Lecture 04: Laws of Thermodynamics

We review the laws of thermodynamics.

1   Laws of physics

Each of the foundational subjects in physics has its central core of laws from which the subject deduces important quantitative explanations of nature. In mechanics, the principles (or, at least, one set of them) are Newton's three laws of motion, and if you continue learning physics you will discover that electromagnetism, quantum mechanics, and special relativity are all grounded in their own principles[1].

Statistical physics is no different. Its principles constitute the laws of thermodynamics and these laws govern all phenomena in the physical universe and are in particular applied to situations where exchanges in heat and changes in entropy are relevant. In these notes we present these laws and discuss their implications.

Our framing question is as follows

> **Framing Question**
> What are the laws of thermodynamics and what are their implications?

Unlike our previous or future "Framing Questions" we will not answer this question through exploration or derivation, but rather through postulation and discussion. The nature of physical laws is that such laws are the starting point of physical theories and therefore, within the context of the theory, they must be postulated without derivation. Thus, our statement of these laws will seemingly come from thin air, but these laws are the results of many scientists over many years studying physical phenomena and trying to reduce and clarify their observations into something general.

2   Zeroth Law of Thermodynamics

Zeroth Law: If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C.
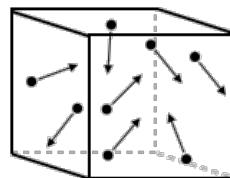

Figure 1: Many particles in a box in a room at constant temperature. The particles in the box can behave quite dynamically in time, but if we consider, say, the total energy of the system, then as time goes on the average total energy will relax to a constant time-independent value.

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[1]That would be Maxwell's equations and the Lorentz force law, the principles of quantum mechanics, and the postulates of special relativity, respectively.
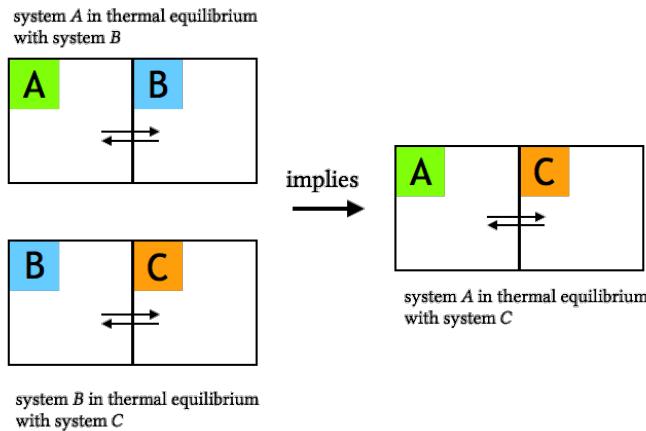
Figure 2: The zeroth law of thermodynamics: System A and system B can exchange energy (represented by the two arrows in opposite directions) and are in thermal equilibrium. The zeroth law presents the existence of thermal equilibrium as a transitive property in which if system B is also in thermal equilibrium with system C, then system A is in thermal equilibrium with system C.

Say we had a system of N motile particles in a volume V, and this system was placed in our classroom such that the system exchanged energy with its surrounding but did not exchange particles. Such a system is clearly dynamic in the sense that the individual particles are moving in time. However, if we wait long enough, the time-average of macroscopic properties of the system (such as energy) would relax to a constant value. Because these quantities have relaxed to a constant value, we need no longer keep track of the specific time dynamics of the system and can instead analyze the system in terms of probabilities to be in the various possible states.

When the time-average of macroscopic properties has reached a constant (within some desired level of accuracy), we say the system is in **thermal equilibrium**. From an experimental perspective a system is at thermal equilibrium if it is at a constant and uniform **temperature**. In this way, the zeroth law is essentially a definition of temperature. In every day usage, the most common metric for temperature uses liquid mercury. Liquid mercury expands when it is heated, and we can use the extent of this expansion along with the zeroth law as a measure of temperature.

Say, we can take a cylinder of liquid mercury to be our system B. If we place the cylinder next to a system A, and the column does not rise (i.e., the macroscopic property of the mercury remains constant in time), then we say system A is in thermal equilibrium with system B. If we place the cylinder of liquid mercury next to a system C, and the column again does not rise, then we say system C is in thermal equilibrium with system B. From these observations we then claim that system A and system C are in thermal equilibrium with each other and are, moreover, at the common temperature defined by the height of the liquid mercury column in system B. We can summarize this relationship between the thermal equilibrium of a system and temperature as follows:

> **Thermal equilibrium and temperature:** If two systems are in thermal equilibrium with each other, then they will register the same **temperature**. Conversely, if two systems register the same **temperature** (through a liquid mercury measurement), then, when they are put into contact with each other, they will be in thermal equilibrium.
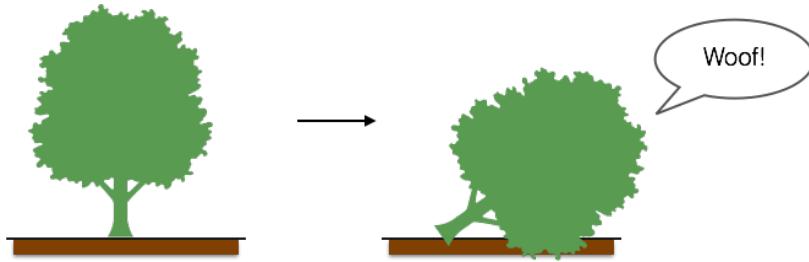
Figure 3: By conservation of energy, we know that a falling tree dissipates its gained energy into the ground and the surrounding air molecules as it falls. This tree releases some of this energy as sound waves, and it indeed makes a sound. But conservation of energy, makes no claim as to what kind of sound the tree makes[3]!

3   First Law of Thermodynamics

> **First Law:** The energy of the universe (or any **isolated system**[2]) is does not change in time (i.e., is conserved). If there are changes in energy, heat, or work in a system they must all balance and result in zero net change in the energy of such a system.

If a tree falls in the forest, does it make a sound? Yes! Because conservation of energy says so!

A tall tree stands up against the force of gravity, and Newtonian mechanics tells us it has potential energy in proportion to its height and mass. When the tree begins to fall over it does so slowly at first, and then it eventually speeds up until right before it reaches the ground, at which point it is at its maximum fall speed. Then, a moment later, the tree smacks into the ground and all of a sudden all of the kinetic energy it began with is gone.
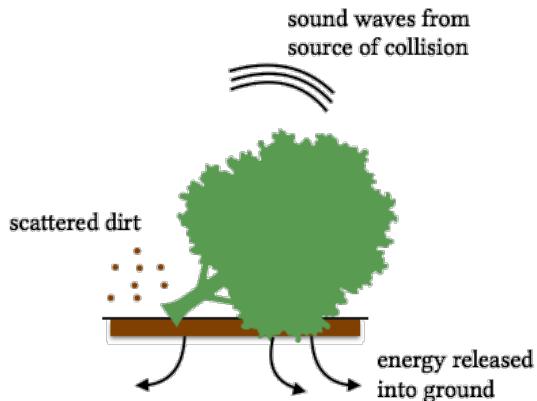

Figure 4: A fallen tree has released all of its kinetic energy into the surrounding environment. It must make a sound!

Where did all that energy go? It was transferred! As the tree was falling, the earth's gravitational force did **work** on the tree, and increased the tree's kinetic energy. As the tree continued to fall, some of the kinetic energy was **dissipated** through air drag. That means the kinetic energy of the tree was transferred to the kinetic energy of the surrounding air particles. When the tree collided with the ground, the tree's

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[2]A system is isolated if it does not exchange matter or energy with its surroundings.
[3]But, of course, one should not fear hearing a tree make this sound, for its bark is worse than its bite.
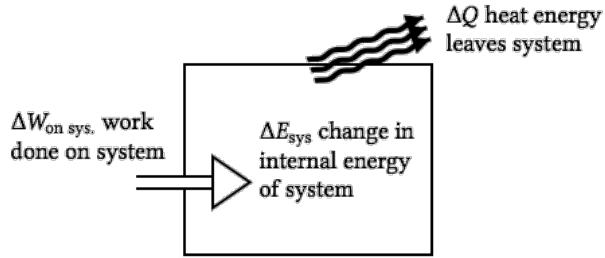
Figure 5: Conservation of energy: Any change in the energy of a system must be due to work being done on the system or heat leaving the system.

remaining kinetic energy was dissipated further by being transferred to the ground, the surrounding dirt, and still more to the air. The energy transferred to the earth was quickly lost; the surrounding dirt was perhaps launched into the air for a few seconds; but the air itself was so disturbed that waves of air pressure were released in what we know of as sound.

The main point is that energy can be transferred and converted from one form to another, but it cannot be created or destroyed. However, there is a caveat to this claim. Not all forms of energy are equally useful. Often when we convert from kinetic to potential energy or from potential to kinetic energy, we can use either manifestation of energy to do work. The kinetic energy of a waterfall can power electric motors, and catapults convert potential energy to kinetic energy by doing work on projectiles. However, the released sound energy from the fallen tree and the energy from the scattered dirt are not useful forms of energy for doing work. The main reason for their lack of usefulness is these energies have a high degree of randomness, or (using the language of statistical physics) are highly entropic. The general label for energy that cannot be completely converted back into work is **heat**.

A common theoretical depiction of the relationship between energy, work, and heat is as follows.

– We do work $\Delta W_{\text{on sys.}}$ on the system (e.g., the earth's gravity doing work on the tree)

– The internal energy of the system changes by $\Delta E_{\text{sys.}}$ (e.g., the tree's kinetic energy increases)

– An amount of heat ΔQ_{exits} leaves the system (e.g., kinetic energy is lost through friction).

In Fig. 5, we represent this system as a **black box** meaning, the precise internal properties of the system are not important. In order for energy to be conserved in this system, the total change in internal energy must equal the sum of the work done on the system minus the heat leaving the system:

$$\Delta E_{\text{sys.}} = \Delta W_{\text{on sys.}} - \Delta Q_{\text{exits}} \qquad \text{[Conservation of energy]} \tag{1}$$

The above equation is the most common formal way of presenting conservation of energy in thermodynamics. We can rearrange Eq.(1) to express how the work done on a system relates to the change in internal energy of the system. Putting the work done on one side, we have

$$\Delta W_{\text{on sys.}} = \Delta E_{\text{sys.}} + \Delta Q_{\text{exits}}. \tag{2}$$

Taking the heat leaving the system to be greater than or equal to zero, we find that $\Delta W_{\text{on sys.}} \geq \Delta E_{\text{sys.}}$. Thus the change in the internal energy of the system is always less than or equal to the work done on the system. The work done on the system can be interpreted as the energy we put into the system, and the internal energy of the system can be interpreted as the energy the system stores. Thus, Eq.(2) tells us

$$\text{Energy put into system} \geq \text{Energy stored in system.} \tag{3}$$

In other words, we can never store more energy in a system than we have already put in. In fact, for real life

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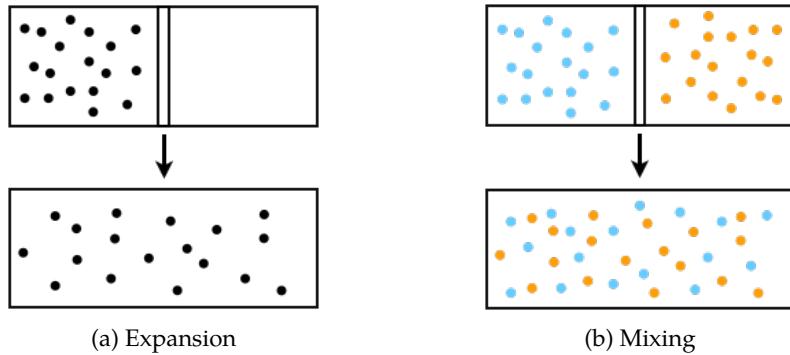(a) Expansion   (b) Mixing

Figure 6: Expansion/Mixing. In the top figures we show the system prior to the release of a constraint. In the bottom figures we show the corresponding system after the release of the constraint. The second law of thermodynamics asserts that we only observe the systems moving from bottom to top, rather than from top to bottom.

systems at nonzero temperature, since the increase in entropy always leads to some energy being released as heat, Eq.(3) is always an inequality and only an equality when the entropy of a system is zero.

4   Second law of Thermodynamics

Second Law: The entropy of the universe (or any **isolated system**) increases or remains constant in time. When this entropy is constant, the system is in thermal equilibrium.

You drop a blot of ink into a glass of water and after some time (if the density of the drop is approximately equal to that of water) the drop has spread throughout the glass of water. Or you take your hot cup of coffee, soup, or tea out of the microwave, and if you let it sit on the counter, it loses heat until it has assumed the temperature of the room. Or you take an ice cube from your freezer and after some time the ice cube has turned into a pool of water.

What unifies all of these examples is that physicists interpret them as consequences of the second law of thermodynamics. In the first case, a relatively ordered system consisting of an ink droplet at a single point evolves in time toward a disordered system where the constituents of the droplet have spread throughout the water. Depicting the system somewhat schematically, we have a situation in which one system (the ink droplet) was confined in space, but eventually expanded to fill its entire volume (Fig. 6a). In the second case, there is an overall increase in entropy of the composite system consisting of of the coffee mug and the the room. Here, we again a mixing phenomena (Fig. 6b), in which the high temperature air particles near the coffee mug mix with the lower temperature air particles within the room. In the third case, the highly ordered state of an ice cube absorbs heat from its surroundings and becomes the much less ordered state of a pool of water.

We have been using the terms "ordered" and "disordered" to informally describe what would more precisely be termed **entropy**. In each scenario, the entropy of the closed system (ink droplet + water, coffee + room, ice + room) increased as time evolved. A schematically clean representation of such increases in entropy are shown in Fig. 6. In the two figures, the second law asserts that the processes always evolve spontaneously (i.e., without the external input of work) in the direction of the arrow. This law was formulated by Rudolf Clausius in 1864 in an attempt to explain the exchanges of heat between gases. In his explanation, he stated that if a system is at a temperature T and gains a heat ΔQ from its surroundings, then the entropy of the system increases by

$$\Delta S = \frac{\Delta Q}{T}. \qquad \text{[For reversible processes]} \tag{4}$$

To be precise, Eq.(4) is only true for processes which can be reversed and still be physically tenable. For,

example Eq.(4) is not valid for the rapid expansion of a gas into a room because the reverse process cannot occur, but it is valid for the controlled expansion of a gas with a piston.

We can rearrange Eq.(4) to write the increase in heat of a system in terms of increase in entropy:

$$\Delta Q = T\Delta S \qquad \text{[For reversible processes]} \tag{5}$$

Taking entropy to be the more fundamental quantity, we therefore see that the heat entering a system is proportional to the temperature of the system. Therefore, when temperature is zero ($T = 0$), the heat ΔQ is also zero. By our previous calculation, a zero ΔQ implies $\Delta W_{\text{on sys.}} = \Delta E_{\text{sys.}}$. In other words, only at $T = 0$ is the energy we put into the system equal to the resulting energy stored in the system.

5   Third Law of Thermodynamics

Third Law: The entropy of a crystalline solid (or any system where there is only a single microstate in the ground state) goes to zero as the temperature of the system goes to absolute zero.

Of the four laws of thermodynamics, the third law is the odd-one out. It seems to be on a different level from the other laws partly because it does not introduce a new thermodynamic concept but rather extends the concept of temperature introduced by the zeroth law. Also, given statistical physics, this law follows as a consequence of the definition of entropy and thus need not be taken as a foundational principle of thermodynamics like the other laws. Still, it is included in the pantheon of thermodynamic laws, so we present it here for historical (if not intellectual) completeness.

The law has two forms, but one form is the more fundamental one. The more fundamental form is stated above. From this statement, the second law extends the concept of temperature to include a value at which the entropy of certain systems is zero. **Absolute zero** temperature is the temperature at which all thermal motion stops and the macrostate of the system is associated with only one microstate.
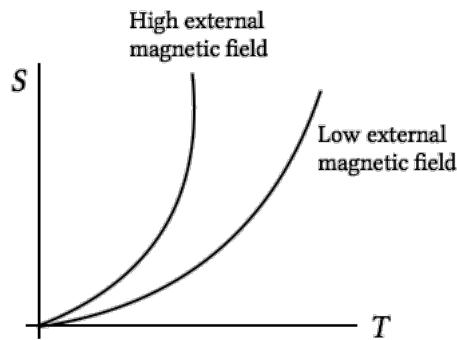

Figure 7: As we lower the temperature of a system with a single state for its ground state (e.g., a spin system in a constant magnetic field), the entropy of the system goes to zero.

Another form of the third law follows from the more fundamental statement above. This form is

Third Law (alternative form): It is not possible to reach absolute zero temperature through successive finite implementations of a cyclic process.

A **cyclic process** is a a process of taking a system through many iterations of a number of stages where the last stage in one iteration returns the system to the initial stage for the next iteration. This alternative form of the third law follows from the first form because we can show graphically that when the entropy goes to zero as T goes to zero (Fig. 7), then the steps of the cyclic process which allow us to iteratively

approach this zero entropy state become smaller and smaller, thus requiring more of them up to an infinite number to reach the zero entropy state.

6 Summary of laws

We can summarize the laws of thermodynamics as follows

- **Zeroth law of thermodynamics:** If system A is in thermal equilibrium with system B, and system C is in thermal equilibrium with system B, then system A and system C are in thermal equilibrium with each other.

- **First law of thermodynamics:** The energy of the universe (or any isolated system) is does not change in time (i.e., is conserved). If there are changes in energy, heat, or work in a system they must all balance and result in zero net change in the energy of such a system.

- **Second law of thermodynamics:** The entropy of the universe (or any system which is allowed to evolve in time without external constraints) increases or remains constant in time. When this entropy is constant, we say the system is in thermal equilibrium.

- **Third law of thermodynamics:** The entropy of a crystalline solid (or any system where there is only a single microstate in the ground state) goes to zero as the temperature of the system goes to absolute zero.

In statistical physics, the second law reigns supreme and is used to derive much of the analytical framework of the theory. In the subsequent notes, we will use the second law to derive the concept of Helmholtz free energy and use this concept to understand the properties of systems at thermal equilibrium.

Resource: Introduction to Statistical Physics
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