CHEM-UA 652: Thermodynamics and Kinetics

Notes for Lecture 2

I. THE IDEAL GAS LAW

In the last lecture, we discussed the Maxwell-Boltzmann velocity and speed distribution functions for an ideal gas. Remember that, in an ideal gas, there are no interactions between the particles, hence, the particles do not exert forces on each other. However, particles do experience a force when they collide with the walls of the container. Let us assume that each collision with a wall is elastic. Let us assume that the gas is in a cubic box of legnth a and that two of the walls are located at $x = 0$ and at $x = a$. Thus, a particle moving along the x direction will eventually collide with one of these walls and will exert a force on the wall when it strikes it, which we will denote as F_x. Since every action has an equal and opposite reaction, the wall exerts a force $-F_x$ on the particle. According to Newton's second law, the force $-F_x$ on the particle in this direction gives rise to an acceleration via

$$-F_x = ma_x = m\frac{\Delta v_x}{\Delta t} \tag{1}$$

Here, Δt represents the time interval between collisions with the same wall of the box. In an elastic collision, all that happens to the velocity is that it changes sign. Thus, if v_x is the velocity in the x direction before the collision, then $-v_x$ is the velocity after, and $\Delta v_x = -v_x - v_x = -2v_x$, so that

$$-F_x = -2m\frac{v_x}{\Delta t} \tag{2}$$

In order to find Δt, we recall that the particles move at constant speed. Thus, a collision between a particle and, say, the wall at $x = 0$ will not change the particle's speed. Before it strikes this wall again, it will proceed to the wall at $x = a$ first, bounce off that wall, and then return to the wall at $x = 0$. The total distance in the x direction traversed is $2a$, and since the speed in the x direction is always v_x, the interval $\Delta t = 2a/v_x$. Consequently, the force is

$$-F_x = -\frac{mv_x^2}{a} \tag{3}$$

Thus, the force that the particle exerts on the wall is

$$F_x = \frac{mv_x^2}{a} \tag{4}$$

The mechanical definition of pressure is

$$P = \frac{\langle F \rangle}{A} \tag{5}$$

where $\langle F \rangle$ is the average force exerted by all N particles on a wall of the box of area A. Here $A = a^2$. If we use the wall at $x = 0$ we have been considering, then

$$P = \frac{N\langle F_x \rangle}{a^2} \tag{6}$$

because we have N particles hitting the wall. Hence,

$$P = \frac{Nm\langle v_x^2 \rangle}{a^3} \tag{7}$$

from our study of the Maxwell-Boltzmann distribution, we found that

$$\langle v_x^2 \rangle = \frac{k_{\mathrm{B}}T}{m} \tag{8}$$

Hence, since $a^3 = V$,

$$P = \frac{Nk_{\mathrm{B}}T}{V} = \frac{nRT}{V} \tag{9}$$

which is the ideal gas law.

The ideal gas law is an example of an equation of state, which was introduced in lecture 1. One way to visualize any equation of state is to plot the so-called *isotherms*, which are graphs of P vs. V at fixed values of T. For the ideal-gas equation of state $P = nRT/V$, some of the isotherms are shown in the figure below (left panel): If we plot P vs. T
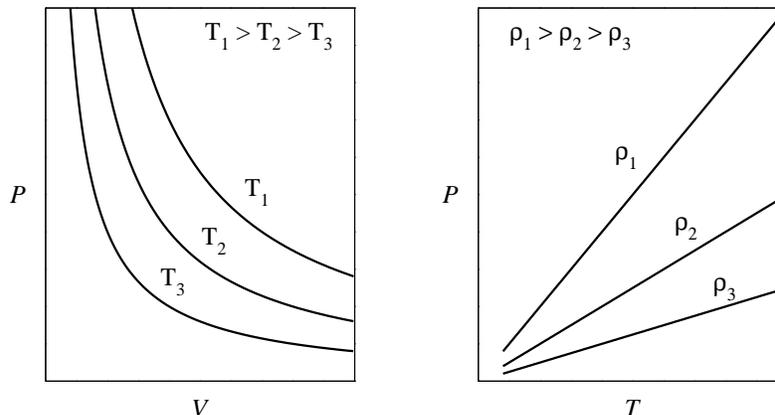

FIG. 1: (*Left*) Pressure vs. volume for different temperatures (isotherms of the ideal-gas equation of state. (*Right*) Pressure vs. temperature for different densities $\rho = N/V$.

at fixed volume (called the *isochores*), we obtain the plot in the right panel. What is important to note, here, is that an ideal gas can exist *only* as a gas. It is not possible for an ideal gas to condense into some kind of "ideal liquid". In other words, a phase transition from gas to liquid can be modeled only if interparticle interactions are properly accounted for.

Note that the ideal-gas equation of state can be written in the form

$$\frac{PV}{nRT} = \frac{P\bar{V}}{RT} = \frac{P}{\rho RT} = 1 \tag{10}$$

where $\bar{V} = V/n$ is called the molar volume. Unlike V, which increases as the number of moles increases (an example of what is called an *extensive* quantity in thermodynamics), $\bar{V}$ does not exhibit this dependence and, therefore, is called *intensive*. The quantity

$$Z = \frac{PV}{nRT} = \frac{P\bar{V}}{RT} = \frac{P}{\rho RT} \tag{11}$$

is called the *compressibility* of the gas. In an ideal gas, if we "compress" the gas by increasing P, the density ρ must increase as well so as to keep $Z = 1$. For a real gas, Z, therefore, gives us a measure of how much the gas deviates from ideal-gas behavior.
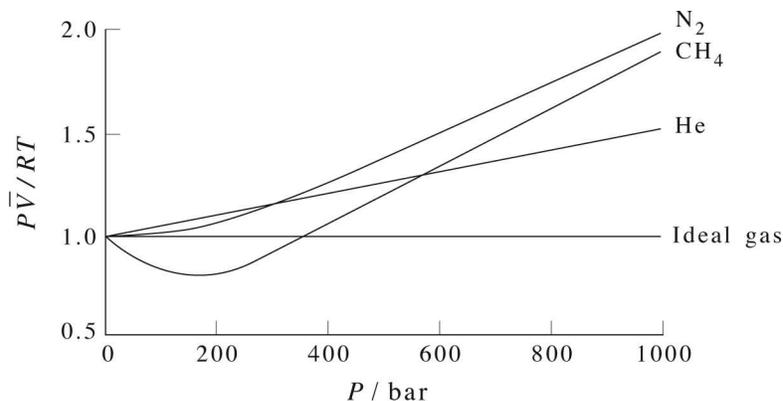
FIG. 2: Plot of the compressibility Z vs. P for several gases, together with the ideal gas, where $Z = 1$.

The figure below shows a plot of Z vs. P for several real gases and for an ideal gas. The plot shows that for sufficiently low pressures (hence, low densities), each gas approaches ideal-gas behavior, as expected.

II.   INTRODUCTION TO STATISTICAL MECHANICS

Defining statistical mechanics: Statistical Mechanics provies the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc.

Why do we need Statistical Mechanics:

1. Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory.

2. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties – spectra, rate constants, etc., using time correlation functions.

3. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice, be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

A. The microscopic laws of motion

Consider a system of N classical particles. The particles a confined to a particular region of space by a "container" of volume V. In classical mechanics, the "state" of each particle is specified by giving its position and its velocity, i.e., by telling where it is and where it is going. The position of particle i is simply a vector of three coordinates $\mathbf{r}_i = (x_i, y_i, z_i)$, and its velocity $\mathbf{v}_i$ is also a vector $(v_{x_i}, v_{y_i}, v_{z_i})$ of the three velocity components. Thus, if we specify, at any instant in time, these six numbers, we know everything there is to know about the state of particle i.

The particles in our system have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $\mathbf{r}_1(t), ..., \mathbf{r}_N(t)$, and the velocities at t are related to the positions by differentiation

$$\mathbf{v}_i(t) = \frac{d\mathbf{r}_i}{dt} = \dot{\mathbf{r}}_i \tag{12}$$

In order to determine the positions and velocities as function of time, we need the classical laws of motion, particularly, Newton's second law. Newton's second law states that the particles move under the action of the forces the particles exert on each other and under any forces present due to external fields. Let these forces be denoted $\mathbf{F}_1, \mathbf{F}_2, ..., \mathbf{F}_N$. Note that these forces are functions of the particle positions:

$$\mathbf{F}_i = \mathbf{F}_i(\mathbf{r}_1, ..., \mathbf{r}_N) \tag{13}$$

which is known as a "force field" (because it is a function of positions). Given these forces, the time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, ..., \mathbf{r}_N)$$

where $\mathbf{F}_1, ..., \mathbf{F}_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i/dt^2$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivaties, $\{\mathbf{r}_1(0), ..., \mathbf{r}_N(0), \dot{\mathbf{r}}_1(0), ..., \dot{\mathbf{r}}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

III. THE ENSEMBLE CONCEPT (HEURISTIC DEFINITION)

For a typical macroscopic system, the total number of particles $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we contented ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes $= 2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ Gbytes which is also 10^2 Yottabytes! The largest computers we have today have perhaps 10^6 Gbytes of memory, so we are off by 11 orders of magnitude just to specify 1 classical state.

Fortunately, we do not need all of this detail. There are enormous numbers of microscopic states that give rise to the same macroscopic observable. Let us again return to the connection between temperature and kinetic energy:

$$\frac{3}{2}Nk_{\mathrm{B}}T = \sum_{i=1}^{N} \frac{1}{2}m_i\mathbf{v}_i^2 \tag{14}$$

which can be solved to give

$$T = \frac{2}{3k_{\mathrm{B}}} \left(\frac{1}{N} \sum_{i=1}^{N} \frac{1}{2}m_i\mathbf{v}_i^2 \right) \tag{15}$$

Here we see that T is related to the average kinetic energy of all of the particles. We can imagine many ways of choosing the particle velocities so that we obtain the same average. One is to take a set of velocities and simply

assign them in different ways to the N particles, which can be done in $N!$ ways. Apart from this, there will be many different choices of the velocities, themselves, all of which give the same average.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procecure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Ensemble: Consider a large number of systems each described by the same set of microscopic forces and sharing a common set of macroscopic thermodynamic variables (e.g. the same total energy, number of moles, and volume). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time.

The questions that naturally arise are:

1. How do we construct an ensemble?

2. How do we perform averages over an ensemble?

3. How do we determine which thermodynamic properties characterize an ensemble?

4. How many different types of ensembles can we construct, and what distinguishes them?

IV.   EXTENSIVE AND INTENSIVE PROPERTIES IN THERMODYNAMICS

Before we discuss ensembles and how we construct them, we need to introduce an important distinction between different types of thermodynamic properties that are used to characterize the ensemble. This distinction is *extensive* and *intensive* properties.

Thermodynamics always divides the universe into a "system" and its "surroundings" with a "boundary" between them. The unity of all three of these is the thermodynamic "universe". Now suppose we allow the system to grow in such a way that both the number of particles and the volume grow with the ratio N/V remaining constant. Any property that increases as we grow the system in this way is called an *extensive* property. Any property that remains the same as we grow the system in this way is called *intensive*.

Examples of extensive properties are N (trivially), V (trivially), energy, free energy,... Examples of intensive properties are pressure P, density $\rho = N/V$, molar heat capacity, temperature,....

V.   THE MICROCANONICAL ENSEMBLE

Consider a classical system that is completely isolated from its surroundings. Such a system has no external influences acting on it, we can restrict our discussion of the classical forces acting on the system to *conservative* forces. Conservative forces are forces that can be derived from a simple scalar function $U(\mathbf{r}_1, ..., \mathbf{r}_N)$ by taking the negative derivative with respect to position

$$\mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i} \tag{16}$$

which simply means that the three components of $\mathbf{F}_i$ are generated as follows:

$$F_{x_i} = -\frac{\partial U}{\partial x_i}, \quad F_{y_i} = -\frac{\partial U}{\partial y_i}, \quad F_{z_i} = -\frac{\partial U}{\partial z_i} \tag{17}$$

The function $U(\mathbf{r}_1, ..., \mathbf{r}_N)$ is called the "potential" of the system or "potential energy" of the system. When this is added to the kinetic energy, we obtain the total energy $\mathcal{E}$ as

$$\mathcal{E} = \frac{1}{2} \sum_{i=1}^{N} m_i \mathbf{v}_i^2 + U(\mathbf{r}_1, ..., \mathbf{r}_N) \tag{18}$$

If there are *no* external fields acting on the system, then this energy is the mechanical *total internal energy*.

An isolated system will evolve in time according to Newton's second law

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, ..., \mathbf{r}_N) \tag{19}$$

Importantly, when the forces are conservative, $\mathcal{E}$ is constant with respect to time, meaning that it is conserved, and hence it is equivalent to the thermodynamic internal energy E. To see that energy conservation is obeyed, we simply need to take the derivative of $\mathcal{E}$ with respect to time and show that it is 0.

$$\mathcal{E} = \frac{1}{2} \sum_{i=1}^{N} m_i \mathbf{v}_i^2 + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$\frac{d\mathcal{E}}{dt} = \sum_{i=1}^{N} m_i \mathbf{v}_i \cdot \dot{\mathbf{v}}_i + \sum_{i=1}^{N} \frac{\partial U}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i$$

$$= \sum_{i=1}^{N} \dot{\mathbf{r}}_i \cdot \mathbf{F}_i - \sum_{i=1}^{N} \mathbf{F}_i \cdot \dot{\mathbf{r}}_i$$

$$= 0$$

Since the mechanical energy is fixed, we can equate it with the thermodynamic internal energy E, which will also be fixed.

In addition to the energy, two other thermodynamic variables are trivially conserved, and they are the number of particles N, and the containing volume V. If we now imagine a collection of such systems in an ensemble, all having the same values of N, V, and E, the same underlying microscopic forces and laws of motion but all having different microscopic states, then this ensemble would be characterized by the values of N, V, and E and is called a *microcanonical ensemble*.

A. Entropy and the number of microscopic states

Now that we have defined one type of ensemble, the microcanonical ensemble, an important quantity pertaining to this ensemble is the number of microscopic states. For short, we will refer to "microscopic states" as "microstates". In a classical system, a microsate is simply a specification of the positions and velocities of all the particles in the system. Thus, in order to find the number of microstates, we ask the following question: In how many ways can we choose the positions and velocities for a system of N particles in a volume V and forces derived from a potential $U(\mathbf{r}_1, ..., \mathbf{r}_N)$ such that we always obtain the same value of the energy in Eq. (18)? Let us denote this number as Ω, and it is clear to see that Ω is a function of N, V, and E, *i.e.*, $\Omega(N, V, E)$. Even though $\Omega(N, V, E)$ is an enormous number, the fact is that it is always finite (as opposed to infinite). How can we calculate $\Omega(N, V, E)$? In principle, $\Omega(N, V, E)$ can be computed by

$$\Omega(N, V, E) = \frac{1}{h^{3N}} \int_{E=\mathcal{E}} d\mathrm{x} \tag{20}$$

where $\mathcal{E}$ is given by Eq. (18), E is a value for the internal energy, and $\int d\mathrm{x}$ means integrate over all of the positions and velocities! The constant h is Planck's constant, and it accounts for the Heisenberg uncertainty principle. If all of the particles in the system are identical, then we must divide the integral on the right by a factor of $1/N!$, which accounts for the fact that the particles can be exchanged in $N!$ ways without changing the microscopic state of the

system. This seemingly innocent formula is actually rather difficult to apply in practice. The number $\Omega(N, V, E)$ is an example of what is called a *partition function* in statistical mechanics. Here, $\Omega(N, V, E)$ is the partition function of the microcanonical ensemble.

The connection between the microscopic world of positions, velocities, forces, potentials, and Newtonian mechanics and the macroscopic, thermodynamic world is the entropy S, which is computed from Ω via Boltzmann's formula

$$S(N, V, E) = k_{\mathrm{B}} \ln \Omega(N, V, E) \tag{21}$$

This formula was emblazoned on Boltzmann's grave, as the photograph below shows:

FIG. 3: Boltzmann's headstone at the Zentralfriedhof in Vienna, Austria.

This definition of entropy also tells us something important about what entropy means. There is a commonly held

(mis)conception that entropy is a measure of the degree of disorder in a system. The notion of "disorder" is certainly something that we all have an intuitive feel for (it's far easier to create chaos in your room than it is to clean it up, and it's far easier to knock over a large stack of oranges in the grocery store than it is to stack them up in the first place). However, as there is no universal definition of disorder, there is no way to quantify it, and hence, it cannot be used as a route to the entropy in a system; in fact, trying to equate entropy and disorder can even be misleading.

Common sense tells us that certain processes occur spontaneously in one direction but not in the reverse direction. But how do we distinguish between those process that truly cannot happen in reverse (such as the breaking of the glass) and those that *could* potentially happen in reverse if only we waited long enough? This thought experiment gives some idea of what entropy really measures.

Classical mechanics can actually help us understand the distinction. Recall Newton's second law of motion which describes how a system of N classical particles evolves in time:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}(\mathbf{r}_1, ..., \mathbf{r}_N) \tag{22}$$

Let us ask what happens if we start from an initial condition $\mathbf{r}_1(0), ..., \mathbf{r}_N(0), \mathbf{v}_1(0), ..., \mathbf{v}_N(0)$, evolve the system out to a time t, where we have positions and velocities $\mathbf{r}_1(t), ..., \mathbf{r}_N(t), \mathbf{v}_1(t), ..., \mathbf{v}_N(t)$, and from this point, we reverse the direction of time. Where will the system be after another time interval t has passed with the clock running backwards? We first ask what happens to Newton's second law if we reverse time in Eq. (22). If we suddenly set $dt \to -dt$, the positions do not change at the moment, hence, the forces do not change either. Moreover, since $dt^2 \to dt^2$, the accelerations do not change. Thus, Newton's second law will have exactly the same form when time is reversed as then time runs in the normal forward direction. This means that the laws of motion, themselves, cannot distinguish between normal and reversed time! This condition is called *time reversal symmetry*. On the other hand, first time derivatives must change sign, hence, the velocities $\mathbf{v}_i = d\mathbf{r}_i/dt \to d\mathbf{r}_i/(-dt) = -\mathbf{v}_i$ must reverse their direction when time is reversed, hence in order to start running the clock backwards at time t, we must replace all of the velocities $\mathbf{v}_1(t), ..., \mathbf{v}_N(t)$ with $-\mathbf{v}_1(t), ..., -\mathbf{v}_N(t)$. The facts that the velocities simply change sign under time reversal but the laws of motion do not tell us that at each point in the time reversed motion, the particles will experience the same forces and, therefore, will accelerate in the same way only in the opposite direction. Thus, after another time t, the particles should end up exactly where the started, i.e., $\mathbf{r}_1(2t) = \mathbf{r}_1(0), ..., \mathbf{r}_N(2t) = \mathbf{r}_N(0)$. Despite this time reversal symmetry of the laws of motion (the same symmetry exists, by the way, in quantum mechanics), there seems to be a definite "arrow" of time, as many processes are truly unidirectional. A few examples will help to illustrate the point that is being made here.

Consider first a box with a partition. One half contains an ideal gas, and the other is empty. When the partition is removed, the gas will spontaneously expand to fill the box. Once the gas expands, the particles will "never"
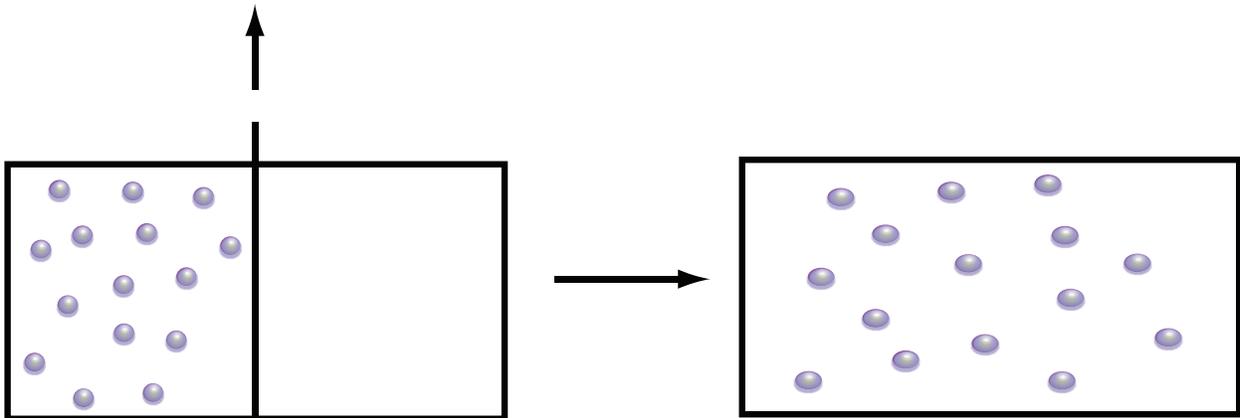

FIG. 4: Expansion of a gas initially partitioned into one-half of its containing volume.

spontaneously return to the left half of the box leaving the right half of the box empty, even though the process is *not* forbidden by the laws of motion or by the first law of thermodynamics. Entropy aims to quantify this tendency

not captured in the first law of thermodynamics. Specifically, what entropy quantifies is the *number of available microscopic states in the system*. Hence, any thermodynamic transformation that cases the number of available microscopic states available to the system to increase will lead to an increase in entropy. While this might seem to be in contradiction to the notion that thermodynamics does not need to refer to the microscopic nature of matter, and while there is a purely thermodynamic definition of entropy that will be introduced shortly, we will see that this connection between entropy and available microstates is both fully consistent with the thermodynamic definition of entropy and intuitively very appealing as a way to understand what entropy is.

Coming back to the gas example, when the partition is in place, the volume of the system is half that of the full box. Thus, when the partition is removed, the volume doubles and the number of available microstates increases significantly. By how much? In order to see this we need to see how Ω depends on V. Recall that for an ideal gas

$$\mathcal{E} = \frac{1}{2} \sum_{i=1}^{N} m\mathbf{v}_i^2 \tag{23}$$

when all of the particles have the same mass m. Note that $\mathcal{E}$ does not depend on positions. Thus, we can write Eq. (20) as

$$\Omega(N, V, E) = \frac{1}{N!h^{3N}} \left[\int_{E=\mathcal{E}} dx_{\mathbf{v}} \right] \left[\int dx_{\mathbf{r}} \right] \tag{24}$$

where $dx_{\mathbf{v}}$ is the integral over velocities, and $dx_{\mathbf{r}}$ is the integral over positions. All we need to do is look at the latter to see how Ω depends on the volume. Suppose the gas occupies a cube of side length a with faces at $x = 0$, $x = a$, $y = 0$, $y = a$, $z = 0$, and at $z = a$. Then, since we have N particles, and we have to integrate over the positions of all of them, we need to integrate each position over the spatial domain defined by this box:

$$\int dx_{\mathbf{r}} = \left[\int_0^a dx_1 \int_0^a dy_1 \int_0^a dz_1 \right] \cdots \left[\int_0^a dx_N \int_0^a dy_N \int_0^a dz_N \right] \tag{25}$$

This means that we have $3N$ integrals that are all exactly the same. Hence, we can write this as

$$\int dx_{\mathbf{r}} = \left[\int_0^a dx_1 \right]^{3N} \tag{26}$$

or

$$\int dx_{\mathbf{r}} = a^{3N} = V^N \tag{27}$$

and therefore, $\Omega(N, V, E) \propto V^N$

Thus, the ratio of available states after the partition is removed to that before the partition is removed is $(2V/V)^N = 2^N$. As we will see shortly, this is equivalent to increase in entropy by $N \ln 2$. Hence, in this thought experiment, entropy increases when the partition is removed because the number of microscopic states increases.

Let us now contrast this thought experiment with another one that differs from the first in one subtle but key respect. Let us suppose that we are somehow able to collect of the gas particles into the left half of the box without having to employ a partition. The situation is shown in the figure below. After the particles are thus collected, we allow them to evolve naturally according to the laws of motion, and not unexpectedly, this evolution causes thme to fill the box, and we never observe them to return to the initial state in which they were prepared. Does the entropy increase in this case? No! Even though it might seem that the system evolves from a (relatively) ordered state to one with greater disorder, the number of microscopic states remains the same throughout the expansion. What distinguishes this case from the previous one is that here, we create a highly unlikely initial state without the use of a device that restricts the number of available states. How unlikely is this initial state? That is, what is the probability that it would occur spontaneously given the total number of available microstates? This probability is given by the fraction of microscopic states represented by the gas occupying half the box to that of the gas occupying the full volume of the box. For an ideal gas, this ratio is $(V/2V)^N = (1/2)^N$. Hence, if $N \sim 10^{23}$, the probability is so small that one would need to wait a time equal to many, many times the current lifetime of the universe to see it happen, even though it is not forbidden by the laws of motion. Even if $N = 100$, the probability is still on the order of 10^{-30}, which is negligible. Even though entropy does not increase, we still observe this process as "one way" because the number
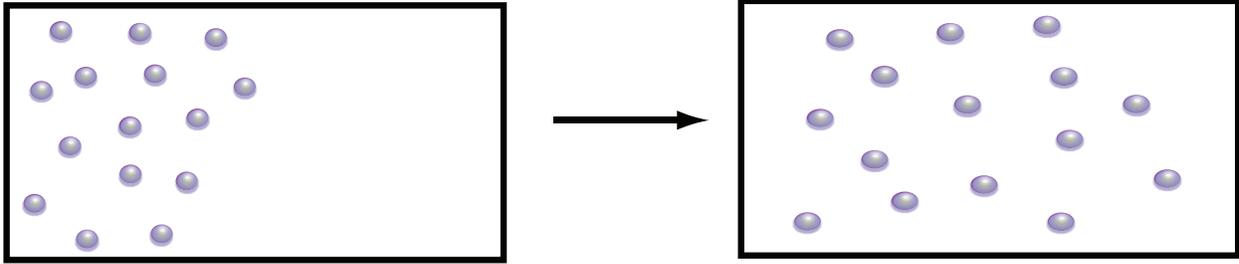
FIG. 5: Expansion of a gas initially located in one-half of its containing volume.

of states in which the gas fills the volume of the box compared to the number of states in which it spontaneously occupies just one half of it, is so astronomically large that it can never find its way to one of the extremely unlikely states in which the particles aggregate into just one half of the box.

An important consequence of Boltzmann's formula is that it proves entropy is an additive quantity, which is always assumed to be true in thermodynamics. Let us consider two independent systems, denoted A and B, and let Ω_A be the number of microstates associated with system A, and let Ω_B be the number of microstates associated with system B. The number of microstates associated with the combined system A+B is then the product $\Omega_{A+B} = \Omega_A \Omega_B$. But what is the entropy of the combined system?

$$
\begin{aligned}
S_{A+B} &= k_B \ln \Omega_{A+B} = k_B \ln (\Omega_A \Omega_B) \\
&= k_B \ln \Omega_A + k_B \ln \Omega_B \\
&= S_A + S_B
\end{aligned}
\tag{28}
$$