Equations of state: interactions and high density

To this point in our discussions about the equation of state, we have assumed an ideal gas. Yes, it might be weird (e.g., degenerate!), and we've taken quantum statistics into account, but we haven't worried about direct interactions between particles. In this lecture, we'll worry a little :)

Coulomb interactions: Back when you first learned about states of matter, you were probably told that there are three: solid, liquid, and gas. The effect we've been ignoring that leads to these states is electrostatic interactions between atoms or molecules. **Ask class**: if we have defined some characteristic electrostatic energy E_c, what is a reasonable energy with which to compare it in order to determine whether it is an important correction? Since we have previously introduced two energies in this context (the thermal energy kT and the Fermi energy E_F), these are good comparison energies. If we assume that the gas is fully ionized and therefore consists, to a first approximation, of a uniform distribution of electrons plus positive charges concentrated in individual nuclei of charge Z, then the electrostatic energy between an electron and its nearest nucleus (assumed to be at a typical distance $\langle r\rangle$) is approximately $E_c = Ze^2/\langle r\rangle$. At an electron number density n_e, $\langle r\rangle \sim n_e^{-1/3}$, so $E_c \sim Ze^2 n_e^{1/3}$. Therefore, the ratio of Coulomb (electrostatic) energy to thermal energy is

$$\frac{E_c}{kT} = \frac{Ze^2 n_e^{1/3}}{kT} \tag{1}$$

and the ratio of Coulomb to Fermi energy (which we assume to be nonrelativistic) is

$$\frac{E_c}{E_F} = \frac{Ze^2 n_e^{1/3}}{p_F^2/2m_e} = \left(\frac{n_e}{Z^3 \times 6 \times 10^{22}\,\mathrm{cm}^{-3}}\right)^{-1/3} . \tag{2}$$

This is not a major correction for most degenerate gases.

Wigner-Seitz approximation: Now we'll try to do things a bit more carefully. We will divide our system into spherical "cells", which at number density n have volume $1/n = 4\pi r_0^3/3$ (where this defines the radius r_0 of the cell) and assume that each cell is electrically neutral because it contains a nucleus of charge $+Ze$ and a uniform sphere of electrons of total charge $-Ze$. The total electrostatic energy per electron is then the electrostatic energy of the electrons with themselves (which is positive), plus the energy of the electrons with the protons (which is negative). The total turns out to be

$$E_c/Z = -\frac{9}{10}\left(\frac{4\pi}{3}\right)^{1/3} Z^{2/3} e^2 n_e^{1/3} . \tag{3}$$

As always we should ask: is this reasonable? For example, is it correct that the energy is negative? Yes, because this configuration is bound; if the energy were positive it would cause the system to fly apart. As another question, we could ask: is it correct that the energy depends directly on density? Yes, because more tightly squeezed means greater electrostatic binding energy.

Because electrostatic interactions add negative energy, they also decrease the pressure compared with what it would be with no interactions. For example, in the nonrelativistic limit,

$$P/P_0 = 1 - \frac{Z^{2/3}}{2^{1/3}\pi a_0 n_e^{1/3}} \,, \tag{4}$$

where P_0 is the degeneracy pressure without interactions and $a_0 = \hbar^2/me^2 \approx 5 \times 10^{-9}$ cm is the Bohr radius. We see that $n_e^{1/3}$ is in the denominator, which means that as the density becomes higher, the fractional correction becomes smaller. This might not initially make sense, because from Equation 3 it is clear that higher densities mean larger electrostatic energies. However, in the nonrelativistic limit, the Fermi energy increases more rapidly with density than the electrostatic energy ($E_F \sim n^{2/3}$), so the fractional correction is smaller.

When we do our usual sanity checks we run into trouble. For example, in the limit $n_e \to 0$ we find that $P/P_0 \to -\infty$. Not good! Another problem is apparent if you ask when $P = 0$, which would be the equilibrium state of zero-pressure material. This formula would predict that the pressure is zero (implying stable matter) at $\rho_0 = 0.4Z^2$ g cm^{-3}, or 250 g cm^{-3} for iron instead of the correct 7.86 g cm^{-3}! When we run into problems such as this it is good to ask ourselves: how might our assumptions fail at low densities? One issue is that we assumed uniformly spread negative charges. But for low densities, the electrons cluster much more towards the nuclei and thus the charge distribution is *not* uniform. Accounting for such effects is the basis of Thomas-Fermi or Thomas-Fermi-Dirac models, but that would take us too far afield.

Formation of crystalline lattice: **Ask class:** what should we compare when trying to determine whether a crystalline lattice will form? It is again an energetics issue; when the lattice energy is large enough compared to the temperature and Fermi energy of the *ions* (we're not talking about electrons at this point), the matter can go from a liquid phase to a crystalline, solid phase in which the Coulomb energy is minimized. **Ask class:** When we're talking about ions, would we expect the thermal energy or Fermi energy to dominate? Usually thermal, because the Fermi energy is a factor m_e/m_i lower than for electrons, and for most densities is small. Therefore, we need to compare $(Ze)^2/r_i$, the Coulomb energy, with kT, the thermal energy. The full calculation is complicated, but one can eventually get an estimate of the critical ratio using Lindemann's empirical rule that the lattice will melt when the mean square fluctuations in the ion position become

$$\frac{\langle(\delta r_i)^2\rangle}{r_i^2} \sim \frac{1}{16} \tag{5}$$

or more. Full inclusion of lots of stuff shows that the critical ratio Γ between the Coulomb energy and the thermal energy necessary to crystallize is $\Gamma \approx 170$. This is important in the late stages of white dwarf cooling; indeed, it delays cooling of white dwarfs because of the energy released during crystallization.

Let's use the $\Gamma = 170$ value to estimate the melting temperature of iron. For iron, $Z = 26$, $A = 56$, and the typical density of solid iron is about 8 g cm^{-3}. Thus $n \approx 8/(56 \times 1.7 \times 10^{-24}) \approx 8 \times 10^{22}$ cm^{-3}, or about 10^{-23} cm^3 per atom. That's about $r = 1.4 \times 10^{-8}$ cm. So, $(Ze)^2/r \approx 10^{-8}$ erg per atom. Dividing this by 170, we get 6×10^{-11} erg, which when we divide by Boltzmann's constant $k \approx 1.38 \times 10^{-16}$ erg K^{-1} gives us about 500,000 K! Wow! What went wrong? The answer is that we used the full, bare charge $Z = 26$ of the iron nucleus. In reality, the electrons in inner orbitals shield the iron, so the effective charge is much less. Therefore, the Coulomb energy is a lot less as well, and the melting temperature is more like 2,000 K. This is an example of the complexities that can enter into these kinds of calculations. It's always a good idea to start off simply, but sometimes you need to include additional effects.

Magnetic fields: Magnetic fields can affect the equation of state or properties of the matter in two ways. One is to make a contribution to the pressure: $P_B = B^2/8\pi$. For example, in the center of the Sun, the ideal gas pressure nkT is about 10^{17} cgs, requiring $B \sim 10^9$ G to compete (the magnetic field is nowhere close to that strong). The other possible effect of magnetic fields to change the opacities significantly. Zeeman splitting can be seen in laboratories even with extremely weak fields, but to really make a big difference, the cyclotron energy $\hbar\omega_c = \hbar eB/mc$ has to be comparable to the binding energy of an electron. This means $B \sim 10^9$ G again for hydrogen, which is only true in neutron stars or possibly some white dwarfs. Note that for more excited states, in which the atomic binding energy is reduced, the threshold magnetic field is less.

Higher densities: Let us now think about what happens to the equilibrium composition of matter as the density increases. Consider a fully ionized gas of protons, neutrons, and electrons (i.e., at this stage we are not including more complicated nuclei). **Ask class:** at low density, what is the equilibrium composition? Just protons and electrons, because neutrons are unstable. That's because the neutron rest mass is greater than the sum of the rest masses of the proton and electron. **Ask class:** energetically, when would one expect it to be favorable for neutrons to exist? When the total energy of the electron becomes large enough that $m_n c^2 \leq m_p c^2 + E_e$, neutrons will be favored. This will occur when the Fermi energy of the electrons plus their rest mass is large enough; $c^2(m_n - m_p - m_e) \approx 1.2$ MeV, so that's what E_F needs to be. **Ask class:** given that electrons, with a mass-energy of 511 keV, become relativistically degenerate at $\rho \sim 10^6$ g cm^{-3}, at approximately what density would we expect their Fermi energy to be 1.2 MeV? In the relativistic regime, $E_F \sim p_F \sim n^{1/3}$, so the expected density is about $\rho \approx 10^6(1.2/0.511)^3 \approx 10^7$ g cm^{-3}.

On to neutron drip: But in reality, there are nuclei around instead of just pne. At low densities, the equilibrium nucleus is ^{56}Fe. As we may remember, this is explained qualitatively by a competition between nuclear and electrostatic forces. At small distances the nuclear strong force is much stronger than the electromagnetic force, so the binding energy increases with more nucleons. However, the strong force has a tiny range (dropping off exponentially with a typical distance $\sim 10^{-13}$ cm), whereas the electrostatic force drops off only as $1/r^2$, without any exponential factor. Thus as the nucleus grows in size the Coulomb energy grows in importance relative to the nuclear energy, and a balance is struck in equilibrium with iron. We might wonder: since the nuclear force is short-range, why couldn't we just make large nuclei a lot denser? Because the (positive) Fermi energy grows with decreasing separation, which is why there is a maximum density for nuclei (called nuclear saturation density) when there is no significant external pressure.

Anyway, as the density increases, the increased Fermi energy of the electrons means that, overall, it becomes energetically more favorable to have extra neutrons, so the equilibrium nuclei become progressively more neutron-rich. The calculation of the equilibrium nucleus at a given density is complicated, and revisions occur from time to time. At about $\rho = 4 \times 10^{11}$ g cm^{-3}, when the equilibrium nuclei are things like ^{118}Kr, the outermost neutrons in the nucleus have zero total energy and hence can "drip" out of the nucleus, producing a system of electrons, neutrons, and nuclei.

Note: Although it is possible to calculate the equilibrium nucleus at a given density there is no guarantee that everything at that density will be in that state. That's good for us, because otherwise we'd all be lumps of iron! In principle the same is true at high densities, where it could have important effects in certain circumstances. For example, impurities can change the conductivity in white dwarfs or neutron stars substantially, although calculations starting in the early 2000s have suggested that at the immense pressure of the inner crusts of neutron stars, impurities and dislocations are squeezed out of the crusts and thus neutron star crusts may be nearly perfect crystals.

Higher densities: Above neutron drip, as the density increases the composition becomes more and more neutron-dominated, with some nuclei in a sea of neutrons. When care is taken to determine the energy of nuclei, including terms such as the surface tension, it is found that as the density increases the shapes of the nuclei change. (Remember that nuclear density is 2.7×10^{14} g cm^{-3}, so at neutron drip we're still a factor of a few hundred away). At the lowest densities of the inner crust we expect spherical nuclei in a tenuous(!) sea of neutrons. At higher densities we expect elongated line-like nuclei. At yet higher densities, 2-D sheets of nuclei with gaps in between. Then with even higher densities the gaps between the sheets shrink, then space is mostly nucleons with line-like "holes", then mostly nucleons with spherical "holes". This is dubbed the "pasta-antipasta" sequence: meatballs (or gnocchi), spaghetti, lasagna, anti-lasagna, anti-spaghetti, anti-meatballs (Swiss cheese?).

At about nuclear density, we expect mostly (>90%) neutrons plus equal numbers of protons and (electrons+muons), where we remember that muons are leptons that are effectively heavy electrons. There might be additional particles that appear at a few times nuclear density. At lowest order we might expect new particles when the Fermi energy of neutrons plus the neutron rest mass-energy is greater than the rest mass-energy of a new particle. For example, lambda hyperons (which have strange quarks) have a rest mass of 1116 MeV. When we estimate the density at which the total energetic cost of a neutron is about 1116 MeV, it's about 10^{15} g cm^{-3}. That's pretty high, but it might be reachable, and the actual needed density will depend on interactions between the new particles and neutrons/protons/themselves. Any such new components (strange matter, quark matter, hyperons, kaons, pions, etc.) tend to soften the equation of state, which would mean that the maximum mass is less than it would have been without the exotica. This, in turn, means that measurements of the masses (and ideally the radii) of neutron stars can give us valuable information about the state of the cores of neutron stars. I'm involved in one project, NASA's NICER (Neutron star Interior Composition ExploreR) mission, whose goal and achievement is to measure the radii of some neutron stars with reliability as well as precision.

Important point: When there is a density-induced phase transition such as this, in which it is energetically favorable to change composition, the equation of state becomes "soft", meaning that the energy density (and hence the pressure) does not increase as rapidly with increasing density as it had been, so it's easier to squeeze (assuming that the new form of matter doesn't rise rapidly in pressure with increasing density). This has crucial consequences for a number of systems. For example, in the early universe there was a QCD phase transition; when matter went from being a quark-gluon soup to being nuclei, the universe was extra squeezeable and black holes may have formed directly. In principle this could mean that black holes of a few to a few hundred solar masses could comprise dark matter in the universe; their formation occurred before big bang nucleosynthesis, so matter in this form would not interfere with BBN. On the other hand, constraints are strong on black holes as dark matter; at this stage, about the only window left open is that primordial black holes with the masses of asteroids ($\sim 10^{17} - 10^{23}$ g) could make up most to all of the dark matter we infer, but outside that mass range the prospects are poor.