

6.04 Computer Simulation of Phases by Molecular Dynamics (6 points)

Relevant lecture course

Molecular Interactions I.

Introduction

In this experiment you will carry out a molecular dynamics simulation of a system of noble gas atoms interacting through a pairwise LJ potential. The atoms are assigned initial (face-centred cubic) crystal lattice starting positions and random initial velocities such that the net momentum of the system is zero. The subsequent trajectories of the atoms are then calculated step by step on the assumption that they obey classical equations of motion subject to certain periodic boundary conditions that are used to mimic the properties of an infinite system.

Each time step corresponds to an interval of the order of 10^{-14} s, and hundreds or thousands of steps are followed, depending on the property under investigation. As the simulation proceeds, running averages and totals are calculated, and from these are obtained the values of various properties of the system such as its temperature, pressure, energy, and the structure of the system in terms of its radial distribution function. By repeating the calculation at various temperatures and densities, the properties of all three (solid, liquid and vapour) phases of the system can be calculated and compared with what one would expect theoretically (e.g. with the predictions of kinetic theory in the case of a simulation of the gas).

Over the past several decades computer experiments have become an invaluable tool in the study of physical properties, especially those of liquids. Such studies employ computer programs to generate the positions and follow the trajectories of a small number of atoms, calculate the effects of collisions between them, and monitor various properties of the system such as the simulated temperature and pressure.

An important part of the computer programs is the potential energy function, which describes the energy of interaction between the atoms as a function of distance. An obvious goal of computer simulation experiments would be to mimic the properties of a real fluid by using an accurate potential energy function. In practice this is very difficult, however, either because the true interactions are unknown or because they are expressed by intractable equations. One therefore typically uses a simple model for the interactions such as the Lennard-Jones (LJ) potential described below. This has the advantage that, although the interactions in the simulated system are not entirely realistic, they are both easy to calculate and unambiguously defined so that precise, quasi-experimental data can be obtained for the model system. Theoretical models of the system can therefore be tested and their properties compared with the results of the simulation, and information may be obtained in this way on properties of theoretical importance which cannot easily be measured in the laboratory.

Background Theory

Interaction Potential

The Lennard-Jones (12-6) potential function provides a convenient approximation to the interaction energy between two noble gas atoms:

$$v(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (1)$$

Here ε is the well depth of the potential and the collision diameter σ is the separation at which $v(r)=0$. Another useful parameter is the equilibrium separation at which $dv(r)/dr$ is zero and there is no net force between the atoms.

The negative r^{-6} term in equation (1) arises from attractive, long-range interactions known as London or dispersion forces. These can be thought of as arising from an instantaneous dipole moment in one atom inducing a dipole in the other atom, which can cause an attractive force. When the atoms approach each other more closely, the overlap of their closed-shell electron densities results in a strong repulsion. It is convenient to express this repulsive interaction as a positive r^{-12} potential as in equation (1), although an exponentially decaying potential would probably have more theoretical justification.

Reduced Variables

For a system of identical noble gas atoms interacting through a pairwise LJ potential, it is natural to use the mass m of a single atom as the unit of mass, the well depth ε as the unit of energy, and the collision diameter σ as the unit of length.

Atom	ε/k_B (K)	σ (nm)
Ar	124	0.342
Kr	190	0.361
Xe	229	0.406

Table 1. Lennard-Jones parameters for Ar, Kr and Xe [1].

Given these definitions, the units of other quantities (pressure, time, momentum, etc.) follow directly, and the properties of the system can be specified in terms of the following reduced variables:

energy	$E^* = E / \varepsilon$	time	$t^* = (\varepsilon / m \sigma^2)^{\frac{1}{2}} t$
density	$\rho^* = \rho \sigma^3$	temperature	$T^* = k_B T / \varepsilon$
pressure	$p^* = p \sigma^3 / \varepsilon$	diffusion coeff.	$D^* = (m / \varepsilon \sigma^2)^{\frac{1}{2}} D$

The use of somewhat different reduced variables is discussed in Atkins' *Physical Chemistry* in connection with the principle of corresponding states, which asserts that the equations of state are very similar for a wide range of real (non-polar) gases when written in terms of the reduced variables $p_r = p/p_c$, $V_{m,r} = V_m / V_{m,c}$ and $T_r = T / T_c$ (where p_c , $V_{m,c}$ and T_c are the critical pressure, critical molar volume and critical temperature of the gas) [2].

In the present context, by analogy with the principle of corresponding states, the use of reduced variables has the advantage that a single computer simulation at a fixed reduced density ρ^* and reduced temperature T^* applies to a wide range of systems with different values of ε , σ and m . For example, a LJ potential with $\varepsilon/k_B = 124$ K and $\sigma = 0.342$ nm provides a reasonable approximation to the interaction between two argon atoms, whereas a LJ potential with $\varepsilon/k_B = 190$ K and $\sigma = 0.361$ nm is more appropriate for the interaction between two krypton atoms (see Table 1). A single computer simulation with $\rho^* = 1$ and $T^* = 1$ therefore corresponds both to a system of argon atoms at $T = 124$ K and $\rho = 25.0$ atoms nm^{-3} and to a system of krypton atoms at $T = 190$ K and $\rho = 21.3$ atoms nm^{-3} .

Phase Diagram

Figure 1 shows the phase diagram for a noble gas [3]. The left-hand side of the diagram shows the projection in the $\rho - T$ plane and the right-hand side shows the projection in the $p - T$ plane. The pressure, density and temperature at the critical point are denoted p_c , ρ_c and T_c , and the corresponding variables at the triple point are p_t , ρ_t and T_t .

The right-hand side of Figure 1 is the most frequently encountered form of the phase diagram, involving the variables p and T . It shows the regions of pressure and temperature at which various phases are thermodynamically stable; each point on the

diagram corresponds to a realisable state of the system. The phase rule due to Gibbs applies to this part of the diagram. Since the system only has one component ($C = 1$), the number of degrees of freedom F and the number of phases in equilibrium P are related in the right-hand side of Figure 1 by

$$F = C + 2 - P = 3 - P \quad (2)$$

Coexistence curves between $P = 2$ phases therefore occur as lines in the figure, and the triple point (where $P = 3$) is the unique point where $F = 0$ and the system is said to be invariant [2].

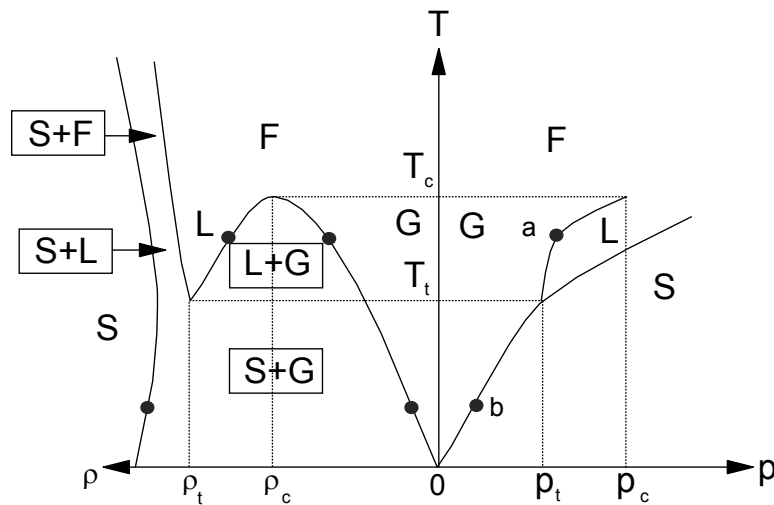


Fig. 1. Phase diagram for a noble gas, showing the boundaries between solid (S), liquid (L) and vapour (G) or fluid (F) phases as solid lines. The subscript t stands for triple point and c for critical point.

The left-hand side of Figure 1 will probably be less familiar to you. Two phases in equilibrium have different densities and this makes the $\rho - T$ phase diagram more complicated. As in the right-hand side of the figure, there are again phase boundaries, but in addition to distinct regions where different phases exist there are now also the *coexistence regions* labelled S+F, S+L, L+G and S+G. These regions arise because (for example) the point marked a on the gas-liquid coexistence curve in the $p - T$ phase diagram corresponds to two points in the $\rho - T$ diagram along the same isotherm between $T = T_t$ and $T = T_c$, one at the low density of the gas phase and the other at the higher density of the liquid phase. Similarly, the point marked b on the gas-solid coexistence curve corresponds to two points in the $\rho - T$ phase diagram, one at the low density of the gas phase and the other at the considerably higher density of the solid phase.

Now suppose that the system is prepared at a density ρ and temperature T inside the L+G coexistence region in Figure 1. The point in question does not have the correct density of either the gas or the liquid phase, and must therefore correspond to both phases simultaneously. The nature of the correspondence is illustrated in Figure 2: a certain fraction $(\rho - \rho_G) / (\rho_L - \rho_G)$ of the system will be in the liquid phase at density

ρ_L and the remaining fraction $(\rho_L - \rho) / (\rho_L - \rho_G)$ will be in the gas phase at density ρ_G , in accordance with the 'lever' rule. A macroscopic system at a density ρ and temperature T in the L+G coexistence region will therefore consist of different proportions of the liquid and gas phases with a phase boundary between the two.

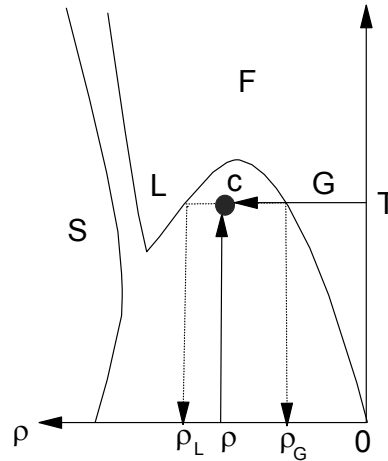


Fig. 2. The lever rule. A macroscopic system prepared with a density ρ and temperature T in the L+G coexistence region will phase-separate into a fraction $(\rho - \rho_G) / (\rho_L - \rho_G)$ of the liquid phase at density ρ_L and a fraction $(\rho_L - \rho) / (\rho_L - \rho_G)$ of the gas phase at density ρ_G .

The reason for stressing this here is that this situation is almost impossible to mimic in a computer simulation, where the inevitable restriction to a small finite number of atoms (albeit with periodic boundary conditions) results in an unrealistically large free energy penalty for forming the phase boundary. Thus a finite-sized computer simulation will generally *not* form a phase boundary between the liquid and gas phases in the coexistence region. Instead, it will spend some of its time exclusively in one phase and the rest of its time in the other, and the statistical fluctuations in the simulated properties of the system will consequently be very large [4].

In view of this situation, you should try to avoid the L+G and S+G coexistence regions in this practical, and concentrate instead on reduced densities (ρ^*) and temperatures (T^*) well inside the solid (S), liquid (L) and vapour (G) regions in Figure 1. In order to help you to do this, it may be useful for you to know that the reduced density and the reduced temperature at the triple point of a Lennard-Jones fluid are approximately $\rho_t^* = 0.85$ and $T_t^* = 0.70$ and that the critical temperature is close to $T_c^* = 1.35$. The liquid phase can therefore be simulated by specifying $\rho^* = 0.85$ and $T^* = 1.0$, and the solid and gas phases can be simulated at the same reduced temperature by specifying $\rho^* = 1.0$ and $\rho^* = 0.1$ respectively.

Computational Details

Periodic Boundary Conditions

A major limitation of any computer simulation is the number of atoms that can be included. There are 6×10^{23} atoms in a mole, but a present-day computer would take longer than the age of the universe (10 - 20 billion years) to calculate the forces between this number of atoms. The size N of the sample that is studied in practice is therefore typically less than 1000 atoms, and in the present experiment N is 108.

To minimise surface effects, and simulate more closely the properties of an infinite system, periodic boundary conditions are imposed on the simulation. The 108 atoms under investigation are chosen to lie in a central cell or "simulation box". When an atom leaves the box, the move is balanced by a periodic copy of the atom entering the box with the same velocity through the opposite face (Figure 3). The only interactions that are calculated are those between each atom within the box and the *closest* periodic copy of each other atom, whether or not this copy lies within the box. This procedure is known as minimum imaging, and it is the standard way to impose periodic boundary conditions on a molecular dynamics simulation [4].

In this experiment we use a cubic simulation box, arranging the atoms initially in a face-centred cubic lattice corresponding to the crystal structure of solid argon. Such an arrangement requires $N = 4n^3$ atoms, where n is an integer, and a 108-atom calculation clearly satisfies this requirement with $n = 3$.

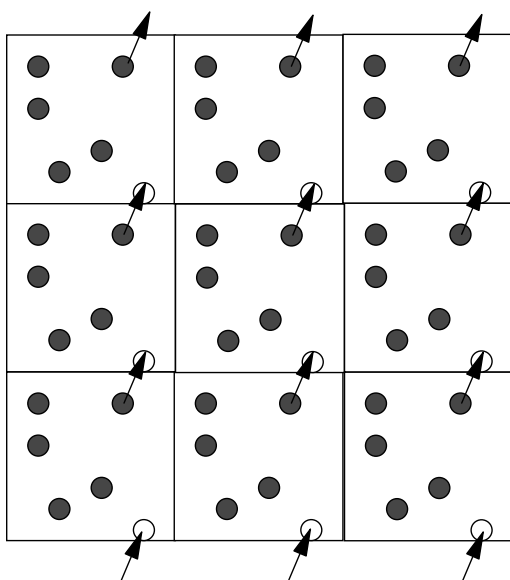


Fig. 3. A two-dimensional periodic system. Atoms can enter and leave the central simulation square across any of its four edges, but each time an atom leaves the square the move is balanced by a periodic image of it entering through the opposite edge. In a three-dimensional simulation, atoms are free to cross any of the six faces of the simulation cube in the same way.

If you want to view the initial arrangement of the atoms, you can do so by performing a simulation with an equilibration time of zero and a simulation time of zero, as described in Section 5, and then typing the command **ATM** (for "atomic motion"). The effect of the periodic boundary conditions on the simulation can be seen by typing the same command after a longer simulation of the gas phase and holding down the right

bracket key (]) to see a movie: provided the simulation has run for long enough the tagged (red) atom will eventually leave the simulation box while a periodic copy of it arrives through the opposite face.

Equilibration

The heart of any molecular dynamics simulation program is a computer subroutine that follows a classical trajectory of the system by numerically integrating Hamilton's equations of motion

$$\frac{dr_i}{dt} = + \frac{\partial K}{\partial p_i} \quad (3) \quad \text{and} \quad \frac{dp_i}{dt} = - \frac{\partial V}{\partial r_i} \quad (4)$$

where K and V are the total kinetic and potential energies

$$K = \sum_{i=1}^N \frac{p_i^2}{2m} \quad (5) \quad \text{and} \quad V = \sum_{i<j}^N v(|r_i - r_j|) \quad (6)$$

and $r_i(t)$ and $p_i(t)$ are the position and momentum vectors of each atom $I = 1, 2, \dots, N$ at time t . (Equation (3) is simply the definition of momentum as $p_i = m dr_i/dt$ and equation (4) is Newton's second law in the form $F_i = dp_i/dt$.)

Since the total energy $E = K + V$ of the system is conserved by these equations, and N and V are conserved by the periodic boundary conditions described above, each point along the trajectory corresponds to a system with the same values of N , V , and E (i.e., to a system in a microcanonical ensemble [2]). The instantaneous kinetic and potential energies K and V are not conserved, however, and they fluctuate during the simulation subject to the constraint that $E = K + V$. An important consequence of this is that the instantaneous temperature T also fluctuates, since it is related to the kinetic energy K by the equipartition formula

$$K = \frac{3}{2} N k_B T \quad (7)$$

(or equivalently, in terms of the reduced variables defined in Section 2, by $K^* = (\frac{3}{2}) N T^*$). The question that this clearly raises is how to allow for these temperature fluctuations when performing a simulation at a specified reduced temperature T^* in the desired region of the $\rho - T$ phase diagram.

The standard answer to this question is to begin the simulation with an *equilibration stage* during which the instantaneous speeds of the atoms are scaled after each time step so as to make the instantaneous reduced temperature T^* equal to the specified temperature T^* [4]. If this procedure is carried out for sufficiently many time steps, the kinetic and potential energies will equilibrate and the resulting atomic speed distribution will approach a Maxwell-Boltzmann distribution at the specified temperature. At this point one can proceed to the *simulation stage* of the calculation in which the speeds are not scaled after each time step and the total energy E is rigorously conserved: during this stage the instantaneous temperature T^* will

fluctuate around the specified temperature resulting in a time-averaged temperature $\langle T^* \rangle$ close to T^* .

In the present experiment, you can specify both the equilibration time $t^*(\text{equil})$ and the simulation time $t^*(\text{sim})$ as input parameters, and you should ensure in particular that $t^*(\text{equil})$ is large enough to give a well-equilibrated atomic speed distribution before proceeding to the simulation stage of the calculation. Although the initial velocity components of the atoms are chosen at random, the initial speed distribution is chosen to be a delta function at the root-mean-square (rms) speed corresponding to the specified temperature T^* (i.e., the initial speeds of the atoms are all the same). The first of the numerical experiments described below is a study of how rapidly this initial speed distribution equilibrates into a Maxwell-Boltzmann distribution in each of the simulated phases.

Simulated Properties

The properties of the system that are calculated during the simulation stage of the calculation include the instantaneous kinetic and potential energies K and V , the radial (or "pair") distribution function $g(r)$, and the diffusion coefficient D . The last two of these properties characterise the structure and the dynamics of the system respectively, and their behaviour is especially interesting to study because it changes so dramatically as a function of r and T .

Kinetic and Potential Energies

Although the instantaneous kinetic and potential energies K and V fluctuate during the simulation, the fluctuations are typically fairly mild and the average values of these energies contain valuable information about the simulated system. In particular, the average value of the reduced potential energy provides an indication of the number of "nearest neighbours" of each atom. Suppose, for example, that the system of N atoms consists on average of $N/2$ isolated diatomics with a bond-length equal to the Lennard-Jones equilibrium separation r_e . Then the total potential energy will be $N/2$ times the well depth $-\epsilon$ and hence the reduced potential energy per atom (V^*/N) will be $-\frac{1}{2}$. The same argument also applies in other circumstances and shows that the reduced potential energy per atom will always be approximately $-\frac{1}{2}$ times the average number of nearest neighbours of each atom, which is simply one in the case of $N/2$ isolated diatomics.

In addition to this interpretation of the potential energy, the calculated values of K and V provide a useful check on the internal consistency of the calculation: their sum $E = K + V$ is expected to be conserved during the simulation stage of the calculation as described in Section 3.2 and the average value of K is expected to be proportional to the simulated temperature as in equation (7). Experiment 2 is based on these remarks.

Radial Distribution Function

The radial distribution function $g(r)$ is defined as the density of atoms in the volume element $dV=4\pi r^2 dr$ at a distance r from a given "test" atom, divided by the average density $\rho = N/V$. Clearly, since the size of the volume element dV increases as r^3 , the density within this volume element will approach the average density and hence $g(r)$ will tend to 1 in the limit as r tends to infinity. Furthermore, since the short-range repulsion between atoms precludes the possibility of finding any other atoms within much less than one collision diameter of the test atom, $g(r)$ will tend to 0 in the limit as r tends to 0.

The behaviour of $g(r)$ between these two limits is more interesting. As discussed in Atkins' Physical Chemistry and your Molecular Interactions lectures, $g(r)$ can range from a periodic array of sharp spikes in the case of a perfect crystal through to a bland statistical curve of the form $g(r) \approx \exp[-v(r)/k_B T]$ for a low-density gas. In Experiment 3, you will simulate the radial distribution function of the Lennard-Jones system in all three (solid, liquid and vapour) phases and so see for yourself how $g(r)$ behaves between these two extremes.

Diffusion Coefficient

The calculated diffusion coefficient D in the gas phase can be compared with what one would expect from kinetic theory, which gives the diffusion coefficient of a gas of "hard sphere" atoms in terms of the mean free path λ and the mean speed \bar{c} of the atoms as [2]

$$D = \frac{1}{3} \lambda \bar{c} \quad (8) \quad \text{where } \lambda = \frac{1}{\sqrt{2} \pi d^2 \rho} \quad (9) \quad \text{and } \bar{c} = \left(\frac{8k_B T}{\pi m} \right)^{\frac{1}{2}} \quad (10)$$

Combining these three equations, and converting everything into the reduced variables defined above, one finds that the reduced diffusion coefficient D^* of the hard-sphere gas is given by

$$D^* = \frac{2(T^*)^{\frac{1}{2}}}{3\pi^{\frac{3}{2}} (d^*)^2 \rho^*} \quad (11)$$

where $d^* = d/\sigma$ is the ratio of the hard-sphere and Lennard-Jones collision diameters. Therefore, in so far as the Lennard-Jones potential can be approximated by a hard-sphere potential, one would expect the calculated diffusion coefficient D^* in the gas phase to be proportional to $\sqrt{T^*} / \rho^*$. The extent to which equation (11) is actually satisfied by a Lennard-Jones gas is the subject of Experiment 4.

Experimental Procedure

The simulation program for this practical runs on the workstation **jeroboam** in the computing area in the Upper Laboratory. Ask a demonstrator for the current username and password for the experiment, then log on to **jeroboam**.

When you log on, a window in which you can type commands should be visible. If there is none, click on the **winterm** icon to create one. In the window type **cd md** then press the return key to change into the appropriate directory.

The following commands are available, all of which must be typed in capital letters:

RUN

This command performs a new (statistically-independent) simulation, prompting you to input the reduced density ρ^* , the reduced temperature T^* , the equilibration time $t^*(\text{equil})$ and the simulation time $t^*(\text{sim})$ from the screen. As the simulation proceeds, the number of time steps that have been completed will appear periodically on the screen. Note that the time step used to integrate equations (3) and (4) is set internally within the program to $dt^*=0.02$, so that (for example) a simulation with $t^*(\text{equil}) = 10.0$ and $t^*(\text{sim}) = 10.0$ will require a total of $20/0.02 = 1000$ time steps to complete. Ideally one would like to use a larger time step to reduce the computer time, but $dt^* = 0.02$ turns out to be the largest time step that results in a stable numerical integration. If you find that the calculation is taking too long and you decide to abort it, you can do so by typing the letter **c** (for cancel) while holding down the **CTRL** key. Note also that the data saved from each new simulation overwrites the data from the previous simulation in order to save on disc space, so you should ensure that you have extracted all of the information you want from the previous simulation before typing a new **RUN** command.

Once the simulation has finished, you can type any of the following commands to analyse the results retrospectively, as indicated on the computer screen:

ATM ("atomic motion")

This command shows a movie of the latest simulation. When you type **ATM**, a new window will appear on the screen showing a picture of the simulation box. The program that generated this window will then read in the positions of the atoms after each of the last 500 time steps of the simulation, which may take a couple of minutes. Once all of the atomic positions have been read, you will see the prompt **<start..>** in the bottom left-hand corner of the window: the right and left bracket keys (**])** and (**[**) can then be used to move the atoms forwards and backwards in time (respectively). Notice that one of the 108 atoms is 'tagged' in red to help you follow its motion, and that several of the surrounding atoms are displayed in green: these green atoms are those within 1.25 s of the red atom and are used to count 'nearest neighbours' in Experiment 2. When you have seen enough, you can type **Q** (shift q) to exit **ATM** and return control to the terminal window.

ASD ("atomic speed distribution")

This command plots a graph of the atomic speed distribution averaged over the equilibration period $t^*(\text{equil})$ of the simulation. The Maxwell-Boltzmann distribution corresponding to the input temperature T^* is also shown (in red) for comparison. To exit **ASD** click the left-hand mouse button on the "Exit" panel.

VCD ("velocity component distribution")

This command works in exactly the same way as **ASD**, but shows a graph of the atomic *velocity component* distribution rather than the atomic speed distribution.

EKV (" E , K and V ")

This command shows the evolution of the total energy E , the kinetic energy K , and the potential energy V during the equilibration and simulation stages of the calculation. Note that all three energies are plotted *per atom* in terms of the reduced energy variable E^* defined in Section 2.

RDF ("radial distribution function")

This command plots a graph showing the calculated radial distribution function $g(r^*)$ as a function of r^* . The plot corresponds to a histogram average over the simulation period $t^*(\text{sim})$ of the calculation. As in the case of the atomic speed distribution, the radial distribution function can be printed if required by selecting "Print" from the "File" menu.

SUM ("summary")

This final command displays a summary of the simulation within the terminal window, including the average values of the simulated reduced temperature $\langle T^* \rangle$, reduced pressure $\langle p^* \rangle$ and reduced diffusion coefficient $\langle D^* \rangle$.

Numerical "Experiments"

Experiment 1: Equilibration

The first stage of every computer simulation is a series of convergence tests, and this practical is no exception: the aim of this first experiment is to establish reliable equilibration times $t^*(\text{equil})$ for simulations of the solid, liquid and vapour phases.

In order to do this, you can simply set the simulation time $t^*(\text{sim})$ equal to zero and perform calculations with increasing values of $t^*(\text{equil}) = 0, 10, 20, \dots$ until the calculated atomic speed and velocity component distributions are converged. Appropriate reduced densities ρ^* and temperatures T^* to use for the three phases are given at the end of Section 2, and the only commands you need are **RUN**, **ASD** and **VCD**. Once you have printed the data you need, close the graphics program **xmgr** (which is automatically started by **ASD** and **VCD**) by clicking on the **Exit** command in the **File** menu. Also check with **ATM** that the motion of the atoms does indeed

correspond to what you would expect to see in each phase. Can you see the effect of periodic boundary conditions in the liquid and gas phase simulations?

Once you are satisfied that you have established reliable equilibration times for all three phases, you should get a demonstrator to check your results before proceeding to Experiment 2. Note that your final equilibration times may well be different in the solid, liquid and vapour phases, and if they are you should think about why it is that the system equilibrates more rapidly in one phase than another.

[To print your results: Data displayed using the **xmgr** graphing package can be printed on the inkjet plotter by using the **Printer Setup...** command in the **File** menu. In the **Print Control String** box enter **lpr -Pps** and then click on the **Print** button.]

Experiment 2: Energetics

The aim of this second experiment is to illustrate the behaviour of the instantaneous kinetic and potential energies K and V discussed in Sections 3.2 and 4.1.

In order to perform the experiment, simply repeat the (equilibrated) solid, liquid and vapour phase calculations you performed in Experiment 1, but now set the simulation time $t^*(\text{sim})$ equal to $t^*(\text{equil})$ rather than to zero. After each simulation, type the command **EKV** to see the evolution of K and V during the equilibration and simulation phases, and plot out the results. Discuss these in your write-up, comparing in particular the number of nearest neighbours implied by the average value of the potential energy with a direct count of the average number of neighbouring (green) atoms within 1.25σ of the tagged (red) atom in 10 randomly selected frames of **ATM**.

Experiment 3: Structure

This third experiment investigates the structure of the system in each of the three simulated phases in terms of the radial distribution function $g(r)$.

In order to perform the experiment, repeat the simulations you did in Experiment 2 and type **RDF** after each simulation, increasing the simulation time $t^*(\text{sim})$ if necessary to reduce the statistical fluctuations in $g(r)$ and obtain a smoother curve. Also vary the reduced temperature in the range $0.5 \leq T^* \leq 1.5$ in the solid ($\rho^* = 1.0$) and vapour ($\rho^* = 0.1$) phases to see the effect of temperature on the simulated radial distribution function.

Plot your results on the printer and discuss them as fully as possible in your write-up in light of the comments in Section 4.2 and the material in your Molecular Interactions lecture notes.

Experiment 4: Dynamics

This final experiment investigates the dynamics of the system in the gas phase in terms of the simulated diffusion coefficient D^* , and also provides an exercise in the use of the principle of corresponding states. The reduced diffusion coefficient D^* is calculated during the simulation using the following simple formula involving the mean square displacement $\langle |r^*(t^*) - r^*(0)|^2 \rangle$ of the atoms from their initial positions [4]:

$$D^* = \lim_{t^* \rightarrow \infty} \frac{1}{6t^*} \langle |r^*(t^*) - r^*(0)|^2 \rangle \quad (12)$$

The limit as t^* tends to infinity in this equation is approximated by the total simulation time $t^*(\text{sim})$, and several statistically-independent simulations are usually required to obtain a reliable estimate of D^* from Eq. (12).

In order to perform the experiment, simply use the commands **RUN** and **SUM** to complete the following table of simulated diffusion coefficients at $T^* = 1.0$, most of which has already been filled in for you to save on computer time:

ρ^*	$r^*(\text{equil})$	$r^*(\text{sim})$	D^*	$\langle D^* \rangle$
0.05	200	200	3.42 2.68 2.39 2.56 3.00	2.81 ± 0.41
0.1	100	100	(5 separate runs)	(average)
0.15	67	67	0.99 0.74 0.79 1.00 0.90	0.99 ± 0.12
0.2	50	50	(5 separate runs)	(average)
0.25	40	40	0.46 0.48 0.46 0.52 0.46	0.47 ± 0.03

Once you have completed the table, plot a graph of D^* against $1/\rho^*$ and explain physically why you might expect this plot to deviate from linearity. Estimate the ratio of the hard-sphere and Lennard-Jones collision diameters $d^* = d/\sigma$, and comment on the value you obtain. Hence use the information in Section 2.2 to estimate the physical diffusion coefficients D of Ar and Kr at 1 atm pressure and 293 K. (If you are interested in how realistic this calculation is you can compare your results with the experimental viscosity coefficients $\varepsilon \approx m \rho D$ of the two gases in Atkins' *Physical Chemistry*, which are quoted there in micropoise ($1 \mu\text{P} = 10^{-7} \text{ kg m}^{-1}\text{s}^{-1}$).

References

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