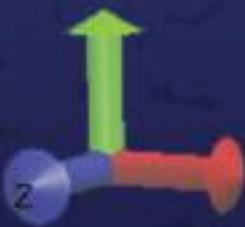
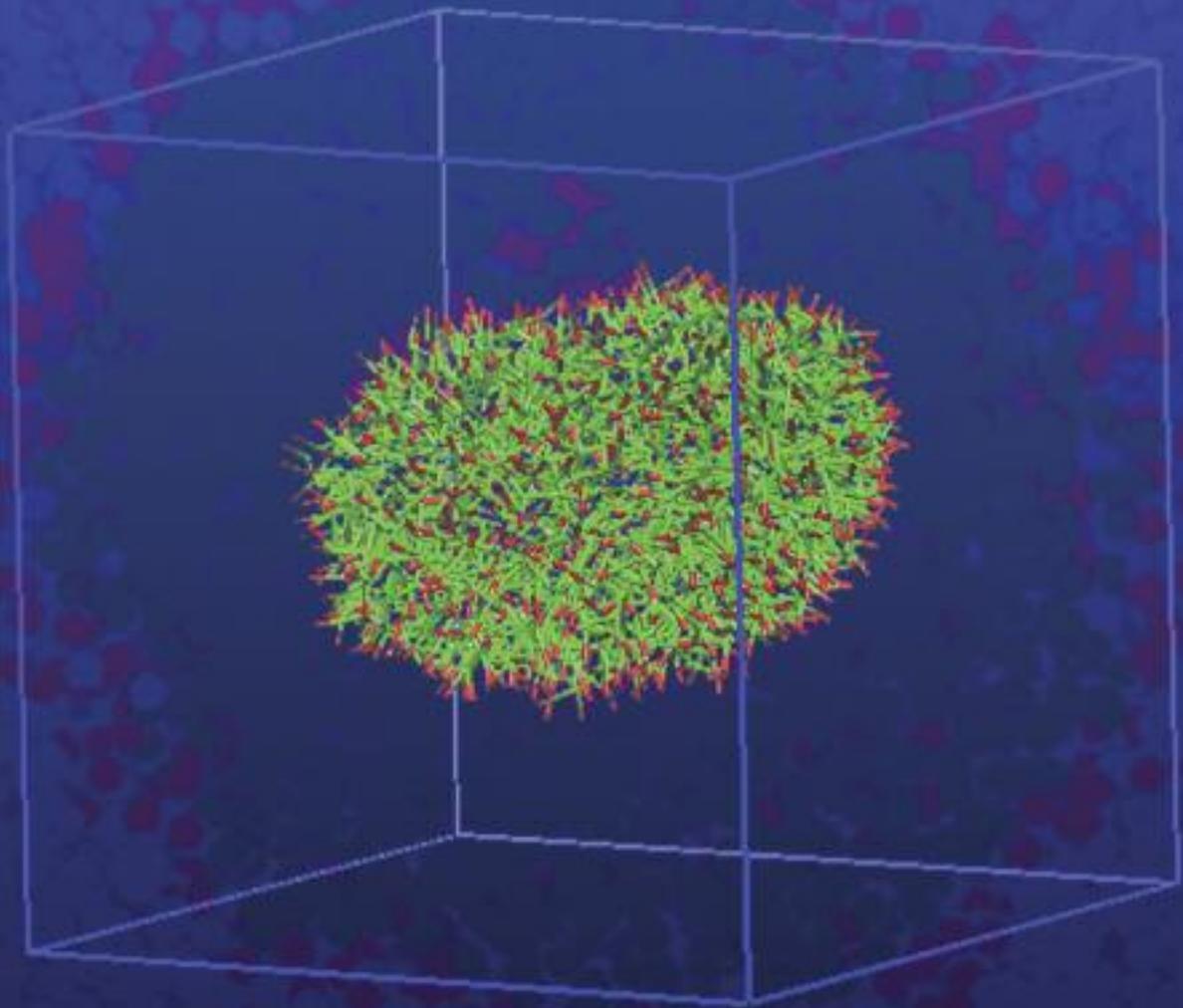


New capabilities and software for materials modelling



Thermodynamic properties of materials are important for many industrial applications in fields such as chemical engineering, metallurgy and geology. While molecular dynamics codes such as DL_POLY^[1] are well-suited for modelling kinetic properties, long and expensive simulations are often required to determine observables such as diffusivity and phase behaviour. Software packages are being developed at Daresbury Laboratory to examine the thermodynamics of a broad range of materials using alternative modelling strategies such as mesoscale and Monte Carlo methods. This work is being carried out under the auspices of the Engineering and Physical Sciences Research Council (EPSRC) for their Collaborative Computational Project for the Computer Simulation of Condensed Phases (CCP5). Both packages, DL_MESO and DL_MONTE, are supplied to individuals under an academic licence, making them free of cost to academic scientists pursuing research of a non-commercial nature. For more information, please visit their respective websites at www.ccp5.ac.uk/DL_MESO and www.ccp5.ac.uk/DL_MONTE

Mesososcopic simulation: DL_MESO

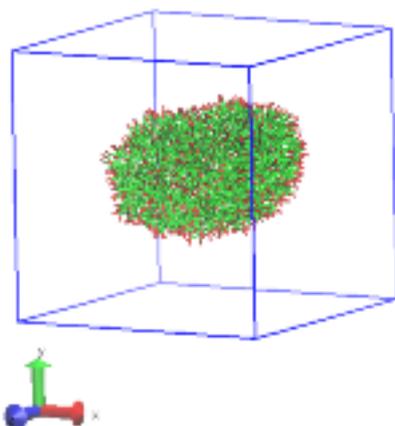
A wide range of complex materials operate at length and time scales between those for microscopic (i.e. atomistic) and macroscopic (continuum-based) systems, for which thermodynamic and hydrodynamic behaviours are equally important. As more efficient alternatives to atomistic simulations, mesoscopic methods have been developed to study such materials, including their underlying dynamics and structures.

DL_MESO is a general-purpose mesoscale simulation package consisting of separate codes for different modelling methods which can run either serially or in parallel with MPI. Two mesoscopic methods are available in the current version of DL_MESO: the Lattice Boltzmann Equation (LBE) method and Dissipative Particle Dynamics (DPD). The LBE code in DL_MESO (DL_MESO_LBE) is well-established and written in modular C++. It is made massively parallel by means of domain decomposition, i.e. dividing the lattice points representing the system volume equally among processing units. Current features in DL_MESO_LBE include: single and

multiple relaxation time collision schemes, various boundary conditions (e.g. fixed densities and velocities), mesophase interactions between different fluid species^[2] and couplings of mass and heat transfers to fluid flows.

More recent developments in DL_MESO have focussed on the DPD code, DL_MESO_DPD, which is written in modular Fortran 90: each major feature is given its own code module. Both the language and some functionality is shared with DL_POLY^[1], such as the use of domain decomposition for parallelisation. A computationally efficient code dedicated to DPD is justified, however, as this modelling method requires stochastic pairwise thermostatting and simulations may reach length and time scales close to those of continuum fluids. Beyond the standard conservative, random and dissipative interactions between pairs of DPD particles ("beads"), the inclusion of bonds between beads to give semblances of molecular structures vastly expands the range of systems that can be modelled. Other features in the current version of DL_MESO_DPD include:

(a)



(b)

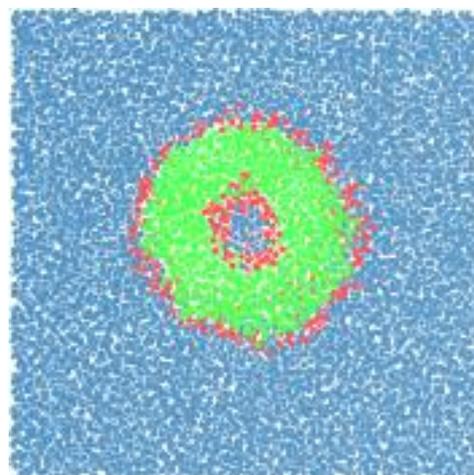


Figure 1: (a) Vesicle formed from amphiphilic molecules initially randomly distributed in aqueous solution^[5] (red denotes hydrophilic head group, green hydrophobic tail); (b) Cross-section of vesicle showing encapsulated water.

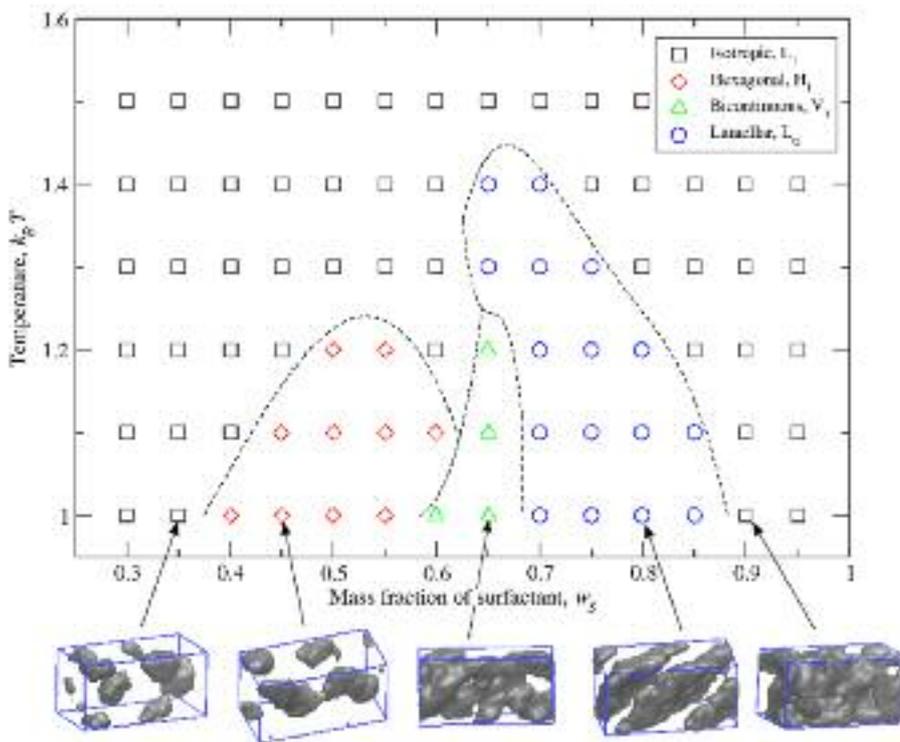


Figure 2: Phase diagram of a non-ionic amphiphilic surfactant as derived from DPD simulations, with illustrations of each mesophase depicting isosurfaces of hydrophobic species. (Proposed phase boundaries given to guide the eye.)

- Many-body (density dependent) interactions between DPD beads to apply alternative equations of state;
- Electrostatic interactions between (soft) charged beads with Ewald sums and smeared charges^[3];
- Hard adsorbing surfaces in place of selected periodic boundaries;
- Alternative thermostats e.g. ^[4] for high viscosity fluids, in place of dissipative and random forces, and barostats for constant pressure (NPT ensemble) systems.

Very good to excellent parallel scaling is achieved due to domain decomposition. Some loss of scaling occurs when using quadratically-scaling Ewald-based electrostatics and/or alternative thermostats that require a replicated data strategy.

One example of a system that can be modelled using DPD is spontaneous

self-assembly of amphiphilic molecules into a vesicle^[5], as illustrated in Figure 1. This simulation of 41,472 beads was carried out on HECToR^[6] (Phase 2b: Cray XE6) using 96 processor cores: formation of a stable vesicle was achieved within 85 minutes. DPD may also be used to predict properties of liquid formulations, e.g. mesophase behaviour^[7]. Figure 2 gives an example phase diagram based on DPD simulations for a typical non-ionic surfactant.

Future versions of the DPD code in DL_MESO will include Lees-Edwards shearing boundary conditions, frozen beads for solid surfaces, more efficient electrostatic force calculations using the particle-particle particle-mesh (PPPM) method and algorithms for reducing bond crossings.

Monte Carlo simulation: DL_MONTE

DL_POLY is a widely used program to model a wide range of systems including ceramics, metals, semiconductors and molecular systems from a number of disciplines such as chemistry, chemical engineering, geology and biology. Whilst the molecular dynamics technique is excellent for calculating kinetic properties of materials, it may not be the most suitable approach for the computation of thermodynamic properties. In contrast Monte Carlo (MC) is ideally suited to the calculation of thermodynamic properties of compounds. Therefore, a MC program, DL_MONTE, was written to complement DL_POLY and provide access to new areas of science. DL_MONTE is written in a modular style using Fortran 95; Fortran was chosen since it shares some functionality with DL_POLY^[11]

(especially DL_POLY Classic). Unfortunately, complete correspondence is impossible due to the different nature of the calculations. DL_MONTE has been written to take advantage of both OpenMP and MPI (replicated data); future developments are likely to take advantage of hybrid schemes.

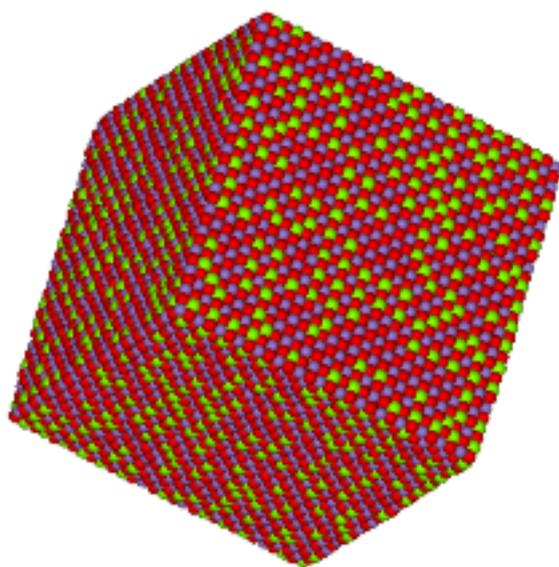


Figure 3: Distribution of Magnesium (green) and Manganese (purple) in a 27,000 atom “nanocube” of $Mn_xMg_{1-x}O$ ($x=0.1$).

The current release of DL_MONTE includes the following interaction potentials:

- Coulomb interactions evaluated using the Ewald sum – for larger simulations the k-vectors can be distributed over nodes to reduce memory use;
- Two-body and three-body non-bonded interactions;

- Bond and angle potentials;
- Metal potentials (Sutton-Chen^[8], embedded atom method^[9], Finnis-Sinclair);
- Tersoff potentials^[10].

Currently the ensembles available are NVT, NPT, Grand Canonical, Semi Grand Canonical and transmutation. The next release of DL_MONTE will also include the Gibbs ensemble.

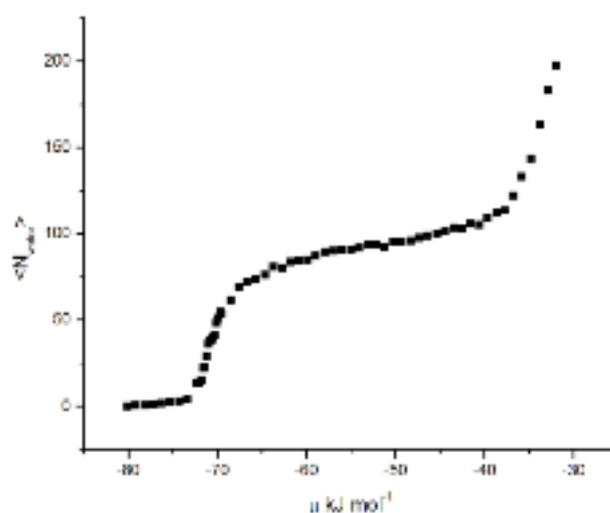


Figure 4: An isotherm calculated using the Grand Canonical ensemble. This example is for the adsorption of water on the MgO(100) surface (similar calculations have been undertaken for CO₂ adsorption in zeolites).

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- [1] I. T. Todorov, W. Smith, K. Trachenko and M. T. Dove, “DL_POLY_3: new dimensions in molecular dynamics simulations via massive parallelism”, *J. Mat. Chem.*, 16 (2006), 1911–1918; http://www.ccp5.ac.uk/DL_POLY
- [2] X. Shan and H. Chen, “Simulation of nonideal gases and liquid-gas phase transitions by the lattice Boltzmann equation”, *Phys. Rev. E*, 49 (1994), 2941–2948
- [3] M. González-Melchor, E. Mayoral, M. E. Velázquez and J. Alejandro, “Electrostatic interactions in dissipative particle dynamics using the Ewald sums”, *J. Chem. Phys.*, 125 (2006), 224107
- [4] C. P. Lowe, “An alternative approach to dissipative particle dynamics”, *EPL*, 47 (1999), 145–151
- [5] S. Yamamoto, Y. Maruyama, and S. Hyodo, “Dissipative particle dynamics study of spontaneous vesicle formation of amphiphilic molecules”, *J. Chem. Phys.*, 116 (2002), 5842–5849
- [6] <http://www.hector.ac.uk>
- [7] P. Prinsen, P. B. Warren and M. A. J. Michels, “Mesoscale simulations of surfactant dissolution and mesophase formation”, *Phys. Rev. Lett.*, 89 (2002), 148302
- [8] A. P. Sutton and J. Chen, “Long-range Finnis-Sinclair potentials”, *Phil. Mag. Lett.*, 61 (1990), 139–146
- [9] M. S. Daw and M. I. Baskes, “Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals”, *Phys. Rev. B*, 29 (1984), 6443–6453
- [10] J. Tersoff, “New empirical approach for the structure and energy of covalent systems”, *Phys. Rev. B*, 37 (1988), 6991–7000