The DL_POLY Molecular Dynamics Package.

W. Smith, I.T. Todorov and M. Leslie

Computational Science & Engineering Department
CCLRC Daresbury Laboratory, Daresbury
Warrington WA4 4AD, United Kingdom

E-mail: W.Smith@dl.ac.uk I.T.Todorov@dl.ac.uk M.Leslie@dl.ac.uk
Molecular Simulation Group: http://www.cse.clrc.ac.uk/msi/index.shtml
DL_POLY: http://www.cse.clrc.ac.uk/msi/software/DL_POLY/index.shtml

Abstract

The DL_POLY package provides a set of molecular dynamics programs that have application over a wide range of atomic and molecular systems. Written for parallel computers they offer capabilities stretching from small systems consisting of a few hundred atoms running on a single processor, up to systems of several million atoms running on massively parallel computers with thousands of processors. In this article we describe the structure of the programs and some applications.

Keywords: DL_POLY, Molecular Dynamics simulation, Software

Introduction

The DL_POLY package was developed at Daresbury Laboratory to support the research interests of the CCP5 project [1]; one of several computational projects set up to foster computational science in the UK. It is a general purpose molecular dynamics package, capable of simulating a wide range of molecular systems, and able to exploit to the full the enormous potential of parallel computers. The code is supplied in source form, so that extensions may be added by the user, building on an already advanced code. DL_POLY has been applied in a broad range of scientific studies since its public release in 1996 [2] as DL_POLY_2. Over 1000 user licences have since been released worldwide.

The original public version of DL_POLY (DL_POLY_2), was based on a Replicated Data (RD) [3] parallelisation strategy, which works well for typical simulations of less than 30,000 atoms on computers with fewer than 100 processors. More recently we have introduced a Domain Decomposition (DD) [4,5] version (DL_POLY_3 [6]), which permits simulation of systems of order of one million atoms (and beyond) on computers with over 1000 processors. The full specification may be found in the DL_POLY User Manual [7].

DL_POLY is currently available under a licence that is free of cost to academic scientists pursuing research of non-commercial nature. Commercial organisations wishing to obtain the code can purchase a licence from the CCLRC (contact Dr. W. Smith (W.Smith@dl.ac.uk) at Daresbury Laboratory in the first instance). Copies of the academic licences and more information about DL_POLY packages can be found on the DL_POLY website: http://www.cse.clrc.ac.uk/msi/software/DL_POLY/index.shtml.

Functionality

DL_POLY has an extremely wide range of applications. These are possible through a comprehensive functionality with many levels of complexity. We shall deal with each of these in turn. Readers wishing to know more about molecular dynamics and underlying theory are recommended to consult the books by Allen and Tildesley [8], Frenkel and Smit [9] or Hansen and McDonald [10].

1. ***Molecular Structures***. The simplest entities recognised by DL_POLY are atoms, which are regarded as point particles interacting with neighbouring particles via a centro-symmetric potential function. Simple atomic ions are also represented in this way. Their dynamics are described by translational motion as in a classical Newtonian treatment. Also possible are rigid molecules, which are point atoms maintained in a fixed geometry. These entities possess both translational (Newtonian) motion and rotational (Eulerian) motion and are useful for describing small molecules, such as water. For larger and more flexible structures, such as polymers, point atoms may be connected by rigid bonds allied with some intramolecular interactions, such as bond angle and dihedral angle potentials, which maintain the basic molecular geometry but permit intramolecular conformational changes, which are an essential feature of the dynamics (and chemistry) of chains. Sometimes completely flexible molecules are required, in which case the rigid bonds are replaced by extensible bond potentials. All of these molecular entities are permitted by DL_POLY_2. DL_POLY_3 is similar in capability, but does not permit rigid bodies. Any combination of the permitted entities is allowed by both programs, so that (in DL_POLY_2) a rigid body solvent and a flexible chain polymer may be simulated together, for example.
2. ***Force Field***. The DL_POLY package does not support a unique force field, as is common in other packages (e.g GROMOS[11], AMBER[12] etc) where specialisation of the applications makes such a feature sensible. However the programs recognise most of the standard potential forms found in other packages, so the user is free to design and

incorporate alternative force fields for any particular application. The intramolecular terms include bond, bond angle, dihedral, inversion and improper dihedral potentials. In each case several analytical forms are available. The intermolecular terms include van der Waals, coulombic, polarization, three-body (angular), four-body (angular), many body (metal) and many body (covalent) potentials. The possible van der Waals potentials are many in number and several options are available for the three- and four-body interactions (which help define structures such as zeolites and glasses). The many body potentials are currently confined to the Sutton-Chen [13] form for metals and the Tersoff [14] form for covalent systems. The treatment of coulombic interactions is a large issue in its own right, owing to the difficulty of calculating long range terms. DL_POLY has several options available including the standard Ewald sum [15]; Smoothed Particle Mesh Ewald (SPME) [16], Hautman-Klein Ewald [17], Reaction Field [18], distance dependant dielectric [19], shifted coulombic sum and direct sum. The Ewald based schemes are by far the most accurate and well founded. The Reaction Field scheme is less accurate but physically sound. The direct sum method is accurate and suitable for finite clusters of atoms. The remaining methods are merely cheap, historical alternatives. A particular feature of the DL_POLY package that is of significance to those studying molecular crystals is the program known as DL_MULTI [20], which is a derivative of DL_POLY_2 that uses distributed multipoles within the Ewald scheme to model molecular crystals. The treatment of polarisable ions in DL_POLY is based on the adiabatic shell model [21]. Finally, there exists within DL_POLY the possibility of adding an external field to the forces acting in a system. Common external fields include electric, shear and confining fields. The richness of the force field terms in DL_POLY provides the possibility of simulating of extremely complex systems, for example including bio-inorganic and bio-metallic interfaces.

3. ***Integration algorithms***. The DL_POLY integration algorithms were originally based on the Verlet leapfrog algorithm [22]. This is a simple and economic algorithm possessed of great stability and is highly suitable for simulations of long duration. The leapfrog algorithm integrates the translational equations of motion. The rotational motion is handled by an algorithm that updates the angular velocity through Euler's equations [23], and updates the molecular orientation by means of quaternion equations [24]. Quaternion parameters are used to define the molecular orientation so that the resulting equations of motion are free of singularities, unlike the more familiar Euler angles [24]. The dynamics of rigid bonds is handled using the well known Shake [25] and Rattle [26] algorithms, and the dynamics of rigid bodies interlinked by rigid bonds is obtained by a hybrid algorithm of our own devising called Qshake [27]. Recently in the molecular simulation community

greater emphasis has been placed on symplectic and time-reversible algorithms [28], which are guaranteed to preserve certain mathematical properties of the system under investigation (such as the Boltzmann distribution function) despite the approximations inherent in any numerical solution of the equations of motion. This has led to the adoption of the velocity Verlet algorithm [29] as the main integration method in DL_POLY_3, with similar changes scheduled for DL_POLY_2. As well as generating molecular trajectories, integration algorithms may also be used to define the statistical mechanical ensemble. The standard fixed particle number (N) – constant volume (V) – constant energy (E) ensemble associated with the simplest implementation of Verlet's integration algorithms is generally referred to (slightly inaccurately) as the NVE ensemble. More significant ensembles are also possible, such as the canonical or NVT ensemble [30] and the isobaric-isothermal or NPT ensemble [31]. The NσT ensemble [32], a variant of the NPT ensemble, responds to anisotropic stress within a (solid state) system and enables the study of solid-solid phase transitions. There are many methods available for generating such ensembles. The methods in DL_POLY are based on the work of Hoover [30], Berendsen *et al.* [33], Evans *et al.* [34], Melchionna *et al.* [35] and Martyna *et al.* [36].

4. ***Boundary Conditions.*** The specification of the boundary conditions is an essential aspect of any finite simulation. DL_POLY provides for the specification of the following boundary conditions, all of which replicate an infinite system: cubic periodic boundaries; orthorhombic periodic boundaries; and parallelepiped (or triclinic) periodic boundaries. DL_POLY_2 additionally provides: truncated octahedral periodic boundaries and rhombic dodecahedral periodic boundaries [37] (which have particular efficiency for simulating isotropic solutions); and slabs (*x*,*y* – periodic, *z* – non-periodic). Systems with no boundaries at all (e.g. an isolated biopolymer in space) are also permitted.

Applications

The range of applications of DL_POLY in molecular systems is enormous, as may be gleaned from a recent review of DL_POLY applications [38]. Known application areas of the package include: structure and dynamics of liquids and solutions; spectroscopy (origin of band shapes); ionic solids; molecular crystals; polymer structure and dynamics; silicate and borate glasses; biological membranes; proteins; solid and liquid interfaces; surfaces; zeolite catalysis; liquid crystals; and clathrates. To give a flavour of some of the many possible applications we present some recent examples of the use of DL_POLY in studies of condensed phase systems.

1. ***Radiation Damage.*** Highly energetic particles progressing through a crystal structure produce cascades of ions within the matrix, giving rise to structural changes and defect formation. Specific materials such as zircon ($ZSiO_4$), which have potential for immobilisation of nuclear waste, have been studied with DL_POLY [39]. Bombardment of the zircon by alpha-particles is known to create permanent amorphous regions in the crystal. If the number of amorphous regions increases with bombardment, a percolation transition takes place at amorphous fraction $p_1 \approx 0.3$ which connects the amorphous regions and gives rise to increased ionic diffusion in the system. However another significant rise in diffusion occurs at $p_2 \approx 0.7$ following increased bombardment. It was suggested that this was due to the amorphous regions having low and high density regions, due to formation of (high density) polymerised silica and regions of depleted matter in between. The depleted matter regions themselves undergo a percolation transition at $p_2 \approx 0.7$, which signals a further enhancement in diffusion. This suggestion was investigated by molecular dynamics simulations of zircon systems of 1,029,000 ions and it was shown that the obtained fraction of depleted matter regions was entirely consistent with the percolation theory result. Very large simulations were necessary in this instance to provide reliable statistical data.

2. ***Contact forces in ceramics.*** For some years we have been studying the origins of friction between crystal surfaces of MgO [40,42], TiO_2 [41] and NaCl [41,43]. Contact between surfaces was modelled as a probe making contact with a surface of the same material. The approach and withdrawal of the probe was done in a series of discrete steps, which allowed for re-establishment of equilibrium at each stage. A thermal bath maintained the temperature of the system. Several significant phenomena were observed, the most important of which was the `jump-to-contact' in which the probe made a discontinuous advance towards the surface to form a contiguous material. After the jump, the probe could not in general be withdrawn without strong hysteresis, which was manifested in damage to the probe or surface, in some instances leading to drawn out `wires' of material between the probe and surface [40]. Entropic effects were shown to be important inasmuch as the force on the probe was not simply the derivative of the configurational energy [41]. Other important factors included the commensurability of the probe and surface at contact, which was sufficient to inhibit the jump-to-contact in some cases [42] and probe shape, which had strong influence on the nature of the hysteresis on retraction. Efforts are currently being made to link the observed behaviour with macroscopic theories of friction, as applied to microscopic contact [43].

3. ***Ion transport and the mixed alkali effect in silicate glasses***. DL_POLY has recently been employed to provide the ionic trajectories in a virtual reality study of alkali ion diffusion in silicate glasses [44]. With the aid of isosurfaces and traced particle trajectories in immersive videos it has been possible to reveal clearly the coupling that exists between the diffusing ions and the low frequency modes of the glass network. Ions were shown to hop cooperatively between sites in the glass. A relationship was shown to exist between the free volume in the glass structure, which is occupied by alkali ions, and the cooperative events, so that a reduction in the free volume available mirrors the fall in ionic conductivity. These novel observations shed new light on the mixed alkali effect in these materials.

4. ***Molecular Crystals.*** DL_MULTI [20] is a derivative of DL_POLY_2 that uses distributed multipoles [45] within the Ewald scheme. The extension to multipoles has been used by Liem and Popelier to study liquid hydrogen fluoride as an example of a simple molecular liquid [46]. The electrostatic potential of an *ab initio* calculation on a single molecule was expanded in spherical tensor multipoles up to L = 5. To validate the potential the geometry of the gas phase HF dimer was calculated, using a hard sphere repulsion for the short range interactions. The results show that for L = 5 agreement between the simulation and *ab initio* calculations is good. For the liquid simulations an empirical Lennard-Jones potential was used to describe the short range repulsion, with the parameters adjusted to reproduce the density and first peak in the F – F radial distribution function. Five experimental properties of liquid HF were calculated (total energy, density, diffusion coefficient, isobaric heat capacity and thermal expansion coefficient) Agreement with experiment was very good. The liquid contaqins chains of HF molecules up to 10 molecules long.
   This type of potential model has also been used in recent years in studies of polymorphism in organic crystals [47] using static lattice simulation codes [48]. Work is currently underway to investigate this type of polymorphism by molecular dynamics.

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