

Introduction to Physical Chemistry – Supplemental Lecture

I. LECTURE OVERVIEW

This supplemental lecture covers some additional material that is not normally part of an introductory physical chemistry course. Specifically, I will derive the ideal gas law using statistical mechanics, discuss some philosophical issues related to entropy, the connection between thermodynamics and other branches of science, and provide some references for further reading.

None of this material will be on the final. I am including this lecture in order to give you a taste of what is studied in more advanced courses in thermodynamics and statistical mechanics, and also to discuss some philosophical issues related to entropy. Unfortunately, I will not have time during the remainder of the course to actually give this lecture in class. Nevertheless, I do hope you read it, and if you have any questions, you should feel free to come to me with any questions.

II. DERIVATION OF THE IDEAL GAS LAW

The Boltzmann formula for entropy, $S = k \ln \Omega$, derived in Lecture 6, may be used to derive the ideal gas law.

Suppose we can derive an expression for the entropy of N ideal gas particles with internal energy E occupying a volume V (we are using E instead of U now, following the convention in statistical mechanics). That is, suppose we can derive a formula $S = S(E, V, N)$. The question is, what is the connection between P , V , N , and T for this gas?

From the First Law of Thermodynamics for a reversible process, we have, for fixed N ,

$$dE = TdS - PdV \quad (1)$$

so that,

$$P = -\frac{\partial E}{\partial V} \quad (2)$$

We also, have, for fixed N ,

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV \quad (3)$$

Setting $dS = 0$ gives,

$$\frac{dE}{dV} = -\frac{\left(\frac{\partial S}{\partial V}\right)_{E,N}}{\left(\frac{\partial S}{\partial E}\right)_{V,N}} \quad (4)$$

which gives, from the definition of P and $1/T = (\partial S/\partial E)_{V,N}$, that,

$$P = T\left(\frac{\partial S}{\partial V}\right)_{E,N} \quad (5)$$

This equation is completely general. It is true for any material, not just an ideal gas. However, we will now proceed to compute $(\partial S/\partial V)_{E,N}$ for an ideal gas.

From the Boltzmann formula, we have that $S(E, V, N) = k \ln \Omega(E, V, N)$, where Ω denotes the degeneracy of the most probable state at energy E , V , and particle number N . However, remember that, as E , V , and N become large, the degeneracy of the most probable state becomes so much larger than the degeneracies of all other states combined that the maximal degeneracy becomes essentially equal to the total degeneracy (if you're confused by this statement, go back to Lecture 6, and read the example of the gas spreading throughout the box). This means that we can replace the maximal degeneracy by the total degeneracy when computing S , which is good because this will ease the computation (I should point out that because the ratio of the degeneracy of the most probable state to the total degeneracy approaches 1 as the system size becomes infinite, when computing entropy it is equivalent to use the total degeneracy or the maximal degeneracy).

Now, in an ideal gas, the particles do not interact, so there is no potential energy term for the interparticle interactions. Therefore, if the ideal gas has a total energy E , then numbering the particles $1, \dots, N$ gives that the particles have energies E_1, \dots, E_N consistent with the constraint $E = E_1 + \dots + E_N$. In principle, the energy E may be distributed in any way we like among the N particles (and in any mode we like for a given particle), giving a total energy degeneracy of $\Omega_{Energy}(E, N)$.

We are not done yet, however, because we have only considered the particle energy (this includes particle velocity, rotation, vibration, etc.), but not the particle position. To calculate the total degeneracy of the system consistent with the total energy E , we have to now include the degeneracy associated with particle position.

Each particle has a volume V in which to spread out and "choose" its location. Therefore, we expect the position degeneracy of each particle to be proportional to V . Since there are N particles, we multiply V N times to get a total position degeneracy proportional to V^N (see Figure 1). Again, multiplying this position degeneracy by the degeneracy in energy, gives a total degeneracy of,

$$\Omega(E, V, N) = \gamma V^N \Omega_{Energy}(E, N) \quad (6)$$

where γ is some proportionality constant.

Therefore,

$$S = k \ln \Omega(E, V, N) = k \ln \gamma + kN \ln V + k \ln \Omega_{Energy}(E, N) \quad (7)$$

and so,

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{kN}{V} \quad (8)$$

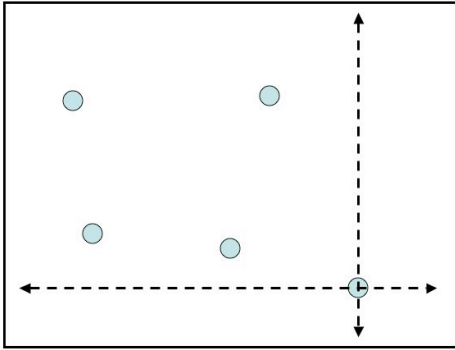


FIG. 1: A particle in a box has a position degeneracy proportional to the total volume V .

Plugging this into our earlier relationship gives,

$$P = T \times \frac{kN}{V} \Rightarrow PV = kNT \quad (9)$$

Using the relationship $k = R/N_A$, and $n = N/N_A$ gives, finally,

$$PV = nRT \quad (10)$$

which you should all recognize as the Ideal Gas Law.

We can actually go further than this, and compute the relationship between the energy and temperature of an ideal gas. This will allow us to compute the heat capacity.

In what follows, we will assume that the gas is *monatomic*. This means that there are no vibrational or rotational modes where the energy of the gas can be distributed. All of the internal energy of the gas is simply kinetic energy of the individual gas particles. If $(\dot{x}_i, \dot{y}_i, \dot{z}_i)$ denotes the velocity vector of particle i , and if each gas particle has a mass m , then the total energy E of the gas is given by the sum of the kinetic energies of the individual particles, and so,

$$\frac{1}{2}m(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2 + \dots + \dot{x}_N^2 + \dot{y}_N^2 + \dot{z}_N^2) = E \quad (11)$$

so that,

$$(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2 + \dots + \dot{x}_N^2 + \dot{y}_N^2 + \dot{z}_N^2) = \frac{2E}{m} \quad (12)$$

Now, notice that the vector $(\dot{x}_1, \dot{y}_1, \dot{z}_1, \dots, \dot{x}_N, \dot{y}_N, \dot{z}_N)$ has a total length $(2E/m)^{1/2}$ (remember the length formula for vectors), and so it lies on a $(3N-1)$ -dimensional sphere of radius $(2E/m)^{1/2}$. Because any vector lying on this sphere corresponds to an energy distribution among the particles consistent with the total energy E , intuitively we expect that the surface area of the sphere provides a measure of the total energy degeneracy (see Figure 2).

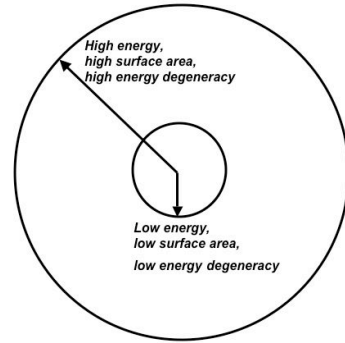


FIG. 2: Illustration of the connection between energy degeneracy and sphere surface area for an ideal gas.

Now, the circumference of a circle (a one-dimensional sphere) is $2\pi r$, and the surface area of a sphere (a two-dimensional sphere) is $4\pi r^2$. Following this pattern, we see that the surface area of an m -dimensional sphere is proportional to r^m , so that the energy degeneracy of the monatomic ideal gas is given by,

$$\Omega_{Energy}(E, N) = A \left(\frac{2E}{m} \right)^{\frac{3N-1}{2}} \quad (13)$$

Notice that we earlier showed that $S = k \ln \gamma + kN \ln V + k \ln \Omega_{Energy}(E, N)$. But this means that,

$$\left(\frac{\partial S}{\partial E} \right)_{V,N} = k \left(\frac{\partial}{\partial E} \right)_{V,N} (\ln \Omega_{Energy}(E, N)) \quad (14)$$

so for the monatomic ideal gas,

$$\begin{aligned} \left(\frac{\partial S}{\partial E} \right)_{V,N} &= k \left(\frac{\partial}{\partial E} \right)_{V,N} (\ln A + \frac{3N-1}{2} \ln \frac{2}{m} + \frac{3N-1}{2} \ln E) \\ &= k \frac{3N-1}{2} \frac{1}{E} \end{aligned} \quad (15)$$

and so,

$$\frac{1}{T} = k \frac{3N-1}{2} \frac{1}{E} \Rightarrow E = k \frac{3N-1}{2} T \quad (16)$$

For large N , this simply becomes,

$$E = \frac{3}{2} kNT = \frac{3}{2} nRT \quad (17)$$

Therefore, the internal energy per mole of a monatomic ideal gas is simply $E/n = (3/2)RT$, which of course implies that $\bar{C}_V = (3/2)R$.

So, we have just proved that the constant volume heat capacity of a monatomic ideal gas is $(3/2)R$. To understand what is going on here, it should be pointed out that we can show, along similar lines of reasoning to what was used just now, that every degree of freedom adds a heat capacity of $(1/2)R$ for an ideal gas.

For example, in three dimensions, a monatomic gas particle has three degrees of freedom: Movement in the x direction, movement in the y direction, and movement in the z direction. Each degree of freedom adds $(1/2)R$ to the heat capacity, giving a total heat capacity of $(3/2)R$.

As an exercise, try going through the above derivation for a monatomic ideal gas, but now in two dimensions, instead of three dimensions. You will see that, instead of computing the surface area of a $(3N - 1)$ -dimensional sphere, you will need to compute the surface area of a $(2N - 1)$ -dimensional sphere, giving, finally, a heat capacity of $(1/2)R + (1/2)R = R$.

Now, a diatomic molecule, in addition to having translational degrees of freedom (i.e., movement in the x , y , and z directions), also has two rotational degrees of freedom and a vibrational degree of freedom. However, at room temperature, vibrational energy spacing are sufficiently large that quantum-mechanical effects are important. The result of this is that the molecules are essentially in their vibrational ground states, so the vibrational degree of freedom is hidden, and may therefore be ignored. This gives a total heat capacity of $5 \times (1/2)R = (5/2)R$.

Finally, for a monatomic ideal gas, we can compute the average kinetic energy of a particle. This is simply $E/N = (3/2)kT$. But, since the average kinetic energy is also, $(1/2)m\langle v \rangle^2$, we have that,

$$v_{rms} = \sqrt{\langle v \rangle^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{\mu_g}} \quad (18)$$

where v_{rms} denotes the *root mean square velocity* and μ_g denotes the molar mass of the gas. The root mean square velocity provides a measure of the average speed of the gas particles as a function of temperature and particle mass. Note that the heavier the particles, the slower they move on average, and the higher the temperature, the faster they move.

For helium we have $\mu_g = 4g/mol = 0.004kg/mol$, so that at $25^\circ C = 298 K$ we have,

$$\begin{aligned} v_{rms}(He, 298K) &= \sqrt{3 \times 298K \times 8.314 \frac{J}{Kmol} \times \frac{mol}{0.004kg}} \\ &= 473m/s = 1702km/hr \end{aligned} \quad (19)$$

As a final note for this section, the derivations done here are only a taste of the full power of statistical mechanics. It is possible to dissect the ideal gas even further and derive the actual distribution of particle velocities for an ideal gas.

III. ENTROPY, THE UNIVERSE, AND THE ARROW OF TIME

The discovery of the Second Law of Thermodynamics in the 19th century led to all kinds of philosophical speculations regarding the ultimate fate of the universe, and

the arrow of time. We will explore these issues here, and attempt to address them within one framework.

A. The “heat death” of the universe

We have already shown that the Second Law of Thermodynamics implies that entropy is always increasing in an isolated system. This has led to speculation that the Second Law implies that the universe as a whole is increasing in entropy, and therefore, that the universe will gradually become more and more disordered, until it eventually undergoes a so-called “heat death.”

There is a lot of controversy surrounding this idea. It may very well be true, but it may turn out to be nonsense as well. The central reason for the idea that the universe will undergo a heat death is the association of entropy and disorder. Therefore, as a system goes to states of higher entropy, it becomes more “disordered.” Applying this to the universe, we could imagine that the most disordered state of the universe is where all the matter has decayed, and energy is simply dispersed throughout the vacuum of space, so that the universe, at its end, consists of a diffuse, cold, matter-energy distribution.

It makes sense that entropy and disorder would be associated with one another. After all, the entropy of a system is simply the maximal degeneracy, and is therefore the degeneracy of the most probable state. In the context of an ideal gas, this means that maximal entropy is attained when the gas is spread throughout its container. In the context of temperature, this means that maximal entropy is attained when the temperature is the same throughout a system. Therefore, it is natural to associate maximal degeneracy with maximal disorder.

However, we have to keep in mind that the Second Law is true by definition, because it is nothing more than a statement from probability theory. Therefore, while in some cases the maximally degenerate configuration of a system fits well with our subjective notions of disorder, in other cases it may not.

Applying this to the universe, we should note that the “Big Bang” theory of the universe argues that the universe began as a singularity that spread out and formed all the matter and energy we see today. One of the major research efforts in cosmology is to determine exactly how much matter and energy is in the universe. If there is too little, then the universe will expand forever, and the universe will ultimately face the predicted “heat death.” However, above a critical mass-energy density, the gravitational attractions between the various parts of the universe will be enough to eventually stop and then reverse the expansion. The result will be the ultimate collapse of all the matter-energy of the universe into a singularity. This end for the universe is called the “Big Crunch.” It is possible that this singularity could expand again in a new “Big Bang,” and so, like a ball bouncing elastically and without friction, it is possible that our universe is stuck in an endless cycle of “Big Bangs” and “Big Crunches,”

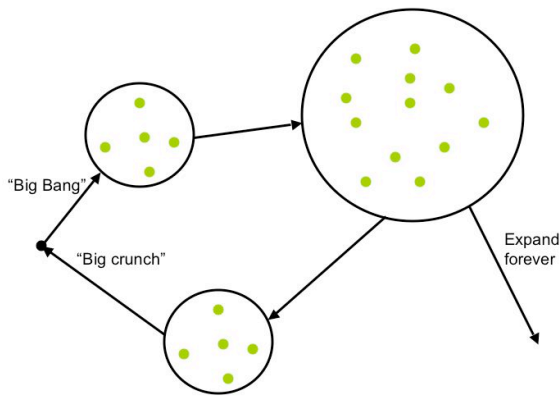


FIG. 3: Two possible scenarios for the ultimate fate of our universe. Either the expansion reverses and the universe collapses in a “big crunch,” or the universe expands forever.

so that there is no heat death at all.

Currently, evidence is suggesting that the expansion of the universe is actually accelerating, due to the presence of a kind of negative energy of the vacuum whose strength is defined by a term called the *cosmological constant*. However, all of this is still largely speculative. In any event, there are theories that universes are constantly being created and destroyed, and that our particular universe, whatever its fate, is but one particular instantiation of this process (all of this is intimately connected to quantum mechanics and quantum measurement theory).

Figure 3 illustrates various theories surrounding the origins and evolution of the universe.

B. Entropy and the arrow of time

It is also said that the increase of entropy is what defines the arrow of time. The reason for this is that the Second Law of Thermodynamics provides a unidirectionality to thermodynamic processes, thereby allowing one to distinguish between a process that goes forward in time, and one that does not.

The reason why this is problematic is that the basic laws of physics do not have a preference for time. Light can travel forwards or backwards. If we saw a film of the Earth orbiting the sun, and then saw the film run backwards, this would not violate any laws of physics. In principle, the Earth can orbit the sun in either direction. A ball hitting the ground in reverse is a ball leaving the ground with some initial velocity. This is also fine.

But, with thermodynamics, things are different. Ice at ten degrees celsius will melt into water. If you ran the film of the melting ice backwards, you would know that you were watching the film in the reverse direction.

How is this to be reconciled with the law of physics? After all, the ice is nothing more than a huge collection of water molecules, moving under the action of Newton’s

laws of motion. If there is enough total energy inside the ice, then the dynamics is such that the water molecules will break their bonds and start to flow. But again, since we are dealing with a deterministic system, why isn’t the reverse film correct?

The answer is that the reverse film *is* correct. The apparent discrepancy comes from our applying the laws of probability to a deterministic system. I will explain what I mean by this:

For a small number of particles, the time behavior of a dynamical system can be determined by solving Newton’s laws of motion. The result is a trajectory giving us the positions and velocities of all the particles as a function of time.

Now suppose we have a large number of particles, say a mole’s worth. The time behavior of the dynamical system is again determined by solving Newton’s laws of motion. However, there is a problem here: For such a large number of particles, it is generally not practical to determine the collective motion of a system (imagine trying to track Avogadro’s number worth of particles!). Also, even if it were possible to determine the collective motion of all the particles, it may not be necessary. For example, to compute the pressure that a gas exerts on the walls of a container, it is not necessary to know the position and velocity of every single particle in the container. We simply need to know what the particles are doing on average. Finally, to accurately determine the motions of a large collection of particles over a meaningful period of time would require such high precision in the initial state of the system that such a task is essentially impossible (there is therefore a strong connection between statistical mechanics and *chaos theory*).

The result of all this is that we replace a deterministic description of a system with a large number of particles with a *probabilistic* description, one that uses a small number of variables to determine what the particles are doing on average, and not what any specific particle is doing at any given time.

As the number of particles becomes infinite, this probabilistic description becomes increasingly accurate (because then the hypothesis of most probable states will be more likely to hold, as Lecture 6 discussed). However, for any finite system, the principle of most probable states will be violated from time to time. This is not a problem with classical mechanics or thermodynamics, however. It is simply a consequence of the fact that we were using a theory that is strictly correct in the limit of infinite system size to describe a finite system.

So, in the case of the water-ice system, at a system energy corresponding to a temperature of ten degrees celsius, the number of configurations corresponding to an ice structure is far, far smaller than the number of configurations corresponding to a water structure. However, because there are a finite number of water molecules, there will be a finite, though small, fraction of all configurations that will be consistent with an ice configuration.

So, regarding the ice-water system as a classical system

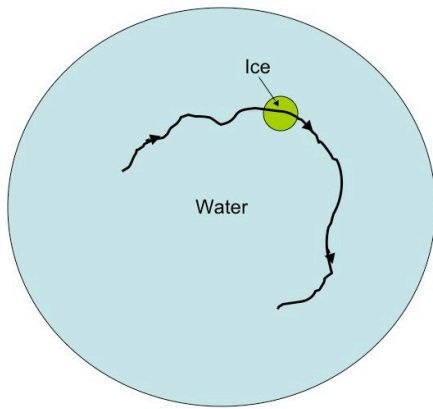


FIG. 4: The number of configurations corresponding to an ice structure versus a liquid water structure. A classical trajectory passes through the ice region, so that running the trajectory forward or backwards from within that ice region will always show ice melting. However, if we only record the forward trajectory starting from the ice region, and then view the film backwards, it will appear as if the liquid water freezes to ice and stays there. This is misleading, as the full configuration diagram shows.

of particles, let us assume that we start with ice, and now run the dynamics forward in time. As Figure 4 shows, the number of configurations corresponding to liquid water is far greater than the number of configurations corresponding to ice. Therefore, as time goes forward, the dynamics of the particles will most likely follow a trajectory that will bring them to what we call a liquid state (the chances that the particles won't do this is so small that we would have to wait much longer than the age of the universe to observe it).

But now, if we start somewhere along this trajectory where the system is now water and run it backwards, then the classical system will simply retrace its route, and eventually return to the ice state. However, this does not indicate that time has gone backwards. Indeed, if we keep running the film backwards, then, as Figure 4 shows, the system will again leave the “ice island” and enter a region corresponding to a liquid configuration. In other words, if we truly run the film backwards, we will once again see the ice melt.

The reason why it appears that the film running backwards is a contradiction, is because the film *starts* with a block of ice, and then initially runs forward to form liquid water. Therefore, we were never able to record the what the ice would have done had we been able to go backwards, before we started with the ice. Had we been truly been able to extend the dynamics “back in time,” we would have seen the ice melt in any event.

IV. HOW IS THERMODYNAMICS CONNECTED TO OTHER BRANCHES OF SCIENCE?

Thermodynamics is important in almost every branch of science and engineering. The reason for this is that thermodynamics is concerned with developing a probabilistic description of many-particle systems that involve a relatively small number of variables (compared an Avogadro's number worth of position and momenta versus temperature, pressure, number of moles, and volume).

The central assumption making this probabilistic description possible is that the system will go into its most probable state given a certain set of constraints. By a *constraint*, I mean something about the system that we know. This includes total energy and volume, for example. The idea is that, given what you know about the system, all system possibilities consistent with what you know are equally likely. The motivation for such an assumption is that without additional information, there is no reason *a priori* to assume that the system possibilities are not equally likely.

Because thermodynamics is in many ways a general methodology for analyzing the behavior of many-particle systems, it is a science that is applicable to a wide range of fields. In this course, we have seen how it is important for understanding heat engines, chemical reactions, and phase equilibria.

Thermodynamics may also be used to understand the collective behavior of light particles, and, when combined with quantum mechanics, may be used to understand the structure of materials at any energy. The application of statistical thermodynamics to materials falls under the rubric of *condensed matter physics*. *Hard condensed matter physics* is often referred to as *solid state physics*, and is concerned with the behavior of semiconductor devices, crystals, and superconductivity, to name a few applications. *Soft condensed matter physics* deals with polymers dissolved in water, and is therefore particularly relevant to biology. Applications include protein folding, DNA and RNA structure, the formation of micelles and membranes, and diffusion processes.

Thermodynamics has been useful in astrophysics, in understanding the interactions between the matter and electromagnetic field of the sun. It has been applied to theoretical studies of black holes, and thermodynamic and statistical-mechanical ideas have even been used to study the global structure of the universe itself.

In computer science and engineering, thermodynamics has found application by way of its generalization, *Information Theory*. Information Theory concerns itself with the error-prone transmission of data across communication channels. As a result, probability theory and therefore the concepts of uncertainty are essential components of this theory. What is interesting is that if one takes a broader view of “data” and “communication channels,” then any physical system may be seen to be defined by the transmission of data across a communication channel.

Therefore, Information Theory has returned to its roots and has become an incredibly powerful framework for understanding physical systems (in quantum mechanics, it is intimately connected to the idea of a measurement and the nature of consciousness).

V. FURTHER READING

This officially concludes all the lecture material covered in this course. For those of you interested in learning more, I highly recommend taking more advanced courses in thermodynamics and statistical mechanics, if you can.

A course in quantum mechanics is also recommended. A number of books that you may find useful are:

1. *Physical Chemistry*, by Ira N. Levine.
2. *Introduction to Statistical Mechanics*, by David Chandler.
3. *Statistical Mechanics*, by Donald A. McQuarrie.

Also, the online encyclopedia Wikipedia is a good source of general information on thermodynamics (including some of the philosophical issues discussed here).