

### Fundamental Postulate. Entropy

Of our world the following facts are known:

1. An isolated system has a set of quantum states.
2. The isolated system flips from one quantum state to another rapidly and ceaselessly.
3. After being isolated for a long time, the system can flip to any one of its quantum states with equal probability.

Thus, a system isolated for a long time behaves like a fair die:

1. A die has six faces.
2. The die is rolled from one face to another.
3. If the die is fair, the die can be rolled to any one of its faces with equal probability.

What is an isolated system? What is a quantum state? How long is a long time? The following notes relate these fundamental concepts to things familiar to us. We then translate the theory of probability of rolling a fair die to the thermodynamics of an isolated system.

In developing the theory of probability, the nature of the die is unimportant, whether the die is made of wood or silver. Woodworking and metallurgy do not concern us. Also unimportant is the nature of the individual faces of the die, whether the dots are carved or painted. What matters is that the number of faces of the die is 6, and that a roll of the die results in any one of the faces with equal probability,  $1/6$ .

Similarly, in developing the thermodynamics of an isolated system, the nature of the isolated system is unimportant, whether the system is a glass of wine or a piece of cheese. The arts of wine and cheese making do not concern us. Also unimportant is the nature of the individual quantum states of the isolated system. What matters is that the isolated system has a certain number of quantum states, and that the system isolated long enough can flip to any one of its quantum states with equal probability.

Instead of “the number of quantum states”, we find it more convenient to use the phrase “the logarithm of the number of quantum states”. The phrase is given shorthand: *entropy*.

**System.** We can regard any part of the world as a *system*. For example, a proton and an electron constitute a system, which we call a hydrogen atom. A glass of wine is also a system. This system is composed of water, ethanol, and other molecules. Do we include the glass as a part of the system? Maybe, if we decide to study the reaction between water and glass. The decision is ours. We can regard any part of the world as a system.

**System interacts with the rest of the world.** The hydrogen atom interacts with the rest of the world, for example, by absorbing or emitting photons. A system like the glass of wine may interact with the rest of the world in many ways. We see the wine because it reflects light. We smell the wine because molecules escape from the wine and reach our noses. We hear the wine when we move a wet finger around the edge of the glass. We warm up the wine when the vibration of the molecules in our hands transfers energy to the vibration of the molecules in the wine. We taste the wine when we drink it.

We can augment our five senses by using other things to interact with the wine. We subject the wine to a pressure to find out how tightly the molecules can be packed together. We subject the wine to an electric field to find out how electric charges on the molecules move around. We pour fruit juice into the wine and watch they mix. We place the wine on a flame and watch the wine evaporate.

Our subject—thermodynamics—is about the interactions between a system and the rest of the world. But our narrative begins with something opposite: a system that does not interact with the rest of the world.

**Isolated system.** A system is said to be an *isolated system* if it does not interact with the rest of the world. To make a glass of wine an isolated system, we seal the glass to prevent molecules from escaping, place the glass in a thermos to prevent energy from escaping, and make the seal unmovable so that the external pressure cannot do work to the wine. We are alert to any other modes of interaction between the wine and the rest of the world. Does the magnetic field of the earth affect the wine? If it does, we will shield the glass of wine from the magnetic field also.

Of course, nothing is perfectly isolated. Like any idealization, the isolated system is a useful approximation of the reality, so long as the interaction between the system and the rest of the world negligibly affects a phenomenon that we choose to study.

For example, it may be too much trouble for us to isolate the wine from gravity. Few of us are inclined to study the wine under the zero-gravity condition. Gravity is important if we carry the wine around, but is unimportant if we want to study the interactions between the molecules in the wine.

**An isolated system has a set of quantum states.** A hydrogen atom consists of a proton and an electron. Even when isolated from the rest of the world, the hydrogen atom can still be in one of multiple quantum states. For example, when the hydrogen atom is isolated at the ground energy level, the

atom has two quantum states. As another example, when the hydrogen atom is isolated at the second energy level, the atom has six quantum states.

A quantum state of the glass of wine is described by a collective cloud of all electrons and positions of all nuclei. An isolated system like the glass of wine has a huge number of quantum states.

**Use quantum states without knowing much quantum mechanics.** In principle, given an isolated system, all its quantum states are determined by quantum mechanics. In practice, however, it is only possible to perform quantum-mechanical calculation for extremely idealized systems. We can perform quantum-mechanical calculation for the hydrogen atom, but we cannot do so for the glass of wine.

We cannot wait for the brute-force quantum-mechanical computation to answer practical questions. We need to develop other methods. After all, we have all learned to ride bicycles without any use of Newton's mechanics. Our bodies and bicycles know enough mechanics.

Similarly, our experimental instruments and the glass of wine know more quantum mechanics than computers do. We can readily see the color of the wine, measure the density of the wine, and analyze its molecular composition—all without performing quantum-mechanical computation.

To a large extent, thermodynamics is an algorithm to obtain and organize useful information from experiments, without quantum-mechanical computation. These lectures teach you this algorithm. What is the algorithm? What is its empirical basis? How does it answer practical questions?

**An isolated system flips from one quantum state to another rapidly and ceaselessly.** An isolated system is not static: it rapidly and ceaselessly flips from one quantum state to another.

For example, in the glass of wine, molecules move rapidly and ceaselessly. Even though you cannot see the movement of the molecules with your own eyes, you can smell the movement with your own nose. When you smell the wine, it is because molecules jump off the wine, entering your nose.

Thus, an isolated system behaves like a die of many faces, perpetually rolled by a madman. The madman is named *energy*.

**Fundamental postulate.** The isolated system flips from one quantum state to another rapidly and ceaselessly. Will the isolated system be more probable in one quantum state than another? The fundamental postulate states that

*A system isolated for a long time can flip to any one of its quantum states with equal probability.*

Thus, a system isolated for a long time behaves like a *fair* die. The fundamental postulate cannot be proved from more elementary facts, but its predictions have been confirmed without exception by empirical observations. We will regard the fundamental postulate as an empirical fact, and build thermodynamics upon the fundamental postulate. We next describe several elementary consequences of the fundamental postulate.

**The number of quantum states of an isolated system.** A coin has two sides: head and tail. A die has six faces. An isolated system has a specific set of quantum states. The number of quantum states of the isolated system is denoted as  $\Omega$ .

When the coin is flipped, the probability for the coin to land on either side is  $1/2$ . When the die is rolled, the probability for the die to settle to a particular face is  $1/6$ . When the system is isolated for a long time, the probability for the isolated system to be in any one of its quantum states is

$$\frac{1}{\Omega}.$$

A glass of wine has a huge number  $\Omega$  of quantum states, so that the probability for the glass of wine to be in any particular quantum state is tiny.

In principle, given an isolated system, its number of quantum states is determined by quantum mechanics. For example, when the hydrogen atom is isolated at the second energy level, the isolated system has  $\Omega = 6$  states.

In practice, the number of quantum states can only be calculated from quantum mechanics for a few idealized systems. We hasten to note that the number of quantum states of an isolated system, such as the glass of wine, can be determined by experimental measurements, as described in later notes.

Even without any calculation or measurement, several trends can be readily anticipated:

- Two glasses of wine have more quantum states than either one glass of wine—the more molecules, the larger the number of quantum states.
- A piece of warm cheese has more quantum states than a piece of cold cheese has—the more energy, the larger the number of quantum states.
- Molecules in vapor phase have more quantum states than the same number of molecules in liquid phase—the larger the volume, the larger the number of quantum states.

**Subset of quantum states.** A die has six faces, labeled as  $\{1,2,3,4,5,6\}$ . When the die is rolled, what is the probability to obtain an even face? We can discover this probability experimentally, by rolling the die many times, and recording the result every time. The probability to obtain an even face is the recorded number of even faces divided by the total number of rolling.

Alternatively, we can calculate this probability. We dissect the whole set  $\{1,2,3,4,5,6\}$  into two subsets: the subset of the even faces  $\{2,4,6\}$ , and the subset of the odd faces  $\{1,3,5\}$ .

$$\text{The probability to obtain an even face} = \frac{3}{6}.$$

An isolated system flips among a set of  $\Omega$  quantum states. Consider a subset of the quantum states. The subset is designated A, and consists of  $\Omega_A$  number of quantum states. After the system is isolated for a long time, the system can flip to in any one of its quantum states with equal probability. Consequently, the probability for the isolated system to be in subset A is

$$\frac{\Omega_A}{\Omega}.$$

A subset is more probable if the subset consists of more quantum states.

**Macrostate.** For an isolated system with a whole set of  $\Omega$  quantum states, we can form a total of  $2^\Omega$  subsets. We will not be interested in that many subsets. A useful subset of the quantum states of an isolated system often consists of a large number of quantum states. What do we mean by the word “useful”? The subset of quantum states is useful typically because we can identify them collectively through an experimental observation.

A useful subset is often called a *macrostate* of the isolated system. Other phrases are often used to describe a useful subset, such as a conformation of a molecule, or a thermodynamic state of a glass of wine, or a configuration of colloidal particles. Useful subsets are illustrated by the following example.

**Half bottle of water.** In a half bottle of water, the bottom half is liquid water, while the top half is vapor. We make the bottle as a whole into an isolated system. The bottle is capped, so that no water molecules will escape from the bottle, and no nitrogen or oxygen molecules from the air will enter the bottle. We also wrap the bottle with a thermal insulator, so that the water in the bottle and the air outside does not exchange energy by heat. We further make the bottle rigid, so that the pressure inside the bottle does no work to the environment.

The water-moisture composite—as an isolated system—contains a total of  $N_{tot}$  water molecules, and can be in a total number  $\Omega_{tot}$  of quantum states.

Let  $N$  be the number of water molecules in the top half of the bottle. When  $N = 0$ , the top half of the bottle has no molecule, but the isolated system—the half bottle of water—can still flip among a large subset of quantum states. Similarly, when the top half of the bottle has  $N = 1$  molecule, the isolated system flips among another subset of quantum states. Let  $\Omega(N)$  be the number of quantum states when  $N$  water molecules are in the gas.

The half bottle of water can be in all  $\Omega_{tot}$  number of quantum states with equal probability. The probability for moisture to have  $N$  number of water molecules is

$$\frac{\Omega(N)}{\Omega_{tot}}.$$

**Constraint internal to an isolated system. Internal variable.** As a variation of the half bottle of water, consider a glass of wine and a piece of cheese together as a single system, isolated from the rest of the world. Initially the wine and the cheese are sealed from each other. Now we puncture the seal, so that water molecules (for example) can escape from the wine and move into the cheese, or the other way around. The seal provides a *constraint* internal to the isolated system. The act of puncturing the seal lifts the constraint, making the partition of water between the wine and the cheese an *internal variable*.

**Use an internal variable to dissect the set of quantum states of an isolated system into a family of subsets.** Implicit in the above discussion is an idea, which is so significant that we now make it explicit. We can dissect the whole set of the quantum states of the half bottle of water into a family of subsets depending on the number of molecules in the top half of the bottle. We name each subset by the number of water molecules in the top half of the bottle, as follows:

- Subset 0 is the subset of quantum states when no molecule is in the top half of the bottle. This macrostate consists of  $\Omega(0)$  quantum states.
- Subset 1 is the subset of quantum states when 1 molecule is in the top half of the bottle. This macrostate consists of  $\Omega(1)$  quantum states.

Let us summarize this idea in generic terms. An isolated system flips among a set of quantum states. A function maps each quantum state of the isolated system to a number,  $Y$ . When the variable assumes a specific value  $Y_i$ ,

the isolated system flips among a subset of the quantum states; we denote by  $\Omega(Y_i)$  the number of quantum states in this subset.

Instead of using a natural language (English, Chinese, etc.), we now use a real variable to dissect the set of quantum states of an isolated system into a family of macrostates. Using a real variable has an obvious advantage: the variable will allow us to use mathematics effectively. One game of thermodynamics is to identify an internal variable for an isolated system, and use the internal variable to dissect the set of the quantum states of the isolated system into a family of macrostates.

**Irreversible change. The arrow of time.** We make the half bottle of water as an isolated system. The bottle is partitioned into two parts by a seal. The bottom half of the bottle contains liquid water, and the top half is a vacuum. When we remove the seal in the middle of the bottle, molecules escape from the water, and fill the top half of the bottle with moisture. Our experience indicates that this process of evaporation is spontaneous. The molecules in the top half of the bottle, however, will not spontaneously all go back to water. That is, the evaporation of a liquid into a vacuum is an *irreversible change*.

What causes this irreversibility? This question presented the founders of our subject a paradox. The movements of the molecules are governed by, say, Newton's laws of mechanics. The laws of mechanics take the same form when time is reversed. If the molecules can escape the liquid, the laws of mechanics predict that the same molecules can also go back to the liquid. Then why the evaporation from a liquid to a vacuum is irreversible?

This irreversibility can be explained in terms of the fundamental postulate. The composite—water and moisture together—constitute an isolated system, which flips among a set of quantum states. The seal in the middle of the bottle provides a *constraint* internal to the isolated system. The act of removing the seal lifts the constraint, making the number of molecules in the top half of the bottle an *internal variable*. When the top half of the bottle is sealed from the bottom half, the top half of the bottle has no molecule, and the isolated system flips among a subset of quantum states. When the seal is removed, there will be other subsets that may consist of more quantum states of the isolated system. Consequently, the change from the initial subset to the final subset appears to be irreversible.

While all other fundamental laws of nature are time-reversible, the fundamental postulate of thermodynamics implies irreversible changes. Thus, the fundamental postulate gives a direction of time: the arrow of time.

**An isolated system approaches equilibrium.** For the isolated system of water-vapor mixture, right after the seal is removed, the isolated system still flips among the quantum states corresponding to the initial partition of water, even though the quantum states corresponding to other partitions are now accessible to the composite. To flip into the new quantum states, water molecules must escape from the liquid, and diffuse into the moisture. The process of evaporation takes time. Given enough time, the isolated system can be in any one of its quantum states with equal probability, and the isolated system is said to be in *equilibrium*.

**From probability to (almost) certainty.** According to the fundamental postulate, the most probable number of molecules in the moisture,  $N$ , maximizes the function  $\Omega(N)$ . The isolated system is said to reach a thermodynamic state (or macrostate) of equilibrium. Or we say that the liquid equilibrates with the gas. Any other partitions of water molecules are also possible, but are less probable than the equilibrium partition.

Our experience indicates that the equilibrium partition is much, much more probable than other partitions. We therefore often focus our attention on the partition that maximizes the function,  $\Omega(N)$ , rather than be bothered with the probability of less probable partitions. This is why a large part of thermodynamics is a game of maximization or minimization.

**Dispersion of a drop of ink in a glass of wine.** To have some feel for numbers, consider a drop of ink in a glass of wine. The ink contains small solid particles (e.g., carbon black) that give the color. After some time, the ink particles disperse in the wine. Our experience indicates that dispersion of ink in a liquid is an irreversible process: the ink particles will spontaneously disperse in the liquid, but the dispersed ink particles will not spontaneously all come back to form a drop of ink. What causes the irreversible dispersion?

At the beginning, all the ink particles are in a small volume in the wine. As time proceeds, each ink particle is free to move in the entire volume of the wine. We call a spatial arrangement of all the ink particles a placement. A placement that all ink particles localize in a small region in the glass is just as probable as a placement that the ink particles disperse in the entire glass. However, there are many more placements that the ink particles disperse in the entire glass than the placements that the ink particles localize in a small region. Consequently, dispersion is more likely than localization.

How many more likely? We view the wine and the ink as a single system, and isolate the system from the rest of the world. Let  $V$  be the volume of the

glass of wine, and  $N$  be the number of the ink particles. We have a dilute concentration of the ink particles suspended in the wine. The interaction between the ink particles is negligible, so that each particle is free to explore everywhere in the wine. Consequently, the number of placements of each ink particle is proportional to  $V$ . The number of placements of the  $N$  ink particles is proportional to  $V^N$ . On the other hand, if the  $N$  particles localize in a small region, say of volume  $V/7$ , the number of placements is proportional to  $(V/7)^N$ . Since all placements are equally likely, the probability to find the  $N$  ink particles in a given volume is proportional to the number of placements. Thus,

$$\frac{\text{probability for } N \text{ particles in volume } V}{\text{probability for } N \text{ particles in volume } V/7} = \frac{V^N}{(V/7)^N} = 7^N.$$

This ratio is huge if we have more than a few ink particles, a fact that explains why the ink particles much, much prefer dispersion to localization.

**How long is a long time?** Right after the small drop of ink is put in the glass of wine, the ink particles are all localized in a small volume. Subsequently, the ink particles move around as molecules in the wine kick the ink particles. After some time, the ink particles disperse throughout the entire volume of the wine. The ink particles are said to attain an equilibrium configuration.

How much time is needed for the isolated system to regain equilibrium? The question depends on individual system. For the system of ink in the wine, clearly the time to attain equilibrium depends on how fast the ink particles move, and how large is the volume of the wine. Indeed, if the drop of ink is in a glass of honey, the ink particles will disperse after a longer time that they disperse in the glass of wine. The study of how long a system attains equilibrium is a subject of *kinetics*.

**Algorithm to apply the fundamental postulate.** On the basis of the fundamental postulate, the entire thermodynamics reduces to an art to construct an isolated system, identify useful subsets of quantum states, and then count—or measure—the number of quantum states that constitute each subset. The fundamental postulate can be applied to analyze experimental observations by using the following algorithm.

1. Construct an isolated system, which has a set of quantum states.
2. Internal to the isolated system is a constraint, and associated with the constraint is an internal variable.
3. When the internal variable is at a particular value, the isolated system flips among a subset of the quantum states.

4. After the constraint is removed for a long time, the probability for the isolated system to be in a subset is the number of quantum states in the subset divided by the total number of quantum states of the isolated system.
5. The most probable value of the internal variable corresponds to the subset having the largest number of quantum states.

**The use of mathematics.** By now we have described the physical content of the fundamental postulate, and an algorithm to use the fundamental postulate to answer practical questions. To use the algorithm effectively, we will need mathematics. The following paragraphs describe several elementary mathematical ideas. None of these ideas will add any new physical content, but they will be handy when practical questions become complex.

**A composite of two separately isolated systems.** A coin has two sides:  $\{H, T\}$ . A die has six faces:  $\{1, 2, 3, 4, 5, 6\}$ . Simultaneously throwing the coin and the die will result in one of the  $2 \times 6$  outcomes:

$$\{H1, H2, H3, H4, H5, H6, T1, T2, T3, T4, T5, T6\}.$$

Now consider two isolated systems  $A'$  and  $A''$ , such as the glass of wine and the piece of cheese. Isolated system  $A'$  has a total of  $\Omega'$  number of quantum states, labeled as  $\{\gamma'_1, \gamma'_2, \dots\}$ . Isolated system  $A''$  has a total of  $\Omega''$  number of quantum states, labeled as  $\{\gamma''_1, \gamma''_2, \dots\}$ .

We keep the two systems *separately isolated*, and view them together as a single isolated system. A quantum state of this composite is any combination of a quantum state chosen from the set  $\{\gamma'_1, \gamma'_2, \dots\}$  and a quantum state chosen from the  $\{\gamma''_1, \gamma''_2, \dots\}$ . For example, one quantum state of the composite is when system  $A'$  is in state  $\gamma'_2$  and system  $A''$  is in state  $\gamma''_3$ . The total number of all such combinations is

$$\Omega' \Omega''.$$

This is the number of quantum states of the composite. Thus,

*The number of quantum states of the composite of two separately isolated systems is the product of the quantum states of the individual isolated systems.*

In the above, we have kept the two systems separately isolated. That is, both the glass of wine and the piece of cheese are separately sealed. The wine

keeps flipping among its quantum states, and the cheese keeps flipping among its quantum states. The wine and the cheese do not interact. What if we seal them together as an isolated system, and remove the seal between them, so that the wine and the cheese can exchange molecules and energy? This action lifts constraint internal to the isolated system, and creates internal variables: the partition of molecules and the partition of energy. This far more interesting situation will be analyzed in subsequent lectures.

**Logarithm turns a product into a sum.** Recall an identity of the logarithm:

$$\log_b(\Omega'\Omega'') = \log_b \Omega' + \log_b \Omega''.$$

Thus, when two separately isolated systems together are regarded as a composite, the logarithm of the number of quantum states of the composite is the sum of the logarithm of the number of quantum states of one isolated system and that of the other isolated system.

The base of the logarithm is arbitrary. Anticipating many uses of derivatives, we adopt the number  $e$  as the base, such that

$$\frac{d(\log \Omega)}{d\Omega} = \frac{1}{\Omega}.$$

**Entropy.** If you are tired of the phrase “the logarithm of the number of quantum states”, you may as well join the crowd and replace the phrase with a cryptic word: *entropy*. That is, you call the quantity  $\log \Omega$  entropy, and give it a symbol  $S$ . Thus, an isolated system with  $\Omega$  number of quantum states has the entropy

$$S = \log \Omega.$$

By replacing a phrase with a word you should not trick yourself into believing that you have learned anything new. When you speak of entropy, you simply paraphrase what you already know about “the logarithm of the number of quantum states”.

**Entropy as a number in the theory of probability.** Entropy may be viewed just a number in the theory of probability. No more, no less. The entropy of a fair coin is  $\log 2$ , and the entropy of a fair die is  $\log 6$ . For any experiment with a total of  $\Omega$  equally probable outcomes, the entropy is  $\log \Omega$ .

The situation is rather like taking differentiation of a function. Differentiation is a mathematical operation: you can take a differentiation if you have a smooth function. You may make interesting applications in engineering

and economics, but there is no point to make a distinction about an engineer's differentiation and an economist's differentiation. The distinction is in the applications, not in the concept of differentiation itself.

**Entropy of a macrostate.** The isolated system flips among a set of  $\Omega$  quantum states. For a subset of quantum states, A, the number of the quantum states in the subset is denoted by  $\Omega_A$ . We call the number

$$S_A = \log \Omega_A$$

the entropy of the subset A.

**The second law of thermodynamics.** Here is a paraphrase of the second law:

*After a system is isolated for a long time, of a given family of macrostates, the most probable macrostate has the largest entropy.*

The second law of thermodynamics is implied by the fundamental postulate. The former is an incomplete expression of the latter.

**A longer paraphrase of the second law of thermodynamics.** We have used the zeroth law to formulate a function of state, the temperature. We have used the first law to formulate another function of state, the internal energy. We may regard the second law as a formulation of yet another function of state, the entropy.

In thermodynamics, we call a subset of quantum states a macrostate, or a thermodynamic state, or simply a state. We specify the state of a system by a list of properties (i.e., functions of state), such as pressure, temperature, volume, and internal energy. The content of the second law consists of the following statements:

1. Entropy is a function of state. For example, for a system of two independent variations such as water, we may name all states of the system by values of two independent properties, such as internal energy  $U$  and volume  $V$ . The entropy  $S$  is a function of the internal energy and the volume,  $S(U, V)$ .
2. For a system consists of several parts, the entropy of the system is the sum of the entropies of the parts.
3. For an isolated system with an internal constraint, upon lifting the constraint, the entropy of the system increases, and the system reaches a state of equilibrium when the entropy is maximized.

## Summary

- Any part of the world can be regarded as a system.
- A system is called an isolated system if it does not interact with the rest of the world.
- An isolated system flips rapidly among a set of quantum states.
- The fundamental postulate: a system isolated for a long time is equally probable to be in any one of its quantum states.
- The probability for an isolated system to be in a subset of quantum states equals the number of quantum states constituting the subset divided by the number of all quantum states of the isolated system.
- The second law of thermodynamics: after a system is isolated for a long time, of a given family of subsets of quantum states, the most probable subset has the largest number of quantum states.

## References

**Textbooks beginning with statistical description.** Our presentation above deviates significantly from how the second law was discovered historically. Our presentation, however, is not new. Similar presentations can be found in many textbooks, such as

- K.A. Dill and S. Bromberg, *Molecular Driving Forces*, 2<sup>nd</sup> edition, Garland Science, 2010.
- C. Kittel and H. Kroemer, *Thermal Physics*, W. H. Freeman and Company, New York, 1980.
- L.D. Landau and E.M. Lifshitz, *Statistical Physics*, Butterworth-Heinemann, 1980.
- R.K. Pathria, *Statistical Mechanics*, Pergamon Press, 1972.
- F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill, Inc., New York, 1965.
- D.V. Schroeder, *Thermal Physics*, Addison Wesley Longman, 2000.

**Classical thermodynamics.** There are many carefully written textbooks on classical thermodynamics. These textbooks do not rely on the fundamental postulate. Here are a few such textbooks:

- C.J. Adkins, *Equilibrium Thermodynamics*, 3<sup>rd</sup> edition, Cambridge University Press, 1983.
- H.B. Callen, *Thermodynamics and Introduction to Thermostatistics*, 2<sup>nd</sup> edition, Wiley, 1985.

- E. Fermi, Thermodynamics, Dover Publications, 1956.
- D.S. Lemons, Mere Thermodynamics, The Johns Hopkins University Press, 2009.
- A.B. Pippard, The elements of Classical Thermodynamics, Cambridge University Press, 1957.
- M.W. Zemansky and R.H. Dittman, Heat and Thermodynamics, McGraw-Hill, Inc. 7<sup>th</sup> edition, 1997.

**Engineering thermodynamics.** Texts used by undergraduate students in mechanical engineering. Engines and refrigerators.

- C. Borgnakke and R.E. Sonntag, Fundamentals of Thermodynamics, 7<sup>th</sup> edition, Wiley, 2009.
- Y.A. Cengel and M.A. Boles, Thermodynamics, 7<sup>th</sup> edition, McGraw Hill, 2010.
- J.H. Keenan, Thermodynamics, Wiley, 1941.
- M.J. Moran, H.N. Shapiro, D.D. Boettner and M.B. Bailey, Fundamentals of Engineering Thermodynamics, 7<sup>th</sup> edition, 2011.
- W.C. Reynolds and H.C. Perkins, Engineering Thermodynamics, McGraw Hill, 1977.
- G. Rogers and Y. Mayhew, Engineering Thermodynamics, 4<sup>th</sup> edition, Longman, 1992.

**Chemical thermodynamics.** Reactions. Mixtures. Phases. Electrochemistry.

- K. Denbigh, The Principles of Chemical Equilibrium, 4<sup>th</sup> edition, Cambridge University Press, 1981.
- H. Devoe, Thermodynamics and Chemistry, Prentice Hall, 2001.
- G.N. Lewis and M. Randall, Thermodynamics and the Free Energy of Chemical Substances, 1923.
- A.P.H. Peters, Concise Chemical Thermodynamics, 3<sup>rd</sup> edition, CRC Press, 2010.
- S.I. Sandler, Chemical, Biological, and Engineering Thermodynamics, 4<sup>th</sup> edition, Wiley, 2006.
- E.B. Smith, Basic Chemical Thermodynamics, 5<sup>th</sup> edition, Oxford University Press, 2004.

**Biological thermodynamics.**

- D.T. Haynie, Biological Thermodynamics, 2<sup>nd</sup> edition, Cambridge University Press, 2008.
- G.G. Hammes, Thermodynamics and Kinetics for Biological Sciences, Wiley, 2000.

#### **Nonequilibrium thermodynamics.**

- S.R. De Groot and P. Mazur, Non-equilibrium Thermodynamics, Dover publications.
- I. Prigogine, Introduction to Thermodynamics of Irreversible Processes.

#### **Popular accounts of thermodynamics.**

- P.W. Atkins, The 2<sup>nd</sup> Law: Energy, Chaos, and Form, W.H. Freeman, 2<sup>nd</sup> edition, 1994.
- P.W. Atkins, Four Laws That Drive the Universe, Oxford University Press, 2007.
- A. Ben-Naim, Entropy Demystified: The Second Law Reduced to Plain Common Sense, World Scientific Publishing Company, 2007.
- P.W. Bridgman, The Nature of Thermodynamics, Harper & Row, 1941.
- J.B. Fenn, Engines, Energy, and Entropy, W.H. Freeman, 1982.
- I. Prigogine and I. Stengers, Order out of Chaos, Bantam Books, 1984.

**History of thermodynamics.** Thermodynamics was established well within the span of the lifetimes of Carnot (1796-1832) and Boltzmann (1844-1906). The history is short and interesting, involving about a handful of main characters. You can have a quick introduction to the history of thermodynamics on Wikipedia. The following items will lead you to the primary sources.

- M. Baily, A Survey of Thermodynamics. AIP press, 1994.
- J. Kestin, ed., The Second Law of Thermodynamics. A selection of original papers by Carnot, Clausius, Kelvin, Gibbs, etc.
- S.I. Sandler, L.V. Woodcock, Historical observations on laws of thermodynamics. Journal of Chemical Engineering Data 55, 4485-4490 (2010).
- I. Muller, A History of Thermodynamics. Springer, 2006.

**Appendix A: Theory of probability of rolling a fair die vs. thermodynamics of an isolated system.** For a brief introduction to the theory of probability, see <http://imechanica.org/node/289>. We now translate

words in the theory of probability of rolling a fair die into the words in the thermodynamics of an isolated system

- The die has 6 faces; the set of all the 6 faces,  $\{1,2,3,4,5,6\}$ , is called the sample space of the die. The isolated system has a specific number of quantum states; we may as well call the set of all these quantum states the sample space of the isolated system.
- The die is rolled to flip from one face to another. The isolated system flips by itself from one quantum state to another.
- A subset of the faces of the die is called an event; for example, the event of getting an even number is the subset  $\{2,4,6\}$ . A subset of the quantum states of the isolated system is called a macrostate, or conformation, or configuration, or thermodynamic state.
- For the die, a random variable is a function that maps each face to a number. For the isolated system, a random variable is a function that maps each quantum state to a number.

**Appendix B: Random variable.** A die has six faces, labeled as A, B, C, D, E, F. Before we roll the die, we agree on a rule of winning: \$200 for face A, \$600 for face B, \$50 for face C, \$1000 for face D, \$700 for face E, \$0 for face F. This rule is a function that maps every face to an amount of winning. The domain of the function is the set of the faces, and the range of the function is a set of numbers. While the rule is deterministic, the amount of winning is random. In the theory of probability, such a function is known as a *random variable*.

An isolated system flips among a set of quantum states. Consider a function that maps every quantum state to a number. That is, the domain of the function is the set of the quantum states of the isolated system, and the range of the function is a set of numbers.

As an example, revisit the half bottle of water. The bottle is an isolated system, and has a set of quantum states. The number of water molecules in the top half of the bottle,  $N$ , is a random variable. Such a function is usually a many-to-one function: many quantum states map to the same number. When the top half of the bottle has a number  $N$  of water molecules, the isolated system flips among a subset of quantum states, and the number of quantum states in this subset is denoted as  $\Omega(N)$ .

**Appendix C: Logarithm.** Consider the relation

$$y = b^x,$$

where  $b$  is a positive number. If  $b = 1$ , this relation reduces to  $y = 1$ , and is of no interest to us. If  $b \neq 1$ , this relation is a one-to-one map between a number  $x$  in the interval  $(-\infty, +\infty)$  and a number  $y$  in the interval  $(0, +\infty)$ . We call  $y$  the exponential of  $x$  to the base  $b$ .

Any one-to-one map can be inverted. Given a number  $y$  in the interval  $(0, +\infty)$ , we can find a number  $x$  in the interval  $(-\infty, +\infty)$  to satisfy the relation  $y = b^x$ . We call  $x$  the logarithm of  $y$  to the base  $b$ , and write

$$x = \log_b y.$$

The following identities hold:

$$\log_b(yz) = \log_b y + \log_b z$$

for any two positive numbers  $y$  and  $z$ , and

$$\log_b(y^p) = p \log_b y$$

for any positive number  $y$  and any real number  $p$ .

The base  $b$  can be changed to any other positive number  $a$  by using

$$\log_a y = \frac{\log_b y}{\log_b a}.$$

Why do we use the logarithm function to define the entropy in the first place? It is because the logarithm function has the following property:

$$\log_b(yz) = \log_b y + \log_b z.$$

Is this property unique to the logarithm function? The answer is yes. To prove this statement, consider a function  $f$  of the property

$$f(yz) = f(y) + f(z)$$

for any two positive numbers  $y$  and  $z$ . We next look for all functions that have this property.

In the special case  $z = 1$ , the above property reduces to  $f(y) = f(y) + f(1)$ , so that

$$f(1) = 0.$$

Setting  $yz = 1$ , we obtain that

$$f(y^{-1}) = -f(y)$$

The property  $f(yz) = f(y) + f(z)$  also implies that

$$f(a^m) = mf(a)$$

$$f(b) = nf(b^{1/n})$$

for any positive real numbers  $a$  and  $b$  any integers  $m$  and  $n$ , where  $n \neq 0$ .

Setting  $a = b^{1/n}$ , we obtain that

$$f(b^{m/n}) = (m/n)f(b)$$

Any real number  $x$  may be approximated by a rational number  $m/n$ . Consequently, we can re-write the above equation as

$$f(b^x) = xf(b).$$

Let  $y = b^x$ , so that  $x = \log_b y$ .  $A = f(b)$  is a constant independent of  $y$ . The above equation is written as

$$f(y) = A \log_b y.$$

Thus, the function has to be logarithm, and the arbitrary constant  $A$  allows us to choose any number as the base.

**Appendix D: Why do we prefer one base over another?** The preference has to do with derivatives. The derivative of a function  $y(x)$  is defined as

$$\frac{dy(x)}{dx} = \lim_{h \rightarrow 0} \left[ \frac{y(x+h) - y(x)}{h} \right].$$

Consider the derivative of the exponential function  $y(x) = b^x$ . Note that

$$\frac{y(x+h) - y(x)}{h} = \left( \frac{b^h - 1}{h} \right) b^x.$$

Consequently, to calculate the derivative of the exponential function, we need to know

$$\lim_{h \rightarrow 0} \left( \frac{b^h - 1}{h} \right).$$

For a given base  $b$ , we can use a calculator to obtain an approximate value of this limit by calculating  $(b^h - 1)/h$  with a small number  $h$ , say  $h = 0.0000$ . For example,  $(b^h - 1)/h \approx 0.92$  when  $b = 2.5$ , and  $(b^h - 1)/h \approx 1.10$  when  $b = 3$ . By try and error, we find that the above limit is 1 for a particular base,  $b \approx 2.718$ . This particular base is denoted as  $b = e$ . That is, the number  $e$  is defined through the expression

$$\lim_{h \rightarrow 0} \left( \frac{e^h - 1}{h} \right) = 1.$$

When the number  $e$  is used as the base, the derivative of the exponential function takes a particularly simple form:

$$\frac{d(e^x)}{dx} = e^x.$$

By contrast, when an arbitrary number  $b$  is used as the base, the derivative of the exponential function is

$$\frac{d(b^x)}{dx} = b^x \log b.$$

When the number  $e$  is used as the base, we write the logarithm function as  $x = \log y$ , and call it the natural logarithm. Thus, in the above equation,  $\log b$  means  $\log_e b$ . The derivative of the natural logarithm also takes a particularly simple form:

$$\frac{d(\log y)}{dy} = \frac{1}{y}.$$

When an arbitrary number  $b$  is used as the base, the derivative of the logarithm function is

$$\frac{d(\log_b y)}{dy} = \frac{1}{y \log b}.$$

If you loath writing the number  $\log b$  in many formulas, you set the base to be  $e$ . The choice of the base  $e$  keeps mathematics tidy, but adds no physical content.