Lecture 2: Thermodynamics - Equilibrium, Temperature and Heat

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In this lecture we discussed the definitions of three important concepts - equilibrium, temperature and internal energy. The last two are defined by the so called Zeroth and First laws of thermodynamics.

1 Equilibrium

We begin by discussing equilibrium. This requires first a discussion of two important concepts - thermodynamic variables, and the possibility of constructing an isolated system.

A thermodynamic system is essentially a (macroscopic) big system, composed of many sub parts (eg. atoms). A thermodynamic variable is one that describes a property of the system as a whole - for example the volume, energy or pressure of a system would be a thermodynamic variable; but the trajectory of some particular atom in a gas would not. Note some of these variables are meaningful for single particles as well eg. energy, but we will encounter thermodynamic variables that have no analogue in the world of small objects (made up of few atoms). These variables will capture the random motions of the constituents making up the thermodynamic system. The collection of thermodynamic variables defines the thermodynamic state of the system. Note, this is a small subset of the variables required for a complete description of the system - which is actually composed of many particles. Nevertheless, thermodynamics only views the system in terms of these variables and places restrictions on how they can change. An isolated system is one that does not couple to the external world. While this is an idealization it can be very nearly approached in reality, by surrounding the system with perfect (adiabatic) walls.

If we take an isolated system and wait long enough, the thermodynamic variables will reach a steady value after some time and there will be no further change. This is the state of equilibrium. In this context, the following observations should be made:
1. One can make a loose analogy to a particle sitting at the bottom of a potential well. However, in an equilibrium thermodynamic system, there is much more action; for example if one drops a light particle into a liquid in equilibrium it is seen to be in a state of constant random motion; nevertheless thermodynamic quantities are stationary.

2. Notice, the isolation of the system is very important. For example, if we consider a resistor connected to a battery, and exposed to air - a steady current flows through it. Now if we focus only on the resistor, it is in steady state. However, it is not isolated and is not in equilibrium. If we consider the system as a whole (battery+resistor in a box), this system will clearly not be in a steady state. For example, in a conventional battery the concentrations of the chemicals involved change with time; or if we imagine the current being produced by discharging a large capacitor, then the charge on the capacitor is changing with time.

3. A final point to be made here is regarding the time scales involved in defining equilibrium. How long should we wait in order to check that the system has settled down to a stationary state? This is a tricky question and there is no single answer that covers all cases. Often, if the changes involved are extremely slow over the time scales of interest the system may be regarded as being in equilibrium. For example a mixture of hydrogen and oxygen at room temperature hardly react and can stay that way for a long period of time. Then over the timescales of even slow experiments, one can assume that they are two distinct species that do not react, and the system can be taken to be at equilibrium. However, if a match is applied to the mixture, then under these new conditions the previous assumptions will have to be reexamined.

2 Temperature

In this section we discuss the Zeroth law of thermodynamics that provides a definition of temperature.

We first introduce the concept of Thermal Equilibrium. Eventually this will just be the fact that we are all aware of from experience, that two bodies brought into thermal contact are in equilibrium only if they have the same temperature. But at this stage we have not defined thermal contact and temperature; this is what we do now.

We have already discussed the concept of a perfect wall that is impervious to everything. Let us consider a less perfect wall (a diathermal wall) that does not allow pressure to be transmitted but is otherwise not specially constructed. (If we take no special precautions, then the wall will transfer heat.)

If we take two systems that are in equilibrium when isolated, and put them in contact with each other separated by a diathermal wall - they may not continue
to be in equilibrium. Then, their state will change till they ultimately come into equilibrium with each other. Since this occurs as a result of contact through a diathermal wall, we will define this as a state of Thermal Equilibrium. This will define the temperature for us - which is formally done via the following statement called the Zeroth Law of Thermodynamics.

'Consider three thermodynamic systems A, B and C. If systems A and B are in thermal equilibrium with each other, and systems A and C are also in thermal equilibrium with each other then systems B and C must be in thermal equilibrium with each other.'

This fact, which we are aware of from experience, means that we can use a thermometer (A) to measure whether two objects (B and C) are in equilibrium. Therefore we can associate a number with the system in a particular state (lets call it the temperature); if two systems have the same value of this number then they are in thermal equilibrium. Two bodies in thermal equilibrium have the same temperature. for a more mathematical derivation of this see the book by Pippard, page 8. Since we can choose any system A as the thermometer, let us make life easier for ourselves and choose a simple system - the ideal gas (experimentally one can realize an ideal gas by taking a sufficiently dilute gas). The equilibrium state of a fixed amount of this gas is completely specified if we know the Pressure (P) and volume(V). Consider the state of this ideal gas at different P,V and ask when it is equilibrium with a fixed test system. This is just a way of asking for what values of P and V does the ideal gas have the same temperature (iso-therms in the PV diagram)? This is well known and goes under the name of Boyle’s law - if you take the gas in two different states \((P_1, V - 1)\) and \((P_2, V_2)\) then they have the same temperature (are in thermal equilibrium with the same test body) if \(P_1V_1 = P_2V_2\). Thus, the product \(PV\) for an ideal gas serves as a measure of the temperature - if we want to find the temperature of any object we find a pair of values \(P, V\) of the ideal gas at which it is in thermal equilibrium with the object, and call the product \(PV\) the temperature. In fact we could call any function of that product the temperature, but it is convenient to define it just as the product, with an appropriate numerical factor, so we get the standard scale of temperature. Note that this definition does not capture the idea of hotness or coldness that we associate with temperature (two temperatures are either equal or different in the above, no importance is assigned to the sign of their difference). This will be introduced once we discuss the second law; the scale of temperature defined from there will coincide with the ideal gas scale if we make the choice above of relating temperature simply to the product \(PV\), times an appropriate constant that depends on the amount of the gas.

Temperature is really just a way of accounting for the internal thermal agitation (eg. thermal motion of molecules in a gas). Therefore it only applies to thermodynamic systems. For an ideal gas one can actually derive that it is these internal motions that lead to the requirement of equal temperature for equilibrium between two systems (see Feynman Lectures on Physics, Vol 1, 39-4
for a nice derivation).

3 Work, Heat and Internal Energy

Mechanics tells us how to measure the amount of work done on an object. This applies equally to a single particle as it does to a thermodynamic system. For example if we have a volume of fluid at a pressure $P$ arising from a moveable piston, then a change in volume $\delta V$ results in an amount $\delta W = -P\delta V$ being done ON the system. Another example might be a soap film of area $A$ with a surface tension $\sigma$. Then, changing the area of the film results in work $\delta W = \sigma \delta a$ being done on the film. For other systems the work done by a change in the parameters of the system is easily calculated - examples can be found in Pippard (page 23) and take the general form $f \delta x$ where $f$ is a generalized force and $\delta x$ is a generalized displacement. (In the example above, $\delta x = -\delta V$, and the generalized force is pressure.)

However, we can also change the state of a system without doing ANY work on it. For example, we can keep the fluid at constant volume ($\delta V = 0$) but yet change its state by bringing it into thermal contact with another object - for example a flame. In order to account for such changes we introduce the concept of heat. We say that the state of the body is changed because heat is added. How can we measure this quantity of heat? It turns out that exactly the same change of state can be affected by doing work alone. For example, if we want to change the state of a fluid, we can imagine inserting a small paddle and rotating this paddle. Clearly, rotating the paddle requires doing work against viscosity in the fluid. Experimentally it can be demonstrated that exactly the same effect as, for example, applying a flame to the fluid, can be obtained by doing work using the paddle described above. Therefore it is natural to equate the amount of heat transferred to the system by the flame $\delta Q$ to the amount of work needed in the paddle experiment to achieve the same result $\delta W$. Therefore, since the effect of heat can be mimicked by work we may conclude that heat is a form of energy (actually it is the energy stored in the disordered motion of the constituents). Notice that throughout, if we need work to mimic the action of adding heat, we need some form of friction (viscosity, friction or in the case of an electrical circuit, resistance). Since these are the only two ways of changing the properties of a system, we can conclude that we can keep track of the energy of a thermodynamic system if we simply keep track of the amount of heat added to it and the amount of work done on it. This is the first law of thermodynamics - that we can define a property of the system, the internal energy $U$, whose changes can be calculated by:

$$\delta U = \delta Q + \delta W$$

This is nothing but the conservation of energy, recognizing the fact that heat is a form of energy. Note that $U$ is a property of the state of a system.
the change in $U$ on changing the state of a system only depends on the initial and final points; not on the path in state space used to make this change. This is not the case with heat and work. The heat added to a body during a change of state depends on the details of that change and not only on the end points. Similarly with work - it is only their sum that is solely a function of the end points and independent of path. Therefore we can speak of the internal energy of a system - it is fixed by the state of a system; but we can’t talk about the heat or the work of a system, only on how much heat is added or taken away, and how much work is done. \footnote{Note that if the internal energy dependend on paths (lets say path 1 from points $a$ to $b$ gave energy $\delta U_1$ while path 2 gave energy $\delta U_2 > \delta U_1$, and if these changes are reversible, then we can go from $a$ to $b$ on path 1 and return on path 2 and get a net gain in energy for free which violates the conservation of energy).}