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

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

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

$$\frac{N}{V} = \int dN_{\mathbf{p}} = \frac{4\pi a}{(2\pi\hbar)^3}\int_0^\infty p^2\exp\left(-\frac{c\sqrt{m^2c^2+p^2}}{T}\right)dp\,. \tag{2}$$

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

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

Then we have

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

Note that [**?** , p. 351]

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

for $\mathrm{Re}(u\mu) > 0$, 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 $x \to u$, $u \to mc$, $\nu \to 3/2$, and $\mu \to c/T$. Note also that $\Gamma(3/2) = \sqrt{\pi}/2$. Then, evaluating Eq. (3),

$$\frac{N}{V} = \frac{4\pi a}{(2\pi\hbar)^3}Tm^2c\,K_2(\beta mc^2) \qquad \Longrightarrow \qquad a = \frac{N}{V}\frac{(2\pi\hbar)^3}{4\pi}\frac{1}{Tm^2c\,K_2(\beta mc^2)}.$$

Substituting into Eq. (1), we obtain

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

as the occupation number distribution in momentum space. Multiplying by V/N, we find the momentum distribution, which is normalized to unity:

$$dP = \frac{\exp\left(-\beta c\sqrt{m^2c^2 + \mathbf{p}^2}\right)}{4\pi T m^2 c\, K_2(\beta mc^2)}\, d^3p\,. \tag{6}$$

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

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

we have

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

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

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

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

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

so the statistical distribution in energy space is

$$dN_\epsilon = \frac{N}{V}\frac{e^{-\beta\epsilon}\epsilon\sqrt{\epsilon^2 - m^2c^4}}{T m^2 c^4\, K_2(\beta mc^2)}\, d\epsilon \qquad \Longrightarrow \qquad d\mathcal{E} = \frac{e^{-\beta\epsilon}\epsilon\sqrt{\epsilon^2 - m^2c^4}}{T m^2 c^4\, K_2(\beta mc^2)}\, d\epsilon\,. \tag{7}$$

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

$$dN_{\mathbf{p}} = \frac{N}{V}\frac{1}{(2\pi mT)^{3/2}}\exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}\right) dp_x\, dp_y\, dp_z \qquad \Longrightarrow \qquad dP = \frac{1}{(2\pi mT)^{3/2}}\exp\left(-\frac{\mathbf{p}^2}{2mT}\right) d^3p\,. \tag{8}$$

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

$$d\mathcal{E} = \frac{2}{\sqrt{\pi T^3}}e^{-\epsilon/T}\sqrt{\epsilon}\, d\epsilon\,. \tag{9}$$

Both distributions are similar to the relativistic ones in Eqs. (6–7). The Maxwell distributions have the kinetic energy $\epsilon = \mathbf{p}^2/2m$ in the exponent, whereas Eqs. (6–7) have the relativistic energy $\epsilon = c\sqrt{m^2c^2 + \mathbf{p}^2}$. The factor of β in the exponent is the same in both cases. However, Eq. (7) goes as $e^{-\beta\epsilon}\epsilon^2$ while Eq. (9) goes as $e^{-\beta\epsilon}\sqrt{\epsilon}$.

The normalization of Eqs. (6–7) is different than that of Eqs. (8–9) in order to account for the relativistic energy. The factor of $1/K_2\beta mc^2$ 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. (7) becomes

$$\lim_{u\to 0} d\mathcal{E} = \lim_{u\to 0} \frac{1}{T^2}\frac{e^{-\beta\epsilon}\epsilon\sqrt{\epsilon^2/T^2-u^2}}{u^2\,K_2(u)}\,d\epsilon = \frac{1}{2T^3}e^{-\beta\epsilon}\epsilon^2\,d\epsilon\,,$$

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:

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

where we integrate from $\epsilon = 0$ since $mc^2 \to 0$ 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

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

and the second moment of energy can be found by

$$\begin{aligned}\langle E^2\rangle &= \int\sum_{i=1}^N\left(\epsilon_i^2+\sum_{j<i}\epsilon_i\epsilon_j\right)\prod_{k=1}^N d\mathcal{E}_k = \sum_{i=1}^N\left(\int\epsilon_i^2\prod_{k=1}^N d\mathcal{E}_k + \sum_{j<i}\int\epsilon_i\epsilon_j\prod_{k=1}^N d\mathcal{E}_k\right)\\ &= \sum_{i=1}^N\left(\int\epsilon_i^2\,d\mathcal{E}_i + \sum_{j<i}\int\epsilon_i\,d\mathcal{E}_i\int\epsilon_j\,d\mathcal{E}_j\right),\end{aligned} \tag{10}$$

where in going to the final equality we have used the fact that $\int d\mathcal{E}_k = 1$. For the first term,

$$\int\epsilon_i^2\,d\mathcal{E}_i = \lim_{u\to 0}\int\epsilon_i^2\,d\mathcal{E}_i = \frac{1}{2T^3}\int_0^\infty \epsilon_i^4 e^{-\beta\epsilon_i}\,d\epsilon_i = \frac{1}{2T^3}4!\,T^5 = 12T^2.$$

For the second term,

$$\int\epsilon_i\,d\mathcal{E}_i\int\epsilon_j\,d\mathcal{E}_j = \langle\epsilon_i\rangle\langle\epsilon_j\rangle = 9T^2.$$

Then Eq. (10) becomes

$$\langle E^2\rangle = N(12T^2) + N(N-1)(9T^2) = 3N(3N+1)T^2.$$

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

$$dP = \frac{e^{-\beta\mathbf{p}^2/2m}}{Z_i}\,d^3p \quad\Longrightarrow\quad Z_i = (2\pi mT)^{3/2}.$$

Applying this procedure to Eq. (6), and assuming the gas molecules are indistinguishable, we find

$$Z_i = 4\pi Tm^2c\,K_2(\beta mc^2) \quad\Longrightarrow\quad Z = \frac{1}{N!}\left[4\pi Tm^2c\,K_2(\beta mc^2)\right]^N.$$

For the ultra-relativistic case,

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

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

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

In the high-temperature limit,

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

In the low-temperature limit,

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

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

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

in spatial dimensions $d = 2, 3$ (here i, j enumerate spatial dimensions). [r_{ij} is the uncentered "correlation coefficient". $a_{ij} = 1$ in the classical (Gaussian) case by Wick's theorem.] Compare them to the non-relativistic case. Discuss their meaning and dependence on d (at least based on $d = 2, 3$).

Solution. In the ultra-relativistic case, Eq. (6) becomes

$$\lim_{u\to 0} dP = \lim_{u\to 0}\frac{c^3}{T^3}\frac{\exp\!\left(-\sqrt{u^2+c^2\mathbf{p}^2/T^2}\right)}{4\pi u^2\,K_2(u)}\,d^3p = \frac{c^3}{8\pi T^3}\exp(-\beta c|\mathbf{p}|)\,d^3p\,. \tag{11}$$

Clearly this represents the three-dimensional case. For this case,

$$\langle p_i^2\rangle = \langle p_z^2\rangle = \int p_z^2\,dP = \frac{c^3}{8\pi T^3}\int_0^{2\pi} d\phi\int_{-1}^{1}\cos^2\theta\,d(\cos\theta)\int_0^\infty p^4 e^{-\beta cp}\,dp = \frac{c^3}{8\pi T^3}2\pi\frac{2}{3}\frac{4!}{(\beta c)^5} = 4\frac{T^2}{c^2},$$

$$\langle p_i^4\rangle = \langle p_i^2 p_i^2\rangle = \int p_z^4\, dP = \frac{c^3}{8\pi T^3}\int_0^{2\pi} d\phi \int_{-1}^{1}\cos^4\theta\, d(\cos\theta)\int_0^\infty p^6 e^{-\beta c p}\, dp = \frac{c^3}{8\pi T^3}2\pi\frac{2}{5}\frac{6!}{(\beta c)^7} = 72\frac{T^4}{c^4},$$

$$\langle p_i^2 p_j^2\rangle = \langle p_x^2 p_y^2\rangle = \int p_x^2 p_y^2 = \frac{c^3}{8\pi T^3}\int_0^{2\pi}\cos^2\phi\sin^2\phi\, d\phi\int_0^\pi \sin^5\theta\, d\theta\int_0^\infty p^6 e^{-\beta c p}\, dp = \frac{c^3}{8\pi T^3}\frac{\pi}{4}\frac{16}{15}\frac{6!}{(\beta c)^7} = 24\frac{T^4}{c^4},$$

where we have used $p_x = p\cos\phi\sin\theta$, $p_y = p\sin\phi\sin\theta$, and $p_z = p\cos\theta$. So we find

$$a_{ij} = \begin{cases} 3/2 & i = j, \\ 1/2 & i \neq j, \end{cases} \qquad\qquad r_{ij} = \begin{cases} 1 & i = j, \\ 1/3 & i \neq j, \end{cases} \tag{12}$$

for the three-dimensional ultra-relativistic gas.

In the two-dimensional case, we need to return to Eq. (1), which becomes

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

To integrate over all of momentum space and find a, we use the plane polar coordinates $d^2p = p\, dp\, d\theta$. We find

$$\begin{aligned}\frac{N}{V} &= \int dN_{\mathbf{p}} = \frac{2\pi a}{(2\pi\hbar)^2}\int_0^\infty p\exp\left(-\frac{c\sqrt{m^2c^2+p^2}}{T}\right) dp = \frac{2\pi a}{(2\pi\hbar)^2}\int_{mc}^\infty u e^{-\beta c u}\, du \\ &= \frac{2\pi a}{(2\pi\hbar)^2}\left(\left[-\frac{T}{c}ue^{-\beta c u}\right]_{mc}^\infty + \frac{T}{c}\int_{mc}^\infty e^{-\beta c u}\, du\right) = \frac{2\pi a}{(2\pi\hbar)^2}\left(mTe^{-\beta mc^2} - \frac{T}{c}\left[\frac{T}{c}e^{-\beta c u}\right]_{mc}^\infty\right) \\ &= \frac{2\pi a}{(2\pi\hbar)^2}e^{-\beta mc^2}\left(mT + \frac{T^2}{c^2}\right),\end{aligned}$$

so

$$a = \frac{N}{V}\frac{(2\pi\hbar)^2}{2\pi}\frac{e^{\beta mc^2}}{mT + T^2/c^2} \qquad\Longrightarrow\qquad dN_{\mathbf{p}} = \frac{N}{V}\frac{1}{2\pi}\frac{e^{\beta mc^2}}{mT+T^2/c^2}\exp\left(-\frac{c\sqrt{m^2c^2+\mathbf{p}^2}}{T}\right) d^2p$$

Then we have

$$dP = \frac{1}{2\pi}\frac{e^{\beta mc^2}}{mT+T^2/c^2}\exp\left(-\frac{c\sqrt{m^2c^2+\mathbf{p}^2}}{T}\right) d^2p\,.$$

Taking the ultra-relativistic limit,

$$\lim_{u\to 0} dP = \lim_{u\to 0}\frac{c^2}{2\pi T^2}\frac{e^u}{u+1}\exp\left(-\sqrt{u^2 + c^2\mathbf{p}^2/T^2}\right) d^2p = \frac{c^2}{2\pi T^2}\exp(-\beta c|\mathbf{p}|)\, d^2p\,.$$

For this case,

$$\langle p_i^2\rangle = \langle p_x^2\rangle = \frac{c^2}{2\pi T^2}\int_0^{2\pi}\cos^2\theta\, d\theta\int_0^\infty p^3 e^{-\beta c p}\, dp = \frac{c^2}{2\pi T^2}\frac{3!\,\pi}{(\beta c)^4} = 3\frac{T^2}{c^2},$$

$$\langle p_i^4\rangle = \langle p_i^2 p_i^2\rangle = \frac{c^2}{2\pi T^2}\int_0^{2\pi}\cos^4\theta\, d\theta\int_0^\infty p^5 e^{-\beta c p}\, dp = \frac{c^2}{2\pi T^2}\frac{3\pi}{4}\frac{5!}{(\beta c)^6} = 45\frac{T^4}{c^4},$$

$$\langle p_i^2 p_j^2\rangle = \langle p_x^2 p_y^2\rangle = \frac{c^2}{2\pi T^2}\int_0^{2\pi}\cos^2\theta\sin^2\theta\, d\theta\int_0^\infty p^5 e^{-\beta c p}\, dp = \frac{c^2}{2\pi T^2}\frac{\pi}{4}\frac{5!}{(\beta c)^6} = 15\frac{T^4}{c^4},$$

where we have used $p_x = p\cos\theta$ and $p_y = p\sin\theta$. So we find

$$a_{ij} = \begin{cases} 5/3 & i=j, \\ 5/9 & i\neq j, \end{cases} \qquad r_{ij} = \begin{cases} 1 & i=j, \\ 1/3 & i\neq j, \end{cases} \tag{13}$$

for the two-dimensional ultra-relativistic gas.

For the non-relativistic case, the three-dimensional momentum distribution is given by Eq. (8). This gives us

$$\begin{aligned}
\langle p_i^2 \rangle = \langle p_z^2 \rangle &= \frac{1}{(2\pi mT)^{3/2}} \int_0^{2\pi} d\phi \int_{-1}^{1} \cos^2\theta \, d(\cos\theta) \int_0^\infty p^4 e^{-\beta p^2/2m}\, dp = \frac{1}{(2\pi mT)^{3/2}} 2\pi \frac{2}{3} \frac{\Gamma(5/2)}{2(2mT)^{-5/2}} \\
&= \frac{1}{(2\pi mT)^{3/2}} \frac{\pi^{3/2}(2mT)^{5/2}}{2} = mT,
\end{aligned}$$

$$\begin{aligned}
\langle p_i^4 \rangle = \langle p_i^2 p_i^2 \rangle &= \frac{1}{(2\pi mT)^{3/2}} \int_0^{2\pi} d\phi \int_{-1}^{1} \cos^4\theta \, d(\cos\theta) \int_0^\infty p^6 e^{-\beta p^2/2m}\, dp = \frac{1}{(2\pi mT)^{3/2}} 2\pi \frac{2}{5} \frac{\Gamma(7/2)}{2(2mT)^{-7/2}} \\
&= \frac{1}{(2\pi mT)^{3/2}} \frac{3\pi^{3/2}(2mT)^{7/2}}{4} = 3m^2T^2,
\end{aligned}$$

$$\begin{aligned}
\langle p_i^2 p_j^2 \rangle = \langle p_x^2 p_y^2 \rangle &= \frac{1}{(2\pi mT)^{3/2}} \int_0^{2\pi} \cos^2\phi \sin^2\phi \, d\phi \int_0^{\pi} \sin^5\theta \int_0^\infty p^6 e^{-\beta p^2/2m}\, dp = \frac{1}{(2\pi mT)^{3/2}} \frac{\pi}{4} \frac{16}{15} \frac{\Gamma(7/2)}{2(2mT)^{-7/2}} \\
&= \frac{1}{(2\pi mT)^{3/2}} \frac{\pi^{3/2}(2mT)^{7/2}}{4} = m^2T^2,
\end{aligned}$$

where we have used

$$\int_0^\infty x^m \exp(-\beta x^n)\, dx = \frac{\Gamma(\gamma)}{n\beta^\gamma}, \qquad \gamma = \frac{m+1}{n}, \tag{14}$$

for $\mathrm{Re}(\beta), \mathrm{Re}(m), \mathrm{Re}(n) > 0$ [**?** , p. 337]. So we find

$$a_{ij} = \begin{cases} 1 & i=j, \\ 1/3 & i\neq j, \end{cases} \qquad r_{ij} = \begin{cases} 1 & i=j, \\ 1/3 & i\neq j, \end{cases} \tag{15}$$

for the three-dimensional non-relativistic gas.

For the two-dimensional non-relativistic case, we return to Eq. (1) with $r = 2$ and $\epsilon = \mathbf{p}^2/2m$:

$$dN_{\mathbf{p}} = \frac{a}{(2\pi\hbar)^2} \exp\left(-\frac{\mathbf{p}^2}{2mT}\right) d^3p\,.$$

Integrating to find a,

$$\frac{N}{V} = \frac{2\pi a}{(2\pi\hbar)^2} \int p e^{-p^2/2mT}\, dp = \frac{2\pi a}{(2\pi\hbar)^2} \frac{\Gamma(1)}{2(2mT)^{-1}} = \frac{2\pi a}{(2\pi\hbar)^2} mT \quad \Longrightarrow \quad a = \frac{N}{V}\frac{(2\pi\hbar)^2}{2\pi mT},$$

which gives us

$$dN_{\mathbf{p}} = \frac{N}{V} \frac{e^{-\mathbf{p}^2/2mT}}{2\pi mT}\, d^3p \quad \Longrightarrow \quad dP = \frac{e^{-\mathbf{p}^2/2mT}}{2\pi mT}\, d^3p\,.$$

Then we find

$$\langle p_i^2 \rangle = \langle p_x^2 \rangle = \frac{1}{2\pi mT} \int_0^{2\pi} \cos^2\theta \, d\theta \int_0^{\infty} p^3 e^{-\mathbf{p}^2/2mT} \, dp = \frac{\pi}{2\pi mT} \frac{\Gamma(2)}{2(2mT)^{-2}} = mT,$$

$$\langle p_i^4 \rangle = \langle p_i^2 p_i^2 \rangle = \frac{1}{2\pi mT} \int_0^{2\pi} \cos^4\theta \, d\theta \int_0^{\infty} p^5 e^{-\mathbf{p}^2/2mT} \, dp = \frac{1}{2\pi mT} \frac{3\pi}{4} \frac{\Gamma(3)}{2(2mT)^{-3}} = 3m^2T^2,$$

$$\langle p_i^2 p_j^2 \rangle = \langle p_x^2 p_y^2 \rangle = \frac{1}{2\pi mT} \int_0^{2\pi} \cos^2\theta \sin^2\theta \, d\theta \int_0^{\infty} p^5 e^{-\mathbf{p}^2/2mT} \, dp = \frac{1}{2\pi mT} \frac{\pi}{4} \frac{\Gamma(3)}{2(2mT)^{-3}} = m^2T^2,$$

which give us

$$a_{ij} = \begin{cases} 1 & i = j, \\ 1/3 & i \neq j, \end{cases} \qquad\qquad r_{ij} = \begin{cases} 1 & i = j, \\ 1/3 & i \neq j, \end{cases} \tag{16}$$

for the two-dimensional non-relativistic gas.

Clearly $r_{ii} = 1$ and $r_{ij} = 1/3$ $(i \neq j)$ in four cases. Thus, we see that r_{ij} has no dependence upon dimension or upon whether the particles are non- or ultra-relativistic.

In both the $d = 2$ and $d = 3$ classical cases, $a_{ii} = 1$ and $a_{ij} = 1/3$ $(i \neq j)$ as well. In the ultra-relativistic cases, however, this is not so; $a_{ii} > 1$ and $a_{ij} > 1/3$ $(i \neq j)$ for both $d = 2$ and $d = 3$. Additionally, a_{ij} (in general) is greater for $d = 2$ that for $d = 3$ in the ultra-relativistic case. This shows that a_{ij} does depend on dimension in this case.

What do they actually mean, though? And their dependence on dimension? I have no clue.

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.

Solution. We will consider particles colliding with a wall located on the yz plane. The number of particles colliding with an area A of this wall in a time δt is given by

$$d\mathcal{N}(\mathbf{p}) = A v_x \, \delta t \, dN_{\mathbf{p}} \,,$$

where v_x is velocity in the x direction and $dN_{\mathbf{p}}$ is the distribution of the number of particles in momentum space. This expression indicates that a particle must be a distance of no more than $v_x \, \delta t$ from the wall in order to collide with it during the time δt [**?** , p. 77].

Each particle that collides with the wall transfers $2p_x$ of momentum to it. Only particles moving toward (rather than away from) the wall can hit it, so we must integrate p_x from $-\infty$ to 0. However, on average half of the particles have $p_x < 0$, meaning that

$$\int_{-\infty}^{0} p_x \, dp_x = \frac{1}{2} \int_{-\infty}^{\infty} p_x \, dp_x \,.$$

The net force exerted by all of the particles is the change in the total momentum, P, which we can now write as

$$F = \frac{\delta P}{\delta t} = \frac{1}{2\delta t} \int 2p_x \, d\mathcal{N}(\mathbf{p}) = A \int v_x p_x \, dN_{\mathbf{p}} \,,$$

where the integral is over all of momentum space [**?** , p. 77]. Then the pressure is simply the force per unit area:

$$P = \frac{F}{A} = \int v_x p_x \, dN_{\mathbf{p}} \,. \tag{17}$$

In the relativistic case, $dN_{\mathbf{p}}$ is given by Eq. (5) and

$$v_x = \frac{p}{\gamma m} = \frac{c^2 p}{\epsilon} = \frac{c p_x}{\sqrt{m^2c^2 + \mathbf{p}^2}}, \tag{18}$$

since $\epsilon = \gamma mc^2$. So Eq. (17) becomes

$$\begin{aligned} P &= \frac{N}{V}\frac{1}{4\pi T m^2 c\, K_2(\beta mc^2)} \int \frac{c p_x^2}{\sqrt{m^2c^2+\mathbf{p}^2}} \exp\Big(-\beta c\sqrt{m^2c^2+\mathbf{p}^2}\Big)\, d^3p \\ &= \frac{N}{V}\frac{1}{4\pi T m^2 c\, K_2(\beta mc^2)} \int_0^{2\pi} \cos^2\phi\, d\phi \int_0^{\pi} \sin^3\theta\, d\theta \int_0^\infty \frac{c p^4}{\sqrt{m^2c^2+p^2}} \exp\Big(-\beta c\sqrt{m^2c^2+p^2}\Big)\, dp \\ &= \frac{N}{V}\frac{1}{4\pi T m^2 c\, K_2(\beta mc^2)} \frac{4\pi}{3} \int_0^\infty \frac{c p^4}{\sqrt{m^2c^2+p^2}} \exp\Big(-\beta c\sqrt{m^2c^2+p^2}\Big)\, dp\,. \end{aligned}$$

Note that $\epsilon = c\sqrt{m^2c^2+p^2}$, and that

$$\epsilon^2 = m^2c^4 + c^2p^2 \quad\Longrightarrow\quad \epsilon\, d\epsilon = pc^2\, dp \quad\Longrightarrow\quad dp = \frac{\epsilon}{pc^2}\, d\epsilon\,.$$

Making this substitution, we find

$$P = \frac{N}{V}\frac{1}{4\pi T m^2 c\, K_2(\beta mc^2)} \frac{4\pi}{3} \int_{mc^2}^\infty \frac{c^2p^4}{\epsilon} e^{-\beta\epsilon} \frac{\epsilon}{pc^2}\, d\epsilon = \frac{N}{V}\frac{1}{4\pi T m^2 c\, K_2(\beta mc^2)} \frac{4\pi}{3}\frac{1}{c^3} \int_{mc^2}^\infty (\epsilon^2 - m^2c^4)^{3/2} e^{-\beta\epsilon}\, d\epsilon\,.$$

Using the integral formula [**?** , p. 350]

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

where $u > 0$, $\mathrm{Re}(\mu), \mathrm{Re}(\nu) > 0$, we see that $x \to \epsilon$, $u \to mc^2$, $\nu \to 5/2$, $\mu \to \beta$. Noting that $\Gamma(5/2) = 3\sqrt{\pi}/4$, We find

$$P = \frac{N}{V}\frac{1}{4\pi T m^2 c\, K_2(\beta mc^2)} \frac{1}{c^3}\frac{4\pi}{3} 4m^2c^4T^2 \frac{3}{4}\, K_2(\beta mc^2) = \frac{NT}{V},$$

and so we have recovered the equation of state $PV = NT$ in the relativistic case.

In the non-relativistic case, $v_x = p_x/m$ and $dN_{\mathbf{p}}$ is given by the Maxwell distribution in Eq. (8). So Eq. (17) becomes in this case

$$\begin{aligned} P &= \frac{N}{V}\frac{1}{(2\pi mT)^{3/2}} \int \frac{p_x^2}{2} \exp\left(-\frac{\mathbf{p}^2}{2mT}\right) d^3p \\ &= \frac{N}{V}\frac{1}{2(2\pi mT)^{3/2}} \int_0^{2\pi}\int_0^{\pi}\int_0^\infty p^2\cos^2\phi\sin^2\theta \exp\left(-\frac{p^2}{2mT}\right) p^2 \sin\theta\, dp\, d\theta\, d\phi \\ &= \frac{N}{V}\frac{1}{2(2\pi mT)^{3/2}} \int_0^{2\pi} \cos^2\phi\, d\phi \int_0^{\pi}\sin^3\theta\, d\theta \int_0^\infty p^4 \exp\left(-\frac{p^2}{2mT}\right) dp \\ &= \frac{N}{V}\frac{1}{2(2\pi mT)^{3/2}} \frac{4\pi}{3} \frac{\Gamma(5/2)}{2(2mT)^{-5/2}} = \frac{N}{V}\frac{1}{2(2\pi mT)^{3/2}} \frac{4\pi}{3}\frac{3\sqrt{\pi}}{4}\frac{(2mT)^{5/2}}{2} = \frac{NV}{T}, \end{aligned}$$

where we have used Eq. (14). So we have once again recovered the equation of state.

In the ultra-relativistic case, $m \to 0$. Applying this limit to Eq. (18),

$$\lim_{m\to 0} v_x = \lim_{m\to 0} \frac{c p_x}{\sqrt{m^2c^2+\mathbf{p}^2}} = \frac{c p_x}{|\mathbf{p}|}.$$

Also, $dN_{\mathbf{p}} = (N/V)\,dP$, where dP is given by Eq. (11). Equation (17) then becomes

$$\begin{aligned}P &= \frac{N}{V}\frac{c^3}{8\pi T^3}\int c\frac{p_x^2}{|\mathbf{p}|}e^{-\beta c|\mathbf{p}|}\,d^3p = \frac{N}{V}\frac{c^4}{8\pi T^3}\int_0^{2\pi}\cos^2\phi\,d\phi\int_0^{\pi}\sin^3\theta\,d\theta\int_0^{\infty}p^3e^{-\beta cp}\,d^3p\\ &= \frac{N}{V}\frac{c^4}{8\pi T^3}\frac{4\pi}{3}\frac{3!}{(\beta c)^4} = \frac{N}{V}\frac{c^4}{8\pi T^3}\frac{4\pi}{3}\frac{6T^4}{c^4} = \frac{NT}{V},\end{aligned}$$

and so we recover the equation of state for a third time.

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 $\epsilon \geq \epsilon_1 = \hbar\omega(n_1 + 1/2)$.

Solution. In quantum statistical mechanics, the Boltzmann distribution is

$$\langle n_k\rangle = ae^{-\epsilon_k/T},$$

where $\langle n_k\rangle$ is the mean number of molecules in state k, which has energy ϵ_k. To find a, we normalize to $\langle n_k\rangle = 1$. We know that the energy associated with quantum number n is $\epsilon_n = \hbar\omega(n + 1/2)$. Then

$$1 = a\sum_{n=0}^{\infty}e^{-\epsilon_n/T} = a\sum_{n=0}^{\infty}\exp\left[-\frac{\hbar\omega}{T}\left(n+\frac{1}{2}\right)\right] = a\frac{e^{-\hbar\omega/2T}}{1-e^{-\hbar\omega/T}} = aZ,$$

where Z is the partition function for a one-dimensional quantum harmonic oscillator, and was found in Prob. 3.2 of Homework 1. Note that

$$Z = \frac{e^{-\hbar\omega/2T}}{1-e^{-\hbar\omega/T}} = \frac{1}{e^{\hbar\omega/2T}-e^{-\hbar\omega/2T}} = \frac{2}{\sinh(\hbar\omega/2T)},$$

so we have

$$\langle n_k\rangle = \frac{\sinh(\hbar\omega/2T)}{2}e^{-\epsilon_k/T} = \frac{\sinh(\hbar\omega/2T)}{2}\exp\left[-\frac{\hbar\omega}{T}\left(n_k+\frac{1}{2}\right)\right].$$

With this normalization, $\langle n_k\rangle$ represents the probability that a single oscillator is in state k. In order to find the probability that a single oscillator has $\epsilon \geq \epsilon_1$, we simply need to add up the probabilities:

$$\begin{aligned}P(\epsilon\geq\epsilon_1) &= \sum_{n_k=n_1}^{\infty}\langle n_k\rangle = \frac{\sinh(\hbar\omega/2T)}{2}\sum_{n=n_1}^{\infty}\exp\left[-\frac{\hbar\omega}{T}\left(n+\frac{1}{2}\right)\right] = \frac{\sinh(\hbar\omega/2T)}{2}e^{-\hbar\omega/2T}\sum_{n=n_1}^{\infty}(e^{-\hbar\omega/T})^n\\ &= \frac{\sinh(\hbar\omega/2T)}{2}e^{-\hbar\omega/2T}\left(\sum_{n=0}^{\infty}(e^{-\hbar\omega/T})^n - \sum_{n=0}^{n_1-1}(e^{-\hbar\omega/T})^n\right)\\ &= \frac{\sinh(\hbar\omega/2T)}{2}e^{-\hbar\omega/2T}\left(\frac{1}{1-e^{-\hbar\omega/T}} - \frac{1-(e^{-\hbar\omega/T})^{n_1}}{1-e^{-\hbar\omega/T}}\right) = \frac{\sinh(\hbar\omega/2T)}{2}e^{-\hbar\omega/2T}\frac{(e^{-\hbar\omega/T})^{n_1}}{1-e^{-\hbar\omega/T}}\\ &= \frac{\sinh(\hbar\omega/2T)}{2}\frac{2}{\sinh(\hbar\omega/2T)}(e^{-\hbar\omega/T})^{n_1} = \exp\left(-\frac{\hbar\omega}{T}n_1\right),\end{aligned}$$

where we have used [**?**]

$$\sum_{k=0}^{n}r^k = \frac{1-r^{n+1}}{1-r}.$$

To obtain the number of particles with energies $\epsilon \geq \epsilon_1$, we simply need to multiply the single-particle probability by the total number of particles, N:

$$N(\epsilon\geq\epsilon_1) = N\exp\left(-\frac{\hbar\omega}{T}n_1\right).$$

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

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