Chain of 1D classical harmonic oscillators

We use this system as a very simplified model of a 1D crystal (1D just so as to make things simpler, but the generalization to 3D is straightforward – see assignment sets).

Assume we have $N$ atoms in a 1D crystal, such that their equilibrium positions are at locations $X_i = ia$, where $a$ is some given distance (called the lattice constant). However, these atoms can still vibrate around these equilibrium positions. We want to study the properties of this system if we assume that the motion of the atoms are classical harmonic oscillations. More precisely, we would like to know what is the entropy of an isolated chain made of $N$ such classical harmonic oscillators, if the energy of the system is between $E, R + \delta E$.

The macrostate of interest, then, is characterized by $E, \delta E$ and $N$. Note that the “volume” (length of the chain) is not a variable since once we know $N$, the length is automatically set to $L = Na$. In other words, $N$ and $L$ are not independent of one another as is the case for gases, where atoms are free to move everywhere, and we only need to keep one. $N$ is the usual choice.

As we know, we need to find the multiplicity $\Omega$ for this macrostate, from which we get the entropy $S = k_B \ln \Omega$; from $S$ we can calculate everything else by taking the appropriate derivatives.

To find the multiplicity, we decided we need to go through the following steps:

(i) figure out the number of degrees of freedom, $f$. Here $f = 1$ because the atoms can only move in one dimension, say along the $x$-axis. Then, a microstate is given by $(x_1, ..., x_N, p_{x1}, ..., p_{xN})$.

(ii) figure out the Hamiltonian. Each atom contributes its kinetic energy, $p_i^2/(2m)$. However, this cannot be all – if it was, these atoms would be free to move everywhere like in a gas, whereas we know that each oscillates near its own equilibrium position. So there must also be some potential energy for each atom, $V_i(x_i)$. Different atoms should have different potentials, since they have equilibriums in different places – remember that for each particle, the equilibrium position is where its potential energy has a minimum. So $V_i(x_i)$ must have a minimum at $X_i = ia$. If we do a Taylor expansion about this minimum and stop to the first non-trivial contribution, we find:

$$V_i(x_i) = V_i(X_i) + \frac{k}{2} (x_i - X_i)^2$$

Here $k > 0$ is just the second derivative of $V_i$ at $x_i = X_i$. The first derivative is zero because $X_i$ is a maximum. We can also choose our energy scale so that $V_i(X_i) = 0$ (those are just some overall constant terms in the Hamiltonian, not doing anything).

If the atoms are identical, they must all have the same $k$ value. This is so because $k = m\omega^2$, where $\omega$ is the frequency of the oscillations (remember classical mechanics) and if the atoms are identical and at equal distances from each other, we expect the frequency of oscillations to be the same for all of them – no reason why some should oscillate faster or slower.

Adding everything together, we conclude that the Hamiltonian for a chain of 1D Harmonic oscillators is:

$$\mathcal{H} = \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} + \frac{m\omega^2 u_i^2}{2} \right]$$

where I switched to $u_i = x_i - X_i$ to simplify the notation a bit. Note that the momentum is still $p_i = m\dot{x}_i = m\dot{u}_i$, so the kinetic energy is not affected by this change.
(iii) Now comes the important step – finding the phase-space volume \( \omega \), which is defined as:

\[
\omega(E, N) = \int_{-\infty}^{\infty} du_1 \cdots \int_{-\infty}^{\infty} du_N \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_N \Theta \left( E - \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} + \frac{m\omega^2 u_i^2}{2} \right] \right)
\]

Note that now both the \( u \) and the \( p \) variables enter in the argument of the Heaviside function. In fact, if you think about it, what we have here is similar to a hyper-ellipse more than to a hyper-sphere, since the terms with \( p \) seem to suggest one radius, and the ones with \( u \) another radius.

We can deal with this by rescaling all terms so that we do have a hyper-sphere of radius 1. To obtain this, let us define new variables:

\[
\frac{p_i^2}{2mE} = z_i^2, \quad \frac{m\omega^2 u_i^2}{2E} = z_{i+N}^2
\]

Note: in class we called these new variables \( p'_i \) and \( u'_i \). One can give them any names, it doesn’t matter what we call the variables of integration. Then, the Heaviside function becomes (after we divide the argument by \( E \), which we can do since this is a positive number and dividing by it doesn’t change the sign of the argument):

\[
\Theta \left( 1 - \sum_{i=1}^{N} z_i^2 - \sum_{i=1}^{N} z_{i+N}^2 \right) = \Theta \left( 1 - \sum_{i=1}^{2N} z_i^2 \right)
\]

This is precisely what we want to see. From the change of variables we have \( dp_i = \sqrt{2mE} dz_i \), \( du_i = \sqrt{\frac{2E}{m\omega^2}} dz_{i+N} \) and the integral is:

\[
\omega(E, N) = \left[ \sqrt{2mE} \right]^N \left[ \sqrt{\frac{2E}{m\omega^2}} \right]^N \int_{-\infty}^{\infty} dz_1 \cdots \int_{-\infty}^{\infty} dz_{2N} \Theta \left( 1 - \sum_{i=1}^{2N} z_i^2 \right)
\]

The multiple integrals are now just \( V_{2N}(1) \), the volume of a \( 2N \)-dimensional hypersphere of radius 1. Using the formula for that, we find:

\[
\omega(E, N) = \left[ \sqrt{2mE} \right]^N \left[ \sqrt{\frac{2E}{m\omega^2}} \right]^N \frac{\pi^N}{\Gamma(N+1)}
\]
After simplifications, this finally gives:
\[
\omega(E, N) = \left(\frac{2\pi E}{\omega}\right)^N \frac{1}{N!}
\] (2)

This was the most difficult step, and I hope you see that the only trick is to figure out how to rewrite the multiple integrals as the volume of some hypersphere. That’s really all there is to it.

Now we just follow the steps:
\[
\Omega(E, \delta E, N) = \frac{1}{G_N h^{Nf}} \frac{\partial \omega}{\partial E} \delta E
\]
The Gibbs factor is $G_N = 1$, as discussed – atoms stay far from each other at all times, so they’re distinguishable through their locations. After taking the derivative and simplifying a bit, we find:
\[
\Omega(E, \delta E, N) = \frac{E^{N-1} \delta E}{(N-1)!} \left(\frac{2\pi}{\hbar \omega}\right)^N
\]

The entropy is then:
\[
S(E, N) = k_B \ln \Omega = (N-1)k_B \ln E + Nk_B \ln \left(\frac{2\pi}{\hbar \omega}\right) + k_B \ln \delta E - (N-1) \ln(N-1) - 1
\]

Here we do the usual fudging bits: we ignore $+k_B \ln \delta E$ because it’s just a tiny constant and won’t influence any derivatives; and because $N$ is very very large, we change $N-1 \rightarrow N$ everywhere, so that we end up with the nice result:
\[
S(E, N) = Nk_B \ln \frac{E}{N\hbar \omega} + Nk_B
\]

Note that this is an extensive, as it should be, and the units are correct as well (I hope you know that $\hbar \omega$ is an energy).

Since $dS = \frac{1}{T} dE - \frac{\mu}{T} dN$, we can find the temperature
\[
\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = Nk_B \frac{1}{E} \rightarrow E = Nk_BT
\]
and then the specific heat is simply
\[
C = \left(\frac{\partial E}{\partial T}\right)_N = Nk_B.
\]

We will redo this problem for quantum oscillators very soon, and we will see that these classical results are indeed correct at high energies/temperatures, but wrong at low energies/temperatures. That is to be expected, since at low energies we expect the role of level quantization to become important, and therefore the classical model (which ignores quantization) should fail.

It turns out that for a 3D crystal, the result is $C = 3Nk_B$ – assuming that there are $N$ sites in the crystal, but each atom is now allowed to oscillate in any direction (not just along the $x$-axis). You should be able to derive this result!

Indeed, at high temperatures this agrees with the measured specific heat of solids – this is known as the Dulong-Petit law. At low temperatures this estimate fails miserably, because quantum effects become important, as I just said. Once we solve the quantum problem, we’ll be able to figure out what “high” and “low” temperatures mean, i.e. what sets the comparison. In fact, one can use common sense to guess the answer: the only energy scale we can make from the parameters of this problem $a, m, \omega$ is $\hbar \omega$, which is the spacing between consecutive allowed energies for a quantum oscillator of frequency $\omega$. As we’ll see, if $k_BT \gg \hbar \omega$ then we’re in the classical limit – at such high temperatures the spacing between the allowed quantum energies can be ignored, so approximating the energy as a continuous variable is ok and thus, the classical approximation becomes accurate.