Entropy of an Extremely Relativistic Gas of Particles

In Discussion Question 3 you found that, for a gas of extremely relativistic particles where we can take the energy of a given particle i to be $\epsilon_i = p_i c$, where p_i is the magnitude of the relativistic momentum, then the average energy of the gas is,

$$E = 3Nk_BT \qquad \Rightarrow \qquad \frac{1}{T} = \frac{3k_B}{u} \qquad \text{where} \qquad u = \frac{E}{N} \tag{1}$$

You were told that, for such a gas, the ideal gas law continues to hold,

$$pV = Nk_BT \qquad \Rightarrow \qquad \frac{p}{T} = \frac{k_B}{v} \qquad \text{where} \qquad v = \frac{V}{N} \tag{2}$$

With these two pieces of information, let us compute the entropy $S(E, V, N)$ of such an extremely relativistic gas.

Classical Thermodynamic Approach

We will first use the method of classical thermodynamics, that we used previously for the non-relativistic ideal gas.

The Gibbs-Duhen relation, written in the entropy formulation of Eq. (1.3.20) is,

$$d\left(\frac{\mu}{T}\right) = u\,d\left(\frac{1}{T}\right) + v\,d\left(\frac{p}{T}\right) \tag{3}$$

Now use the results of Eqs. (1) and (2) above to write,

$$d\left(\frac{\mu}{T}\right) = u\,d\left(\frac{3k_B}{u}\right) + v\,d\left(\frac{k_B}{v}\right) = -\frac{3k_B}{u}\,du - \frac{k_B}{v}\,dv \tag{4}$$

Integrate to get,

$$\left(\frac{\mu}{T}\right) - \left(\frac{\mu}{T}\right)_0 = -3k_B \ln\left(\frac{u}{u_0}\right) - k_B \ln\left(\frac{v}{v_0}\right) \tag{5}$$

where $(\mu/T)_0$, u_0, and v_0 are constants of integration.

We can now use the analog of Euler's relation for the entropy,

$$S = \frac{1}{T}E + \frac{p}{T}V - \frac{\mu}{T}N \tag{6}$$

with Eqs. (1) and (2) to write

$$S = 3k_BN + Nk_B + 3Nk_B \ln\left(\frac{u}{u_0}\right) + Nk_B \ln\left(\frac{v}{v_0}\right) - \left(\frac{\mu}{T}\right)_0 N \tag{7}$$

$$= 4Nk_B - \left(\frac{\mu}{T}\right)_0 N + Nk_B \ln\left[\left(\frac{u}{u_0}\right)^3 \left(\frac{v}{v_0}\right)\right] \tag{8}$$

Now define, $S_0/N_0 = 4k_B - (\mu/T)_0$, $E = uN$, $E_0 = uN_0$, $V = vN$, $V_0 = v_0N_0$, and one gets,

$$S(E, V, N) = \frac{N}{N_0}S_0 + Nk_B \ln\left[\left(\frac{E}{E_0}\right)^3 \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-4}\right] \qquad \text{for an extremely relativistic gas} \tag{9}$$

We can compare that to our earlier result for a non-relativistic gas,

$$S(E, V, N) = \frac{N}{N_0}S_0 + Nk_B \ln\left[\left(\frac{E}{E_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2}\right] \qquad \text{for a non-relativistic gas} \tag{10}$$

Microcanonical Ensemble Approach

In the microcanonical ensemble, where the gas has a Hamiltonian,

$$\mathcal{H} = \sum_{i=1}^{N} \epsilon_i = \sum_{i=1}^{N} p_i c \tag{11}$$

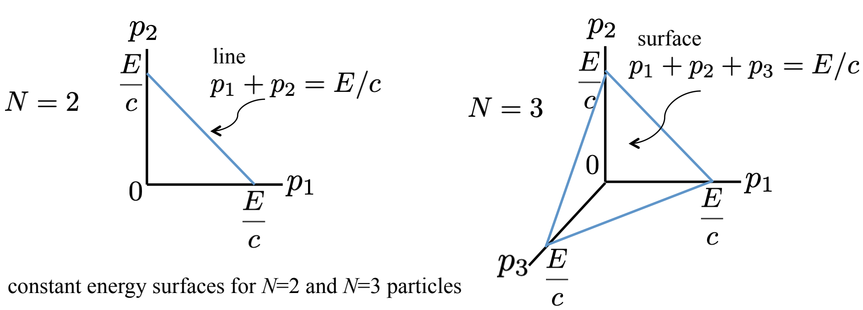
we can write for the density of states $g(E)$,

$$g(E) = \frac{1}{h^{3N}} \prod_{i=1}^{N} \int_V d^3 r_i \int_{-\infty}^{\infty} d^3 p_i \; \delta\left(\sum_{i=1}^{N} p_i c - E\right) = \frac{V^N}{h^{3N}} \prod_{i=1}^{N} \int_{-\infty}^{\infty} d^3 p_i \; \delta\left(\sum_{i=1}^{N} p_i c - E\right) \tag{12}$$

$$= \frac{V^N}{h^{3N}} (4\pi)^N \prod_{i=1}^{N} \int_0^{\infty} dp_i \, p_i^2 \, \delta\left(\sum_{i=1}^{N} p_i c - E\right) \tag{13}$$

where in the last step we integrated over all the directions of each $\mathbf{p}_i$ and are left only with the integral over the magnitude of each momentum p_i.

Now we can't do the integral over the delta function quite so easily as we did for the non-relativistic gas. The delta function restricts the integration to the surface of constant energy E. For the non-relativistic gas, that surface was just the surface of a sphere in $3N$ dimensional momentum space. That made the integral easy to do. But in the extreme relativistic case, that surface is more complicated. To give some examples, below we show the constant energy line in (p_1, p_2) space for $N = 2$ particles, and the constant energy surface in (p_1, p_2, p_3) space for $N = 3$ particles. Clearly, as N increases, the description of this surface gets more and more complicated!



constant energy surfaces for N=2 and N=3 particles

However we can make progress using a trick! Write

$$\delta(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \, \mathrm{e}^{ikx} \tag{14}$$

and substitute in for the delta function in Eq. (13),

$$g(E) = \left(\frac{4\pi V}{h^3}\right)^N \prod_{i=1}^{N} \int_0^{\infty} dp_i \, p_i^2 \, \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \, \mathrm{e}^{i\left(\sum_{i=1}^{N} p_i c - E\right)x} \tag{15}$$

$$= \frac{1}{2\pi} \left(\frac{4\pi V}{h^3}\right)^N \int_{-\infty}^{\infty} dx \, \mathrm{e}^{-iEx} \prod_{i=1}^{N} \left\{ \int_0^{\infty} dp_i \, p_i^2 \, \mathrm{e}^{ip_i cx} \right\} \tag{16}$$

where in the second step we switched the order of the integrals around, and factored the exponential of a sum into a product of exponentials.

To do the integral over p_i, we can make the substitution of variables, $y = pcx$, to get,

$$\int_0^{\infty} dp \, p^2 \, \mathrm{e}^{ipcx} = \frac{1}{c^3 x^3} \int_0^{\infty} dy \, y^2 \, \mathrm{e}^{iy} = \frac{\kappa}{c^3 x^3} \tag{17}$$

Here $\kappa = \int_0^\infty dy\, y^2\, \mathrm{e}^{iy}$ is a constant (in actuality, this integral does not converge! but we will pretend it does). Then,

$$g(E) = \frac{1}{2\pi}\left(\frac{4\pi V}{h^3}\right)^N \int_{-\infty}^{\infty} dx\, \mathrm{e}^{-iEx} \left(\frac{\kappa}{c^3 x^3}\right)^N \tag{18}$$

To do the integral over x, we can make the substitution of variables, $y = Ex$, to get,

$$g(E) = \frac{1}{2\pi}\left(\frac{4\pi V\kappa}{h^3 c^3}\right)^N \int_{-\infty}^{\infty} dx\, \mathrm{e}^{-iEx}\, \frac{1}{x^{3N}} = \frac{1}{2\pi}\left(\frac{4\pi V\kappa}{h^3 c^3}\right)^N E^{3N-1} \int_{-\infty}^{\infty} dy\, \mathrm{e}^{-iy}\, \frac{1}{y^{3N}} \tag{19}$$

Now I don't really know how to evaluate the integral, so let me just call it $C(N)$ (in actuality, this integral does not converge!). Then,

$$\Omega(E) = g(E)\Delta E = \frac{1}{2\pi}\left(\frac{4\pi V\kappa}{h^3 c^3}\right)^N E^{3N} C(N) \frac{\Delta E}{E} \tag{20}$$

and then we have,

$$S(E, V, N) = k_B \ln \Omega(E) = -k_B \ln(2\pi) + k_B \ln\left(\frac{\Delta E}{E}\right) + N k_B \ln\left[\left(\frac{4\pi V\kappa}{h^3 c^3}\right) E^3 C^{1/N}(N)\right] \tag{21}$$

We can compare the above to S in Eq. (9), obtained from classical thermodynamics. Inside the logarithm we have the same factor VE^3 as in Eq. (9). But since we don't really know what is $C(N)$, we can't say if the N-dependence agrees. We are also missing the first term of Eq. (9) that is proportional to N, but that too might appear if we knew what $C(N)$ was.

So this was a valiant attempt, but did not entirely lead to success! It illustrates what is in general the problem with computing things in the microcanonical ensemble: it is hard to specify the constant energy surface in phase space and to compute averages restricted to that surface. We will soon see that computations go much more easily in the *canonical* ensemble, where we integrate over all of phase space, weighting states of different total energy E by the Boltzmann factor $\mathrm{e}^{-E/k_B T}$.

Fortunately, the computation of $g(E)$ for the extreme relativistic gas is given in Pathria and Beale – see Chapter 2, problem 2.8, page 38, with reference to Appendix C. There they indicate how to compute $G(E) = \int_0^E dE' g(E')$, from which one can get $g(E) = dG/dE$. From the result given in problem 2.8 we can write,

$$G(E) = \frac{V^N}{h^{3N}} \frac{[8\pi(E/c)^3]^N}{(3N)!} \tag{22}$$

from which we get

$$g(E) = \frac{dG}{dE} = \frac{V^N}{h^{3N}} \frac{3N[8\pi(E/c)^3]^N}{(3N!)} \frac{1}{E} \tag{23}$$

and so

$$\Omega(E) = g(E)\Delta E = \frac{V^N}{h^{3N}} \frac{3N[8\pi(E/c)^3]^N}{(3N!)} \frac{\Delta E}{E} \tag{24}$$

and then

$$S(E, V, N) = k_B \ln \Omega = k_B \ln(3N) + k_B \ln\left(\frac{\Delta E}{E}\right) + N k_B \ln\left[\frac{8\pi E^3 V}{c^3 h^3}\right] - k_B \ln[(3N)!] \tag{25}$$

We can use Stirling's approximation to write, $\ln[(3N)!] = 3N\ln(3N) - 3N$. Using that in the above we get,

$$S(E, V, N) = 3Nk_B + Nk_B \ln\left[\frac{8\pi E^3 V}{c^3 h^3 (3N)^3}\right] + k_B \ln(3N) + k_B \ln\left(\frac{\Delta E}{E}\right) \tag{26}$$

$$= 3Nk_B + Nk_B \ln\left[\frac{8\pi}{27 c^3 h^3}\left(\frac{E}{N}\right)^3 V\right] + k_B \ln(3N) + k_B \ln\left(\frac{\Delta E}{E}\right) \tag{27}$$

The last two terms become negligible compared to the first two terms in the thermodynamic limit of $N \to \infty$.

Note, this expression above is not so terribly different from our attempt in Eq. (21). Inside the logarithm we again find the same term E^3V, which is also in our thermodynamic result of Eq. (9). But the above Eq. (27) also gives the N dependence of the argument of the logarithm, which we did not know from our previous attempt of Eq. (21). We see it is N^{-3}. We can compare that, however, to what we see in the thermodynamic result of Eq. (9) where we have N^{-4} inside the logarithm.

This missing factor of N^{-1} inside the logarithm that we see in our microcanonical calculation of S as compared to the classical thermodynamic calculation, is exactly the missing factor of N^{-1} that we found for the non-relativistic gas: compare Eqs. (2.5.7) with (2.5.10). The solution to this discrepancy for the relativistic gas is the same as it is for the non-relativistic gas. Our microcanonical calculation above treated the particles as if they were *distinguishable*. And as Gibbs showed, we need to treat them as if they are *indistinguishable*. The result is that the Ω above must be replaced by $\Omega/N!$, as discussed in Notes 2-7. If we do that, then S for the relativistic gas becomes,

$$S(E,V,N) = 3Nk_B + Nk_B \ln\left[\frac{8\pi}{27c^3h^3}\left(\frac{E}{N}\right)^3 V\right] + k_B\ln(3N) + k_B\ln\left(\frac{\Delta E}{E}\right) - k_B \ln N! \tag{28}$$

$$= 4Nk_B + Nk_B \ln\left[\frac{8\pi}{27c^3h^3}\left(\frac{E}{N}\right)^3 \left(\frac{V}{N}\right)\right] + k_B\ln(3N) + k_B\ln\left(\frac{\Delta E}{E}\right) \tag{29}$$

where we used Stirling's approximation to write, $\ln N! = N\ln N - N$.

Comparing the above to our thermodynamic result of Eq. (9), we now see the same initial term proportional to N, and the same dependence of the argument of the logarithm on E, V, and N.

If I have time, perhaps I will try to show you just how to derive $G(E)$ in Eq. (22). But you could look up the problem in Pathria and Beale and try to work on it yourself!

Method of Pathria and Beale

We want to compute the integrated density of states $G(E)$. Using Eq. (13) we get,

$$G(E) = \int_0^E dE'\, g(E') = \frac{V^N}{h^{3N}}(4\pi)^N \int dp_1\, p_1^2 \int dp_2\, p_2^2 \,\cdots \int dp_N\, p_N^2 \tag{30}$$

where the integrals over the p_i are restricted by the condition $\displaystyle\sum_{i=1}^N p_i c \le E$.

We can make a transformation of variables to $q_i = p_i c/E$. Then we get,

$$G(E) = \frac{V^N}{h^{3N}}(4\pi)^N \left(\frac{E}{c}\right)^{3N} \int dq_1\, q_1^2 \int dq_2\, q_2^2 \,\cdots \int dq_N\, q_N^2 \tag{31}$$

where the integrals over the q_i are restricted by the condition $\displaystyle\sum_{i=1}^N q_i \le 1$. Let us denote the integrals over the q_i as the N-dependent value C_N. Since the region of integration is bounded, these integrals give a finite value for C_N. We can then write,

$$I(E) \equiv \int dp_1\, p_1^2 \int dp_2\, p_2^2 \,\cdots \int dp_N\, p_N^2 = C_N \left(\frac{E}{c}\right)^{3N} \quad , \qquad p_i \text{ restricted so that } \sum_{i=1}^N p_i c = E \tag{32}$$

We now want to determine the values C_N.

Suppose we wanted to compute the average of some quantity X, that depended on the p_i only via the total energy $E=\sum_{i=1}^N p_i c$, so $X(p_1,\ldots,p_N)=X(E(p_1,\ldots,p_N))$, and we want to average over all states with any value of $E\le\infty$. We could then write,

$$\int_0^\infty dp_1\, p_1^2 \int_0^\infty dp_2\, p_2^2\ \cdots \int_0^\infty dp_N\, p_N^2 X(E(p_1,\ldots,p_N)) = \int_0^\infty dE\, X(E)\,\frac{dI(E)}{dE} = \frac{3NC_N}{c^{3N}}\int_0^\infty dE\, X(E) E^{3N-1} \quad (33)$$

In the integration over the p_i on the left side of the equation, we can take the integrals over the p_i in an unrestricted way since we want to average over all possible values of E. In the integration on the right side of the equation, we imagine doing that integral over the surfaces of constant E, then integrating over E.

Now we take for the function $X(E)=\mathrm{e}^{-E/c}=\mathrm{e}^{-\sum_{i=1}^N p_i}=\mathrm{e}^{-p_1}\mathrm{e}^{-p_2}\cdots\mathrm{e}^{-p_N}$. Putting this into the left side of the above equation give,

$$\int_0^\infty dp_1\, p_1^2 \int_0^\infty dp_2\, p_2^2\ \cdots \int_0^\infty dp_N\, p_N^2 \mathrm{e}^{-p_1}\mathrm{e}^{-p_2}\cdots\mathrm{e}^{-p_N} = \left(\int_0^\infty dp\, p^2\, \mathrm{e}^{-p}\right)^N = 2^N \quad (34)$$

The right side of Eq. (33) becomes,

$$\frac{3NC_N}{c^{3N}}\int_0^\infty dE\, \mathrm{e}^{-E/c} E^{3N-1} = 3NC_N \int_0^\infty dx\, \mathrm{e}^{-x} x^{3N-1} = 3NC_N\Gamma(3N) = 3NC_N(3N-1)! \quad (35)$$

where in the second step we made the substitution of variables, $x=E/c$, and in the third and last steps we used the definition and properties of the Gamma function. Equating Eqs. (34) and (35) then gives,

$$2^N = 3NC_N(3N-1)! \qquad \Rightarrow \qquad C_N = \frac{2^N}{3N(3N-1)!} = \frac{2^N}{(3N)!} \quad (36)$$

and so

$$I(E) = \frac{2^N}{(3N)!}\left(\frac{E}{c}\right)^{3N} \quad (37)$$

Finally, combining with Eq. (30) we get,

$$G(E) = \frac{V^N}{h^{3N}}(4\pi)^N \frac{2^N}{(3N)!}\left(\frac{E}{c}\right)^{3N} = \left(\frac{8\pi V E^3}{h^3 c^3}\right)^N \frac{1}{(3N)!} \quad (38)$$

which is the same as Eq. (22).