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

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

Thermodynamics

$dE = TdS + đW$ $\qquad$ For a gas: $đW = -PdV$ $\qquad$ 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. *Poisson brackets:* Consider the integral over a multidimensional phase space $\Gamma \equiv [\mathbf{p}, \mathbf{q}]$:

$$I = \int d\Gamma A\{B, C\},$$

where $A(\mathbf{p}, \mathbf{q})$, $B(\mathbf{p}, \mathbf{q})$, and $C(\mathbf{p}, \mathbf{q})$ are functions over phase space, and

$$\{B, C\} \equiv \left(\frac{\partial B}{\partial \mathbf{q}} \cdot \frac{\partial C}{\partial \mathbf{p}} - \frac{\partial B}{\partial \mathbf{p}} \cdot \frac{\partial C}{\partial \mathbf{q}}\right),$$

denotes the Poisson bracket of B and C.

(a) Prove the following identity (which you can use in subsequent parts of this problem)

$$I = \int d\Gamma A\{B, C\} = \int d\Gamma B\{C, A\}.$$

• **(2 points)** Writing out the Poisson bracket explicitly yields

$$I = \int d\Gamma A \sum_{i=1}^{3N} \left(\frac{\partial B}{\partial q_i}\frac{\partial C}{\partial p_i} - \frac{\partial B}{\partial p_i}\frac{\partial C}{\partial q_i}\right).$$

(Here the index i is used to label the 3 coordinates, as well as the N particles, and hence runs from 1 to $3N$.) Integrating the above expression by parts so as to remove derivatives of B gives

$$\begin{aligned}
I &= \int d\Gamma \sum_{i=1}^{3N} \left[B\frac{\partial}{\partial p_i}\left(A\frac{\partial C}{\partial q_i}\right) - B\frac{\partial}{\partial q_i}\left(A\frac{\partial C}{\partial p_i}\right)\right] \\
&= \int d\Gamma B \sum_{i=1}^{3N} \left(A\frac{\partial^2 C}{\partial p_i \partial q_i} + \frac{\partial A}{\partial p_i}\frac{\partial C}{\partial q_i} - A\frac{\partial^2 C}{\partial q_i \partial p_i} - \frac{\partial A}{\partial q_i}\frac{\partial C}{\partial p_i}\right] \\
&= \int d\Gamma B \sum_{i=1}^{3N} \left[\frac{\partial C}{\partial q_i}\frac{\partial A}{\partial p_i} - \frac{\partial C}{\partial p_i}\frac{\partial A}{\partial q_i}\right] \\
&= \int d\Gamma B\{C, A\}.
\end{aligned}$$

(b) Show that when $C(\mathbf{p}, \mathbf{q}) = F(A(\mathbf{p}, \mathbf{q}))$, where $F(x)$ denotes any function of x,

$$\int d\Gamma A\{B, C\} = 0.$$

• **(2 points)** The Poisson bracket of A and $C = F(A)$ is zero, since

$$\{C, A\} = \sum_{i=1}^{3N}\left[\frac{\partial F(A)}{\partial q_i}\frac{\partial A}{\partial p_i} - \frac{\partial F(A)}{\partial p_i}\frac{\partial A}{\partial q_i}\right] = F'(A)\sum_{i=1}^{3N}\left[\frac{\partial A}{\partial q_i}\frac{\partial A}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial A}{\partial q_i}\right] = 0\,.$$

Using the identity of part (a), we thus have

$$I = \int d\Gamma A\{B, C\} = \int d\Gamma B\{F(A), A\} = 0\,.$$

(c) The phase space density $\rho(\Gamma, t)$ satisfies the equation $\partial_t \rho = \{H, \rho\}$, and an associated entropy is given by $S(t) = -\int d\Gamma \rho(\Gamma, t)\ln\rho(\Gamma, t)$. Prove that $dS/dt = 0$.

• **(2 points)** The entropy associated with the phase space probability is

$$S(t) = -\int d\Gamma \rho(\Gamma, t)\ln\rho(\Gamma, t) = -\left\langle \ln\rho(\Gamma, t)\right\rangle .$$

Taking the derivative with respect to time gives

$$\frac{dS}{dt} = -\int d\Gamma \left(\frac{\partial \rho}{\partial t}\ \ln\rho + \rho\frac{1}{\rho}\frac{\partial \rho}{\partial t}\right) = -\int d\Gamma \frac{\partial \rho}{\partial t}\left(\ln\rho + 1\right).$$

Substituting the expression for $\partial\rho/\partial t$ obtained from Liouville's theorem gives

$$\frac{dS}{dt} = \int d\Gamma \{\mathcal{H}, \rho\}\left(\ln\rho + 1\right).$$

The result in the previous section, with $A = \rho$ and $F(\rho) = (\ln\rho + 1)$ now implies

$$\frac{dS}{dt} = \int d\Gamma \{\mathcal{H}, \rho\}\left(\ln\rho + 1\right) = 0.$$

(d) The average of function $A(\mathbf{p}, \mathbf{q})$ is given by $\langle A\rangle(t) = \int d\Gamma \rho(\Gamma, t) A(\mathbf{p}, \mathbf{q})$. Prove that

$$\frac{d\left\langle A\right\rangle}{dt} = \left\langle \{A, \mathcal{H}\}\right\rangle \,.$$

• **(1 points)** The time evolution of the ensemble average is given by

$$\frac{d\left\langle A\right\rangle}{dt} = \int d\Gamma \frac{\partial \rho(\mathbf{p}, \mathbf{q}, t)}{\partial t} A(\mathbf{p}, \mathbf{q}) = \int d\Gamma A(\mathbf{p}, \mathbf{q})\{\mathcal{H}, \rho\}.$$

Using the result of part (a), the integral over phase space can be rewritten as

$$\frac{d\langle A\rangle}{dt} = \int d\Gamma A\{\mathcal{H},\rho\} = \int d\Gamma \rho\{A,\mathcal{H}\} = \langle\{A,\mathcal{H}\}\rangle \, .$$

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2. *Three gas mixture:* Consider a mixture of three gases (a), (b) and (c), in a box.

(a) Write down the Boltzmann equations for the one particle densities f_a, f_b and, f_c, in terms of the Liouville operators $\mathcal{L}_\alpha \equiv [\partial_t + (\vec{p}_\alpha/m_\alpha)\cdot\nabla]$, and appropriate collision operators

$$C_{\alpha,\beta} = -\int d^3\vec{p}_2 d^2\vec{b}_{\alpha\beta}\ |\vec{v}_1 - \vec{v}_2| \left[f_\alpha(\vec{p}_1,\vec{q}_1)f_\beta(\vec{p}_2,\vec{q}_1) - f_\alpha(\vec{p}_1{}',\vec{q}_1)f_\beta(\vec{p}_2{}',\vec{q}_1)\right],$$

for $\alpha,\beta = a,b,c$.

• **(1 points)** The Boltzmann equation for one type of gas is easily generalized to two as

$$\begin{cases} \mathcal{L}_a f_a = C_{a,a} + C_{a,b} + C_{a,c} \\ \mathcal{L}_b f_b = C_{b,a} + C_{b,b} + C_{b,c} \\ \mathcal{L}_c f_c = C_{c,a} + C_{c,b} + C_{c,c} \end{cases} .$$

(b) If there are no interactions between particles of different species, i.e. $C_{\alpha,\beta} = 0$ for $\alpha \neq \beta$, write down the most general zeroth order solution for the densities f_a, f_b and, f_c.

• **(2 points)** The zeroth order solution is obtained by setting the integrand of the self-collision terms $C_{\alpha,\alpha}$ to zero. For each gas species, this is achieved by setting $\ln f_\alpha$ as a sum of collision conserved quantities, as $\ln f_\alpha = a_\alpha + \vec{b}_\alpha\cdot\vec{p} + \beta_\alpha p^2/(2m_\alpha)$ for $\alpha = a,b,c$, since particle number, momentum $\vec{p}$, and kinetic energy $p^2/(2m_\alpha)$ are conserved in the collision. Exponentiating the above and casting the result in standard form yields

$$\begin{cases} f_a^0(\vec{q},\vec{p},t) = n_a(\vec{q},t)\left(\frac{\beta_a(\vec{q},t)}{2\pi m_a}\right)^{3/2}\exp\left[-\frac{\beta_a(\vec{q},t)(\vec{p}-m_a\vec{u}_a(\vec{q},t))^2}{2m_a}\right] \\ f_b^0(\vec{q},\vec{p},t) = n_b(\vec{q},t)\left(\frac{\beta_b(\vec{q},t)}{2\pi m_b}\right)^{3/2}\exp\left[-\frac{\beta_b(\vec{q},t)(\vec{p}-m_b\vec{u}_b(\vec{q},t))^2}{2m_b}\right] \\ f_c^0(\vec{q},\vec{p},t) = n_c(\vec{q},t)\left(\frac{\beta_c(\vec{q},t)}{2\pi m_c}\right)^{3/2}\exp\left[-\frac{\beta_c(\vec{q},t)(\vec{p}-m_c\vec{u}_c(\vec{q},t))^2}{2m_c}\right] \end{cases} ,$$

i.e. there can be distinct $\vec{u}_\alpha$ and β_α for each gas species.

(c) How does including interactions between (a) and (b) particles, but no interactions between the (a) and (c) or (b) and (c) particles modify the form of f_a, f_b and, f_c?

• **(2 points)** Setting $C_{a,b}$ to zero requires $\ln f_a + \ln f_b$ to be the same before and after collisions. Using the forms $\ln f_\alpha = a_\alpha + \vec{b}_\alpha \cdot \vec{p} + \beta_\alpha p^2/(2m_\alpha)$ obtained previously from same species collisions, this implies that

$$a_a + \vec{b}_a \cdot \vec{p}_1 + \beta_a \frac{p_1^2}{2m_a} + a_b + \vec{b}_b \cdot \vec{p}_2 + \beta_b \frac{p_2^2}{2m_b} = a_a + \vec{b}_a \cdot \vec{p}_1' + \beta_a \frac{p_1'^2}{2m_a} + a_b + \vec{b}_b \cdot \vec{p}_2' + \beta_b \frac{p_2'^2}{2m_b}.$$

The above identity must hold for any quartet of $\{\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2'\}$ as long as $\vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2'$, and $p_1^2/m_a + p_2^2/m_b = p_1'^2/m_a + p_2'^2/m_b$. For this to hold, we need $\vec{b}_a = \vec{b}_b$ and $\beta_a = \beta_b$ for each $\vec{q}$ and t. The resulting one particle densities are now given by

$$\begin{cases} f_a^0(\vec{q},\vec{p},t) = n_a(\vec{q},t) \left(\dfrac{\beta_b(\vec{q},t)}{2\pi m_a}\right)^{3/2} \exp\left[-\dfrac{\beta_b(\vec{q},t)(\vec{p}-m_a\vec{u}_b(\vec{q},t))^2}{2m_a}\right] \\ f_b^0(\vec{q},\vec{p},t) = n_b(\vec{q},t) \left(\dfrac{\beta_b(\vec{q},t)}{2\pi m_b}\right)^{3/2} \exp\left[-\dfrac{\beta_b(\vec{q},t)(\vec{p}-m_b\vec{u}_b(\vec{q},t))^2}{2m_b}\right] \\ f_c^0(\vec{q},\vec{p},t) = n_c(\vec{q},t) \left(\dfrac{\beta_c(\vec{q},t)}{2\pi m_c}\right)^{3/2} \exp\left[-\dfrac{\beta_c(\vec{q},t)(\vec{p}-m_c\vec{u}_c(\vec{q},t))^2}{2m_c}\right] \end{cases},$$

i.e. with the same $\vec{u}_b$ and β_b for (a) and (b) gas species.

(d) What is the corresponding form of f_a, f_b and, f_c upon including interactions between (a) and (b) particles, (c) and (b) particles, but no interactions between the (a) and (c) particles?

• **(1 points)** Setting $C_{c,b}$ to zero requires $\ln f_c + \ln f_b$ to be the same before and after collisions. Using the forms $\ln f_\alpha = a_\alpha + \vec{b}_\alpha \cdot \vec{p} + \beta_\alpha p^2/(2m_\alpha)$ obtained previously from same species collisions, this implies that

$$a_c + \vec{b}_c \cdot \vec{p}_1 + \beta_c \frac{p_1^2}{2m_c} + a_b + \vec{b}_b \cdot \vec{p}_2 + \beta_b \frac{p_2^2}{2m_b} = a_c + \vec{b}_c \cdot \vec{p}_1' + \beta_c \frac{p_1'^2}{2m_c} + a_b + \vec{b}_b \cdot \vec{p}_2' + \beta_b \frac{p_2'^2}{2m_b}.$$

The above identity must hold for any quartet of $\{\vec{p}_1, \vec{p}_2, \vec{p}_1', \vec{p}_2'\}$ as long as $\vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2'$, and $p_1^2/m_c + p_2^2/m_b = p_1'^2/m_c + p_2'^2/m_b$. For this to hold, we need $\vec{b}_c = \vec{b}_b$ and $\beta_c = \beta_b$ for each $\vec{q}$ and t. Given the equality $\vec{b}_a = \vec{b}_b$ and $\beta_a = \beta_b$, we now have $\vec{b}_a = \vec{b}_b = \vec{b}_c$ and $\beta_a = \beta_b = \beta_c \equiv \beta$, resulting in

$$\begin{cases} f_a^0(\vec{q},\vec{p},t) = n_a(\vec{q},t) \left(\dfrac{\beta(\vec{q},t)}{2\pi m_a}\right)^{3/2} \exp\left[-\dfrac{\beta(\vec{q},t)(\vec{p}-m_a\vec{u}(\vec{q},t))^2}{2m_a}\right] \\ f_b^0(\vec{q},\vec{p},t) = n_b(\vec{q},t) \left(\dfrac{\beta(\vec{q},t)}{2\pi m_b}\right)^{3/2} \exp\left[-\dfrac{\beta(\vec{q},t)(\vec{p}-m_b\vec{u}(\vec{q},t))^2}{2m_b}\right] \\ f_c^0(\vec{q},\vec{p},t) = n_c(\vec{q},t) \left(\dfrac{\beta(\vec{q},t)}{2\pi m_c}\right)^{3/2} \exp\left[-\dfrac{\beta(\vec{q},t)(\vec{p}-m_c\vec{u}(\vec{q},t))^2}{2m_c}\right] \end{cases}.$$

Similar to the zeroth law of thermodynamics if (a) and (c) are separately in equilibrium with (b), they are also in equilibrium with each other.

(e) Including interactions among all particles, i.e. with all $C_{\alpha,\beta} \neq 0$, what are the slow (hydrodynamic) modes of this gas mixture?

• **(1 points)** The hydrodyamic modes are the three gas densities $n_a(\vec{q},t)$, $n_b(\vec{q},t)$, and $n_c(\vec{q},t)$, the velocity vector $\vec{u}$, and the energy density (related to $\beta(\vec{q},t)$).

(f) Starting with a configuration of N_a, N_b, and N_c particles in a box of volume V, what are the final (equilibrium) forms of f_a, f_b and, f_c?

• **(1 points)** The equilibrium configuration has uniform densities $n_\alpha = N_\alpha/V$, is stationary $\vec{u} = 0$, with uniform temperature T, i.e.

$$f_\alpha(\vec{q},\vec{p}) = n_\alpha \left(\frac{\beta}{2\pi m_\alpha}\right)^{3/2} \exp\left[-\frac{\beta \vec{p}^{\,2}}{2m_\alpha}\right] .$$

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