

PHYSICS 115/242
Molecular Dynamics Project

Due in class, Wednesday, May 4.

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

$$P(\{x, p\}) \propto \exp(-E(\{x, p\})/k_B T) \quad (1)$$

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

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

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

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

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

$$\langle v^2 \rangle_{\text{equil}} = T. \quad (4)$$

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

$$V(x_l - x_{l+1}) = \frac{1}{2}(x_l - x_{l+1} - 1)^2 + \frac{1}{4}(x_l - x_{l+1} - 1)^4 = \frac{1}{2}(y_l - y_{l+1})^2 + \frac{1}{4}(y_l - y_{l+1})^4, \quad (5)$$

where

$$y_l = x_l - l \quad (6)$$

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.

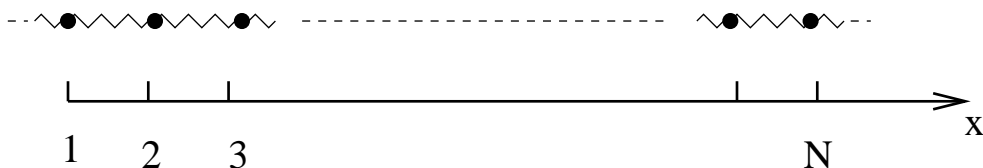
(Note that $v_l \equiv \dot{x}_l = \dot{y}_l$.)

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

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

(notice the signs) where

$$f(t) = -t - t^3. \quad (8)$$



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

$$v_l(t = 0) = \sin \left[\frac{2\pi l}{N} \right]. \quad (9)$$

To understand this, note that the wave-vectors of the “normal modes” compatible with periodic boundary conditions are $k_m = 2\pi m/N$, where $m = 0, 1, 2, \dots, N - 1$. 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. N in the range 20–30 should do.
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. After some time t_{equil} (which you may need to estimate by trial and error) compute $\langle v^2 \rangle$ by averaging both over the N particles and times greater than t_{equil} . Hence estimate the temperature according to Eq. (4).
Note: The time t is related to the number of updates N_u by $t = N_u h$.
4. Produce a histogram of the velocity distribution and show that it fits the expected Gaussian distribution in Eq. (3).
5. Repeat parts 3 and 4 with the anharmonic (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 velocities of a single particle (you should average over all the particles) is *not* Gaussian. In the absence of anharmonicity, all the modes oscillate independently, with frequency given by

$$\omega_n = 2 \sin \left(\frac{n\pi}{N} \right). \quad (10)$$

Hence the energy will stay forever in the 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 cubic, rather than 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

$$a_k = \sqrt{\frac{2}{N}} \sum_{l=0}^N y_l \sin \left[\frac{2\pi k l}{N} \right], \quad (11)$$

for $k = 1, 2, \dots, N/2$. They also Fourier transformed the velocity and computed the energy in the different modes from

$$E_k = \frac{1}{2} (\dot{a}_k^2 + \omega_n^2 a_k^2). \quad (12)$$

FPU did *not* find equipartition, to their great surprise.

Determine whether you have equipartition in your model by computing E_k at different times for $k = 1$ and several other values of k . Note that at $t = 0$ all the E_k are zero except for $k = 1$, and $E_1 = N/4$.

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_1^2 in Eq. (12) with $k = 1$. The modern view is that FPU would have found equipartition if they had put considerably more energy into the system initially.

Note: 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. It include the function definition for the force:

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

void update_1_step(int N, double h, double y[], double v[]) // position Verlet
{
    double f(double x);
    int i;
    for (i = 0; i < N; i++) // half-step in x
        {y[i] += 0.5 * h * v[i];}
```

```

//
// full-step in v;
// v[0] and v[N-1] treated separately because of periodic boundary conditions.
//
v[0] += h * (f(y[0] - y[1]) - f(y[N-1] - y[0]));
for (i = 1; i < N-1; i++)
    {v[i] += h * (f(y[i] - y[i+1]) - f(y[i-1] - y[i]));}
v[N-1] += h * (f(y[N-1] - y[0]) - f(y[N-2] - y[N-1]));

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

```

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