PHYSICS 115/242

Molecular Dynamics Project

Due in class, Wednesday May 14.

Give yourself plenty of time for this assignment. Don't leave it to the last minute.

In this mini-project you will show that an interacting, classical system comes to equilibrium in which the probability of having a particular configuration in "phase-space" (i.e. the positions and momenta of the particles) is given by the Boltzmann distribution

$$P(\{x,p\}) \propto \exp(-E(\{x,p\})/k_BT) \tag{1}$$

where $\{x,p\}$ refers to the set of all positions, x_i, and momenta, p_i, E is the energy, k_B is Boltzmann's constant, and T is the temperature in Kelvin.
Here we will consider particles of unit mass (so $p_i = v_i$) moving in one dimension. Hence the Hamiltonian (energy) is given by

$$E = \sum_{i=1}^{N} \tfrac{1}{2} v_i^2 + \sum_{i<j} V(x_i - x_j)\,. \tag{2}$$

The probability that a particle has velocity v in equilibrium is therefore given by the Maxwell distribution

$$P_{\text{equil}}(v) = \frac{1}{\sqrt{2\pi T}} \exp\left(-\frac{v^2}{2T}\right)\,, \tag{3}$$

where, from now on, we use units where $k_B = 1$. The coefficient in front of the exponential is to ensure that the probability is normalized. By doing the appropriate Gaussian integrals you should be able to show this, and also to show that the mean square velocity is given by

$$\langle v^2 \rangle_{\text{equil}} = T\,. \tag{4}$$

Consider a system of particles coupled by "anharmonic springs" such that they are in mechanical equilibrium (i.e. the potential is a minimum) if the spacing between them is 1, and the potential energy between an adjacent pair is given by

$$\begin{aligned} V(x_l - x_{l+1}) &= \tfrac{1}{2}(x_l - x_{l+1} + 1)^2 + \tfrac{1}{3}(x_l - x_{l+1} + 1)^3 + \tfrac{1}{4}(x_l - x_{l+1} + 1)^4, \\ &= \tfrac{1}{2}(y_l - y_{l+1})^2 + \tfrac{1}{3}(y_l - y_{l+1})^3 + \tfrac{1}{4}(y_l - y_{l+1})^4\,, \end{aligned} \tag{5}$$

where

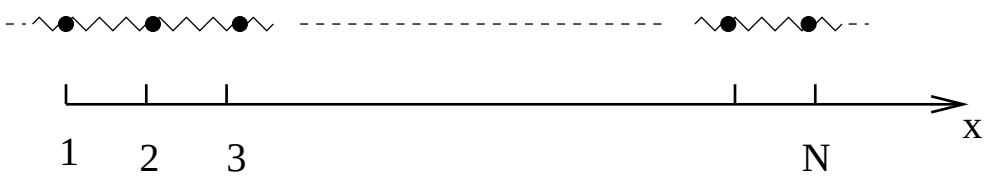
$$y_l = x_l - l \tag{6}$$

is the *deviation* of the particle away from its equilibrium position $x_l = l$.
It will be most convenient to use y_ℓ as the basic variable in your calculations.
(Note that $v_l \equiv \dot{x}_l = \dot{y}_l$.)
Assume that a particle only interacts with its two neighbors; see the figure below. It follows that the force on particle l is given by

$$F(y_l) = -\left[\frac{\partial V(y_l - y_{l+1})}{\partial y_l} + \frac{\partial V(y_{l-1} - y_l)}{\partial y_l}\right] = f(y_l - y_{l+1}) - f(y_{l-1} - y_l) \tag{7}$$

(notice the signs) where

$$f(t) = -(t + t^2 + t^3)\,. \tag{8}$$



Use "periodic boundary conditions" in which the right hand neighbor of the last particle ($l = N$) is the first particle ($l = 1$) and vice versa. (This means that the system has no edges.) You may find it convenient to imagine that the particles are placed around a ring of length L.
Start the system off with the positions of the particles at the minimum of the potential energy, $y_l(t = 0) = 0$, so the potential energy is zero, and set the velocities to be

$$v_l(t = 0) \;=\; \sin\left[\frac{2\pi(l + \delta)}{N}\right] , \tag{9}$$

where the "shift" δ is there to avoid a symmetry in the initial conditions which is preserved by the equations of motion. It can be any value between 0 and 1 except $0, 1$ or $1/2$. To understand these initial conditions, note that the wave-vectors of the "normal modes" compatible with periodic boundary conditions are $k_m = 2\pi m/N$, where $m = 0, 1, 2, \cdots , N - 1$. The $m = 0$ mode is just uniform motion, which persists unchanged because total momentum is conserved. Hence Eq. (9) puts all the energy in the lowest (non-zero) mode ($m = 1$). It is easy to see that the average of v^2 (averaged over sites) is $1/2$ and so the total energy (which is, of course, a constant of the motion) is equal to $\frac{1}{4}N$ (i.e. energy per particle is $\frac{1}{4}$).
The energy will stay constant but, a central assumption of statistical mechanics is that, after an "equilibration" time, it will be divided between the potential and kinetic energy according to the Boltzmann distribution. In particular the probability of a particle having velocity v will be given by Eq. (3).
For this project you are to show that this is true and determine the temperature T the system settles down to. More precisely, you need to do the following:

1. Decide on a value of N. Don't make it too large because the simulation will then take a long time to run. On the other hand, don't make it too small. The reason is that the Boltzmann distribution in Eq. (1) applies to a system which can exchange energy with a much bigger system, called a reservoir. In statistical physics jargon, this is called the "canonical ensemble". However, in the simulation, the energy is conserved, so the system can not explore as many configurations as when the energy is allowed to fluctuate. The case with energy conservation is called the "microcanonical ensemble". The two ensembles are argued to be equivalent for large sizes, but there are differences for small sizes. A value of N around 30 should be large enough that the differences between canonical and microcanonical ensembles will be minor, but small enough that the simulation will not take for ever to run on a PC.

2. Decide on an algorithm for integrating the equations of motion. I strongly suggest the position Verlet method since this is simple and, being symplectic, the energy will stay close to its initial value. You should take a fairly small step-size h, say $h = 0.02$, to get accurate results.

3. Initially, the system will not have equilibrated, so it is useful to run for an initial time $t_{\rm equil}$ without measurements and follow this by running for a longer time $t_{\rm equil}$ during which an

average of $\langle v^2 \rangle$ is made. Hence estimate the temperature according to Eq. (4).
Note:

(a) The "equilibration" phase is not essential if the run is long enough, but the initial transient during which the system is not equilibrated will give a correction which only decreases slowly as the length of the run is increased. It is therefore better to include an equilibration phase. A value for t_{equil} of a few hundred to a thousand would suffice for the range sizes proposed above.

(b) The time t is related to the number of updates N_u by $t = N_u h$.

(c) To do the average, you should average over particles for a given time, and also over times.

4. Produce a histogram of the velocity distribution and show that it fits the expected Gaussian distribution in Eq. (3).
Note: You need to carefully normalize the histogram from the simulation so that it corresponds to Eq. (3). In particular, note that the Maxwell distribution is normalized,

$$\int_{-\infty}^{\infty} P_{\text{equil}}(v)\, dv = 1, \tag{10}$$

so the area under the curve is unity. The same must be true for the histograms, which implies that, if the height of the i-th histogram is h_i and the width of the bins is Δv, then

$$\Delta v \sum_i h_i = 1. \tag{11}$$

5. Repeat parts 3 and 4 with the anharmonic (cubic and quartic) interactions turned off, so $f(y)$ in Eq. (8) is given by $f(y) = -y$. You should find (i) the temperature is precisely 1/4, and (ii) the distribution of particle velocities is *not* Gaussian.
Note:

(a) To see the detailed structure in the histogram, I suggest that you use a rather smaller value for N; a value around 15–20 should do.

(b) In the absence of anharmonicity, all the modes oscillate independently, with frequency given by

$$\omega_m = 2 \sin\left(\frac{m\pi}{N}\right). \tag{12}$$

Hence the energy will stay forever in the single mode where it was put initially, see Eq. (9). **Anharmonicity is needed for equilibration.**

6. **242 students only**
This problem is essentially a very old one first studied by Fermi Pasta and Ulam (FPU) in the 1950's in what was probably the first molecular dynamics simulation. Like you, they considered a chain of anharmonic springs in one dimension, and put all the energy initially into the longest wavelength mode. Some differences are (i) they used open, rather than periodic, boundary conditions, and (ii) they considered only cubic, rather than cubic *and*

quartic, anharmonicity in the potential. They looked more carefully at whether equilibration occurs by considering whether there was equipartition of energy between the different modes. Hence they Fourier transformed the displacement, which in our case corresponds to

$$a_m = \sqrt{\frac{1}{N}} \sum_{l=1}^{N} y_l \ \exp\left[\frac{2\pi i m\, l}{N}\right] , \tag{13}$$

for $m = -N/2+1, -N/2+2, \cdots, N/2-1, N/2$. They also Fourier transformed the velocity and computed the energy in the different modes from[1]

$$E_m = \tfrac{1}{2}\left(|\dot{a}_m|^2 + \omega_m^2\, |a_m|^2\right) . \tag{14}$$

(Note that there is no energy in the $m = 0$ mode[2] but the other $N-1$ modes are expected to have equipartition.) However, FPU did *not* find equipartition, to their great surprise.

You should do the following:

(a) At $t = 0$ all the E_m are zero except for $m = \pm 1$, for which $E_{\pm 1} = N/8$. Verify that the E_m stay at their initial values for the harmonic case.

(b) Including the anharmonic terms, determine whether you have equipartition in your model by computing E_m at different times for $m = 1$ and several other values of m.

Note:

- Actually FPU initialized the displacements (rather than the velocities), essentially in the form $y_l = \sin(2l\pi/N)$, which has much less energy than in our case because of the factor of ω_m^2 in Eq. (14) with $m = 1$. The modern view is that FPU would have found equipartition if they had put considerably more energy into the system initially.
- I have put on the class web site a talk on the FPU problem given by David Campbell (Boston University) at a recent meeting of the American Physical Society. I suggest you look at this for more background. The reference is
  http://physics.ucsc.edu/~peter/115/FPU-birth-of-nonlinear-science-Lilienfeld.pdf

Hint: Here is a suggestion for a position Verlet code to update one timestep. I put this in a separate file, `pos_verlet.c`. The force $f(x)$ is defined in the main program. Note the way I deal with periodic boundary conditions. (An alternative approach is to put in a bunch of `if` statements to detect when one is at the boundary. However, these slow down the program.)

[1] This includes the kinetic energy and the harmonic part of the potential energy.

[2] With the given initial conditions, the center of mass momentum is zero so there is no contribution to E_0 from the kinetic energy, and there is also no contribution from the potential energy because $\omega_0 = 0$.

```
pos_verlet(int N, double h, double x[], double v[], double f(double))
{
    int i;

    for (i = 0; i < N; i++) x[i] += 0.5 * h * v[i]; // half-step in x
//
// Full-step in v; v[0] and v[N-1] treated separately because of periodic bc's
//
    v[0] +=  h * (f(x[0] - x[1]) - f(x[N-1] - x[0]));
    for (i=1; i<N-1; i++) v[i] += h * (f(x[i]-x[i+1]) - f(x[i-1] - x[i]));
    v[N-1] += h * (f(x[N-1] - x[0]) - f(x[N-2] - x[N-1]));

    for (i = 0; i < N; i++) x[i] += 0.5 * h * v[i]; // half-step in x
}
```

This routine is called from the main program as follows:

```
    pos_verlet(N, h, y, v, f);
```

where `y` and `v` are declared to be arrays of dimension N. For the anharmonic interactions specified in the problem, the function $f(x)$ is defined by

```
double f(double y)                        // Computes the force
{
       return -y - y*y - y*y*y;
}
```

One can then very change to the harmonic model simply by replacing the one executable line by `return -y`.

Note: Please ask me, well in advance of the deadline, if you are not clear what is expected.