Solution 4 for Chapter 4 and 5

4.7 Entropy of a Classical, Norelativistic, Monatomic Gas in the Microcanonical Ensemble

(a) Total energy $E \Rightarrow \sum_{A=1}^{N} \frac{1}{2m}|P_A|^2 = E$

$|x^j_A| < L/2$ because particles are comfined in the box.

(b) It's a 5-D hypersurface which has measure 0 in the 6-D phase space

(c) $\int \prod_A d^3 P_A = S_{3N} \int_{E-\delta E}^{E} p^{3N-1} dp$ where $|P|$ is between $\sqrt{2mE}$ and $\sqrt{2m(E-\delta E)}$, so $\Delta\Gamma = V^N(V_\nu(a) - V_\nu(a-\delta a))$

(d) Since $V_\nu(a) = \frac{\pi^{\nu/2}}{(\nu/2)!} a^\nu \Rightarrow \frac{V_\nu(a-\delta a)}{V_\nu(a)} = (1-\frac{\delta a}{a})^\nu = e^{\nu\log(1-\frac{\delta a}{a})}$
$= e^{-\nu\delta a/a}$

$\nu\frac{\delta a}{a} = \frac{1}{2}\frac{\delta E}{E} 3N \gg 1 \Rightarrow e^{-\nu\delta a/a} \ll 1 \Rightarrow V_\nu(a) - V_\nu(a-\delta a) \approx V_\nu(a)$

The number of available states is $\frac{g_s^N}{N!\,h^{3N}} V_{3N}(a) V^N$

$\Rightarrow k_B \log\Delta\Gamma = N k_B \log\left(\frac{g_s}{\sqrt[N]{N!}\,h^3} \frac{\pi^{3/2}}{(\frac{3}{2}N)!^{1/N}} (2mE)^{3/2} V\right)$

$\Rightarrow S \approx N k_B \log\left[\frac{V}{N}\left(\frac{E}{N}\right)^{3/2} g_s \left(\frac{4\pi m}{3h^2}\right)^{3/2} e^{5/2}\right]$

4.7 (e) $S = Nk_B\left[\frac{5}{2} + \log\left(\frac{h^3}{g_s}\frac{1}{(2\pi m k_B T)^{3/2}} e^{-\mu/k_BT}\left(\frac{4\pi mT}{3h^2}\right)^{3/2} g_s\right)\right]$

$= Nk_B\left(\frac{5}{2} - \frac{\mu}{k_B}\right)$ $\qquad E = \frac{3}{2}Nk_BT$

5.4. Adiabatic Index for Ideal Gas

(a) $dE = TdS - pdV \Rightarrow \left(\frac{\partial E}{\partial S}\right)\Big|_V = T$ or $\left(\frac{\partial S}{\partial E}\right)\Big|_V = \frac{1}{T}$

$$\frac{\partial E}{\partial T} = \frac{\partial E}{\partial S}\frac{\partial S}{\partial T} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = C_V$$

Adiabatic expansion $(dS=0)$ $dE = C_V dT = -PdV$

(b) $dT = \frac{-P}{C_V}dV = -\frac{Nk_BT}{C_V}dV$

$\Rightarrow \log T = -\frac{Nk_B}{C_V}\log(V) + C$

$\Rightarrow -\partial \log P = \partial \log V + \frac{Nk_B}{C_V}\log V \Rightarrow \gamma = 1 + \frac{Nk_B}{C_V}$

(c) $C_P = T\frac{\partial S}{\partial T}\Big|_{P,N} = T\left(\frac{\partial E}{\partial T} + P\frac{\partial V}{\partial T}\right)_{N,P}$

$= C_V + Nk_BT \Rightarrow \gamma = C_P/C_V$

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5.3 Grand Canonical Ensemble for Ideal Relativistic Gas [by Alexei Dvoretskii, edited by Geoffrey Lovelace]

(a) Suppose there are N identical particles in the volume. Since the gas is in a classical regime, the average occupation number for each state is low ($\bar{\eta} \ll 1$), so it is highly unlikely that a state will contain more than one quanta. A given configuration thus has N particles in N states, which can be done in $N!$ different ways. Therefore

$$\boxed{\mathcal{M} = N!}$$

(b) Each particle can move in three dimensions; since the gas is monatomic, there are no rotational or vibrational degrees of freedom. Therefore, the total number of degrees of freedom is $W = 3N$. We know that $\mathcal{N} = \frac{1}{\mathcal{M}h^{3N}}$, so, using the result from part (a), $\mathcal{N} = \frac{1}{N!h^{3N}}$. The particles travel freely for most of the time, so all of the energy is kinetic:

$$\boxed{\mathcal{E}_N = \sum_{A=1}^{N} \sqrt{\mathbf{p}_A^2 + m^2}}$$

(c) So far, we've been treating N as a constant. However, in reality the system may have any number of particles, from 0 to ∞. For each system with N particles, we must sum over the possible states, weighting each term by the exponential given in Eq. (3.40a). The sum over all states of a system with N particles confined to a volume each confined to a volume V can be expressed as $\int dN_{\text{states}}$. Therefore, using Eq. (3.40a), we have

$$Z = \sum_n \exp\left(\frac{-\mathcal{E} + \mu_R N_n}{kT}\right) = \sum_{N=0}^{\infty} \int dN_{\text{states,N}} e^{\frac{-\mathcal{E}_{\text{state}} + \mu_R N}{kT}}.$$

Consider a single particle in the gas (say, particle A). It is confined to the volume V that the gas occupies, so $dN_{\text{states,N,A}} = \frac{V d^3 p_A}{h^3} = 4\pi p_A^2 dp_A V$. The number of states available to the entire gas of N particles, then, is

$$dN_{\text{states,N}} = \frac{\prod_{A=1}^{N} 4\pi p_A^2 dp_A V^N}{h^{3N} N!}.$$

Note that we have divided by $N!$, since the particles are identical; interchanging any two particles does not give a new state. We already found $\mathcal{E} = E_{\text{state}}$ in part (b).

Inserting these expression into the equation for Z, we have

$$\begin{aligned} Z &= \sum_{N=0}^{\infty} \int \frac{\prod_{A=1}^{N} 4\pi p_A^2 dp_A V^N}{h^{3N} N!} e^{\frac{-\left(\Sigma_{A=1}^{N} \sqrt{\mathbf{p}_A^2 + m^2}\right) + \mu_R N}{kT}} \\ &= \sum_{N=0}^{\infty} e^{\frac{\mu_R N}{kT}} \frac{V^N}{N! h^{3N}} \prod_{A=1}^{N} \left[\int e^{-\sqrt{\mathbf{p_A}^2 + m^2}} 4\pi p_A^2 dp_A \right] \\ &= \sum_{N=0}^{\infty} e^{\frac{\mu_R N}{kT}} \frac{V^N}{N! h^{3N}} \left[\int_0^{\infty} e^{-\sqrt{p^2+m^2}} 4\pi p^2 dp \right]^N \end{aligned}$$

In the last line, we note that dp_A is just a dummy variable.

(d) For the non-relativistic limit, write $\sqrt{\mathbf{p}^2 + m^2} = m + \frac{\mathbf{p}^2}{2m}$, which is the non-relativistic energy. Then we have

$$\int_0^{\infty} e^{-\frac{\sqrt{p^2+m^2}}{kT}} 4\pi p^2 dp = \int_0^{\infty} e^{\frac{-m-\frac{p^2}{2m}}{kT}} 4\pi p^2 dp = e^{-m/kT} (2\pi mkT)^{3/2}.$$

Let $\mu \equiv \mu_R - m$, so that

$$Z = \sum_{N=0}^{\infty} \frac{V^N}{N! h^{3N}} e^{\frac{\mu N}{kT}} (2\pi mkT)^{3N/2} = \exp\left(\frac{V}{h^3} e^{\frac{\mu}{kT}} (2\pi mkT)^{3/2} \right).$$

From Z, it is straightforward to get the grand potential Ω:

$$Z = e^{-\Omega/kT} \Rightarrow -kT \log Z = \Omega = -kT e^{\frac{\mu}{kT}} \frac{V}{h^3} (2\pi mkT)^{3/2}.$$

This is Eq. 3.47a.

For the ultrarelativistic limit, let $m \to 0$, so that the particles travel near the speed of light. Then

$$\int_0^{\infty} e^{-\frac{\sqrt{p^2+m^2}}{kT}} 4\pi p^2 dp = \int_0^{\infty} e^{-p/kT} 4\pi p^2 dp = 8\pi (kT)^3.$$

It is straightforward to evaluate this integral. The rest of the problem proceeds analogously to the nonrelativistic case, except you keep the relativistic chemical potential:

$$\boxed{-kT \log Z = \Omega = -8\pi \tfrac{V}{h^3} (kT)^4 e^{\mu_R/kT}}$$

(e) The quantities you are asked to calculate in part (e) are all partial derivatives of the potential you calculated in part (d). Eqs. (3.47c) tells you how to get $\bar{N}$, S, and P: Take minus the partial derivative of Ω with respect to

μ_R, T. and V, respectively. The results are then

$$\bar{N} = \frac{8\pi V(kT)^3}{h^3} e^{\mu_R/kT}$$
$$P = \frac{8\pi (kT)^4}{h^3} e^{\mu_R/kT}$$
$$S = k\bar{N}(4 - \frac{\mu_R}{kT}).$$

To calculate $\bar{\mathcal{E}}$, use Eq. (3.43):

$$\bar{\mathcal{E}} = \Omega + TS + \mu_R \bar{N} = 3\bar{N}kT.$$

Then it immediately follows that

$$\boxed{\bar{\mathcal{E}}/\bar{N} = 3kT \text{ and } \bar{\mathcal{E}}/V = 3P}$$

5.2 Energy Representation for a Nonrelativistic Monatomic Gas [by Dan Grin]

(a) We begin with an expression for the fundamental potential E of a nonrelativistic gas in the energy representation, (see Eq. 4.9c in the text)

$$E(V,S,N) = N\left(\frac{3h^2}{4\pi m}\right)\left(\frac{V}{N}\right)^{-2/3} \exp\left(\frac{2}{3k_B}\frac{S}{N} - 5/3\right). \tag{1}$$

To derive the desired relations, we need only substitute Eqn. (1) into the following expressions for the intensive variables in terms of variables of the fundamental potential (Eqns. 4.10a in the text):

$$T = \left(\frac{\partial E}{\partial S}\right)_{\text{V,N}}, \ \mu = \left(\frac{\partial E}{\partial N}\right)_{\text{V,S}}, \ P = -\left(\frac{\partial E}{\partial V}\right)_{\text{S,N}}. \tag{2}$$

In the case of temperature, this derivative is trivial, as E only depends on S through the exponent, and yields

$$\boxed{T = \tfrac{h^2}{2\pi k_B m}\left(\tfrac{N}{V}\right)^{2/3} \exp\left[\tfrac{2}{3k_B}\tfrac{S}{N} - 5/3\right].}$$

In the case of pressure, the derivative is trivial, as E only depends on V through the pre-factor in front, and so,

$$\boxed{P = -\left(\tfrac{\partial E}{\partial V}\right)_{\text{S,N}} = \tfrac{h^2}{2\pi m}\left(\tfrac{N}{V}\right)^{5/3} \exp\left[\tfrac{2}{3k_B}\tfrac{S}{N} - 5/3\right].}$$

The chemical potential is a little trickier, but we can simplify our lives a little by re-writing E in the following form

$$E = \left(\frac{N}{V}\right)^{5/3}\left(\frac{3h^2}{4\pi m}\right) \exp\left[\frac{2}{3k_B}\frac{S}{N} - 5/3\right] V \tag{3}$$

Then, calling on the product (Leibniz) rule, we see that

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\rm V,S} = \frac{5}{3}\left(\frac{N}{V}\right)^{2/3}\frac{3h^2}{4\pi m}\exp\left[\frac{2}{3k_B}\frac{S}{N} - 5/3\right] - \frac{2S}{3k_B N^2}\left(\frac{N}{V}\right)^{5/3}\exp\left[\frac{2}{3\rm k_B}\frac{\rm S}{\rm N} - 5/3\right]\rm V \tag{4}$$

$$\boxed{\Rightarrow \mu = \frac{h^2}{4\pi m}\left(\frac{N}{V}\right)^{2/3}\left(5 - 2\frac{S}{k_B N}\right)\exp\left[\frac{2}{3k_B}\frac{S}{N} - 5/3\right].}$$

(b) We verify that the Maxwell relations are satisfied by taking the appropriate derivatives of the Eqns. derived in part a).

$$-\left(\frac{\partial P}{\partial S}\right)_{\rm N,V} = -\left(\frac{h^2}{3k_B\pi N m}\right)\left(\frac{N}{V}\right)^{5/3}\exp\left[\frac{2}{3k_B}\frac{S}{N} - 5/3\right] = \left(\frac{\partial T}{\partial V}\right)_{\rm S,N} \tag{5}$$

$$\left(\frac{\partial \mu}{\partial V}\right)_{\rm N,S} = \left(\frac{h^2}{6\pi m N}\right)\left(\frac{N}{V}\right)^{5/3}\left(5 - 2\frac{S}{k_B N}\right)\exp\left[\frac{2}{3k_B}\frac{S}{N} - 5/3\right] = -\left(\frac{\partial P}{\partial N}\right)_{\rm S,V} \tag{6}$$

$$\left(\frac{\partial T}{\partial N}\right)_{\rm S,V} = \left\{\frac{h^2}{3\pi m k_{\rm B} V}\left(\frac{V}{N}\right)^{1/3} - \frac{h^2 S}{3\pi m k_B^2 N^2}\left(\frac{N}{V}\right)^{2/3}\right\}\times \exp\left[\frac{2}{3k_B}\frac{S}{N} - 5/3\right] = \left(\frac{\partial \mu}{\partial S}\right)_{\rm N,V}. \tag{7}$$

(c) To derive the ideal gas gas equation, we solve the temperature equation for the exponential expression to obtain

$$\exp\left[\frac{2}{3k_B}\frac{S}{N} - 5/3\right] = \frac{2\pi k_B m T}{h^2}\left(\frac{V}{N}\right)^{2/3}. \tag{8}$$

Plugging this into the pressure equation, oodles of factors cancel out to yield the desired ideal gas law:

$$\boxed{P = Nk_B T/V.}$$

4.10 Primordial Element Formation [by Alexei Dvoretskii, edited by Geoffrey Lovelace, Dan Grin, Nate Bode]

In the early universe, the protons and neutrons travelled at non-relativistic speeds, so they can be described as a monatomic, non-relativistic gas. The photons travel at the speed of light and make up an ultrarelativistic gas. We solve the problem by considering the gas in two different epochs and suppose that the transition is rapid. Initially we have a gas made up of solely neutrons and protons. The entropy per 2 protons and 2 neutrons is (ignoring the small mass difference between the proton and neutron)

$$\begin{aligned}\sigma_{\text{init}} &= 4\left(\frac{5}{2}+\ln\left[\frac{2m_p}{\rho}\left(\frac{2\pi m_p k T_{\text{f}}}{h^2}\right)^{3/2}\right]\right) \\ &= 10+4\ln\left[\frac{2m_p}{\rho}\left(\frac{2\pi m_p k T_{\text{f}}}{h^2}\right)^{3/2}\right]\end{aligned}$$

In the final state the entropy will be given by the α-particle entropy per α-particle added to the photon entropy per photon. Note that the 7 MeV is the binding energy per nucleon. Therefore, the total binding energy of an α-particle is 28 MeV (so the problem incorrectly gives 7 MeV). Therefore

$$\sigma_{\text{final}} = \frac{5}{2}+\ln\left[\frac{8m_p}{\rho}\left(\frac{8\pi m_p k T_{\text{f}}}{h^2}\right)^{3/2}\right]+\sigma_\gamma,$$

where σ_γ is the photon entropy per photon and can be roughly found from the thermodynamic equation

$$\sigma_\gamma \sim S_\gamma/k = U/T = 28\text{ MeV}/kT \approx 4.49\times10^{-5}\text{ ergs}/kT\ . \tag{9}$$

Now we must calculate ρ at the transition point. As nucleosynthesis occurs after inflation the universe expands adiabatically except when particle species annihilate. At the $\sim$ MeV temperatures under consideration, the last annihilation event ($e^+e^- \to \gamma\gamma$) has occurred, so we may treat the expansion of the universe as adiabatic. This means that the density of baryons is given by

$$\rho_{\text{baryon,init}} = \rho_{\text{baryon,now}}\left(\frac{T_{\text{init}}}{T_{\text{now}}}\right)^3 . \tag{10}$$

Currently the total matter density is $\rho_{\text{total,now}} \approx 1.7\times10^{-29}\text{g/cm}^3$, and the mass fraction of baryons is about 2%. Therefore to we need to equate σ_{init} and σ_{final}, plugging in Eqns. 10 and 9. Solving using your favorite numerical solver gives

$$\boxed{T_{\text{crit}} = 1.0\times10^9\text{K}\ .}$$

The time of nucleosynthesis can be found by plugging this temperature into

$$T(t) = \frac{T_{\text{init}}}{\sqrt{t/t_{\text{init}}}} \Rightarrow t_{\text{crit}} = t_{\text{init}}\left(\frac{T_{\text{init}}}{T_{\text{crit}}}\right)^2 \tag{11}$$

Therefore,

$$\boxed{t_{\text{crit}} \sim 100\text{ s.}}$$

In Fig. 1, we can see that at early times (high temperatures), the higher entropy (preferred) state is $2p+2n$, while at late times (low temperatures $T < T_{\text{crit}}$), the higher entropy (preferred) state is $\alpha+\gamma$, indicating that helium production does not occur until $T \sim T_{\text{crit}}$.

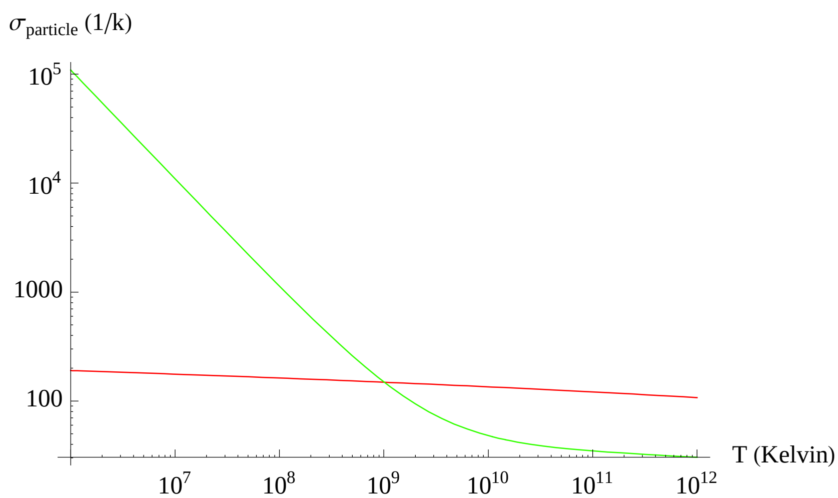

Figure 1: Particle Entropy per Particle in units of k^{-1} as a function of temperature in Kelvin. Red curve shows entropy per particle for collection of protons and neutrons only (initial state), while the green curve shows entropy per particle for α-particles and photons in the final state.