

Equations of state, introduction

Our next three lectures will be on another aspect of the microphysics of stars: the equation of state. In general, the equation of state tells us the pressure as a function of quantities such as the density, temperature, and composition. The direct utility of the equation of state comes in the equation of hydrostatic equilibrium: $dP/dr = -\rho GM/r^2$ if we assume spherical symmetry. But as we will discuss, we can also understand more about the gas in a star, including the ionization fraction, which in turn has important implications for how energy is transported.

Throughout our discussion we will assume that the matter is in equilibrium. As we recall from the first lecture, this has many meanings and we won't, for example, demand that the matter is in nuclear equilibrium because that would preclude fusion! But we will assume that locally matter is in pressure equilibrium, thermal equilibrium, and ionization equilibrium, for example.

Before we go into details it's useful to check our understanding of everyday states of matter. Consider in particular air versus water. If you squeeze a container of air you can reduce the volume easily. That is, the pressure does not increase a lot with increasing density. Indeed, if you think about an ideal gas, then $P = nkT$ for number density n and temperature T . In contrast, water is *very* difficult to compress. In fact, hydraulic lifts are based on the principle that water is essentially incompressible. Thus for water, the pressure increases dramatically with increasing density (or if you like, to increase the density of water you need a *lot* of pressure).

We will now start considering our equation of state through the lens of thermodynamics. Our starting point for this will be the chemical potential:

$$\mu_i = \left(\frac{\partial E}{\partial N_i} \right)_{S,V} . \quad (1)$$

Here N_i is the number of the i th species, and the subscript S, V means that for this computation the entropy S and the volume V are held constant. Thermodynamic and chemical equilibrium require that if there are reactions that might change the N_i , then $\sum_i \mu_i dN_i = 0$. Photon number is not conserved, which means that $\mu_\gamma = 0$. Note that here we're interested in reactions that take place fairly rapidly, so things like nuclear reactions (which usually take years to billions of years) aren't included. Technically, these reactions mean that the system is *not* in equilibrium (as we noted earlier), but this is another example of how we simplify by dropping small terms. However, we should remember that it is possible to get to a lower-energy state via these reactions, and that at some point if the reactions are fast compared to chemical reactions then they must be included.

The dN_i are related to each other by particular reactions, so that means we can also write $\sum_i \mu_i \nu_i = 0$, where ν_i are the stoichiometric coefficients. For example, consider the two-way reaction by which water can be formed or dissociated: $2\text{H}_2\text{O} \leftrightarrow 2\text{H}_2 + \text{O}_2$. This implies that in equilibrium $2\mu_{\text{H}_2\text{O}} = 2\mu_{\text{H}_2} + \mu_{\text{O}_2}$, which means that $2\mu_{\text{H}_2} + \mu_{\text{O}_2} - 2\mu_{\text{H}_2\text{O}} = 0$ in equilibrium.

From thermodynamics we will now move to quantum statistical mechanics. Suppose that we have some species of particle (e.g., an electron, or an ion, or a photon, or whatever). Assume thermodynamic equilibrium at temperature T , and say that the particle has chemical potential μ , momentum p and kinetic energy at that momentum $E(p)$, and that if the particle has internal structure (e.g., an atom with different electronic configurations) that the internal energy of the particle relative to a reference point (e.g., the ground state) is $E(\text{state})$. Then the distribution function, which is the number of particles expected per volume in six-dimensional phase space (three dimensions for the coordinate and three dimensions for the momentum), is

$$n(p) = \frac{1}{h^3} \sum_{\text{states}} \frac{1}{e^{E_{\text{tot}}(\text{state})/kT} \pm 1} . \quad (2)$$

Here h is Planck's constant and $E_{\text{tot}} = -\mu + E(\text{state}) + E(p)$. Note that the energy level relative to which one determines E_{state} is a free parameter, but $-\mu + E_{\text{state}}$ isn't, which can lead to varying definitions for μ (beware!). For degenerate energy states (meaning states with the same energy) the distribution function is sometimes written with a g_j in the numerator, which is the number of states having the same energy E_j .

The ± 1 in the denominator indicates whether the particle obeys Fermi (for $+$) or Bose (for $-$) statistics. The point is that Fermi wavefunctions (for half-integral spin particles) are antisymmetric, so they avoid each other and the "occupation number" (the $1/[\exp(\text{blah}) + 1]$ bit in the distribution function) is always less than 1 because two identical fermions can't be in the same state. Electrons are examples of fermions, as are protons or neutrons or quarks. Bose wavefunctions (for integral spin particles) are symmetric, and can have occupation numbers from 0 to infinity. Photons are the best known bosons among the elementary particles, but there are other examples including the Higgs boson and, more prosaically, any nucleus with an even number of nucleons (such as helium-4).

The distribution function is in $(\text{cm-momentum})^{-3}$ units. We usually assume that momentum space is spherically symmetric (i.e., isotropic), which means that the physical number density is

$$n = \int_p n(p) 4\pi p^2 dp . \quad (3)$$

In general, the kinetic energy is $E(p) = (p^2 c^2 + m^2 c^4)^{1/2} - mc^2$. For an isotropic system the

pressure is

$$P = \frac{1}{3} \int_p n(p) p v 4\pi p^2 dp \quad (4)$$

where the velocity is $v = \partial E / \partial p$, and the internal energy density is

$$E = \int_p n(p) E(p) 4\pi p^2 dp. \quad (5)$$

We will now use this formalism to revisit some system with which we are already familiar, but from a different standpoint. Our first application will be to “perfect” noninteracting particles, for simplicity, and we will continue to assume isotropy.

Blackbody radiation. For photons, $\mu = 0$, $g = 2$ (because there are two polarizations), $E(\text{state}) = 0$ (because there are no excited states), $E(p) = pc$, and we use the minus in the denominator because photons are bosons. The photon number density is then

$$n_\gamma = \frac{8\pi}{h^3} \int_0^\infty \frac{p^2 dp}{\exp(pc/kT) - 1} \approx 20 T^3 \text{ cm}^{-3}. \quad (6)$$

The radiation pressure is $aT^4/3$ and the energy density is aT^4 , where $a = 8\pi^5 k^4 / 15c^3 h^3 = 7.6 \times 10^{-15} \text{ erg cm}^{-3} \text{ K}^{-4}$.

Monatomic ideal gas. Now let’s think about an ideal gas. Ideal means that the gas is sparse (i.e., the gas molecules don’t encroach on each other), and we’ll make the gas monatomic with no internal structure to make things simple. Since the gas is sparse, the occupation number must be $1/[\exp(E_{\text{tot}}(\text{state})/kT) \pm 1] \ll 1$, so $\exp(E_{\text{tot}}(\text{state})/kT) \gg 1$ and thus $E_{\text{tot}}(\text{state}) \gg kT$, where we recall that $E_{\text{tot}}(\text{state}) = -\mu + E(\text{state}) + E(p)$. The assumption of no internal structure means that $E(\text{state}) = 0$, and if the motion of the particles is drawn from a thermal distribution then the kinetic energy $E(p)$ is typically of the order of kT rather than being much larger than kT . This means that for an ideal gas $-\mu \gg kT$, or $\mu \ll -kT$. The chemical potential is therefore very negative for an ideal gas.

What?!? How can that make sense? I used to think that the chemical potential for a given type of particle was the change in energy of a system when you added a particle of that type. Then $\mu \ll -kT$ would be nonsensical. But what I had missed is that the chemical potential is the change in energy of a system when you add a particle of your given type *and you keep the entropy and the volume constant*. The entropy is proportional to the log of the number of equivalent microphysical ways to make the same macroscopic system. But if you add a particle to a sparse system, the number of microphysical states in the system increases a lot, just because now you have more particles and thus more states. To keep the entropy the same as it was before the addition of the particle, while also fixing the volume, you have to decrease the temperature of the system so that there are fewer momentum states for the

particles. This reduction in temperature also reduces the energy of the system, which is how the chemical potential can be very negative for ideal gases. Just another physics subtlety...

In any case, given that $\mu \ll -kT$, the ± 1 in the denominator of the distribution function can be neglected. We will assume a nonrelativistic gas for starters, so $E(p) = p^2/2m$ and $v = p/m$. The number density is then

$$n = \frac{4\pi}{h^3} g \int_0^\infty p^2 e^{\mu/kT} e^{-p^2/2mkT} dp . \quad (7)$$

This can be integrated to find the relation between μ and n , the total number density. This relation is

$$e^{\mu/kT} = \frac{nh^3}{g(2\pi mkT)^{3/2}} . \quad (8)$$

If you have a state with an energy E_j relative to the reference energy, then with this simplification the equation above would have to be multiplied by $e^{E_j/kT}$ on the rhs. Similar integrations show that $P = nkT$ (big surprise!) and $E = \frac{3}{2}nkT$.

Saha equation. This is *thermal* ionization. Consider a hydrogen atom with a single energy level (i.e., it only has a ground state rather than also having excited states), and consider the ionization reaction



where $\chi_H=13.6$ eV is the ground state binding energy. The question posed by Meghnad Saha is then: in equilibrium, what can be said about the abundance of neutral hydrogen atoms versus ionized hydrogen? In this case, let the reference energy ($E = 0$) be for the free electron and proton. The statistical weights are 2 for the hydrogen atom (one when the electron and proton spins are in the same direction, and when when they are opposite to each other), and two combined for the proton and electron (again, one where the spins are in same direction, and when when they are in opposite directions). The number densities are then

$$n_e = \frac{2[2\pi m_e kT]^{3/2}}{h^3} e^{\mu^-/kT} , \quad (10)$$

$$n^+ = \frac{[2\pi m_p kT]^{3/2}}{h^3} e^{\mu^+/kT} , \quad (11)$$

and

$$n^0 = \frac{2[2\pi(m_p + m_e)kT]^{3/2}}{h^3} e^{\mu^0/kT} e^{\chi_H/kT} . \quad (12)$$

If we were being *really* accurate, would the actual mass in the third equation be $m_p + m_e$? (No, because we'd have to subtract the binding energy. But this is only a correction of magnitude 13.6/511,000, and can thus be ignored. In the same spirit, the electron mass is only a 1/1,800 correction and can be ignored here.)

Forming the product n^+n_e/n^0 , we find

$$\frac{n^+n_e}{n^0} = \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{(\mu^- + \mu^+ - \mu_0)/kT} e^{-\chi_H/kT} . \quad (13)$$

Given our assumption of equilibrium, $\mu^- + \mu^+ - \mu_0 = 0$. The numerical factor is about $2.4 \times 10^{15} T^{3/2} \text{ cm}^{-3}$. But this equation by itself is not sufficient to determine the abundances of electrons, protons, and neutral hydrogen, because we have only one equation for three unknowns. What are reasonable auxiliary conditions? Charge balance implies $n^+ = n^-$, and conservation of nucleons means that $n^0 + n^+ = n$, where n is the total number density. With these extra conditions, the degree of ionization $y \equiv n^+/n = n_e/n$ is, numerically,

$$\frac{y^2}{1-y} = \frac{4 \times 10^{-9}}{\rho} T^{3/2} e^{-1.6 \times 10^5/T} , \quad (14)$$

where as usual quantities such as ρ and T are referenced to the appropriate cgs unit.

When we look at this equation we see that the ionization fraction for a fixed temperature goes up when the density goes down. Why is that? This is thermal ionization, so you can imagine some radiation field pervading the region. The ionization rate per volume, therefore, just goes like the number density. However, the recombination rate involves two particles, and hence must go as the product of their densities. Therefore, the recombination rate increases more rapidly than the ionization rate when the density goes up, and the resulting ionization fraction goes down.

We always must make sure to use equations only in their domain of applicability! As an example using the Saha equation, let's compute the ionization fraction in the center of the Sun. Using $T = 1.5 \times 10^7 \text{ K}$ and $\rho = 100 \text{ g cm}^{-3}$, we find that $y^2/(1-y) = 2.3$. This has a solution of $y = 0.75$, so the center of the Sun is 25% neutral (!). This is nonsense, of course. The resolution is that at such densities, the separation between atoms is much less than the size of an individual free atom, so the electrons get squeezed up to continuum states and *pressure* ionization dominates.

Returning to the Saha equation, and assuming that only thermal ionization matters, we run into what appears to be a big problem. What we really should have included was *all* energy states of the atom. This sum would diverge because there are in principle an infinite number of finite terms that would have to be summed in this way. This would mean that all atoms are neutral, all the time. What is the resolution of this apparent paradox?