

## The hard sphere system

One of the simplest systems that exhibits a phase transition is the system of identical hard spheres. It seems surprising that a system without an energy scale could possess distinct phases. Configurations either have zero energy, when all spheres are disjoint, or infinite energy (and are forbidden) when this is not true. It is therefore not the energy of the system (or the temperature of the external environment with which it exchanges energy) that determines the phase of the system, but the total volume available to the spheres (or the pressure imposed by the external environment). When the system volume is large (low pressure), the phase is a (non-ideal) gas. When the volume is small (high pressure), the hard spheres form a periodic crystal.

In this project you will learn how to efficiently simulate a system of hard spheres in three dimensions in the fixed temperature and pressure ensemble. To see the first-order gas/crystal transition you will have to perform very many Metropolis-Monte-Carlo steps, otherwise the equilibrium phase will not spontaneously switch at the transition pressure. Observing the system switch spontaneously is much more convincing (of the first order transition) than the widespread practice of measuring and comparing properties after *preparing* the system in each of the two phases. In the latter method one measures the average volume per sphere in the two phases as a function of pressure,  $v_{\text{gas}}(p)$  and  $v_{\text{cryst}}(p)$ , and infers the transition pressure by the value of  $p$  where the two curves cross. This approach suffers from the problem that technically the system is not in equilibrium when, at a given  $p$ , it has the larger of the two volumes. More seriously, this method limits the possible phases to those the investigator considered worth investigating<sup>1</sup>.

The degrees of freedom are the positions (in three dimensions)  $x_1, \dots, x_N$  of  $N$  spheres of diameter  $a$  in a cubic box with periodic boundary conditions. The volume  $V$  of the box is another degree of freedom. You should think of the cubic box as immersed in an environment at pressure  $p$ , so that it performs work (and changes its internal energy) when it changes its volume. The Gibbs measure of the hard sphere system is

$$d\mu(p) \propto d^3x_1 \cdots d^3x_n dV e^{-\beta(H_0 + pV)},$$

where  $H_0 = 0$  when all pairs of spheres are separated by at least distance  $a$ , and  $H_0 = \infty$  otherwise. Using the sphere diameter  $a$  as the unit of length, the measure can be rewritten in the dimensionless form

$$d\mu(\tilde{p}) \propto d^3\tilde{x}_1 \cdots d^3\tilde{x}_n d\tilde{V} e^{-(\tilde{H}_0 + \tilde{p}\tilde{V})}, \quad (1)$$

---

<sup>1</sup>In three dimensions, where we can draw from naturally occurring packings, this is not a serious issue. On the other hand, in as few as 10 dimensions there is a zoo of dense packing candidates, some of which are not even periodic!

where

$$\beta p V = \tilde{p} \tilde{V}$$

defines the dimensionless pressure  $\tilde{p}$  and the unit of pressure

$$p/\tilde{p} = \frac{k_B T}{a^3}.$$

You should use the standard Metropolis algorithm to sample the distribution (1). In addition to transitions that move one sphere at a time (rejecting when it impinges on another), you will have to sample the volume  $V$  of the box. When you expand the box to a larger volume (rescaling the sphere positions correspondingly), the only penalty is the work  $\tilde{p} \Delta \tilde{V}$  performed on the environment. When you shrink the box to a smaller volume you also need to check that the minimum distance 1 between all pairs of spheres is maintained (rejecting the proposed transition when this is not true). In my simulation I propose a change to the volume only after I have made a complete round of proposed moves on all the spheres. The range of sphere moves and volume changes is adjusted to keep the Metropolis acceptance rate near 50%.

The hard sphere model has one parameter<sup>2</sup>, the system pressure  $p$ . Phase behavior is revealed by the specific volume

$$v(p) = \frac{1}{N} \langle V \rangle.$$

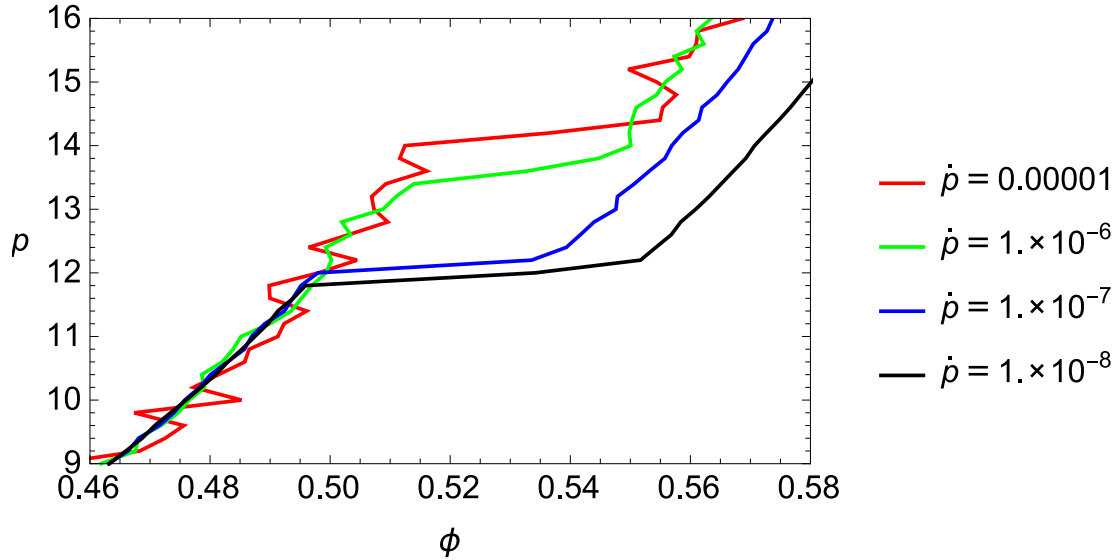
Researchers usually plot the packing fraction

$$\phi(p) = \frac{(4\pi/3)(1/2)^3}{v(p)}$$

horizontally, even though  $p$  (vertical axis) is the independent variable. On the next page is a detail of such a plot I produced for a system of 108 spheres. The four curves show the effect of increasing the equilibration time (slowing the compression rate  $\dot{p}$ ) by four orders of magnitude. I chose 108 spheres because this number fills a cubic periodic box as an fcc crystal without defects. However, I suspect for  $N$  in this range the presence of defects has little effect on the plot of  $\phi(p)$  vs.  $p$ .

---

<sup>2</sup>All symbols now are in the length and pressure units defined above.



If you choose to work on this project, here are the specific tasks.

- Read *Event-chain Monte Carlo algorithms for hard-sphere systems* by E. P. Bernard, W. Krauth and D. B. Wilson (Phys. Rev. E, 2009, 80: 056704) for inspiration on faster equilibration. I don't know if this method solves the ice-9 problem (especially in higher dimensions), but it had a decisive impact on resolving a long-standing debate about hard disks.
- Implement an efficient fixed- $(T, P)$  hard (3D) sphere simulator and estimate the phase coexistence pressure and range of packing fractions at this pressure.
- For fun, try your code on 4D hard spheres. As far as I know, no one has ever achieved phase equilibrium in this system.