Problem 1. *H*-theorem and Pauli kinetic balance equation The Pauli balance equation (a version of the Boltzmann kinetic equation more suitable for a quantum setting) reads

$$\dot{w}_i = \sum_j (P_{ij} w_j - P_{ji} w_i), \tag{1}$$

where w_i is the probability of a system to be in the state $|i\rangle$ and P_{ij} is a transition probability rate (i.e. the probability of a state $|i\rangle$ to transition to $|j\rangle$ during unit time). In addition, a detailed balance condition is imposed: $P_{ij} = P_{ji}$.

1.1(a) Show that the Pauli balance equation respects the normalization condition $\sum_i w_i = 1$.

Solution. Since $P_{ij} = P_{ji}$,

$$\sum_i \sum_j P_{ij} w_j = \sum_i \sum_j P_{ji} w_j.$$

Swapping indices on the right side,

$$\sum_i \sum_j P_{ij} w_j = \sum_i \sum_j P_{ij} w_i = \sum_i \sum_j P_{ji} w_i,$$

where we have once again applied $P_{ij} = P_{ji}$. Then, by Eq. (1),

$$\sum_i \dot{w}_i = \sum_i \sum_j (P_{ij} w_j - P_{ij} w_i) = 0. \tag{2}$$

This implies $\sum_i w_i = k$, where k is some constant. If $k \neq 1$, we may redefine $w_i \to w_i/k$ without affecting the validity of the proof. Thus, we have shown that Eq. (1) respects the normalization condition. $\square$

1.1(b) Show that the Pauli balance equation is time irreversible.

Solution. We will first provide an example and then give a more general treatment. We assume the probabilities are properly normalized, so $\sum_i P_{ij} = \sum_j P_{ij} = 1$.

Consider a two-state system with states $|1\rangle$ and $|2\rangle$, which has

$$P = \begin{bmatrix} 1 - \mu & \mu \\ \mu & 1 - \mu \end{bmatrix},$$

where $0 \leq \mu \leq 1$. Applying Eq. (1), we obtain the system of differential equations

$$\dot{w}_1 = (P_{11} w_1 - P_{11} w_1) + (P_{12} w_2 - P_{21} w_1) = \mu(w_2 - w_1),$$
$$\dot{w}_2 = (P_{21} w_1 - P_{12} w_2) + (P_{22} w_2 - P_{22} w_2) = \mu(w_1 - w_2).$$

This system can be written as the matrix equation

$$\frac{d}{dt} \begin{bmatrix} w_1 \\ w_2 \end{bmatrix} = \mu \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} w_1 \\ w_2 \end{bmatrix} \equiv A \begin{bmatrix} w_1 \\ w_2 \end{bmatrix}, \tag{3}$$

where we have defined the matrix A. A has eigenvalues λ given by

$$0 = \begin{vmatrix} -(\mu + \lambda) & \mu \\ \mu & -(\mu + \lambda) \end{vmatrix} = (\mu + \lambda)^2 - \mu^2 \quad \implies \quad (\mu + \lambda)^2 = \mu^2 \quad \implies \quad \lambda = -2\mu, 0.$$
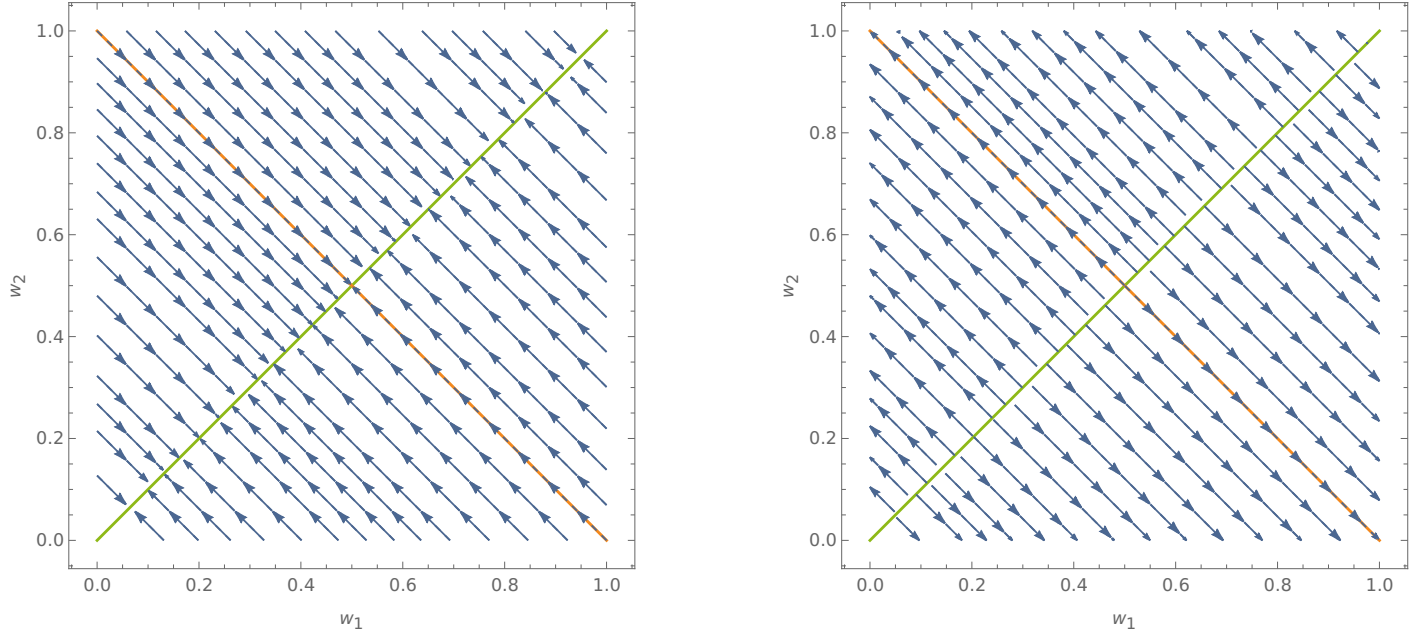
Figure 1: Plot of the (w_1, w_2) phase plane indicating trajectories for (left) the nominal system and (right) the system with $t \to -t$. The normalization $\sum_i w_i = 1$ confines the system to the orange line. The green line represents the equilibrium, which is stable for the nominal system and unstable for the time-reversed system.

The respective eigenvectors u, v can be found by

$$\mu \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = -2\mu \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \implies -u_1 + u_2 = -2\mu u_1 \implies u_1 = 1, u_2 = -1,$$

$$\mu \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = 0 \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} \implies -v_1 + v_2 = 0 \implies v_1 = v_2 = 1.$$

We can analyze the behavior of the system using stability analysis methods which are well known in applied mathematics, but which we will not prove here [**?** , pp. 127–130]. Since one of the eigenvalues is 0, there is a line of fixed points along the direction of the corresponding eigenvector, $\mathbf{v} = (1, 1)$. Since the other eigenvalue is negative, these fixed points are stable; all trajectories are along $\mathbf{u} = (-1, 1)$ and point toward the fixed points.

In practice, however, the normalization condition $\sum_i w_i = 1$ restricts the system to a line. The blue arrows in Fig. 1 (left) shows trajectories in the (w_1, w_2) phase plane. The green line indicates the line of stable fixed points. The orange line indicates the allowed values of w_1, w_2 under the normalization condition. For any initial condition along the line, the system will tend toward the point $w_1 = w_2 = 1/2$.

Under time reversal $t \to -t$, the directions of the trajectories change. This scenario is shown in Fig. 1 (right). Clearly the equilibrium has switched stability under this transformation. Thus, the system evolves in the opposite direction for any initial condition (unless the systems starts out at equilibrium, in which case it will not evolve in either case). So this system is time irreversible.

Now we will generalize the argument to an N-state system. From Eq. (1), note that

$$\dot{w}_i = P_{ii}(w_i - w_i) + \sum j \neq i^N P_{ij}(w_j - w_i) = \sum j \neq i^N P_{ij}w_j - \left(\sum j = 1^N P_{ij} - P_{ii} \right) w_i$$

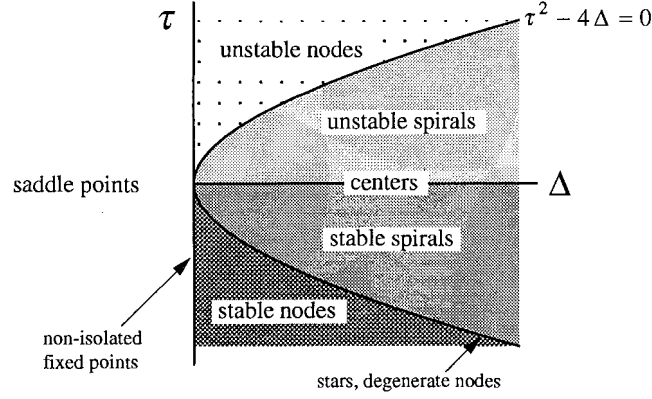$$= \sum j \neq i^N P_{ij}w_j + (P_{ii} - 1)w_i.$$

Figure 2: Fixed point classification scheme using $\tau = \text{Tr}(A)$ and $\Delta = \det(A)$ [? , p. 137]

Then A is an $N \times N$ matrix,

$$
A = \begin{bmatrix}
P_{11} - 1 & P_{12} & P_{13} & \cdots & P_{1N} \\
P_{21} & P_{22} - 1 & P_{23} & \cdots & P_{2N} \\
P_{31} & P_{32} & 1 - P_{33} & \cdots & P_{3N} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
P_{N1} & P_{N2} & P_{N3} & \cdots & 1 - P_{NN}
\end{bmatrix},
\tag{4}
$$

and the generalization of Eq. (3) is

$$
\frac{d}{dt}\begin{bmatrix}
w_1 \\ w_2 \\ w_3 \\ \vdots \\ w_N
\end{bmatrix} = \begin{bmatrix}
P_{11} - 1 & P_{12} & P_{13} & \cdots & P_{1N} \\
P_{21} & P_{22} - 1 & P_{23} & \cdots & P_{2N} \\
P_{31} & P_{32} & 1 - P_{33} & \cdots & P_{3N} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
P_{N1} & P_{N2} & P_{N3} & \cdots & 1 - P_{NN}
\end{bmatrix}\begin{bmatrix}
w_1 \\ w_2 \\ w_3 \\ \vdots \\ w_N
\end{bmatrix}.
$$

Another method of analyzing stability in applied mathematics is by analyzing the signs of the trace and determinant of A [? , pp. 136–137]. Let $\tau = \text{Tr}(A)$ and $\Delta = \det(A)$. Referring to Eq. (4), clearly τ is negative (unless it is precisely 0, which would not be very interesting). For Δ, we note that the columns of A are *not* linearly independent due to the normalization constraint on P_{ij}, meaning A is not invertible [?]. Thus, it is a singular matrix with zero determinant [?].

The stability and type of fixed point(s) of the system can be determined using Fig. 2 [? , p. 137]. For $\tau < 0$ and $\Delta = 0$, the system has a stable non-isolated fixed point, which manifested as a line of stable fixed point in the two-state example. Due to the normalization condition, the system is confined to a $N - 1$ dimensional region of the N dimensional phase space. The equilibrium is a generalization of a stable node, so all trajectories in the N-dimensional phase space end on the allowed equilibrium point. Under $t \to -t$, then, the trajectories change direction as in the two-state example. (This is in contrast to, say, a stable "center" whose trajectories are orbits that would change direction under time reversal, but remain stable.) In other words, the stable equilibrium becomes an unstable one, so the system described by Eq. (1) is time irreversible. $\qquad\square$

1.1(c) Show that the entropy $S = -\sum_i w_i \ln w_i$ is non-decreasing: $\dot{S} \geq 0$.

Solution. Note that

$$\dot{S} = -\sum_i \frac{d}{dt}(w_i \ln w_i) = -\sum_i \frac{dw_i}{dt}\frac{d}{dw_i}(w_i \ln w_i) = -\sum_i \dot{w}_i(\ln w_i + 1) = -\sum_i \dot{w}_i \ln w_i,$$

where we have applied Eq. (2). We now apply Eq. (1):

$$\dot{S} = -\sum_i \sum_j (P_{ij}w_j - P_{ji}w_i) \ln w_i = -\frac{1}{2}\left(\sum_i \sum_j (P_{ij}w_j - P_{ji}w_i) \ln w_i + \sum_j \sum_i (P_{ji}w_i - P_{ij}w_j) \ln w_j\right),$$

where we have split the sum in half and swapped indices for the second half. Then, using the symmetry of P,

$$\dot{S} = -\frac{1}{2}\sum_i \sum_j P_{ij}[(w_j - w_i)\ln w_i + (w_i - w_j)\ln w_j] = \frac{1}{2}\sum_i \sum_j P_{ij}[(w_i - w_j)\ln w_i - (w_i - w_j)\ln w_j]$$

$$= \frac{1}{2}\sum_i \sum_j P_{ij}(w_i - w_j)(\ln w_i - \ln w_j).$$

Since w_i represent probabilities, $0 \leq w_i \leq 1$ for all i, which implies $\ln w_i \leq 0$. If $w_i > w_j$, $\ln w_j$ is more negative than $\ln w_i$. That is,

$$w_i \geq w_j \implies \ln w_i - \ln w_j \geq 0 \quad \text{and} \quad w_i - w_j \geq 0,$$
$$w_i \leq w_j \implies \ln w_i - \ln w_j \leq 0 \quad \text{and} \quad w_i - w_j \leq 0.$$

Thus, $\dot{S} \geq 0$ as desired. $\qquad\square$

1.2 Rényi entropy of the order α is defined by the formula $S_\alpha = 1/(1-\alpha)\ln\sum_i w_i^\alpha$.

1.2(a) Show that Rényi entropy of the order 1 is the Boltzmann entropy (in the context of information theory, Boltzmann entropy is called Shannon entropy).

Solution. Firstly,

$$S_\alpha = \lim_{\alpha \to 1}\frac{1}{1-\alpha}\ln\sum_i w_i^\alpha.$$

Note that

$$\lim_{\alpha \to 1}\ln\sum_i w_i^\alpha = \ln\sum_i w_i = \ln(1) = 0, \qquad\qquad \lim_{\alpha \to 1}(1-\alpha) = 0,$$

where we have used the result of Prob. 1.1(a). Applying L'Hôpital's rule, we find

$$\lim_{\alpha \to 1}S_\alpha = \lim_{\alpha \to 1}\frac{d(\ln\sum_i w_i^\alpha)/d\alpha}{d(1-\alpha)/d\alpha} = \lim_{\alpha \to 1}-\frac{d(\sum_i w_i^\alpha)/d\alpha}{\sum_i w_i^\alpha} = \lim_{\alpha \to 1}-\sum_i w_i^\alpha \ln w_i = -\sum_i w_i \ln w_i,$$

where we have used $d(a^x)/dx = (\ln a)a^x$ [?]. This is the Shannon entropy, as desired. $\qquad\square$

1.2(b) Show that Rényi entropy doesn't decrease: $\dot{S}_\alpha \geq 0$.

Solution. We note that

$$\dot{S}_\alpha = \frac{d}{dt}\left(\frac{1}{1-\alpha}\ln\sum_i w_i^\alpha\right) = \frac{1}{1-\alpha}\frac{d}{dt}\left(\ln\sum_i w_i^\alpha\right) = \frac{1}{1-\alpha}\frac{1}{\sum_i w_i^\alpha}\frac{d}{dt}\left(\sum_i w_i^\alpha\right) = \frac{1}{1-\alpha}\frac{1}{\sum_i w_i^\alpha}\alpha\sum_i \dot{w}_i w_i^{\alpha-1}$$

$$= \frac{\alpha}{1-\alpha}\frac{\sum_i \dot{w}_i w_i^{\alpha-1}}{\sum_i w_i^\alpha}.$$

Applying Eq. (1) and the same trick as in Prob. 1.1(c),

$$\dot{S}_\alpha = \frac{\alpha}{1-\alpha}\frac{1}{\sum_i w_i^\alpha}\sum_i w_i^{\alpha-1}\sum_j(P_{ij}w_j - P_{ji}w_i)$$

$$= \frac{\alpha}{1-\alpha}\frac{1}{2\sum_i w_i^\alpha}\left(\sum_i w_i^{\alpha-1}\sum_j(P_{ij}w_j - P_{ji}w_i) + \sum_j w_j^{\alpha-1}\sum_i(P_{ji}w_i - P_{ij}w_j)\right)$$

$$= \frac{\alpha}{1-\alpha}\frac{1}{2\sum_i w_i^\alpha}\sum_i\sum_j P_{ij}[w_i^{\alpha-1}(w_j - w_i) + w_j^{\alpha-1}(w_i - w_j)]$$

$$= \frac{\alpha}{1-\alpha}\frac{1}{2\sum_i w_i^\alpha}\sum_i\sum_j P_{ij}[(w_i^{\alpha-1} - w_j^{\alpha-1})(w_j - w_i)].$$

Keeping in mind that $0 \leq w_i \leq 1$, this result is non-negative in all possible regimes:

$$w_j \geq w_i \quad\text{and}\quad \alpha < 1 \quad\Longrightarrow\quad \frac{\alpha}{1-\alpha} > 0 \quad\text{and}\quad w_i^{\alpha-1} - w_j^{\alpha-1} \geq 0 \quad\text{and}\quad w_j - w_i \geq 0,$$

$$w_j \geq w_i \quad\text{and}\quad \alpha > 1 \quad\Longrightarrow\quad \frac{\alpha}{1-\alpha} < 0 \quad\text{and}\quad w_i^{\alpha-1} - w_j^{\alpha-1} \leq 0 \quad\text{and}\quad w_j - w_i \geq 0,$$

$$w_j \leq w_i \quad\text{and}\quad \alpha < 1 \quad\Longrightarrow\quad \frac{\alpha}{1-\alpha} > 0 \quad\text{and}\quad w_i^{\alpha-1} - w_j^{\alpha-1} \leq 0 \quad\text{and}\quad w_j - w_i \leq 0,$$

$$w_j \leq w_i \quad\text{and}\quad \alpha > 1 \quad\Longrightarrow\quad \frac{\alpha}{1-\alpha} < 0 \quad\text{and}\quad w_i^{\alpha-1} - w_j^{\alpha-1} \geq 0 \quad\text{and}\quad w_j - w_i \leq 0.$$

Of course $\sum_i w_i^\alpha > 0$ in any case. Thus, $\dot{S}_\alpha \geq 0$ as desired. $\qquad\square$

Problem 2. Pauli paramagnetism Cold atomic gases could be realized by atomic isotopes which are fermions (^{6}Li, ^{40}K, etc.). Such isotopes may have a large atomic spin. Assuming that the Fermi gas is degenerate and its constituents have a spin $s > 1/2$, compute the Pauli magnetic susceptibility.

Solution. According to p. 2 of Lecture 12, the magnetic susceptibility is defined

$$\chi = \frac{1}{V}\frac{\partial N}{\partial \mu},$$

where $N = \partial\Omega/\partial\mu$, and

$$\Omega(\mu, B) = \frac{1}{2}\Omega_0(\mu + B) + \frac{1}{2}\Omega_0(\mu - B) \approx \Omega_0(\mu) + \frac{B^2}{2}\frac{\partial^2\Omega_0}{\partial\mu^2},$$

where B is the strength of the magnetic field and Ω_0 is the thermodynamic potential with no field present. <mark>but I think this doesn't work because it is only for spin 1/2</mark>

For a Fermi gas, the thermodynamic potential is [**?** , p. 145]

$$\Omega_0 = -T \sum_k \ln\left(1 + e^{(\mu - \epsilon_k)/T}\right).$$

Note that

$$\frac{\partial \Omega_0}{\partial \mu} =$$

Then the thermodynamic potential in the magnetic field is

$$\Omega =$$

Problem 3. Landau diamagnetism

3.1 Compute the Landau diamagnetic susceptibility for ultra-relativistic Fermi gas.

3.2 (*) Compute the Landau diamagnetic susceptibility for a Fermi gas confined to a box whose linear size in the z direction is $L_z \ll L_x, L_y$. The magnetic field is directed along the z direction. Consider two cases when the energy spacing $(2\pi\hbar/L_z)^2/2m$ is much larger/smaller than the cyclotron energy $\mu_B B$.

Problem 4.   Fluctuations of thermodynamics

4.1 Find the energy fluctuation $\langle(\Delta E)^2\rangle = \langle(E - \langle E\rangle)^2\rangle$ and the number fluctuation $\langle(\Delta N)^2\rangle = \langle(N - \langle N\rangle)^2\rangle$ for photons in the black body radiation.

Solution.   Planck's distribution, which gives the occupation number for state k of a blackbody, is [**?** , p. 163]

$$\langle n_k\rangle = \frac{1}{e^{\hbar\omega_k/T} - 1}.$$

This is a special case of the Bose distribution with $\mu = 0$ and $\epsilon_k = \hbar\omega_k$. The Bose distribution is [**?** , p. 146]

$$\langle n_k\rangle = \frac{1}{e^{(\epsilon_k - \mu)/T} - 1}.$$

Applying $\langle(\Delta N)^2\rangle = T\, \partial\langle N\rangle/\partial\mu$, which is derived in Prob. 4.2, we find [**?** , p. 355]

$$\langle(\Delta n_k)^2\rangle = T\frac{\partial\langle n_k\rangle}{\partial\mu} = T\frac{\partial}{\partial\mu}\left(\frac{1}{e^{(\epsilon_k - \mu)/T} - 1}\right) = T\frac{e^{(\epsilon_k - \mu)/T}}{T(e^{(\epsilon_k - \mu)/T} - 1)^2} = \frac{e^{(\epsilon_k - \mu)/T} - 1 + 1}{(e^{(\epsilon_k - \mu)/T} - 1)^2}$$

$$= \frac{1}{e^{(\epsilon_k - \mu)/T} - 1} + \frac{1}{(e^{(\epsilon_k - \mu)/T} - 1)^2} = \langle n_k\rangle\,(1 + \langle n_k\rangle)$$

The number of photons in the frequency interval $d\omega$ is [**?** , p. 163]

$$dN_\omega = \frac{V}{\pi^2 c^3}\frac{\omega^2}{e^{\hbar\omega/T} - 1}\,d\omega = \frac{V}{\pi^2 c^3}\omega^2\,\langle n_k\rangle\,d\omega\,,$$

where $\langle n_k\rangle = 1/(e^{\hbar\omega/T} - 1)$ is the Planck distribution. By analogy,

$$\langle(\Delta\,dN_\omega)^2\rangle = \frac{V}{\pi^2 c^3}\omega^2\,\langle(\Delta n_k)^2\rangle\,d\omega = \frac{V}{\pi^2 c^3}\omega^2\,\langle n_k\rangle\,(1 + \langle n_k\rangle)\,d\omega = dN_\omega + \langle n_k\rangle\,dN_\omega\,.$$

For the total number of particles, we integrate over $\omega \in (0, \infty)$ [**?** , p. 165]:

$$\langle(\Delta N)^2\rangle = \int_0^\infty \langle(\Delta\,dN_\omega)^2\rangle = \int_0^\infty (dN_\omega + \langle n_k\rangle\,dN_\omega) = N + \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^2}{(e^{\hbar\omega/T} - 1)^2}\,d\omega$$

$$= N + \frac{VT^3}{\pi^2 c^3 \hbar^3}\int_0^\infty \frac{x^2}{(e^x - 1)^2}\,dx = \frac{VT^3}{\hbar^3 c^3}\frac{2\,\zeta(3)}{\pi^2} + \frac{VT^3}{\pi^2 c^3 \hbar^3}\left(\frac{\pi^2}{3} - 2\,\zeta(3)\right) = \frac{VT^3}{3c^3 \hbar^3},$$

where N is given in the book, and we have evaluated the second integral using Mathematica.

Likewise, the radiation energy in the interval $d\omega$ is [**?** , p. 163]

$$dE_\omega = \frac{V}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/T} - 1}\,d\omega = \frac{V}{\pi^2 c^3}\omega^3\,\langle n_k\rangle\,d\omega\,,$$

so, as before, $\langle(\Delta\,dE_\omega)^2\rangle = dE_\omega + \langle n_k\rangle\,dE_\omega$. Then the total energy is

$$\langle(\Delta E)^2\rangle = \int_0^\infty (dE_\omega + \langle n_k\rangle\,dE_\omega) = E + \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^3}{(e^{\hbar\omega/T} - 1)^2}\,d\omega = E + \frac{VT^4}{\pi^2 c^3 \hbar^3}\int_0^\infty \frac{x^3}{(e^x - 1)^2}\,dx$$

$$= \frac{\pi^2 VT^4}{15\hbar^3 c^3} + \frac{VT^4}{\pi^2 c^3 \hbar^3}\left(6\,\zeta(3) - \frac{\pi^4}{15}\right) = \frac{6\,\zeta(3)\,VT^4}{\pi^2 c^3 \hbar^3} = \frac{7.212\,VT^4}{\pi^2 c^3 \hbar^3}.$$

4.2 Show that the number of particles in a sub-volume of a gas fluctuates according the formula $\langle (\Delta N)^2 \rangle = T\, \partial \langle N \rangle / \partial \mu$. Furthermore, apply this formula to the Boltzmann, Fermi, and Bose ideal gases.

Solution. Let $p(x)$ denote the probability of a fluctuation in x. Then $p(x) \propto e^{S(x)}$, where $S(x)$ is the entropy of a closed system representing a sub-volume of a gas [**?** , pp. 343, 348]. It follows that $p(x) \propto e^{\Delta S(x)}$, where $\Delta S(x)$ is the change in the entropy due to the fluctuation [**?** , p. 348]. This change is equal to the difference between $S(x)$ and its equilibrium value, which is given by

$$\Delta S(x) = -\frac{\Delta E - T\, \Delta S + P\, \Delta V}{T},$$

where T and P are the equilibrium values [**?** , pp. 60, 349]. Assuming small fluctuations and thus small ΔE, we can expand ΔE as

$$\Delta E = \frac{\partial E}{\partial S} \Delta S + \frac{\partial E}{\partial V} \Delta V + \frac{1}{2} \left[\frac{\partial^2 E}{\partial S^2}^2 + 2 \frac{\partial^2 E}{\partial S \partial V} \Delta S\, \Delta V + \frac{\partial E}{\partial V}^2 \right]$$

$$= T\, \Delta S - P\, \Delta V + \frac{1}{2} \left[\left(\Delta \frac{\partial E}{\partial S} \right)_V \Delta S + \left(\Delta \frac{\partial E}{\partial V} \right)_S \Delta V \right] = T\, \Delta S - P\, \Delta V + \frac{\Delta S\, \Delta T - \Delta P\, \Delta V}{2},$$

where we have used $\partial E / \partial S = T$ and $\partial E / \partial V = -P$ [**?** , pp. 60, 349]. Then the fluctuation probability has the proportionality

$$p \propto e^{\Delta S(x)} = \exp\left(\frac{\Delta P\, \Delta V - \Delta S\, \Delta T}{2T} \right).$$

Expanding ΔS and ΔP in terms of V and T, we find

$$\Delta P = \left(\frac{\partial P}{\partial T} \right)_V \Delta T + \left(\frac{\partial P}{\partial V} \right)_t \Delta V, \qquad \Delta S = \left(\frac{\partial S}{\partial T} \right)_V \Delta T + \left(\frac{\partial S}{\partial V} \right)_T \Delta V = \frac{C_v}{T} \Delta T + \left(\frac{\partial P}{\partial T} \right)_V \Delta V,$$

where we have used $(\partial S / \partial V)_T = (\partial P / \partial T)_V$ and $C_v = T(\partial S / \partial T)_V$ [**?** , pp. 45, 50, 349]. Making these substitutions,

$$p \propto \exp\left\{ \frac{1}{2T} \left[\left(\frac{\partial P}{\partial T} \right)_V \Delta T\, \Delta V + \left(\frac{\partial P}{\partial V} \right)_t (\Delta V)^2 - \frac{\partial C_v}{\partial T}^2 - \left(\frac{\partial P}{\partial T} \right)_V \Delta V\, \Delta T \right] \right\}$$

$$= \exp\left[\left(\frac{1}{2T} \frac{\partial P}{\partial V} \right)_t (\Delta V)^2 - \frac{C_v}{2T^2}(\Delta T) \right] = \exp\left[\left(\frac{1}{2T} \frac{\partial P}{\partial V} \right)_t (\Delta V)^2 \right] \exp\left[-\frac{C_v}{2T^2}(\Delta T) \right]. \tag{5}$$

Thus, the expression is separable and fluctuations in V and in T can be regarded as independent [**?** , p. 349].

We will focus on fluctuations in volume, and assume their probability to be Gaussian distributed. The Gaussian distribution is given by [**?** , p. 345]

$$p(x)\, dx = \frac{1}{\sqrt{2\pi \langle x^2 \rangle}} \exp\left(-\frac{x^2}{2 \langle x^2 \rangle} \right) dx\,.$$

Comparing Eq. (5), we find that [**?** , p. 350]

$$\langle (\Delta V)^2 \rangle = -T \left(\frac{\partial V}{\partial P} \right)_T.$$

Dividing both sides by N^2 [**?** , p. 351],

$$\langle [\Delta(V/N)]^2 \rangle = -\frac{T}{N^2} \left(\frac{\partial V}{\partial P} \right)_T.$$

Now we fix V and consider fluctuations in N. Note that

$$\Delta(V/N) = V\,\Delta(1/N) = -\frac{V}{N^2}\,\Delta N,$$

so we have

$$\langle(\Delta N)^2\rangle = -\frac{TN^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_T.$$

Since $N = V\,f(P,T)$, we can write

$$-\frac{N^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_T = N\left[\frac{\partial}{\partial P}\left(\frac{N}{V}\right)\right]_{T,N} = N\left[\frac{\partial}{\partial P}\left(\frac{N}{V}\right)\right]_{T,v} = \frac{N}{V}\left(\frac{\partial N}{\partial P}\right)_{T,v} = \left(\frac{\partial P}{\partial\mu}\right)_{T,V}\left(\frac{\partial N}{\partial P}\right)_{T,V} = \left(\frac{\partial N}{\partial\mu}\right)_{T,V},$$

where we have used $N/V = (\partial P/\partial\mu)_T$ [**?** , pp. 351–352]. Since we associated all quantities with those at equilibrium, we have shown that

$$\langle(\Delta N)^2\rangle = T\frac{\partial\langle N\rangle}{\partial\mu} \tag{6}$$

as desired. $\qquad\square$

For a classical Boltzmann gas, the number of particles in a interval d^3p is [**?** , pp. 108–109]

$$dN_\mathbf{p} = \frac{V}{(2\pi mT)^{3/2}}\exp\left(\frac{\mu}{T} - \frac{\mathbf{p}^2}{2mT}\right)d^3p,$$

so the total number of particles is

$$N = \frac{V}{(2\pi mT)^{3/2}}\int\exp\left(\frac{\mu}{T} - \frac{\mathbf{p}^2}{2mT}\right)d^3p.$$

To apply Eq. (6), note that

$$T\frac{\partial\langle N\rangle}{\partial\mu} = T\frac{\partial}{\partial\mu}\left(\frac{V}{(2\pi mT)^{3/2}}\int\exp\left(\frac{\mu}{T} - \frac{\mathbf{p}^2}{2mT}\right)d^3p\right) = T\frac{V}{(2\pi mT)^{3/2}}\int\frac{d}{dT}\left(e^{\mu/T}e^{-\mathbf{p}^2/(2mT)}\,d^3p\right)$$

$$= \frac{T}{T}\frac{\partial}{\partial\mu}\left(\frac{V}{(2\pi mT)^{3/2}}\int\exp\left(\frac{\mu}{T} - \frac{\mathbf{p}^2}{2mT}\right)d^3p\right) = N.$$

Thus,

$$\langle(\Delta N)^2\rangle - \langle N\rangle.$$

For the Fermi and Bose gases, the number of particles is given by

$$N = \frac{gV}{\pi^2\hbar^2}\sqrt{\frac{m^3T^3}{2}}\int_0^\infty\frac{\sqrt{z}}{e^{z-\mu/T}\pm 1}\,dz\begin{cases}\text{Fermi,}\\ \text{Bose,}\end{cases}$$

where $z = \epsilon/T$ [**?** , pp. 149, 354]. Evaluating the integrals using

$$\int_0^\infty\frac{k^s}{e^{k-\mu}\pm 1}\,dk = -\Gamma(s+1)\,\mathrm{Li}_{1+s}(\mp e^\mu),$$

where Li is the polylogarithm [**?**], we have

$$N = \mp\frac{gV}{\pi^2\hbar^2}\sqrt{\frac{m^3T^3}{2}}\Gamma(3/2)\,\mathrm{Li}_{3/2}(\mp e^{\mu/T}) = \mp\frac{gV}{\pi^2\hbar^2}\left(\frac{mT}{2}\right)^{3/2}\mathrm{Li}_{3/2}(\mp e^{\mu/T}).$$

Using the formula $d\mathrm{Li}_n(x)/dx = \mathrm{Li}_{n-1}(x)/x$ [**?**], we find

$$\frac{\partial}{\partial \mu}[\mathrm{Li}_{3/2}(\mp e^{\mu/T})] = \mp \frac{\partial}{\partial \mu}\Big(\mp e^{\mu/T}\Big)\frac{\mathrm{Li}_{3/2}(\mp e^{\mu/T})}{e^{\mu/T}} = \frac{\mathrm{Li}_{3/2}(\mp e^{\mu/T})}{T}.$$

So the fluctuations are

$$\langle (\Delta N)^2 \rangle = \mp \frac{gV}{\pi^2 \hbar^2}\sqrt{\frac{m^3}{2^3 T}}\,\mathrm{Li}_{3/2}(\mp e^{\mu/T})\begin{cases}\text{Fermi,}\\ \text{Bose.}\end{cases}$$

Problem 5.   Pair correlation function

5.1 Compute the pair correlation of density $C(r) = \langle\langle n(r)\, n(0)\rangle\rangle$ and the fluctuation of the occupation number $\langle |n_k|^2 \rangle$ of the degenerate Fermi gas $(T \ll E_F)$ in dimensions $d = 1, 2, 3$. Discuss various distance regimes.

5.2 Repeat the above for the Bose gas above the condensation temperature.