Isolated Systems

Of our world the following facts are known:

- An isolated system has a set of quantum states.
- The isolated system ceaselessly flips from one quantum state to another.
- A system isolated for a long time is equally probable to be in any one of its quantum states.

Thus, an isolated system behaves like a fair die:

- A die has six faces.
- The die is rolled to flip from one face to another.
- A fair die is equally probable to be in any one of its faces.

The following notes remind us what an isolated system is, and translate the theory of probability of rolling a fair die to the thermodynamics of an isolated system.

These facts of our world enable us to study experimental phenomena by following an algorithm. For a given phenomenon, we construct an isolated system, which flips among a set of quantum states. We then construct subsets of the quantum states. Each subset is called a macrostate of the isolated system. The probability for the system to be in a macrostate is the number of quantum states in the macrostate divided by the number of quantum states in the whole set.

We will mostly follow a sub-algorithm. Of all macrostates of an isolated system, the most probable macrostate has the largest number of quantum states. This statement is known as the second law of thermodynamics. The fundamental postulate implies the second law of thermodynamics. The latter is an incomplete expression of the former.

We will find it convenient to use the phrase "the logarithm of the number of quantum states". The phrase is given shorthand: entropy. We can speak of the entropy of an isolated system, as well as the entropy of a macrostate of the isolated system.

A system. We can regard any part of the world as a *system*. A glass of wine, for example, is a system. This system is composed of water, alcohol, and other molecules. Do we include the glass as a part of the system? Maybe, if we decide to study the reaction between alcohol and glass. The decision is ours. We can regard any part of the world as a system.

An isolated system. A system is said to be *isolated* 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 happen to study.

An isolated system has a set of quantum states. An isolated system has a set of quantum states. For example, a proton and an electron form a system known as a hydrogen atom. When the motion of the proton is neglected, a quantum state of the hydrogen atom is characterized by an electron cloud, or the wave function of the electron. The hydrogen atom interacts with the rest of the world, for example, by absorbing photons, so that the energy of the electron can change. Even when the hydrogen atom is isolated from the rest of the world, the isolated system can still be in multiple quantum states. The hydrogen atom has two quantum states if the atom is isolated at the ground energy level, six quantum states if the atom is isolated at the second energy level, and so on.

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

An isolated system ceaselessly flips from one quantum state to another. An isolated system is not static: it constantly flips from one quantum state to another. Thus, an isolated system behaves like a die of a large number of faces, and a madman rolls the die perpetually. For example, in the glass of wine, molecules ceaselessly move. Molecules even jump off the wine: you smell the molecules.

The fundamental postulate. The isolated system ceaselessly flips from one quantum state to another. 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 is equally probable to be in any one of its quantum states.*

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 the entire thermodynamics upon the fundamental postulate. We next describe several elementary consequences of the fundamental postulate.

The number of quantum states of an isolated system. An isolated system has a set of quantum states. The number of quantum states of the isolated system is denoted by Ω. In principle, for a given isolated system, its number of quantum states may be calculated using 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 states of an isolated system can be determined by experimental measurements; see notes on Temperature (http://imechanica.org/node/291).

Because every quantum state is equally probable, the probability P_{state} for the isolated system to be in any one quantum state is

$$P_{\text{state}} = \frac{1}{\Omega}.$$

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

A macrostate of an isolated system. A subset of the quantum states of an isolated system is called a *macrostate*. A macrostate is also designated by using other words, such as a *conformation* of a molecule, or a *thermodynamic state* of a glass of wine, or a *configuration* of ink particles in a liquid.

Consider a short RNA molecule in a large quantity of a liquid as an isolated system. Let us say that the RNA molecule can be in two conformations: chains or loops. Each conformation is a gross description, consisting of many quantum states. For example, both a straight chain and a wiggled chain belong to the same conformation, the chains. Even when the shape of the RNA molecule is fixed, the molecules in the surrounding liquid can be in many quantum states. The two conformations of the RNA molecule interest us because they have different biophysical functions. By contrast, the individual quantum states are too numerous to interest us.

The number of quantum states in a macrostate of an isolated system. Let Ω be the number of quantum states of an isolated system. A subset of the quantum states is called macrostate A. The macrostate has Ω_A number quantum states. Because all individual quantum states of the isolated system are equally probable, the probability for the isolated system to be in macrostate A is

$$P_{\text{macrostate A}} = \frac{\Omega_A}{\Omega}.$$

Thus, on the basis of the fundamental postulate, the entire thermodynamics reduces to an art to identify useful macrostates, and then count the number of states that constitute each macrostate.

Irreversible change in an isolated system. Now consider a half glass of wine. We seal the bottom half of the glass, evacuate the top half of the glass, and isolate the whole glass from the rest of the world. Then we remove the seal, and allow molecules to escape from the liquid to fill the top half of the glass with a gas.   Our experience indicates that the process of evaporation is spontaneous, but the molecules in the gas will not spontaneously all go back to the liquid. That is, the evaporation of a liquid into a vacuum is an irreversible change in an isolated system. What causes this irreversibility?

We can explain this irreversibility in terms of the fundamental postulate. The seal in the middle of the glass 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 glass a *variable*. We name a macrostate of the isolated system by the number of molecules in the top half of the glass. Thus,

- Macrostate 0 consists of $\Omega(0)$ states in which no molecule is in the top half of the glass,

- Macrostate 1 consists of $\Omega(1)$ states in which 1 molecule is in the top half of the glass, and so on.

The half glass of wine, which is an isolated system, ceaselessly flips among a set of quantum states. When the top half of the glass has a particular number of molecules, the isolated system flips among a particular subset of quantum states. According to the fundamental postulate, a macrostate of an isolated system is more probable if the macrostate consists of more quantum states of the isolated system. When the constraint is lifted, there will be other macrostates that may consist of more states of the isolated system. Consequently, the change from the initial to the final macrostate appears to be irreversible.

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 spontaneous 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,

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

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.

An internal variable of an isolated system. Consider a function that maps a quantum state of an isolated system 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 real number. This function is known as an *internal variable* of the isolated system.

In the theory of probability, such a function of quantum state is called a *random variable*. For example, consider the following rule of winning after a roll of a fair die: $200 for face 1, $600 for face 2, $50 for face 3, $1000 for face 4, $700 for face 5, $0 for face 6. This rule is a function of face. While the rule is deterministic, the winning is a random variable, depending on the face obtained in a roll of the die.

$$\Omega_{tot}$$

An isolated system has a set of Ω_{tot} states.

$$\Omega(Y_1)$$
$$\Omega(Y_2)$$
$$\Omega(Y_3)$$
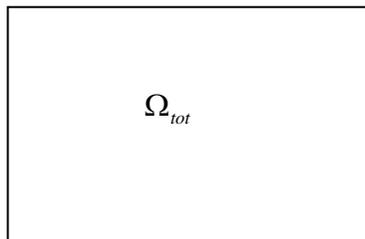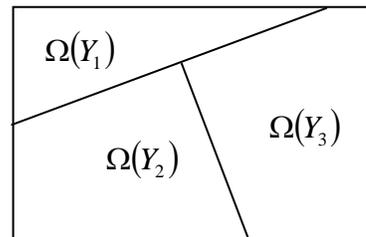
The set of states is dissected into a family of subsets. Each subset is known as a macrostate. All states in a given macrostate have the same value of *Y*.

Dissect the whole set of quantum states of an isolated system into a family of subsets by using an internal variable. For the isolated system such as a half glass of wine, we are interested in the number *N* of molecules in the top half of the glass, i.e., the number of molecules in the gas. This number is a function of the state of the isolated system. Such a function is usually a many-to-one function: many quantum states of the isolated system give the same number of molecules in the gas.

When $N = 0$, the top half of the glass is devoid of any molecule. Even in this case, the isolated system flips among a large subset of quantum states. This subset of quantum states constitutes a macrostate, called macrostate 0; we denote by $\Omega(0)$ the number of quantum states of the isolated system when no molecule is in the top half glass. Similarly, when the top half of the glass has $N = 1$ molecules, the isolated system flips another subset of quantum states. The subset of quantum states constitutes another macrostate, called macrostate 1; we denote by $\Omega(1)$ the number of quantum states of the isolated system when 1 molecule is in the top half glass. Thus we can dissect the whole set of the quantum states of the half glass of wine into a family of macrostates depending on the number of molecules in the top half of the glass.

This idea is so important that we formalize it now. An isolated system flips among a set of quantum states. A function maps each quantum state of the

isolated system to a real variable, *Y*. When the variable is held at a specific value Y_i, the isolated system flips among a subset of the quantum states. This subset of quantum states constitutes a macrostate; we denote by $\Omega(Y_i)$ the number of quantum states in this subset.

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

The second law of thermodynamics. Consider a constraint internal to an isolated system. When this constraint is lifted, we observe that an internal variable changes with time.

We can use the internal variable *Y* to dissect the set of quantum states of the isolated system into a family of subsets, each subset (called a macrostate) consisting of all the quantum states having the same value of the internal variable. Each macrostate of the isolated system has its own number of quantum states.

As the isolated system ceaselessly flips from one quantum state to another, we observe a sequence of values of the internal variable. Associated with this sequence of values is a sequence of macrostates, along with a sequence of the numbers of quantum states in the macrostates:

- sequence of time: $t_1, t_2, t_3, \ldots$
- sequence of values of the internal variable: $Y(t_1), Y(t_2), Y(t_3), \ldots$
- sequence of macrostates: $A(t_1), A(t_2), A(t_3), \ldots$
- sequence of numbers of states: $\Omega(t_1), \Omega(t_2), \Omega(t_3), \ldots$

The fundamental postulate implies that the last sequence must be in an increasing order. This statement is perhaps the most useful version of the second law of thermodynamics.

A thermodynamic model. Consider the half glass of wine again. When the number of molecules in the top half of the glass is *N*, the isolated system has $\Omega(N)$ states. What is the most probable number of molecules in the gas?

For most isolated systems, the number of molecules is so large that we may as well regard *N* as a continuous variable. This simplification allows us to use the calculus of real variables.

Consider two microstates of the half glass of wine. In one macrostate, the gas has *N* molecules, and the macrostate has $\Omega(N)$ quantum states. The function $\Omega(N)$ specify a *thermodynamic model* of the system.

In another macrostate, the gas has $N + dN$ molecules, and the macrostate has $\Omega(N + dN)$ states. The numbers of states in the two microstates differ by

$$\Omega(N + dN) - \Omega(N) = \frac{\partial \Omega(N)}{\partial N} dN.$$

Of the two directions of change, the gas gaining and losing molecules, the more probable direction of change increases the number of the states. This statement is a direct consequence of the fundamental postulate, and is translated into the following conclusions.

- If $\partial \Omega / \partial N > 0$, the gas will more probably gain molecules.
- If $\partial \Omega / \partial N < 0$, the gas will more probably lose molecules.
- If $\partial \Omega / \partial N = 0$, the gas will be equally probable to gain or lose molecules.

From probability to (almost) certainty. According to the fundamental postulate, the most probable number of molecules in the gas, *N*, maximizes the function $\Omega(N)$. The isolated system of the half glass of wine is said to reach a *thermodynamic state of equilibrium*. Or we say that the liquid equilibrates with the gas.

Any other partitions of molecules are also probable, 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 an endless game of maximization or minimization.

A kinetic model. Consider the half glass of wine again. The system is isolated from the rest of the world. The two halves are separated by a membrane, which allows molecules to go across slowly. How does the number of molecules in the top half of the glass evolve with time?

As before, we regard the number of molecules in the top half of the glass, *N*, as an internal variable of the isolated system, and use *N* to dissect the set of quantum states of the isolated system into subsets, each subset consisting of all the quantum states having the same value of *N*. Let the number of quantum states in the subset be $\Omega(N)$. When the number of gas molecules in the top half changes by
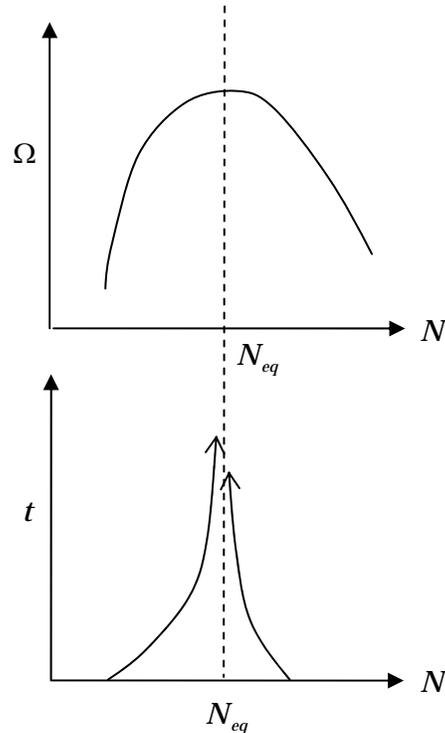
$$\delta N = N_{\text{later}} - N_{\text{earlier}},$$

The number of quantum states in the subset changes by

$$\delta \Omega = \frac{\partial \Omega(N)}{\partial N} \delta N.$$

The fundamental postulate implies that

$$\frac{\partial \Omega(N)}{\partial N} \delta N \geq 0.$$

One way to satisfy the above condition is to set

$$\frac{\partial N(t)}{\partial t} = K \frac{\partial \Omega(N)}{\partial N},$$

with $K > 0$. The coefficient K models the conductance of the membrane, and may vary with N. We may determine the function $K(N)$ by experiments. The above equation is known as a *kinetic model* of the system. The equation is an ordinary differential equation. Once the functions $\Omega(N)$ and $K(N)$ are known, the above equation evolves N in time.

In the graph, the function $\Omega(N)$ has a maximum at $N = N_{eq}$. When $N(0) < N_{eq}$, the number of molecules in the gas phase increases over time and approaches the equilibrium value. When $N(0) > N_{eq}$, the number of molecules in the gas phase decreases over time and approaches the equilibrium value.

Exponential decay. We can even obtain an analytical solution by linearizing the above ordinary differential equation. When $N(0)$ is not too far from N_{eq}, we can expand the two functions $\Omega(N)$ and $K(N)$ into Taylor series, and retain only leading terms:

$$\Omega(N) = \Omega(N_{eq}) - \frac{1}{2} \alpha (N - N_{eq})^2,$$

$$K(N) = k,$$

where α and k are positive constants. Thus, the ordinary differential equation becomes

$$\frac{\partial N(t)}{\partial t} = -k\alpha(N - N_{eq}).$$

The solution to this linear ordinary differential equation is

$$\frac{N(t) - N_{eq}}{N(0) - N_{eq}} = \exp(-k\alpha t).$$

This example shows why exponential decay is such a prevalent process.

Theory of probability of rolling a fair die vs. thermodynamics of an isolated system. 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 ceaselessly 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, an internal variable is a function that maps each quantum state to a number.

A composite of two isolated systems. Simultaneously rolling a die and flipping a coin will result in one of the $6 \times 2 = 12$ outcomes.

Now consider two isolated systems A' and A''. Isolated system A' has a total of Ω' number of quantum states, labeled as $\{\gamma'_1, \gamma'_2, ...,\}$. Isolated system A'' has a total of Ω'' number of quantum states, labeled as $\{\gamma''_1, \gamma''_2, ...,\}$.

A composite of the two isolated systems is still an isolated system. A quantum state of the composite is any combination of a quantum state chosen from the set $\{\gamma'_1, \gamma'_2, ...,\}$ and a quantum state chosen from the $\{\gamma''_1, \gamma''_2, ...,\}$. For example, one quantum state of the composite is when system A' is in state γ'_2 and system A'' is in state γ''_3. The total number of all such combinations is

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

This is the number of quantum states of the composite.

Entropy. Entropy is shorthand for the phase "the logarithm of the number of quantum states". That is, the entropy S of an isolated system is defined by

$$S = \log \Omega.$$

Entropy so defined is a pure number, and needs no unit. The base of the logarithm is arbitrary, and we will adopt the natural base, such that

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

Just like the number of states, entropy is a pure number associated with any probability distribution, not just the probability distribution of quantum states of an isolated system. For example, we can talk about the entropy of rolling a fair die ($S = \log 6$), or the entropy of tossing a fair coin ($S = \log 2$).

The isolated system flips among a set of quantum states. A subset of the quantum states is called a macrostate of the isolated system. Denote the number of the quantum states in the subset by Ω_A. We call the number

$$S_A = \log \Omega_A$$

the entropy of the macrostate A.

By changing a phrase 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", $\log \Omega$. The following statements are banal, but may sound profound if you forget what the word entropy means.

Entropy is defined for an isolated system even when the system is not in equilibrium. Thus, entropy is a property of an isolated system, in or out of equilibrium.

Entropy is an extensive quantity. For a composite of several systems, the entropy of the composite is the sum of the entropies of the individual systems. This statement follows from a property of the logarithmic function:
$$\log\left(\Omega'\Omega''\right) = \log\Omega' + \log\Omega''.$$
A few more states are concerned with the entropy of a macrostate.

Of all the macrostates, the most probable macrostate has the highest entropy. This statement is known as the second law of thermodynamics.

We will use the second law of thermodynamics extensively in subsequent notes. As examples, we will use the second law of thermodynamics to define temperature (http://imechanica.org/node/291), and understand phase transition (http://imechanica.org/node/4878).