Exercises

4.1 **Equilibration.**[1] [2] (Computation) ②

Can we verify that realistic systems of atoms equilibrate? As we have discussed in Section 4.2, we do not know how to prove that systems of realistic atoms are ergodic. Also, phase space is so large we cannot verify ergodicity by checking computationally that a trajectory visits all portions of it.

(a) *For 20 particles in a box of size $L \times L \times L$, could we hope to test if our trajectory came close to all spatial configurations of the atoms? Let us call two spatial configurations 'nearby' if the corresponding atoms in the two configurations are in the same $(L/10) \times (L/10) \times (L/10)$ subvolume. How many 'distant' spatial configurations are there? On a hypothetical computer that could test 10^{12} such configurations per second, how many years would it take to sample this number of configurations?* (Hint: Conveniently, there are roughly $\pi \times 10^7$ seconds in a year.

We certainly can solve Newton's laws using molecular dynamics to check the equilibrium *predictions* made possible by assuming ergodicity. You may download our molecular dynamics software [10] and hints for this exercise from the text web site [129].

Run a constant-energy (microcanonical) simulation of a fairly dilute gas of Lennard–Jones particles (crudely modeling argon or other noble gases). Start the atoms at rest (an atypical, non-equilibrium state), but in a random configuration (except ensure that no two atoms in the initial configuration overlap, less than $|\Delta \mathbf{r}| = 1$ apart). The atoms that start close to one another should start moving rapidly, eventually colliding with the more distant atoms until the gas equilibrates into a statistically stable state.

We have derived the distribution of the components of the momenta (p_x, p_y, p_z) for an equilibrium ideal gas (eqn 3.19 of Section 3.2.2),

$$\rho(p_x) = \frac{1}{\sqrt{2\pi m k_B T}} \exp\left(-\frac{{p_x}^2}{2mk_B T}\right) \qquad (4.10)$$

This momentum distribution also describes interacting systems such as the one we study here (as we shall show in Chapter 6).

(b) *Plot a histogram of the components of the momentum in your gas for a few time intervals, multiplying the averaging time by four for each new graph, starting with just the first time-step. At short times, this histogram should be peaked around zero, since the atoms start at rest. Do they appear to equilibrate to the Gaussian prediction of eqn 4.10 at long times? Roughly estimate the equilibration time, measured using the time dependence of the velocity distribution. Estimate the final temperature from your histogram.*

These particles, deterministically following Newton's laws, spontaneously evolve to satisfy the predictions of equilibrium statistical mechanics. This equilibration, peculiar and profound from a dynamical systems point of view, seems obvious and ordinary from the perspective of statistical mechanics. See Fig. 4.3 and Exercise 4.4 for a system of interacting particles (planets) which indeed does not equilibrate.

[1] From *Statistical Mechanics: Entropy, Order Parameters, and Complexity* by James P. Sethna, copyright Oxford University Press, 2007, page 69. A pdf of the text is available at pages.physics.cornell.edu/sethna/StatMech/ (select the picture of the text). Hyperlinks from this exercise into the text will work if the latter PDF is downloaded into the same directory/folder as this PDF.

[2] This exercise and the associated software were developed in collaboration with Christopher Myers.