Equations of state, introduction

Discuss homework. Very pleased in general. Remember to take the problem algebraically to where you were asked! (Problem 1). Apologize for not making expectations clear for fourth problem (rough answer would have been fine! For current I. M. N. Sane problem, all they need to do is disprove his model, it doesn't have to be done to lots of significant figures. But a numerical estimate is important). **Mention**: Greenland story (Maryland is about 10,000 sq. mi.), make hamster estimates. Explain constancy of angular momentum (torque is $\mathbf{r} \times \mathbf{F}$, so changing the central force does not change the angular momentum). Also report that the music on the front cover is definitely "Twinkle, Twinkle, Little Star", or more precisely the sixth variation that Mozart composed on that theme.

The equation of state, in general, is the relation between pressure, density, and temperature. Included in this is the idea of the ionization level. Go through states of matter in ordinary experience: gas, liquid, solid. What are the kinds of things that determine what state you're in? Composition matters as well as density and temperature.

Recap why LTE is a good approximation. Also recap why it is that we care about the equation of state. LTE is a good approximation **Ask class** because the distances over which important things change (for example, the pressure or temperature) are much greater than the mean free path of a photon (assuming radiative transfer is most important). Calculate this: pressure scale height is

$$\lambda_P = -\left(\frac{d\ln P}{dr}\right)^{-1} = \frac{P}{g\rho} = \frac{R^2}{2r}\left[1-\left(\frac{r}{R}\right)^2\right] , \qquad (1)$$

where the last equality holds for a constant-density star. This is infinite at the center and of order R for most of the star. The temperature gradient we already went through: if we take 10^7 K over 10^{11} cm as an approximate value, that's 10^{-4} K cm^{-1}. By comparison (**ask class**), the distance typically traveled by a photon is $(n\sigma)^{-1} = (\kappa\rho)^{-1}$, or about 1 cm. Thus, although there is energy flow, it occurs on large length scales and locally, thermodynamic equilibrium is usually an excellent approximation. **Ask class:** what are some circumstances in which this might not be a good approximation? (supernova, nova, possibly large-scale convection). Also not a great approximation anywhere outside the stellar photosphere, where the material is optically thin (e.g., the corona). Is LTE a reasonable approximation in the classroom? Cold air from outside, hot air from professors. Again, need $(n\sigma)^{-1}$, which is about $(10^{20}10^{-16})^{-1} = 10^{-4}$ cm, so probably yess.

Chemical potential:

$$\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V} . \qquad (2)$$

Here N_i is the number density per gram of the ith species, so that $N_i = n_i/\rho$. 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, so $\mu_\gamma = 0$. 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, 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. From this, can see in another way that $\mu_\gamma = 0$: if a reaction of the form $A \to B + \gamma$ is allowed, so is $A \to B + \gamma + \gamma$. If μ_γ were nonzero, equilibrium would not be possible.

A lot of the interesting thermodynamic quantities can be calculated from the distribution function in 6-dimensional phase space (three coordinate, three momentum). This is also called the occupation number. For a given species, the distribution function for a particular momentum is

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

Here $E_{\rm tot} = -\mu + E({\rm state}) + {\rm E(p)}$, where E(state) is the energy of the state of that species relative to some level (often the ground state energy) and $E(p)$ is the kinetic energy for momentum p. For degenerate energy states this is sometimes written with a g_j in the numerator, which is the number of states having the same energy E_j. Same deal. Of course (**ask class**) the ± 1 refers to Fermi or Bose statistics. The distribution function is in (cm-momentum)$^{-3}$ units. Usually assume that momentum space is spherically symmetric, so that the physical number density is

$$n = \int_p n(p) 4\pi p^2 \, dp \; . \tag{4}$$

In general, the kinetic energy is **Ask class:** $E(p) = (p^2c^2 + m^2c^4)^{1/2} - mc^2$. The isotropic pressure is

$$P = \frac{1}{3} \int_p n(p) p v 4\pi p^2 \, dp \tag{5}$$

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

$$E = \int_p n(p) E(p) 4\pi p^2 \, dp \; . \tag{6}$$

Tell class: we are now going to concentrate for a while on "perfect" noninteracting particles, for simplicity. Later, we will think about the interactions of particles with other particles, which is what produces the liquid and solid states. Still later, we will talk about really high densities and some of the things that can arise in white dwarfs and neutron stars.

Specific application: blackbody radiation. **Ask class**: for photons, what is μ (0), g (2, because there are two polarizations), E_j (zero, because there are no excited states), $E(p)$ ($E(p)=pc$), and plus or minus in the denominator (minus, because photons are bosons). Put it together and what have you got? (bippity boppity boo, but never mind that). The photon number density is then

$$n_\gamma = \frac{8\pi}{h^3}\int_0^\infty \frac{p^2\,dp}{\exp(pc/kT)-1} \approx 20\,T^3\ \mathrm{cm}^{-3}\ . \tag{7}$$

The radiation pressure is $aT^4/3$ and the energy density is aT^4, where $a=8\pi^5k^4/15c^3h^3=7.6\times10^{-15}$ erg cm^{-3} K^{-4}. **Ask class**: we talked about gamma-law equations of state earlier. What does this mean for gamma? ($P=(\gamma-1)E$, so $\gamma=4/3$). What consequence does that have for a star whose pressure and energy density are dominated by radiation? Close to instability. This is one of the reasons that very high-mass stars $M>100\,M_\odot$ are not very stable. For somewhat separate reasons having to do with cooling, accretion disks that are dominated by radiation pressure are also unstable.

From this, we can also get the spectral distribution for a blackbody.

$$u_\nu\,d\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}d\nu\ \mathrm{erg\ cm^{-3}\ Hz^{-1}\ Hz}\ . \tag{8}$$

Monatomic Gas: The bit about $\mu\ll0$ for an ideal gas can be derived by computing the number density and then getting μ from it; can assume it now and find that it is correct.

Given that it is, the ±1 in the denominator is superfluous. Assume a nonrelativistic gas for starters, so **Ask class**: $E(p)=p^2/2m$ and $v=p/m$. Assume only one energy level, $E=E_0$; we can reference the energy to this single energy level and define $E_0=0$ (this simply redefines μ relative to that energy level, and different definitions exist in the literature). For an ideal gas $\mu\ll-kT$. The number density is then

$$n=\frac{4\pi}{h^3}g\int_0^\infty p^2e^{\mu/kT}e^{-p^2/2mkT}\,dp\ . \tag{9}$$

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

$$e^{\mu/kT}=\frac{nh^3}{g(2\pi mkT)^{3/2}}\ . \tag{10}$$

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.

Ask class: for, say, hydrogen gas, when would one expect this expression to be self-inconsistent such that $\mu\not\ll-kT$, meaning that $e^{\mu/kT}\ll1$? Ask them to make an estimate for the density given room temperature of $\sim$ 300 K, then work out on the board. Reasonable to expect that when the orbitals overlap the expression is no longer valid. This would be the case when the average separation is comparable to the size of each atom, so if separation is about 10^{-8} cm, then $n = 10^{24}$ cm^{-3} is the density. For T=300 K, $e^{\mu/kT} = 1$ at $n = 2 \times 10^{24}$ cm^{-3} if $g = 2$, so this conforms to intuition.

Similar integrations show that $P = nkT$ (big surprise!) and $E = \frac{3}{2}nkT$. What is gamma-law for this equation of state? ($P = (\gamma - 1)E$, so $\gamma = 5/3$).

Saha equation: This is *thermal* ionization. Consider a hydrogen atom with a single energy level (ground state), and consider the ionization reaction

$$H^+ + e^- \longleftrightarrow H^0 + \chi_H \ , \tag{11}$$

where χ_H=13.6 eV is the ground state binding energy. In equilibrium, what can be said about the abundances? In this case, let the reference energy ($E = 0$) be for the free electron and proton. Statistical weights: 2 for the hydrogen atom, two combined for the proton and electron (spins in same direction, spins in opposite directions). The number densities are then

$$n_e = \frac{2[2\pi m_e kT]^{3/2}}{h^3} e^{\mu^-/kT} \ , \tag{12}$$

$$n^+ = \frac{[2\pi m_p kT]^{3/2}}{h^3} e^{\mu^+/kT} \ , \tag{13}$$

and

$$n^- = \frac{2[2\pi(m_p + m_e)kT]^{3/2}}{h^3} e^{\mu^0/kT} e^{\chi_H/kT} \ . \tag{14}$$

Ask class: 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 13.6/511,000 or a 1/40,000 correction, and can be dumped. 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

$$\frac{n^+ n_e}{n^0} = \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{(\mu^- + \mu^+ - \mu_0)}/kT e^{-\chi_H/kT} \ . \tag{15}$$

Ask class: what is $(\mu^- + \mu^+ - \mu_0)$ in equilibrium, which we've been assuming? It's zero. The numerical factor is about $2.4 \times 10^{15} T^{3/2}$ cm^{-3}. **Ask class**: is this equation sufficient to determine the abundances of electrons, protons, and neutral hydrogen? No, because we have only one equation for three unknowns. **Ask class**: what are reasonable auxilliary conditions? Charge balance implies $n^+ = n^-$, and conservation of nucleons means that $n^0 + n^+ = n$, the total number density. With these extra conditions, the degree of ionization $y \equiv n^+/n = n_e/n$ is, numerically,

$$\frac{y^2}{1-y} = \frac{4 \times 10^{-9}}{\rho} T^{3/2} e^{-1.6 \times 10^5/T} \ , \tag{16}$$

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

Ask class: what does this mean about the degree of ionization for a fixed temperature but varying density? (degree of ionization goes up when 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 when the density goes up, and the resulting ionization fraction goes down.

Ask class to compute ionization fraction in the center of the Sun. Suppose **Ask class** $T = 1.5 \times 10^7$ K and $\rho = 100$ g cm^{-3}, for round numbers. Then $y^2/(1-y) = 2.3$. This has a solution of $y = 0.75$, so the center of the Sun is 25% neutral (!). **See if this poses a problem for anyone in class!**. This is nonsense, of course. 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. Go back to the original Saha equation and indicate that what really should have been included was *all* energy states of the atom, and that this sum would diverge because there are in principle an infinite number of finite terms that would have to be summed in this way. In reality, the size of the orbital increases like n^2, so in most circumstances only the first term needs to be kept, as we did.

Idea of degeneracy. Note, however, that uncertainty principle means that even for bosons the energy goes up with increasing density, and so provides support. At some point I do want to go into topics appropriate for high density, i.e., white dwarfs and neutron stars.