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Dynam: The Molecular Dynamics Simulator

Windows-compatible computers

Instructor Notes

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Answers to Questions

1. Describe in your own words the nature of molecular motion in each of the liquid, solid, and gas phases.

In a solid, molecules move about their equilibrium positions in the crystal lattice, but they cannot interchange their positions. In a liquid they move past each other in complex curved trajectories. In a gas they move in straight lines until they collide, at which point they repel each other and move off in different directions.

2. Explain why the radial distribution plot for a solid consists of a series of sharp peaks while that of a liquid has only one sharp peak together with one or more rounded ones.

The peak that occurs at the smallest internuclear distance corresponds to the distance of closest approach, which is about the same for liquids and solids. Solids exhibit other sharp peaks because the long-range order in the solid gives rise to longer repeat distances. In a face-centered cubic lattice, the distance of closest approach is half the face diagonal of the unit cell, but other distances that occur include the unit cell edge, the face diagonal, etc. No long-range order occurs in liquids, but there are still some distances that are somewhat more likely than others to occur. These longer distances appear as broad peaks in the radial distribution plot.

3. Why are there essentially no peaks in the radial distribution plot of a gas?

Molecular motion in a gas is completely random, so all internuclear distances are equally likely. However there is sometimes a small peak at the distance of closest approach because any two molecules spend a little time in each other's vicinity when they collide.

4a. For a series of similar (monatomic) molecules, the noble gases He, Ne, Ar and Xe, plot the collision diameter σ and well depth ε (as given by Dynam) against the number of electrons in the molecule. Is the dependence what you would expect? Explain.

Plots of the collision diameter and the well depth against the atomic number of the noble gas are approximately linear, but with some scatter. This is what would be expected. The collision diameter of an atom depends on the number of shells of electrons in the atom and the well depth on the strength of the instantaneous dipole-dipole interactions between the atoms, which in turn depends on the number of electrons in them.

b. Use your plot to predict the collision diameter and well depth of krypton, Kr. Compare your results to the literature values, which are σ = 390 pm and ε = 155 K.

From a least-squares fit of the data, σ = 360 pm and ε = 160 K for Z = 36.

5. Use the ideal gas law to calculate the pressure of the gas at the conditions of your gas-phase plot. Does your result agree with the value given by Dynam? If not, why not?

A typical result given by Dynam is that for reduced temperature $T^* = 1.041$ and reduced density $d^* = 0.040$, the reduced pressure $p^* = 0.034$. The corresponding ideal gas value is $p^* = T^* d^* = 1.041 * 0.040 = 0.0416$. The two values are different because the program takes intermolecular attractions into account but the ideal gas law does not.

6. According to the kinetic molecular theory of gases, the average kinetic energy of a gas is proportional to its temperature in Kelvins. Run Dynam at various temperatures and the smallest possible density (0.01 reduced units) to see if this is so. If not, account for any differences.

Dynam's output shows the total energy rather than the kinetic energy. However, the potential energy of a gas is zero, making the total energy and kinetic energy the same. The following data, obtained at d* = 0.01 and various temperatures and using a step time of 0.002, clearly show that the total energy (and thus the kinetic energy) is proportional to the temperature.

T*	E*
0.281	11.96
0.491	22.3
0.76	35.31
0.982	45.78
1.476	69.09