Lecture 13 Summary

Phys 404

The goal of this lecture is to set up a purely classical theory of statistical mechanics. In other words, if all we want to do is study thermodynamics and statistical mechanics in the high-temperature and dilute (concentration $n \ll n_Q$) limit, why do we need to start with a quantum mechanical solution? Let's consider the limit where the temperature $\tau \gg \varepsilon_{n+1} - \varepsilon_n$, so that the quantized nature of the energy levels do not play a role in the statistical properties. We will use classical expressions for the dynamics of the system and calculate a classical partition function. With that we can then do the standard calculations to get all of the thermodynamic quantities we need. To attack this problem, we first have to do a little quantum mechanics!

In the semi-classical limit of quantum mechanics, one finds that the Bohr-Sommerfeld quantization condition holds to good approximation. This condition is stated as $\oint p\, dq = nh$, where p is the non-relativistic momentum of the particle, q is its coordinate, $n = 1, 2, 3, 4, \ldots$ is a positive integer, and h is Planck's constant. The integral is taken over a closed 'orbit' or motion of the particle. Bohr used this idea to quantize the angular momentum of the electron in its orbit around the proton and created the first quantum model of the hydrogen atom. His idea was that the electron completed a journey around the proton in such a way that its matter wave function oscillated exactly an integer number of wavelengths around the closed orbit. This can be stated as $\oint \frac{dq}{\lambda_{dB}} = n$, where λ_{dB} is the deBroglie wavelength of the matter wave that describes the particle, and is given by $\lambda_{dB} = h/p$. Substituting this into the integral gives $\oint \frac{dq}{h/p} = n$, or $\oint p\, dq = nh$, which is the Bohr-Sommerfeld quantization condition. A similar result can be derived in the semi-classical limit of quantum mechanics using the WKB approximation (Griffiths, *Quantum Mechanics*, Chapter 8). Hold on to this thought…

Going back to pure classical physics, consider the harmonic oscillator in one dimension. This is a model of a mass m, connected to a stationary wall by a Hooke's law spring of spring constant k, and sitting on a friction-less surface. The spring has an equilibrium length, and under that condition the particle resides at coordinate $x = 0$. If the mass is moved left or right, the spring exerts a restoring force, and the mass oscillates in time with a frequency given by $\omega = \sqrt{k/m}$. The **Hamiltonian** is an expression for the total energy of a particle (or system of particles) in terms of the coordinates and momenta of the particles. The Hamiltonian for a one-dimensional harmonic oscillator is $H = \frac{p^2}{2m} + kx^2/2$. The total energy remains fixed as the motion evolves, meaning that the Hamiltonian is equal to a fixed constant, the total energy E. The motion of the particle can be represented in a phase space spanned by the coordinate x and the momentum p. The instantaneous disposition of the particle is represented as a single point (the phase point) in this two-dimensional plane. As the particles moves, it will trace out a continuous curve in phase space (see this animation). In fact it traces out a closed curve in the shape of an ellipse. The phase point will move clockwise on the ellipse as time evolves. Note that the phase point is a mathematical point, because we can specify the position and momentum of the particle with arbitrary precision in classical mechanics. The size of the ellipse can be continuously varied as well, simply by changing the total energy E of the particle slightly.

If we apply the ideas of quantum mechanics to phase space, we see a couple of interesting things. First the disposition of the system is smeared out in phase space by the Heisenberg Uncertainty principle. We cannot simultaneously specify the coordinate and momentum of the particle to arbitrary precision, but we are limited to $\Delta x \, \Delta p_x \geq \hbar/2$. Thus the phase point becomes a phase blob. In addition, the Bohr-Sommerfeld quantization condition says that the area enclosed by the orbits in phase space (that's the geometrical interpretation of $\oint p \, dq$) must be quantized in units of Planck's constant h! Planck's constant has a new role as the quantum of phase space volume. It is the minimum volume that is taken up by the phase blob, and it sets the scale for the granularity or discrete structure of phase space. Two states whose phase points are within h of each other in phase space are indistinguishable, at least quantum mechanically. Hence there is a limit to how many states can fit in phase space, and this forms the basis for counting the states of a system (an essential step in calculating a partition function!) The number of states with energy less than or equal to a given orbit in phase space is given by $n = \frac{1}{h}\oint p \, dq$. With this simple prescription we can count states simply by calculating areas in phase space. In other words, a sum over states (as in the partition function) can be replaced with an integral over phase space, normalized by Planck's constant.

We can now write the classical partition function for N particles in three dimensions in the canonical ensemble (i.e. the system is in thermal equilibrium with a large reservoir at temperature τ): $Z_{classical} = \frac{1}{h^{3N}} \iiint \quad \ldots \iiint e^{-H/\tau} \, dx_1 dy_1 dz_1 dp_{x1} dp_{y1} dp_{z1} \ldots dx_N dy_N dz_N dp_{xN} dp_{yN} dp_{zN}$, where $H = H(x_1, y_1, z_1, p_{x1}, p_{y1}, p_{z1}, \ldots, x_N, y_N, z_N, p_{xN}, p_{yN}, p_{zN})$ is the Hamiltonian of the $N-$particle system. The Hamiltonian is an expression for the total energy of the system in terms of all the coordinates and momenta of all the particles. Note that there are $6N$ infinite integrals over all of the coordinates and momenta of all the particles. The pre-factor is the quantum volume of this $6N-$dimensional phase space.

As an example, consider a single particle in a three-dimensional box, just as we did before in the ideal gas calculation (Z_1 calculation, Lecture 10). The particle is of mass m and is confined inside a cube of sides $L \; x \; L \; x \; L$ by an infinite square well potential. The classical Hamiltonian is $H = \frac{\vec{p}\cdot\vec{p}}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$, and the classical partition function has only 6 integrals: $Z_{classical} = \frac{1}{h^3}\int_0^L dx \int_0^L dy \int_0^L dz \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \, e^{-p_x^2 + p_y^2 + p_z^2/2m\tau}$. The coordinate integrals yield a factor of $L^3 = V$, while the momentum integrals break into a product of three Gaussian integrals, and the result is $Z_{classical} = V\left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$, which was previously written as $Z_{classical} = Vn_Q$, where n_Q is called the quantum concentration. This is exactly the result that we derived using the full-blown quantum partition function in Lecture 10. This result demonstrates that one can solve classical statistical mechanics problems by using only the classical Hamiltonian (rather than solving the quantum problem from scratch), along with the 'hybrid' expression for the classical partition function above.

We then considered the 1-dimensional harmonic oscillator, a problem that was previously solved with quantum statistical mechanics in lecture 11. The classical Hamiltonian is $H = \frac{p^2}{2m} + kx^2/2$, as stated above. The classical partition function is written as $Z_{classical} = \frac{1}{h}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp\, e^{-p^2/2m\tau} e^{-kx^2/2\tau}$. Note that the coordinate and momentum are integrated over every possible value, out to $\pm\infty$. In other words, we assume that the system can borrow any amount of energy from the reservoir to explore every possible location in phase space. In fact the reservoir is finite, and the energy borrowed from it must also be finite. However, these high energy states come into the integral with very small weight in the Boltzmann factor, and we make little error by extending the limits of integration to $\pm\infty$. The partition function is just the product of two Gaussian integrals and can be quickly evaluated as $Z_{classical} = \tau/\hbar\omega$. Note that this does not agree with the quantum statistical mechanics result, $Z_{quantum} = \frac{1}{1-e^{-\hbar\omega/\tau}}$. This is expected because the classical calculation is done in the high temperature limit where $\tau \gg \varepsilon_{n+1} - \varepsilon_n = \hbar\omega$ in this case. Take the high-temperature limit of the quantum mechanical partition function, and you find $Z_{quantum} \cong \frac{1}{1-(1-\frac{\hbar\omega}{\tau})} = \tau/\hbar\omega$, which agrees with the classical result. From this we see that the classical partition function is not always equal to the full quantum partition function, but they should agree in the high temperature limit.