Mesoscale Physical Chemistry Simulations Using The DL_MESO Software Package

[v1.0]

Molecular Dynamics Simulations

In general computer modellers can create programmes to model what is going on in chemical systems.
The assumptions used include:

- treating atoms as single particles (i.e. there are no separate electrons)
- atoms move using Newton's laws of motion
- Interactions between atoms include both bonds and electrostatic charges

The constructed simulations must explain experimental observations at the molecular level. The simulations can then be used to assist in the design new materials in, for example, drug delivery.

What is DL_MESO?

Mesoscale modelling methods fit between those used for molecular dynamics and computational fluid dynamics. These operate at length and time scales suited for modelling complex materials with both atom-like effects and bulk fluid properties such as viscosity. Examples of systems that can be modelled at the mesoscale include solute diffusion, conductive and convective heat transfers, phase behaviours of fluids and polymers (e.g. surfactants, amphiphiles), self-assembly of chemical structures and adsorption onto surfaces.

The Computational 'Geeky Stuff'

DL_MESO is a general-purpose mesoscale simulation package developed by Michael Seaton under a research grant provided by EPSRC. It is written in the Fortran90 and C++computing languages.

DL_MESO supports both Lattice Boltzmann Equation (LBE) and Dissipative Particle Dynamics (DPD) methods. It is supplied with its own Java-based Graphical User Interface (GUI) and is capable of both serial and parallel execution.

DL_MESO was created to provide a comprehensive mesoscale modelling package capable of bridging the gap between atomistic and continuum methods that can exploit emerging parallel computing architectures. It consists of codes for frequently-

used mesoscale methods (e.g. LBE, DPD), which can be verified and extended by registered users of the package. The codes can be considered as flexible 'simulation engines': setup and analysis of simulations can be achieved by pre- and post-processing utilities and scripts.

More information can be found at: https://www.scd.stfc.ac.uk/Pages/DL_MESO.aspx

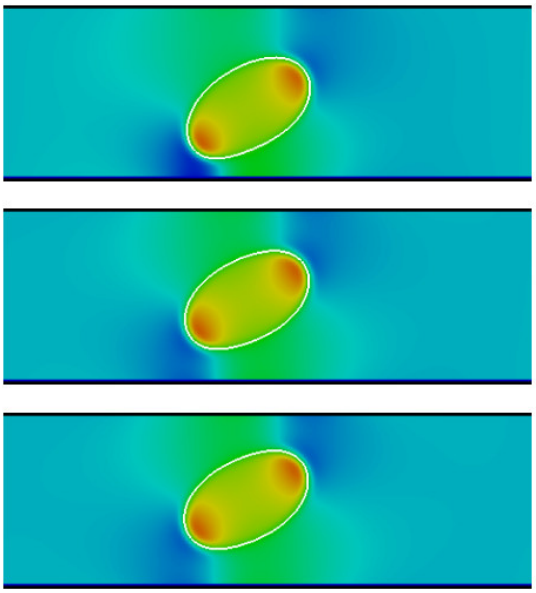
The Chemistry 'Geeky Stuff'

Historically the study of fluid matter (gases and liquids/solutions) depends on consideration of whether fluids are considered as a continuum or atomistic. In a continuum, fluids have properties (density, velocity, pressure) that are considered almost uniform in terms of space and time. This is usually an adequate description for most applications. However fluids are known to be made up of atoms and molecules whose individual properties should be considered when working at the nanoscale. ($1x\ 10^{-9}$ m). A third description of fluids with an intermediate level of the two previous descriptions has existed since the mid-1970s, where fluids are represented in terms of the probability of finding a given particle at a given position in space and time with a given velocity. The DL_MESO software considers fluids in the third descriptor.

Examples of the DL_MESO Software in Use

The results of simulations will be of importance to chemist, physicists, biochemist and engineers.

A Two Dimensional (2D) Drop Shear



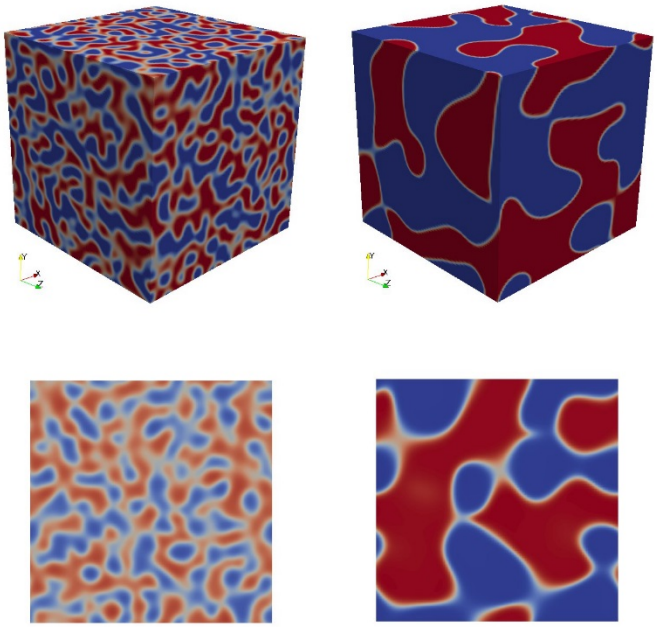
Experiments show that two immiscible liquids (liquids that do not mix) will try to reduce the surface area between them whereas a small amount of one liquid in another will often form into round drops. How big the drops become depends on the liquids and their interfacial tension. This in turn depends on the intermolecular bonds (forces) that are present in each liquid.

Computer models can be used to look at liquids that do not mix and see what happens to liquid drops when flows are applied. We used the program (DL_MESO program) to model a drop surrounded by another liquid placed between two walls. The walls were at the top and bottom.

Initially, when at rest, the drop is close to the bottom wall. We slide the top wall to move at a constant speed. This causes the drop to move up towards the top wall as well as across. The shape of the drop also stretches out from its original circle: how

much it stretches can be controlled by the interfacial tension between the two liquids. The colour in the video shows the pressure acting on the fluids, with a white line showing the drop. (Video).

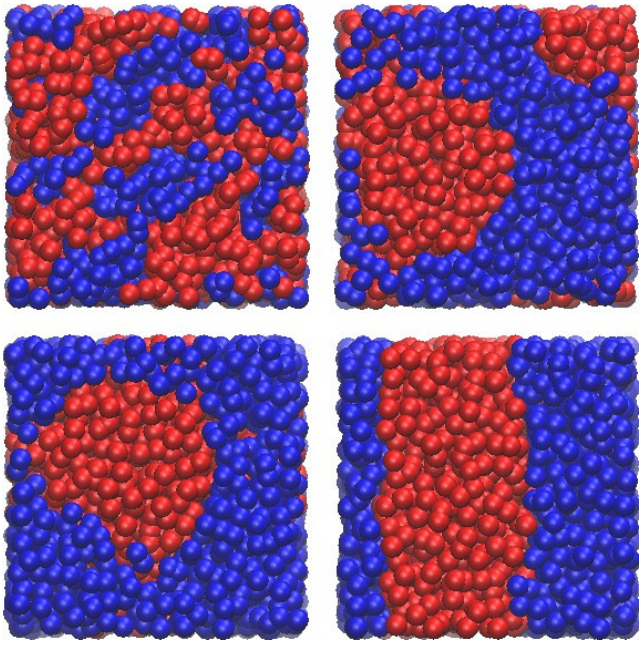
A Three-Dimensional (3D) Phase Separation



If you try to mix together two liquids that do not usually mix, due to intermolecular bonding, they will separate out. The interfacial tension between the two liquids gives an idea of how quickly they will separate.

We used the DL_MESO program to model two liquids that are mixed together, in an open box, at the start. We applied an interfacial tension between the two liquids. This interfacial tension pushes the two liquids apart, causing them to separate. Drops of each liquid eventually come together and form liquid layers. The videos show each liquid as a different colour (red or blue). Video 1

Phase Separation

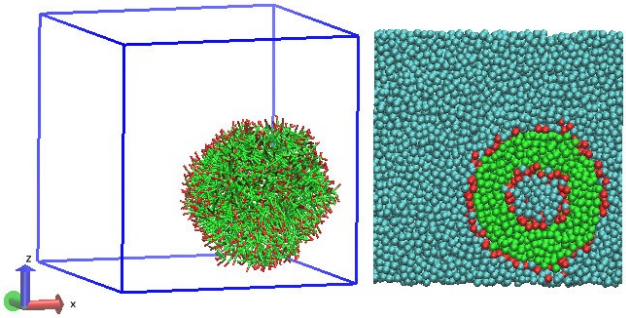


Observation shows that if you try to mix together two liquids that do not tend to mix, they will separate out. The interfacial tension between two liquids gives an idea of how much force they will apply to each other and how quickly they will separate.

We used the DL_MESO program to model two liquids as different types of particle in an open box (shown as two different colours in the video, red and blue). The 3000 particles are mixed together at the start, but we applied a

strong interfacial tension between the two particle types. This tension pushes the particles apart, causing them to separate and form liquid layers. (Video)

Vesicle Formation



Soap molecules can be thought of looking like tadpoles. They have a long hydrocarbon chain 'tail' which can only form van der Waals bonds (AKA Instantaneous dipole-dipole interactions) and a charged 'head' capable of forming hydrogen bonds. These molecules, therefore, have sections that 'like' and 'dislike' water. When in water these hydrophilic and hydrophobic sections will arrange themselves so the shorter water-loving parts stay in the water and the longer water-hating sections will bunch together. The shape of these arrangements depends on how many molecules you add!

We used the DL_MESO program to model molecules with water-loving (hydrophilic) and water-hating (hydrophobic) sections in water. The hydrophilic head sections of the molecules are shown as red, while the hydrophobic tail sections are green. The hydrophilic sections interact less strongly with water, while the hydrophobic sections repel water more strongly. The simulation comprises 37 440 unbonded water particles and 1008 molecules!

After a while, a sphere-like structure forms in the box. Taking a slice through it, you can see water has found its way inside. This structure is termed a vesicle and forms to allow the hydrophobic parts of molecules to avoid water: the water inside the vesicle is in contact with the hydrophilic parts. The amount of water inside the vesicle depends on the number of molecules used. Vesicles can be used to collect up exact doses of an active chemical, which can be put into drugs given to people to cure illnesses. Vesicles have important uses in cellular biology. (Video)

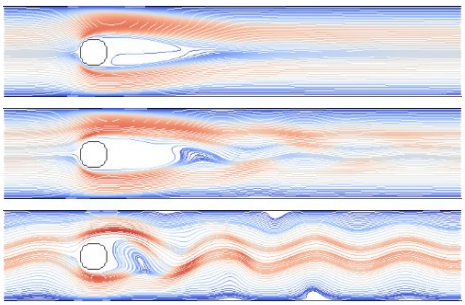
Surface Drop

If a small amount of water is in a box, it will collect up into drops. If the drops land on a solid surface, the shape of the drop on the surface will depend on the surface tension between the water and the wall. This can be measured by looking at the contact angle between the wall and the water.

We used the DL_MESO program to model water particles in a large box with solid walls at the top and bottom. A constant force due to gravity is applied to all water particles, while interactions are used to make sure water particles can collect together and control the surface tension between the water and the wall. The wall is shown as particles that are fixed in position and do not move.

As the simulation runs, the water particles collect up together into drops and land on the wall at the bottom of the box. These drops eventually collect up together (coalesce) into larger drops, which remain in contact with the wall particles. The strength of the interaction between water and wall particles determines the contact angle: the more the wall repels the water, the less surface area of water makes contact with the wall. (Video)

A Two-Dimensional (2D) Karman Vortex



Seeing how obstacles affect flows of liquids and gases can be important. For example, wind flowing past a car aerial can make it vibrate, while strong winds past a power station cooling tower might apply stress and even cause it to collapse! More Commonly used in Engineering or Physics than Chemistry.

We can use computer models to work out what happens to the fluid when it flows past an object. Here we modelled a fluid (gases or liquids) flowing in a channel: the video shows the speed of the fluid. (Video)

Putting a solid circle as an obstacle into the flow changes its flow pattern. If the flow is fast enough, the flow separates around the object and produces an unsteady swirling pattern. This is known as a von Kármán vortex street. Note adding a fin to the object can reduce the swirling.

Images https://www.scd.stfc.ac.uk/Pages/DL_MESO-example.aspx