

PHYSICS 715 COURSE NOTES
WEEK 1

1 Thermodynamics

1.1 Introduction

When we start to study physics, we learn about particle motion. First one particle, then two. It is dismaying to learn that the motion of three particles moving under the influence of mutual forces is already a problem so difficult that it is normally impossible to solve analytically. When it is visualized on a computer, we see why: except for anomalous situations, the motion is extremely complicated. One of the great surprises in physics is that the motion of many, many particles is, in certain respects, simpler than the motion of three, and we can understand quite a bit of what is happening. That is what we will be doing this semester.

We must be prepared for some differences from classical and quantum mechanics of one- and two-particle systems, however. First, we cannot understand everything about the motion of 10^{25} particles. We will only be able to understand statistical properties of their motion. The predictability of the system's behavior will also be uncertain, in a sense that we will make clear as we progress. Second, we must be prepared to use different mathematics than we usually use. Most of the time in dealing with single particles, we are solving differential equations: Newton's 2nd law, the Schrodinger equation, and so on. In this course, we will, for the most part, be using probability theory and statistics.

The subject is very powerful in understanding what happens in everyday life. We very often deal with macroscopic objects made of very many particles, and with temperature, a concept that does not even make sense when talking about a single particle.

There are two ways to regard the subject of thermodynamics. It can be thought of as an empirical set of laws constructed from the observation of macroscopic systems, or as a consequence of microscopic statistical mechanics. These are the historical and logical views, respectively.

I follow the first approach in these notes, which also dictates the order of the syllabus. I do this to emphasize that the concepts of thermodynamics are autonomous and that we can use intuition from everyday observations to build them up. Also, I wish to point out the crucial role that intermediate levels of description play in physics. It is rare that we can use microscopic theory *directly* to understand the observed world - instead we must try to build up a set of rules for macroscopic phenomena and understand experimental facts first on that basis. Only then do we try to derive the rules from some underlying theory. This view has always been common except in particle physics, which has been regarded as a "fundamental" subject. Now even the standard model of elementary particles is regarded as an "effective" theory, to be derived from some other theory at some future date. This point of view solves at a

stroke the conceptual difficulty of infinities in the renormalization of field theories.

Thermodynamics therefore comes first. Statistical mechanics comes later.

1.2 Equilibrium

Thermodynamics deals with the states of macroscopic bodies and is based on two everyday observations:

(a) If left in given external conditions, a body will come to a certain unique state and stay in that state. This is called its equilibrium state.

(b) The number of external parameters which need to be specified in order to determine the equilibrium state is not too large, and we can discover them all if we are careful.

The equilibrium state is unique and determines all the properties of the body, such as its volume, its color, its hardness, etc. The concept of equilibrium does, however, depend on the time scale of observation. For example, the gas in an inflated balloon is at a certain pressure which is greater than atmospheric pressure because of the stretched rubber. If we know the number of gas molecules, the temperature and the pressure, we will see that we can calculate the volume of the balloon, assuming that the gas inside is in equilibrium. This equilibrium is established a fraction of a second after the balloon is blown up. If we wait long enough, however, the gas diffuses out through the rubber, and the volume decreases. A new equilibrium state is reached where the internal and external pressures are equal. 'Equilibrium' is therefore always relative to a certain set of processes and a corresponding time scale. Feynman said something like "Equilibrium is what you have after the fast things have happened and the slow things haven't happened yet". For thermodynamics to be useful at all, it is necessary that the various time scales can be separated. There are systems in nature, such as spin glasses, where relaxation processes probably take place on all (or a wide range of) time scales. To these systems, thermodynamics (in our sense of the word) does not apply. There are also systems where the state determined by the external conditions is not unique. In some cases if the number of such states is not too large (such as a ferromagnet undergoing hysteresis), we can extend the concept of equilibrium.

Some important external parameters are: temperature T , which is always important; pressure P , particularly important for gases; magnetic field H , which is important for magnets and superconductors, external electric fields E . Any mechanical constraints on the system must also be specified. In equilibrium, we can often find a relation between the external parameters and the properties of the body. This is called an equation of state. For an ideal gas, we have $f(P, V, T) = 0$, where $f(P, V, T) = PV - NkT$. Here N is the number of molecules and k is the Boltzmann constant. This equation defines a surface in the state space defined by the three variables P , V , and T . For a magnet, the equation of state would look like $f(H, M, T) = 0$, where H is the external magnetic field, and M is the magnetic moment.

In any transformation of the gas which takes place slowly enough that equilibrium is maintained throughout, called a quasistatic process, the system remains always on the surface. Alternatively, if we perturb the system violently, it will leave the surface. If we then leave it alone, however, it will relax back to equilibrium and back to the surface.

Particularly simple are quasistatic transformations in which one parameter is held fixed. For example at constant temperature, a system will move along an isotherm. For an ideal gas, this is a hyperbola on a $P-V$ diagram: $P = NkT / V = \text{const.} / V$. We could also arrange experiments at constant pressure or volume, in which case the curves are called isobars and isochors, respectively. A magnetic system would have a corresponding surface in the state space on which quasistatic processes take place. These quasistatic transformations are also reversible, in a sense which I will make precise below.

1.3 Thermodynamic quantities

We now wish to make use of our knowledge from outside thermodynamics, starting from mechanics. We expect that any isolated system contains a certain well-defined and measurable amount of energy U . Again using a gas as an example, the energy is just the total kinetic energy of the molecules and the potential energy of their interaction. Then U for an *equilibrium* state is determined by two variables: $U = U(P, V)$, for example. Because there is a relation between P , V , and T , we could also write $U = U(V, T)$, etc. U is of course well defined for any state, equilibrium or not, but in a non-equilibrium state U will not be a function of only the two variables. More details about the system would be needed.

We can add energy to the system by doing work on it. The work done in changing the volume of the gas by a very small amount dV is $-dW$, as the symbol W is conventionally defined as work done *by* the gas, (coming from engineering roots of the subject, positive work is good) which is the negative of work done *on* the gas: $-dW = -Fdl = -\frac{F}{A}d(Al) = -PdV$, where A is the area, and F is the component of the force normal to the area. Finally $dW = PdV$ and the total work done by a finite change in volume is

$$\Delta W = \int_{V_i}^{V_f} P(V)dV \quad (1)$$

where V_i is the initial volume and V_f in the final volume. If no other energy leaves or enters the system, then $\Delta U = \Delta W$, i. e. , the change in energy of the system is equal to the work done by the system. In that case mechanical considerations alone are sufficient to understand what has happened. Thermodynamics is almost superfluous. However, it is often found that $\Delta U \neq \Delta W$ when a gas does work. This means that some other energy, which we call heat, has entered or left the gas. This is a natural thing to suppose, since the temperature of the gas often changes during such processes.

Let's look at the extreme case when we change the energy by heating the system without doing *any* work on it. For a gas this means the process takes place at constant

volume: $dW = PdV = 0$. We have added energy to the system. We now *define* heat by the equation $dQ = dU$ for a process in which no work is done. The first law of thermodynamics is the statement that heat is a form of energy and energy is additive, therefore

$$dU = dQ - dW. \quad (1st\ Law) \quad (2)$$

This holds for *all* transformations, quasistatic or not. We nowhere needed the requirement that the system was in equilibrium.

The form of the first law suggests that we could break up the energy content of the system into two parts, heat and work. This is *not* possible. This is shown by the following example. Allow a gas to expand from V_i to V_f by (a) free expansion by removing a partition and by (b) isothermal expansion by pushing a piston.

In (a), there is no time for heat to enter or leave the system $-dQ = 0$; also the system does no work on the outside world, since the motion of the partition is perpendicular to the pressure $\vec{F} \perp d\vec{\ell} = dW_a = 0$. Hence, for (a)

$$\Delta U_a = \Delta Q_a - \Delta W_a = 0. \quad (3)$$

In (b), we do the process sufficiently slowly in a temperature bath at a fixed T. The bath exchanges heat ΔQ_b with the system. It does work

$$\Delta W_b = \int_{V_i}^{V_f} PdV \quad (4)$$

on the piston.

The energy U of the system has a definite value in every state of the system. This means that the change ΔU depends only on the initial and final states of the system. For our example, ΔU is the same for (a) and (b) since the initial and final states are the same: $\Delta U_a = \Delta U_b$. But for (a), we have that $\Delta U_a = 0$, so that for (b), we have that $\Delta U_b = \Delta Q_b - \Delta W_b = 0$. Finally we see that

$$\Delta Q_b = \Delta W_b \neq 0. \quad (5)$$

Both the work and the heat transferred are different for the two processes, even though the initial and final states are the same. Thus work and heat cannot be attributes of the system itself. Work and heat are attributes of the *process* which the system undergoes and in fact only their changes are therefore meaningful. They are not things that the system *contains*. Another way to see this is that $\Delta W = \int PdV$ is the area under the curve on the P-V diagram. Two different processes will have two different curves and different areas even though the initial and final states are the same. Reference to example (b) shows that ΔQ also shows the property of path dependence. For this reason dW and dQ are sometimes written dW and dQ to indicate that they are "imperfect differentials", i. e. , not derivatives of functions W and Q . We conclude that pressure, volume and energy are thermodynamical variables of a mechanical kind which describe equilibrium states. Work and heat, though useful for calculating the energy, are not variables which can be used to describe states of a thermodynamic system. We shall have to develop other variables to characterize the specifically thermal character of a thermodynamic state.

1.4 Thermal variables

The difficulties we encountered in defining the quantity of heat leave us with a problem. We still need to find variables which will enable us to understand what is happening to the system as heat is added or taken away, i.e., thermal quantities that are attributes of the system itself. Let us try again a thought experiment to discover these variables. This time use a gas which is thermally isolated from its surroundings. Then $dQ = 0$ for any process, so $dU = -dW$ from the first law. We can therefore determine the energy of the system up to an arbitrary constant from $dW = PdV$. Quasistatically change the volume. Repeat the experiment a number of times, each time plotting U vs V . We will find a set of curves which characterize the gas. Label these by S_1, S_2 , etc. *The curves are found experimentally not to cross, meaning that S is a well defined function.* So $S = S(U, V)$ is a variable which characterizes the state of the gas. We can also write $U = U(S, V)$. Define the temperature T by the equation $T = \left(\frac{\partial U}{\partial S}\right)_V$. The derivative of U is taken at constant volume, which means that it describes a process in which no work is done. By the first law, then:

$$dQ = dU = \left(\frac{\partial U}{\partial S}\right)_V dS. \quad (6)$$

The equation $dQ = TdS$ is what we are looking for. It expresses the heat change in terms of actual thermodynamical variables T and S which characterize the system itself. S is called the entropy. Even though dQ is path dependent $dS = dQ/T$ is not. Multiplication by $1/T$ turns dQ into a perfect differential. In the theory of differential equations $1/T$ would be called an integrating factor. The way we defined entropy is not unique, since there was arbitrariness in how the curves were labelled. Any monotonic function of S would have done just as well. This arbitrariness is removed in practice by empirically defining a temperature scale rather than an entropy scale. The scale is defined in terms of measurable properties of a given reference system. Any other system whose temperature is desired is placed in thermal contact with the reference system. When the total system consisting of the two subsystems comes to equilibrium, they have the same temperature. This defines a universal scale since equilibrium is a transitive relation: if system 1 is in equilibrium with system 2 and 2 with 3, then system 1 is in equilibrium with system 3, and so on. This last, empirical, fact is sometimes called the zeroth law of thermodynamics. We now have the desired thermal variables, temperature T and entropy S . The first law now takes the more useful form:

$$dU = TdS - PdV. \quad (7)$$

The entropy has the property that a system constrained to be at fixed U and V (but allowed to exchange heat with its surroundings), will evolve towards a state of maximum entropy. Alternatively stated: among all states of a system having the same energy and volume, the equilibrium state is the state of maximum entropy. Any internal variables will relax until the system comes to such a state. To illustrate this, let us construct a system with only one variable to make things easy to visualize.

The system consists of two gases separated by a fixed conducting partition. The two gases are initially at different temperatures T_1 and T_2 . The energy of the total system is $U = U_1 + U_2$ and is held constant (no heat or work to outside world). The total entropy is $S = S_1 + S_2$. The volumes V_1 and V_2 are fixed. We allow U_1 to change by the exchange of heat. Then

$$\frac{dS_{tot}}{dU_1} = \left(\frac{\partial S_1}{\partial U_1} \right)_{V_1} + \left(\frac{\partial S_2}{\partial U_1} \right)_{V_2} = \left(\frac{\partial S_1}{\partial U_1} \right)_{V_1} - \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2} = \frac{1}{T_1} - \frac{1}{T_2} \quad (8)$$

Now we know that $T_1 = T_2$ in equilibrium, in accord with ordinary experience. Hence

$$\frac{dS_{tot}}{dU_1} = 0. \quad (9)$$

It is also the case that

$$\frac{d^2 S_{tot}}{dU_1^2} \leq 0, \quad (10)$$

though we won't show this. Hence the total entropy is maximized in the equilibrium state.

We may generalize this by allowing the partition to move so that only the sum $V_1 + V_2 = V_{tot}$ is fixed. Varying V_1 and U_1 (again with $U_1 + U_2$ fixed) then gives

$$dS_{tot} = \left(\frac{\partial S_{tot}}{\partial V_1} \right)_{U_1, V_2, U_2} dV_1 + \left(\frac{\partial S_{tot}}{\partial U_1} \right)_{V_1, V_2, U_2} dU_1 \quad (11)$$

$$+ \left(\frac{\partial S_{tot}}{\partial V_2} \right)_{V_1, V_1, U_2} dV_2 + \left(\frac{\partial S_{tot}}{\partial U_2} \right)_{U_1, V_2, V_2} dU_2. \quad (12)$$

Using the first law

$$dU = TdS - PdV, \quad (13)$$

we see that

$$\left(\frac{\partial S}{\partial V} \right)_U = \frac{P}{T}, \quad (14)$$

is true for any system. For our partitioned gas, the equation $S_{tot}(U_1, V_1, V_2, U_2) = S_1(U_1, V_1) + S_2(V_2, U_2)$ shows that

$$\left(\frac{\partial S_{tot}}{\partial V_1} \right)_{U_1, V_2, U_2} = \left(\frac{\partial S_1}{\partial V_1} \right)_{U_1} = \frac{P_1}{T_1}. \quad (15)$$

Since we also have that $dV_1 = -dV_2$ and $dU_1 = -dU_2$,

$$dS_{tot} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1, \quad (16)$$

Since $T_1 = T_2$ and $P_1 = P_2$, the total entropy is stationary (and actually maximal) with respect to all changes, once the system has come to equilibrium

This thought experiment may be generalized: forget about the partition and think only about two halves of a homogeneous system. Then the principle of maximal entropy implies that pressure and temperature gradients do not occur in equilibrium. The maximum property of the entropy leads us to the Second Law of Thermodynamics.

1.5 The Second Law

The second law is of interest to us particularly because it clarifies the notion of equilibrium. We will look at one particular formulation first, that of Kelvin: "It is impossible to convert heat into work with no other effect". The meaning of the law is often explained using cyclical processes. This is convenient for the practical reason that engines run in cycles, but also because we wish to understand a general law which is independent of any particular state of the system. Therefore we consider the general problem of what happens when we come back to the same state we started in, i.e., one cycle. Let us again think about the simplest example of a gas at pressure P and volume V which can exchange both heat and work with the outside world. One particularly interesting cycle is the Carnot cycle.

The top and bottom curves are isotherms at T_2 and T_1 , respectively. The left and right curves are adiabats - constant entropy curves. On these $dS = 0$ so $dQ = 0$. No heat is absorbed. Heat Q_2 is absorbed on the top curve $a \rightarrow b$, and heat Q_1 is given off on $c \rightarrow d$. The total work done in one cycle is $W = (\int_a^b + \int_b^c + \int_c^d + \int_d^a)PdV$, the area inside the cycle curves. By the first law $W = Q_2 - Q_1$. We define the efficiency $\eta \equiv \text{work done/heat added} = W/Q_2 = 1 - Q_1/Q_2$. Note that if the cycle is run in reverse, we would do work W on the system and absorb heat Q_2 from outside. This would be a refrigerator. The efficiency may be expressed in terms of the temperatures T_1 and T_2 because by hypothesis $S_a = S_d$ and $S_b = S_c$; since $Q_2 = T_2(S_b - S_a)$ and $Q_1 = -T_1(S_c - S_d)$, we have $Q_1/Q_2 = T_1/T_2$ and the efficiency is $\eta = 1 - T_1/T_2$.

The reason that the Carnot cycle is special is that, according to the Second Law, it has the maximum efficiency among all engines operating between the temperatures T_1 and T_2 , and this is due to its reversibility. For imagine another engine, not necessarily reversible, that operates between the two reservoirs, absorbing heat Q'_2 at T_2 and giving off Q'_1 at T_1 . It does work W' during one cycle. The change in entropy Δ_{tot} of the engine+reservoirs in the cycle is that of the reservoir alone since the engine comes back to the initial state. So $\Delta_{tot} = Q'_1/T_1 - Q'_2/T_2 = (Q'_2 - W)/T_1 - Q'_2/T_2$ and we must have that $\Delta_{tot} \geq 0$, so $W' \leq Q'_2(1 - T_1/T_2)$, which is to say that $\eta \leq 1 - T_1/T_2$.

I think the following proof, as given in the book and in the lecture, is saying the same thing in a less clear way.

"Let us run this engine through N' cycles in conjunction with a Carnot engine in reverse through N cycles, where N is chosen so that the heat absorbed at T_2 is zero, i. e. , so that $Q_2^{tot} = N'Q'_2 - NQ_2 = 0$. Then we also have $W^{tot} = N'W' - NW$ and $Q_1^{tot} = N'Q'_1 - NQ_1$. By the first law $W^{tot} = Q_2^{tot} - Q_1^{tot} = -Q_1^{tot}$. By the second law,

we must have $W^{tot} \leq 0$, (we are doing work on the composite system) otherwise we would be extracting heat from the reservoir at T_1 and turning it entirely into work. But $W^{tot} \leq 0$ implies $Q_1^{tot} \geq 0$ so $N'Q'_1 - NQ_1 \geq 0$. By the choice of N , this gives $Q_2Q'_1 - Q'_2Q_1 \geq 0$ and finally $Q_1/Q_2 \leq Q'_1/Q'_2$, which implies $1 - Q_1/Q_2 \geq 1 - Q'_1/Q'_2$. Thus no engine is more efficient than the reversible Carnot engine. So $\eta_{Carnot} \geq \eta'$ which is to say that the Carnot efficiency is the maximum efficiency”.

As an explicit example, let us construct a Carnot engine using an ideal gas. We wish to determine the shape of the cycle on the P-V diagram. The isothermal parts are easy. Since $PV = NKT$, we have $P_aV_a = P_bV_b$ and $P_cV_c = P_dV_d$. The sections a-b and c-d are hyperbolas. a-b is described by the equation $P = (P_aV_a)/V$ and c-d by $P = (P_cV_c)/V$. In general, the isotherms are the family of curves $PV = \text{constant}$, where the constant labels the different curves.

It takes a bit more work to figure out the equations of the adiabatic paths b-c and d-a. First of all, they must satisfy $dQ = 0$. The first law then gives $dU = -PdV$. We may get rid of U by using the fact that for an ideal gas $U = C_vT$, where C_v , the specific heat, is a constant. Thus

$$C_v dT = -PdV. \quad (17)$$

Now the equation of state $PV = NkT$ gives

$$PdV + VdP = NkdT. \quad (18)$$

We can eliminate the unwanted variable T between these two equations:

$$\frac{1}{Nk}C_v(PdV + VdP) = -PdV. \quad (19)$$

Defining

$$c_v = C_v/Nk, \quad (20)$$

$$(c_v + 1)\frac{dV}{V} = -c_v\frac{dP}{P}. \quad (21)$$

This is now a relation for the path in terms of P and V alone. Integrating from the point b, we find

$$(c_v + 1)\int_b^V \frac{dV}{V} = -c_v\int_b^P \frac{dP}{P}, \quad (22)$$

which is

$$(c_v + 1)\log \frac{V}{V_b} = -c_v\log\left(\frac{P}{P_b}\right), \quad (23)$$

or

$$\left(\frac{V}{V_b}\right)^{(c_v+1)} = \left(\frac{P_b}{P}\right)^{c_v}, \quad (24)$$

which may also be written as

$$P^{c_v}V^{c_v+1} = P_b^{c_v}V_b^{c_v+1}, \quad (25)$$

which is the equation for the curve b-c. The curve d-a is given analogously by

$$P^{c_v} V^{c_v+1} = P_d^{c_v} V_d^{c_v+1}. \quad (26)$$

More generally, the adiabatic curves are the family

$$P^{c_v} V^{c_v+1} = \text{constant}. \quad (27)$$

The constant labels the various curves.

For a monatomic ideal gas $c_v = 3/2$ and $P^{3/2} V^{5/2} = \text{constant}$ is the equation of an adiabat. You will calculate the total work and heat in the exercises.

A practical motor should have the maximum possible efficiency. It should be run in a Carnot cycle, taking in heat at a very high temperature T_2 and giving it off at a very low temperature T_1 . For ordinary applications, T_1 is room temperature, about 300K. For external combustion engines, such as the steam engine, T_2 is limited certainly by the melting temperature of the vessel containing the water, (maybe 1500K) and actually must be considerably lower to avoid degrading the vessel, around 800K. Internal combustion engines operate at considerably higher T_2 by absorbing heat in a short burst, within the working substance (in this case air) which gives this sort of engine a large advantage. The cycle used in automobile engines is called the Otto cycle and looks roughly like this: Two of the legs are adiabatic, as in a Carnot cycle. The other two are more like isochors than isotherms, however, for practical reasons.

As a final example of a thermodynamic transformation, which illustrates the role of entropy, let us revisit the reversible isothermal expansion of an ideal gas. It expands with $T = T_0 = \text{constant}$, which implies $U = U_0 = \text{constant}$. By the first law $dQ = dW = PdV$. Hence

$$\Delta Q = \int_{V_i}^{V_f} PdV = \int_{V_i}^{V_f} \frac{NkT_0}{V} = NkT_0 \log\left(\frac{V_f}{V_i}\right). \quad (28)$$

Also

$$\Delta S = \frac{\Delta Q}{T_0} = Nk \log\left(\frac{V_f}{V_i}\right). \quad (29)$$

In this isothermal case, the heat source provides heat ΔQ to the system. The entropy change of the source is $\Delta S = -\Delta Q/T_0 = -\Delta S$. Hence $\Delta_{tot} = \Delta S + \Delta S_s = 0$. The entropy of the composite system does not change, and the whole transformation is reversible. In contrast, for free expansion of the gas from V_i to V_f , we have $\Delta Q = \Delta W = 0$, i. e. , no heat is provided to the system. Since S is a state function, we must have that $\Delta S = Nk \log(\frac{V_f}{V_i})$ as before. In this case the total entropy of the universe has increased, because of the irreversibility of the process.