

Reading

This week, we'll concentrate on the material in K&K chapter 4. This might be called the thermodynamics of oscillators.

Classical Statistical Mechanics

Recall that statistical mechanics was developed before quantum mechanics. In our discussions, we've made use of the fact that quantum mechanics allows us to speak of discrete states (sometimes we have to put our system in a box of volume V), so it makes sense to talk about the number of states available to a system, to define the entropy as the logarithm of the number of states, and to speak of maximizing the number of states (entropy) available to the system. If one didn't know about quantum mechanics and didn't know about discrete states, how would one do statistical mechanics?

Answer: in classical statistical mechanics, the phase space volume plays the role of the number of states. We've mentioned phase space briefly. Here's a slightly more detailed description. In classical mechanics, one has the Lagrangian, $L(q, \dot{q}, t)$ which is a function of generalized coordinates q , their velocities, \dot{q} , and possibly the time, t . The equations of motion are Lagrange's equations

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) - \frac{\partial L}{\partial q} = 0.$$

Note that q might be a single variable or it might stand for a vector of coordinates. In the latter case, there is one equation of motion for each coordinate. The Hamiltonian is defined by a Legendre transformation,

$$H(q, p, t) = p\dot{q} - L(q, \dot{q}, t),$$

where

$$p = \frac{\partial L}{\partial \dot{q}},$$

is called the momentum conjugate to q (or the canonical momentum). The equations of motion become (assuming neither L nor H is an explicit function of time)

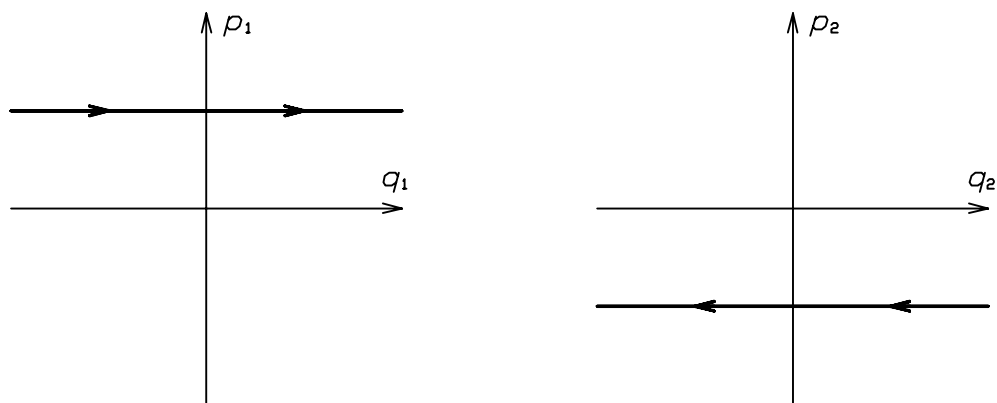
$$\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q},$$

so that each second order equation of motion has been replaced by a pair of first order equations of motion.

If p and q are given for a particle at some initial time, then the time development of p and q are determined by the equations of motion. If we consider a single pair of conjugate

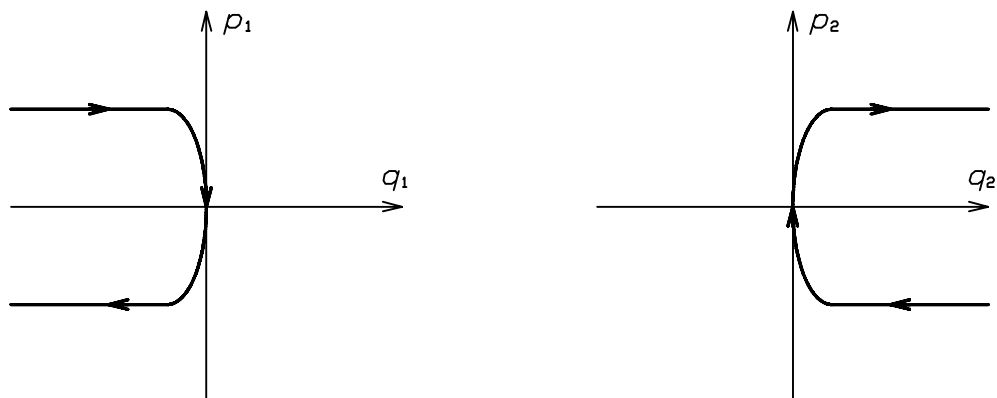
coordinates, p and q (i.e., a one-dimensional system), and we consider a space with axes q and p , then a point in this space represents a state of the system. The equations of motion determine a trajectory (or orbit) in this space that the system follows. The q - p space is called phase space. If we consider a 3-dimensional particle, then three coordinates and three momenta are required to describe the particle. Phase space becomes 6-dimensional and is a challenge to draw. If we consider N 3-dimensional particles, then phase space becomes $6N$ -dimensional. Or, one might draw N trajectories in a 6-dimensional space.

As an example of a phase space that we might actually be able to draw, consider two 1-dimensional particles moving along a common line. Suppose they are essentially free particles. The phase space coordinates are $q_1, p_1, q_2,$ and p_2 . (Subscripts refer to particles 1 and 2.) The figure shows an attempt at drawing a trajectory in the 4-dimensional phase



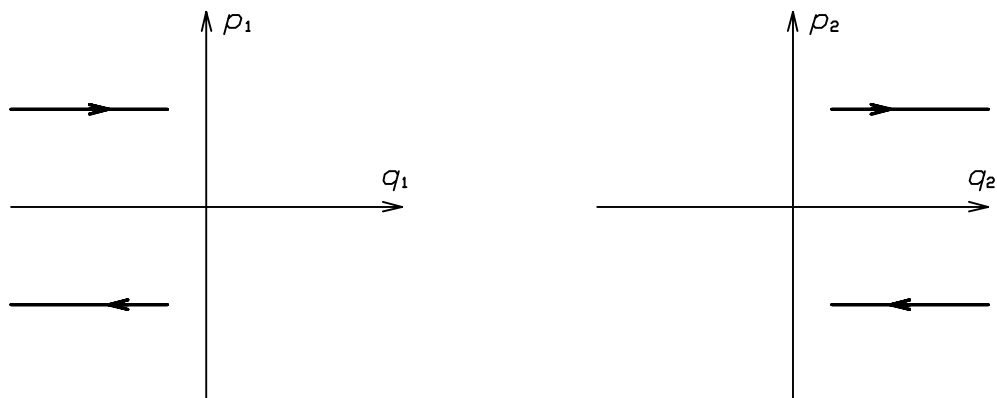
space. Since we have free particles, p_1 and p_2 are constants and q_1 and q_2 are linear functions of time, for example, $q_1 = p_1 t / m_1$. The figure shows a trajectory for q_1 and for q_2 . As shown, q_1 has a positive momentum, so its trajectory is from left to right, while q_2 has a negative momentum, so its trajectory is from right to left. Each point on the trajectory of q_1 corresponds to exactly one point on the trajectory of q_2 —the points are labeled by time and points at the same time are corresponding points. If we could draw in four dimensions, there would be a single line representing both particles and we would not have to point out this correspondence.

Note that at some time, both particles are at the same physical place in space and simply pass through each other as we've drawn the trajectories above. Instead of passing through each other, suppose they have a collision and "bounce backwards." This might be represented by the diagram shown in the next figure. This has been drawn assuming equal



masses, equal and opposite momenta, and an elastic collision. I'm sure you can work out diagrams for other cases.

Suppose we are considering a low density gas (again!). We certainly would not want to try to draw a phase space for all the particles in the gas and we certainly wouldn't want to try to draw all the trajectories including collisions. In the two particle case we've been considering, suppose we blinked while the collision occurred. What would we see? The answer (for a suitable blink) is shown in the next figure. We'd see particles 1 and 2



moving along as free particles before we blinked and again after we blinked, but while we blinked, they changed their momenta. We've already mentioned that in a low density gas, the molecules travel several molecular diameters between collisions while collisions occur only when molecules are within a few molecular diameters of each other. One way to treat a low density gas is to treat the molecules as free particles and to try to add in something to account for the collisions. By looking at the drawing of the collision (where we blinked), we can see that one way is to say that the particles follow phase space trajectories for a free particle, except every now and then a trajectory ends and reappears—somewhere else. The disappearance and reappearance of phase space trajectories does not really happen; it's an approximate way to treat collisions.

All this is motivation for the idea that collisions randomize the distribution of particles in phase space. Of course the randomization must be consistent with whatever constraints are placed on the system (such as fixed total energy, etc.) In general, if a system is in thermal contact with another system, we would expect that the exchanges of energy,

required for thermal equilibrium, would result in randomization of the phase space location.

The classical statistical mechanics analog of our postulate that all accessible states are equally probable is the postulate that all accessible regions of phase space are equally probable. In other words, a point in phase space plays the role of a state. The leveling of the probabilities is of course accomplished by the collisions and energy transfers we've just been discussing. It shouldn't be too hard to convince yourself that any concept we've discussed that doesn't explicitly require Planck's constant can just as easily be done with classical statistical mechanics as with quantum statistical mechanics. Even in cases where we used \hbar , if there is a reasonable mapping of quantum states to phase space volume, the classical treatment will give the same results as the quantum treatment (but of course, lacking an \hbar).

As an example, suppose we consider a single free particle in a box of volume V in thermal contact with a reservoir at temperature τ . Our derivation of the Boltzmann factor did not depend on quantum mechanics, so the probability of finding this particle in a state with energy E is $\exp(-E/\tau)$, just as before. The partition function is no longer a sum over states, but an integral over phase space volume,

$$Z_C = \int_{-L/2}^{+L/2} dx \int_{-L/2}^{+L/2} dy \int_{-L/2}^{+L/2} dz \int_{-\infty}^{+\infty} dp_x \int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z \exp(-(p_x^2 + p_y^2 + p_z^2)/2m\tau) ,$$

where Z_C stands for the classical partition function, and the volume is taken to be a cube of side L for convenience. The integrals over the coordinates give V and each integral over a momentum gives $\sqrt{2\pi m\tau}$. The result is

$$Z_C = V(2\pi m\tau)^{3/2} .$$

Recall our previous result for the free particle partition function,

$$Z_Q = V(2\pi m\tau)^{3/2} \left(\frac{1}{h}\right)^3 ,$$

where the subscript Q indicates the "quantum" partition function. Note that the expression includes h , not \hbar . So, in this case, the classical and quantum partition functions are the same except for a factor of h^{-3} . Mostly, we use the logarithm of the partition function. This means that many results that we derive from the partition function will not depend on whether we use Z_C or Z_Q . For example, the energy is $\tau^2 \partial(\log Z)/\partial\tau$, so the h^3 factor has no effect on the energy. An important exception is the entropy. The entropy is missing an additive constant. This has no effect on relative entropy, but it does matter for absolute entropy. (How would you measure absolute entropy?) By comparing the two expressions one sees that for each pair of conjugate phase space coordinates, such as x and p_x , one should assign the volume h to a single state. Using classical considerations, we can (at least for a low density gas) reproduce the quantum results simply by using

$$\frac{dx dp_x}{h} \frac{dy dp_y}{h} \frac{dz dp_z}{h} ,$$

as the appropriate volume in phase space. This works in general provided the average occupancy is very low.

We see that the Maxwell velocity distribution falls out of the classical approach and the h^{-3} even if included, would get erased in the normalization factor for the probability density.

A Classical Harmonic Oscillator

Now suppose we have a one dimensional harmonic oscillator, whose Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{kq^2}{2} = \frac{1}{2m} (p^2 + m^2\omega^2q^2) ,$$

where $\omega^2 = k/m$ is the natural frequency of the oscillator, Suppose this oscillator is in thermal equilibrium at temperature τ . What is the mean value of its energy? One way we can work this out is to take the Boltzmann factor as the probability density in phase space. So

$$P(E) dq dp = C \exp(-(p^2 + m^2\omega^2q^2)/2m\tau) dq dp ,$$

where uppercase P is used for probability density to distinguish it from momentum. The normalization constant, C , is set by requiring that the integral of the probability density over phase space be unity. The position and momentum integrals can be done separately and lead to normalization factors $m\omega/\sqrt{2\pi m\tau}$ for the position coordinate and $1/\sqrt{2\pi m\tau}$ for the momentum coordinate. To get the average energy of this oscillator, we have

$$\begin{aligned} \langle E \rangle &= C \int_{-\infty}^{+\infty} dq \int_{-\infty}^{+\infty} dp \frac{1}{2m} (p^2 + m^2\omega^2q^2) \exp(-(p^2 + m^2\omega^2q^2)/2m\tau) , \\ &= \frac{m\omega}{\sqrt{2\pi m\tau}} \int_{-\infty}^{+\infty} dq \frac{m^2\omega^2q^2}{2m} e^{-m^2\omega^2q^2/2m\tau} + \frac{1}{\sqrt{2\pi m\tau}} \int_{-\infty}^{+\infty} dp \frac{p^2}{2m} e^{-p^2/2m\tau} , \\ &= \frac{\tau}{2} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx x^2 \exp(-x^2/2) + \frac{\tau}{2} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dy y^2 \exp(-y^2/2) , \\ &= \frac{\tau}{2} + \frac{\tau}{2} = \tau . \end{aligned}$$

Of course, we could obtain the same result by calculating the partition function and going from there. Note that the harmonic oscillator has two ways to store energy: as kinetic energy or as potential energy. Each of these can be considered a *degree of freedom* and each stores, on the average, $\tau/2 = kT/2$. This is an example related to equipartition of energy discussed by K&K in chapter 3.

Classical Cavity Radiation

We're familiar with the idea that hot objects radiate energy. There are the expressions "red hot" and "white hot" denoting very hot objects. The color comes from the appearance of the objects and is the color of the electromagnetic energy radiated by the object. Allowing two objects to exchange radiation is a way to place them in thermal contact. For ordinary temperatures this may not be a very efficient method of heat exchange compared to conduction or convection, but at high temperatures (in stars, for example) it can become the dominant method of energy transfer. Also, when working at cryogenic temperatures, one needs to shield the experiment from direct exposure to room temperature radiation because this can be an important heat load on the cold apparatus.

How can we make a perfect absorber of radiant energy? If we could, what would it look like? If it absorbed all the radiation that hit it, then nothing would be reflected back, so we couldn't see anything and it would appear black. A perfect absorber is called a *blackbody*. We could make a perfect absorber by making a large cavity with a small hole connecting the cavity to the outside world. Then, as seen from the outside, any radiation hitting the hole, passes through the hole and bounces around inside the cavity until it is absorbed. By making the cavity sufficiently big and the hole sufficiently small, we can make the chances of the radiation coming back out the hole before it's absorbed as small as we like. (Of course, when the wavelength of the radiation is comparable to or larger than the size of the hole, then we have to worry about diffraction...)

A cavity containing a hole must also radiate energy. If not, it would heat up to arbitrarily high temperatures (and of course, this violates the second law of thermodynamics by transferring heat from a cold object to a hot object with no other change). So when a cavity is in thermal equilibrium with its surroundings, it must radiate energy out through the hole at the same rate that energy is absorbed through the hole. A hole has no properties, so the radiated spectrum (energy at each frequency or wavelength or color) can only depend on the temperature. This spectrum is called the blackbody (or thermal or cavity) radiation spectrum. A real physical object which is a perfect absorber must radiate the same spectrum. We can place a physically black object into thermal contact with a cavity radiator. In order to avoid violating the second law, the energy absorbed must equal the energy radiated. If we consider a filter which is perfectly transparent in some frequency range and perfectly reflecting outside this range and we insert this filter between the two objects, then we conclude that the perfect absorber and the cavity radiator must radiate the same spectrum (the same amount of energy at each frequency). Finally, real absorbers are not perfect. If in equilibrium, a fraction a of the incident radiation is absorbed, with the rest being reflected, then it must be the case that it emits the fraction a of the ideal blackbody radiation, otherwise we can arrange to violate the second law. Finally, by using our filter again, we conclude that if it absorbs the fraction $a(\omega)$ at frequency ω , it must radiate the same fraction $e(\omega) = a(\omega)$ of the ideal blackbody radiation spectrum. Jargon: a is called the *absorptivity* and e is called the *emissivity*.

The upshot of all this is that there is a universal radiation spectrum that depends only on temperature and is called the blackbody, thermal or cavity radiation spectrum. Let us try to calculate this spectrum.

The spectrum is produced by electromagnetic fields inside the cavity. These fields contain energy and they are in equilibrium with the walls of the cavity at temperature τ . To make life simple, let's suppose our cavity is a cube of side L . You may recall from your studies of electromagnetism that the fields in the cavity can be divided into modes with each mode oscillating like a harmonic oscillator. Electromagnetic energy oscillates back and forth between the electric field (like the position coordinate in a standard harmonic oscillator) and the magnetic field (like the momentum coordinate).

Each mode can store energy independently, so each mode contributes a harmonic oscillator term to the Hamiltonian of the cavity. Different modes have different frequencies and this is where the spectrum comes from. So we are getting close: we've already calculated the average energy in a harmonic oscillator; all we have to do now is enumerate the modes and their frequencies and we'll have the calculation of the blackbody spectrum.

As you may know, the electric field for a given mode in a perfectly conducting cavity has components of the form

$$E_z = E_0 \sin(\omega t) \sin(n_x \pi x / L) \sin(n_y \pi y / L) \cos(n_z \pi z / L),$$

where E_0 is the amplitude of the mode (an electric field, not an energy!), ω is the frequency of oscillation, and n_x , n_y , and n_z are integers. The cavity is assumed to run from 0 to L in each coordinate. The sine terms ensure that electric field component parallel to a perfectly conducting wall is zero at the wall. (Electric field is always perpendicular to the surface of a perfect conductor). The cosine term ensures that the magnetic field (related to the E-field by Maxwell's equations) has no perpendicular component at the wall. The integers n_x , n_y , n_z are related to the number of half wavelengths that fit in the cavity. Maxwell's equations tell us that

$$\omega^2 = \frac{\pi^2 c^2}{L^2} (n_x^2 + n_y^2 + n_z^2).$$

We can think of a mode as a wave bouncing around inside the cavity and when it has bounced around once, it must be in phase with the original wave in order to have resonance and a mode. This is another way of seeing how the integers arise. We also know that any electromagnetic wave in a vacuum has two polarizations. So for each set of positive integers there are two independent oscillators. And each oscillator has average energy τ according to our earlier calculation.

To calculate the spectrum, we need to know how many sets of integers correspond to a given range in ω . We start by considering the number that correspond to a frequency less than a particular ω . If we consider a three dimensional space with axes n_x , n_y , and

n_z , then the number is the number of lattice points in this space in the positive octant with $\sqrt{n_x^2 + n_y^2 + n_z^2} < r = \omega L / \pi c$. This is just the volume of 1/8 of a sphere of radius r ,

$$N(< \omega) = 2 \frac{1}{8} \frac{4\pi}{3} \left(\frac{\omega L}{\pi c} \right)^3 ,$$

where the factor of 2 accounts for the two polarizations. This should be reminding you very strongly of what we did when counting the states of a particle in a box. The number of oscillators in the frequency range $\omega \rightarrow \omega + d\omega$ is found by differentiating the above, and

$$n(\omega) d\omega = \frac{V\omega^2}{\pi^2 c^3} d\omega ,$$

where V has been inserted in place of L^3 .

Now, each oscillator has average energy τ , so the energy per unit frequency in the cavity is

$$\frac{dU}{d\omega} d\omega = \frac{V\omega^2 \tau}{\pi^2 c^3} d\omega ,$$

and the total energy in the cavity is found by integrating over all frequencies,

$$U = \int_0^{+\infty} d\omega \frac{V\omega^2 \tau}{\pi^2 c^3} = \infty !!!$$

This says there is an infinite energy in the cavity and this can't be right! Also the energy per unit frequency result says that the energy is concentrated towards the high frequencies in proportion to ω^2 . This is called the *ultraviolet catastrophe*. It says that if you made a cavity and put a small hole in it to let the radiation out, you'd be instantly incinerated by the flux of X-rays and gamma rays! Of course, we're all still here, so this doesn't happen. Where did we go wrong? This is the same question physicists were asking themselves in the latter part of the nineteenth and the early part of the twentieth century.

The answer is, we didn't go wrong, at least as far as classical physics is concerned. Everything we did leading up to infinite energy density in a cavity is perfectly legal according to classical physics. It is one of the many contradictions that arose around the turn of the century that led to the development of quantum mechanics. One of the things to note is that cavity radiation could be measured and at low frequencies it gave results in agreement with what we've just derived. That is, the spectral density $(1/V) dU/d\omega$ is proportional to τ and to ω^2 . For higher frequencies the measured result falls far below our calculation. The ω^2 region is called the Rayleigh-Jeans part of the spectrum. What's needed to cure our calculation is a way to keep the high frequency modes from being excited. We shall see that it is the discreteness of the energy levels provided by quantum mechanics that keeps these modes quiescent.