Answer all three problems, but note that the first parts of each problem are easier than its last parts. Therefore, make sure to proceed to the next problem when you get stuck.

You may find the following information helpful:

Physical Constants

Electron mass	$m_e \approx 9.1 \times 10^{-31} Kg$	Proton mass	$m_p \approx 1.7 \times 10^{-27} Kg$
Electron Charge	$e \approx 1.6 \times 10^{-19} C$	Planck's const./2π	$\hbar \approx 1.1 \times 10^{-34} Js^{-1}$
Speed of light	$c \approx 3.0 \times 10^{8} ms^{-1}$	Stefan's const.	$\sigma \approx 5.7 \times 10^{-8} Wm^{-2}K^{-4}$
Boltzmann's const.	$k_B \approx 1.4 \times 10^{-23} JK^{-1}$	Avogadro's number	$N_0 \approx 6.0 \times 10^{23} mol^{-1}$

Conversion Factors

$1atm \equiv 1.0 \times 10^5 Nm^{-2}$ $\quad$ $1\mathring{A} \equiv 10^{-10} m$ $\quad$ $1eV \equiv 1.1 \times 10^4 K$

Thermodynamics

$dE = TdS + đW$ $\quad$ For a gas: $đW = -PdV$ $\quad$ For a wire: $đW = Jdx$

Mathematical Formulas

$\int_0^\infty dx\ x^n\ e^{-\alpha x} = \frac{n!}{\alpha^{n+1}}$ $\qquad$ $\left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$

$\int_{-\infty}^{\infty} dx \exp\left[-ikx - \frac{x^2}{2\sigma^2}\right] = \sqrt{2\pi\sigma^2} \exp\left[-\frac{\sigma^2 k^2}{2}\right]$ $\qquad$ $\lim_{N\to\infty} \ln N! = N \ln N - N$

$\left\langle e^{-ikx} \right\rangle = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle$ $\qquad$ $\ln \left\langle e^{-ikx} \right\rangle = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle_c$

$\cosh(x) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots$ $\qquad$ $\ln(1-x) = -\sum_{n=1}^{\infty} \frac{x^n}{n}$

Surface area of a unit sphere in d dimensions $\qquad$ $S_d = \frac{2\pi^{d/2}}{(d/2-1)!}$

1. *Hard core gas:* A gas obeys the equation of state $P(V - Nb) = Nk_BT$, and has a heat capacity C_V independent of temperature. (N is kept fixed in the following.)

(a) Find the Maxwell relation involving $\partial S/\partial V|_{T,N}$.

- For $dN = 0$,

$$d(E - TS) = -SdT - PdV, \quad \Longrightarrow \quad \left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N}.$$

(b) By calculating $dE(T, V)$, show that E is a function of T (and N) only.

- Writing dS in terms of dT and dV,

$$dE = TdS - PdV = T\left(\left.\frac{\partial S}{\partial T}\right|_{V,N} dT + \left.\frac{\partial S}{\partial V}\right|_{T,N} dV\right) - PdV.$$

Using the Maxwell relation from part (a), we find

$$dE(T, V) = T\left.\frac{\partial S}{\partial T}\right|_{V,N} dT + \left(T\left.\frac{\partial P}{\partial T}\right|_{V,N} - P\right) dV.$$

But from the equation of state, we get

$$P = \frac{Nk_BT}{(V - Nb)}, \quad \Longrightarrow \quad \left.\frac{\partial P}{\partial T}\right|_{V,N} = \frac{P}{T}, \quad \Longrightarrow \quad dE(T, V) = T\left.\frac{\partial S}{\partial T}\right|_{V,N} dT,$$

i.e. $E(T, N, V) = E(T, N)$ does not depend on V.

(c) Show that $\gamma \equiv C_P/C_V = 1 + Nk_B/C_V$ (independent of T and V).

- The heat capacity is

$$C_P = \left.\frac{\partial Q}{\partial T}\right|_P = \left.\frac{\partial E + P\partial V}{\partial T}\right|_P = \left.\frac{\partial E}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P.$$

But, since $E = E(T)$ only,

$$\left.\frac{\partial E}{\partial T}\right|_P = \left.\frac{\partial E}{\partial T}\right|_V = C_V,$$

and from the equation of state we get

$$\left.\frac{\partial V}{\partial T}\right|_P = \frac{Nk_B}{P}, \quad \Longrightarrow \quad C_P = C_V + Nk_B, \quad \Longrightarrow \quad \gamma = 1 + \frac{Nk_B}{C_V},$$

which is independent of T, since C_V is independent of temperature. The independence of C_V from V also follows from part (a).

(d) By writing an expression for $E(P, V)$, or otherwise, show that an adiabatic change satisfies the equation $P(V - Nb)^{\gamma}$ =constant.

• Using the equation of state, we have

$$dE = C_V dT = C_V d\left(\frac{P(V - Nb)}{Nk_B}\right) = \frac{C_V}{Nk_B}\left(PdV + (V - Nb)dP\right).$$

The adiabatic condition, $dQ = dE + PdV = 0$, can now be written as

$$0 = dQ = \left(1 + \frac{C_V}{Nk_B}\right) Pd(V - Nb) + \frac{C_V}{Nk_B}(V - Nb)dP.$$

Dividing by $C_V P(V - Nb)/(Nk_B)$ yields

$$\frac{dP}{P} + \gamma\frac{d(V - Nb)}{(V - Nb)} = 0, \quad \Longrightarrow \quad \ln\left[P(V - Nb)^{\gamma}\right] = constant.$$

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2. *Energy of a gas:* The probability density to find a particle of momentum $\mathbf{p} \equiv (p_x, p_y, p_z)$ in a gas at temperature T is given by

$$p(\mathbf{p}) = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left(-\frac{p^2}{2mk_B T}\right), \qquad \text{where} \qquad p^2 = \mathbf{p}\cdot\mathbf{p} \quad .$$

(a) Using Wick's theorem, or otherwise, calculate the averages $\left\langle p^2 \right\rangle$ and $\langle(\mathbf{p}\cdot\mathbf{p})(\mathbf{p}\cdot\mathbf{p})\rangle$.

• From the Gaussian form we obtain $\langle p_\alpha p_\beta\rangle = mk_B T\delta_{\alpha\beta}$, where α and β label any of the three components of the momentum. Therefore:

$$\left\langle p^2 \right\rangle = \langle p_\alpha p_\alpha\rangle = mk_B T\delta_{\alpha\alpha} = 3mk_B T,$$

and using Wick's theorem

$$\langle(\mathbf{p}\cdot\mathbf{p})(\mathbf{p}\cdot\mathbf{p})\rangle = \langle p_\alpha p_\alpha p_\beta p_\beta\rangle = (mk_B T)^2\left[\delta_{\alpha\alpha}\delta_{\beta\beta} + 2\delta_{\alpha\beta}\delta_{\alpha\beta}\right] = 15\,(mk_B T)^2.$$

(b) Calculate the characteristic function for the energy $\varepsilon = p^2/2m$ of a gas particle.

• The characteristic function ε is the average $\left\langle e^{ik\varepsilon}\right\rangle$, which is easily calculated by Gaussian integration as

$$\left\langle e^{ik\varepsilon}\right\rangle = \left\langle e^{ikp^2/2m}\right\rangle = \int \frac{d^3\mathbf{p}}{(2\pi m k_B T)^{3/2}} \exp\left[\left(ik - \frac{1}{k_B T}\right)\frac{p^2}{2m}\right] = (1 - ikk_B T)^{-3/2}.$$

(c) Using the characteristic function, or otherwise, calculate the m^{th} cumulant of the particle energy $\langle \varepsilon^m \rangle_c$.

• The cumulants are obtained from the expansion

$$\ln \left\langle e^{ik\varepsilon} \right\rangle = \sum_{m=1}^{\infty} \frac{(ik)^m}{m!} \left\langle \varepsilon^m \right\rangle_c = -\frac{3}{2} \ln \left(1 - ikk_BT\right) = \frac{3}{2} \sum_{m=1}^{\infty} \frac{\left(k_BT\right)^m}{m} (ik)^m,$$

as

$$\left\langle \varepsilon^m \right\rangle_c = \frac{3}{2}(m-1)! \left(k_BT\right)^m .$$

(d) The total energy of a gas of N (independent) particles is given by $E = \sum_{i=1}^{N} \varepsilon_i$, where ε_i is the kinetic energy of the i^{th} particle, as given above. Use the central limit theorem to compute the probability density for energy, $p(E)$, for $N \gg 1$.

• Since the energy E is the sum of N identically distributed independent variables, its cumulants are simply N times those for a signle variable, i.e.

$$\left\langle E^m \right\rangle_c = N \left\langle \varepsilon^m \right\rangle_c = \frac{3}{2} N (m-1)! \left(k_BT\right)^m .$$

According to the central limit theorem, in the large N limit the mean and variance are sufficient to describe the probability density, which thus assumes the Gaussian form

$$p(E) = \frac{1}{\sqrt{3\pi N k_B T}} \exp\left[-\frac{\left(E - 3Nk_BT/2\right)^2}{3Nk_BT} \right].$$

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3. *'Relativistic' gas:* Consider a gas of particles with a 'relativistic' one particle Hamiltonian $\mathcal{H}_1 = c|\mathbf{p}|$, where $|\mathbf{p}| = \sqrt{p_x^2 + p_y^2 + p_z^2}$ is the magnitude of the momentum. (The external potential is assumed to be zero, expect at the edges of the box confining the gas particles.) Throughout this problem treat the two body interactions and collisions precisely as in the case of classical particles considered in lectures.

(a) Write down the Boltzmann equation for the one-particle density $f_1(\mathbf{p}, \mathbf{q}, t)$, using the same collision form as employed in lectures (without derivation).

• The Boltzmann equation has the general form

$$\mathcal{L} f_1 = C[f_1, f_1].$$

The collision term is assumed to be the same as in the classical case derived in lectures, and thus given by

$$C[f_1, f_1] = -\int d^3\mathbf{p_2} d^2\mathbf{b} |\mathbf{v_2} - \mathbf{v_1}| \left[f_1(\mathbf{p_1}) f_1(\mathbf{p_2}) - f_1(\mathbf{p_1'}) f_1(\mathbf{p_2'}) \right].$$

(There are various subtleties in treatment of relativistic collisions, such as the meaning of $|\mathbf{v_2} - \mathbf{v_1}|$, which shall be ignored here.) The streaming terms have the form

$$\mathcal{L} f_1(\mathbf{p}, \mathbf{q}, t) = \partial_t f_1 + \{\mathcal{H}_1, f_1\} = \left[\partial_t + \frac{\partial \mathcal{H}_1}{\partial p_\alpha} \partial_\alpha \right] f_1 = \left[\partial_t + c \frac{p_\alpha}{|\mathbf{p}|} \partial_\alpha \right] f_1.$$

(b) The two body collisions conserve the number of particles, the momentum, and the particle energies as given by $\mathcal{H}_1$. Write down the most general form $f_1^0(\mathbf{p}, \mathbf{q}, t)$ that sets the collision integrand in the Boltzmann equation to zero. (You do not need to normalize this solution.)

• The integrand in $C[f_1, f_1]$ is zero if at each $\mathbf{q}$, $\ln f_1(\mathbf{p_1}) + \ln f_1(\mathbf{p_2}) = \ln f_1(\mathbf{p_1'}) + \ln f_1(\mathbf{p_2'})$. This can be achieved if $\ln f_1 = \sum_\mu a_\mu(\mathbf{q}, t) \chi_\mu(\mathbf{p})$, where $\chi_\mu(\mathbf{p})$ are quantities conserved in a two body collision, and a_μ are functions independent of $\mathbf{p}$. In our case, the conserved quantities are 1 (particle number), $\mathbf{p}$ (momentum), and $c|\mathbf{p}|$ (energy), leading to

$$f_1^0(\mathbf{p}, \mathbf{q}, t) = \exp\left[-a_0(\mathbf{q}, t) - \mathbf{a_1}(\mathbf{q}, t) \cdot \mathbf{p} - a_2(\mathbf{q}, t) c |\mathbf{p}| \right].$$

For any function $\chi(\mathbf{p})$ which is conserved in the collisions, there is a hydrodynamic equation of the form

$$\partial_t \left(n \langle \chi \rangle \right) + \partial_\alpha \left(n \left\langle c \frac{p_\alpha}{|\mathbf{p}|} \chi \right\rangle \right) - n \langle \partial_t \chi \rangle - n \left\langle c \frac{p_\alpha}{|\mathbf{p}|} \partial_\alpha \chi \right\rangle = 0,$$

where $n(\mathbf{q}, t) = \int d^3\mathbf{p} f_1(\mathbf{p}, \mathbf{q}, t)$ is the local density, and

$$\langle \mathcal{O} \rangle = \frac{1}{n} \int d^3\mathbf{p} f_1(\mathbf{p}, \mathbf{q}, t) \mathcal{O}.$$

(c) Obtain the equation governing the density $n(\mathbf{q}, t)$, in terms of the average local velocity $u_\alpha = \langle c p_\alpha / |\mathbf{p}| \rangle$.

• Substituting $\chi = 1$ in the conservation equation gives

$$\partial_t n + \partial_\alpha (n u_\alpha) = 0, \qquad \text{with} \qquad u_\alpha = \langle c p_\alpha / |\mathbf{p}| \rangle.$$

(d) Find the hydrodynamic equation for the local momentum density $\pi_\alpha(\mathbf{q}, t) \equiv \langle p_\alpha \rangle$, in terms of the pressure tensor $P_{\alpha\beta} = nc \left\langle (p_\alpha - \pi_\alpha)(p_\beta - \pi_\beta) / |\mathbf{p}| \right\rangle$.

• Since momentum is conserved in the collisions, we can obtain a hydrodynamic equation by putting $\chi_\alpha = p_\alpha - \pi_\alpha$ in the general conservation form. Since $\langle \chi_\alpha \rangle = 0$, this leads to

$$\partial_\beta \left(n \left\langle c \frac{\chi_\beta + \pi_\beta}{|\mathbf{p}|} \chi_\alpha \right\rangle \right) + n \partial_t \pi_\alpha + n u_\beta \partial_\beta \pi_\alpha = 0.$$

Further simplification and rearrangements leads to

$$D_t \pi_\alpha \equiv \partial_t \pi_\alpha + u_\beta \partial_\beta \pi_\alpha = -\frac{1}{n} \partial_\beta P_{\beta\alpha} - \frac{1}{n} \partial_\beta \left(n \pi_\beta c \left\langle \frac{\chi_\alpha}{|\mathbf{p}|} \right\rangle \right).$$

(Unfortunately, as currently formulated, the problem does not lead to a clean answer, in that there is a second term in the above result that does not depend on $P_{\alpha\beta}$.)

(e) Find the (normalized) one particle density $f_1(\mathbf{p}, \mathbf{q}, t)$ for a gas of N such particles in a box of volume V, in equilibrium at a temperature T.

• At equilibrium, the temperature T and the density $n = N/V$ are uniform across the system, and there is no local velocity. The general form obtained in part (b) now gives

$$f_1^0(\mathbf{p}, \mathbf{q}, t) = \frac{N}{V} \exp\left(-\frac{c|\mathbf{p}|}{k_B T} \right) \frac{1}{8\pi} \left(\frac{c}{k_B T} \right)^3.$$

The normalization factor is obtained by requiring $N = V \int d^3\mathbf{p} f_1$, noting that $d^3\mathbf{p} = 4\pi p^2 dp$, and using $\int_0^\infty dp p^n e^{-p/a} = n! a^{n+1}$.

(f) Evaluate the pressure tensor $P_{\alpha\beta}$ for the above gas in equilibrium at temperature T.

• For the gas at equilibrium $\pi_\alpha = u_\alpha = 0$, and the pressure tensor is given by

$$P_{\alpha\beta} = nc \left\langle \frac{p_\alpha p_\beta}{|\mathbf{p}|} \right\rangle = nc \delta_{\alpha\beta} \left\langle \frac{p_x p_x}{|\mathbf{p}|} \right\rangle = \delta_{\alpha\beta} \frac{nc}{3} \left\langle \frac{\mathbf{p} \cdot \mathbf{p}}{|\mathbf{p}|} \right\rangle.$$

In rewriting the above equation we have taken advantage of the rotational symmetry of the system. The expectation value is simply

$$\langle |\mathbf{p}| \rangle = \frac{\int_0^\infty dp p^2 p e^{-cp/k_B T}}{\int_0^\infty dp p^2 e^{-cp/k_B T}} = 3 \frac{k_B T}{c},$$

leading to

$$P_{\alpha\beta} = \delta_{\alpha\beta} n k_B T,$$

which is the usual formula for an ideal gas.

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