Notes for Lecture 1

Thermodynamics

1.1 Thermodynamics and Statistical Physics

Thermodynamics deals with macroscopic phenomena in a phenomenological way, while statistical physics tries to establish the microscopic origin of thermodynamic laws from the dynamics of many particles. Both are fundamental parts of our trying to understand the Nature around us. In this course, we will spend most of our time studying the statistical physics of particles and fields. In this lecture and the next, however, we make sure that we establish solid understanding of bare essentials of the thermodynamics. A sharp analytical mind armed with the reductionist idealism may sometimes misled to think that the law of thermodynamics is unimportant or uninteresting—quite the opposite is more like it[1].

1.2 Fundamental physics like no other

The subject of thermodynamics and statistical physics seems quite "applied," or "not so fundamental," from the following point of view. Consider other subjects—classical mechanics, electro-magnetism, quantum mechanics, etc. In all of these disciplines, what one usually starts with is a "particle." How nice! And a nice set of equations written in stone! Like Newton's equation, or others. How relieving to start in such

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[1] Einstein has a famous quote in this regard. "A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts."

a fundamental manner from an authoritative set of principles! However, instead of starting from such boiled-down essence as particle and equation of motion, thermodynamics starts with something that seem so . . . down to earth . . . like engine, heat, reservoir, probability. A possible reaction by a student, like my former self in an undergraduate school, is a bit of bewilderment towards such a "non-fundamental looking discipline." It seems that this might even be a typical response by many students.

Clearly, one might proclaim, statistical mechanics is inferior in the sense that it relies on other first principles like Newton's equation, Maxwell's equations, or Schrödinger equation.

Moreover, statistical physics seems fundamentally non-exact. What do I mean by this? By the time students learn statistical physics, they have already gone through a process of getting used to "not being exact" in this sense: many problems in such beautiful subjects such as classical mechanics, quantum mechanics etc. are simply not solvable. So, one has to apply approximate methods. Well, that might have been disappointing to some students. However, this statistical mechanics is quite another beast, seemingly offering another dimension of ugliness or non-exactness. Even the first principle of the statistical mechanics has to be established *probabilistically*! We are told that the principle such as the 2nd law of thermodynamics must be interpreted "in a probabilistic sense"—e.g. the law of mechanics does not disallow the heat going from a cool object to a hot object, it is just very improbable that such an event will occur. This may definitely be another level of blow to a kind of idealistic attitude of a student. Physics is called an "exact science." Here, in statistical physics, it seems that the laws themselves are not something that we can rely on as being exact! What kind of compromised subject is this? Where is the beauty of the "exact science"?

Of course, these "concerns" are exaggerated grotesquely, just for my argument's sake, while I believe that a line of thought can go as described, sometimes.

And of course, these concerns are in large part misconceptions. The truth is that everything that one does in science is statistical, in multiple senses. Every measurement that establishes the fact and the law and such are governed by statistics. Every law has a chance to fail, if a new phenomenon that defies the existing paradigm is discovered. Last but not least, the modern view of fundamental particles require many body physics such as expressed by the renormalization group theory. (And indeed the explicit acknowledgement of the many body nature of the world is what makes thermodynamics down to earth and the probability matter a lot in statistical mechanics.) So the many body nature of the world permeates even the most beloved "fundamental particle" that we so love to see on page 1 of classical mechanics, or quantum mechanics, etc. And along those lines, we invoke the concept such as "symmetry breaking" and renormalized particles, to define the fundamental particles.

So, in these senses, my (long-ago-renewed) opinion is that the statistical physics is fundamental physics like no other, pointing out how probabilistic concepts underpin all of physics and how really certain and sure things can become even if the fundamental principle is based on the probability. This way, various disciplines of the whole of physics seem to make a sort of a strange feedback loop.

1.3 Thermodynamic variables

Thermodynamic variables = thermodynamic coordinates = state functions = state variables. Like pressure, volume, surface tension, area, number of particles, chemical potential, etc. These are related to mechanical and chemical work. We will shortly see that temperature and entropy are important state functions, and they are not related to work. And of course, energy is a thermodynamic variable as well.

1.4 Transformation

A transformation is defined as a process in which the thermodynamic variables change. During a transformation, thermodynamic variables may not be well-defined. "Transformation" and "process" will be used loosely to mean the same.

1.5 The equilibrium

We all know that everything changes. However, in a longish but limited time window of observation, many things can be approximated as not changing at all. This is the concept of the equilibrium. We define the **equilibrium state** as a state where the thermodynamic variables are constant *and* there are no macroscopic currents. If a state satisfies the first condition but not the latter, then it is called a "**steady state**."

The equilibrium is a concept that needs to be interpreted with the right time scale in mind. When time scale is too long, then the thermodynamic variables may change. When time scale is too short (than the relaxation time of the system), then the thermodynamic variables generally fluctuate rapidly. Indeed, the fluctuation is an important concept. It is essential that the equilibrium coexists with temporal and spatial fluctuations.

1.6 The zeroth law

The zeroth law of thermodynamics seems simple enough, but is not trivial.

If two systems A and B are in equilibrium, and if B and C are in equilibrium, then A and C are also in equilibrium.

Importantly, we note that an equilibrium can be established without necessarily exchanging any (macroscopic) mechanical forces or constituent particles.

This law is shown to lead to the fact that there must be an empirical thermodynamic variable, **temperature**.

Why is this? Imagine three gas systems, A, B, and C, just to be concrete. Each system is characterized by pressure and volume. We do not consider any other work related variables, for simplicity. These three gas systems are in contact with one another through "heat-conducting" walls, which do not move. So, these systems cannot exchange work.

When the two gas systems come to a mutual equilibrium, it is clear that the pressure and the volume of each system will adjust upon interaction. So, the very fact that the two systems come to a mutual equilibrium can be expressed as a constraint

$$f_{AB}(P_A, V_A; P_B, V_B) = 0$$

Now we shall show that this constraint can be re-written as

$$\Theta_A(P_A, V_A) = \Theta_B(P_B, V_B)$$

assuming the zero-th law, establishing the Θ function, as the *empirical temperature* state function.

Inverting f_{AB} one can write, for example,

$$P_B = F_{AB}(P_A, V_A; V_B)$$

Similarly, considering B and C, we can write

$$P_B = F_{BC}(V_B; P_C, V_C)$$

So,

$$F_{AB}(P_A, V_A; V_B) = F_{BC}(V_B; P_C, V_C)$$

By taking just one specific value of V_B, we get

$$\Theta_A(P_A, V_A) = \Theta_C(P_C, V_C)$$

where Θ_A and Θ_C are some functions of P_A, V_A and P_C, V_C respectively.

But the zero-th law says that there must be a constraint

$$f_{AC}(P_A, V_A; P_C, V_C) = 0$$

For the equilibrium to be uniquely defined, this constraint must be the same as the above. QED.

So, the temperature becomes equal when two systems come into equilibrium by exchange of "heat." This is not all, however. As we will see later, if two systems are allowed to exchange volume (V), then they will come into equilibrium by equalizing pressure (P). And, if two systems are allowed to exchange particles (N), then they will come into equilibrium by equalizing chemical potential (μ). In a heat exchange, one can view the entropy (S) as being exchanged for the equalization of temperature (T).

1.7 The first law

The first law of thermodynamics is the principle of energy conservation, and is best summarized by the following equation.

$$dE = đQ + đW \tag{1.1}$$

Here, E is the energy of the system. dE is the total differential of the energy function in terms of independent thermodynamic variables. $đQ$ is not a total differential since Q is not a state function. Neither is the work W. Instead, the amount of heat that the system receives ($đQ$) and the amount of work that the system receives ($đW$) depends on *how* the process of heat transfer or the process of work is carried out[2]. The notation $đ$ to denote a non-total-differential is standard in thermal/statistical physics.

If there is no heat transfer (**adiabatic process**), then $đW$ is independent of how the work is performed, e.g. independent of the path that is taken to go from the initial state to the final state. From mechanics, we are familiar with this situation—this is the case of a purely mechanical system, where there is no dissipation. So, the first law of thermodynamics above is the generalization of the energy conservation principle that now includes the heat. In a phenomenological sense, it gives the definition of heat.

The above law is valid whether or not the system is in equilibrium during the process.

However, we often consider cases—**quasi-static processes**—where the system is in equilibrium at each point of the process because the system is driven slowly enough so that it has time to relax into equilibrium at each point. In such quasi-static processes, the thermodynamic variables are then well-defined at each point, and so it is possible to write down the work in terms of those thermodynamic variables.

Also, we consider **reversible processes**, which are literally those that can be run backward in time by changing input and output. Reversible processes are necessarily quasi-static processes, since non-equilibrium processes are not reversible[3] (e.g., a free expansion of a gas).

Question: is any quasi-static process a reversible process also? No, not necessarily. An easy example is the following. Take a Carnot engine involving an ideal gas (see below). Now, introduce friction between the cylinder wall and the top lid of the gas. This new engine is non-reversible (and thus is not a Carnot engine). Now, the work put out by the engine will be less than the enclosed area in the P-V diagram (see below). When the process is reversed by changing the sign of the work put in, it does not result in the same process. Other examples include the Joule-Thomson throttling process and a quasi-static stirring.

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[2] Note that here, we define $đW$ as the work done *on* the system. Some textbook defines it as the work done by the system, which is the negative of our $đW$.

[3] Here, what is really meant is that a non-equilibrium to equilibrium process is not reversible. Somewhat "artificial" examples of non-equilibrium processes such as a mass on spring or a pendulum *without* any damping *are* clearly reversible (in a single period of motion the motion of such an oscillator/pendulum reverses itself once). Note that this fact is true even if such a system is non-linear (a free non-linear one dimensional oscillator is not chaotic): any bound motion in one dimension is periodic. For a real macroscopic system, however, there *almost always is* damping, and such a periodic motion will come to a halt, in an irreversible process.

We will show this important fact in the next lecture: **for an adiabatic process, a reversible process is equivalent to an isentropic process**, i.e. a process in which entropy does not change.

We are rather familiar with the concept of work from mechanics. It is given by force times the displacement. This can be now applied to quasi-static processes, since the thermodynamic coordinates are well-defined during the process. Typically, one can divide state functions into a set of generalized forces (J) and a set of generalized displacements (x). Here are some typical examples: F tension and L length, S surface tension and A area, $-P$ pressure and V volume, H and M, E (electric field) and P (polarization), and μ and N are examples of J and x pairs. Given a set of force and displacement pair, the work is given by $đW = J\,dx$, and thus, in general, when there are multiple forces in operation

$$đW = \sum_i J_i\,dx_i. \qquad \text{(reversible process only)} \tag{1.2}$$

Here, we added the stipulation "reversible only," as this stipulation is necessary from general consideration (LN 2). In this paragraph, though, we implicitly considered a purely mechanical process only, in which no heat is involved; such process is always reversible.

One may note that the forces are **intensive** quantities, independent of the system size, while the displacements are **extensive** quantities, proportional to the system size.

1.8 Temperature

With the zero-th law and the first law, it is possible to define temperature. Bodies in equilibrium are at the same temperature. When heat flows from one body to another body, the first body is defined as a "hotter" object and the second body as a "colder" object. We can then define that hotter means higher temperature while colder means lower temperature.

This much definition of temperature is enough as the basis for the second law. In turn, we will see that the absolute temperature can be defined using the second law.

1.9 The second law

So, the zero-th law implies that there is a thing called "temperature" and the first law shows that there is a thing called "heat transfer." Just as Newton's first two laws of mechanics can be taken as mere definitions, these two laws of thermodynamics can be taken as definitions. There is then the second law, which is not just a definition, just as Newton's third law cannot be taken as a mere definition.

The second law is a well-tested law, which is true as far as we know.

Kelvin's postulate: No process is possible whose sole result is the complete conversion of heat to work *from a source at a constant temperature throughout.* (There is no perfect engine.)

Clausius's postulate: No process is possible whose sole result is the transfer of heat from a colder body to a hotter body. (There is no perfect refrigerator.)

Note that each of these statements says "sole result." A process can involve a complete conversion of heat to work if it involves other changes. For instance, suppose in a cylinder there is an ideal gas. The bottom end of the gas is a reservoir with temperature T_0. All other enclosures of the gas is adiabatic. Let us assume that the top lid of the gas is movable. Let the gas expand slowly (while you are pushing down on the top, to balance). Since we are considering an ideal gas, the energy is independent of volume. Also, because of the quasi-static process assumption, the expansion is an iso-thermal expansion. The gas clearly does work on the top lid (and your hand does a negative work, equal and opposite to the work by the gas). How did this happen? Where did this work come from? Since the gas did not change its energy, the work must have come from the heat intake from the reservoir. So, a perfect conversion of heat into work! However, notice that this is not the sole result. The gas has changed its volume! Why does this matter, you might complain. It is a perfect engine, this way. Somewhat true, but this engine will definitely not be a practical thing, since it cannot run in cycles to generate work again and again. Instead, we will run out of space pretty quickly and this machine has to stop at some point.

Also, note that Kelvin's postulate is stipulated with "from a source at a constant temperature throughout."

Historically, these two equivalent statements were possible thanks to the previous work by Carnot, who importantly contributed the concept of Carnot engine, and the corresponding Carnot's theorem. It is left as an exercise to show that these two statements are equivalent.

Now, we shall explore some general properties derived from the above postulates. We will consider the Carnot engine and non-Carnot engines. We require that this engine is cyclic. Namely, after a period it comes back to the same state.

First, let us consider any engine that operates between two heat reservoirs. Suppose that the engine takes heat Q_H from the hot reservoir, and deposits heat Q_C to the cold reservoir, in a cycle. The work is then given by $W = Q_H - Q_C$. We shall prove that

$$Q_C, Q_H > 0 \quad \text{if} \quad W > 0 \qquad \text{(any engine)} \tag{1.3}$$

To prove this, suppose $Q_C \leq 0$. This means that the cold reservoir lost the heat. We can then simply connect the hot reservoir and the cold reservoir to replenish this heat, leaving the cold reservoir unchanged at all. After this step, then, the net effect is the total conversion of the heat from a single source $(Q_H - Q_C)$ into work—this violates the Kelvin's postulate. So, $Q_C > 0$. It then follows trivially that $Q_H > 0$ also, since $Q_H = W + Q_C$.

Second, for any engine, we can define the efficiency as

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \tag{1.4}$$

Third, a Carnot engine is defined as a reversible engine that does the above. If the Carnot engine process is reversed, it is a refrigerator, and its figure of merit is defined as $\omega = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$.

It is of interest to "build a Carnot engine" using an ideal gas. The full process can be taken as the following: iso-thermal expansion at T_H, adiabatic expansion to T_C, iso-thermal compression at T_C, and adiabatic compression to T_H. It can easily be shown that the total work that the engine does is the enclosed area of the two isotherms and the two adiabatics in the $P - V$ plane.

Adiabatic process for a monatomic gas: $E = \frac{3}{2} N k_B T = \frac{3}{2} PV$. $đQ = dE - đW = dE + PdV = 0$. $VdP + \frac{5}{3} PdV = 0$. So, $PV^\gamma = \text{constant}$ with $\gamma = 5/3$.

Carnot's theorem: No engine operating between two reservoirs can be more efficient than a Carnot engine operating between them.

You are probably very familiar with this fact. The proof is rather simple. Suppose that a general engine (Carnot or non-Carnot) is doing work W while drawing Q_H and depositing Q_C. Suppose that a Carnot engine is doing work W while drawing Q'_H

and Q'_C. Such an engine can always be built to the right size for any specified amount of work W (as is clear from the above example of an ideal gas based engine). So, we can assume, without loss of generality, that the two engines do the same amount of work, W. By definition, the Carnot engine is reversible and so we can combine the non-Carnot engine and the reversed Carnot engine to form a new composite engine. This new engine does not do any work, since $W + (-W) = 0$, but it takes heat $Q_H - Q'_H$ while it deposits heat $Q_C - Q'_C$. By energy conservation, these two must be equal. Note then that $Q_H - Q'_H$ must be positive or zero, since otherwise it will break the Clausius postulate. Thus, $Q_H \geq Q'_H$. Therefore, the efficiency of the general engine $= W/Q'_H \leq W/Q_H = \eta_{Carnot}$.

It follows immediately that any two Carnot engines connected to the same two heat reservoirs must extract the same Q_H and deposit the same Q_C in order to do a certain given amount of work W (since if the two engines are both Carnot engines, then $Q_H \geq Q'_H$ and $Q'_H \geq Q_H$, and thus $Q_H = Q'_H$). As $W = Q_H - Q_C$, we then conclude that *any* Carnot engine operating between two heat baths has the same *universal efficiency*, $\eta_{Carnot} = \frac{Q_H - Q_C}{Q_H}$. It then follows that Q_C/Q_H is the same for all Carnot engines operating from the same two reservoirs.

This fact makes it possible to define the *absolute temperature scale* simply as the ratio

$$\frac{T_C}{T_H} \equiv \frac{Q_C}{Q_H} \tag{1.5}$$

According to this, the absolute temperature must be positive[4], as we already showed that $Q_C > 0$ (Eq. 1.3).

Note that the above definition defines the temperature up to a scale. This scale can be fixed by, e.g., setting the value of the triple point of the water as 273.16 K.

Furthermore, one can show that this absolute temperature scale identical with the definition of the temperature using the ideal gas.

Lastly, note that the above equation Eq. 1.5 applies even when the engine is reversed to act as a refrigerator. In that case, both Q_C and Q_H will be negative.

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[4] However, here, we assume that the reference temperature is positive. This assumption, while sounding reasonable, is *not* valid in general.