

Problem 1. Thermodynamics of a relativistic gas

1.1 Find the statistical distribution of a relativistic gas in momentum space, and in energies. Discuss the relativistic corrections compared to the Maxwell distribution.

Solution. We will use the Boltzmann distribution for an ideal gas in the classical limit. The distribution of the density of states in phase space is

$$n(p, q) = a \exp\left(-\frac{\epsilon(p, q)}{T}\right),$$

where $n(p, q)$ is the mean number of molecules of energy $\epsilon(p, q)$ in a phase space volume element $dp dq$. Here a is a normalization constant, determined by normalizing to N/V particles per unit volume, where N is the total number of gas molecules and V is the total volume. The mean number of molecules contained in a single volume element is

$$dN = \frac{n(p, q)}{(2\pi\hbar)^r} dp dq,$$

where r is the number of translational degrees of freedom [?, p. 107–108]. We assume $r = 3$.

The energy of a single relativistic particle is $\epsilon = c\sqrt{m^2c^2 + \mathbf{p}^2}$, where m is its mass, \mathbf{p} its three-dimensional momentum, and c the speed of light [?, p. 110]. This gives us

$$dN_{\mathbf{p}} = \frac{a}{(2\pi\hbar)^3} \exp\left(-\frac{c\sqrt{m^2c^2 + \mathbf{p}^2}}{T}\right) d^3p, \quad (1)$$

where we are ignoring the coordinate-space volume dq , because it would disappear anyway upon normalization.

Now we must find a by integrating over all of momentum space, which we will carry out using spherical coordinates with $d^3p = p^2 \sin\theta dp d\theta d\phi$. We find

$$\frac{N}{V} = \iiint dN = \frac{4\pi a}{(2\pi\hbar)^3} \int_0^\infty p^2 \exp\left(-\frac{c\sqrt{m^2c^2 + p^2}}{T}\right) dp. \quad (2)$$

Let $u = \sqrt{m^2c^2 + p^2}$. Then the lower bound of integration for u is mc , and

$$\frac{du}{dp} = \frac{p}{\sqrt{m^2c^2 + p^2}} = \frac{\sqrt{u^2 - m^2c^2}}{u} \implies dp = \frac{u}{\sqrt{u^2 - m^2c^2}} du.$$

Then we have

$$\frac{N}{V} = \frac{4\pi a}{(2\pi\hbar)^3} \int_{mc}^\infty u \sqrt{u^2 - m^2c^2} e^{-cu/T} du. \quad (3)$$

Note that [?, p. 351]

$$\int_u^\infty x(x^2 - u^2)^{\nu-1} e^{-\mu x} dx = \frac{2^{\nu-1/2}}{\sqrt{\pi}} \mu^{1/2-\nu} u^{\nu+1/2} \Gamma(\nu) K_{\nu+1/2}(u\mu) \quad (4)$$

for $\text{Re}(u\mu) > 0$, where $\Gamma(z)$ is the Gamma function and $K_n(z)$ is a modified Bessel function of the second kind [?, p. 175]. Comparing with Eq. (3), we have $x \rightarrow u$, $u \rightarrow mc$, $\nu \rightarrow 3/2$, and $\mu \rightarrow c/T$. Note also that $\Gamma(3/2) = \sqrt{\pi}/2$ [?]. Then, evaluating Eq. (3),

$$\frac{N}{V} = \frac{4\pi a}{(2\pi\hbar)^3} T m^2 c K_2(\beta m c^2) \implies a = \frac{N}{V} \frac{(2\pi\hbar)^3}{4\pi} \frac{1}{T m^2 c K_2(\beta m c^2)}.$$

Substituting into Eq. (1), we obtain

$$dN_{\mathbf{p}} = \frac{N}{V} \frac{\exp\left(-\beta c \sqrt{m^2 c^2 + \mathbf{p}^2}\right)}{4\pi T m^2 c K_2(\beta m c^2)} d^3 p \quad (5)$$

as the statistical distribution in momentum space.

To find the distribution in energy space, we will change variables in Eq. (1) to $\epsilon = c \sqrt{m^2 c^2 + \mathbf{p}^2}$. Noting that

$$\frac{dp}{d\epsilon} = \frac{cp}{\sqrt{m^2 c^2 + p^2}} \implies dp = \frac{\epsilon}{c^2} \sqrt{\epsilon^2/c^2 - m^2 c^2} = \frac{\epsilon}{c^3} \sqrt{\epsilon^2 - m^2 c^4},$$

we have

$$dN_{\epsilon} = \frac{4\pi b}{(2\pi\hbar)^3} \frac{1}{c^3} \epsilon \sqrt{\epsilon^2 - m^2 c^4} e^{-\epsilon/T} d\epsilon,$$

where b is a normalization constant, which we will find by integration:

$$\frac{N}{V} = \frac{4\pi b}{(2\pi\hbar)^3} \frac{1}{c^3} \int_{mc^2}^{\infty} \epsilon \sqrt{\epsilon^2 - m^2 c^4} e^{-\epsilon/T} d\epsilon$$

Again comparing to Eq. (4), we have $x \rightarrow \epsilon$, $u \rightarrow mc^2$, $\nu \rightarrow 3/2$, and $\mu \rightarrow \beta$. This gives us

$$\frac{N}{V} = \frac{4\pi b}{(2\pi\hbar)^3} T m^2 c K_2(\beta m c^2) \implies b = a,$$

so the statistical distribution in energy space is

$$dN_{\epsilon} = \frac{N}{V} \frac{e^{-\beta\epsilon} \epsilon \sqrt{\epsilon^2 - m^2 c^4}}{T m^2 c^4 K_2(\beta m c^2)} d\epsilon. \quad (6)$$

The Maxwell distribution in momentum space is [?, p. 109]

$$dN_{\mathbf{p}} = \frac{N}{V (2\pi m T)^{3/2}} \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}\right) dp_x dp_y dp_z. \quad (7)$$

From p. 2 of Lecture 4, the Maxwell distribution in energy space is

$$dN_{\epsilon} = \frac{N}{V} \frac{2}{\sqrt{\pi T^3}} e^{-\epsilon/T} \sqrt{\epsilon} d\epsilon. \quad (8)$$

Both distributions are similar to the relativistic ones in Eqs. (5–6). The Maxwell distributions have the kinetic energy $\epsilon = \mathbf{p}^2/2m$ in the exponent, whereas Eqs. (5–6) have the relativistic energy $\epsilon = c \sqrt{m^2 c^2 + \mathbf{p}^2}$. The factor of β in the exponent is the same in both cases. However, Eq. (6) goes as $e^{-\beta\epsilon} \epsilon^2$ while Eq. (8) goes as $e^{-\beta\epsilon} \sqrt{\epsilon}$.

The normalization of Eqs. (5–6) is different than that of Eqs. (7–8) in order to account for the relativistic energy. The factor of $1/K_2 \beta m c^2$ means that the relativistic “occupation number densities” fall off much more rapidly with T than the nonrelativistic ones. This is sensible because the relativistic particles are able to access a much larger range of momenta at high temperatures, which spreads them out over a larger range of energies.

1.2 Now take the ultra-relativistic limit. Find the mean energy $\langle E \rangle$ and the second moment of energy $\langle E^2 \rangle$. Find the free energy and the entropy in the limits of high and low temperature.

Solution. The ultra-relativistic limit is $T \gg mc^2$ [?, p. 175]. Let $u = mc^2/T$. Then Eq. (6) becomes

$$\lim_{u \rightarrow 0} dN_\epsilon = \lim_{u \rightarrow 0} \frac{N}{V} \frac{1}{T^2} \frac{e^{-\beta\epsilon} \epsilon \sqrt{\epsilon^2/T^2 - u^2}}{u^2 K_2(u)} d\epsilon = \frac{N}{V} \frac{1}{2T^3} e^{-\beta\epsilon} \epsilon^2 d\epsilon,$$

where we have used Mathematica to evaluate the limit of the denominator.

The mean energy can be found by $\langle E \rangle = N \langle \epsilon \rangle$, where $\langle \epsilon \rangle$ is the mean energy per molecule:

$$\langle E \rangle = N \langle \epsilon \rangle = V \lim_{u \rightarrow 0} \int \epsilon dN_\epsilon = \frac{N}{2T^3} \int_0^\infty \epsilon^3 e^{-\beta\epsilon} d\epsilon = \frac{N}{2T^3} 3! T^4 = 3NT,$$

where we integrate from $\epsilon = 0$ since $mc^2 \rightarrow 0$ in this limit, and we have used $\int_0^\infty x^n e^{-\mu x} dx = n! \mu^{-n-1}$ [?, p. 340].

The second moment of energy is not an additive quantity, so we cannot simply compute $N \langle \epsilon^2 \rangle$. Let $E = \sum_{i=1}^N \epsilon_i$, where ϵ_i is the energy of a given molecule. Then

$$E^2 = \left(\sum_{i=1}^N \epsilon_i \right) \left(\sum_{j=1}^N \epsilon_j \right) = \sum_{i=1}^N \epsilon_i^2 + \sum_{i \neq j} \epsilon_i \epsilon_j,$$

and the second moment of energy can be found by

$$\langle E^2 \rangle = \int \left(\sum_{i=1}^N \epsilon_i^2 + \sum_{i \neq j} \epsilon_i \epsilon_j \right) \prod_{i=1}^N$$

The Helmholtz free energy is $F = -T \ln Z$, where Z is the partition function [?, p. 87]. According to p. 1 of Lecture 4, the single-particle partition function of the Maxwell distribution can be found by

$$dN_{\mathbf{p}} = \frac{N}{V} \frac{1}{Z_i} e^{-\beta \mathbf{p}^2 / 2m} d^3 p \implies Z_i = (2\pi m T)^{3/2}.$$

Applying this procedure to Eq. (5), we find

$$Z_i = 4\pi T m^2 c K_2(\beta m c^2).$$

Assuming the gas molecules are indistinguishable, this gives the many-particle partition function

$$Z = \frac{1}{N!} [4\pi T m^2 c K_2(\beta m c^2)]^N.$$

For the ultra-relativistic case,

$$\lim_{u \rightarrow 0} Z_i = 4\pi \frac{T^3}{c^3} \lim_{u \rightarrow 0} u^2 K_2(u) = 8\pi \frac{T^3}{c^3} \implies Z = \frac{1}{N!} \left(8\pi \frac{T^3}{c^3} \right)^N.$$

Then the free energy is

$$F = -T \ln Z = -T \left(N \ln \left(8\pi \frac{T^3}{c^3} \right) - \ln N! \right) \approx -NT \left(\ln \left(\frac{8\pi}{N} \frac{T^3}{c^3} \right) + 1 \right),$$

where we have used Stirling's approximation $\ln N! \approx N \ln N - N$. The entropy can be found by $S = -(\partial F / \partial T)_V$ [?, p. 47], which gives us

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T} \left[NT \left(\ln \left(\frac{8\pi T^3}{N c^3} \right) + 1 \right) \right] = N \left(\ln \left(\frac{8\pi T^3}{N c^3} \right) + 1 \right) + NT \frac{\partial}{\partial T} \left[\ln \left(\frac{8\pi}{N c^3} \right) + 3 \ln T + 1 \right] \\ &= N \left(\ln \left(\frac{8\pi T^3}{N c^3} \right) + 4 \right). \end{aligned}$$

In the high-temperature limit,

$$\begin{aligned} \lim_{T \rightarrow \infty} F &= \lim_{T \rightarrow \infty} -NT \left(\ln \left(\frac{8\pi T^3}{N c^3} \right) + 1 \right) = \lim_{T \rightarrow \infty} -3NT \ln T = \infty, \\ \lim_{T \rightarrow \infty} S &= \lim_{T \rightarrow \infty} N \left(\ln \left(\frac{8\pi T^3}{N c^3} \right) + 4 \right) = \lim_{T \rightarrow \infty} 3N \ln T = \infty. \end{aligned}$$

In the low-temperature limit,

$$\begin{aligned} \lim_{T \rightarrow 0} F &= \lim_{T \rightarrow 0} -NT \left(\ln \left(\frac{8\pi T^3}{N c^3} \right) + 1 \right) = \lim_{T \rightarrow 0} -3NT \ln T = 0, \\ \lim_{T \rightarrow 0} S &= \lim_{T \rightarrow 0} N \left(\ln \left(\frac{8\pi T^3}{N c^3} \right) + 4 \right) = \lim_{T \rightarrow 0} 3N \ln T = -\infty. \end{aligned}$$

1.3 In the non-relativistic Maxwell distribution, the different translational degrees of freedom are independent as the kinetic energy is the sum of three independent terms $K = \sum_{i=1}^3 p_i^2 / 2m$. This is not so in the relativistic case. For the ultra-relativistic gas compute the quantities

$$a_{ij} = \frac{\langle p_i^2 p_j^2 \rangle}{3 \langle p_i^2 \rangle \langle p_j^2 \rangle}, \quad r_{ij} = \frac{\langle p_i^2 p_j^2 \rangle}{\sqrt{\langle p_i^4 \rangle \langle p_j^4 \rangle}},$$

in spatial dimensions $d = 2, 3$ (here i, j enumerate spatial dimensions). Compare them to the non-relativistic case. Discuss their meaning and dependence on d (at least based on $d = 2, 3$).

Problem 2. Collision frequency and pressure Consider an ideal relativistic gas in a container. Given the rate of the collisions of molecules with the wall of the container per unit area per unit time, find the pressure of the gas in the relativistic, non-relativistic, and ultra-relativistic cases, and compare the results.

Problem 3. Boltzmann distribution Consider an ideal gas consisting of N identical one-dimensional quantum harmonic oscillators with Hamiltonian $H(p, q) = p^2 / 2m + m\omega q^2 / 2$. Determine the total number of oscillators in states with energies $\epsilon \geq \epsilon_1 = \hbar\omega(n_1 + 1/2)$.

Problem 4. Boltzmann H -function The equilibrium distribution function $f(p, q)$ of a non-interacting gas is a Maxwell-Boltzmann distribution. Show that the entropy of such a system satisfies $S = -k_B H + \text{const.}$, where $H = \int f \ln f d\Gamma$ is the Boltzmann H -function.

Problem 5. BBGKY Consider for simplicity a 1D system (a system on a circle) of N particles with an arbitrary two-body interaction:

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_i U(x_i) + \sum_{i>j} V(x_i - x_j).$$

Give a derivation of the first equation of the BBGKY hierarchy at equilibrium for this system, which is a relation between the 1-point and 2-point distribution (correlation) functions.

Problem 6. Partition function as a generating functional Consider the Gibbs distribution of the system described in Problem 5. For simplicity neglect the kinetic energy. Let $n(x) = \sum_i \delta(x - x_i)$ be the density, and $\langle n(x) \rangle$ its expectation value. Let $C(x, y) = \langle \delta n(x) \delta n(y) \rangle$, where $\delta n(x) = n(x) - \langle n \rangle$, be the two-point correlation function.

6.1 Show that $\langle n(x) \rangle = -T \delta \ln Z / \delta U(x)$, where $Z[U(x)]$ is the partition function of the Gibbs distribution treated as a functional of the potential U .

6.2 Show that

$$C(x, y) = T^2 \frac{\delta^2 \ln Z}{\delta U(x) \delta U(y)} = -T \frac{\delta \langle n(x) \rangle}{\delta U(y)} = -T \frac{\delta \langle n(y) \rangle}{\delta U(x)}.$$