Unit 6

Equation of state: Ideal gas

6.1 Preliminaries

- First we recall the distribution function and do a little thermodynamics with them.
- A distribution function simply measures the number density of a species in 6D space of position and momentum.
- If we know this function for a gas, all thermodynamic quantities can be derived (pressure, temperature, density, composition).
- Equations of state relate pressure, temperature, and number of particles.
- An ideal gas is one in which the particles don't interact (except through elastic collisions). They can exchange energy though, but have to conserve it.
- This approximation breaks down when matter is degenerate, and particles begin to "sense" each other and interact in quantum fashion or otherwise.
- An important thermodynamical quantity is the chemical potential μ_c for each species, that was introduced earlier. For classical particles, $\mu_c \to -\infty$, for degenerate fermions $\mu_c \to \epsilon_{\mathrm{F}}$, for bosons $\mu_c = 0$.
- Chemical changes in the gas use the chemical potential to monitor particle numbers, and thus to achieve a chemical equilibrium (in addition to thermodynamic equilibrium).
- In thermodynamic equilibrium, statistical mechanics tells us the relationship between the number density (of phase space, ie, number per unit volume per unit momentum: $\mathrm{d}^3\boldsymbol{r}\,\mathrm{d}^3\boldsymbol{p}$) of a species

$$n(p) = \frac{1}{h^3} \sum_j \frac{g_j}{\exp\left\{\left[E_j + E(p) - \mu_c\right]/k_{\mathrm{B}}T\right\} \pm 1}, \tag{6.1}$$

  where

  - j are the possible energy states of the species (like energy levels in an ion), and E_j is the energy of that level
  - $E(p)$ is the kinetic energy
  - g_j is the degeneracy of state j (number of states with same energy)
  - ± is either for fermions or bosons, respectively.

  Note that the units of Planck's constant are length times momentum (remember the uncertainty principle). We will come back to this frequently.

- To find the number density (particles cm^{-3}) we integrate $n(p)\,\mathrm{d}^3 p$ over momentum space (assumed to be symmetric)

$$n = \int_p 4\pi p^2 n(p)\,\mathrm{d}p. \tag{6.2}$$

- To remain completely general, the kinetic energy of a particle of rest mass m is

$$E(p) = (p^2c^2 + m^2c^4)^{1/2} - mc^2. \tag{6.3}$$

IN CLASS WORK

What does this expression reduce to in the nonrelativistic limit?

Answer: In this limit, we note that $pc \ll mc^2$, so one can expand the term in the square root:

$$\begin{aligned} E(p) &= mc^2\left(1+\frac{p^2c^2}{m^2c^4}\right)^{1/2} - mc^2, \\ &\approx mc^2\left(1+\frac{1}{2}\frac{p^2c^2}{m^2c^4}\right) - mc^2, \\ &\approx \frac{p^2}{2m}, \end{aligned}$$

which is the expression we'd expect.

- Now we can define three general quantities:
  1. Velocity:

$$v = \frac{\partial E}{\partial p}. \tag{6.4}$$

  2. Pressure:

$$P = \int_{\boldsymbol{p}} n(\boldsymbol{p})\boldsymbol{v}\cdot\boldsymbol{p}\,\mathrm{d}^3\boldsymbol{p} = \frac{1}{3}\int_p n(p)v\,p\,4\pi p^2\,\mathrm{d}p, \tag{6.5}$$

     where the last equality comes from assuming isotropy of pressure.
  3. Internal energy density (energy per unit volume):

$$u = \int_p n(p)E(p)4\pi p^2\,\mathrm{d}p. \tag{6.6}$$

- These general considerations can soon be applied to specific cases.

6.2 Maxwell-Boltzmann statistics

- The relation of Equation (6.1) to classical probability functions is found through Equation (6.11) and Equation (6.12). These tell us the fraction of particles within an infinitesimal element of 3-dimensional space (velocity, energy, or momentum space).

- In momentum space

$$f(p)\,\mathrm{d}p = \frac{4\pi}{(2\pi m k_{\mathrm{B}}T)^{3/2}} e^{-p^2/2mkT} p^2\,\mathrm{d}p. \tag{6.7}$$

- In energy space

$$f(E)\,\mathrm{d}E = \frac{2}{\sqrt{\pi}(k_{\mathrm{B}}T)^{3/2}} e^{-E/kT}\sqrt{E}\,\mathrm{d}E. \tag{6.8}$$

- In velocity space
$$f(v)\,\mathrm{d}v = 4\pi\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} e^{-mv^2/2kT} v^2\,\mathrm{d}v. \tag{6.9}$$

- These are normalized such that the integrals of each quantity over velocity, momentum, or energy are equal to 1.

6.3 Ideal monatomic gas

- As a first demonstration, we consider a gas of single species nonrelativistic particles. We will be using Equation (6.1).

- Their energy is $E = p^2/2m$. Consider one energy level $E_j = E_0$.

- For this system, the chemical potential goes to negative infinity (as we'll see), so the exponential term is large, and the ±1 term can be safely ignored.

- The number density of particles in any given momentum state p is
$$n(p) = \frac{g}{h^3} e^{-p^2/2mkT} e^{-E_0/kT} e^{\mu_{\mathrm{c}}/kT}, \tag{6.10}$$
and so the total number density over all momenta is
$$n = \frac{4\pi g}{h^3}\int_0^\infty p^2 e^{-p^2/2mkT} e^{-E_0/kT} e^{\mu_{\mathrm{c}}/kT}\,\mathrm{d}p. \tag{6.11}$$

- The integral is straightforward and gives an expression
$$n = \frac{(2\pi m k_{\mathrm{B}}T)^{3/2} g}{h^3} e^{-E_0/kT} e^{\mu_{\mathrm{c}}/kT}. \tag{6.12}$$

- Another way to write this is
$$e^{\mu_{\mathrm{c}}/kT} = \frac{nh^3}{g(2\pi m k_{\mathrm{B}}T)^{3/2}} e^{E_0/kT}. \tag{6.13}$$
Since we are assuming that the term on the left is small (since $\mu_{\mathrm{c}} \ll -1$), then the right hand side must also be small. Specifically, $nT^{-3/2}$ cannot be too large. If that were the case, then we would not be able to ignore the ±1 term in the distribution function.

- Returning to the definition of gas pressure in Equation (6.5), we can compute the integral to find
$$P = g\frac{4\pi}{h^3}\frac{\pi^{1/2}}{8m}(2mk_{\mathrm{B}}T)^{5/2} e^{-E_0/kT} e^{\mu_{\mathrm{c}}/kT}. \tag{6.14}$$

- Using the generalized number density from Equation (6.12), this gives what you thought it would
$$P = nk_{\mathrm{B}}T\ [\mathrm{dyne\,cm^{-2}}]. \tag{6.15}$$
This is the equation of state for an ideal gas.

- Similarly we can compute the internal energy density from Equation (6.6)
$$u = \frac{3}{2}nk_{\mathrm{B}}T = \frac{3}{2}P;\ [\mathrm{erg\,cm^{-3}}]. \tag{6.16}$$

- Note that the units of pressure and internal energy density are the same.

- From what we saw before with the mean molecular weight, we can also express these quantities as

$$n = \frac{\rho}{\mu m_{\mathrm{u}}}, \tag{6.17}$$

$$P = \frac{\rho k_{\mathrm{B}} T}{\mu m_{\mathrm{u}}}, \tag{6.18}$$

$$P = \frac{\rho R T}{\mu}, \tag{6.19}$$

where μ is the mean molecular weight, and $R = k_{\mathrm{B}}/m_{\mathrm{u}}$ is the ideal gas constant $R = 8.31 \times 10^7\,\mathrm{erg\,K^{-1}\,mol^{-1}}$.

EXAMPLE PROBLEM 6.1: Instead of arriving at Equation (6.16) through the energy formulation, one can use velocity to show that the average internal kinetic energy per particle is $3/2 k_{\mathrm{B}} T$. Hint: Start with the Maxwellian distribution for a classical gas in velocity (Equation (6.9)) and then compute the mean square speed $\langle v^2 \rangle$. The integration limits of v should be from zero to infinity.

Answer: The mean square speed can be written as

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v) \mathrm{d}v,$$

where $f(v)$ is the Maxwell distribution. One can (and should) use a table of integrals to find that

$$\int_0^\infty x^n e^{-ax^2} \mathrm{d}x = \frac{(2k-1)!!}{2^{k+1} a^k} \left(\frac{\pi}{a}\right)^{1/2},$$

where $n = 2k$ and in our case $a = m/2k_{\mathrm{B}}T > 0$. Note the double factorial, which, for $k = 2$, is $3 \times 1 = 3$. The result is

$$\langle v^2 \rangle = 4\pi \left(\frac{m}{2\pi k_{\mathrm{B}} T}\right)^{3/2} \cdot \frac{3}{8} \frac{\pi^{1/2}}{a^{5/2}},$$

and after cancellation becomes

$$\langle v^2 \rangle = \frac{3 k_{\mathrm{B}} T}{m}.$$

The kinetic energy is then $1/2 m \langle v^2 \rangle = 3/2 k_{\mathrm{B}} T$, precisely what we set out to prove.