Gas physics: macroscopic processes

We've made progress in understanding many astrophysical processes by focusing on just gravity. However, we now need to move on to consider other interactions. Of particular importance is gas physics. Most things that we can see outside the solar system are in the gas phase, even though (as in the case of stars in a cluster) their gaseous nature is not necessarily essential to the description of a particular phenomenon. However, the properties of stars, the formation of structure, and innumerable other phenomena depend strongly on how gases interact, so that's where we will turn our attention. We will begin with a review of thermodynamics, which we will find has many things in common with n-body gravity.

Thermodynamics is a bit of a strange theory, in that the "laws" of thermodynamics aren't laws on a par with, say, the law of gravity. The law of gravity, or Maxwell's equations, or any of a number of similar laws, are usually considered to be fundamental laws that act on a particle by particle (or field by field) basis, and are therefore deterministic and immutable. On the other hand, the laws of thermodynamics aren't fundamental laws at all. They are merely statements of tendencies. For example, one of the laws is that heat diffuses from a hot system to a cold system. But in any particular case, for a short time, a few energetic particles from the cold system may make their way to the hot system, thereby going against this "law". Should this make us uncomfortable?

No, for a couple of reasons. First, although the laws of thermodynamics "merely" describe tendencies, when one has an enormous number of particles those tendencies are so strong that they are basically inevitable. This is the nature of statistics. For example, suppose I decide on a "law of flipping coins". This law states that when the coin is fair, there will be an equal number of heads and tails in a series of flips. Now, you know from experience that this isn't always true. If you flip a coin six times, getting two heads and four tails is perfectly reasonable. If you flip it more often, in fact, the chance that you will get exactly half diminishes; you'd be mildly surprised if you got exactly 50 heads in 100 throws. However, as the number of flips goes up, the fraction of heads gets closer and closer to 50% assuming a fair coin. Therefore, the deviations from this "law" become less and less with more trials. Indeed, decades after thermodynamics was largely developed, it was found that its laws could be derived from statistical mechanics, in the sense that treating umpteen zillion molecules interacting with each other gives you thermodynamics, on average. This is similar to our development of gravitational interactions, where we went from lots of chaos in three-body systems to strong and predictable tendencies in n-body systems.

The second reason one shouldn't dismiss thermodynamics compared to, say, Newton's laws is that our current understanding is that these, too, are approximations. From the quantum standpoint, the path taken by, say, a baseball has some "fuzziness" associated with it. It has an overwhelming likelihood of moving along the classical trajectory, but that's just a "tendency" in the same way that the laws of thermodynamics are tendencies. Therefore, thermodynamics works just fine when there are enough particles that the statistics are good. Like anything else, you have to make sure that you use thermodynamics only in its domain of applicability.

With that said, what are the laws of thermo?

- 0th law: Heat diffuses from a hot system to a cold system. Thermal equilibrium occurs when the temperatures of the two systems are equal. If two systems are both in thermal equilibrium with a third system, the two are in thermal equilibrium with each other.
- 1st law: An equilibrium system can be characterized by its internal energy U. If there is no interaction with the outside world, U is conserved. If there is interaction but no exchange of particles, then
$$dU = dQ + dW \ , \tag{1}$$
where dQ is the heat added and dW is the work done on the system.
- 2nd law: Entropy never decreases; $dS \geq 0$ in any interaction, and $dS = 0$ only for reversible interactions.
- 3rd law: As temperature goes to absolute zero, the entropy approaches a constant, $S \to S_0$ as $T \to 0$, which is a state of complete order.

Let's consider some details about these laws. The first law says that the energy content of the gas can change, meaning that the system the gas interacts with must have its energy change in the opposite sense because energy is still conserved in any interaction. **Ask class:** what is the work done on the system? Work equals force times distance, and pressure is force per area, so work equals pressure times area times distance, or pressure times change in volume:
$$dW = -PdV \tag{2}$$
where the negative sign is because if the volume decreases then the internal energy content must increase. Note that here we have an example of a law that applies only when there are a large number of particles. Imagine that the gas is in a container with walls. Work is done by shrinking the size of the container. On a particle by particle basis, the way that work is done is that if you imagine moving the walls of the container inwards, a particle bouncing off the wall will leave with greater speed than it started (assuming elastic collisions). Now, if there are a small number of particles, you could imagine sneakily waiting until no particle was near the wall to shrink the container, and no change would occur in the energy. Put another way, if there are few enough particles that at some instant none are in contact with the container, then at that instant there is no effective pressure, so the volume can be changed without affecting the internal energy of the gas. If instead you have an effectively

unlimited number of particles, there is always a steady pressure and any change in the volume of the container adds internal energy to the gas.

What about entropy? This is a slippery concept. From the standpoint of statistical mechanics, entropy is a measure of the disorder of a system. However, let's define it in the way first used in thermodynamics. Suppose you have a system at temperature T, with fixed volume and number of particles. You add some heat dQ to this system. Then the change in entropy dS is $dS = dQ/T$. Therefore, entropy has units of energy divided by temperature, e.g., erg K^{-1}.

Whoop de do. What can we do with this quantity? For various insights into the meaning of entropy, I recommend that you look at the Feynman Lectures on Physics, chapters 44 and 46 in Volume 1. Here I'll pick a few highlights.

First, suppose you bring two systems into contact, one with a high temperature T_1 and the other with a low temperature $T_2 < T_1$. **Ask class:** in which direction will the heat flow? From the hotter to the cooler, so from system 1 to system 2. Call the amount of energy flowing from 1 to 2, dQ, which must be greater than zero. **Ask class:** what is the net change in entropy for the systems? System 1 loses heat, so it has $dS_1 = -dQ/T_1$. System 2 gains heat, so it has $dS_2 = dQ/T_2$. The total change in the entropy for both systems combined is $dS = dS_1 + dS_2 = dQ(1/T_2 - 1/T_1)$. But since $T_2 < T_1$, this means that $dS > 0$. In fact, you can see that the only way to have $dS = 0$ is if $T_2 = T_1$. Stated another way, the only way to have no change in entropy as a system changes is to make sure that all the changes are reversible.

This example shows that although the *total* entropy can't decrease, the entropy of an individual component of a system *can* decrease (in this case, the hotter system 1). This means you have to be careful to consider all of a system. For example, the highest entropy state of snow after a snowfall is for it to be at a uniform height. However, interactions with bumps on the ground, wind, buildings, etc. produce drifts in complicated patterns. Also, as living beings we take low-entropy food and convert it into high-entropy heat and waste, allowing our bodies to maintain or increase complexity. Evolution and development of structure can occur without violating the second law of thermodynamics because these are not closed systems, and the system as a whole does increase its entropy.

An additional point about entropy is that it relates to the amount of useful work that can be extracted from a system, in the sense, say, of running a machine. If a system has the maximum entropy possible (meaning, in practice, that it is in complete thermal equilibrium), then no work can be obtained. As we saw above, however, a temperature difference means that the system is not in a state of maximal entropy. The maximum efficiency of an engine, defined as the energy in useful work divided by the heat transferred, is $W/Q = (T_1 - T_2)/T_1$, where $T_1 \geq T_2$. Since $T_2 \geq 0$ (third law), this can never be greater than unity but one can always get some work done if $T_1 > T_2$. This leads to the old proof that hell must be isothermal; if it weren't, then some clever engineer could devise a machine to use the temperature differences to run air conditioners!

Entropy is a fundamental concept of thermodynamics, but pursuing it in detail can make your head spin around. One issue is that it produces a clear direction of time, since entropy increases as time goes on. This is perfectly in agreement with everyday experience. If you drop a cup, it shatters, but you'd be astonished if shards of a cup spontaneously reassembled. So what's the big deal? The issue is that the fundamental microscopic laws of physics all seem to be time-reversible. Stars moving around in a cluster will be quite happy to go exactly in the opposite sense; if you looked at a movie of a cluster, then watched it backwards, then star by star you would see nothing out of order. That's also true if you were to look at each of the atoms, photons, etc. in the shards of the cup. In a deep sense, looked at classically, this is because equations of motion involve accelerations, which have two time derivatives and are therefore symmetric if $t \to -t$. What, then, is the origin of the asymmetry associated with entropy and seen in everyday life?

It's a deep question, but a reasonable answer is that it is associated with initial conditions. That is, the universe started out with low entropy, so it has lots of room to evolve to different states. Return to the analogy of flipping coins. Suppose I start out with all one million coins with the heads side up. Say that there is some process which, once per second per coin, has a 1% chance of flipping over the coin. After one second one would expect roughly 10,000 coins to have their tails side up. In the next second there is some chance that all 10,000 will flip back to heads, but it is exceedingly improbable. Nonetheless, since this law is reversible, it is possible. This will continue until roughly half the coins are tails. When it is half and half, an observer would not note any particular changes in the system. At the beginning, though, the observer might formulate a "law of increase in tails". So why did the universe start with a low entropy? I certainly don't know the answer, and I think this is a puzzle not yet solved.

One final comment on entropy. From the statistical mechanics standpoint, every microscopic state of a system with a given total energy has the same probability as every other such microscopic state. The question is, what are the most probable *macroscopic* states? Let me clarify by returning to the coin flipping example. Suppose you flipped a million fair coins. The probability that you get all heads, HHHH..., is exactly the same as the probability that you will get some random specified sequence HTHHT... or anything else. If that doesn't make intuitive sense, think of it this way. Yes, you'd be amazed (and suspicious!) if you got nothing but heads for a million flips. But you'd be equally amazed and suspicious if I correctly predicted, in advance, the results of the coin flips, regardless of the sequence. Therefore, each microstate (specific sequence) has the same probability. However, you can ask about the macrostate, which in this case is the total number of heads regardless of order. There is one way, in a million flips, to get a million heads. There are a million ways to get 999,999 heads and one tail. There are roughly $10^{300,000}$ ways to get 500,000 heads and 500,000 tails. Thus, it is a lot more probable to get roughly 50% heads than all heads.

To complete our discussion of thermodynamics, we need to complete our inventory of things that can change the internal energy of a gas. So far, we have included work done by pressure, and heat added to the gas. In addition, since real gases aren't isolated inside walls, there can be exchange of particles. There is a quantity, called the chemical potential μ, that is used to indicate the change in the internal energy of a substance when particles are added. Therefore, if the gas has pressure P, temperature T, and chemical potential μ, then the change in energy is

$$dU = -PdV + TdS + \mu dN \ , \tag{3}$$

where dV is the change in volume, dS is the change in entropy, and dN is the change in the number of particles. The use of differentials indicates that one assumes infinitesimal changes; finite changes are built up using the infinitesimal changes as usual in calculus.

We have focused in this class on general thermodynamic properties. In order to treat a particular gas or fluid, however, we need a description of that particular gas. For example, we would like to know how U, T, P, and V relate to each other. These local, microscopic relations are wrapped up in the *equation of state*. To understand this in more detail we need a specific statistical description of the particular gas. This will be our task in the next class.