

PHYS 617 - Statistical Mechanics  
A Modern Course in Statistical Physics by *Linda E. Reichl*  
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## Homework 2

### Problem 1

Derive the multiplicity factor  $\Omega(E, V)$  and the equation of state for a relativistic gas of particles.  
Recall the formula relating energy and momentum

$$\epsilon^2 = p^2 c^2 + m^2 c^4$$

and assume the system is ultra-relativistic, so that  $p^2 c^2 \gg m^2 c^4$ .

What is the total energy  $E$  of the system as a function of the temperature  $T$ ?

What is the pressure  $P$  as a function of the temperature?

What is the adiabatic index  $\gamma$  describing this system? (i.e.  $P = Kn^\gamma$  for adiabatic expansion or compression, where  $n$  is the number density).

*Proof.* Assume our system has  $N$  particles in 3 dimensions. We know the description for that system is equivalent to  $3N$  particles in 1 dimension or 1 particle in  $3N$  dimensions.

Since the system is ultra-relativistic, then  $p^2 c^2 \gg m^2 c^4 \implies \epsilon = pc \implies p = \frac{\epsilon}{c}$ . Additionally, since this is a system of  $3N$  particles in 1 dimension, each with energy  $\epsilon_i$ , then the total energy of the system  $E$  is given by

$$E = \sum_{i=1}^{3N} \epsilon_i = c \sum_{i=1}^{3N} p_i.$$

The possible positions is given by the hypervolume of the position space, which is  $\frac{V^N}{N!}$ . The possible momenta is given by the hypervolume of the momentum space, which is  $\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} R^{3N-1}$ , where  $R = \sum_i p_i = \frac{E}{c}$ .

Then, the multiplicity factor is

$$\begin{aligned} \Omega(E, V) &= \frac{(\# \text{ possible positions})(\# \text{ possible momenta})}{h^{3N}} \\ &= \frac{(\text{area of position space})(\text{area of momentum space})}{h^{3N}} \\ &= \frac{\left(\frac{V^N}{N!}\right) \left(\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} R^{3N-1}\right)}{h^{3N}} \\ &= \frac{\left(\frac{V^N}{N!}\right) \left(\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} \left(\frac{E}{c}\right)^{3N-1}\right)}{h^{3N}} \\ &\sim \frac{\left(\frac{V}{N}\right)^N \left(2 \left(\frac{2\pi}{3N}\right)^{\frac{3N}{2}} \left(\frac{E}{c}\right)^{3N}\right)}{h^{3N}} \quad (\text{since } N \gg 1) \\ &\sim \frac{\left(\frac{V}{N}\right)^N \left(\frac{E}{c\sqrt{N}}\right)^{3N}}{h^{3N}}, \end{aligned}$$

and

$$\ln(\Omega) \sim N \ln\left(\frac{V}{N}\right) + 3N \ln\left(\frac{E}{c\sqrt{N}}\right) - 3N \ln(h).$$

To derive an equation for the total energy  $E$  of the system as a function of temperature  $T$ , we first find

$$\begin{aligned}\beta &= \frac{1}{k_B T} = \frac{\partial \ln(\Omega)}{\partial E} \\ &= \frac{\partial}{\partial E} \left[ N \ln \left( \frac{V}{N} \right) + 3N \ln \left( \frac{E}{c\sqrt{N}} \right) - 3N \ln(h) \right] \\ &= \frac{3N}{E}, \\ &\implies E = 3Nk_B T.\end{aligned}$$

In other words, the average energy per particle is  $3k_B T$ , which is significantly greater than the classical average energy per particle which is  $k_B T$ .

To derive an equation for the pressure as a function of temperature  $T$ , we first find

$$\begin{aligned}\beta P &= \frac{\partial \ln(\Omega)}{\partial V} \\ &= \frac{\partial}{\partial V} \left[ N \ln \left( \frac{V}{N} \right) + 3N \ln \left( \frac{E}{c\sqrt{N}} \right) - 3N \ln(h) \right] \\ &= \frac{N}{V}, \\ &\implies P = \frac{Nk_B T}{V}.\end{aligned}$$

In other words, the relativistic gas of particles can still be treated as an ideal gas.

To find the adiabatic index  $\gamma$ , this means  $dS = 0$ , as our system is in adiabatic expansion or compression and the overall entropy does not change. We have

$$S = k_B \ln(\Omega) \sim k_B \left[ N \ln \left( \frac{V}{N} \right) + 3N \ln \left( \frac{E}{\sqrt{N}} \right) - 3N \ln(h) \right],$$

then

$$\begin{aligned}dS &= \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV \\ &= \frac{3Nk_B}{E} dE + \frac{Nk_B}{V} dV \\ &= 0 \\ &\implies \frac{3}{E} dE = -\frac{1}{V} dV \\ &\implies 3 \ln(E) = -\ln(V) + \text{const.} \\ &\implies E^3 \propto V^{-1} \\ &\implies \frac{E}{V} \propto V^{-\frac{4}{3}},\end{aligned}$$

and the adiabatic index  $\gamma = \frac{4}{3}$ . ■

**Problem 2**

Van Der Waals came up with a method for describing a system of hard spheres with a physical size  $R_0$ . The only difference to the multiplicity factor is that each hard sphere removes some volume  $V_0 \sim R_0^3$  from the system, such that the total volume that the particles have available to them is actually  $V - NV_0$ , instead of  $V$ . Derive the multiplicity factor and equation of state for this system (assuming a monotonic, non-relativistic gas, and answering the same questions as in Problem 1 except show that it is not really consistent with a simple  $\gamma$ -law; derive a relationship between pressure and density for this system while undergoing adiabatic changes in density and pressure. There should be some unusual behavior when the number density  $n$  is close to some  $n_{crit}$ . How do we interpret this behavior and what is the value of  $n_{crit}$ ?

*Proof.* Assume our system has  $N$  particles in 3 dimensions (as before). Van Der Waals' method proposes to take  $V \rightarrow V - NV_0$  to account for the volumes taken up by the hard spheres.

The possible positions is given by the hypervolume of the position space, which is  $\frac{(V - NV_0)^N}{N!}$ . The possible momenta is given by the hypervolume of the momentum space, which is  $\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} R^{3N-1}$ , where  $R = \sqrt{2mE}$ .

Then, the multiplicity factor is

$$\begin{aligned}
 \Omega(E, V) &= \frac{(\# \text{ possible positions})(\# \text{ possible momenta})}{h^{3N}} \\
 &= \frac{(\text{area of position space})(\text{area of momentum space})}{h^{3N}} \\
 &= \frac{\left(\frac{(V - NV_0)^N}{N!}\right) \left(\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} R^{3N-1}\right)}{h^{3N}} \\
 &= \frac{\left(\frac{(V - NV_0)^N}{N!}\right) \left(\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} (2mE)^{\frac{3N-1}{2}}\right)}{h^{3N}} \\
 &\sim \frac{\left(\frac{V - NV_0}{N}\right)^N \left(2 \left(\frac{2\pi}{3N}\right)^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}\right)}{h^{3N}} \quad (\text{since } N \gg 1) \\
 &\sim \frac{\left(\frac{V - NV_0}{N}\right)^N \left(\frac{mE}{N}\right)^{\frac{3N}{2}}}{h^{3N}},
 \end{aligned}$$

and

$$\ln(\Omega) \sim N \ln\left(\frac{V - NV_0}{N}\right) + \frac{3N}{2} \ln\left(\frac{mE}{N}\right) - 3N \ln(h).$$

To derive an equation for the total energy  $E$  of the system as a function of temperature  $T$ , we first find

$$\begin{aligned}
 \beta &= \frac{1}{k_B T} = \frac{\partial \ln(\Omega)}{\partial E} \\
 &= \frac{\partial}{\partial E} \left[ N \ln\left(\frac{V - NV_0}{N}\right) + \frac{3N}{2} \ln\left(\frac{mE}{N}\right) - 3N \ln(h) \right] \\
 &= \frac{3N}{2E},
 \end{aligned}$$

$$\implies E = \frac{3}{2} N k_B T.$$

In other words, the average energy per particle is  $\frac{3}{2} k_B T$ .

To derive an equation for the pressure as a function of temperature  $T$ , we first find

$$\begin{aligned}\beta P &= \frac{\partial \ln(\Omega)}{\partial V} \\ &= \frac{\partial}{\partial V} \left[ N \ln \left( \frac{V - NV_0}{N} \right) + \frac{3N}{2} \ln \left( \frac{mE}{N} \right) - 3N \ln(h) \right] \\ &= \frac{N}{V - NV_0}, \\ &\implies P = \frac{Nk_B T}{V - NV_0}.\end{aligned}$$

To find the adiabatic index  $\gamma$ , this means  $dS = 0$ , as our system is in adiabatic expansion or compression and the overall entropy does not change. We will show that this does not follow the simple  $\gamma$ -law. We have

$$S = k_B \ln(\Omega) \sim k_B \left[ N \ln \left( \frac{V - NV_0}{N} \right) + \frac{3N}{2} \ln \left( \frac{mE}{N} \right) - 3N \ln(h) \right],$$

then

$$\begin{aligned}dS &= \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV \\ &= \frac{3Nk_B}{2E} dE + \frac{Nk_B}{V - NV_0} dV \\ &= 0 \\ \implies \frac{3}{2} \frac{1}{E} dE &= - \frac{1}{V - NV_0} dV \\ \implies \frac{3}{2} \ln(E) &= - \ln(V - NV_0) + \text{const.} \\ \implies E^{\frac{3}{2}} &\propto (V - NV_0)^{-1} \\ \implies E &\propto (V - NV_0)^{-\frac{2}{3}} \\ \implies \frac{E}{V} &\propto V^{-\frac{5}{3}} \left( 1 - \frac{NV_0}{V} \right)^{-\frac{2}{3}},\end{aligned}$$

which doesn't follow the adiabatic  $\gamma$ -law.

Instead, we will derive a relationship between pressure and density for this system undergoing adiabatic changes in pressure and density. First, denote by  $n = \frac{N}{V}$  the particle density. We will rewrite the equation for entropy as

$$S = k_B \ln(\Omega) \sim k_B \left[ N \ln \left( \frac{k_B T}{P} \right) + \frac{3N}{2} \ln \left( \frac{3mP}{2} \right) + \frac{3N}{2} \ln \left( \frac{1}{n} - V_0 \right) - 3N \ln(h) \right],$$

We have

$$\begin{aligned}dS &= \frac{\partial S}{\partial P} dP + \frac{\partial S}{\partial n} dn \\ &= \left( -\frac{Nk_B}{P} + \frac{3Nk_B}{2P} \right) dP + \frac{3Nk_B}{2} \frac{1}{\frac{1}{n} - V_0} \left( -\frac{1}{n^2} \right) dn \\ &= 0 \\ \implies \frac{1}{P} dP &= \frac{3}{n - V_0 n^2} dn \\ \implies \ln(P) &= -3 \ln \left( \frac{1}{n} - V_0 \right) + \text{const.} \\ \implies P &\propto \left( \frac{1}{n} - V_0 \right)^{-3}.\end{aligned}$$

For  $n = n_{crit} = \frac{1}{\sqrt{v_0}}$ , an unusual behavior occurs. This is because entire volume is filled with these hard spheres and there is no more free space, i.e. the entire space is filled with particles. ■

### Problem 3

Imagine you have a room filled with  $N$  gas particles. What is the probability that if you observe this room at some instant, all of the particles will be in the left half of the room, with none in the right half (suffocating half the class)?

If  $N$  is Avogadro's number, how small is this probability? Are we safe from spontaneous death?

*Proof.* Initially, one could say that, assuming the probability of finding a particle anywhere in the room is uniform, then the probability of finding it in one-half of the room is 0.5. If we have  $N$  particles, then the probability would just be  $(0.5)^N$ . Although this is a really good estimate for all practical purposes, this reasoning is flawed, as we are assuming the particles are independent and will just pop into existence at sometime without any collisions happening, which is unrealistic because collisions are significant at the scale involved.

The number of collisions a particle experiences is

$$n = \frac{L/2}{\lambda},$$

where  $L$  is the length of the room and  $\lambda$  is the mean free path. Let's assume, as stated before, that there is a 0.5 probability that, with each collision, the particle will bounce with an angle which directs it towards the half of the room we are interested in. Then, considering that there are  $N/2$  particles in half-room, the probability of them spontaneously moving to the our half of the room at once is

$$P(N) = (0.5^n)^{\frac{N}{2}} = 0.5^{\frac{LN}{4\lambda}}.$$

Letting  $N = N_A = 6.022 \times 10^{23}$ , and considering an average classroom with  $L = 10$  m and a mean free path of a particle in the air to be  $\lambda = 64$  nm, we have

$$P(N_A) = 0.5^{\frac{10(6.022 \times 10^{23})}{4(64 \times 10^{-9})}} \approx 0.5^{2.35 \times 10^{31}} \approx 10^{-7 \times 10^{30}},$$

which is unimaginably small. So yes, I'm pretty sure we are safe from spontaneous death. ■

### Problem 4

Estimate the temperature below which you do not excite a single quantum rotational mode in a diatomic gas (as a function of the molecular moment of inertia  $I$ ).

For molecular Hydrogen, where the hydrogen atoms are separated by about 3 Angstroms, what is this temperature in Kelvin?

*Proof.* New degrees of freedom open up at higher temperatures because, with the possible exception of translational kinetic energy, degrees of freedom are quantized. Due to quantum mechanics, the molecules can only vibrate/rotate/get excited with certain discrete energies, and there is a lowest energy at which this happens. The particular energy of this "lowest excited state" determines the temperature at which the degree of freedom "turns on" or "freezes", by which we mean that it is accessible to a large number of particles in the ensemble (in reality, there will nearly always be a few highly excited particles at any temperature simply due to the nature of the statistical distribution of the particles, but in most situations this tiny fraction is irrelevant). As such, the temperature at which new degrees of freedom turn on is highly dependent on the specific material that is being examined.

Every degree of freedom in a molecule accounts for  $\frac{1}{2}k_B T$ . A diatomic gas molecule has an energy of  $\frac{5}{2}k_B T$ : 3 translational degrees of freedom accounting for  $\frac{3}{2}k_B T$  and 2 rotational degrees of freedom accounting for  $\frac{2}{2}k_B T$ . We need to find the temperature  $T$  at which the rotational degrees of freedom get "frozen". Since we are talking about one particle, then we can take  $N = 1$ . Thus, the energy as to which are are prescribed is

$$E = k_B T = \frac{I\omega^2}{2} \implies T = \frac{I\omega^2}{2k_B},$$

where  $I$  is the moment of inertia, and we get the spacing of energy levels for this degree of freedom from the quantization rule  $I\omega \sim n\hbar$ . For the ground state ( $n = 1$ ), we have that  $I\omega \sim \hbar$ . Then

$$T = \frac{I \left(\frac{\hbar}{I}\right)^2}{2k_B} = \frac{\hbar^2}{2k_B I} = \frac{4 \times 10^{-46}}{I} \sim \frac{10^{-46}}{I}.$$

For a hydrogen molecule, we have two hydrogen atoms, each of mass  $m_H = 1.67 \times 10^{-27}$  kg, and they are separated at a distance of  $d = 3 \text{ \AA} = 3 \times 10^{-10}$  m, then

$$I = MR^2 = 2m_H \left(\frac{d}{2}\right)^2 = 7.515 \times 10^{-47} \text{ kg m}^2 \sim 10^{-47} \text{ kg m}^2,$$

and, thus,

$$T \sim 10 \text{ K}.$$

■

### Problem 5

Estimate the temperature of the interior of the sun, knowing the mass  $M_\odot \sim 10^{33}$  g and radius  $R_\odot \sim 10^{11}$  cm. Assume the pressure in the sun is sufficient to keep it supported against gravitational collapse.

*Note:* Be careful when googling this number. It might give you a much smaller answer than your estimate! Don't trust google.

*Proof.* Since the pressure in the sun is sufficient to keep it supported against gravitational collapse, then we know the equation of hydrostatic equilibrium holds, stating

$$\frac{dP}{dr} = -\rho \frac{Gm}{r^2}.$$

Assume the sun is purely made of hydrogen atoms. At the center, the hydrogen atoms are fully ionized, so that there are two free particles (one proton, one electron) for every hydrogen mass. The formula for heat pressure is

$$P_h = \frac{2Nk_B T}{V} = 2nk_B T,$$

where  $n$  is the number density of hydrogen atoms and the factor of 2 accounts for the fact that there are two free particles per hydrogen atom.

To estimate  $n$ , we assume that the sun has uniform density. The total number of hydrogen atoms in the sun is then

$$N = \frac{M_\odot}{m_H}$$

The density of hydrogen atoms is the total number divided by the volume of the sun

$$n = \frac{N}{V} = \frac{\frac{M_\odot}{m_H}}{\frac{4}{3}\pi R_\odot^3} = \frac{3M_\odot}{4\pi R_\odot^3 m_H}$$

Estimating the inward pressure due to gravity, we have that the force of the gravitational attraction between two masses  $M_1$  and  $M_2$  is given by Newton's law of gravitation

$$F = G \frac{M_1 M_2}{d^2},$$

where  $d$  is the distance between the two masses.

Now, for the sun, there's only one mass,  $M_\odot$ , and it's attracting itself. So let's simply replace both  $M_1$  and  $M_2$  by  $M_\odot$ . Moreover, there's only one characteristic distance in the picture, and that's the radius,  $R_\odot$  of the sun itself.

Pressure is force divided by area, which is the surface area of the sun,  $A = 4\pi R_\odot^2$ . Dividing the force of gravity by  $A$  to find an expression for the pressure exerted by gravity, we get

$$P_g = G \frac{M_\odot^2}{4\pi R_\odot^4}$$

Setting  $P_h = P_g$ , we get

$$T = \frac{GM_\odot m_H}{6k_B R_\odot}$$

Estimating the internal temperature of the Sun, we get

$$T \sim \frac{(10^{-11})(10^{30})(10^{-27})}{(10^{-23})(10^9)} = 10^6 \text{ K.}$$

■

### Problem 6

Pathria & Beale derive the multiplicity for an ideal gas using quantum mechanics. Imagine a 3D infinite square well with sides of length  $L$ . As we are all experts on quantum mechanics, we know the infinite square well admits energy eigenvalues of

$$\epsilon(n_x, n_y, n_z) = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2).$$

Given the constraint that the total energy

$$E = \sum_{i=1}^N \epsilon_i$$

for a fixed total number of particles  $N$  estimate the multiplicity factor  $\Omega(E, V)$ , i.e. for a given energy, how many possible quantum states of  $N$  particles can have that energy? You can assume large  $N$  and large  $E$  (large enough total energy that the average energy per particle is way above the ground state, that will help a lot). You should only worry about dependence on  $E$  and  $V$ , don't worry about terms that look like  $N^N$  unless you really want to. It should be equivalent to what we derived in class.

*Note:* the full formula they give is:

$$\ln(\Omega) = N \ln \left( \frac{V}{N h^3} \left( \frac{4\pi m E}{3N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} N.$$

*Proof.* Our system has  $N$  particles in 3 dimensions. The given constraint is that the total energy of the system  $E$  is given by

$$E = \sum_{i=1}^N \epsilon_i,$$

where  $\epsilon_i = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)_i$  is the energy of the  $i$ th particle.

The possible positions is given by the hypervolume of the position space, which is  $\frac{V^N}{N!}$ . The possible momenta is given by the hypervolume of the momentum space, which is  $\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} R^{3N-1}$ , where  $R = \sqrt{2mE}$ .

Then, the multiplicity factor is

$$\begin{aligned}
 \Omega(E, V) &= \frac{(\# \text{ possible positions})(\# \text{ possible momenta})}{h^{3N}} \\
 &= \frac{(\text{area of position space})(\text{area of momentum space})}{h^{3N}} \\
 &= \frac{\left(\frac{V^N}{N!}\right) \left(\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} R^{3N-1}\right)}{h^{3N}} \\
 &= \frac{\left(\frac{V^N}{N!}\right) \left(\frac{2\pi^{\frac{3N}{2}}}{(\frac{3N}{2}-1)!} (2mE)^{\frac{3N-1}{2}}\right)}{h^{3N}} \\
 &\sim \frac{\left(\frac{Ve}{N}\right)^N \left(\frac{4\pi emE}{3N}\right)^{\frac{3N}{2}}}{h^{3N}} \quad (\text{since } N \gg 1)
 \end{aligned}$$

and

$$\ln(\Omega) \sim N \ln \left( \frac{V}{Nh^3} \left( \frac{4\pi mE}{3N} \right)^{\frac{3}{2}} \right) + \frac{5}{2}N.$$

■