G25.2651: Statistical Mechanics

Notes for Lecture 3

I. MICROCANONICAL ENSEMBLE: CONDITIONS FOR THERMAL EQUILIBRIUM

Consider bringing two systems into thermal contact. By thermal contact, we mean that the systems can only exchange heat. Thus, they do not exchange particles, and there is no potential coupling between the systems. In this case, if system 1 has a phase space vector x_1 and system 2 has a phase space vector x_2, then the total Hamiltonian can be written as

$$H(\mathrm{x}) = H_1(\mathrm{x}_1) + H_2(\mathrm{x}_2)$$

Furthermore, let system 1 have N_1 particles in a volume V_1 and system 2 have N_2 particles in a volume V_2. The total particle number N and volume V are $N = N_1 + N_2$ and $V = V_1 + V_2$. The entropy of each system is given by

$$S_1(N_1, V_1, E_1) = k \ln \Omega_1(N_1, V_1, E_1)$$
$$S_2(N_2, V_2, E_2) = k \ln \Omega_2(N_2, V_2, E_2)$$

The partition functions are given by

$$\Omega_1(N_1, V_1, E_1) = C_{N_1} \int d\mathrm{x}_1 \delta(H_1(\mathrm{x}_1) - E_1)$$
$$\Omega_2(N_2, V_2, E_2) = C_{N_2} \int d\mathrm{x}_2 \delta(H_2(\mathrm{x}_2) - E_2)$$
$$\Omega(N, V, E) = C_N \int d\mathrm{x} \delta(H_1(\mathrm{x}_1) + H_2(\mathrm{x}_2) - E) \neq \Omega_1(N_1, V_1, E_1)\Omega_2(N_2, V_2, E_2)$$

However, it can be shown that the total partition function can be written as

$$\Omega(E) = C' \int_0^E dE_1 \Omega_1(E_1)\Omega_2(E - E_1)$$

where C' is an overall constant independent of the energy. Note that the dependence of the partition functions on the volume and particle number has been suppressed for clarity.

Now imagine expressing the integral over energies in the above expression as a Riemann sum:

$$\Omega(E) = C'\Delta \sum_{i=1}^{P} \Omega_1(E_1^{(i)})\Omega_2(E - E_1^{(i)})$$

where Δ is the small energy interval (which we will allow to go to 0) and $P = E/\Delta$. The reason for writing the integral this way is to make use of a powerful theorem on sums with large numbers of terms.

Consider a sum of the form

$$\sigma = \sum_{i=1}^{P} a_i$$

where $a_i > 0$ for all a_i. Let $a_{\max}$ be the largest of all the a_i's. Clearly, then

$$a_{\max} \leq \sum_{i=1}^{P} a_i$$
$$P a_{\max} \geq \sum_{i=1}^{P} a_i$$

Thus, we have the inequality

$$a_{\max} \leq \sigma \leq P a_{\max}$$

or

$$\ln a_{\max} \leq \ln \sigma \leq \ln a_{\max} + \ln P$$

This gives upper and lower bounds on the value of $\ln \sigma$. Now suppose that $\ln a_{\max} >> \ln P$. Then the above inequality implies that

$$\ln \sigma \approx \ln a_{\max}$$

This would be the case, for example, if $a_{\max} \sim e^P$. In this case, the value of the sum is given to a very good approximation by the value of its maximum term.

Why should this theorem apply to the sum expression for $\Omega(E)$? Consider the case of a system of free particles $H = \sum_{i=1}^N \mathbf{p}_i^2/2m_i$, i.e., no potential. Then the expression for the partition function is

$$\Omega(E) \sim \int_{D(V)} d^N\mathbf{r} \int d^N\mathbf{p}\delta\left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} - E\right) \sim V^N$$

since the particle integrations are restricted only the volume of the container. Thus, the terms in the sum vary exponentially with N. But the number of terms in the sum P also varies like N since $P = E/\Delta$ and $E \sim N$, since E is extensive. Thus, the terms in the sum under consideration obey the conditions for the application of the theorem.

Let the maximum term in the sum be characterized by energies $\bar{E}_1$ and $\bar{E}_2 = E - \bar{E}_1$. Then, according to the above analysis,

$$S(E) = k\ln\Omega(E) = k\ln\Delta + k\ln\left[\Omega_1(\bar{E}_1)\Omega_2(E-\bar{E}_1)\right] + k\ln P + k\ln C'$$

Since $P = E/\Delta$, $\ln\Delta + \ln P = \ln\Delta + \ln E - \ln\Delta = \ln E$. But $E \sim N$, while $\ln\Omega_1 \sim N$. Since $N >> \ln N$, the above expression becomes, to a good approximation

$$S(E) \approx k\ln\left[\Omega_1(\bar{E}_1)\Omega_2(E-\bar{E}_1)\right] + \mathcal{O}(\ln N) + \text{const}$$

Thus, apart from constants, the entropy is approximately additive:

$$\begin{aligned} S(E) &= k\ln\Omega_1(\bar{E}_1) + k\ln\Omega_2(\bar{E}_2) \\ &= S_1(\bar{E}_1) + S_2(\bar{E}_2) + \mathcal{O}(\ln N) + \text{const} \end{aligned}$$

Finally, in order to compute the temperature of each system, we make a small variation in the energy $\bar{E}_1, d\bar{E}_1$. But since $\bar{E}_1 + \bar{E}_2 = E$, $d\bar{E}_1 = -d\bar{E}_2$. Also, this variation is made such that the total entropy S and energy E remain constant. Thus, we obtain

$$\begin{aligned} 0 &= \frac{\partial S_1}{\partial \bar{E}_1} + \frac{\partial S_2}{\partial \bar{E}_1} \\ 0 &= \frac{\partial S_1}{\partial \bar{E}_1} - \frac{\partial S_2}{\partial \bar{E}_2} \\ 0 &= \frac{1}{T_1} - \frac{1}{T_2} \end{aligned}$$

from which it is clear that $T_1 = T_2$, the expected condition for thermal equilibrium.

It is important to point out that the entropy $S(N,V,E)$ defined via the microcanonical partition function is not the only entropy that satisfies the properties of additivity and equality of temperatures at thermal equilibrium. Consider an ensemble defined by the condition that the Hamiltonian, $H(\mathrm{x})$ is less than a certain energy E. This is known as the *uniform ensemble* and its partition function, denoted $\Sigma(N,V,E)$ is defined by

$$\Sigma(N,V,E) = C\int_{H(\mathrm{x})<E} d\mathrm{x} = C\int d\mathrm{x}\,\theta(E - H(\mathrm{x}))$$

where $\theta(x)$ is the Heaviside step function. Clearly, it is related to the microcanonical partition function by

$$\Omega(N,V,E) = \frac{\partial}{\partial E}\Sigma(N,V,E)$$

Although we will not prove it, the entropy $\tilde{S}(N,V,E)$ defined from the uniform ensemble partition function via

$$\tilde{S}(N,V,E) = k\ln\Sigma(N,V,E)$$

is also approximately additive and will yield the condition $T_1 = T_2$ for two systems in thermal contact. In fact, it differs from $S(N,V,E)$ by a constant of order $\ln N$ so that one can also define the thermodynamics in terms of $\tilde{S}(N,V,E)$. In particular, the temperature is given by

$$\frac{1}{T} = \left(\frac{\partial\tilde{S}}{\partial E}\right)_{N,V} = k\left(\frac{\partial\ln\Sigma}{\partial E}\right)_{N,V}$$

II. REVERSIBLE LAWS OF MOTION AND THE ARROW OF TIME

Hamilton's equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

are invariant under a reversal of the direction of time $t \to -t$. Under such a transformation, the positions and momenta transform according to

$$\begin{aligned} q_i &\to q_i \\ p_i &= m_i\frac{dq_i}{dt} \to m_i\frac{dq_i}{d(-t)} = -p_i \end{aligned}$$

Thus,

$$\frac{dq_i}{d(-t)} = -\frac{\partial H}{\partial p_i}, \qquad \frac{d(-p_i)}{d(-t)} = -\frac{\partial H}{\partial q_i}$$

or

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

The form of the equations does not change! One of the implications of time reversal symmetry is as follows: Suppose a system is evolved forward in time starting from some initial condition up to a maximum time t; at t, the evolution is stopped, the sign of the velocity of each particle in the system is reversed, i.e., a time reversal transformation is performed, and the system is allowed to evolve once again for another time interval of length t; the system will return to its original starting point in phase space, i.e., the system will return to its initial condition. Now from the point of view of mechanics and the microcanonical ensemble, the initial conditions (for the first segment of the evolution) and the conditions created by reversing the signs of the velocities for initiating the second segment are equally valid and equally probably, both being points selected from the constant energy hypersurface. Therefore, from the point of view of mechanics, without *a priori* knowledge of which segment is the forward evolving trajectory and which is the time reversed trajectory, it should not be possible to say which is which. That is, if a movie of each trajectory were to be made and shown to an ignorant observer, that observer should not be able to tell which is the forward-evolving trajectory and which the time-reversed trajectory. Therefore, from the point of view of mechanics, which obeys time-reversal symmetry, *there is not preferred direction for the flow of time.*

Yet our everyday experience tells us that there are plenty of situations in which a system seems to evolve in a certain direction and not in the reverse direction, suggesting that there actually is a preferred direction in time. Some common examples are a glass falling to the ground and smashing into tiny pieces or the sudden expansion of a gas into a large box. These processes would *always* seem to occur in the same way and never in the reverse (the glass shards never reassemble themselves and jump back onto the table forming an unbroken glass, and the gas particles never suddenly all gather in one corner of the large box). This seeming inconsistency with the reversible laws of mechanics is known as *Loschmidt's paradox.* Indeed, the second law of thermodynamics, itself, would seem to be at odds with the reversibility of the laws of mechanics. That is, the observation that a system naturally evolves in such a way as to increase its entropy cannot obviously be rationalized starting from the microscopic reversible laws of motion.

Note that a system being driven by an external agent or field will not be in equilibrium with its surroundings and can exhibit irreversible behavior as a result of the work being done on it. The falling glass is an example of such a system. It is acted upon by gravity, which drives it uniformly toward a state of ever lower potential energy until the glass smashes to the ground. Even though it is possible to write down a Hamiltonian for this system, the treatment of the external field is only approximate in that the true microscopic origin of the external field is not taken into account. This also brings up the important question of how one exactly defines non-equilibrium states in general, and how do they evolve, a question which, to date, has no fully agreed upon answer and is an active area of research. However, the expanding gas example does not involve an external driving force and still seems to exhibit irreversible behavior. How can this observation be explained for such an isolated system?

One possible explanation was put forth by Boltzmann, who introduced the notion of *molecular chaos.* Under this assumption, the momenta of two particles do not become correlated as the result of a collision. This is tantamount to the assumption that microscopic information leading to a correlation between the particles is lost. This is not inconsistent with microscopic reversibility from a probabilistic point of view, as the momenta of two particles before a collision are certainly uncorrelated with each other. The assumption of molecular chaos allows one to prove the so called Boltzmann *H-theorem*, a theorem that predicts an increase in entropy until equilibrium is reached. For more details see Chapters 3 and 4 of Huang.

Boltzmann's assumption of molecular chaos remains unproven and may or may not be true. Another explanation due to Poincaré is based on his *recurrence theorem.* The Poincaré recurrence theorem states that *a system having a finite amount of energy and confined to a finite spatial volume will, after a sufficiently long time, return to an arbitrarily small neighborhood of its initial state.*

Proof of the recurrence theorem (taken almost directly from Huang, pg. 91):

Let a state of a system be represented by a point x in phase space. As the system evolves in time, a point in phase space traces out a trajectory that is uniquely determined by any given point on the trajectory (because of the deterministic nature of classical mechanics). Let g_0 be an arbitrary volume element in the phase space in the volume ω_0. After a time t all points in g_0 will be in another volume element g_t in a volume ω_t, which is uniquely determined by the choice of g_0. Assuming the system is Hamiltonian, then by Liouville's theorem:

$$\omega_0 = \omega_t$$

Let $?_0$ denote the subspace of phase space that is the union of all g_t for $0 \leq t < \infty$. Let its volume be Ω_0. Similarly, let $?_\tau$ denote the subspace that is the union of all g_t for $\tau \leq t < \infty$. Let its volume be Ω_τ. The numbers Ω_0 and Ω_τ are finite because, since the energy of the system is finite and the spatial volume occupied is finite, a representative point is confined to a finite region in phase space. The definitions immediately imply that $?_0$ contains $?_\tau$.

We may think of $?_0$ and $?_\tau$ in a different way. Imagine the region $?_0$ to be filled uniformly with representative points. As time progresses, $?_0$ will evolve into some other regions that are uniquely determined. It is clear, from the definitions, that after a time τ, $?_0$ will become $?_\tau$. Also, by Liouville's theorem:

$$\Omega_0 = \Omega_\tau$$

Recall that $?_0$ contains all the future destinations of the points in g_τ, which in turn is evolved from g_0 after a time τ. It has been shown that $?_0$ has the same volume as $?_\tau$ since $\Omega_0 = \Omega_\tau$ by Liouville's theorem. Therefore, $?_0$ and $?_\tau$ must contain the same set of points (except possibly for a set of zero measure).

In particular, $?_\tau$ contains all of g_0 (except possibly for a set of zero measure). But, by definition, all points in $?_\tau$ are future destinations of the points in g_0. Therefore all points in g_0 (except possibly for a set of zero measure) must return to g_0 after a sufficiently long time. Since g_0 can be made arbitrarily small, Poincaré's theorem follows.

Now consider an initial condition in which all the gas particles are initially in a corner of a large box. By Poincaré's theorem, the gas particles must eventually return to their initial state in the corner of the box. How long is this recurrence time? In order to answer this, consider dividing the box up into M small cells of volume v. The total number of microstates available to the gas varies with N like V^N. The number of microstates corresponding to all the particles occupying a single cell of volume v is v^N. Thus, the probability of observing the system in this microstate is approximately $(v/V)^N$. Even if $v = V/2$, for $N \sim 10^{23}$, the probability is vanishingly small. The Poincaré recurrence time, on the other hand, is proportional to the inverse of this probability or $(V/v)^N$. Again, since $N \sim 10^{23}$, if $v = V/2$, the required time is

$$t \sim 2^{10^{23}}$$

which is many orders of magnitude longer than the current age of the universe. Thus, although the system will return arbitrarily close to its initial state, the time required for this is unphysically long and will never be observed. Over times relevant for observation, given similar such initial conditions, the system will essentially always evolve in the same way, which is to expand and fill the box and essentially never to the opposite.