1   Project Summary

Phase behavior is a widely studied phenomena in physics. Mathematically describing, for example, liquid-vapor phase transitions is a complicated process and requires lots of approximations and extrapolations. The most simple approximation of (non-interacting) gases is the ideal gas law which relates pressure, density and temperature. A relation between these quantities fully describes the state of a system and is therefore also called an equation of state. The ideal gas law holds for high temperatures and low densities. For atmospheric circumstances, gases like oxygen, nitrogen, hydrogen, noble gases and even some heavier gases like carbon dioxide can to a reasonable extent be described by the ideal gas law.

For more dense systems, extensions of the ideal gas law are provided in the literature, of which the virial (or cluster) expansions is the most famous one. It describes many particle interactions via a pair-interaction route. It is an expansion in terms of density and, although it is more accurate than the ideal gas, it still only converges for small enough densities and high temperatures. For sufficiently high temperatures (above a certain critical temperature) substances will go continuously from a gas type of behaviour to a liquid type of behaviour. These transitions are called second order phase transitions and they can quite accurately be described by expansions around this critical temperature. First order phase transitions occur below the critical temperature and they involve latent heat. During such a transition, a system either absorbs or releases a fixed (and typically large) amount of energy. They are much more complex and interesting to study since higher order interactions play a role. Yet pairwise interactions are the state of the art.

We will study liquid vapor systems for a Van der Waals type of fluid. Such a fluid is described by an equation of state which is an extension of the ideal gas law. It takes into account a sence of incompressibility beyond a certain density and an attractive force. This results in isotherms as shown in (the right pressure volume $(p-V)$ diagram) in figure 1. Above the critical temperature, the isotherms are monotonically deacrasing with volume. The state points between point 2 and 6 are described by the line straightly connecting them. This is so since by the second law of thermodynamics, any system tends to an equilibrium state with maximal entropy ('disorder'), or, equivalently, minimal free energy. The corresponding (Gibbs) free energy is shown left in figure 1. This shows that the pure states on the isotherm between points 2 and 6 are unstable since these states have a higher free energy, than
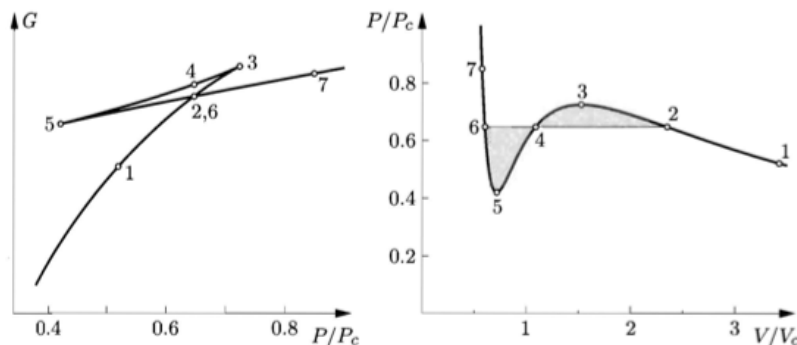
Figure 1: Gibbs free energy as a function of pressure for a Van der Waals fluid at $T=0.9T_c$. The corresponding isotherm is shown at the right. States in the range 2-3-4-5-6 are unstable. The coordinates are normalized by the critical values[1].

the staight line which represents a liquid vapor mixture.

We will solve such an equation of state for a typical noble gas to obtain point 2 and 6 as in figure 1^1, for a range of temperatures, up to the critical temperature. This will be done in the formalism of classical density functional theory (classical DFT) which was developed in the sixties to describe molecular fluids, derived from the quantum equivalent which describes electron systems. The difficulty in solving the equation of state is obtaining a correlation function between particles. We will obtain it from a powerful theory called fundamental measure theory (FMT), which was originally designed to describe interactions of hard sphere mixtures by convoluting the particles weighted over their fundamental measures (hence the name FMT) and proven to be very accurate and fast compared to computer simulations. The theory is developed about two decades ago, but only recently (2002) it was used to obtain correlation functions for hard spheres. We will try to extend this to systems of soft particles with long ranged attractions and short ranged repulsions. Mathematically this leads to an integral equation which is very challenging to solve. It is a first step towards solving a system of particles with long ranged interactions fully selfconsistent within FMT.

---

[1]Schroeder D.V. (2000). An introduction to thermal physics. Addison Wesley