes will be briefly reviewed. Second, the importance of the discrete atomistic structure of the crack tip will be discussed together with the so-called lattice trapping effects. Third, the dynamics of the brittle fracture process and the critical velocities which can be attained by the crack and by emitted dislocations will be investigated.

### **The importance of microscopic contributions to condensed phase macroscopic properties in empirical force field calculations.**

Alex MacKerell

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Empirical force field calculations apply simplistic mathematical models to study complex chemical systems. The results from such calculations are directly dependent on the quality of the empirical force field parameters used in the computations. We will present a methodology for the development of force field parameters that takes into account both microscopic (e.g. specific interactions between water molecules and model compounds) and macroscopic (e.g. heats of vaporization or free energies of solvation) properties. Examples from protein, lipid and nucleic acid calculations will be presented.

### **Molecular dynamics simulations of the $a \rightarrow b$ pressure-induced reconstructive phase transformation in crystals of resorcinol.**

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The ability to predict new polymorphic phases of a substance as well as its phase stability is of considerable scientific interest and technological importance. The molecular dynamics simulation technique using the Parrinello-Rahman boundary conditions offers a potentially powerful approach for investigating both polymorphism and polymorphic phase transformations.

This study presents results of molecular dynamics simulations of a reconstructive polymorphic transformation in a strongly hydrogen-bonded molecular crystal, namely resorcinol. The focus has been on the  $a \rightarrow b$  transformation as a function of pressure, which has been successfully simulated. The effects of some of the important variables associated with simulations of crystals have been

explored. Simulations were carried out using both a partially rigid and a flexible representation of the resorcinol molecule as well as different force-field parameters. In addition, the effects of variations in the temperature and pressure relaxation constants, system size and starting configuration were examined.

This success with a hydrogen-bonded structure, along with a better understanding of the variables associated with molecular dynamics simulations of crystals opens up the possibility of exploring structure, phase stability, and kinetic aspects of polymorphic crystals of molecular systems.

### Many-body effects in the interaction potentials of ionic materials.

Paul Madden.

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Anions in the condensed phase have profoundly different properties from their free counterparts. This is a consequence of the strong confining potential exerted on the anionic electron density by surrounding ions. Depending on the precise shape of the potential (which, in thermal motion, will vary from one instant to the next), the anion may be more-or-less compressed, deformed and polarized and hence its interaction potential with the other ions in the system will also vary. Only for the simplest ionic systems (*e.g.* alkali halides) can this variation be neglected and the interactions described by some average pair potential. Most other systems exhibit "covalent effects" in their structure and dynamical properties – that is to say that these properties are not describable as a consequence of pairwise additive ionic interactions.

For some time (see *Chem.Soc.Rev.*, **25**, 339-350 (1996)), my group has been examining how to represent in computer simulations the *many-body* aspects of the interaction potentials, which arise as a consequence of the variation of the confining potential. Some of these effects (notably polarization and ion compression) can be unambiguously characterized by performing electronic structure calculations on ions in suitable idealized environments. These allow the partial parameterization of an "extended" ionic model, in which the variation in the ionic properties are represented by additional dynamical variables (alongside the ionic coordinates) which are handled by borrowing ideas from the Car-Parrinello method. For other effects, we have to resort to more empirical methods or to total energy calculations to characterize them. The calculations reveal that a surprisingly large range of "covalent" behaviour can be recovered within this extended ionic model.

In the talk I will illustrate these ideas by describing the development of many-body potentials for oxides by Adrian Rowley. The basic potential is refined in careful, quantitative studies of MgO (see *J.Chem.Phys.*, **108**, 10209 (1998)). It is then shown how, by simply scaling some of the potential parameters to allow for the change of cation radius, this potential may be *transferred* to other oxides, even if this involves a change of stoichiometry. Applications to the surface relaxation of Cr<sub>2</sub>O<sub>3</sub> and to the different crystalline polymorphs of GeO<sub>2</sub> will be described.

## Oral Presentations

\* indicates speaker

### Parallelisation of molecular dynamics simulations: an introduction.

David Henty.

Edinburgh Parallel Computing Centre, Kings Buildings,  
University of Edinburgh, Edinburgh EH9 3JZ, UK.

Modern supercomputers are parallel machines, and these pose certain problems for the coding of simulations such as molecular dynamics. This talk aims to give insight into these problems, and how they are overcome for state-of-the-art machines. Those planning a career in high performance computation should appreciate how powerful these machines may be in the near future.

### Anticipating potential problems.

Graeme Ackland.

Department of Physics, King's Buildings,  
University of Edinburgh, Edinburgh EH9 3JZ, UK.

This introductory talk will discuss transferability of interatomic potentials. In particular the need to consider the types of interactions which are likely to be important in a given simulation is discussed. Selection of a functional form and appropriate fitting data for a potential is then investigated and a few examples are discussed.

### Mean-field and large-scale simulation approaches to the molecular design of liquid crystals.

Maja Nendel<sup>1\*</sup>, M.A. Glaser<sup>2</sup>, Y. Lansac<sup>2</sup>, N.A. Clark<sup>2</sup> and D.M. Walba<sup>1</sup>.

<sup>1</sup> Department of Chemistry and Biochemistry, Campus Box 215,  
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<sup>2</sup> Condensed Matter Laboratory, Department of Physics, Campus Box 390,  
University of Colorado, Boulder, CO 80309-0390, USA.

The Boulder model constitutes a mean-field approach to predict certain properties of tilted smectic liquid crystals, i.e. the spontaneous polarization density  $P$ , the non-zero second-order hyperpolarizability  $\chi^{(2)}$ , optical dichroism and refractive indices. In this model, a single liquid crystal molecule is placed into a bent cylindrical-shaped binding site, or mean-field potential, analogous to the binding cavity in enzymes. The shape of the binding site is chosen to have a symmetry corresponding to that of the phase. The underlying hybrid force-fields are developed using *ab initio* and DFT calculations on small model systems, and they are parametrized to fit experimental data. The development of these force fields will be discussed, as will be the performance of the Boulder model in specific cases as compared to large-scale molecular dynamics calculations and to experimental data.

### Interaction laws used in the simulation of granular materials.

D.M. Heyes<sup>1\*</sup>, J. Baxter<sup>2</sup>, U. Tüzün<sup>2</sup> and P.A. Langston<sup>3</sup>.

<sup>1</sup> Department of Chemistry, University of Surrey,

<sup>2</sup> Department of Chemical Engineering, University of Surrey,

<sup>3</sup> Department of Chemical Engineering, University of Nottingham.

Molecular Dynamics simulation has been used many times to model the physical properties of granular materials since the pioneering work of Cundall & Strack (*Geotechnique* **29**, 47 (1979)). A wide range of processes, including simple shear, compaction, mixing by churning and vibration, transportation by conveyance, hopper filling and discharge and heap formation have been simulated. Highly idealised interaction laws have typically been employed (*e.g.* spring-and-dashpot, and Hertz – the classical solution for two elastic spheres in compressed contact) with the implicit assumption that the physical phenomena produced are insensitive to the interaction law between the grains. In recent years our MD work in this area has shown that this is far from the case. For example, the granular assembly structure, the stress distribution in the system and at its boundaries, and even the bulk flow characteristics are highly sensitive to the analytic form chosen for the interaction potential. We have established simple interaction laws that give a more realistic representation of granular system behaviour than those used in the past. A discussion of the terms in this interaction law, and the issues raised will be given. Examples of results taken from our simulations of hoppers and heap formation will be presented (Langston, Tüzün & Heyes, *Chem.Eng.Sci.* **50**, 967 (1995) & **51**, 863 (1995); *Powder Tech.* **85**, 153 (1995); Baxter, Tüzün, Burnell & Heyes, *Phys.Rev.E* **55**, 3546 (1997); Langston, Nikitidis, Tüzün, Heyes & Spyrou, *Powder Tech.* **94**, 59 (1997)).

### Effects of hard cores – purely viscous liquids?

J.G. Powles<sup>1\*</sup> and D.M. Heyes<sup>2</sup>.

<sup>1</sup> Physics Department, University of Kent, Canterbury,

<sup>2</sup> Chemistry Department, University of Surrey, Guildford.

It is shown that if an intermolecular potential has a hard core of **any sort**, the infinite-frequency shear modulus  $G_\infty$  and the bulk modulus  $K_\infty$  of the fluid are infinite (Powles & Heyes, in preparation). This is a generalisation and extended application of the analysis of Zwanzig (Zwanzig & Mountain, *J.Chem.Phys.* **43**, 4464 (1965); Schofield, *Proc.Phys.Soc.* **88**, 149 (1966)), which has recently been investigated in detail for hard spheres (Heyes & Aston, *J.Chem.Phys.* **100**, 2149 (1994)) and for increasingly steeply repulsive potentials (Heyes, *J.Chem.Phys.* **107**, 63 (1997); Heyes & Powles, *Molec.Phys.* in press) showing explicitly that  $G_\infty$  and  $K_\infty$  are infinite. This result has also been noted in passing, for hard spheres, elsewhere (Schofield, p.583 in *Physics of Simple Liquids*, ed: Temperley et al., North Holland (1968); Groot & Aghurof, *Macromolecules* **28**, 6284 (1995)).

According to Maxwell (*Phil.Trans.Roy.Soc.* **157**, 49 (1867)), and the experimental evidence, all real fluids are “viscoelastic”. However, if the infinite-frequency elastic moduli are infinite, the Maxwell relaxation time is zero and the fluid is purely viscous at all finite frequencies. Thus the non-physical assumption of a hard core interaction leads to non-physical behaviour and the repercussions of this demand further analysis (Powles & Heyes *loc. cit.*).

## Modelling aluminium clusters with an empirical many-body potential.

L.D. Lloyd.

School of Chemistry,  
University of Birmingham, Birmingham B15 2TT, UK.

An empirical two-plus-three-body atomistic potential, derived by fitting experimental data pertaining to bulk aluminium, has been applied to the study of structures and growth patterns of small aluminium clusters. The high dimensionality of the nuclear configuration space for clusters results in an extremely large number of isomers and local minima on the potential energy hypersurface. Global optimisation (i.e. searching for the lowest energy structure) was carried out using Random Search and Monte Carlo Simulated Annealing methods, for  $Al_2$  to  $Al_{20}$ . The results of random searching have been used to put lower bounds on the number of minima for these nuclearities, and the efficiency of the Monte Carlo Simulated Annealing approach has been demonstrated. Comparisons have generally been in good agreement with results of previous calculations using electronic structure and empirical potential methods. While many of the global minima were also global minima for Lennard-Jones or Morse clusters, a number of new structures have been identified for  $Al_N$  clusters, notably for  $N = 9, 16, 17, 18$  and  $20$ .

## Cluster geometry optimization using genetic algorithms.

Roy L. Johnston\* and Chris Roberts.

School of Chemistry, The University of Birmingham,  
Edgbaston, Birmingham B15 2TT, UK.

Atomic clusters are aggregates of anywhere between 2 and (of the order of)  $10^6$  atoms. The atoms may all be of the same type (elemental clusters) or of different types (e.g. alloy clusters, ionic clusters). Clusters can be formed by nearly all the elements in the Periodic Table, such as the noble gases (e.g. argon), semi-conducting elements (e.g. carbon and silicon) and metals (e.g. sodium and iron). The bonding in these different types of clusters is very different, ranging from weak dispersion forces (noble gas clusters) to covalent (carbon and silicon clusters) and delocalized/metallic (metal clusters). Clusters are of interest from a theoretical viewpoint as well as for their possible application in the growing field of nano-electronics. For an  $N$ -atom cluster there are a very large number of possible structures (isomers), many of which correspond to local minima on the Potential Energy Hypersurface. The problem we face is trying to find the lowest energy isomer (Global Minimum). In this presentation, I will discuss the application of Genetic Algorithms to achieve this global minimization, giving examples ranging from argon clusters (bound by a simple Lennard-Jones potential) to metal clusters bound by Morse and many-body potentials and carbon clusters, including the fullerenes.

## The Road to Ammonium Nitrate.

K.A. Mort\*, R.A. Jackson, P.J. Wilde.

Department of Chemistry, Keele University,  
Keele, Staffs, ST5 5BG, UK.

Ammonium nitrate is an industrially important chemical which exists in several phases. A good starting point in trying to model this complex system is to develop potentials for the constituent

molecular ions separately by using empirical fitting to ammonium halides and alkali nitrates. We have developed potentials for the ammonium ion and the nitrate ion using the GULP program developed by J. Gale (Imperial College). We present these results together with results from molecular dynamics simulations using these fitted potentials. We also present preliminary results for transferring these potentials into simulations of ammonium nitrate.

### How complex should a potential be?

Stuart Pawley

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University of Edinburgh, Edinburgh EH9 3JZ, UK.

We should always ask whether the potential function that we are using for a particular modelling task has sufficient mathematical complexity for the task, but does not have more complexity than the task needs. Some examples will be presented, starting from the early days of lattice dynamics. Why is it that the Lennard-Jones atom-atom model, which was much maligned years ago, has now an enviable pedigree? Why is it that some molecular dynamics models need a time-step as small as a femto-second? And how can I somehow bring quaternions into my talk?

### *Ab initio* interatomic potentials of silica from a genetic algorithm.

T. Uchino<sup>1,\*</sup>, S.N. Taraskin<sup>2</sup>, S.R. Elliott<sup>2</sup>, and D.C. Clary<sup>1</sup>.

<sup>1</sup> Department of Chemistry, University College London,

<sup>2</sup> Department of Chemistry, University of Cambridge.

A new method to provide interatomic potentials from *ab initio* Hartree-Fock (HF) cluster calculations is proposed. We employ a cluster consisting of five SiO<sub>4</sub> tetrahedra. More than 250 *ab initio* points are calculated at the HF/6-31G(d) level on the basis of the normal coordinates of five different vibrational modes of the cluster. The force-field parameters are then determined based on a genetic algorithm. These parameters are tested in the molecular dynamics simulation of some silica polymorphs.

### The extended overlap model and its application to calculating anion polarizabilities in ionic solids.

Richard J. Wheatley.

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University Park, Nottingham NG7 2RD, UK.

The overlap model is based on the assumption that the intermolecular exchange-repulsion energy is proportional to the overlap between the ground-state molecular charge densities. It has been used successfully for obtaining semi-empirical potentials involving neutral molecules.

An extended overlap model has recently been introduced for ionic interactions, taking into account the effect of polarization on the anion charge density. In an A<sup>+</sup>B<sup>-</sup> dimer, a "monomer" *ab initio* calculation is performed on B<sup>-</sup>, using as a perturbation the electrostatic potential due to the interaction with A<sup>+</sup>, plus an effective potential due to the overlap of electrons between the two ions.

This effective potential reduces the polarization of the anion, and can be regarded as providing an exchange-induction contribution to the potential, to infinite order.

The model can also be used for estimating the polarizabilities of ions in solids. Again, only a monomer calculation is required on the anion, perturbed by the electrostatic and effective potentials of the surrounding ions. The computational time required to calculate polarizabilities is reduced by several orders of magnitude in this way. Basis set superposition error is also eliminated. Results for LiF and LiCl crystals indicate that the model provides in-crystal polarizabilities for the anions in essentially exact agreement with expensive direct calculations, at both the Hartree-Fock and MP2 levels of theory.

### Deviations from the predicted behaviour of a polarisable and compressible ion model of zirconia.

N.A. Marks\*, S. Fabris and M.W. Finnis.

School of Mathematics and Physics,  
Queen's University of Belfast,  
Belfast BT7 1NN, Northern Ireland.

We examine a model of zirconia in which the ions carry formal charges and the anions are both compressible and polarisable. The compression aspect of the model is parametrised from *ab initio* calculations, while the polarisation effects are to the quadrupolar level and include the short-range damping effect demonstrated by Fowler and Madden. The paper which presents the zirconia model (Wilson *et al.* Phys.Rev.B **54**, 9147 (1996)) claims to reproduce both the experimentally observed monoclinic ground state as well as the tetragonal double well distortion. In attempting to break this model, we find that the ground state of the potential is a rutile-like structure, which has not been observed experimentally in zirconia. This situation can be explained as a manifestation of overly large quadrupole moments and a born-mayer term which is too repulsive. We examine how this has arisen and suggest ways in which the model can be corrected. One of these improvements is a new representation of the short-range damping.

### Derivation of potential models for MgO from *ab initio* data.

Maurice Leslie.

CLRC, Daresbury Laboratory, Warrington WA4 4AD, UK.

A number of models for ionic materials are compared using magnesium oxide as an example material. *Ab initio* Hartree Fock data are used as the observables in a least-squares fit. A number of different shell models will be presented and their limitations discussed. Particular emphasis will be placed on the L-point LA phonons which can only be adequately described by allowing the oxygen shells to become non-spherical.

## Posters

\* indicates presenter

### First principles computer simulations of liquid crystal molecules.

C.J. Adam\*, S.J. Clark, G.J. Ackland and J. Crain.

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University of Edinburgh, Edinburgh EH9 3JZ, UK.

The molecular properties of the prototypical liquid-crystal molecule 4-4'pentyl-cyano- biphenyl (5CB) are investigated using an accurate first principles quantum mechanical method. A detailed study of the molecular structure and bonding in 5CB as well as the intra-molecular degrees of freedom is performed, which provide information on the conformational dynamics and vibrational molecular motions. Also investigated are the electrostatic properties of 5CB and the influence that the condensed phase may have on molecular properties.

### Solvent polarisation and dynamics in hybrid QM/MM methods.

R.A. Bryce\*, N.A. Burton, I.H. Hillier and R. Buesnel.

Department of Chemistry,  
University of Manchester,  
Manchester M13 9PL, UK.

Hybrid QM/MM potentials are now increasingly used in the study of dynamics and reactivity in the condensed phase. It is important to consider the mutual polarisation of the QM and MM regions. We have developed such a model of solvation to include these effects based on the principle of electronegativity equalisation (Bryce, Buesnel, Hillier & Burton, *Chem.Phys.Lett.* **279**, 367 (1997)). Here the partial atomic charges of the classical region are treated as dynamical variables and propagated in a fashion analogous to the Car-Parrinello method. Applications to the study of properties of ion-water clusters are discussed.

### Calculation of helical twisting power for liquid crystal chiral dopants.

Melanie J. Cook\* and Mark R. Wilson.

Department of Chemistry, University of Durham,  
South Road, Durham DH1 3LE, UK.

The helical twisting power (HTP) determines the pitch of the chiral nematic phase produced when a nematic liquid crystal is doped with a low concentration of chiral solute molecules. Molecules with large HTP values have major applications in electro-optic displays and in optical data processing.

We have developed a new simulation technique that allows accurate calculation of HTP values for a range of chiral dopant molecules. We employ twisted periodic boundary conditions, together with a Gay-Berne solvent, to produce a twisted nematic phase with a 90° rotation in the director across the simulation box. We then carry out a sequence of Monte Carlo fluid simulations to grow

an atomistic model of a chiral dopant into the Gay-Berne solvent. Statistical perturbation theory gives a measure of the change in free energy for this process. Comparison of the free energy difference for an enantiomer and its mirror image allows us to calculate HTP values.

We find that we are able successfully to predict the direction of twist for each enantiomer. Within statistical errors the computed HTP values are in good agreement with experimental data.

### A model potential for metal surface studies.

Dr Hazel Cox<sup>1\*</sup>, Roy L. Johnston<sup>2</sup> and John N. Murrell<sup>1</sup>.

<sup>1</sup> School of Chemistry, Physics and Environmental Sciences,  
University of Sussex, Falmer, Brighton BN1 9QJ, UK,

<sup>2</sup> School of Chemistry,  
The University of Birmingham, UK.

An empirical potential energy function, comprising two- and three-body terms, has been derived for several cubic atomic solids (Pt, Pa, Yb, etc.) by fitting parameters to the phonon dispersion curves, elastic constants, lattice energy and lattice spacings of the most stable phase of the solid (fcc for the examples above), and the vacancy formation energy. These potentials reproduce the fitted structural data very well, and some other properties such as the Cauchy pressure (+ve and -ve) and phase changes along the Bain deformation path, which are not fitted. The potential is then used to calculate surface energies and relaxations of the high symmetry surfaces, which tend to agree well with experimental values. For example, the potential for Pt reproduces the energies and relaxations of the (111), (110) and (100) surfaces of fcc Pt to a high degree of accuracy, and correctly predicts the relaxation, pairing and buckling of the  $1 \times 2$  reconstruction of the (110) Pt surface.

### Studies in the dissolution of calcite.

N.H. De Leeuw<sup>1</sup>, S.C. Parker<sup>1</sup> and J.H. Harding<sup>2\*</sup>.

<sup>1</sup> School of Chemistry, University of Bath,

<sup>2</sup> University College, London.

Atomistic simulation techniques were used to model two stepped {10.4} surfaces of the calcium carbonate polymorph calcite. The obtuse monatomic steps were found to be more stable than the acute monatomic steps. The initial stages of growth at the steps were considered in vacuo and in water. In vacuo  $\text{CaCO}_3$  was shown to adsorb preferentially at the acute step. However, the energies of the adsorption were modified by the geometry of adsorbed water molecules. The calculations predict that including water molecules in the simulations causes the obtuse step to grow preferentially, in agreement with experimental findings of calcite growth in solution. On using potential parameters which reproduce experimental enthalpies of the dissolution of the calcite crystal, the addition of a full obtuse step is found to be exothermic in contrast to the endothermic process of adding an acute step. This explains why obtuse steps are experimentally found to grow faster than acute steps.

### Molecular and bulk properties by molecular mechanics.

Martin Grayson.

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University of Sheffield,  
Sheffield S3 7HF, UK.

Molecular Mechanics uses a parameterized 2/3/4-body force-field to provide an estimate of the energy of an assembly of molecules. This work is concerned with the production of "property surfaces" to provide an estimate of quantities such as bulk magnetic susceptibility, NMR spectra from estimated shieldings and coupling constants, polarizabilities, or optical activity for the same assembly of molecules. This can also be expressed in parameterized 2/3/4-body form, 2-body forms being bond properties, their bond-length derivatives and their derivatives with respect to the surrounding coulomb field. Such bond properties have a very old pedigree right back to J.J. Thomson. A well-known 4-body parameterization is the Karplus Equation for the variation of spin-spin coupling constants with dihedral angle.

### The renormalized potential for cubic crystals.

Tomasz Gwizdalla.

Department of Solid State Physics,  
University of Lodz, Pomorska 149/153,  
90-236 Lodz, Poland.

The shape of the potential curve for some fcc and bcc crystals has been determined. Starting from the basic shape appropriate for the elastic properties for the temperature 0K and using the anharmonic renormalization method proposed by Siklos and Plakida, we obtained potentials for temperatures up to the melting point. These potentials were used for subsequent SLAB calculations of the dynamical properties of the samples studied, performing equally well for bulk as for thin film or surface calculations.

### Conformational transitions in amylose strands.

Michelle M. Kuttel\* and Kevin J. Naidoo.

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Rondebosch, 7701, South Africa.

Development of a biodegradable alternative to imperishable plastic polymers is becoming increasingly necessary. A potential candidate is starch, a naturally-occurring and enzymatically degradable biopolymer comprising two polysaccharides: amylose (a linear polymer with  $\alpha(1\rightarrow4)$  linked D-glucopyranose units) and amylopectin (a branched polymer with short  $\alpha(1\rightarrow4)$  glucose chains connected by  $\alpha(1\rightarrow6)$  bonds).

However, in order to render starch-based plastics commercially viable, some undesirable physical properties of starch (eg. brittleness and rapid physical aging) should be eliminated. It is necessary to understand the underlying folding mechanisms of starch in a number of environments to determine which modifications should be made to the starch molecule to achieve this end. Our first approach is to explore the mechanisms of folding of a 6-unit amylose strand in vacuum. This strand constitutes a single turn in both the B and V helical form of amylose.

We compute the potential of mean force of the amylose strand as a function of the end-to-end distance (the distance between O4 on the first glucose residue and O1 on the sixth glucose residue), using an iterative constraining potential method, previously developed by us (Naidoo & Brady, *J.Am.Chem.Soc.*, submitted 1998). We use CHARMM (Brooks, Bruccoleri, Olafson, States, Swaminathan & Karplus, *J.Comput.Chem.*, 4(2), 187) and a CHARMM-like force field for carbohydrates (Liang & Brady, unpublished, 1998), for all the molecular dynamics calculations.

### Computer simulation of confined liquid crystal mixtures.

R. Latham\* and D.J. Cleaver.

Materials Research Institute, Sheffield Hallam University,  
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We present preliminary results from a molecular dynamics study a confined liquid crystal mixture. This study uses a fluid composed of two species of rod-like particles of differing lengths confined between two solid substrates. The fluid interaction is modelled using a generalised Gay-Berne potential and a non-separable anisotropic molecule-wall potential is employed. The molecule-wall potential includes a term which breaks the azimuthal symmetry, in order both to aid equilibration and to simulate a "rubbed" surface.

### Molecular dynamics simulations of particle bombardment induced desorption process: enhancement of Au-thiolate clusters by the use of a modified pairwise potential.

K.S.S. Liu <sup>1\*</sup>, C.W. Yong <sup>2</sup>, B.J. Garrison <sup>3</sup> and J.C. Vickerman <sup>1</sup>.

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<sup>3</sup> Dept. of Chemistry, The Pennsylvania State University,  
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Molecular dynamics simulations have been used to model the process of Ar bombardment onto a system of n-alkanethiolate molecules adsorbed on a Au(111) surface. A blend of pairwise and many-body potentials are used for various interatomic interactions. Of note are the potentials for S-S and Au-S interactions which are essentially pairwise but with an energy parameter,  $D_e$ , which varies according to the heights of S and Au atoms above the surface. It is found that the modified Au-S potential enhances the formation of a variety of Au thiolate clusters. The ejected species calculated from the simulation correlate well with those recorded by the secondary ion mass spectrometry (SIMS).

### Molecular dynamics simulation of flexible liquid crystal molecules.

Carl McBride\* and Mark R. Wilson.

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Molecular dynamics simulations have been performed for a liquid crystal molecule composed of a Gay-Berne core unit connecting a three-site and a seven-site Lennard-Jones flexible alkyl chain. Calculations have been carried out for 512 molecules in the NVT ensemble for simulation times of up to 8.0 ns at two distinct densities. The liquid crystal phases of the material have been fully characterised by measurements of orientational order parameters and structure factors in each phase. Results are also presented for conformational distributions and effective torsional potentials of the system as well as results for translational diffusion and reorientational dynamics. We conclude that models of this nature represent a powerful approach to the study of flexibility in mesogenic systems and open up possibilities for predicting both the phase behaviour and bulk properties of liquid crystals based solely on a prior knowledge of intermolecular interactions. See McBride, Wilson & Howard, *Mol.Phys.* **93**, 955 (1998); Wilson, *J.Chem.Phys.* **107**, 8654 (1997).

We also present results for a fully atomistic model of the mesogen 4, 4'-dipentyl- 1, 1'-bibicyclo[2.2.2]octane (5,5-BBCO) in which we show growth of a nematic phase directly from the isotropic liquid.

### The structure of small gold clusters.

Nicholas T. Wilson\* and Roy L. Johnston.

School of Chemistry, The University of Birmingham,  
Edgbaston, Birmingham B15 2TT, UK.

Molecular Dynamics Simulated Annealing techniques have been used to probe the structure of small gold clusters consisting of between 2 and 40 atoms. The interatomic interactions within these clusters are described using a Murrell-Mottram potential (Murrell & Mottram, *Mol.Phys.*, **69**, 571 (1990)) which is an empirical atomistic [2+3]-body potential energy function parameterised to bulk experimental data such as lattice energy, lattice separation and phonon frequencies.

The Molecular Dynamics Simulated Annealing protocol involves the slow quenching of a cluster from a high, usually molten, temperature into its lowest energy conformation. If the annealing is performed infinitely slowly then the cluster should be quenched into the global minimum of the potential. The efficiency of this method as a tool for probing the potential energy surface of this system is explored with relation to other methods of determining the global minimum.

### The effects of segment-segment repulsion on model polymers.

Cheng Xiao and David M. Heyes

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University of Surrey, Guildford GU2 5XH, UK.

The effects of segment-segment interactions on polymer solutions are examined by Brownian Dynamics simulation in the free-draining limit. The bead-and-spring model is used to describe polymer chains and the segment-segment interactions are modeled by a pair-potential of Gaussian

type  $u(r)/kT = A \exp(-r^2/a^2)$ . The chain dimensions and viscoelastic properties of the system are studied as functions of chain-length and concentration.

### Computer simulations of orientational behaviour of strained polymer networks.

C.W. Yong\* and P.G. Higgs.

School of Biological Sciences, Stopford Building,  
The University of Manchester, M13 9PT, UK.

Monte Carlo simulations of dense polymer networks under uniaxial strain were carried out using a three-dimensional bond fluctuation chain model. A simple excluded volume (EV) rule is applied in order to take into account both inter- and intra-molecular interactions. Symmetrised distribution functions of segmental orientations are being calculated which show characteristic doublet structures as has also been observed in deuterium nuclear magnetic resonance experiments (D-NMR). The splittings are believed to be due to reorientations of polymer segments about a macroscopic axis parallel to the direction of the uniaxial strain. Such observations are in contradiction to the predictions of the classical "phantom" network theory. Different parts of interactions are systematically switched on or off in order to study in detail the factors which affect the orientational behaviour of a polymer segment. The uniformity of the average segmental uniaxial orientations along a chain will also be addressed.

## CCP5 visit of Dennis Rapaport

Bar-Ilan University  
Ramat-Gan  
Israel

During the course of an extended visit to the Physics Department at Edinburgh University, which was sponsored by the TRACS program of the Edinburgh Parallel Computing Center (EPCC), a short lecture tour was arranged for me under the auspices of CCP5. So, during a hot week in August 1997, I found myself visiting the Daresbury Laboratory, UMIST (Manchester), and Reading University, with lots of train mileage in between (despite using a sophisticated algorithm to minimize the distance).

The visit began in Daresbury where my hosts were Bill Smith and Phil Lindan. I had visited the lab on two previous occasions to work on parallel processing, so this provided a welcome opportunity to renew old acquaintances. I gave a talk on interactive simulation and visualization (some of this material is described in [1,2]) with live demonstrations using a Silicon Graphics workstation and large-screen projector kindly arranged by Phil. The visit gave me a chance to talk at length with Bill about subjects of mutual interest, parallel computing in particular.

It was only a short hop to Manchester, where my my host at UMIST was Julian Clarke. I gave a seminar describing some of my recent work on granular material simulation (see [3-5]). There was time for plenty of discussion with Julian, with Les Woodcock who came over from Bradford and who also finds granular matter fascinating, and with the members of Julian's group.

Then south to Reading, home also to a famous place of incarceration. My hosts were Mark Rodger and Mike Drew. The colloquium was on the methodology of molecular dynamics, based on my recent book [6]. A number of members of the audience who had come from universities nearby were people I had encountered in various places in the past but had not met for many years, so it was nice to see some familiar faces. I had discussions with Mark and Mike and the members of their groups; it was also an opportunity to catch up on the latest Australian news from Mark, a fellow antipodean expatriate.

I would like to thank my hosts at each of the ports of call for their warm hospitality and for making this little trip a most rewarding experience. It provided a welcome opportunity to talk to people working on challenging computational problems in a number of different fields, and it was encouraging to see that computer simulation has such a dedicated following in the physics and chemistry communities. Thanks also to CCP5 for sponsoring the trip, and to Stuart Pawley, who was my host in Edinburgh, for putting the program together.

### References:

- [1] *An Introduction to Interactive Molecular Dynamics Simulations*, D. C. Rapaport, *Computers in Physics* **11** (4), 337 (1997).
- [2] *Interactive Molecular Dynamics*, D. C. Rapaport, *Physica A*, **240**, 246 (1997).
- [3] *Molecular Dynamics Studies of Grain Segregation in Sheared Flow*, D. Hirshfeld and D. C. Rapaport, *Phys. Rev. E* **56**, 2012 (1997).
- [4] *Molecular Dynamics Studies of Granular Flow Through an Aperture*, D. Hirshfeld, Y. Radzyner and D. C. Rapaport, *Phys. Rev. E* **56**, 4404 (1997).
- [5] *Subharmonic Surface Waves in Vibrated Granular Media*, D. C. Rapaport, *Physica A* (in press, 1997).
- [6] *The Art of Molecular Dynamics Simulation*, D. C. Rapaport (Cambridge University Press, 1995); paperback edn. (1997).