Gas physics: microscopic processes

From the previous work we know something about the properties of gas as a whole. What we don't know yet is how this relates to the properties or populations of individual states within the gas. This is the domain of microscopic gas processes, or statistical physics. Now, it should be clear that if the gas is allowed to be in any arbitrary state whatsoever, then one can't make any statements about, e.g., how many atoms are in one state compared to another. That's because we could in principle set up the gas any way we liked. It would then evolve in a certain way, which we could calculate, but at any given instant we wouldn't know much about the system. Therefore, we will assume that the gas is in thermal equilibrium. If so, how many molecules are in a given state? We'll use for our discussion the Feynman Lectures on Physics, chapter 40 in volume 1.

Suppose that we have a gas, and we imagine two parallel planes in the gas separated by distance dx. Let there be some force F on the atoms in the gas. Suppose that the gas has a number density of n atoms per volume. We will consider an ideal gas, which has a pressure of $P = nkT$ at temperature T. In order for the system to be in equilibrium, the force due to the pressure must be balanced by the effect of the force F. However, there will not be any *net* force if the pressure is constant, because the atom has equal force from all around itself. You, for example, are in an atmosphere that exerts a pressure of roughly 10 Newtons per square centimeter, the equivalent of thousands of kilograms over your whole body, yet you aren't squeezed to pulp! It is a *change* in pressure (gradient of pressure) that can exert a net force. Therefore, the force F must balance the gradient of the pressure P.

Let's assume that the system has a constant temperature T, as it will in thermal equilibrium. Pressure (and change in pressure dP) has units of force per area. Therefore, we have

$$Fn\,dx = dP = kT\,dn\ . \tag{1}$$

Note that $-F\,dx$ is the work involved in moving a molecule from x to $x+dx$. Now suppose that the force is derived from a potential V. We found before that $F = -\nabla V = -dV/dx$ in our case. Therefore, we have

$$\begin{aligned} kT\,dn &= -n\,dV \\ dn/n &= -dV/kT \\ n &= \text{const} \times \exp(-V/kT)\ . \end{aligned} \tag{2}$$

Therefore, if the force derives from a potential, the number of molecules in a particular location depends on the negative exponential of the potential energy, divided by kT. This is called *Boltzmann's law*. It is remarkably general. *Any* force that is derived from a potential leads to Boltzmann's law, in classical physics. For example, one could think of an isothermal column of gas in a uniform gravitational field of acceleration g. The number density decreases with height h in accordance with $n \propto \exp(-mgh/kT)$. As usual, we can check various limits: when h increases the pressure decreases (correct); when T decreases the pressure decreases at a fixed h (correct); and so on. Note that the decrease is faster for heavier molecules. This is one reason why at high altitudes we have an oxygen deficit: our natural breathing rate is controlled by the level of CO_2 in the bloodstream, and this decreases rapidly at high altitude so we don't breathe as often as we should until we acclimate.

But what if the force *isn't* derived from a potential? In that case, thermal equilibrium isn't possible at all! Sound bizarre? Consider the following. Suppose you have a bunch of balls in a container, and the balls have friction with each other. To be truly dissipative, the energy released in friction must leave the container entirely. Then you can see that no thermal equilibrium is possible, because energy continues to be lost from the system. In the general case, if a force isn't derived from a potential then there are closed loops in the system that lose or gain net energy, so there is no equilibrium.

We now have the distribution in space, but what about in velocity? It turns out that there is a remarkable (and not accidental) parallel with the distribution in space. Following Feynman again, let's consider a column of gas in thermal equilibrium in a uniform gravitational field. Let's say that there are no collisions between molecules. Let us consider arbitrarily some height $h = 0$ (a reference height; there could be molecules at negative h). How many molecules make it from $h = 0$ to $h = h_0 > 0$? It's not all of them, since some molecules don't have the required energy and will fall down before getting to $h = h_0$. In fact, it is exactly the molecules with enough kinetic energy that populate the higher level. We saw from before that the relative number of molecules at each height is $n(h = h_0)/n(h = 0) = \exp(-mgh_0/kT)$. Therefore, the relative fraction of molecules with enough energy to make it from $h = 0$ to $h = h_0$ must also be $\exp(-mgh_0/kT)$. By conservation of energy, the kinetic energy of those molecules must be at least $\frac{1}{2}mv_0^2$, where v_0 is the vertical speed needed to just make it to h_0 from 0. Therefore,

$$\frac{n(v > v_0)}{n(v > 0)} = \exp(-\text{kinetic energy}/kT) \ . \tag{3}$$

Adding collisions doesn't change this; we could, for example, imagine moving only a tiny height dh such that no collisions occurred in the meantime.

Combined, these two results imply something remarkable. The number of molecules in a particular state (which now includes a position, velocity, and any internal states) in thermal equilibrium is proportional to the exponential of the negative of the total energy divided by kT. Therefore, schematically,

$$N(\text{state}) \propto \exp(-E_{\text{tot}}/kT) \ . \tag{4}$$

Just for reference, in quantum mechanics this is modified in accordance with the nature of the particle in question, to

$$N(\text{state}) \propto 1/[\exp(E_{\text{tot}}/kT) \pm 1] \tag{5}$$

where the $+1$ applies to fermions (such as electrons) and the -1 applies to bosons (such as photons). In classical physics, $E_{\text{tot}} \gg kT$, so the two formulae are essentially equivalent. This, therefore, is our new grand statement of statistical physics in thermal equilibrium.

Consider an application of this in three dimensions. How many particles in a gas have total three-dimensional speed $v > v_0$? Above, we derived the distribution for one dimension. For three dimensions it must be the product of three functions of the same type. Therefore, in Cartesian coordinates,

$$f(v_x, v_y, v_z)dv_x\, dv_y\, dv_z \propto e^{-mv_x^2/2kT} e^{-mv_y^2/2kT} e^{-mv_z^2/2kT} dv_x dv_y dv_z \ . \tag{6}$$

The total velocity is $v^2 = v_x^2 + v_y^2 + v_z^2$. Therefore, we can rewrite this as

$$f(v)d^3v \propto e^{-mv^2/2kT} d^3v \propto e^{-mv^2/2kT} v^2 dv \ . \tag{7}$$

This is the Maxwell-Boltzmann distribution for the velocities of particles in a gas in thermal equilibrium. If you want the fractional distribution, such that $\int f(v)d^3v = 1$, then you get factors in front.

We may rewrite the number in a state to say that

$$\mathcal{N} = \frac{dN}{d^3x\, d^3p} \propto e^{-E_{\text{tot}}/kT} \tag{8}$$

in equilibrium, for a classical substance such that the ± 1 doesn't enter in the denominator. This is called the *distribution function.* The distribution function, and its quantum extension, are fundamental to the description of all sorts of phenomena at the microscopic level. Note that this looks odd, in the sense that it is one differential (dN) over six ($dx\, dy\, dz\, dp_x\, dp_y\, dp_z$, in Cartesian coordinates). What it means is that you can integrate the distribution function over some of the differentials to get different quantities. For example, the ordinary number density n is $n = dN/d^3x$, so $n = \int \mathcal{N}\, d^3p$. The kinetic energy density u is the same integral except weighted by the kinetic energy in each state, so $u = \int \mathcal{N} \sqrt{p^2c^2 + m^2c^4}\, d^3p$ in full relativity, and so on. Using the distribution function, one can compute, for a particular gas or substance, relations between the temperature, pressure, and density; that is, one can compute the *equation of state.*

For a couple of specific cases, one can derive the equation of state from simpler considerations. We'll start with an ideal gas, and follow Feynman, volume 1, chapter 39.

Suppose we have an ideal gas in a container, moving isotropically (equal probability to move in all directions). One end of the container is fixed, and the other has a piston that we can use to measure the force exerted by the gas. Suppose that the axis of the container is the x axis, and that the piston has an area A perpendicular to the axis. With this situation, we only have to worry about forces in the x direction. Let's pretend that every time a molecule hits the piston, it undergoes an elastic collision. Then if the molecule initially had an x speed v_x, then if its mass is m the momentum delivered to the piston by that molecule was $2mv_x$ (the factor of 2 is because after the collision the molecule has x speed $-v_x$). The force is the momentum per time, $F = dp/dt$, so we need to know the number of collisions per time. If the gas has number density n, then the number per time is nv_xA, so $F = nv_xA \cdot 2mv_x$. The pressure is force per area, so

$$P = 2nmv_x^2 \ . \tag{9}$$

That would be the case if all molecules had the same x component of speed, v_x. But it doesn't. Therefore, we need to take the average, so we're tempted to write $P = 2nm\langle v_x^2\rangle$. However, the molecules moving *away* from the piston don't contribute to the pressure, so only half the molecules are involved. Therefore,

$$P = nm\langle v_x^2\rangle \ . \tag{10}$$

We've only thought about the x direction, for convenience. If the gas moves isotropically, then the y and z directions must be equivalent to the x direction, so they're equal. But that also means that $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \langle v^2\rangle/3$, so we have

$$P = \frac{1}{3}nm\langle v^2\rangle = \frac{2}{3}n\langle mv^2/2\rangle = \frac{2}{3}u \ , \tag{11}$$

where u is the energy density. Therefore, pressure is proportional to energy density. Since pressure and energy density have the same units, this is something that is true in general; the proportionality factor, however, differs depending on the situation.

Keeping that in mind, what about radiation? Radiation has a momentum related to its energy by $E = pc$. As before, we can think of a piston perpendicular to the x axis, and we find that

$$P = 2np_xv_x \ . \tag{12}$$

As before, when we average we eliminate the factor of 2, and then can reexpress p_xv_x as $\mathbf{p}\cdot\mathbf{v}/3$ from isotropy, so we get

$$P = n\langle\mathbf{p}\cdot\mathbf{v}\rangle/3 \ . \tag{13}$$

In fact, this is exactly what we had before. But we also know that $\mathbf{p}$ is in the same direction as $\mathbf{v}$ and that $|\mathbf{v}| = c$, so $\mathbf{p}\cdot\mathbf{v}$ is just the energy, and $n\langle\mathbf{p}\cdot\mathbf{v}\rangle$ is the energy density. Therefore, we find for radiation

$$P = u/3 \ . \tag{14}$$

Radiation and an ideal gas both have relations between pressure and energy density that may be expressed as

$$P = (\gamma - 1)u \ , \tag{15}$$

with the property (that you can find by integrating) that

$$PV^\gamma = \text{constant} \ . \tag{16}$$

For an ideal gas, $\gamma = 5/3$; for radiation, $\gamma = 4/3$. This means that radiation is somewhat more compressible than an ideal gas. Remarkably, for stars we almost always find that $4/3 < \gamma < 5/3$, and when $\gamma \to 4/3$ the star becomes unstable. This is one example of how the equation of state can make a major difference!

Let's finish up with an example of how to manipulate thermodynamic differentials. We will use this to show that the energy density of radiation is proportional to the fourth power of temperature. From the first law of thermodynamics with $dN = 0$, we have for radiation

$$\begin{aligned} dU &= -PdV + TdS \\ d(uV) &= -(u/3)dV + TdS \\ Vdu + udV &= -(u/3)dV + TdS \\ Vdu + \tfrac{4}{3}udV &= TdS \ . \end{aligned} \tag{17}$$

We assume (correctly!) that the pressure and energy density of radiation are functions of just the temperature: $u = u(T)$. Then we have $dS = (V/T)(du/dT)dT + (4/3)(u/T)dV$. This implies $\partial S/\partial V|_T = (4/3)(u/T)$, which is a function of T. Therefore,

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial}{\partial T}\left(\frac{4}{3}\frac{u}{T}\right)\bigg|_V = \frac{4}{3}\frac{\partial}{\partial T}\left(\frac{u}{T}\right) \ . \tag{18}$$

We can also take the partial derivatives of S in the other order:

$$\begin{aligned} (\partial S/\partial T)\Big|_V &= (V/T)(du/dT) \\ (\partial^2 S/\partial V \partial T) &= (\partial/\partial V)\left((V/T)(du/dT)\right)\Big|_T = (1/T)(du/dT) \ . \end{aligned} \tag{19}$$

But partial derivatives commute, so we have

$$\begin{aligned} (4/3)(d/dT)(u/T) &= (1/T)(du/dT) \\ (1/T)(4/3)(du/dT) - (4/3)(u/T^2) &= (1/T)(du/dT) \\ (1/3)(1/T)(du/dT) &= (4/3)(u/T^2) \\ du/u &= 4dT/T \\ u &\propto T^4 \ . \end{aligned} \tag{20}$$

The constant of proportionality is $a = 7.565 \times 10^{-15}$ erg cm^{-3} K^{-4}, and depends only on fundamental constants. One can use this, and similar relations, to derive the entropy of radiation or other quantities.