PHYS2020 Week 5 Project Milestone

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1 Background

Phase diagrams plot the conditions of a system (e.g. volume, temperature, pressure, enthalpy, entropy, etc.) against each other, and are partitioned to show where and under what circumstances certain phases of matter exist.

Under certain conditions, many substances have properties which don't match a single, commonly-known state of matter such as solid, liquid or gas. Rather, they need the more generalised idea of "phase" to describe them.

One feature is the line(s) of equilibrium, which visually separate(s) different phases. Along these lines, matter exists at more than one phase, and undergoes phase transitions (for example, sublimation occurs along the red line in Figure 1, and matter exists in both solid and gaseous phases)
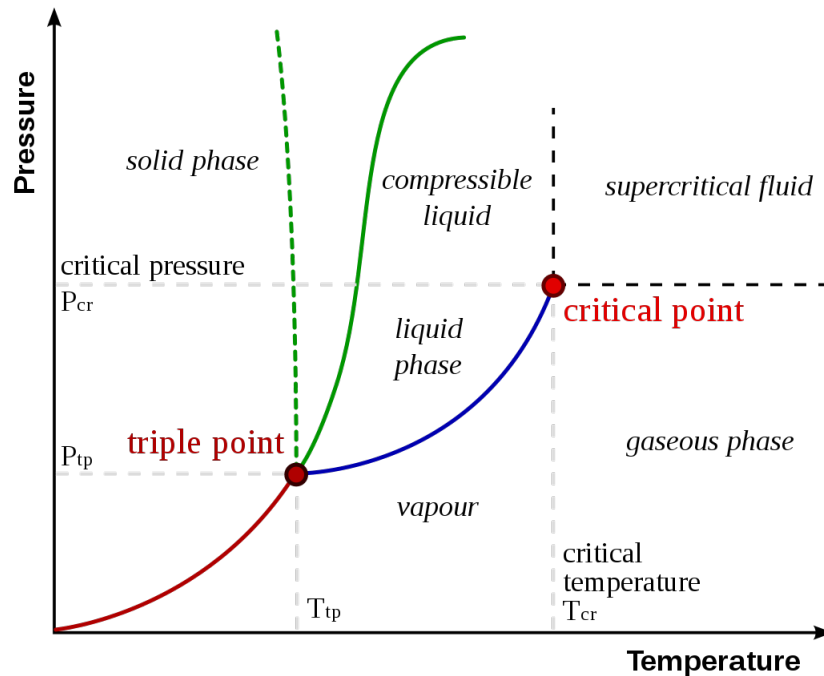
Figure 1: A phase diagram of water. There are some phases which do not nicely
fit into the categories solid/liquid/gas. The red line separates solid and gaseous
forms, so corresponds to the processes of sublimation and deposition. The
blue line separates liquid and gas (vapourisation, condensation). The dotted
green line separates liquid and solid (melting, freezing). Unlike water, most
substances have denser solid forms than liquid forms, so the slope of this line
is usually positive (as shown in the solid green line). Two points of interest are
the triple point (where solid, liquid and gaseous forms coexist), and the critical
point (beyond which the fluid has properties of both liquid and gas). `Image
source: Wikimedia Commons`

2 Aims

This project aims to simulate the molecular dynamics of a substance, given different a pair of input conditions corresponding to what might be found in a phase diagram, for example a pressure-temperature pair.

Hamiltonian dynamics will be helpful, in particular the following pair of differential equations relating momentum $\mathbf{q}$ and position $\mathbf{p}$ to time t and Hamiltonian $H = V + T$ (where V is potential energy and T kinetic energy):

$$\frac{d\mathbf{p}}{dt} = \frac{\partial H}{\partial \mathbf{q}} \qquad \text{and} \qquad \frac{d\mathbf{q}}{dt} = -\frac{\partial H}{\partial \mathbf{p}}$$

It will also be helpful to find the averages of different properties over time. This can be done with the following integral for some property A:

$$\langle A \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A(\mathbf{q}(t), \mathbf{p}(t)) dt$$

Since functions of most thermodynamic properties are discontinuous at lines and points of equilibrium (as this is where phase transition occurs), this integral cannot be solved analytically, so a numerical approximation method will be needed.

Some restrictions might be needed to make the simulation feasible, such as:

- Restricting to 2 dimensions (also easier to visualise)

- Limited number of particles

- A smaller space over which to simulate (e.g. assuming the system "looks the same everywhere" at a certain scale)

- Larger time steps (but this greatly reduces accuracy of equations, as they assume infinitesimal dt)

If time permits, some possible extensions to the project include:

- Extending simulation to 3 or more dimensions, investigating whether this affects the shape or location of lines and points of equilibrium (with possible differences due to higher degrees of freedom)

- Allowing choice of which quantities and pairs of quantities to use (between pressure, volume, entropy, etc.)

- How/if things change if ergodicity (every microstate is equally likely over long time periods) is not assumed

- Mixtures of different species of particles, or allowing for differences such as monatomic vs polyatomic molecules

3   Planning

I will use Python. Position and momentum will be represented as different arrays, with as many elements as there are spatial dimensions. This means that for each particle, there will be a pair of corresponding variables for each dimension, with each pair related by the Hamiltonian equations.

To find an appropriate value for the time step dt, I will program a simple and entirely analytical system and compare the analytical results (where dt is infinitesimal) to computations with non-infinitesimal values of dt, and choose a value that balances accuracy and computational time.

4   Some other ideas I had, just in case

If the idea above doesn't suit the project, here are some others I was considering:

- Simulating different models and types of perpetual motion machines, with toggles for the assumptions that make them work or not work

- Modelling viscosity of different phases, and comparing solids ("infinite" viscosity) to superfluids (0 viscosity) by simulating things in between