Apr. 4

Microcanonical Ensemble (continued)

In the previous lecture, I proposed the *microcanonical ensemble* as a model of thermodynamic equilibrium. The proposal, specifically, was that the macroscopic observables in a thermodynamic equilibrium state would be well approximated by averaging these observables in the ensemble of states in which all states of fixed energy appear with constant probability per phase space volume. I applied this model to the *ideal gas* and derived the basic properties of the ideal gas that you know from undergraduate chemistry. Our discussion also illustrated some points of principle that I will now analyze further.

For the ideal gas, we saw that typical states averaged in the microcanonical ensemble have a uniform density of particles and uniform partitioning of energy among macroscopic clusters of particles. The ensemble that we average over contains special states, for example, the state in which most of the atoms are on one side of the container. However, states which are special in any way are *rare*. For a subsystem of M particles, the fluctuations about the average values are of the order of $1/\sqrt{M}$, a level that is very small when $M \sim N_A$. Much larger fluctuations are suppressed exponentially in M.

The point is worth emphasizing. To do this, I will introduce some useful nomenclature. In statistical mechanics, we deal with systems of N particles or degrees of freedom with N very large, of the order of 10^{20} or higher. These values of N are large enough to justify defining *densities* of observable quantities or quantities per particle. Let us then define

- an *intensive* quantity is one that tends to *constant* as N becomes very large
- an *extensive* quantity is one that grows proportional to N as N becomes very large

Then, density, pressure, energy per particle, and 'temperature' (as defined in the previous lecture) are *intensive*, while total energy, and total volume are *extensive*. In general, local properties of a thermodynamic system are intensive, while global sums are extensive.

In addition to this distinction, there is another important distinction in the way quantities scale with N. This is expressed by what Daniel Schroeder refers to as *ordinary*, *large*, and *very large* numbers. *Ordinary numbers* are numbers such as 2, π, and 196,883. In a thermodynamic system with local interactions, per-atom properties are given by an ordinary number times a quantity with dimensions at the atomic scale. *Large numbers* are numbers of the order of Avogadro's number N_A. The energy of a whole system will be of the order of an atomic energy times N_A. *Very large numbers* are are numbers of the order of

$$e^{N_A}$$

The total number of states averaged in the microcanonical ensemble is is a very large number in this sense, while special states appear with numbers of order 1. It hardly matters whether the exact ratio is

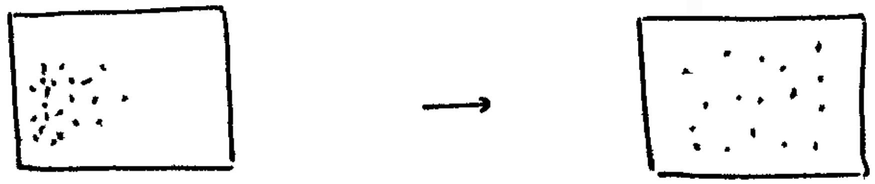
$$e^{N_A}, \qquad e^{\frac{1}{\pi}N_A}, \text{ or } \qquad e^{+10^{-6}N_A}$$

In all cases, the huge number of states into which a large number of particles can rearrange themselves crushes all other factors.

With these ideas, I would give to give the following picture of thermal equilibrium: Consider a system of a large number of particles in a definite initial state. Following the dynamics, this state will evolve into other states on the surface of fixed energy. In principle, each state will have different properties. However, typical states will have the same macroscopic properties, with a smooth partitioning of the particles and of the energy among the various parts of the system. I will put this as the basic assumption underlying statistical mechanics:

> All typical states of fixed energy have the same macroscopic properties. Atypical states exist, but the probability of such a state among all states of fixed energy is the inverse of a *very large number.* These atypical states rapidly evolve into typical states, in a time of the order of the atomic timescale. Typical states can evolve into atypical states, but only with very small (and negligible) probability.

The transition from an atypical states on the energy surface to a typical state gives a concrete picture of the approach to thermodynamic equilibrium:



I hope that you accept this picture, which I will use as the basis of the rest of the discussion in this course.

The postulate implies that we can calculate the macroscopic properties of any large assemblage of atoms as those of any typical state of given energy. The problem with this idea is that we need to know which states are typical. The solution to that problem is to average over all states with the given energy, that is, to average over the microcanonical ensemble of states.

There is one point here that I should clarify. Why do we integrate over states using a uniform density in phase space rather than some other measure? There is a well-defined answer to this question. In classical mechanics, there is a theorem, Liouville's theorem, that states that volumes in phase space are not changed under Hamiltonian time evolution. Thus, the microcanonical average as I have defined it is time-independent, as would be appropriate for a description of equilibrium. More general averages over phase space do not have this property.

Here is a proof of Liouville's theorem: Start from a small volume in phase space

$$dq_1 \cdots dq_N \, dp_1 \cdots dp_N$$

Let the points in this volume evolve over a small time interval

$$q_i \to q_i' = q_i + \dot{q}_i \Delta t \qquad p_i \to p_i' = p_i + \dot{p}_i \Delta t$$

These points now occupy a volume

$$dq'_1 \cdots dq'_N = \left| \frac{\partial(q'_i\, p'_i)}{\partial(q_j\, p_j)} \right| dq_1 \cdots dq_N\, dp_1 \cdots dp_N$$

The ratio of volumes is the Jacobian determinant

$$\left| \det \begin{bmatrix} \frac{\partial q'_i}{\partial q_j} & \frac{\partial p'_i}{\partial q_j} \\ \frac{\partial q'_i}{\partial p_j} & \frac{\partial p'_i}{\partial p_j} \end{bmatrix} \right| = \left| \det \begin{bmatrix} \delta_{ij} + \frac{\partial}{\partial q_j} \dot{q}_i \Delta t & \frac{\partial}{\partial q_j} \dot{p}_i \Delta t \\ \frac{\partial}{\partial p_j} \dot{q}_i \Delta t & \delta_{ij} + \frac{\partial}{\partial p_j} \dot{p}_i \Delta t \end{bmatrix} \right|$$

We can now expand the determinant in the small parameter Δt. The general formula for the expansion of the determinant of a matrix $\mathcal{A}$ follows from the expression

$$\det A = \prod_a \lambda_a = \exp\left[\sum_a \log \lambda_a\right] = \exp\left[\operatorname{tr} \log A\right]$$

where λ_a are the eigenvalues of $\mathcal{A}$. If

$$A = \underset{\sim}{1} + a\, \Delta t$$

then

$$\det(1 + a\,\Delta t) = \exp \operatorname{tr} \log(1 + a\,\Delta t)$$
$$= \exp\left[\operatorname{tr} a\, \Delta t + \cdots\right] = 1 + \operatorname{tr} a\, \Delta t + \cdots$$

Using these formulae, the Jacobian above is

$$1 + \sum_{i=1}^{N} \left(\frac{\partial}{\partial q_i} \dot{q}_i + \frac{\partial}{\partial p_i} \dot{p}_i \right) \Delta t + O(\Delta t^2)$$

$$= 1 + \sum_{i=1}^{N} \left[\frac{\partial}{\partial q_i} \left(\frac{\partial H}{\partial p_i} \right) + \frac{\partial}{\partial p_i} \left(-\frac{\partial H}{\partial q_i} \right) \right] \Delta t + O(\Delta t^2)$$

$$= 1 + 0 + O(\Delta t^2)$$

So indeed

$$\frac{d}{dt} (\text{Jacobian}) = 0$$

and the volume in phase space is preserved when we integrate the equations of motion. Since energy is conserved by Hamiltonian evolution, the same conclusion applies to areas on a surface of constant energy.

This argument tells us that the microcanonical ensemble gives a consistent description of thermal equilibrium. It does not explain why a system that evolves from a single point in phase space resembles the average over the energy surface. If we would like to go beyond the intuition above that typical points on the energy surface are identical macroscopically, we get into very deep water indeed. An explanation that has been proposed is that systems of many particles have the property of being *ergodic*, that is, the time average of any observable is equal to the average over the energy surface. Roughly, a system is ergodic if the time evolution of a point on the energy surface eventually comes close to any other points on the energy surface. Ergodicity can be proved for certain simple systems, for example, a gas of hard spheres. However, there are other systems that are known *not* to be ergodic. For example, many systems in one dimension are *integrable*, that is, their equations of motion imply an infinite number of conservation laws in addition to the conservation of energy and momentum. Then the time evolution of a point on the energy surface can only evolve to points with the same values of these conservation laws. More commonly, many systems have additional approximate conservation laws in special regions of phase space that prevent trajectories from going out of those regions. This is the content of the KAM theorem, described in Sethna's book.

In any case, ergodicity is not very attractive as an explanation of the validity of the microcanonical ensemble, because it takes a long time for a system to explore its whole energy surface. This time grows exponentially with the size of the system. On the other hand, in our experience, the time for the approach to thermal equilibrium is determined by local conditions and does not grow with the size of the system. Further aspects of the theory of ergodicity and the attempts to use this to derive properties of thermodynamic equilibrium are discussed in the classic but very instructive treatise by Paul and Tatiana Ehrenfest, *The Conceptual Foundations of the Statistical Approach in Mechanics* (1912).

I think that the explanation that typical states on the energy surface are macroscopically identical is closer to the truth, but it lacks a rigorous justification. For the purpose of this course, I will take the statement above as a postulate and claim that we are studying only systems to which it applies. Fortunately, it does seem to apply to most interacting systems of atoms that we study in practice. The success of the predictions that we will make from this postulate is its real justification.

Using these ideas, we can now analyze the following question: Given two assemblages of particles, each of which is in equilibrium, what happens when they are brought together and allowed to exchange energy? Which way does the energy flow? What state of each system results from this process?

Each initial state can be represented by a microcanonical ensemble of the fixed initial energy. As the system exchange energy, they evolve on the energy surface of the total system. Eventually, they reach a typical state of this sytem. We can describe this process quantitatively as follows: Initially, the two systems 1 and 2 have energies E_{01} and E_{02} such that

$$E_{01} + E_{02} = E$$

Each system occupies an energy surface of area

$$\Omega_1(E_{10}) \qquad\qquad \Omega_2(E_{20})$$

After the systems have interacted, the area of the energy surface for the combined system is

$$\Omega(E) = \int dE_1 \, \Omega_1(E_1) \, \Omega_2(E - E_1)$$

Now we can use the fact that $\Omega_i(E)$ is a *very large number*. For the idea gas, we found a behavior like

$$\Omega(E) \sim \left(\frac{E}{N}\right)^{\frac{3}{2}N}$$

It is convenient to define

$$S(E) = \log \Omega(E)$$

This quantity $S(E)$ is already an extensive quantity, that is, a quantity that grows proportional to N as N becomes large.

Since $\Omega(E)$ has dimensions, the logarithm is not yet well defined. We can fix it by convention by dividing Ω by a power of a convenient phase space volume. Looking ahead to the quantum theory, we note that $dq\,dp$ has the units of g cm^2/sec or the units of $\hbar$, and we can choose $2\pi\hbar$ per degree of freedom as the unit of phase space volume. Then, more precisely,

$$S(E) = \log \frac{\Omega(E)}{(2\pi\hbar)^D} \qquad D \text{ degrees of freedom}$$

The quantity $S(E)$ is called the *entropy* of the thermodynamic system. Again, $S(E)$ is *extensive*,

$$S(E) \sim N$$

In terms of the entropies of the systems 1 and 2, we can write the integral representing the $\Omega(E)$ for the combined system as

$$\Omega(E) = \int dE_1 \; e^{[S_1(E_1) + S_2(E-E_1)]}$$

Whereever the maximum of the exponent occurs, states with those values of the two energies are dominant by absurb amounts over all other states on the combined energy surface. The fluctuations about the dominant values of the energies will be of the order of $1/\sqrt{N}$. Thus, the criterion for the equilibrium state of the two systems is

$$\frac{d}{dE_1}\left[S_1(E_1) + S_2(E-E_1)\right] = 0$$

or

$$\frac{dS_1}{dE}(E_1) = \frac{dS_2}{dE}(E_2)$$

If the two systems were in this relation before there were brought into contact, no energy would flow and the two systems would remain in their initial states.

This result gives a precise meaning to the intuitive concept of *temperature*. Temperature gives the direct of the flow of energy between two systems in contact. Energy flows from the hotter system to the cooler one, and there is no flow if the two systems are at the same temperature. It thus makes sense to *define* temperature by the equation

$$\frac{1}{T} = \frac{dS}{dE}$$

Then, by the above argument, the approach to equilibrium will always increase the energy of a system at lower temperature at the expense of the energy of a system at higher temperature.

We need to check that this definition of temperature agrees with the definition given in the previous lecture for an ideal gas. I will do that before the end of this lecture.

I should note one aspect of this definition. Since S is dimensionless and E has the dimensions of energy, T as defined in the above equation has the units of energy. Usually temperature is defined in units called *degrees Kelvin* or, with a change in the choice of zero, *degrees Celsius*. In this course, I will continue to consider T as an energy. If you would like to measure T in °K, replace T by $k_B T$ where k_B is *Boltzmann's constant*,

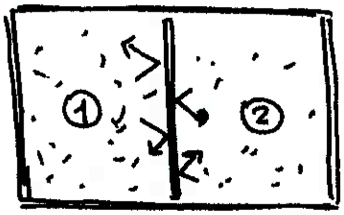
$$k_B = 1.38 \times 10^{-23} \; J/{}^\circ K \approx 0.86 \times 10^{-4} \; eV/{}^\circ K$$

Then the Boltzmann distribution is written as

$$\exp\left[- \frac{\varepsilon}{k_B T} \right] \qquad \varepsilon = \text{particle energy}$$

If Boltzmann's constant is used, it is conventional to multiply $S(E)$ by Boltzmann's constant and measure entropy in units of $J/{}^\circ K$. Please excuse me that I prefer to measure T in ergs or eV, keep $S(E)$ dimensionless as it should be, and ignore k_B.

I will now consider some other ways that two systems can interact. If two systems are separated by a wall



the wall could in principle move to allow the combined system to attain a better equilibrium. For each system, $\Omega_i(E)$ depends parametrically on the volme of the system V_i. If we can increase V_1 and decrease V_2 in such a way as to create a more generic state of the combined system, this state will give the new macroscopic properties of the system. In terms of the microcanonical ensemble, the system will move to a new microcanonical distribution with a higher entropy. Similarly, if the two systems 1 and 2 can exchange particles and some exchange of particles leads to a higher entropy, the system will move to that new configuration.

We are now entering the subject of *thermodynamics.* Thermodynamics is a method for discussing the macroscopic behavior of physical systems phenomenologically. The basic assumption of thermodynamics is that, for any system, there exists a *state function*, for example, the entropy S, that has a unique value for given thermal conditions, for example, for fixed E, V, and N. This hypothesis together with very general identities for partial derivatives turns out to have surprising power in constraining the properties of the system described by $S(E, V, N)$.

In this more precise language,

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

To discuss interactions that change V and N, we can give interpretations to the other first partial derivatives of S. Before I do this, I will review some properties of partial derivatives.

There are four important properties of partial derivatives that are used repeatedly in thermodynamics. First and most obviously,

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial f}\right)_y}$$

Second, the order of partial differentiation can be exchanged,

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y$$

This will lead to physically interesting relations, called *Maxwell relations.* Third, the derivative of $f(x, y)$ with respect to a third quantity is given by

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

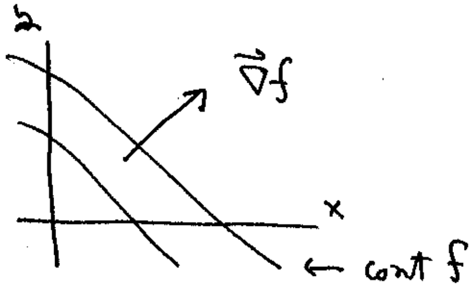
$$\text{or} \quad \frac{df}{dz} = \left(\frac{\partial f}{\partial x}\right)_y \frac{dx}{dz} + \left(\frac{\partial f}{\partial y}\right)_x \frac{dy}{dz}$$

Finally, there is a triple derivative relation

$$\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1$$

To derive this, note that a line of constant f in the (x, y) plane has slope

$$\left(\frac{\partial y}{\partial x}\right)_f$$



and the vector along the gradient of $f(x, y)$, which is orthogonal to this line, has slope

$$\frac{\left(\frac{\partial f}{\partial y}\right)_x}{\left(\frac{\partial f}{\partial x}\right)_y}$$

Now return to the problem of analyzing changes in a pair of interacting systems that result from changes in V_i and N_i. These changes might or might not be associated with changes in the energy of these systems. In general, the energies will change. For example, when the volume of 1 increases and the volume of 2 decreases, system 1 does work on system 2. This work is accounted by accounting the force times distance involved in the volume change. If the area is indefinite, we can write this equally well as pressure times the change in volume. We define the *pressure* of a system formally by

$$\mathcal{P} = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$$

It is convenient to make a similar definition for the change in energy due to a change in particle number. We define the *chemical potential* associated with a particle species by

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

For most processes in which two systems interact and change their energies, volumes, and particle numbers, the overall entropy will increase. Then system will proceed from the initial state to the final state in an uncontrollable way. However, we can think about special processes in which the total entropy remains constant. Then there is no preferences as to the direction of the change. In this situation, the change can be made arbitrarily slowly. Processes of the first kind are called *irreversible.* Processes of the second kind are called *reversible* or *adiabatic.* In the previous paragraph, pressure and chemical potential are defined in adiabatic processes, which makes sense, because these give well-defined situations in which these quantities can be measured with arbitrary care.

We can relate pressure and chemical potential to derivatives of the entropy by using partial derivative relations. From

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = -\left(\frac{\partial E}{\partial V}\right)_{S,N}\left(\frac{\partial S}{\partial E}\right)_{V,N}$$

we can recognize the partial derivatives on the right-hand side and so derive

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$$

From

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\left(\frac{\partial E}{\partial N}\right)_{S,V}\left(\frac{\partial S}{\partial E}\right)_{V,N}$$

we can derive in a similar way

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$

In summary,

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V,N} \qquad \frac{p}{T} = \frac{\partial S}{\partial V}\bigg|_{E,N} \qquad -\frac{\mu}{T} = \frac{\partial S}{\partial N}\bigg|_{E,V}$$

To conclude this lecture, I will apply the formulae we have just derived to the special case of the ideal gas. In the previous lecture, we found the formula for the phase space volume of an ideal gas of definite E, V, N:

$$\Omega_N(E) = \frac{V^N (2\pi m E)^{3N/2}}{(\frac{3}{2}N-1)!} \cdot (\text{order 1 factor})$$

Since N is very large, we can simplify this using Stirling's formula

$$(\tfrac{3}{2}N-1)! = (\tfrac{3}{2}N-1)^{\frac{3N}{2}-\frac{1}{2}} e^{-\frac{3}{2}N-1} \sqrt{2\pi} = \exp\left[\frac{3N}{2}\log\left(\frac{3N}{2}-1\right)+\cdots\right]$$

This gives

$$S = \log\Omega(E) = N \cdot \log\left[V \cdot \left(\frac{2\pi m E \cdot e}{3/2\, N}\right)^{3/2}\right]$$

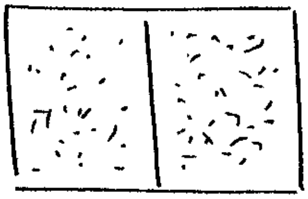
There is something odd about this formula. It is not *extensive*, since for large N it is not proportional to N but rather behaves as $N\log N$. This has real physical consequence. If we take two systems at the same temperature, pressure, and chemical potential and put them in contact, we might expect that the total entropy of the system would be the sum of the entropies of the original individual systems. However, the formula we have derived implies that the entropy of the combined system will be larger, by the change

$$2N \log V \longrightarrow 2N \log 2V$$

so that

$$\Delta S = 2N \log 2$$

This makes some kind of sense. A model of the process we are talking about is to fill the two halves of a chamber separately with gas under the same conditions, and then to take down a wall separating the two halves,



Then the change in entropy makes some sense. The atoms originally in the left-hand side of the chamber can now roam over the whole chamber, and similarly for the atoms orginally on the right. When this experiment is done with *different* gases, the removal of the wall results in irreversible mixing and a higher entropy and lower temperature for the final mixture of gases. However, when the experiment is done with the *same* gas on both sides, there is no effect.

Gibbs realized that this observation tells us something profound about the nature of atoms or molecules in a gas. We must treat different atoms of the same gas as *indistinguishable.* That is, in evaluating the volume of the microcanonical ensemble, we should not treat the configuration

and the configuration obtained by reversing the positions of the two atoms as two distinct configurations. The atoms are *identical*, and the configuration of two atoms should be counted only once. The underlying reason why this is the right prescription comes from quantum mechanics, but this consequence is seen in the macroscopic properties of gases.

The effect of Gibbs' prescription is to change Ω by replacing

$$\int d^{3N}q = V^N \qquad \text{by} \qquad \int [dq] = \frac{V^N}{N!}$$

This removes the multiple counting of identical configurations of atoms. Then the above expression for Ω is replaced by

$$\Omega_N(E) = \frac{V^N}{N!} \frac{(2\pi m E)^{3N/2}}{\left(\frac{3N}{2}-1\right)!} \cdot O(1)$$

and the expression for the entropy is replaced by

$$S = \log \frac{\Omega_N(E)}{(2\pi\hbar)^{3N}}$$

$$= N \left\{ \log \frac{V}{N} + 1 + \frac{3}{2} \log \frac{E}{N} + \frac{3}{2} + \frac{3}{2} \log \left[\frac{2\pi m}{\frac{3}{2}(2\pi\hbar)^2} \right] \right\}$$

Now we can evaluate the temperature and pressure of the ideal gas from our general formalism. We find

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2} \frac{N}{E}$$

and

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{N}{V}$$

so that, finally,

$$E = \frac{3}{2} N T \qquad pV = NT$$

as we found in the previous lecture.

We can put the above expression for S into a nicer form by using more explicitly quantum-mechanical notation. Define the *thermal de Broglie wavelength* by

$$p_{TdB} = [2m E(T)]^{1/2} = (3mT)^{1/2}$$

$$\lambda_{TdB} = 2\pi\hbar / p_{TdB} = 2\pi\hbar / (3mT)^{1/2}$$

Then

$$\frac{S}{N} = \frac{5}{2} + \log\left(\frac{\ell}{\lambda_{TdB}/\sqrt{2\pi}}\right)^3$$

with

$$\ell^3 = V/N$$