Problems & Solutions

for

Statistical Physics of Particles

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by

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Problems for Chapter I - Thermodynamics

1. *Surface tension:* Thermodynamic properties of the interface between two phases are described by a state function called the surface tension $\mathcal{S}$. It is defined in terms of the work required to increase the surface area by an amount dA through $dW = \mathcal{S}dA$.

(a) By considering the work done against surface tension in an infinitesimal change in radius, show that the pressure inside a spherical drop of water of radius R is larger than outside pressure by $2\mathcal{S}/R$. What is the air pressure inside a soap bubble of radius R?

• The work done by a water droplet on the outside world, needed to increase the radius from R to $R + \Delta R$ is

$$\Delta W = (P - P_o) \cdot 4\pi R^2 \cdot \Delta R,$$

where P is the pressure inside the drop and P_o is the atmospheric pressure. In equilibrium, this should be equal to the increase in the surface energy $\mathcal{S}\Delta A = \mathcal{S} \cdot 8\pi R \cdot \Delta R$, where $\mathcal{S}$ is the surface tension, and

$$\Delta W_{\text{total}} = 0, \quad \Longrightarrow \quad \Delta W_{\text{pressure}} = -\Delta W_{\text{surface}} ,$$

resulting in

$$(P - P_o) \cdot 4\pi R^2 \cdot \Delta R = \mathcal{S} \cdot 8\pi R \cdot \Delta R, \quad \Longrightarrow \quad (P - P_o) = \frac{2\mathcal{S}}{R}.$$

In a soap bubble, there are two air-soap surfaces with almost equal radii of curvatures, and

$$P_{\text{film}} - P_o = P_{\text{interior}} - P_{\text{film}} = \frac{2\mathcal{S}}{R},$$

leading to

$$P_{\text{interior}} - P_o = \frac{4\mathcal{S}}{R}.$$

Hence, the air pressure inside the bubble is larger than atmospheric pressure by $4\mathcal{S}/R$.

(b) A water droplet condenses on a solid surface. There are three surface tensions involved $\mathcal{S}_{aw}$, $\mathcal{S}_{sw}$, and $\mathcal{S}_{sa}$, where a, s, and w refer to air, solid and water respectively. Calculate the angle of contact, and find the condition for the appearance of a water film (complete wetting).

• When steam condenses on a solid surface, water either forms a droplet, or spreads on the surface. There are two ways to consider this problem:

Method 1: Energy associated with the interfaces

In equilibrium, the total energy associated with the three interfaces should be minimum, and therefore

$$dE = S_{aw}dA_{aw} + S_{as}dA_{as} + S_{ws}dA_{ws} = 0.$$

Since the total surface area of the solid is constant,

$$dA_{as} + dA_{ws} = 0.$$

From geometrical considerations (see proof below), we obtain

$$dA_{ws}\cos\theta = dA_{aw}.$$

From these equations, we obtain

$$dE = (S_{aw}\cos\theta - S_{as} + S_{ws})\,dA_{ws} = 0, \quad \Longrightarrow \quad \cos\theta = \frac{S_{as} - S_{ws}}{S_{aw}}.$$

Proof of $dA_{ws}\cos\theta = dA_{aw}$: Consider a droplet which is part of a sphere of radius R, which is cut by the substrate at an angle θ. The areas of the involved surfaces are

$$A_{ws} = \pi(R\sin\theta)^2, \quad \text{and} \quad A_{aw} = 2\pi R^2(1 - \cos\theta).$$

Let us consider a small change in shape, accompanied by changes in R and θ. These variations should preserve the volume of water, i.e. constrained by

$$V = \frac{\pi R^3}{3}\left(\cos^3\theta - 3\cos\theta + 2\right).$$

Introducing $x = \cos\theta$, we can re-write the above results as

$$\begin{cases} A_{ws} = \pi R^2\left(1 - x^2\right), \\ A_{aw} = 2\pi R^2\left(1 - x\right), \\ V = \dfrac{\pi R^3}{3}\left(x^3 - 3x + 2\right). \end{cases}$$

The variations of these quantities are then obtained from

$$\begin{cases} dA_{ws} = 2\pi R\left[\dfrac{dR}{dx}(1 - x^2) - Rx\right]dx, \\ dA_{aw} = 2\pi R\left[2\dfrac{dR}{dx}(1 - x) - R\right]dx, \\ dV = \pi R^2\left[\dfrac{dR}{dx}(x^3 - 3x + 2) + R(x^2 - x)\right]dx = 0. \end{cases}$$

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From the last equation, we conclude

$$\frac{1}{R}\frac{dR}{dx} = -\frac{x^2 - 1}{x^3 - 3x + 2} = -\frac{x + 1}{(x - 1)(x + 2)}.$$

Substituting for dR/dx gives,

$$dA_{ws} = 2\pi R^2 \frac{dx}{x + 2}, \qquad \text{and} \qquad dA_{aw} = 2\pi R^2 \frac{x \cdot dx}{x + 2},$$

resulting in the required result of

$$dA_{aw} = x \cdot dA_{ws} = dA_{ws}\cos\theta.$$

Method 2: Balancing forces on the contact line

Another way to interpret the result is to consider the force balance of the equilibrium surface tension on the contact line. There are four forces acting on the line: *(1)* the surface tension at the water–gas interface, *(2)* the surface tension at the solid–water interface, *(3)* the surface tension at the gas–solid interface, and *(4)* the force downward by solid–contact line interaction. The last force ensures that the contact line stays on the solid surface, and is downward since the contact line is allowed to move only horizontally without friction. These forces should cancel along both the y–direction x–directions. The latter gives the condition for the contact angle known as *Young's equation*,

$$\mathcal{S}_{as} = \mathcal{S}_{aw} \cdot \cos\theta + \mathcal{S}_{ws}, \qquad \Longrightarrow \qquad \cos\theta = \frac{\mathcal{S}_{as} - \mathcal{S}_{ws}}{\mathcal{S}_{aw}}.$$

The critical condition for the complete wetting occurs when $\theta = 0$, or $\cos\theta = 1$, i.e. for

$$\cos\theta_C = \frac{\mathcal{S}_{as} - \mathcal{S}_{ws}}{\mathcal{S}_{aw}} = 1.$$

Complete wetting of the substrate thus occurs whenever

$$\mathcal{S}_{aw} \leq \mathcal{S}_{as} - \mathcal{S}_{ws}.$$

(c) In the realm of "large" bodies gravity is the dominant force, while at "small" distances surface tension effects are all important. At room temperature, the surface tension of water is $\mathcal{S}_o \approx 7 \times 10^{-2} N m^{-1}$. Estimate the typical length-scale that separates "large" and "small" behaviors. Give a couple of examples for where this length-scale is important.

- Typical length scales at which the surface tension effects become significant are given by the condition that the forces exerted by surface tension and relevant pressures become comparable, or by the condition that the surface energy is comparable to the other energy changes of interest.

Example 1: Size of water drops not much deformed on a non-wetting surface. This is given by equalizing the surface energy and the gravitational energy,

$$S \cdot 4\pi R^2 \approx mgR = \rho V g R = \frac{4\pi}{3} R^4 g,$$

leading to

$$R \approx \sqrt{\frac{3S}{\rho g}} \approx \sqrt{\frac{3 \cdot 7 \times 10^{-2} N/m}{10^3 kg/m^3 \times 10 m/s^2}} \approx 1.5 \times 10^{-3} m = 1.5 mm.$$

Example 2: Swelling of spherical gels in a saturated vapor: Osmotic pressure of the gel (about 1 atm) = surface tension of water, gives

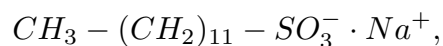$$\pi_{gel} \approx \frac{N}{V} k_B T \approx \frac{2S}{R},$$

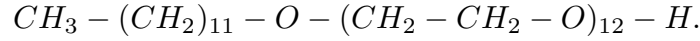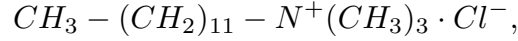where N is the number of counter ions within the gel. Thus,

$$R \approx \left(\frac{2 \times 7 \times 10^{-2} N/m}{10^5 N/m^2} \right) \approx 10^{-6} m.$$

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2. *Surfactants:* Surfactant molecules such as those in soap or shampoo prefer to spread on the air-water surface rather than dissolve in water. To see this, float a hair on the surface of water and gently touch the water in its vicinity with a piece of soap. (This is also why a piece of soap can power a toy paper boat.)

(a) The air-water surface tension $\mathcal{S}_o$ (assumed to be temperature independent) is reduced roughly by $N k_B T/A$, where N is the number of surfactant particles, and A is the area. Explain this result qualitatively.

- Typical surfactant molecules have a hydrophilic head and a hydrophobic tail, and prefer to go to the interface between water and air, or water and oil. Some examples are,

$$CH_3 - (CH_2)_{11} - SO_3^- \cdot Na^+,$$

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$$CH_3 - (CH_2)_{11} - N^+(CH_3)_3 \cdot Cl^-,$$

$$CH_3 - (CH_2)_{11} - O - (CH_2 - CH_2 - O)_{12} - H.$$

The surfactant molecules spread over the surface of water and behave as a two dimensional gas. The gas has a pressure proportional to the density and the absolute temperature, which comes from the two dimensional degrees of freedom of the molecules. Thus the surfactants lower the free energy of the surface when the surface area is increased.

$$\Delta F_{\text{surfactant}} = \frac{N}{A} k_B T \cdot \Delta A = (S - S_o) \cdot \Delta A, \quad \Longrightarrow \quad S = S_o - \frac{N}{A} k_B T.$$

(Note that surface tension is defined with a sign opposite to that of hydrostatic pressure.)

(b) Place a drop of water on a clean surface. Observe what happens to the air-water-surface contact angle as you gently touch the droplet surface with a small piece of soap, and explain the observation.

• As shown in the previous problem, the contact angle satisfies

$$\cos \theta = \frac{S_{as} - S_{ws}}{S_{aw}}.$$

Touching the surface of the droplet with a small piece of soap reduces S_{aw}, hence $\cos \theta$ increases, or equivalently, the angle θ decreases.

(c) More careful observations show that at higher surfactant densities

$$\left. \frac{\partial S}{\partial A} \right|_T = \frac{N k_B T}{(A - Nb)^2} - \frac{2a}{A} \left(\frac{N}{A} \right)^2 \quad, \quad \text{and} \quad \left. \frac{\partial T}{\partial S} \right|_A = -\frac{A - Nb}{N k_B};$$

where a and b are constants. Obtain the expression for $S(A, T)$ and explain qualitatively the origin of the corrections described by a and b.

• When the surfactant molecules are dense their interaction becomes important, resulting in

$$\left. \frac{\partial S}{\partial A} \right|_T = \frac{N k_B T}{(A - Nb)^2} - \frac{2a}{A} \left(\frac{N}{A} \right)^2,$$

and

$$\left. \frac{\partial T}{\partial S} \right|_A = -\frac{A - Nb}{N k_B}.$$

Integrating the first equation, gives

$$S(A, t) = f(T) - \frac{N k_B T}{A - Nb} + a \left(\frac{N}{A} \right)^2,$$

where $f(T)$ is a function of only T, while integrating the second equation, yields

$$\mathcal{S}(A, T) = g(A) - \frac{Nk_B T}{A - Nb},$$

with $g(A)$ a function of only A. By comparing these two equations we get

$$\mathcal{S}(A, T) = \mathcal{S}_o - \frac{Nk_B T}{A - Nb} + a\left(\frac{N}{A}\right)^2,$$

where $\mathcal{S}_o$ represents the surface tension in the absence of surfactants and is independent of A and T. The equation resembles the van der Waals equation of state for gas-liquid systems. The factor Nb in the second term represents the excluded volume effect due to the finite size of the surfactant molecules. The last term represents the binary interaction between two surfactant molecules. If surfactant molecules attract each other the coefficient a is positive the surface tension increases.

(d) Find an expression for $C_{\mathcal{S}} - C_A$ in terms of $\frac{\partial E}{\partial A}\big|_T$, $\mathcal{S}$, $\frac{\partial \mathcal{S}}{\partial A}\big|_T$, and $\frac{\partial T}{\partial \mathcal{S}}\big|_A$, for $\frac{\partial E}{\partial T}\big|_A = \frac{\partial E}{\partial T}\big|_{\mathcal{S}}$.

- Taking A and T as independent variables, we obtain

$$\delta Q = dE - \mathcal{S} \cdot dA, \quad \Longrightarrow \quad \delta Q = \frac{\partial E}{\partial A}\bigg|_T dA + \frac{\partial E}{\partial T}\bigg|_A dT - \mathcal{S} \cdot dA,$$

and

$$\delta Q = \left(\frac{\partial E}{\partial A}\bigg|_T - \mathcal{S}\right) dA + \frac{\partial E}{\partial T}\bigg|_A dT.$$

From the above result, the heat capacities are obtained as

$$\begin{cases} C_A \equiv \dfrac{\delta Q}{\delta T}\bigg|_A = \dfrac{\partial E}{\partial T}\bigg|_A \\[4mm] C_{\mathcal{S}} \equiv \dfrac{\delta Q}{\delta T}\bigg|_{\mathcal{S}} = \left(\dfrac{\partial E}{\partial A}\bigg|_T - \mathcal{S}\right) \dfrac{\partial A}{\partial T}\bigg|_{\mathcal{S}} + \dfrac{\partial E}{\partial T}\bigg|_{\mathcal{S}} \end{cases},$$

resulting in

$$C_{\mathcal{S}} - C_A = \left(\frac{\partial E}{\partial A}\bigg|_T - \mathcal{S}\right) \frac{\partial A}{\partial T}\bigg|_{\mathcal{S}}.$$

Using the chain rule relation

$$\frac{\partial T}{\partial \mathcal{S}}\bigg|_A \cdot \frac{\partial \mathcal{S}}{\partial A}\bigg|_T \cdot \frac{\partial A}{\partial T}\bigg|_{\mathcal{S}} = -1,$$

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we obtain

$$C_{\mathcal{S}} - C_A = \left(\left. \frac{\partial E}{\partial A} \right|_T - \mathcal{S} \right) \cdot \left(\frac{-1}{\left. \frac{\partial T}{\partial \mathcal{S}} \right|_A \cdot \left. \frac{\partial \mathcal{S}}{\partial A} \right|_T} \right).$$

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3. *Temperature scales:* Prove the equivalence of the ideal gas temperature scale Θ, and the thermodynamic scale T, by performing a Carnot cycle on an ideal gas. The ideal gas satisfies $PV = Nk_B\Theta$, and its internal energy E is a function of Θ only. However, *you may not assume that $E \propto \Theta$.* You may wish to proceed as follows:

(a) Calculate the heat exchanges Q_H and Q_C as a function of Θ_H, Θ_C, and the volume expansion factors.

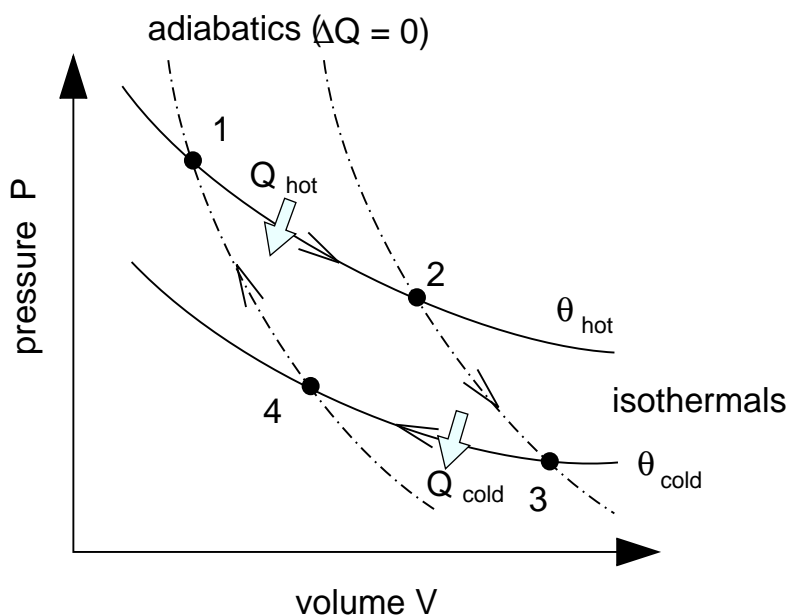• The ideal gas temperature is defined through the equation of state

$$\theta = \frac{PV}{Nk_B}.$$

The thermodynamic temperature is defined for a reversible Carnot cycle by

$$\frac{T_{hot}}{T_{cold}} = \frac{Q_{hot}}{Q_{cold}}.$$

For an ideal gas, the internal energy is a function only of θ, i.e. $E = E(\theta)$, and

$$dQ = dE - dW = \frac{dE}{d\theta} \cdot d\theta + PdV.$$

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Consider the Carnot cycle indicated in the figure. For the segment 1 to 2, which undergoes an isothermal expansion, we have

$$d\theta = 0, \implies dQ_{hot} = PdV, \quad \text{and} \quad P = \frac{Nk_B\theta_{hot}}{V}.$$

Hence, the heat input of the cycle is related to the expansion factor by

$$Q_{hot} = \int_{V_1}^{V_2} Nk_B\theta_{hot}\frac{dV}{V} = Nk_B\theta_{hot}\ln\left(\frac{V_2}{V_1}\right).$$

A similar calculation along the low temperature isotherm yields

$$Q_{cold} = \int_{V_4}^{V_3} Nk_B\theta_{cold}\frac{dV}{V} = Nk_B\theta_{cold}\ln\left(\frac{V_3}{V_4}\right),$$

and thus

$$\frac{Q_{hot}}{Q_{cold}} = \frac{\theta_{hot}}{\theta_{cold}}\frac{\ln\left(V_2/V_1\right)}{\ln\left(V_3/V_4\right)}.$$

(b) Calculate the volume expansion factor in an adiabatic process as a function of Θ.

• Next, we calculate the volume expansion/compression ratios in the adiabatic processes. Along an adiabatic segment

$$dQ = 0, \implies 0 = \frac{dE}{d\theta}\cdot d\theta + \frac{Nk_B\theta}{V}\cdot dV, \implies \frac{dV}{V} = -\frac{1}{Nk_B\theta}\frac{dE}{d\theta}\cdot d\theta.$$

Integrating the above between the two temperatures, we obtain

$$\begin{cases} \ln\left(\frac{V_3}{V_2}\right) = -\frac{1}{Nk_B}\int_{\theta_{cold}}^{\theta_{hot}}\frac{1}{\theta}\frac{dE}{d\theta}\cdot d\theta, \quad \text{and} \\ \ln\left(\frac{V_4}{V_1}\right) = -\frac{1}{Nk_B}\int_{\theta_{cold}}^{\theta_{hot}}\frac{1}{\theta}\frac{dE}{d\theta}\cdot d\theta. \end{cases}$$

While we cannot explicitly evaluate the integral (since $E(\theta)$ is arbitrary), we can nonetheless conclude that

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}.$$

(c) Show that $Q_H/Q_C = \Theta_H/\Theta_C$.

• Combining the results of parts (a) and (b), we observe that

$$\frac{Q_{hot}}{Q_{cold}} = \frac{\theta_{hot}}{\theta_{cold}}.$$

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Since the thermodynamic temperature scale is defined by

$$\frac{Q_{hot}}{Q_{cold}} = \frac{T_{hot}}{T_{cold}},$$

we conclude that θ and T are proportional. If we further define $\theta(\text{triple point}_{H_20}) = T(\text{triple point}_{H_20}) = 273.16$, θ and T become identical.

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4. *Equations of State:* The equation of state constrains the form of internal energy as in the following examples.

(a) Starting from $dE = TdS - PdV$, show that the equation of state $PV = Nk_BT$, in fact implies that E can only depend on T.

• Since there is only one form of work, we can choose any two parameters as independent variables. For example, selecting T and V, such that $E = E(T, V)$, and $S = S(T, V)$, we obtain

$$dE = TdS - PdV = T\left.\frac{\partial S}{\partial T}\right|_V dT + T\left.\frac{\partial S}{\partial V}\right|_T dV - PdV,$$

resulting in

$$\left.\frac{\partial E}{\partial V}\right|_T = T\left.\frac{\partial S}{\partial V}\right|_T - P.$$

Using the Maxwell's relation[†]

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V,$$

we obtain

$$\left.\frac{\partial E}{\partial V}\right|_T = T\left.\frac{\partial P}{\partial T}\right|_V - P.$$

Since $T\left.\frac{\partial P}{\partial T}\right|_V = T\frac{Nk_B}{V} = P$, for an ideal gas, $\left.\frac{\partial E}{\partial V}\right|_T = 0$. Thus E depends only on T, i.e. $E = E(T)$.

(b) What is the most general equation of state consistent with an internal energy that depends only on temperature?

• If $E = E(T)$,

$$\left.\frac{\partial E}{\partial V}\right|_T = 0, \quad \Longrightarrow \quad T\left.\frac{\partial P}{\partial T}\right|_V = P.$$

The solution for this equation is $P = f(V)T$, where $f(V)$ is any function of only V.

[†] $dL = Xdx + Ydy + \cdots, \quad \Longrightarrow \quad \left.\frac{\partial X}{\partial y}\right|_x = \left.\frac{\partial Y}{\partial x}\right|_y = \frac{\partial^2 L}{\partial x \cdot \partial y}.$

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(c) Show that for a van der Waals gas C_V is a function of temperature alone.

- The van der Waals equation of state is given by

$$\left[P - a \left(\frac{N}{V} \right)^2 \right] \cdot (V - Nb) = Nk_BT,$$

or

$$P = \frac{Nk_BT}{(V - Nb)} + a \left(\frac{N}{V} \right)^2.$$

From these equations, we conclude that

$$C_V \equiv \left. \frac{\partial E}{\partial T} \right|_V, \quad \Longrightarrow \quad \left. \frac{\partial C_V}{\partial V} \right|_T = \frac{\partial^2 E}{\partial V \partial T} = \frac{\partial}{\partial T} \left\{ T \left. \frac{\partial P}{\partial T} \right|_V - P \right\} = T \left. \frac{\partial^2 P}{\partial T^2} \right|_V = 0.$$

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5. *Clausius–Clapeyron equation* describes the variation of boiling point with pressure. It is usually derived from the condition that the chemical potentials of the gas and liquid phases are the same at coexistence.

- From the equations

$$\mu_{liquid}(P, T) = \mu_{gas}(P, T),$$

and

$$\mu_{liquid}(P + dP, T + dT) = \mu_{gas}(P + dP, T + dT),$$

we conclude that along the coexistence line

$$\left. \frac{dP}{dT} \right|_{coX} = \frac{\left. \frac{\partial \mu_g}{\partial T} \right|_P - \left. \frac{\partial \mu_l}{\partial T} \right|_P}{\left. \frac{\partial \mu_l}{\partial P} \right|_T - \left. \frac{\partial \mu_g}{\partial P} \right|_T}.$$

The variations of the Gibbs free energy, $G = N\mu(P, T)$ from the extensivity condition, are given by

$$V = \left. \frac{\partial G}{\partial P} \right|_T, \quad S = - \left. \frac{\partial G}{\partial T} \right|_P.$$

In terms of intensive quantities

$$v = \frac{V}{N} = \left. \frac{\partial \mu}{\partial P} \right|_T, \quad s = \frac{S}{N} = - \left. \frac{\partial \mu}{\partial T} \right|_P,$$

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where s and v are molar entropy and volume, respectively. Thus, the coexistence line satisfies the condition

$$\left.\frac{dP}{dT}\right|_{\text{coX}} = \frac{S_g - S_l}{V_g - V_l} = \frac{s_g - s_l}{v_g - v_l}.$$

For an alternative derivation, consider a Carnot engine using one mole of water. At the source (P, T) the latent heat L is supplied converting water to steam. There is a volume increase V associated with this process. The pressure is adiabatically decreased to $P - dP$. At the sink $(P - dP, T - dT)$ steam is condensed back to water.

(a) Show that the work output of the engine is $W = V dP + \mathcal{O}(dP^2)$. Hence obtain the Clausius–Clapeyron equation

$$\left.\frac{dP}{dT}\right|_{\text{boiling}} = \frac{L}{TV}. \tag{1}$$

- If we approximate the adiabatic processes as taking place at constant volume V (vertical lines in the $P - V$ diagram), we find

$$W = \oint P dV = PV - (P - dP)V = V dP.$$
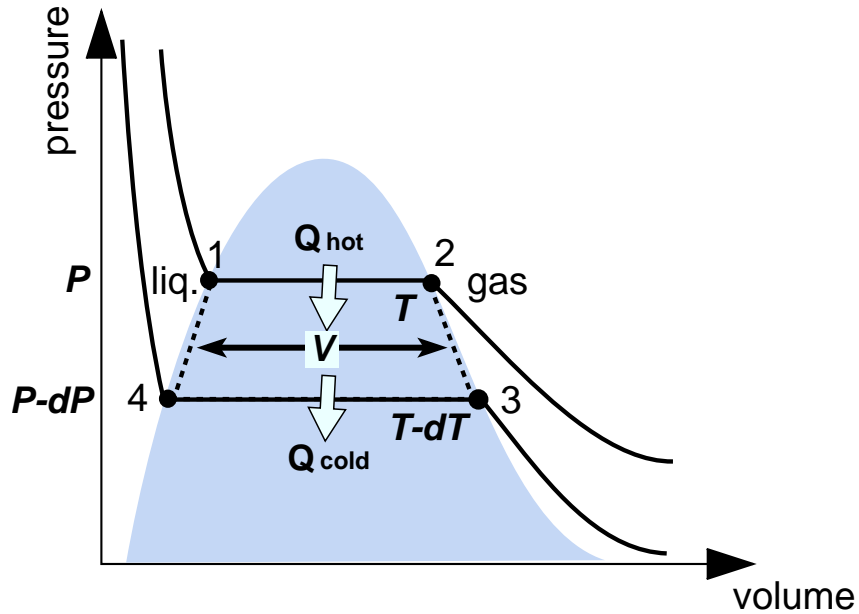
Here, we have neglected the volume of liquid state, which is much smaller than that of the gas state. As the error is of the order of

$$\frac{\partial V}{\partial P}\bigg|_S dP \cdot dP = O(dP^2),$$

we have

$$W = V dP + O(dP^2).$$

The efficiency of any Carnot cycle is given by

$$\eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H},$$

and in the present case,

$$Q_H = L, \quad W = V dP, \quad T_H = T, \quad T_C = T - dT.$$

Substituting these values in the universal formula for efficiency, we obtain the Clausius-Clapeyron equation

$$\frac{V dP}{L} = \frac{dT}{T}, \quad \text{or} \quad \frac{dP}{dT}\bigg|_{coX} = \frac{L}{T \cdot V}.$$

(b) What is wrong with the following argument: "The heat Q_H supplied at the source to convert one mole of water to steam is $L(T)$. At the sink $L(T - dT)$ is supplied to condense one mole of steam to water. The difference $dTdL/dT$ must equal the work $W = V dP$, equal to $L dT/T$ from eq.(1). Hence $dL/dT = L/T$ implying that L is proportional to T!"

• The statement "At the sink $L(T - dT)$ is supplied to condense one mole of water" is incorrect. In the $P - V$ diagram shown, the state at "1" corresponds to pure water, "2" corresponds to pure vapor, but the states "3" and "4" have two phases coexisting. In going from the state 3 to 4 less than one mole of steam is converted to water. Part of the steam has already been converted into water during the adiabatic expansion $2 \to 3$, and the remaining portion is converted in the adiabatic compression $4 \to 1$. Thus the actual latent heat should be less than the contribution by one mole of water.

(c) Assume that L is approximately temperature independent, and that the volume change is dominated by the volume of steam treated as an ideal gas, i.e. $V = Nk_BT/P$. Integrate equation (1) to obtain $P(T)$.

- For an ideal gas

$$V = \frac{Nk_B T}{P}, \quad \Longrightarrow \quad \left.\frac{dP}{dT}\right|_{coX} = \frac{LP}{Nk_B T^2}, \quad \text{or} \quad \frac{dP}{P} = \frac{L}{Nk_B T^2}dT.$$

Integrating this equation, the boiling temperature is obtained as a function of the pressure P, as

$$P = C \cdot \exp\left(-\frac{L}{k_B T_{Boiling}}\right).$$

(d) A hurricane works somewhat like the engine described above. Water evaporates at the warm surface of the ocean, steam rises up in the atmosphere, and condenses to water at the higher and cooler altitudes. The Coriolis force converts the upwards suction of the air to spiral motion. (Using ice and boiling water, you can create a little storm in a tea cup.) Typical values of warm ocean surface and high altitude temperatures are $80^0 F$ and $-120^0 F$ respectively. The warm water surface layer must be at least 200 feet thick to provide sufficient water vapor, as the hurricane needs to condense about 90 million tons of water vapor per hour to maintain itself. Estimate the maximum possible efficiency, and power output, of such a hurricane. (The latent heat of vaporization of water is about $2.3 \times 10^6 \, Jkg^{-1}$.)

- For $T_C = -120^o F = 189^o K$, and $T_H = 80^o F = 300^o K$, the limiting efficiency, as that of a Carnot engine, is

$$\eta_{max} = \frac{T_H - T_C}{T_H} = 0.37.$$

The output power, is equal to (input power) x (efficiency). The input in this case is the energy obtained from evaporation of warm ocean temperature; hence

$$\text{Power output} = \frac{dW}{dt} = \frac{dQ_c}{dt} \times \frac{T_H - T_C}{T_C}$$
$$= \frac{90 \times 10^6 tons}{hr} \cdot \frac{1hr}{3600sec} \cdot \frac{1000kg}{ton} \cdot \frac{2.3 \times 10^6 J}{kg} \times 0.67 \approx 4 \times 10^{13} watts.$$

(e) Due to gravity, atmospheric pressure $P(h)$ drops with the height h. By balancing the forces acting on a slab of air (behaving like a perfect gas) of thickness dh, show that $P(h) = P_0 \exp(-mgh/kT)$, where m is the average mass of a molecule in air.

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- Consider a horizontal slab of area A between heights h and $h + dh$. The gravitational force due to mass of particles in the slab is

$$dF_{\text{gravity}} = mg\frac{N}{V}Adh = mg\frac{P}{k_BT}Adh,$$

where we have used the ideal gas law to relate the density (N/V) to the pressure. The gravitational force is balanced in equilibrium with the force due to pressure

$$dF_{\text{pressure}} = A\left[P(h) - P(h + dh)\right] = -\left.\frac{\partial P}{\partial h}\right|Adh.$$

Equating the two forces gives

$$\left.\frac{\partial P}{\partial h}\right| = -mg\frac{P}{k_BT}, \qquad \Longrightarrow \qquad P(h) = p_0 \exp\left(-\frac{mgh}{k_BT}\right),$$

assuming that temperature does not change with height.

(f) Use the above results to estimate the boiling temperature of water on top of Mount Everest ($h \approx 9km$). The latent heat of vaporization of water is about $2.3 \times 10^6 Jkg^{-1}$.

- Using the results from parts (c) and (e), we conclude that

$$\frac{P_{\text{Everest}}}{P_{\text{sea}}} \approx \exp\left(-\frac{mg}{k_BT}(h_{\text{Everest}} - h_{\text{sea}})\right) \approx \exp\left[-\frac{L}{k_B}\left(\frac{1}{T_{\text{Everest}}(\text{boil})} - \frac{1}{T_{\text{sea}}(\text{boil})}\right)\right].$$

Using the numbers provided, we find $T_{\text{Everest}}(\text{boil}) \approx 346^o\text{K}$ ($74^o\text{C} \approx 163^o\text{F}$).

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6. *Glass:* Liquid quartz, if cooled slowly, crystallizes at a temperature T_m, and releases latent heat L. Under more rapid cooling conditions, the liquid is supercooled and becomes glassy.

(a) As both phases of quartz are almost incompressible, there is no work input, and changes in internal energy satisfy $dE = TdS + \mu dN$. Use the extensivity condition to obtain the expression for μ in terms of E, T, S, and N.

- Since in the present context we are considering only chemical work, we can regard entropy as a function of two independent variables, e.g. E, and N, which appear naturally from $dS = dE/T - \mu dN/T$. Since entropy is an extensive variable, $\lambda S = S(\lambda E, \lambda N)$. Differentiating this with respect to λ and evaluating the resulting expression at $\lambda = 1$, gives

$$S(E, N) = \left.\frac{\partial S}{\partial E}\right|_N E + \left.\frac{\partial S}{\partial N}\right|_E N = \frac{E}{T} - \frac{N\mu}{T},$$

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leading to

$$\mu = \frac{E - TS}{N}.$$

(b) The heat capacity of crystalline quartz is approximately $C_X = \alpha T^3$, while that of glassy quartz is roughly $C_G = \beta T$, where α and β are constants.

Assuming that the third law of thermodynamics applies to both crystalline and glass phases, calculate the entropies of the two phases at temperatures $T \leq T_m$.

• Finite temperature entropies can be obtained by integrating dQ/T, starting from $S(T = 0) = 0$. Using the heat capacities to obtain the heat inputs, we find

$$\begin{cases} C_{crystal} = \alpha T^3 = \dfrac{T}{N}\dfrac{dS_{crystal}}{dT}, & \implies \quad S_{crystal} = \dfrac{N\alpha T^3}{3}, \\[2mm] C_{glass} = \beta T = \dfrac{T}{N}\dfrac{dS_{glass}}{dT}, & \implies \quad S_{glass} = \beta N T. \end{cases}$$

(c) At zero temperature the local bonding structure is similar in glass and crystalline quartz, so that they have approximately the same internal energy E_0. Calculate the internal energies of both phases at temperatures $T \leq T_m$.

• Since $dE = TdS + \mu dN$, for $dN = 0$, we have

$$\begin{cases} dE = TdS = \alpha NT^3 dT & (crystal), \\[2mm] dE = TdS = \beta NT dT & (glass). \end{cases}$$

Integrating these expressions, starting with the same internal energy E_o at $T = 0$, yields

$$\begin{cases} E = E_o + \dfrac{\alpha N}{4}T^4 & (crystal), \\[2mm] E = E_o + \dfrac{\beta N}{2}T^2 & (glass). \end{cases}$$

(d) Use the condition of thermal equilibrium between two phases to compute the equilibrium melting temperature T_m in terms of α and β.

• From the condition of chemical equilibrium between the two phases, $\mu_{crystal} = \mu_{glass}$, we obtain

$$\left(\frac{1}{3} - \frac{1}{4}\right) \cdot \alpha T^4 = \left(1 - \frac{1}{2}\right) \cdot \beta T^2, \quad \implies \quad \frac{\alpha T^4}{12} = \frac{\beta T^2}{2},$$

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resulting in a transition temperature

$$T_{melt} = \sqrt{\frac{6\beta}{\alpha}}.$$

(e) Compute the latent heat L in terms of α and β.

• From the assumptions of the previous parts, we obtain the latent heats for the glass to crystal transition as

$$L = T_{melt} \left(S_{glass} - S_{crystal} \right) = N T_{melt} \left(\beta T_{melt} - \frac{\alpha T_{melt}^3}{3} \right)$$

$$= N T_{melt}^2 \left(\beta - \frac{\alpha T_{melt}^2}{3} \right) = N T_{melt}^2 (\beta - 2\beta) = -N\beta T_{melt}^2 < 0.$$

(f) Is the result in the previous part correct? If not, which of the steps leading to it is most likely to be incorrect?

• The above result implies that the entropy of the crystal phase is larger than that of the glass phase. This is clearly unphysical, and one of the assumptions must be wrong. The questionable step is the assumption that the glass phase is subject to the third law of thermodynamics, and has zero entropy at $T = 0$. In fact, glass is a non-ergodic state of matter which does not have a unique ground state, and violates the third law.

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7. *Filament:* For an elastic filament it is found that, at a finite range in temperature, a displacement x requires a force

$$J = ax - bT + cTx,$$

where a, b, and c are constants. Furthermore, its heat capacity at constant displacement is proportional to temperature, i.e. $C_x = A(x)T$.

(a) Use an appropriate Maxwell relation to calculate $\partial S/\partial x|_T$.

• From $dF = -SdT + Jdx$, we obtain

$$\left. \frac{\partial S}{\partial x} \right|_T = -\left. \frac{\partial J}{\partial T} \right|_x = b - cx.$$

(b) Show that A has to in fact be independent of x, i.e. $dA/dx = 0$.

- We have $C_x = T\frac{\partial S}{\partial T} = A(x)T$, where $S = S(T, x)$. Thus

$$\frac{\partial A}{\partial x} = \frac{\partial}{\partial x}\frac{\partial S}{\partial T} = \frac{\partial}{\partial T}\frac{\partial S}{\partial x} = 0$$

from part (a), implying that A is independent of x.

(c) Give the expression for $S(T, x)$ assuming $S(0, 0) = S_0$.

- $S(x, T)$ can be calculated as

$$S(x, T) = S(0, 0) + \int_{T'=0}^{T'=T}\frac{\partial S(T', x=0)}{\partial T'}dT' + \int_{x'=0}^{x'=x}\frac{\partial S(T, x')}{\partial x'}dx'$$

$$= S_0 + \int_0^T AdT' + \int_0^x (b - cx')dx'$$

$$= S_0 + AT + (b - \frac{c}{2}x)x.$$

(d) Calculate the heat capacity at constant tension, i.e. $C_J = T\,\partial S/\partial T|_J$ as a function of T and J.

- Writing the entropy as $S(T, x) = S(T, x(T, J))$, leads to

$$\left.\frac{\partial S}{\partial T}\right|_J = \left.\frac{\partial S}{\partial T}\right|_x + \left.\frac{\partial S}{\partial x}\right|_T \left.\frac{\partial x}{\partial T}\right|_J.$$

From parts (a) and (b), $\left.\frac{\partial S}{\partial x}\right|_T = b - cx$ and $\left.\frac{\partial S}{\partial T}\right|x = A$. Furthermore, $\left.\frac{\partial x}{\partial T}\right|_J$ is given by $a\frac{\partial x}{\partial T} - b + cx + cT\frac{\partial x}{\partial T} = 0$, i.e.

$$\frac{\partial x}{\partial T} = \frac{b - cx}{a + cT}.$$

Thus

$$C_J = T\left[A + \frac{(b - cx)^2}{(a + cT)}\right].$$

Since $x = \frac{J+bT}{a+cT}$, we can rewrite the heat capacity as a function of T and J, as

$$C_J = T\left[A + \frac{(b - c\frac{J+bT}{a+cT})^2}{(a + cT)}\right]$$

$$= T\left[A + \frac{(ab - cJ)^2}{(a + cT)^3}\right].$$

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8. *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 $dN = 0$,

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

(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

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

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 hear capacity is

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

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

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

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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9. *Superconducting transition:* Many metals become superconductors at low temperatures T, and magnetic fields B. The heat capacities of the two phases at zero magnetic field are approximately given by

$$\begin{cases} C_s(T) = V\alpha T^3 & \text{in the superconducting phase} \\ C_n(T) = V\left[\beta T^3 + \gamma T\right] & \text{in the normal phase} \end{cases},$$

where V is the volume, and $\{\alpha, \beta, \gamma\}$ are constants. (There is no appreciable change in volume at this transition, and mechanical work can be ignored throughout this problem.)

(a) Calculate the entropies $S_s(T)$ and $S_n(T)$ of the two phases at zero field, using the third law of thermodynamics.

- Finite temperature entropies are obtained by integrating $dS = đQ/T$, starting from $S(T = 0) = 0$. Using the heat capacities to obtain the heat inputs, we find

$$\begin{cases} C_s = V\alpha T^3 = T\frac{dS_s}{dT}, & \Longrightarrow \quad S_s = V\frac{\alpha T^3}{3}, \\ C_n = V\left[\beta T^3 + \gamma T\right] = T\frac{dS_n}{dT}, & \Longrightarrow \quad S_n = V\left[\frac{\beta T^3}{3} + \gamma T\right] \end{cases}.$$

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(b) Experiments indicate that there is no latent heat $(L = 0)$ for the transition between the normal and superconducting phases at zero field. Use this information to obtain the transition temperature T_c, as a function of α, β, and γ.

• The Latent hear for the transition is related to the difference in entropies, and thus

$$L = T_c \left(S_n(T_c) - S_s(T_c) \right) = 0.$$

Using the entropies calculated in the previous part, we obtain

$$\frac{\alpha T_c^3}{3} = \frac{\beta T_c^3}{3} + \gamma T_c, \quad \Longrightarrow \quad T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}.$$

(c) At zero temperature, the electrons in the superconductor form bound Cooper pairs. As a result, the internal energy of the superconductor is reduced by an amount $V\Delta$, i.e. $E_n(T = 0) = E_0$ and $E_s(T = 0) = E_0 - V\Delta$ for the metal and superconductor, respectively. Calculate the internal energies of both phases at finite temperatures.

• Since $dE = TdS + BdM + \mu dN$, for $dN = 0$, and $B = 0$, we have $dE = TdS = CdT$. Integrating the given expressions for heat capacity, and starting with the internal energies E_0 and $E_0 - V\Delta$ at $T = 0$, yields

$$\begin{cases} E_s(T) = E_0 + V \left[-\Delta + \dfrac{\alpha}{4}T^4 \right] \\[2mm] E_n(T) = E_0 + V \left[\dfrac{\beta}{4}T^4 + \dfrac{\gamma}{2}T^2 \right] \end{cases}.$$

(d) By comparing the Gibbs free energies (or chemical potentials) in the two phases, obtain an expression for the energy gap Δ in terms of α, β, and γ.

• The Gibbs free energy $G = E - TS - BM = \mu N$ can be calculated for $B = 0$ in each phase, using the results obtained before, as

$$\begin{cases} G_s(T) = E_0 + V \left[-\Delta + \dfrac{\alpha}{4}T^4 \right] - TV\dfrac{\alpha}{3}T^3 = E_0 - V \left[\Delta + \dfrac{\alpha}{12}T^4 \right] \\[2mm] G_n(T) = E_0 + V \left[\dfrac{\beta}{4}T^4 + \dfrac{\gamma}{2}T^2 \right] - TV \left[\dfrac{\beta}{3}T^3 + \gamma T \right] = E_0 - V \left[\dfrac{\beta}{12}T^4 + \dfrac{\gamma}{2}T^2 \right] \end{cases}.$$

At the transition point, the chemical potentials (and hence the Gibbs free energies) must be equal, leading to

$$\Delta + \frac{\alpha}{12}T_c^4 = \frac{\beta}{12}T_c^4 + \frac{\gamma}{2}T_c^2, \quad \Longrightarrow \quad \Delta = \frac{\gamma}{2}T_c^2 - \frac{\alpha - \beta}{12}T_c^4.$$

Using the value of $T_c = \sqrt{3\gamma/(\alpha - \beta)}$, we obtain

$$\Delta = \frac{3}{4}\frac{\gamma^2}{\alpha - \beta}.$$

(e) In the presence of a magnetic field B, inclusion of magnetic work results in $dE = TdS + BdM + \mu dN$, where M is the magnetization. The superconducting phase is a perfect diamagnet, expelling the magnetic field from its interior, such that $M_s = -VB/(4\pi)$ in appropriate units. The normal metal can be regarded as approximately non-magnetic, with $M_n = 0$. Use this information, in conjunction with previous results, to show that the superconducting phase becomes normal for magnetic fields larger than

$$B_c(T) = B_0\left(1 - \frac{T^2}{T_c^2}\right),$$

giving an expression for B_0.

• Since $dG = -SdT - MdB + \mu dN$, we have to add the integral of $-MdB$ to the Gibbs free energies calculated in the previous section for $B = 0$. There is no change in the metallic phase since $M_n = 0$, while in the superconducting phase there is an additional contribution of $-\int M_s dB = (V/4\pi)\int BdB = (V/8\pi)B^2$. Hence the Gibbs free energies at finite field are

$$\begin{cases} G_s(T, B) = E_0 - V\left[\Delta + \frac{\alpha}{12}T^4\right] + V\frac{B^2}{8\pi} \\ G_n(T, B) = E_0 - V\left[\frac{\beta}{12}T^4 + \frac{\gamma}{2}T^2\right] \end{cases}.$$

Equating the Gibbs free energies gives a critical magnetic field

$$\frac{B_c^2}{8\pi} = \Delta - \frac{\gamma}{2}T^2 + \frac{\alpha - \beta}{12}T^4 = \frac{3}{4}\frac{\gamma^2}{\alpha - \beta} - \frac{\gamma}{2}T^2 + \frac{\alpha - \beta}{12}T^4$$

$$= \frac{\alpha - \beta}{12}\left[\left(\frac{3\gamma}{\alpha - \beta}\right)^2 - \frac{6\gamma T^2}{\alpha - \beta} + T^4\right] = \frac{\alpha - \beta}{12}\left(T_c^2 - T^2\right)^2,$$

where we have used the values of Δ and T_c obtained before. Taking the square root of the above expression gives

$$B_c = B_0\left(1 - \frac{T^2}{T_c^2}\right), \quad \text{where} \quad B_0 = \sqrt{\frac{2\pi(\alpha - \beta)}{3}}T_c^2 = \sqrt{\frac{6\pi\gamma^2}{\alpha - \beta}} = T_c\sqrt{2\pi\gamma}.$$

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10. *Photon gas Carnot cycle:* The aim of this problem is to obtain the blackbody radiation relation, $E(T,V) \propto VT^4$, starting from the equation of state, by performing an infinitesimal Carnot cycle on the photon gas.
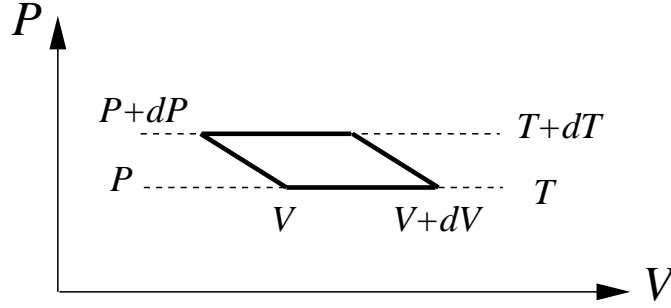
(a) Express the work done, W, in the above cycle, in terms of dV and dP.

• Ignoring higher order terms, net work is the area of the cycle, given by $W = dPdV$.

(b) Express the heat absorbed, Q, in expanding the gas *along an isotherm*, in terms of P, dV, and an appropriate derivative of $E(T,V)$.

• Applying the first law, the heat absorbed is

$$Q = dE + PdV = \left[\left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV + PdV \right]_{\text{isotherm}} = \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] dV.$$

(c) Using the efficiency of the Carnot cycle, relate the above expressions for W and Q to T and dT.

• The efficiency of the Carnot cycle ($\eta = dT/T$) is here calculated as

$$\eta = \frac{W}{Q} = \frac{dP}{[(\partial E/\partial V)_T + P]} = \frac{dT}{T}.$$

(d) Observations indicate that the pressure of the photon gas is given by $P = AT^4$, where $A = \pi^2 k_B^4 / 45 \, (\hbar c)^3$ is a constant. Use this information to obtain $E(T,V)$, assuming $E(T,0) = 0$.

• From the result of part (c) and the relation $P = AT^4$,

$$4AT^4 = \left(\frac{\partial E}{\partial V} \right)_T + AT^4, \quad \text{or} \quad \left(\frac{\partial E}{\partial V} \right)_T = 3AT^4,$$

so that

$$E = 3AVT^4.$$

(e) Find the relation describing the *adiabatic paths* in the above cycle.

• Adiabatic curves are given by $dQ = 0$, or

$$0 = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV = 3VdP + 4PdV,$$

i.e.

$$PV^{4/3} = \text{constant}.$$

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11. *Irreversible Processes:*

(a) Consider two substances, initially at temperatures T_1^0 and T_2^0, coming to equilibrium at a final temperature T_f through heat exchange. By relating the direction of heat flow to the temperature difference, show that the change in the total entropy, which can be written as

$$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{dQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{dQ_1}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} dQ,$$

must be positive. This is an example of the more general condition that "*in a closed system, equilibrium is characterized by the maximum value of entropy S.*"

• Defining the heat flow from substance 1 to 2 as, $dQ_{1 \to 2}$, we get,

$$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{dQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{dQ_2}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} dQ_{1 \to 2}.$$

But according to Clausius' statement of the second law $dQ_{1 \to 2} > 0$, if $T_1 > T_2$ and $dQ_{1 \to 2} < 0$, if $T_1 < T_2$. Hence, $(T_1 - T_2)dQ_{1 \to 2} \geq 0$, resulting in

$$\Delta S \geq \int \frac{T_1 - T_2}{T_1 T_2} dQ_{1 \to 2} \geq 0.$$

(b) Now consider a gas with adjustable volume V, and diathermal walls, embedded in a heat bath of constant temperature T, *and* fixed pressure P. The change in the entropy of the bath is given by

$$\Delta S_{\text{bath}} = \frac{\Delta Q_{\text{bath}}}{T} = -\frac{\Delta Q_{\text{gas}}}{T} = -\frac{1}{T}\left(\Delta E_{\text{gas}} + P\Delta V_{\text{gas}}\right).$$

By considering the change in entropy of the combined system establish that *"the equilibrium of a gas at fixed T and P is characterized by the minimum of the Gibbs free energy $G = E + PV - TS$."*

- The total change in entropy of the whole system is,

$$\Delta S = \Delta S_{\text{bath}} + \Delta S_{\text{gas}} = -\frac{1}{T}(\Delta E_{\text{gas}} + P\Delta V_{\text{gas}} - T\Delta S_{\text{gas}}) = -\frac{1}{T}\Delta G_{\text{gas}}.$$

By the second law of thermodynamics, all processes must satisfy,

$$-\frac{1}{T}\Delta G_{\text{gas}} \geq 0 \quad \Leftrightarrow \quad \Delta G_{\text{gas}} \leq 0,$$

that is, all processes that occur can only lower the Gibbs free energy of the gas. Therefore the equillibrium of a gas in contact with a heat bath of constant T and P is established at the point of minimum Gibbs free energy, i.e. when the Gibbs free energy cannot be lowered any more.

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12. *The solar system* originated from a dilute gas of particles, sufficiently separated from other such clouds to be regarded as an isolated system. Under the action of gravity the particles coalesced to form the sun and planets.

(a) The motion and organization of planets is much more ordered than the original dust cloud. Why does this not violate the second law of thermodynamics?

- The formation of planets is due to the gravitational interaction. Because of the attractive nature of this interaction, the original dust cloud with uniform density has in fact lower entropy. Clumping of the uniform density leads to higher entropy. Of course the gravitational potential energy is converted into kinetic energy in the process. Ultimately the kinetic energy of falling particles is released in the form of photons which carry away a lot of entropy.

(b) The nuclear processes of the sun convert protons to heavier elements such as carbon. Does this further organization lead to a reduction in entropy?

• Again the process of formation of heavier elements is accompanied by the release of large amounts of energy which are carry away by photons. The entropy carry away by these photons is more than enough to compensate any ordering associated with the packing of nucleons into heavier nuclei.

(c) The evolution of life and intelligence requires even further levels of organization. How is this achieved on earth without violating the second law?

• Once more there is usage of energy by the organisms that converts more ordered forms of energy to less ordered ones.

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Problems for Chapter II - Probability

1. *Characteristic functions:*   Calculate the characteristic function, the mean, and the variance of the following probability density functions:

(a) *Uniform* $p(x) = \frac{1}{2a}$ for $-a < x < a$, and $p(x) = 0$ otherwise;

• A *uniform* probability distribution,

$$p(x) = \begin{cases} \dfrac{1}{2a} & \text{for} - a < x < a \\ 0 & \text{otherwise} \end{cases} ,$$

for which there exist many examples, gives

$$f(k) = \frac{1}{2a} \int_{-a}^{a} \exp(-ikx)dx = \frac{1}{2a}\frac{1}{-ik}\exp(-ikx)\Big|_{-a}^{a}$$

$$= \frac{1}{ak}\sin(ka) = \sum_{m=0}^{\infty}(-1)^{m}\frac{(ak)^{2m}}{(2m+1)!}.$$

Therefore,

$$m_1 = \langle x \rangle = 0, \qquad \text{and} \qquad m_2 = \langle x^2 \rangle = \frac{1}{3}a^2.$$

(b) *Laplace* $p(x) = \frac{1}{2a}\exp\left(-\frac{|x|}{a}\right)$;

• The *Laplace* PDF,

$$p(x) = \frac{1}{2a}\exp\left(-\frac{|x|}{a}\right),$$

for example describing light absorption through a turbid medium, gives

$$f(k) = \frac{1}{2a}\int_{-\infty}^{\infty} dx \exp\left(-ikx - \frac{|x|}{a}\right)$$

$$= \frac{1}{2a}\int_{0}^{\infty} dx \exp(-ikx - x/a) + \frac{1}{2a}\int_{-\infty}^{0} dx \exp(-ikx + x/a)$$

$$= \frac{1}{2a}\left[\frac{1}{-ik + 1/a} - \frac{1}{-ik - 1/a}\right] = \frac{1}{1 + (ak)^2}$$

$$= 1 - (ak)^2 + (ak)^4 - \cdots.$$

Therefore,

$$m_1 = \langle x \rangle = 0, \qquad \text{and} \qquad m_2 = \langle x^2 \rangle = 2a^2.$$

(c) *Cauchy* $p(x) = \frac{a}{\pi(x^2+a^2)}$.

● The *Cauchy*, or *Lorentz* PDF describes the spectrum of light scattered by diffusive modes, and is given by

$$p(x) = \frac{a}{\pi(x^2 + a^2)}.$$

For this distribution,

$$f(k) = \int_{-\infty}^{\infty} \exp(-ikx)\frac{a}{\pi(x^2 + a^2)}dx$$

$$= \frac{1}{2\pi i}\int_{-\infty}^{\infty} \exp(-ikx)\left[\frac{1}{x - ia} - \frac{1}{x + ia}\right]dx.$$

The easiest method for evaluating the above integrals is to close the integration contours in the complex plane, and evaluate the residue. The vanishing of the integrand at infinity determines whether the contour has to be closed in the upper, or lower half of the complex plane, and leads to

$$f(k) = \begin{cases} -\dfrac{1}{2\pi i}\displaystyle\int_C \dfrac{\exp(-ikx)}{x + ia}dx = \exp(-ka) & \text{for } k \geq 0 \\[3mm] \dfrac{1}{2\pi i}\displaystyle\int_B \dfrac{\exp(-ikx)}{x - ia}dx = \exp(ka) & \text{for } k < 0 \end{cases} = \exp(-|ka|).$$

Note that $f(k)$ is not an analytic function in this case, and hence does not have a Taylor expansion. The moments have to be determined by another method, e.g. by direct evaluation, as

$$m_1 = \langle x \rangle = 0, \qquad \text{and} \qquad m_2 = \langle x^2 \rangle = \int dx \frac{\pi}{a} \cdot \frac{x^2}{x^2 + a^2} \rightarrow \infty.$$

The first moment vanishes by symmetry, while the second (and higher) moments diverge, explaining the non-analytic nature of $f(k)$.

The following two probability density functions are defined for $x \geq 0$. Compute only the mean and variance for each.

(d) *Rayleigh* $p(x) = \frac{x}{a^2}\exp(-\frac{x^2}{2a^2})$,

● The *Rayleigh* distribution,

$$p(x) = \frac{x}{a^2}\exp\left(-\frac{x^2}{2a^2}\right), \qquad \text{for} \qquad x \geq 0,$$

can be used for the length of a random walk in two dimensions. Its characteristic function is

$$f(k) = \int_0^\infty \exp(-ikx) \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx$$

$$= \int_0^\infty [\cos(kx) - i\sin(kx)] \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx.$$

The integrals are not simple, but can be evaluated as

$$\int_0^\infty \cos(kx) \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = \sum_{n=0}^\infty \frac{(-1)^n n!}{(2n)!} \left(2a^2 k^2\right)^n,$$

and

$$\int_0^\infty \sin(kx) \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = \frac{1}{2} \int_{-\infty}^\infty \sin(kx) \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx$$

$$= \sqrt{\frac{\pi}{2}} ka \exp\left(-\frac{k^2 a^2}{2}\right),$$

resulting in

$$f(k) = \sum_{n=0}^\infty \frac{(-1)^n n!}{(2n)!} \left(2a^2 k^2\right)^n - i\sqrt{\frac{\pi}{2}} ka \exp\left(-\frac{k^2 a^2}{2}\right).$$

The moments can also be calculated directly, from

$$m_1 = \langle x \rangle = \int_0^\infty \frac{x^2}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = \int_{-\infty}^\infty \frac{x^2}{2a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = \sqrt{\frac{\pi}{2}} a,$$

$$m_2 = \langle x^2 \rangle = \int_0^\infty \frac{x^3}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = 2a^2 \int_0^\infty \frac{x^2}{2a^2} \exp\left(-\frac{x^2}{2a^2}\right) d\left(\frac{x^2}{2a^2}\right)$$

$$= 2a^2 \int_0^\infty y \exp(-y) dy = 2a^2.$$

(e) *Maxwell* $p(x) = \sqrt{\frac{2}{\pi}} \frac{x^2}{a^3} \exp(-\frac{x^2}{2a^2})$.

• It is difficult to calculate the characteristic function for the *Maxwell* distribution

$$p(x) = \sqrt{\frac{2}{\pi}} \frac{x^2}{a^3} \exp\left(-\frac{x^2}{2a^2}\right),$$

say describing the speed of a gas particle. However, we can directly evaluate the mean and variance, as

$$m_1 = \langle x \rangle = \sqrt{\frac{2}{\pi}} \int_0^\infty \frac{x^3}{a^3} \exp\left(-\frac{x^2}{2a^2}\right) dx$$

$$= 2\sqrt{\frac{2}{\pi}} a \int_0^\infty \frac{x^2}{2a^2} \exp\left(-\frac{x^2}{2a^2}\right) d\left(\frac{x^2}{2a^2}\right)$$

$$= 2\sqrt{\frac{2}{\pi}} a \int_0^\infty y \exp(-y) dy = 2\sqrt{\frac{2}{\pi}} a,$$

and

$$m_2 = \langle x^2 \rangle = \sqrt{\frac{2}{\pi}} \int_o^\infty \frac{x^4}{a^3} \exp\left(-\frac{x^2}{2a^2}\right) dx = 3a^2.$$

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2. *Directed random walk:* The motion of a particle in three dimensions is a series of independent steps of length ℓ. Each step makes an angle θ with the z axis, with a probability density $p(\theta) = 2\cos^2(\theta/2)/\pi$; while the angle ϕ is uniformly distributed between 0 and 2π. (Note that the solid angle factor of $\sin\theta$ is already included in the definition of $p(\theta)$, which is correctly normalized to unity.) The particle (walker) starts at the origin and makes a large number of steps N.

(a) Calculate the expectation values $\langle z \rangle$, $\langle x \rangle$, $\langle y \rangle$, $\langle z^2 \rangle$, $\langle x^2 \rangle$, and $\langle y^2 \rangle$, and the covariances $\langle xy \rangle$, $\langle xz \rangle$, and $\langle yz \rangle$.

• From symmetry arguments,

$$\langle x \rangle = \langle y \rangle = 0,$$

while along the z-axis,

$$\langle z \rangle = \sum_i \langle z_i \rangle = N \langle z_i \rangle = Na \langle \cos\theta_i \rangle = \frac{Na}{2}.$$

The last equality follows from

$$\langle \cos\theta_i \rangle = \int p(\theta)\cos\theta d\theta = \int_0^\pi \frac{1}{\pi}\cos\theta \cdot (\cos\theta + 1)d\theta$$
$$= \int_0^\pi \frac{1}{2\pi}(\cos 2\theta + 1)d\theta = \frac{1}{2}.$$

The second moment of z is given by

$$\langle z^2 \rangle = \sum_{i,j} \langle z_i z_j \rangle = \sum_i \sum_{i\neq j} \langle z_i z_j \rangle + \sum_i \langle z_i^2 \rangle$$
$$= \sum_i \sum_{i\neq j} \langle z_i \rangle \langle z_j \rangle + \sum_i \langle z_i^2 \rangle$$
$$= N(N-1) \langle z_i \rangle^2 + N \langle z_i^2 \rangle.$$

Noting that

$$\frac{\langle z_i^2 \rangle}{a^2} = \int_0^\pi \frac{1}{\pi}\cos^2\theta(\cos\theta + 1)d\theta = \int_0^\pi \frac{1}{2\pi}(\cos 2\theta + 1)d\theta = \frac{1}{2},$$

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we find
$$\langle z^2 \rangle = N(N-1)\left(\frac{a}{2}\right)^2 + N\frac{a^2}{2} = N(N+1)\frac{a^2}{4}.$$

The second moments in the x and y directions are equal, and given by

$$\langle x^2 \rangle = \sum_{i,j} \langle x_i x_j \rangle = \sum_i \sum_{i \neq j} \langle x_i x_j \rangle + \sum_i \langle x_i^2 \rangle = N \langle x_i^2 \rangle.$$

Using the result

$$\frac{\langle x_i^2 \rangle}{a^2} = \langle \sin^2 \theta \cos^2 \phi \rangle$$

$$= \frac{1}{2\pi^2} \int_0^{2\pi} d\phi \cos^2 \phi \int_0^\pi d\theta \sin^2 \theta (\cos \theta + 1) = \frac{1}{4},$$

we obtain

$$\langle x^2 \rangle = \langle y^2 \rangle = \frac{Na^2}{4}.$$

While the variables x, y, and z are not independent because of the constraint of unit length, simple symmetry considerations suffice to show that the three covariances are in fact zero, i.e.

$$\langle xy \rangle = \langle xz \rangle = \langle yz \rangle = 0.$$

(b) Use the central limit theorem to estimate the probability density $p(x, y, z)$ for the particle to end up at the point (x, y, z).

• From the Central limit theorem, the probability density should be Gaussian. However, for correlated random variable we may expect cross terms that describe their covariance. However, we showed above that the covarainces between x, y, and z are all zero. Hence we can treat them as three *independent* Gaussian variables, and write

$$p(x, y, z) \propto \exp\left[-\frac{(x - \langle x \rangle)^2}{2\sigma_x^2} - \frac{(y - \langle y \rangle)^2}{2\sigma_y^2} - \frac{(z - \langle z \rangle)^2}{2\sigma_z^2}\right].$$

(There will be correlations between x, y, and z appearing in higher cumulants, but all such cumulants become irrelevant in the $N \to \infty$ limit.) Using the moments

$$\langle x \rangle = \langle y \rangle = 0, \qquad \text{and} \qquad \langle z \rangle = N\frac{a}{2},$$

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = N\frac{a^2}{4} = \sigma_y^2,$$

$$\text{and} \quad \sigma_z^2 = \langle z^2 \rangle - \langle z \rangle^2 = N(N+1)\frac{a^2}{4} - \left(\frac{Na}{2}\right)^2 = N\frac{a^2}{4},$$

we obtain

$$p(x,y,z) = \left(\frac{2}{\pi Na^2}\right)^{3/2} \exp\left[-\frac{x^2 + y^2 + (z - Na/2)^2}{Na^2/2}\right].$$

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3. *Tchebycheff inequality:* Consider any probability density $p(x)$ for $(-\infty < x < \infty)$, with mean λ, and variance σ^2. Show that the total probability of outcomes that are more than $n\sigma$ away from λ is less than $1/n^2$, i.e.

$$\int_{|x-\lambda|\geq n\sigma} dx\, p(x) \leq \frac{1}{n^2}.$$

Hint: Start with the integral defining σ^2, and break it up into parts corresponding to $|x - \lambda| > n\sigma$, and $|x - \lambda| < n\sigma$.

- By definition, for a system with a PDF $p(x)$, and average λ, the variance is

$$\sigma^2 = \int (x - \lambda)^2 p(x) dx.$$

Let us break the integral into two parts as

$$\sigma^2 = \int_{|x-\lambda|\geq n\sigma} (x-\lambda)^2 p(x) dx + \int_{|x-\lambda|<n\sigma} (x-\lambda)^2 p(x) dx,$$

resulting in

$$\sigma^2 - \int_{|x-\lambda|<n\sigma} (x-\lambda)^2 p(x) dx = \int_{|x-\lambda|\geq n\sigma} (x-\lambda)^2 p(x) dx.$$

Now since

$$\int_{|x-\lambda|\geq n\sigma} (x-\lambda)^2 p(x) dx \geq \int_{|x-\lambda|\geq n\sigma} (n\sigma)^2 p(x) dx,$$

we obtain

$$\int_{|x-\lambda|\geq n\sigma} (n\sigma)^2 p(x) dx \leq \sigma^2 - \int_{|x-\lambda|<n\sigma} (x-\lambda)^2 p(x) dx \leq \sigma^2,$$

and

$$\int_{|x-\lambda|\geq n\sigma} p(x) dx \leq \frac{1}{n^2}.$$

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4. *Optimal selection:* In many specialized populations, there is little variability among the members. Is this a natural consequence of optimal selection?

(a) Let $\{r_\alpha\}$ be n random numbers, each independently chosen from a probability density $p(r)$, with $r \in [0,1]$. Calculate the probability density $p_n(x)$ for the largest value of this set, i.e. for $x = \max\{r_1, \cdots, r_n\}$.

● The probability that the maximum of n random numbers falls between x and $x + dx$ is equal to the probability that one outcome is in this interval, while all the others are smaller than x, i.e.

$$p_n(x) = p(r_1 = x, r_2 < x, r_3 < x, \cdots, r_n < x) \times \binom{n}{1},$$

where the second factor corresponds to the number of ways of choosing which $r_\alpha = x$. As these events are independent

$$p_n(x) = p(r_1 = x) \cdot p(r_2 < x) \cdot p(r_3 < x) \cdots p(r_n < x) \times \binom{n}{1}$$
$$= p(r = x) \left[p(r < x) \right]^{n-1} \times \binom{n}{1}.$$

The probability of $r < x$ is just a cumulative probability function, and

$$p_n(x) = n \cdot p(x) \cdot \left[\int_0^x p(r) dr \right]^{n-1}.$$

(b) If each r_α is uniformly distributed between 0 and 1, calculate the mean and variance of x as a function of n, and comment on their behavior at large n.

● If each r_α is uniformly distributed between 0 and 1, $p(r) = 1$ ($\int_0^1 p(r) dr = \int_0^1 dr = 1$). With this PDF, we find

$$p_n(x) = n \cdot p(x) \cdot \left[\int_0^x p(r) dr \right]^{n-1} = n \left[\int_0^x dr \right]^{n-1} = nx^{n-1},$$

and the mean is now given by

$$\langle x \rangle = \int_0^1 x p_n(x) dx = n \int_0^1 x^n dx = \frac{n}{n+1}.$$

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The second moment of the maximum is

$$\langle x^2 \rangle = n \int_0^1 x^{n+1} dx = \frac{n}{n+2},$$

resulting in a variance

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{n}{n+2} - \left(\frac{n}{n+1} \right)^2 = \frac{n}{(n+1)^2(n+2)}.$$

Note that for large n the mean approaches the limiting value of unity, while the variance vanishes as $1/n^2$. There is too little space at the top of the distribution for a wide variance.

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5. *Benford's law* describes the observed probabilities of the *first digit* in a great variety of data sets, such as stock prices. Rather counter-intuitively, the digits 1 through 9 occur with probabilities 0.301, .176, .125, .097, .079, .067, .058, .051, .046 respectively. The key observation is that this distribution is invariant under a change of scale, e.g. if the stock prices were converted from dollars to persian rials! Find a formula that fits the above probabilities on the basis of this observation.

• Let us consider the observation that the probability distribution for first integers is unchanged under multiplication by any (i.e. a random) number. Presumably we can repeat such multiplications many times, and it is thus suggestive that we should consider the properties of the *product of random numbers*. (Why this should be a good model for stock prices is not entirely clear, but it seems to be as good an explanation as anything else!)

Consider the $x = \prod_{i=1}^N r_i$, where r_i are *positive*, random variables taken from some reasonably well behaved probability distribution. The random variable $\ell \equiv \ln x = \sum_{i=1}^N \ln r_i$ is the sum of many random contributions, and according to the central limit theorem should have a Gaussian distribution in the limit of large N, i.e.

$$\lim_{N \to \infty} p(\ell) = \exp \left[-\frac{\left(\ell - N\bar{\ell} \right)^2}{2N\sigma^2} \right] \frac{1}{\sqrt{2\pi N\sigma^2}},$$

where $\bar{\ell}$ and σ^2 are the mean and variance of $\ln r$ respectively. The product x is distributed according to the *log-normal distribution*

$$p(x) = p(\ell) \frac{d\ell}{dx} = \frac{1}{x} \exp \left[-\frac{\left(\ln(x) - N\bar{\ell} \right)^2}{2N\sigma^2} \right] \frac{1}{\sqrt{2\pi N\sigma^2}}.$$

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The probability that the first integer of x in a decimal representation is i is now obtained approximately as follows:

$$p_i = \sum_q \int_{10^q i}^{10^q (i+1)} dx p(x).$$

The integral considers cases in which x is a number of magnitude 10^q (i.e. has $q+1$ digits before the decimal point). Since the number is quite widely distributed, we then have to sum over possible magnitudes q. The range of the sum actually need not be specified! The next stage is to change variables from x to $\ell = \ln x$, leading to

$$p_i = \sum_q \int_{q+\ln i}^{q+\ln(i+1)} d\ell p(\ell) = \sum_q \int_{q+\ln i}^{q+\ln(i+1)} d\ell \exp\left[-\frac{(\ell - N\overline{\ell})^2}{2N\sigma^2} \right] \frac{1}{\sqrt{2\pi N\sigma^2}}.$$

We shall now make the *approximation* that over the range of integration ($q + \ln i$ to $q + \ln(i+1)$), the integrand is approximately constant. (The approximation works best for $q \approx N\overline{\ell}$ where the integral is largest.) This leads to

$$p_i \approx \sum_q \exp\left[-\frac{(q - N\overline{\ell})^2}{2N\sigma^2} \right] \frac{1}{\sqrt{2\pi N\sigma^2}} [\ln(i+1) - \ln i] \propto \ln\left(1 + \frac{1}{i}\right),$$

where we have ignored the constants of proportionality which come from the sum over q. We thus find that the distribution of the first digit is *not uniform*, and the properly normalized proportions of $\ln(1+1/i)$ indeed reproduce the probabilities $p_1, \cdots, p_9$ of 0.301, .176, .125, .097, .079, .067, .058, .051, .046 according to Benford's law. (For further information check http://www.treasure-troves.com/math/BenfordsLaw.html.)

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6. *Information:* Consider the velocity of a gas particle in one dimension ($-\infty < v < \infty$).

(a) Find the unbiased probability density $p_1(v)$, subject only to the constraint that the average *speed* is c, i.e. $\langle |v| \rangle = c$.

- For an unbiased probability estimation, we need to maximize entropy subject to the two constraints of normalization, and of given average speed ($\langle |v| \rangle = c.$). Using Lagrange multipliers α and β to impose these constraints, we need to maximize

$$S = -\langle \ln p \rangle = -\int_{-\infty}^{\infty} p(v) \ln p(v) dv + \alpha\left(1 - \int_{-\infty}^{\infty} p(v) dv\right) + \beta\left(c - \int_{-\infty}^{\infty} p(v)|v| dv\right).$$

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Extremizing the above expression yields

$$\frac{\partial S}{\partial p(v)} = -\ln p(v) - 1 - \alpha - \beta|v| = 0,$$

which is solved for

$$\ln p(v) = -1 - \alpha - \beta|v|,$$

or

$$p(v) = Ce^{-\beta|v|}, \qquad \text{with} \quad C = e^{-1-\alpha}.$$

The constraints can now be used to fix the parameters C and β:

$$1 = \int_{-\infty}^{\infty} p(v)dv = \int_{-\infty}^{\infty} Ce^{-\beta|v|}dv = 2C\int_{0}^{\infty} e^{-\beta v}dv = 2C\frac{1}{-\beta}e^{-\beta v}\Big|_{0}^{\infty} = \frac{2C}{\beta},$$

which implies

$$C = \frac{\beta}{2}.$$

From the second constraint, we have

$$c = \int_{-\infty}^{\infty} Ce^{-\beta|v|}|v|dv = \beta\int_{0}^{\infty} e^{-\beta v}vdv,$$

which when integrated by parts yields

$$c = \beta\left[-\frac{1}{\beta}ve^{-\beta v}\Big|_{0}^{\infty} + \frac{1}{\beta}\int_{0}^{\infty} e^{-\beta v}dv\right] = \left[-\frac{1}{\beta}e^{-\beta v}\Big|_{0}^{\infty}\right] = \frac{1}{\beta}.$$

or,

$$\beta = \frac{1}{c}.$$

The unbiased PDF is then given by

$$p(v) = Ce^{-\beta|v|} = \frac{1}{2c}\exp\left(-\frac{|v|}{c}\right).$$

(b) Now find the probability density $p_2(v)$, given only the constraint of average kinetic energy, $\langle mv^2/2 \rangle = mc^2/2$.

• When the second constraint is on the average kinetic energy, $\langle mv^2/2 \rangle = mc^2/2$, we have

$$S = -\int_{-\infty}^{\infty} p(v)\ln p(v)dv + \alpha\left(1 - \int_{-\infty}^{\infty} p(v)dv\right) + \beta\left(\frac{mc^2}{2} - \int_{-\infty}^{\infty} p(v)\frac{mv^2}{2}dv\right).$$

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The corresponding extremization,

$$\frac{\partial S}{\partial p(v)} = -\ln p(v) - 1 - \alpha - \beta \frac{mv^2}{2} = 0,$$

results in

$$p(v) = C \exp\left(-\frac{\beta mv^2}{2}\right).$$

The normalization constraint implies

$$1 = \int_{-\infty}^{\infty} p(v) dv = C \int_{-\infty}^{\infty} e^{-\beta mv^2/2} = C\sqrt{2\pi/\beta m},$$

or

$$C = \sqrt{\beta m/2\pi}.$$

The second constraint,

$$\frac{mc^2}{2} = \int_{-\infty}^{\infty} p(v) \frac{mv^2}{2} dv = \frac{m}{2} \sqrt{\frac{\beta m}{2\pi}} \int_{-\infty}^{\infty} \exp\left(-\frac{\beta mv^2}{2}\right) v^2 dv$$

$$= \frac{m}{2} \sqrt{\frac{\beta m}{2\pi}} \left[\frac{\sqrt{\pi}}{2} \left(\frac{2}{\beta m}\right)^{3/2}\right] = \frac{1}{2\beta},$$

gives

$$\beta = \frac{1}{mc^2},$$

for a full PDF of

$$p(v) = C \exp\left(-\frac{\beta mv^2}{2}\right) = \frac{1}{\sqrt{2\pi c^2}} \exp\left(-\frac{v^2}{2c^2}\right).$$

(c) Which of the above statements provides more information on the velocity? Quantify the difference in information in terms of $I_2 - I_1 \equiv (\langle \ln p_2 \rangle - \langle \ln p_1 \rangle)/\ln 2$.

- The entropy of the first PDF is given by

$$S_1 = -\langle \ln p_1 \rangle = -\int_{-\infty}^{\infty} \frac{1}{2c} \exp\left(\frac{-|v|}{c}\right) \left[-\ln(2c) - \frac{|v|}{c}\right] dv$$

$$= \frac{\ln(2c)}{c} \int_{0}^{\infty} \exp\left(-\frac{v}{c}\right) dv + \frac{1}{c} \int_{0}^{\infty} \exp\left(-\frac{v}{c}\right) \frac{v}{c} dv$$

$$= -\ln(2c) \exp(-v/c)|_0^{\infty} + \frac{1}{c} \left[-c \exp(-v/c)|_0^{\infty}\right]$$

$$= \ln(2c) + 1 = 1 + \ln 2 + \ln c.$$

For the second distribution, we obtain

$$S_2 = -\langle \ln p_2 \rangle = -\frac{1}{\sqrt{2\pi c^2}} \int_{-\infty}^{\infty} \exp\left(-\frac{v^2}{2c^2}\right) \left[-\frac{1}{2}\ln\left(2\pi c^2\right) - \frac{v^2}{2c^2}\right]$$

$$= \frac{\ln\left(2\pi c^2\right)}{2\sqrt{2\pi c^2}} \int_{-\infty}^{\infty} \exp\left(-v^2/2c^2\right) dv + \frac{1}{\sqrt{2\pi c^2}} \int_{-\infty}^{\infty} \frac{v^2}{2c^2} \exp\left(-v^2/2c^2\right) dv$$

$$= \frac{1}{2}\ln\left(2\pi c^2\right) + \frac{1}{c^2\sqrt{2\pi c^2}} \left[\frac{\sqrt{2\pi c^2}c^2}{2}\right]$$

$$= \frac{1}{2}\ln\left(2\pi c^2\right) + \frac{1}{2} = \frac{1}{2} + \frac{1}{2}\ln(2\pi) + \ln c.$$

For a discrete probability, the information content is

$$I_\alpha = \ln_2 M - S_\alpha / \ln 2,$$

where M denotes the number of possible outcomes. While M, and also the proper measure of probability are not well defined for a continuous PDF, the ambiguities disappear when we consider the difference

$$I_2 - I_1 = (-S_2 + S_1)/\ln 2$$

$$= -(S_2 - S_1)/\ln 2$$

$$= -\frac{(\ln \pi - \ln 2 - 1)}{2\ln 2} \approx 0.3956.$$

Hence the constraint of constant energy provides 0.3956 more bits of information. (This is partly due to the larger variance of the distribution with constant speed.)

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7. *Dice:* A dice is loaded such that 6 occurs twice as often as 1.

(a) Calculate the unbiased probabilities for the 6 faces of the dice.

• We want to find p_i that maximizes, $S = -\sum p_i \ln p_i$ with the constraints, $p_6 = 2p_1$ and $\sum p_i = 1$. Since for a fixed sum, $\sum p_i = 1 - 3p_1$, $-\sum_{i=2,\cdots,5} p_i \ln p_i$ is maximized by $p_2 = p_3 = p_4 = p_5$, our problem reduces to maximizing,

$$S(p_1) = -p_1 \ln p_1 - 2p_1 \ln 2p_1 - (1 - 3p_1)\ln\frac{1 - 3p_1}{4}.$$

Differentiating this with respect to p_1, we get,

$$\frac{dS}{dp_1} = 3\ln\left(\frac{1 - 3p_1}{2^{8/3}p_1}\right).$$

Note that this has only one zero and its sign changes from $+$ to $-$ at that zero. The maximum value of S is obtained for at that zero which is,

$$p_1 = \frac{1}{2^{8/3} + 3}.$$

Hence we obtain,

$$p_1 = \frac{1}{2^{8/3} + 3}, \quad p_2 = p_3 = p_4 = p_5 = \frac{1 - 3p_1}{4} = \frac{2^{2/3}}{2^{8/3} + 3}, \quad p_6 = 2p_1 = \frac{2}{2^{8/3} + 3}.$$

(b) What is the information content (in bits) of the above statement regarding the dice?

• By definitiion of the information content,

$$I = \ln_2 6 + \sum_{i=1}^{6} p_i \ln_2 p_i = \ln_2 6 + \ln_2 \frac{2^{2/3}}{3 + 2^{8/3}} = \frac{5}{3} + \ln_2 \frac{3}{3 + 2^{8/3}},$$

which is about 0.03 bits.

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8. *Random matrices:* As a model for energy levels of complex nuclei, Wigner considered $N \times N$ symmetric matrices whose elements are random. Let us assume that each element M_{ij} (for $i \geq j$) is an independent random variable taken from the probability density function

$$p(M_{ij}) = \frac{1}{2a} \quad \text{for} \quad -a < M_{ij} < a, \quad \text{and} \quad p(M_{ij}) = 0 \quad \text{otherwise.}$$

(a) Calculate the characteristic function for each element M_{ij}.

• Since each element is uniformly distributed in the interval $(-a, a)$, the characteristic function is

$$\tilde{p}_{ij}(k) = \int_{-a}^{a} dx \; e^{-ikx} \frac{1}{2a} = \frac{e^{ika} - e^{-ika}}{2aik} = \frac{\sin ak}{ak}.$$

(b) Calculate the characteristic function for the trace of the matrix, $T \equiv \operatorname{tr} M = \sum_i M_{ii}$.

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• The trace of the matrix is the sum of the N diagonal elements which are independent random variables. The characteristic function for the sum of independent variables is simply the product of the corresponding characteristic functions, and thus

$$\tilde{p}_T(k) = \prod_{i=1}^{N} \tilde{p}_{ii}(k) = \left(\frac{\sin ak}{ak} \right)^N.$$

(c) What does the central limit theorem imply about the probability density function of the trace at large N?

• Since the trace is the sum of $N \gg 1$ independent random variables, its cumulants are simply N times those of a single element. The leading cumulants are

$$\langle T \rangle_c = N \langle M_{ij} \rangle = 0,$$

and

$$\langle T^2 \rangle_c = N \langle M_{ij}^2 \rangle = N \int_{-a}^{a} dx \, \frac{x^2}{2a} = N \frac{a^2}{3}.$$

For the qunatity $t = T/\sqrt{N}$, higher order cumulants vanish in the limit of $N \to \infty$, and thus

$$\lim_{N \to \infty} p \left(t = \frac{\text{tr} \, M}{\sqrt{N}} \right) = \exp \left(-\frac{3t^2}{2a^2} \right) \sqrt{\frac{3}{2\pi a^2}}.$$

(d) For large N, each eigenvalue λ_α ($\alpha = 1, 2, \cdots, N$) of the matrix M is distributed according to a probability density function

$$p(\lambda) = \frac{2}{\pi \lambda_0} \sqrt{1 - \frac{\lambda^2}{\lambda_0^2}} \quad \text{for} \quad -\lambda_0 < \lambda < \lambda_0, \quad \text{and} \quad p(\lambda) = 0 \quad \text{otherwise},$$

(known as the Wigner semi-circle rule). Find the variance of λ.

(**Hint:** Changing variables to $\lambda = \lambda_0 \sin \theta$ simplifies the integrals.)

• The mean value of λ is zero by symmetry, and hence its variance is given by

$$\langle \lambda^2 \rangle_c = \int_{-\lambda_0}^{\lambda_0} d\lambda \, \lambda^2 \frac{2}{\pi \lambda_0} \sqrt{1 - \frac{\lambda^2}{\lambda_0^2}}.$$

In the integral, change variables to $\lambda = \lambda_0 \sin \theta$ and $d\lambda = \lambda_0 \cos \theta d\theta$, to get

$$\langle \lambda^2 \rangle_c = \frac{2\lambda_0^2}{\pi} \int_{-\pi/2}^{\pi/2} d\theta \, \cos^2 \theta \sin^2 \theta = \frac{\lambda_0^2}{2\pi} \int_{-\pi/2}^{\pi/2} d\theta \, \sin^2 2\theta = \frac{\lambda_0^2}{4\pi} \int_{-\pi/2}^{\pi/2} d\theta \, (1 - \cos 4\theta) = \frac{\lambda_0^2}{4}.$$

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(e) If in the previous result, we have $\lambda_0^2 = 4Na^2/3$, can the eigenvalues be independent of each other?

• The trace of a matrix is related to its eigenvalues by

$$T = \sum_{\alpha=1}^{N} \lambda_\alpha, \quad \Longrightarrow \quad \langle T^2 \rangle_c = \sum_{\alpha=1}^{N} \langle \lambda_\alpha^2 \rangle + \sum_{\alpha \neq \beta} \langle \lambda_\alpha \lambda_\beta \rangle.$$

The cross-correlations of eigenvalues thus satisfy

$$\sum_{\alpha \neq \beta} \langle \lambda_\alpha \lambda_\beta \rangle = \langle T^2 \rangle_c - \sum_{\alpha=1}^{N} \langle \lambda_\alpha^2 \rangle = N\frac{a^2}{3} - N \times \frac{4Na^2}{3} \neq 0.$$

Clearly, this is inconsistent with independent eigenvalues. In fact, the well known result that eigenvalues do not cross implies a repulsion between eigenvalues which leads to a much wider distribution than would result from independent eigenvalues.

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9. *Random deposition:* A mirror is plated by evaporating a gold electrode in vaccum by passing an electric current. The gold atoms fly off in all directions, and a portion of them sticks to the glass (or to other gold atoms already on the glass plate). Assume that each column of deposited atoms is independent of neighboring columns, and that the average deposition rate is d layers per second.

(a) What is the probability of m atoms deposited at a site after a time t? What fraction of the glass is not covered by any gold atoms?

• This is an example of a Poisson process, for which the probability of m deposition events at average rate d is

$$p(m) = \frac{(dt)^m e^{-dt}}{m!}.$$

The fraction of the glass that is not covered by gold atoms can be obtained by $p(0)$, that is,

$$p(0) = e^{-dt}.$$

An explicit derivation of this follows: First note that in a given time interval Δt, the probability for an atom to stick to a site is Δp. We will eventually send both to zero. In this case, the probability for a column at a site to have m atoms in time t would be,

$$p(m) =_{(t/\Delta t)} C_m (\Delta p)^m (1 - \Delta p)^{t/\Delta t - m}.$$

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So the average number of layers made in time t would be for $N \equiv t/\Delta t$,

$$\sum_{n=0}^{N} n \cdot_N C_n (\Delta p)^n (1 - \Delta p)^{N-n} = N\Delta p = \frac{\Delta p}{\Delta t} t = dt.$$

Hence the relation, $\Delta p = d\Delta t$. Note that this relation was obtained without any assumptions on $\Delta t, \Delta p$. Now let's obtain $p(m)$ as we send $\Delta t, \Delta p \to 0$

$$p(m) = \lim_{\Delta t \to 0} \frac{(t/\Delta t)(t/\Delta t - 1) \cdots (t/\Delta t - m + 1)}{m!} (\Delta p)^m (1 - \Delta p)^{t/\Delta t - m}.$$

Rearranging the terms we get,

$$p(m) = \lim_{\Delta t \to 0} \frac{(t\Delta p/\Delta t) \cdots (t\Delta p/\Delta t - (m-1)\Delta p)}{m!} (1 - \Delta p)^{t/\Delta t - m}.$$

Inserting, $\Delta t = d\Delta p$ we get,

$$p(m) = \lim_{\Delta p \to 0} \frac{(dt)^m}{m!} (1 - \Delta p)^{dt/\Delta p} = \frac{(dt)^m e^{-dt}}{m!}.$$

(b) What is the variance in the thickness?

- We need $\langle m^2 \rangle$, which is,

$$\langle m^2 \rangle = \sum_{m=0}^{\infty} m^2 p(m) = \sum \frac{m(m-1)}{m!} (dt)^m e^{-td} + \sum \frac{m}{m!} (dt)^m e^{-td} = (dt)^2 + dt$$

Since,

$$\langle m \rangle = \sum_{m=0}^{\infty} \frac{m}{m!} (dt)^m e^{-td} = dt.$$

the variance in the thickness is,

$$\langle m^2 \rangle - \langle m \rangle^2 = dt.$$

Note that all cumulants of this Poisson process are equal to dt.
****

10. _Diode:_ The current I across a diode is related to the applied voltage V via $I = I_0 [\exp(eV/kT) - 1]$. The diode is subject to a random potential V of zero mean and variance σ^2 which is Gaussian distributed. Find the probability density $p(I)$ for the current

I flowing through the diode. Find the most probable value for I, the mean value of I, and indicate them on a sketch of $p(I)$.

<center>********</center>

11. *Mutual information:* Consider random variables x and y, distributed according to a joint probability $p(x, y)$. The mutual information between the two variables is defined by

$$M(x, y) \equiv \sum_{x,y} p(x, y) \ln \left(\frac{p(x, y)}{p_x(x) p_y(y)} \right),$$

where p_x and p_y denote the *unconditional* probabilities for x and y.

(a) Relate $M(x, y)$ to the entropies $S(x, y)$, $S(x)$, and $S(y)$ obtained from the corresponding probabilities.

- Expanding the expression for $M(x, y)$, we get

$$M(x, y) = \sum_{x,y} p(x, y) \ln p(x, y) - \sum_{x,y} p(x, y) \ln p_x(x) - \sum_{x,y} p(x, y) \ln p_y(y).$$

Since

$$\sum_y p(x, y) = p_x(x),$$

and

$$\sum_x p(x, y) = p_y(y),$$

we obtain

$$M(x, y) = -S(x, y) + S(x) + S(y).$$

(b) Calculate the mutual information for the joint Gaussian form

$$p(x, y) \propto \exp \left(-\frac{ax^2}{2} - \frac{by^2}{2} - cxy \right).$$

- First, we calculate the normalization factor for the joint probability distribution

$$1 = A_{xy} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp \left(-\frac{a}{2} x^2 - \frac{b}{2} y^2 - cxy \right)$$

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calculating the integral, we get

$$A_{xy} = \frac{1}{2\pi}\sqrt{ab - c^2}.$$

Next, we have to find $p(x)$ and $p(y)$. For that purpose, we "integrate out" y and x respectively:

$$p_x(x) = \int_{-\infty}^{\infty} dy\, p(x,y) = \sqrt{\frac{1}{2\pi}\left(a - \frac{c^2}{b}\right)} \exp\left[-\left(\frac{a}{2} - \frac{c^2}{2b}\right)x^2\right],$$

and

$$p_y(y) = \sqrt{\frac{1}{2\pi}\left(b - \frac{c^2}{a}\right)} \exp\left[-\left(\frac{b}{2} - \frac{c^2}{2a}\right)y^2\right].$$

Thus,

$$M(x,y) = \sum_{x,y} p(x,y)\left[\ln\left(\frac{A_{xy}}{A_x A_y}\right) - cxy - \frac{c^2}{2b}x^2 - \frac{c^2}{2a}y^2\right]$$

$$= \ln\left(\frac{A_{xy}}{A_x A_y}\right) - \frac{c^2}{2b}\int x^2 p_x(x)dx - \frac{c^2}{2a}\int y^2 p_y(y)dy - c\int dx \int dy\, xy\, p(x,y),$$

where $A_{x,y}$ are the normalization factors for $p_x(x)$ and $p_y(y)$. This expression finally leads to

$$M(x,y) = \ln\left(\frac{A_{xy}}{A_x A_y}\right) = -\frac{1}{2}\ln\left(1 - \frac{c^2}{ab}\right).$$

****

12. *Semi-flexible polymer in two dimensions* Configurations of a model polymer can be described by either a set of vectors $\{\mathbf{t}_i\}$ of length a in two dimensions (for $i = 1, \cdots, N$), or alternatively by the angles $\{\phi_i\}$ between successive vectors, as indicated in the figure below.

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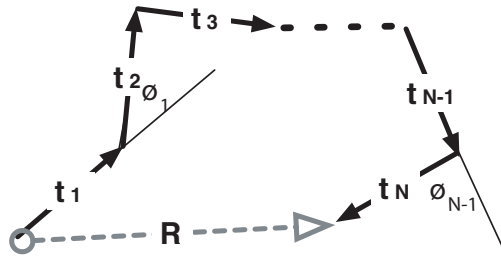
The polymer is at a temperature T, and subject to an energy

$$\mathcal{H} = -\kappa \sum_{i=1}^{N-1} \mathbf{t}_i \cdot \mathbf{t}_{i+1} = -\kappa a^2 \sum_{i=1}^{N-1} \cos \phi_i \quad ,$$

where κ is related to the bending rigidity, such the probability of any configuration is proportional to $\exp\left(-\mathcal{H}/k_B T\right)$.

(a) Show that $\langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle \propto \exp\left(-|n - m|/\xi\right)$, and obtain an expression for the *persistence length* $\ell_p = a\xi$. (You can leave the answer as the ratio of simple integrals.)

• In terms of the angles, the dot product can be written as

$$\mathbf{t}_m \cdot \mathbf{t}_n = a^2 \cos\left(\phi_m + \phi_{m+1} + \cdots + \phi_{n-1}\right) = a^2 \Re\, e^{i(\phi_m + \phi_{m+1} + \cdots + \phi_{n-1})}.$$

Note that the angles $\{\phi_n\}$ are *independent variables*, distributed according to the Boltzmann weight

$$p\left[\{\phi_n\}\right] \propto \prod_{n=1}^{N-1} \exp\left(\frac{\kappa a^2}{k_B T} \cos \phi_n\right) \quad .$$

Hence the average of the product is the product of averages, and

$$\langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle = a^2 \Re \prod_{k=m}^{n-1} \left\langle e^{i\phi_n} \right\rangle = a^2 \left[\frac{\int d\phi \cos \phi \; e^{\frac{\kappa a^2}{k_B T} \cos \phi}}{\int d\phi \; e^{\frac{\kappa a^2}{k_B T} \cos \phi}}\right]^{|n-m|} .$$

The persistence length is thus given by

$$\ell_p = \frac{a}{\ln\left[\int d\phi \; e^{\frac{\kappa a^2}{k_B T} \cos \phi} \middle/ \int d\phi \; \cos \phi \; e^{\frac{\kappa a^2}{k_B T} \cos \phi}\right]}.$$

(b) Consider the end–to–end distance $\mathbf{R}$ as illustrated in the figure. Obtain an expression for $\langle R^2 \rangle$ in the limit of $N \gg 1$.

• Using $\mathbf{R} = \sum_{n=1}^{N-1} \mathbf{t}_n$, we obtain

$$\langle R^2 \rangle = \sum_{m,n} \langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle = \sum_{m,n} a^2 e^{-|n-m|/\xi}.$$

The above sum decays exponentially around each point. Ignoring corrections from end effects, which are asymptotically negligible for $N \to \infty$, we obtain

$$\langle R^2 \rangle \simeq a^2 N \left[1 + 2\frac{e^{-1/\xi}}{1 - e^{-1/\xi}}\right] = a^2 N \coth \frac{1}{2\xi}.$$

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(c) Find the probability $p(\mathbf{R})$ in the limit of $N \gg 1$.

• Since $\mathbf{R} = \sum_{n=1}^{N-1} \mathbf{t}_n$, we can use the central limit theorem to conclude that in the limit of $N \to \infty$, the probability distribution $p(\mathbf{R})$ approaches a Gaussian form. Thus, we just need to evaluate the mean and variance of $\mathbf{R}$. Since the mean $\langle \mathbf{R} \rangle = 0$ by symmetry, the variance is equal to $\langle R^2 \rangle$ calculated in part (b). Noting that in two dimensions, $\langle R_x^2 \rangle = \langle R_y^2 \rangle = \langle R^2 \rangle / 2$, the properly normalized Gaussian form is

$$p(\mathbf{R}) = \frac{1}{\pi \langle R^2 \rangle} \exp\left[-\frac{\mathbf{R} \cdot \mathbf{R}}{\langle R^2 \rangle} \right].$$

(d) If the ends of the polymer are pulled apart by a force $\mathbf{F}$, the probabilities for polymer configurations are modified by the Boltzmann weight $\exp\left(\frac{\mathbf{F} \cdot \mathbf{R}}{k_B T} \right)$. By expanding this weight, or otherwise, show that

$$\langle \mathbf{R} \rangle = K^{-1}\mathbf{F} + \mathcal{O}(F^3) \quad,$$

and give an expression for the Hookian constant K in terms of quantities calculated before.

• Let us indicate by $\langle \rangle_0$ averages taken for $\mathbf{F} = 0$. Then the average of $\mathbf{R}$ at finite $\mathbf{F}$ is given by

$$\langle \mathbf{R} \rangle = \frac{\left\langle \mathbf{R} e^{\beta \mathbf{F} \cdot \mathbf{R}} \right\rangle_0}{\left\langle e^{\beta \mathbf{F} \cdot \mathbf{R}} \right\rangle_0} \quad,$$

where $\beta = 1/(k_B T)$. The exponential factors can now be expanded in powers of F. Noting that zero-force averages of odd powers of R are zero by symmetry, we obtain

$$\langle R_\mu \rangle = \beta F_\nu \langle R_\nu R_\mu \rangle_0 + \mathcal{O}(F^3) \quad.$$

By symmetry $\langle R_\nu R_\mu \rangle_0 = \delta_{\mu\nu} \langle R^2 \rangle_0 / 2$, where $\langle R^2 \rangle_0$ is the zero-force expression calculated in the previous part. Thus,

$$\langle \mathbf{R} \rangle = K^{-1}\mathbf{F} + \mathcal{O}(F^3) \quad, \text{with} \quad K = \frac{2 k_B T}{\langle R^2 \rangle_0}.$$

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13. *The book of records:* Consider a sequence of random numbers $\{x_1, x_2, \cdots, x_n, \cdots\}$; the entry x_n is a *record* if it is larger than all numbers before it, i.e. if $x_n > \{x_1, x_2, \cdots, x_{n-1}\}$.

We can then define an associated sequence of indicators $\{R_1, R_2, \cdots, R_n, \cdots\}$ in which $R_n = 1$ if x_n is a record, and $R_n = 0$ if it is not (clearly $R_1 = 1$).

(a) Assume that each entry x_n is taken independently from the same probability distribution $p(x)$. [In other words, $\{x_n\}$ are *IIDs* (independent identically distributed).] Show that, irrespective of the form of $p(x)$, there is a very simple expression for the probability P_n that the entry x_n is a record.

• Consider the n–entries $\{x_1, x_2, \cdots, x_n\}$. Each one of them has the same probability to be the largest one. Thus the probability that x_n is the largest, and hence a record, is $P_n = 1/n$.

(b) The records are entered in the *Guinness Book of Records*. What is the average number $\langle S_N \rangle$ of records after N attempts, and how does it grow for, $N \gg 1$? If the number of trials, e.g. the number of participants in a sporting event, doubles every year, how does the number of entries asymptotically grow with time.

•

$$\langle S_N \rangle = \sum_{n=1}^{N} P_n = \sum_{n=1}^{N} \frac{1}{n} \approx \ln N + \gamma + \mathcal{O}\left(\frac{1}{N}\right) \quad \text{for} \quad N \gg 1,$$

where $\gamma \approx 0.5772\ldots$ is the Euler number. Clearly if $N \propto 2^t$, where t is the number of years,

$$\langle S_t \rangle \approx \ln N(t) = t \ln 2.$$

(c) Prove that the record indicators $\{R_n\}$ are *independent* random variables (though not identical), in that $\langle R_n R_m \rangle_c = 0$ for $m \neq n$.

• $\langle R_n R_m \rangle = 1 \cdot P_n \cdot P_m$ while $\langle R_n \rangle = 1 \cdot P_n$, hence yielding,

$$\langle R_n R_m \rangle_c = P_n P_m - P_n \cdot P_m = 0.$$

This is by itself not sufficient to prove that the random variables R_n and R_m are independent variables. The correct proof is to show that the joint probability factorizes, i.e. $p(R_n, R_m) = p(R_n)p(R_m)$. Let us suppose that $m > n$, the probability that x_m is the largest of the random variables up to m is $1/m$, irrespective of whether some other random number in the set was itself a record (the largest of the random numbers up to n). The equality of the conditional and unconditional probabilities is a proof of independence.

(d) Compute all moments, and the first three cumulants of the total number of records S_N after N entries. Does the central limit theorem apply to S_N?

- We want to compute $\langle e^{-ikS_N} \rangle$. This satisfies,

$$\langle e^{-ikS_N} \rangle = \frac{e^{-ik}}{N} \langle e^{-ikS_{N-1}} \rangle + \frac{N-1}{N} \langle e^{-ikS_{N-1}} \rangle = \frac{e^{-ik} + N - 1}{N} \langle e^{-ikS_{N-1}} \rangle,$$

since the probability for aquiring an additional phase $-ik$ is $P_N = 1/N$. Since $\langle e^{-ikS_1} \rangle = e^{-ik}$, by recursion we obtain,

$$\langle e^{-ikS_N} \rangle = \frac{1}{N!} \prod_{n=1}^{N} (e^{-ik} + n - 1) = \frac{1}{N!} \sum_{n=0}^{N} S_1(N, n) e^{-ikn},$$

where $S_1(n, m)$ denotes the unsigned Stirling number of the first kind. Expanding the exponent, we obtain,

$$\langle e^{-ikS_N} \rangle = \frac{1}{N!} \sum_{n=0}^{N} S_1(N, n) \sum_{m=0}^{\infty} \frac{n^m (-ik)^m}{m!} = \sum_{m=0}^{\infty} \frac{(-ik)^m}{m!} \left[\frac{1}{N!} \sum_{n=0}^{N} S_1(N, n) n^m \right].$$

Hence we obtain the mth moment,

$$\langle S_N^m \rangle = \frac{1}{N!} \sum_{n=0}^{N} S_1(N, n) n^m.$$

The first three cumulants can be obtained using the moments, but the easier way to obtain them is by using the fact that $S_N = R_1 + \cdots + R_N$ and that R_n are independent variables. Due to the independence of R_n,

$$\langle S_N^m \rangle_c = \sum_{n=1}^{N} \langle R_n^m \rangle_c.$$

From this, and the fact that for any m, $\langle R_n^m \rangle = 1/n$, we easily obtain,

$$\langle S_N \rangle_c = \sum_{n=1}^{N} \langle R_n \rangle_c = \sum_{n=1}^{N} \frac{1}{n},$$

$$\langle S_N^2 \rangle_c = \sum_{n=1}^{N} \langle R_n^2 \rangle_c = \sum_{n=1}^{N} (\frac{1}{n} - \frac{1}{n^2}),$$

$$\langle S_N^3 \rangle_c = \sum_{n=1}^{N} \langle R_n^3 \rangle_c = \sum_{n=1}^{N} (\frac{1}{n} - \frac{3}{n^2} + \frac{2}{n^3}).$$

The central limit theorem applies to S_N since R_n are independent variables. Seeing this in another way is to observe that for large N,

$$\langle S_N^m \rangle_c = \sum_{n=1}^{N} \langle R_n^m \rangle_c < \sum_{n=1}^{N} \langle R_n^m \rangle = \sum_{n=1}^{N} \frac{1}{n} \approx \ln N + \mathcal{O}(1).$$

Since the variance is of order $\ln N$, all the higher moments can be disregarded.

(e) The first record, of course occurs for $n_1 = 1$. If the third record occurs at trial number $n_3 = 9$, what is the mean value $\langle n_2 \rangle$ for the position of the second record? What is the mean value $\langle n_4 \rangle$ for the position of the fourth record?

- The probability for $n_2 = n$ and $n_3 = 9$ is,

$$(1 - R_2) \cdots (1 - R_{n-1}) R_n (1 - R_{n+1}) \cdots (1 - R_8) R_9 = \frac{1}{72(n-1)}.$$

Hence $\langle n_2 \rangle_{n_3=9}$ can be obtained by,

$$\langle n_2 \rangle = \frac{\sum_{n_2=2}^{8} n_2 \cdot \frac{1}{72(n_2-1)}}{\sum_{n_2=2}^{8} \frac{1}{72(n_2-1)}} = \frac{1343}{363} \approx 3.70.$$

As for $\langle n_4 \rangle$, for given value of x_3, define, $P(x_3) = \int_{x_3}^{\infty} dx\, p(x)$. Then we get for a given value of x_3,

$$\langle n_4 \rangle_{x_3=a} = \sum_{n=10}^{\infty} n \cdot (1 - P(a))^{n-10} P(a) = \frac{9P(a)}{1 - (1 - P(a))} + \frac{P(a)}{(1 - (1 - P(a)))^2} = 9 + \frac{1}{P(a)}.$$

Hence we obtain $\langle n_4 \rangle$ by,

$$\langle n_4 \rangle = \frac{\int_{-\infty}^{\infty} da\, p(a)(9 + 1/P(a))}{\int_{-\infty}^{\infty} da\, p(a)} = \int_0^1 dP(9 + \frac{1}{P}) \to \infty,$$

where we used the fact that $p(a) = -dP(a)/da$.
$$********$$

14. *Jarzynski equality:* In equilibrium at a temperature T, the probability that a macroscopic system is in a microstate μ is $p(\mu) = \exp\left[-\beta \mathcal{H}(\mu)\right]/Z$, where $\mathcal{H}(\mu)$ is the energy of the microstate, $\beta = 1/(k_B T)$, and the normalization factor is related to the free energy by $-\beta F = \ln Z$. We now change the macroscopic state of the system by performing external work W, such that the new state is also in equilibrium at temperature T. For example, imagine that the volume of a gas in changed by moving a piston as $L(t) = L_1 + (L_2 - L_1)t/\tau$.

Depending on the protocol (e.g. the speed $u = (L_2 - L_1)/\tau$), the process may be close to or far from reversible. Nonetheless, the Jarzynski equality relates the probability distribution for the work W to the *equilibrium* change in free energy!

(a) Assume that the process by which work is performed is fully deterministic, in the sense that for a given protocol, any initial microstate μ will evolve to a specific final microstate μ'. The amount of work performed $W(\mu)$ will vary with the initial microstate, and there is thus a probability distribution $p_f(W)$ which can be related to the equilibrium $p(\mu)$. The energy of the final microstate, however, is precisely $\mathcal{H}'(\mu') = \mathcal{H}(\mu) + W(\mu)$. Time reversal symmetry implies that if we now instantaneously reverse all the momenta, and proceed according to the reversed protocol, the time-reversed microstate $\overline{\mu'}$ will deterministically evolve back to microstate μ, and the work $-W(\mu)$ is recovered. However, rather than doing so, we first allow the system to equilibrate into its new macrostate at temperature T, before reversing the protocol to recover the work. The recovered work $-W$ will now be a function of the selected microstate, and distributed according to a different probability $p_b(-W)$, related to $p'(\mu') = \exp\left[-\beta\mathcal{H}'(\mu')\right]/Z'$. It is in general not possible to find $p_f(W)$ or $p_b(-W)$. However, by noting that the probabilities of a pair of time-reversed microstates are exactly equal, show that their ratio is given by

$$\frac{p_f(W)}{p_b(-W)} = \exp\left[\beta(W + F - F')\right].$$

While you were guided to prove the above result with specific assumptions, it is in fact more generally valid, and known as the *work–fluctuation theorem*.

• $p_f(W)$ can be defined such that,

$$p_f(W)dW = \sum_{W(\mu)=W} p(\mu)d\mu.$$

Also,

$$p_b(-W)dW = \sum_{W'(\mu')=-W} p'(\mu')d\mu'.$$

We used $W(\mu)$ to denote the work done on the microstate μ in the forward process, and $W'(\mu')$ to denote the work done on the microstate μ' in the backward process. Note that there is a one to one correspondence between initial microstates μ such that $W(\mu) = W$ and final microstates μ' with $W'(\mu') = -W$, since each μ is mapped to a μ' by a given

protocol. Also, since the density of microstates do not change by thermodynamic processes, it is safe to say that at a given microstate μ, $d\mu = d\mu'$. Hence we may write,

$$p_b(-W)dW = \sum_{W'(\mu')=-W} p'(\mu')d\mu' = \sum_{W(\mu)=W} p'(\mu'(\mu))d\mu.$$

Therefore,

$$\frac{p_f(W)}{p_b(-W)} = \frac{\sum_{W(\mu)=W} p(\mu)d\mu}{\sum_{W(\mu)=W} p'(\mu'(\mu))d\mu}.$$

Now since for each μ,

$$\frac{p(\mu)d\mu}{p'(\mu'(\mu))d\mu} = \frac{Z'}{Z}\exp(-\beta(\mathcal{H}(\mu) - \mathcal{H}'(\mu'))) = \exp(\beta(W + F - F')),$$

we finally obtain,

$$\frac{p_f(W)}{p_b(-W)} = \exp(\beta(W + F - F')).$$

(b) Prove the *Jarzynski equality*

$$\Delta F \equiv F' - F = -k_B T \ln \left\langle \mathrm{e}^{-\beta W} \right\rangle \equiv -k_B T \ln \left[\int dW p_f(W) \mathrm{e}^{-\beta W} \right].$$

This result can in principle be used to compute equilibrium free energy differences from an ensemble of non-equilibrium measurements of the work. For example, in *Liphardt, et. al., Science* **296**, *1832 (2002)*, the work needed to stretch a single RNA molecule was calculated and related to the free energy change. However, the number of trials must be large enough to ensure that the averaged exponential, which is dominated by rare events, is accurately obtained.

• From the previous problem,

$$p_f(W)e^{-\beta W} = p_b(-W)e^{\beta(F-F')} = p_b(-W)e^{-\beta\Delta F}.$$

Integrating both sides with respect to W, and using $\int dW p_b(-W) = 1$ we get,

$$\langle e^{-\beta W} \rangle = e^{-\beta\Delta F}.$$

Taking the logarithm of both sides and sorting out the terms we get,

$$\Delta F = -k_B T \ln\langle e^{-\beta W} \rangle.$$

(c) Use the Jarzynski equality to prove the familiar thermodynamic inequality

$$\langle W \rangle \leq \Delta F \qquad .$$

• Since $\exp(-\beta W)$ is a convex function of W, for any distribution $p(W)$ with $p(W) \geq 0$ and $\int dW p(W) = 1$,

$$\langle e^{-\beta W} \rangle = \int dW p(W) \exp(-\beta W) \geq \exp\left(-\beta \int dW p(W) W\right) = e^{-\beta \langle W \rangle}.$$

Hence we obtain,

$$\Delta F = -\frac{1}{\beta} \ln \langle e^{-\beta W} \rangle \leq -\frac{1}{\beta} \ln e^{-\beta \langle W \rangle} = \langle W \rangle.$$

(d) Consider a cycle in which a work $W + \omega$ is performed in the first stage, and work $-W$ is returned in the reversed process. According to the second law of thermodynamics, the net gain ω must be negative. However, within statistical physics, it is always possible that this condition is violated. Use the above results to conclude that the probability of violating the second law decays with the degree of violation according to

$$P_{\text{violating second law}}(\omega) \leq e^{-\beta \omega}.$$

• Let us define $\overline{p}(\omega)$ as the *probability density* to violate the second law by $\omega > 0$. Since the same ω can be obtained for different choices of W, we have

$$\overline{p}(\omega) = \int dW p_f(W - \omega) p_b(-W).$$

By the relation obtained in (a), we get,

$$\frac{p_f(W - \omega) p_b(-W)}{p_b(-W + \omega) p_f(W)} = \frac{\exp(\beta(W - \omega + F - F'))}{\exp(\beta(W + F - F'))},$$

which yields,

$$p_f(W - \omega) p_b(-W) = p_b(-W + \omega) p_f(W) \exp(-\beta \omega),$$

hence,

$$\overline{p}(\omega) = \int dW p_b(-W + \omega) p_f(W) \exp(-\beta \omega) = \overline{p}(-\omega) \exp(-\beta \omega).$$

The cumulative probability of violating the second law by ω *or more* is now obtained as

$$P(\omega) = \int_\omega^\infty \omega' \overline{p}(\omega') = \int_\omega^\infty \omega' \overline{p}(-\omega') \exp(-\beta \omega') < \exp(-\beta \omega) \int_\omega^\infty \omega' \overline{p}(-\omega') < \exp(-\beta \omega).$$

The first inequality is because for all ω' in the integrand, $\exp(-\beta \omega') < \exp(-\beta \omega)$, and the second since any cumulative probability is less than one.

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Problems for Chapter III - Kinetic Theory of Gases

1. *One dimensional gas:* A thermalized gas particle is suddenly confined to a one–dimensional trap. The corresponding mixed state is described by an initial density function $\rho(q, p, t = 0) = \delta(q)f(p)$, where $f(p) = \exp(-p^2/2mk_BT)/\sqrt{2\pi mk_BT}$.

(a) Starting from Liouville's equation, derive $\rho(q, p, t)$ and sketch it in the (q, p) plane.

• Liouville's equation, describing the incompressible nature of phase space density, is

$$\frac{\partial \rho}{\partial t} = -\dot{q}\frac{\partial \rho}{\partial q} - \dot{p}\frac{\partial \rho}{\partial p} = -\frac{\partial \mathcal{H}}{\partial p}\frac{\partial \rho}{\partial q} + \frac{\partial \mathcal{H}}{\partial q}\frac{\partial \rho}{\partial p} \equiv -\{\rho, \mathcal{H}\}.$$

For the gas particle confined to a 1–dimensional trap, the Hamiltonian can be written as

$$\mathcal{H} = \frac{p^2}{2m} + V(q_x) = \frac{p^2}{2m},$$

since $V_{q_x} = 0$, and there is no motion in the y and z directions. With this Hamiltonian, Liouville's equation becomes

$$\frac{\partial \rho}{\partial t} = -\frac{p}{m}\frac{\partial \rho}{\partial q},$$

whose solution, subject to the specified initial conditions, is

$$\rho(q, p, t) = \rho\left(q - \frac{p}{m}t, p, 0\right) = \delta\left(q - \frac{p}{m}t\right)f(p).$$
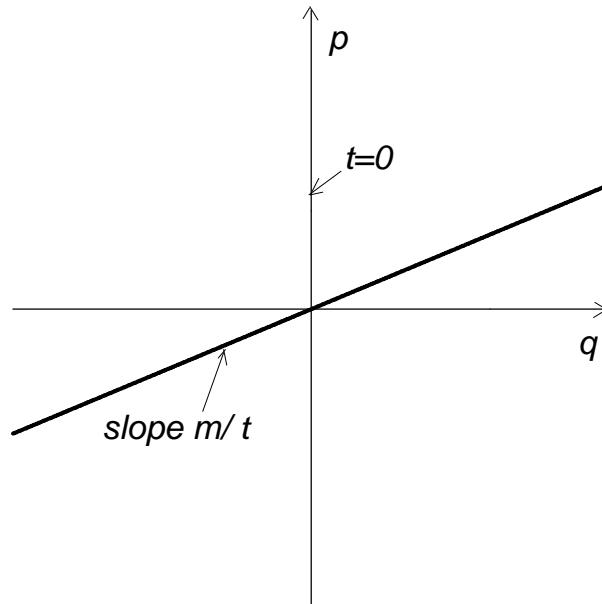
(b) Derive the expressions for the averages $\langle q^2 \rangle$ and $\langle p^2 \rangle$ at $t > 0$.

• The expectation value for any observable $\mathcal{O}$ is

$$\langle \mathcal{O} \rangle = \int d\Gamma \mathcal{O} \rho(\Gamma, t),$$

and hence

$$\langle p^2 \rangle = \int p^2 f(p) \delta \left(q - \frac{p}{m} t \right) dp \ dq = \int p^2 f(p) dp$$

$$= \int_{-\infty}^{\infty} dp \ p^2 \frac{1}{\sqrt{2\pi m k_B T}} \exp \left(-\frac{p^2}{2m k_B T} \right) = m k_B T.$$

Likewise, we obtain

$$\langle q^2 \rangle = \int q^2 f(p) \delta \left(q - \frac{p}{m} t \right) dp \ dq = \int \left(\frac{p}{m} t \right)^2 f(p) dp = \left(\frac{t}{m} \right)^2 \int p^2 f(p) dp = \frac{k_B T}{m} t^2.$$

(c) Suppose that hard walls are placed at $q = \pm Q$. Describe $\rho(q, p, t \gg \tau)$, where τ is an appropriately large relaxation time.

• Now suppose that hard walls are placed at $q = \pm Q$. The appropriate relaxation time τ, is the characteristic length between the containing walls divided by the characteristic velocity of the particle, i.e.

$$\tau \sim \frac{2Q}{|\dot{q}|} = \frac{2Qm}{\sqrt{\langle p^2 \rangle}} = 2Q\sqrt{\frac{m}{k_B T}}.$$

Initially $\rho(q, p, t)$ resembles the distribution shown in part (a), but each time the particle hits the barrier, reflection changes p to $-p$. As time goes on, the slopes become less, and $\rho(q, p, t)$ becomes a set of closely spaced lines whose separation vanishes as $2mQ/t$.
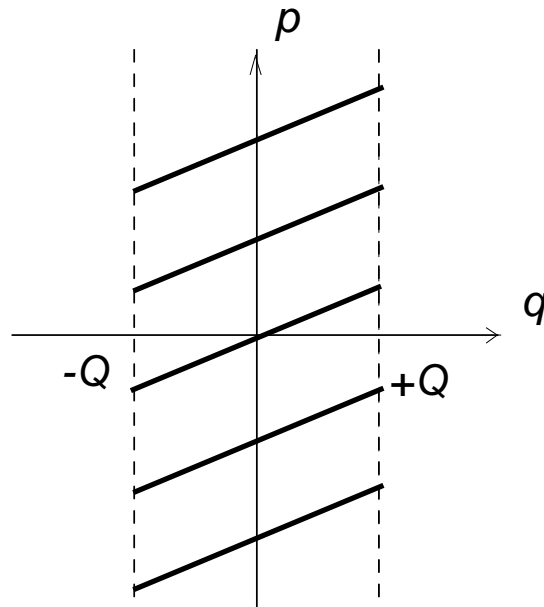
(d) A "coarse–grained" density $\tilde{\rho}$, is obtained by ignoring variations of ρ below some small resolution in the (q, p) plane; e.g., by averaging ρ over cells of the resolution area. Find $\tilde{\rho}(q, p)$ for the situation in part (c), and show that it is stationary.

• We can choose any resolution ε in (p, q) space, subdividing the plane into an array of pixels of this area. For any ε, after sufficiently long time many lines will pass through this area. Averaging over them leads to

$$\tilde{\rho}(q, p, t \gg \tau) = \frac{1}{2Q} f(p),$$

as (i) the density $f(p)$ at each p is always the same, and (ii) all points along $q \in [-Q, +Q]$ are equally likely. For the time variation of this coarse-grained density, we find

$$\frac{\partial \tilde{\rho}}{\partial t} = -\frac{p}{m} \frac{\partial \tilde{\rho}}{\partial q} = 0, \quad \text{i.e.} \quad \tilde{\rho} \text{ is stationary.}$$

****

2. *Evolution of entropy:* The normalized ensemble density is a probability in the phase space Γ. This probability has an associated entropy $S(t) = -\int d\Gamma \rho(\Gamma, t) \ln \rho(\Gamma, t)$.

(a) Show that if $\rho(\Gamma, t)$ satisfies Liouville's equation for a Hamiltonian $\mathcal{H}$, $dS/dt = 0$.

• A candidate "entropy" is defined by

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

Taking the derivative with respect to time gives

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

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

$$\frac{dS}{dt} = -\int d\Gamma \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} \right) (\ln \rho + 1).$$

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(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 yields[†]

$$
\begin{aligned}
\frac{dS}{dt} &= \int d\Gamma \sum_{i=1}^{3N} \left[\rho \frac{\partial}{\partial p_i} \left(\frac{\partial \mathcal{H}}{\partial q_i} (\ln \rho + 1) \right) - \rho \frac{\partial}{\partial q_i} \left(\frac{\partial \mathcal{H}}{\partial p_i} (\ln \rho + 1) \right) \right] \\
&= \int d\Gamma \sum_{i=1}^{3N} \left[\rho \frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i} (\ln \rho + 1) + \rho \frac{\partial \mathcal{H}}{\partial q_i} \frac{1}{\rho} \frac{\partial \rho}{\partial p_i} - \rho \frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i} (\ln \rho + 1) - \rho \frac{\partial \mathcal{H}}{\partial p_i} \frac{1}{\rho} \frac{\partial \rho}{\partial q_i} \right] \\
&= \int d\Gamma \sum_{i=1}^{3N} \left[\frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial \rho}{\partial p_i} - \frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial \rho}{\partial q_i} \right].
\end{aligned}
$$

Integrating the final expression by parts gives

$$
\frac{dS}{dt} = - \int d\Gamma \sum_{i=1}^{3N} \left[-\rho \frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i} + \rho \frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i} \right] = 0.
$$

(b) Using the method of Lagrange multipliers, find the function $\rho_{\max}(\Gamma)$ which maximizes the functional $S[\rho]$, subject to the constraint of fixed average energy, $\langle \mathcal{H} \rangle = \int d\Gamma \rho \mathcal{H} = E$.

• There are two constraints, normalization and constant average energy, written respectively as

$$
\int d\Gamma \rho(\Gamma) = 1, \qquad \text{and} \qquad \langle \mathcal{H} \rangle = \int d\Gamma \rho(\Gamma) \mathcal{H} = E.
$$

[†] This is standard integration by parts, i.e. $\int_b^a F dG = FG|_b^a - \int_b^a G dF$. Looking explicitly at one term in the expression to be integrated in this problem,

$$
\int \prod_{i=1}^{3N} dV_i \frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} = \int dq_1 dp_1 \cdots dq_i dp_i \cdots dq_{3N} dp_{3N} \frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i},
$$

we identify $dG = dq_i \frac{\partial \rho}{\partial q_i}$, and F with the remainder of the expression. Noting that $\rho(q_i) = 0$ at the boundaries of the box, we get

$$
\int \prod_{i=1}^{3N} dV_i \frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} = - \int \prod_{i=1}^{3N} dV_i \rho \frac{\partial}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i}.
$$

Rewriting the expression for entropy,

$$S(t) = \int d\Gamma \rho(\Gamma) \left[-\ln \rho(\Gamma) - \alpha - \beta \mathcal{H} \right] + \alpha + \beta E,$$

where α and β are Lagrange multipliers used to enforce the two constraints. Extremizing the above expression with respect to the function $\rho(\Gamma)$, results in

$$\left. \frac{\partial S}{\partial \rho(\Gamma)} \right|_{\rho = \rho_{max}} = -\ln \rho_{max}(\Gamma) - \alpha - \beta \mathcal{H}(\Gamma) - 1 = 0.$$

The solution to this equation is

$$\ln \rho_{max} = -(\alpha + 1) - \beta \mathcal{H},$$

which can be rewritten as

$$\rho_{max} = C \exp\left(-\beta \mathcal{H} \right), \quad \text{where} \quad C = e^{-(\alpha+1)}.$$

(c) Show that the solution to part (b) is stationary, i.e. $\partial \rho_{\max}/\partial t = 0$.

• The density obtained in part (b) is stationary, as can be easily checked from

$$\frac{\partial \rho_{max}}{\partial t} = -\{\rho_{max}, \mathcal{H}\} = -\left\{ Ce^{-\beta \mathcal{H}}, \mathcal{H} \right\}$$

$$= \frac{\partial \mathcal{H}}{\partial p} C(-\beta) \frac{\partial \mathcal{H}}{\partial q} e^{-\beta \mathcal{H}} - \frac{\partial \mathcal{H}}{\partial q} C(-\beta) \frac{\partial \mathcal{H}}{\partial p} e^{-\beta \mathcal{H}} = 0.$$

(d) How can one reconcile the result in (a), with the observed increase in entropy as the system approaches the equilibrium density in (b)? (Hint: Think of the situation encountered in the previous problem.)

• Liouville's equation preserves the information content of the PDF $\rho(\Gamma, t)$, and hence $S(t)$ does not increase in time. However, as illustrated in the example in problem 1, the density becomes more finely dispersed in phase space. In the presence of any coarse-graining of phase space, information disappears. The maximum entropy, corresponding to $\tilde{\rho}$, describes equilibrium in this sense.

****

3. *The Vlasov equation* is obtained in the limit of high particle density $n = N/V$, or large inter-particle interaction range λ, such that $n\lambda^3 \gg 1$. In this limit, the collision terms are dropped from the left hand side of the equations in the BBGKY hierarchy.

The BBGKY hierarchy

$$
\left[\frac{\partial}{\partial t} + \sum_{n=1}^{s} \frac{\vec{p}_n}{m} \cdot \frac{\partial}{\partial \vec{q}_n} - \sum_{n=1}^{s} \left(\frac{\partial U}{\partial \vec{q}_n} + \sum_l \frac{\partial \mathcal{V}(\vec{q}_n - \vec{q}_l)}{\partial \vec{q}_n} \right) \cdot \frac{\partial}{\partial \vec{p}_n} \right] f_s
$$
$$
= \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial \mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial \vec{q}_n} \cdot \frac{\partial f_{s+1}}{\partial \vec{p}_n},
$$

has the characteristic time scales

$$
\begin{cases}
\dfrac{1}{\tau_U} \sim \dfrac{\partial U}{\partial \vec{q}} \cdot \dfrac{\partial}{\partial \vec{p}} \sim \dfrac{v}{L}, \\[2mm]
\dfrac{1}{\tau_c} \sim \dfrac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \dfrac{\partial}{\partial \vec{p}} \sim \dfrac{v}{\lambda}, \\[2mm]
\dfrac{1}{\tau_X} \sim \displaystyle\int dx \dfrac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \dfrac{\partial}{\partial \vec{p}} \dfrac{f_{s+1}}{f_s} \sim \dfrac{1}{\tau_c} \cdot n\lambda^3,
\end{cases}
$$

where $n\lambda^3$ is the number of particles within the interaction range λ, and v is a typical velocity. The Boltzmann equation is obtained in the dilute limit, $n\lambda^3 \ll 1$, by disregarding terms of order $1/\tau_X \ll 1/\tau_c$. The Vlasov equation is obtained in the dense limit of $n\lambda^3 \gg 1$ by ignoring terms of order $1/\tau_c \ll 1/\tau_X$.

(a) Assume that the N body density is a product of one particle densities, i.e. $\rho = \prod_{i=1}^{N} \rho_1(\mathbf{x}_i, t)$, where $\mathbf{x}_i \equiv (\vec{p}_i, \vec{q}_i)$. Calculate the densities f_s, and their normalizations.

• Let bfx_i denote the coordinates and momenta for particle i. Starting from the joint probability $\rho_N = \prod_{i=1}^{N} \rho_1(\mathbf{x}_i, t)$, for *independent particles*, we find

$$
f_s = \frac{N!}{(N-s)!} \int \prod_{\alpha=s+1}^{N} dV_\alpha \rho_N = \frac{N!}{(N-s)!} \prod_{n=1}^{s} \rho_1(\mathbf{x}_n, t).
$$

The normalizations follow from

$$
\int d\Gamma \rho = 1, \quad \Longrightarrow \quad \int dV_1 \rho_1(\mathbf{x}, t) = 1,
$$

and

$$
\int \prod_{n=1}^{s} dV_n f_s = \frac{N!}{(N-s)!} \approx N^s \qquad \text{for} \qquad s \ll N.
$$

(b) Show that once the collision terms are eliminated, all the equations in the BBGKY hierarchy are equivalent to the single equation

$$\left[\frac{\partial}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{q}} - \frac{\partial U_{\text{eff}}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} \right] f_1(\vec{p}, \vec{q}, t) = 0,$$

where

$$U_{\text{eff}}(\vec{q}, t) = U(\vec{q}) + \int d\mathbf{x}' \mathcal{V}(\vec{q} - \vec{q}') f_1(\mathbf{x}', t).$$

- Noting that

$$\frac{f_{s+1}}{f_s} = \frac{(N-s)!}{(N-s-1)!} \rho_1(\mathbf{x}_{s+1}),$$

the reduced BBGKY hierarchy is

$$\left[\frac{\partial}{\partial t} + \sum_{n=1}^{s} \left(\frac{\vec{p}_n}{m} \cdot \frac{\partial}{\partial \vec{q}_n} - \frac{\partial U}{\partial \vec{q}_n} \cdot \frac{\partial}{\partial \vec{p}_n} \right) \right] f_s$$

$$\approx \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial \mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial \vec{q}_n} \cdot \frac{\partial}{\partial \vec{p}_n} [(N-s) f_s \rho_1(\mathbf{x}_{s+1})]$$

$$\approx \sum_{n=1}^{s} \frac{\partial}{\partial \vec{q}_n} \left[\int dV_{s+1} \rho_1(\mathbf{x}_{s+1}) \mathcal{V}(\vec{q}_n - \vec{q}_{s+1}) \cdot N \right] \frac{\partial}{\partial \vec{p}_n} f_s,$$

where we have used the approximation $(N-s) \approx N$ for $N \gg s$. Rewriting the above expression,

$$\left[\frac{\partial}{\partial t} + \sum_{n=1}^{s} \left(\frac{\vec{p}_n}{m} \cdot \frac{\partial}{\partial \vec{q}_n} - \frac{\partial U_{eff}}{\partial \vec{q}_n} \cdot \frac{\partial}{\partial \vec{p}_n} \right) \right] f_s = 0,$$

where

$$U_{eff} = U(\vec{q}) + N \int dV' \mathcal{V}(\vec{q} - \vec{q}') \rho_1(\mathbf{x}', t).$$

(c) Now consider N particles confined to a box of volume V, with no additional potential. Show that $f_1(\vec{q}, \vec{p}) = g(\vec{p})/V$ is a stationary solution to the Vlasov equation *for any $g(\vec{p})$*. Why is there no relaxation towards equilibrium for $g(\vec{p})$?

- Starting from

$$\rho_1 = g(\vec{p})/V,$$

we obtain

$$\mathcal{H}_{eff} = \sum_{i=1}^{N} \left[\frac{\vec{p_i}^2}{2m} + U_{eff}(\vec{q_i}) \right],$$

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with

$$U_{eff} = 0 + N \int dV' \mathcal{V}(\vec{q} - \vec{q}\,') \frac{1}{V} g(\vec{p}) = \frac{N}{V} \int d^3 q \mathcal{V}(\vec{q}).$$

(We have taken advantage of the normalization $\int d^3 p g(\vec{p}) = 1$.) Substituting into the Vlasov equation yields

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{q}} \right) \rho_1 = 0.$$

There is no relaxation towards equilibrium because there are no collisions which allow $g(\vec{p})$ to relax. The momentum of each particle is conserved by $\mathcal{H}_{eff}$; i.e. $\{\rho_1, \mathcal{H}_{eff}\} = 0$, preventing its change.

****

4. *Two component plasma:* Consider a *neutral* mixture of N ions of charge $+e$ and mass m_+, and N electrons of charge $-e$ and mass m_-, in a volume $V = N/n_0$.

(a) Show that the Vlasov equations for this two component system are

$$\begin{cases} \left[\dfrac{\partial}{\partial t} + \dfrac{\vec{p}}{m_+} \cdot \dfrac{\partial}{\partial \vec{q}} + e \dfrac{\partial \Phi_{\text{eff}}}{\partial \vec{q}} \cdot \dfrac{\partial}{\partial \vec{p}} \right] f_+(\vec{p}, \vec{q}, t) = 0 \\[3mm] \left[\dfrac{\partial}{\partial t} + \dfrac{\vec{p}}{m_-} \cdot \dfrac{\partial}{\partial \vec{q}} - e \dfrac{\partial \Phi_{\text{eff}}}{\partial \vec{q}} \cdot \dfrac{\partial}{\partial \vec{p}} \right] f_-(\vec{p}, \vec{q}, t) = 0 \end{cases},$$

where the effective Coulomb potential is given by

$$\Phi_{\text{eff}}(\vec{q}, t) = \Phi_{\text{ext}}(\vec{q}) + e \int d\mathbf{x}' C(\vec{q} - \vec{q}\,') \left[f_+(\mathbf{x}', t) - f_-(\mathbf{x}', t) \right].$$

Here, Φ_{ext} is the potential set up by the external charges, and the Coulomb potential $C(\vec{q})$ satisfies the differential equation $\nabla^2 C = 4\pi \delta^3(\vec{q})$.

• The Hamiltonian for the two component mixture is

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{\vec{p}_i^{\,2}}{2m_+} + \frac{\vec{p}_i^{\,2}}{2m_-} \right] + \sum_{i,j=1}^{2N} e_i e_j \frac{1}{|\vec{q}_i - \vec{q}_j|} + \sum_{i=1}^{2N} e_i \Phi_{ext}(\vec{q}_i),$$

where $C(\vec{q}_i - \vec{q}_j) = 1/|\vec{q}_i - \vec{q}_j|$, resulting in

$$\frac{\partial \mathcal{H}}{\partial \vec{q}_i} = e_i \frac{\partial \Phi_{ext}}{\partial \vec{q}_i} + e_i \sum_{j \neq i} e_j \frac{\partial}{\partial \vec{q}_i} C(\vec{q}_i - \vec{q}_j).$$

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Substituting this into the Vlasov equation, we obtain

$$\begin{cases} \left[\dfrac{\partial}{\partial t} + \dfrac{\vec{p}}{m_+} \cdot \dfrac{\partial}{\partial \vec{q}} + e\dfrac{\partial \Phi_{eff}}{\partial \vec{q}} \cdot \dfrac{\partial}{\partial \vec{p}}\right] f_+(\vec{p}, \vec{q}, t) = 0, \\ \left[\dfrac{\partial}{\partial t} + \dfrac{\vec{p}}{m_-} \cdot \dfrac{\partial}{\partial \vec{q}} - e\dfrac{\partial \Phi_{eff}}{\partial \vec{q}} \cdot \dfrac{\partial}{\partial \vec{p}}\right] f_-(\vec{p}, \vec{q}, t) = 0. \end{cases}$$

(b) Assume that the one particle densities have the stationary forms $f_\pm = g_\pm(\vec{p})n_\pm(\vec{q})$. Show that the effective potential satisfies the equation

$$\nabla^2 \Phi_{\text{eff}} = 4\pi \rho_{\text{ext}} + 4\pi e \left(n_+(\vec{q}) - n_-(\vec{q})\right),$$

where ρ_{ext} is the external charge density.

• Setting $f_\pm(\vec{p}, \vec{q}) = g_\pm(\vec{p})n_\pm(\vec{q})$, and using $\int d^3p\, g_\pm(\vec{p}) = 1$, the integrals in the effective potential simplify to

$$\Phi_{eff}(\vec{q}, t) = \Phi_{ext}(\vec{q}) + e \int d^3q' C(\vec{q} - \vec{q}\,') \left[n_+(\vec{q}\,') - n_-(\vec{q}\,')\right].$$

Apply ∇^2 to the above equation, and use $\nabla^2 \Phi_{ext} = 4\pi\rho_{ext}$ and $\nabla^2 C(\vec{q}-\vec{q}\,') = 4\pi\delta^3(\vec{q}-\vec{q}\,')$, to obtain

$$\nabla^2 \phi_{eff} = 4\pi\rho_{ext} + 4\pi e \left[n_+(\vec{q}) - n_-(\vec{q})\right].$$

(c) Further assuming that the densities relax to the equilibrium Boltzmann weights $n_\pm(\vec{q}) = n_0 \exp\left[\pm\beta e\Phi_{\text{eff}}(\vec{q})\right]$, leads to the self-consistency condition

$$\nabla^2 \Phi_{\text{eff}} = 4\pi \left[\rho_{\text{ext}} + n_0 e \left(e^{\beta e\Phi_{\text{eff}}} - e^{-\beta e\Phi_{\text{eff}}}\right)\right],$$

known as the *Poisson–Boltzmann equation*. Due to its nonlinear form, it is generally not possible to solve the Poisson–Boltzmann equation. By linearizing the exponentials, one obtains the simpler *Debye* equation

$$\nabla^2 \Phi_{\text{eff}} = 4\pi \rho_{\text{ext}} + \Phi_{\text{eff}}/\lambda^2.$$

Give the expression for the *Debye screening length* λ.

• Linearizing the Boltzmann weights gives

$$n_\pm = n_o \exp[\mp\beta e\Phi_{eff}(\vec{q})] \approx n_o \left[1 \mp \beta e\Phi_{eff}\right],$$

resulting in

$$\nabla^2 \Phi_{eff} = 4\pi \rho_{ext} + \frac{1}{\lambda^2} \Phi_{eff},$$

with the screening length given by

$$\lambda^2 = \frac{k_B T}{8\pi n_o e^2}.$$

(d) Show that the Debye equation has the general solution

$$\Phi_{\text{eff}}(\vec{q}) = \int d^3 \vec{q}' G(\vec{q} - \vec{q}') \rho_{\text{ext}}(\vec{q}'),$$

where $G(\vec{q}) = \exp(-|\vec{q}|/\lambda)/|\vec{q}|$ is the screened Coulomb potential.

• We want to show that the Debye equation has the general solution

$$\Phi_{eff}(\vec{q}) = \int d^3 \vec{q} \, G(\vec{q} - \vec{q}') \rho_{ext}(\vec{q}'),$$

where

$$G(\vec{q}) = \frac{\exp(-|q|/\lambda)}{|q|}.$$

Effectively, we want to show that $\nabla^2 G = G/\lambda^2$ for $\vec{q} \neq 0$. In spherical coordinates, $G = \exp(-r/\lambda)/r$. Evaluating ∇^2 in spherical coordinates gives

$$\nabla^2 G = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial G}{\partial r} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \left[-\frac{1}{\lambda} \frac{e^{-r/\lambda}}{r} - \frac{e^{-r/\lambda}}{r^2} \right]$$

$$= \frac{1}{r^2} \left[\frac{1}{\lambda^2} r e^{-r/\lambda} - \frac{1}{\lambda} e^{-r/\lambda} + \frac{1}{\lambda} e^{-r/\lambda} \right] = \frac{1}{\lambda^2} \frac{e^{-r/\lambda}}{r} = \frac{G}{\lambda^2}.$$

(e) Give the condition for the self-consistency of the Vlasov approximation, and interpret it in terms of the inter-particle spacing?

• The Vlasov equation assumes the limit $n_o \lambda^3 \gg 1$, which requires that

$$\frac{(k_B T)^{3/2}}{n_o^{1/2} e^3} \gg 1, \quad \Longrightarrow \quad \frac{e^2}{k_B T} \ll n_o^{-1/3} \sim \ell,$$

where ℓ is the interparticle spacing. In terms of the interparticle spacing, the self–consistency condition is

$$\frac{e^2}{\ell} \ll k_B T,$$

i.e. the interaction energy is much less than the kinetic (thermal) energy.

(f) Show that the characteristic relaxation time ($\tau \approx \lambda/c$) is temperature independent. What property of the plasma is it related to?

• A characteristic time is obtained from

$$\tau \sim \frac{\lambda}{c} \sim \sqrt{\frac{k_B T}{n_o e^2}} \cdot \sqrt{\frac{m}{k_B T}} \sim \sqrt{\frac{m}{n_o e^2}} \sim \frac{1}{\omega_p},$$

where ω_p is the plasma frequency.

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5. *Two dimensional electron gas in a magnetic field:* When donor atoms (such as P or As) are added to a semiconductor (e.g. Si or Ge), their conduction electrons can be thermally excited to move freely in the host lattice. By growing layers of different materials, it is possible to generate a spatially varying potential (work–function) which traps electrons at the boundaries between layers. In the following, we shall treat the trapped electrons as a gas of classical particles *in two dimensions*.

If the layer of electrons is sufficiently separated from the donors, the main source of scattering is from electron–electron collisions.

(a) The Hamiltonian for non–interacting free electrons in a magnetic field has the form

$$\mathcal{H} = \sum_i \left[\frac{\left(\vec{p}_i - e\vec{A}\right)^2}{2m} \pm \mu_B |\vec{B}| \right].$$

(The two signs correspond to electron spins parallel or anti-parallel to the field.) The vector potential $\vec{A} = \vec{B} \times \vec{q}/2$ describes a uniform magnetic field $\vec{B}$. Obtain the classical equations of motion, and show that they describe rotation of electrons in cyclotron orbits in a plane orthogonal to $\vec{B}$.

• The Hamiltonian for non–interacting free electrons in a magnetic field has the form

$$\mathcal{H} = \sum_i \left[\frac{\left(\vec{p}_i + e\vec{A}\right)^2}{2m} \pm \mu_B |\vec{B}| \right],$$

or in expanded form

$$\mathcal{H} = \frac{p^2}{2m} + \frac{e}{m}\vec{p} \cdot \vec{A} + \frac{e^2}{2m}\vec{A}^2 \pm \mu_B |\vec{B}|.$$

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Substituting $\vec{A} = \vec{B} \times \vec{q}/2$, results in

$$\mathcal{H} = \frac{p^2}{2m} + \frac{e}{2m}\vec{p} \cdot \vec{B} \times \vec{q} + \frac{e^2}{8m}\left(\vec{B} \times \vec{q}\right)^2 \pm \mu_B|\vec{B}|$$

$$= \frac{p^2}{2m} + \frac{e}{2m}\vec{p} \times \vec{B} \cdot \vec{q} + \frac{e^2}{8m}\left(B^2q^2 - (\vec{B} \cdot \vec{q})^2\right) \pm \mu_B|\vec{B}|.$$

Using the canonical equations, $\dot{\vec{q}} = \partial\mathcal{H}/\partial\vec{p}$ and $\dot{\vec{p}} = -\partial\mathcal{H}/\partial\vec{q}$, we find

$$\begin{cases} \dot{\vec{q}} = \dfrac{\partial\mathcal{H}}{\partial\vec{p}} = \dfrac{\vec{p}}{m} + \dfrac{e}{2m}\vec{B} \times \vec{q}, \quad \Longrightarrow \quad \vec{p} = m\dot{\vec{q}} - \dfrac{e}{2}\vec{B} \times \vec{q}, \\[2mm] \dot{\vec{p}} = -\dfrac{\partial\mathcal{H}}{\partial\vec{q}} = -\dfrac{e}{2m}\vec{p} \times \vec{B} - \dfrac{e^2}{4m}B^2\vec{q} + \dfrac{e^2}{4m}\left(\vec{B} \cdot \vec{q}\right)\vec{B}. \end{cases}$$

Differentiating the first expression obtained for $\vec{p}$, and setting it equal to the second expression for $\dot{\vec{p}}$ above, gives

$$m\ddot{\vec{q}} - \frac{e}{2}\vec{B} \times \dot{\vec{q}} = -\frac{e}{2m}\left(m\dot{\vec{q}} - \frac{e}{2}\vec{B} \times \vec{q}\right) \times \vec{B} - \frac{e^2}{4m}|\vec{B}|^2\vec{q} + \frac{e^2}{4m}\left(\vec{B} \cdot \vec{q}\right)\vec{B}.$$

Simplifying the above expression, using $\vec{B} \times \vec{q} \times \vec{B} = B^2\vec{q} - \left(\vec{B} \cdot \vec{q}\right)\vec{B}$, leads to

$$m\ddot{\vec{q}} = e\vec{B} \times \dot{\vec{q}}.$$

This describes the rotation of electrons in cyclotron orbits,

$$\ddot{\vec{q}} = \vec{\omega}_c \times \dot{\vec{q}},$$

where $\vec{\omega}_c = e\vec{B}/m$; i.e. rotations are in the plane perpendicular to $\vec{B}$.

(b) Write down heuristically (i.e. not through a step by step derivation), the Boltzmann equations for the densities $f_\uparrow(\vec{p}, \vec{q}, t)$ and $f_\downarrow(\vec{p}, \vec{q}, t)$ of electrons with up and down spins, in terms of the two cross-sections $\sigma \equiv \sigma_{\uparrow\uparrow} = \sigma_{\downarrow\downarrow}$, and $\sigma_\times \equiv \sigma_{\uparrow\downarrow}$, of *spin conserving* collisions.

• Consider the classes of collisions described by cross-sections $\sigma \equiv \sigma_{\uparrow\uparrow} = \sigma_{\downarrow\downarrow}$, and $\sigma_\times \equiv \sigma_{\uparrow\downarrow}$. We can write the Boltzmann equations for the densities as

$$\frac{\partial f_\uparrow}{\partial t} - \{\mathcal{H}_\uparrow, f_\uparrow\} = \int d^2p_2 d\Omega |v_1 - v_2| \left\{ \frac{d\sigma}{d\Omega}\left[f_\uparrow(\vec{p_1}')f_\uparrow(\vec{p_2}') - f_\uparrow(\vec{p_1})f_\uparrow(\vec{p_2})\right] + \right.$$

$$\left. \frac{d\sigma_\times}{d\Omega}\left[f_\uparrow(\vec{p_1}')f_\downarrow(\vec{p_2}') - f_\uparrow(\vec{p_1})f_\downarrow(\vec{p_2})\right]\right\},$$

and

$$\frac{\partial f_\downarrow}{\partial t} - \{\mathcal{H}_\downarrow, f_\downarrow\} = \int d^2 p_2 d\Omega |v_1 - v_2| \left\{ \frac{d\sigma}{d\Omega} \left[f_\downarrow(\vec{p_1}\,') f_\downarrow(\vec{p_2}\,') - f_\downarrow(\vec{p_1}) f_\downarrow(\vec{p_2}) \right] + \right.$$

$$\left. \frac{d\sigma_\times}{d\Omega} \left[f_\downarrow(\vec{p_1}\,') f_\uparrow(\vec{p_2}\,') - f_\downarrow(\vec{p_1}) f_\uparrow(\vec{p_2}) \right] \right\}.$$

(c) Show that $d\mathrm{H}/dt \leq 0$, where $\mathrm{H} = \mathrm{H}_\uparrow + \mathrm{H}_\downarrow$ is the sum of the corresponding H functions.

- The usual Boltzmann H–Theorem states that $d\mathrm{H}/dt \leq 0$, where

$$\mathrm{H} = \int d^2 q d^2 p f(\vec{q}, \vec{p}, t) \ln f(\vec{q}, \vec{p}, t).$$

For the electron gas in a magnetic field, the H function can be generalized to

$$\mathrm{H} = \int d^2 q d^2 p \left[f_\uparrow \ln f_\uparrow + f_\downarrow \ln f_\downarrow \right],$$

where the condition $d\mathrm{H}/dt \leq 0$ is proved as follows:

$$\frac{d\mathrm{H}}{dt} = \int d^2 q d^2 p \left[\frac{\partial f_\uparrow}{\partial t} (\ln f_\uparrow + 1) + \frac{\partial f_\downarrow}{\partial t} (\ln f_\downarrow + 1) \right]$$

$$= \int d^2 q d^2 p \left[(\ln f_\uparrow + 1) \left(\{f_\uparrow, \mathcal{H}_\uparrow\} + C_{\uparrow\uparrow} + C_{\uparrow\downarrow} \right) + (\ln f_\downarrow + 1) \left(\{f_\downarrow, \mathcal{H}_\downarrow\} + C_{\downarrow\downarrow} + C_{\downarrow\uparrow} \right) \right],$$

with $C_{\uparrow\uparrow}$, etc., defined via the right hand side of the equations in part (b). Hence

$$\frac{d\mathrm{H}}{dt} = \int d^2 q d^2 p (\ln f_\uparrow + 1) (C_{\uparrow\uparrow} + C_{\uparrow\downarrow}) + (\ln f_\downarrow + 1) (C_{\downarrow\downarrow} + C_{\downarrow\uparrow})$$

$$= \int d^2 q d^2 p (\ln f_\uparrow + 1) C_{\uparrow\uparrow} + (\ln f_\downarrow + 1) C_{\downarrow\downarrow} + (\ln f_\uparrow + 1) C_{\uparrow\downarrow} + (\ln f_\downarrow + 1) C_{\downarrow\uparrow}$$

$$\equiv \frac{d\mathrm{H}_{\uparrow\uparrow}}{dt} + \frac{d\mathrm{H}_{\downarrow\downarrow}}{dt} + \frac{d}{dt} (\mathrm{H}_{\uparrow\downarrow} + \mathrm{H}_{\downarrow\uparrow}),$$

where the $\mathrm{H}'s$ are in correspondence to the integrals for the collisions. We have also made use of the fact that $\int d^2 p d^2 q \{f_\uparrow, \mathcal{H}_\uparrow\} = \int d^2 p d^2 q \{f_\downarrow, \mathcal{H}_\downarrow\} = 0$. Dealing with each of the terms in the final equation individually,

$$\frac{d\mathrm{H}_{\uparrow\uparrow}}{dt} = \int d^2 q d^2 p_1 d^2 p_2 d\Omega |v_1 - v_2| (\ln f_\uparrow + 1) \frac{d\sigma}{d\Omega} \left[f_\uparrow(\vec{p_1}\,') f_\uparrow(\vec{p_2}\,') - f_\uparrow(\vec{p_1}) f_\uparrow(\vec{p_2}) \right].$$

After symmetrizing this equation, as done in the text,

$$\frac{d\mathrm{H}_{\uparrow\uparrow}}{dt} = -\frac{1}{4} \int d^2 q d^2 p_1 d^2 p_2 d\Omega |v_1 - v_2| \frac{d\sigma}{d\Omega} \left[\ln f_\uparrow(\vec{p_1}) f_\uparrow(\vec{p_2}) - \ln f_\uparrow(\vec{p_1}\,') f_\uparrow(\vec{p_2}\,') \right]$$

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$$\cdot \left[f_\uparrow(\vec{p}_1) f_\uparrow(\vec{p}_2) - f_\uparrow(\vec{p}_1{}') f_\uparrow(\vec{p}_2{}') \right] \le 0.$$

Similarly, $d\mathrm{H}_{\downarrow\downarrow}/dt \le 0$. Dealing with the two remaining terms,

$$\frac{d\mathrm{H}_{\uparrow\downarrow}}{dt} = \int d^2q d^2p_1 d^2p_2 d\Omega |v_1 - v_2| \left[\ln f_\uparrow(\vec{p}_1) + 1\right] \frac{d\sigma_\times}{d\Omega} \left[f_\uparrow(\vec{p}_1{}') f_\downarrow(\vec{p}_2{}') - f_\uparrow(\vec{p}_1) f_\downarrow(\vec{p}_2) \right]$$

$$= \int d^2q d^2p_1 d^2p_2 d\Omega |v_1 - v_2| \left[\ln f_\uparrow(\vec{p}_1{}') + 1\right] \frac{d\sigma_\times}{d\Omega} \left[f_\uparrow(\vec{p}_1) f_\downarrow(\vec{p}_2) - f_\uparrow(\vec{p}_1{}') f_\downarrow(\vec{p}_2{}') \right],$$

where we have exchanged $(\vec{p}_1, \vec{p}_2 \leftrightarrow \vec{p}_1{}', \vec{p}_2{}')$. Averaging these two expressions together,

$$\frac{d\mathrm{H}_{\uparrow\downarrow}}{dt} = -\frac{1}{2} \int d^2q d^2p_1 d^2p_2 d\Omega |v_1 - v_2| \frac{d\sigma_\times}{d\Omega} \left[\ln f_\uparrow(\vec{p}_1) - \ln f_\uparrow(\vec{p}_1{}')\right]$$
$$\cdot \left[f_\uparrow(\vec{p}_1) f_\downarrow(\vec{p}_2) - f_\uparrow(\vec{p}_1{}') f_\downarrow(\vec{p}_2{}') \right].$$

Likewise

$$\frac{d\mathrm{H}_{\downarrow\uparrow}}{dt} = -\frac{1}{2} \int d^2q d^2p_1 d^2p_2 d\Omega |v_1 - v_2| \frac{d\sigma_\times}{d\Omega} \left[\ln f_\downarrow(\vec{p}_2) - \ln f_\downarrow(\vec{p}_2{}')\right]$$
$$\cdot \left[f_\downarrow(\vec{p}_2) f_\uparrow(\vec{p}_1) - f_\downarrow(\vec{p}_2{}') f_\uparrow(\vec{p}_1{}') \right].$$

Combining these two expressions,

$$\frac{d}{dt} \left(\mathrm{H}_{\uparrow\downarrow} + \mathrm{H}_{\downarrow\uparrow} \right) = -\frac{1}{4} \int d^2q d^2p_1 d^2p_2 d\Omega |v_1 - v_2| \frac{d\sigma_\times}{d\Omega}$$
$$\left[\ln f_\uparrow(\vec{p}_1) f_\downarrow(\vec{p}_2) - \ln f_\uparrow(\vec{p}_1{}') f_\downarrow(\vec{p}_2{}')\right] \left[f_\uparrow(\vec{p}_1) f_\downarrow(\vec{p}_2) - f_\uparrow(\vec{p}_1{}') f_\downarrow(\vec{p}_2{}') \right] \le 0.$$

Since each contribution is separately negative, we have

$$\frac{d\mathrm{H}}{dt} = \frac{d\mathrm{H}_{\uparrow\uparrow}}{dt} + \frac{d\mathrm{H}_{\downarrow\downarrow}}{dt} + \frac{d}{dt} \left(\mathrm{H}_{\uparrow\downarrow} + \mathrm{H}_{\downarrow\uparrow} \right) \le 0.$$

(d) Show that $d\mathrm{H}/dt = 0$ for any $\ln f$ which is, *at each location*, a linear combination of quantities conserved in the collisions.

• For $d\mathrm{H}/dt = 0$ we need each of the three square brackets in the previous derivation to be zero. The first two contributions, from $d\mathrm{H}_{\uparrow\downarrow}/dt$ and $d\mathrm{H}_{\downarrow\downarrow}/dt$, are similar to those discussed in the notes for a single particle, and vanish for any $\ln f$ which is a linear combination of quantities conserved in collisions

$$\ln f_\alpha = \sum_i a_i^\alpha(\vec{q}) \chi_i(\vec{p}),$$

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where $\alpha = (\uparrow \text{ or } \downarrow)$. Clearly at each location $\vec{q}$, for such f_α,

$$\ln f_\alpha(\vec{p}_1) + \ln f_\alpha(\vec{p}_2) = \ln f_\alpha(\vec{p}_1{}') + \ln f_\alpha(\vec{p}_2{}').$$

If we consider only the first two terms of $d\mathrm{H}/dt = 0$, the coefficients $a_i^\alpha(\vec{q})$ can vary with both $\vec{q}$ and $\alpha = (\uparrow \text{ or } \downarrow)$. This changes when we consider the third term $d\left(\mathrm{H}_{\uparrow\downarrow} + \mathrm{H}_{\downarrow\uparrow}\right)/dt$. The conservations of momentum and kinetic energy constrain the corresponding four functions to be the same, i.e. they require $a_i^\uparrow(\vec{q}) = a_i^\downarrow(\vec{q})$. There is, however, no similar constraint for the overall constant that comes from particle number conservation, as the numbers of spin-up and spin-down particles is *separately* conserved, i.e. $a_0^\uparrow(\vec{q}) = a_0^\downarrow(\vec{q})$. This implies that the densities of up and down spins can be different in the final equilibrium, while the two systems must share the same velocity and temperature.

(e) Show that the streaming terms in the Boltzmann equation are zero for any function that depends only on the quantities conserved by the one body Hamiltonians.

• The Boltzmann equation is

$$\frac{\partial f_\alpha}{\partial t} = -\{f_\alpha, \mathcal{H}_\alpha\} + C_{\alpha\alpha} + C_{\alpha\beta},$$

where the right hand side consists of streaming terms $\{f_\alpha, \mathcal{H}_\alpha\}$, and collision terms C. Let I_i denote any quantity conserved by the one body Hamiltonian, i.e. $\{I_i, \mathcal{H}_\alpha\} = 0$. Consider f_α which is a function only of the $I_i's$

$$f_\alpha \equiv f_\alpha(I_1, I_2, \cdots).$$

Then

$$\{f_\alpha, \mathcal{H}_\alpha\} = \sum_j \frac{\partial f_\alpha}{\partial I_j} \{I_j, \mathcal{H}_\alpha\} = 0.$$

(f) Show that angular momentum $\vec{L} = \vec{q} \times \vec{p}$, is conserved during, and away from collisions.

• Conservation of momentum for a collision at $\vec{q}$

$$(\vec{p}_1 + \vec{p}_2) = (\vec{p}_1{}' + \vec{p}_2{}'),$$

implies

$$\vec{q} \times (\vec{p}_1 + \vec{p}_2) = \vec{q} \times (\vec{p}_1{}' + \vec{p}_2{}'),$$

or

$$\vec{L}_1 + \vec{L}_2 = \vec{L}_1{}' + \vec{L}_2{}',$$

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where we have used $\vec{L}_i = \vec{q} \times \vec{p}_i$. Hence angular momentum $\vec{L}$ is conserved during collisions. Note that only the z–component L_z is present for electrons moving in 2–dimensions, $\vec{q} \equiv (x_1, x_2)$, as is the case for the electron gas studied in this problem. Consider the Hamiltonian discussed in (a)

$$\mathcal{H} = \frac{p^2}{2m} + \frac{e}{2m}\vec{p} \times \vec{B} \cdot \vec{q} + \frac{e^2}{8m}\left(B^2 q^2 - (\vec{B} \cdot \vec{q})^2\right) \pm \mu_B |\vec{B}|.$$

Let us evaluate the Poisson brackets of the individual terms with $L_z = \vec{q} \times \vec{p} \mid_z$. The first term is

$$\left\{|\vec{p}|^2, \vec{q} \times \vec{p}\right\} = \varepsilon_{ijk}\left\{p_l p_l, x_j p_k\right\} = \varepsilon_{ijk}2p_l\frac{\partial}{\partial x_l}(x_j p_k) = 2\varepsilon_{ilk}p_l p_k = 0,$$

where we have used $\varepsilon_{ijk}p_j p_k = 0$ since $p_j p_k = p_k p_j$ is symmetric. The second term is proportional to L_z,

$$\left\{\vec{p} \times \vec{B} \cdot \vec{q}, L_z\right\} = \{B_z L_z, L_z\} = 0.$$

The final terms are proportional to q^2, and $\left\{q^2, \vec{q} \times \vec{p}\right\} = 0$ for the same reason that $\left\{p^2, \vec{q} \times \vec{p}\right\} = 0$, leading to

$$\{\mathcal{H}, \vec{q} \times \vec{p}\} = 0.$$

Hence angular momentum is conserved away from collisions as well.

(g) Write down the most general form for the equilibrium distribution functions for particles confined to a circularly symmetric potential.

• The most general form of the equilibrium distribution functions must set both the collision terms, and the streaming terms to zero. Based on the results of the previous parts, we thus obtain

$$f_\alpha = A_\alpha \exp\left[-\beta \mathcal{H}_\alpha - \gamma L_z\right].$$

The collision terms allow for the possibility of a term $-\vec{u} \cdot \vec{p}$ in the exponent, corresponding to an average velocity. Such a term will not commute with the potential set up by a stationary box, and is thus ruled out by the streaming terms. On the other hand, the angular momentum does commute with a circular potential $\{V(\vec{q}), L\} = 0$, and is allowed by the streaming terms. A non–zero γ describes the electron gas rotating in a circular box.

(h) How is the result in part (g) modified by including scattering from magnetic and non-magnetic impurities?

- Scattering from any impurity removes the conservation of $\vec{p}$, and hence $\vec{L}$, in collisions. The γ term will no longer be needed. Scattering from magnetic impurities mixes populations of up and down spins, necessitating $A_\uparrow = A_\downarrow$; non–magnetic impurities do not have this effect.

(i) Do conservation of spin and angular momentum lead to new hydrodynamic equations?

- Conservation of angular momentum is related to conservation of $\vec{p}$, as shown in (f), and hence does not lead to any new equation. In contrast, conservation of spin leads to an additional hydrodynamic equation involving the magnetization, which is proportional to $(n_\uparrow - n_\downarrow)$.

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6. *The Lorentz gas* describes non-interacting particles colliding with a fixed set of scatterers. It is a good model for scattering of electrons from donor impurities. Consider a uniform two dimensional density n_0 of fixed impurities, which are hard circles of radius a.

(a) Show that the differential cross section of a hard circle scattering through an angle θ is

$$d\sigma = \frac{a}{2} \sin \frac{\theta}{2} \, d\theta,$$

and calculate the total cross section.

- Let b denote the impact parameter, which (see figure) is related to the angle θ between $\vec{p}'$ and $\vec{p}$ by

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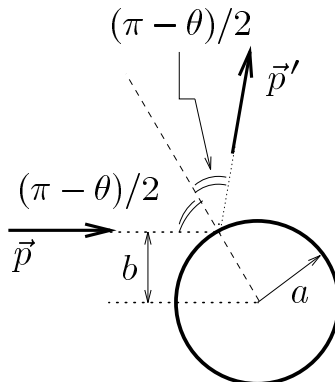
$$b(\theta) = a \sin \frac{\pi - \theta}{2} = a \cos \frac{\theta}{2}.$$

The differential cross section is then given by

$$d\sigma = 2|db| = a \sin \frac{\theta}{2} d\theta.$$

Hence the total cross section

$$\sigma_{tot} = \int_0^\pi d\theta a \sin \frac{\theta}{2} = 2a \left[-\cos \frac{\theta}{2} \right]_0^\pi = 2a.$$

(b) Write down the Boltzmann equation for the one particle density $f(\vec{q}, \vec{p}, t)$ of the Lorentz gas (including only collisions with the fixed impurities). *(Ignore the electron spin.)*

• The corresponding Boltzmann equation is

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial f}{\partial \vec{q}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}}$$
$$= \int d\theta \frac{d\sigma}{d\theta} \frac{|\vec{p}|}{m} n_0 \left[-f(\vec{p})) + f(\vec{p}\,') \right] = \frac{n_o |\vec{p}|}{m} \int d\theta \frac{d\sigma}{d\theta} \left[f(\vec{p}\,') - f(\vec{p}) \right] \equiv C \left[f(\vec{p}) \right].$$

(c) Find the eigenfunctions and eigenvalues of the collision operator.

(d) Using the definitions $\vec{F} \equiv -\partial U / \partial \vec{q}$, and

$$n(\vec{q}, t) = \int d^2 \vec{p} f(\vec{q}, \vec{p}, t), \qquad \text{and} \qquad \langle g(\vec{q}, t) \rangle = \frac{1}{n(\vec{q}, t)} \int d^2 \vec{p} f(\vec{q}, \vec{p}, t) g(\vec{q}, t),$$

show that for any function $\chi(|\vec{p}|)$, we have

$$\frac{\partial}{\partial t} (n \langle \chi \rangle) + \frac{\partial}{\partial \vec{q}} \cdot \left(n \left\langle \frac{\vec{p}}{m} \chi \right\rangle \right) = \vec{F} \cdot \left(n \left\langle \frac{\partial \chi}{\partial \vec{p}} \right\rangle \right).$$

• Using the definitions $\vec{F} \equiv -\partial U / \partial \vec{q}$,

$$n(\vec{q}, t) = \int d^2 \vec{p} f(\vec{q}, \vec{p}, t), \qquad \text{and} \qquad \langle g(\vec{q}, t) \rangle = \frac{1}{n(\vec{q}, t)} \int d^2 \vec{p} f(\vec{q}, \vec{p}, t) g(\vec{q}, t),$$

we can write

$$\frac{d}{dt} (n \langle \chi(|\vec{p}|) \rangle) = \int d^2 p \chi(|\vec{p}|) \left[-\frac{\vec{p}}{m} \cdot \frac{\partial f}{\partial \vec{q}} - \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} + \int d\theta \frac{d\sigma}{d\theta} \frac{|\vec{p}|}{m} n_o (f(\vec{p}) - f(\vec{p}\,')) \right]$$
$$= -\frac{\partial}{\partial \vec{q}} \cdot \left(n \left\langle \frac{\vec{p}}{m} \chi \right\rangle \right) + \vec{F} \cdot \left(n \left\langle \frac{\partial \chi}{\partial \vec{p}} \right\rangle \right).$$

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Rewriting this final expression gives the hydrodynamic equation

$$\frac{\partial}{\partial t}\left(n\left\langle\chi\right\rangle\right) + \frac{\partial}{\partial\vec{q}}\cdot\left(n\left\langle\frac{\vec{p}}{m}\chi\right\rangle\right) = \vec{F}\cdot\left(n\left\langle\frac{\partial\chi}{\partial\vec{p}}\right\rangle\right).$$

(e) Derive the conservation equation for local density $\rho \equiv mn(\vec{q}, t)$, in terms of the local velocity $\vec{u} \equiv \langle\vec{p}/m\rangle$.

- Using $\chi = 1$ in the above expression

$$\frac{\partial}{\partial t}n + \frac{\partial}{\partial\vec{q}}\cdot\left(n\left\langle\frac{\vec{p}}{m}\right\rangle\right) = 0.$$

In terms of the local density $\rho = mn$, and velocity $\vec{u} \equiv \langle\vec{p}/m\rangle$, we have

$$\frac{\partial}{\partial t}\rho + \frac{\partial}{\partial\vec{q}}\cdot(\rho\vec{u}) = 0.$$

(f) Since the magnitude of particle momentum is unchanged by impurity scattering, the Lorentz gas has an infinity of conserved quantities $|\vec{p}|^m$. This unrealistic feature is removed upon inclusion of particle–particle collisions. For the rest of this problem focus only on $p^2/2m$ as a conserved quantity. Derive the conservation equation for the energy density

$$\epsilon(\vec{q}, t) \equiv \frac{\rho}{2}\left\langle c^2\right\rangle, \qquad \text{where} \qquad \vec{c} \equiv \frac{\vec{p}}{m} - \vec{u},$$

in terms of the energy flux $\vec{h} \equiv \rho\left\langle\vec{c}c^2\right\rangle/2$, and the pressure tensor $P_{\alpha\beta} \equiv \rho\left\langle c_\alpha c_\beta\right\rangle$.

- With the kinetic energy $\chi = p^2/2m$ as a conserved quantity, the equation found in (c) gives

$$\frac{\partial}{\partial t}\left(\frac{n}{2m}\left\langle|\vec{p}|^2\right\rangle\right) + \frac{\partial}{\partial\vec{q}}\cdot\left(\frac{n}{2}\left\langle\frac{\vec{p}}{m}\frac{p^2}{m}\right\rangle\right) = \vec{F}\cdot\left(n\frac{\langle\vec{p}\rangle}{m}\right).$$

Substituting $\vec{p}/m = \vec{u} + \vec{c}$, where $\langle\vec{c}\rangle = 0$, and using $\rho = nm$,

$$\frac{\partial}{\partial t}\left[\frac{\rho}{2}u^2 + \frac{\rho}{2}\left\langle c^2\right\rangle\right] + \frac{\partial}{\partial\vec{q}}\cdot\left[\frac{\rho}{2}\left\langle(\vec{u}+\vec{c})(u^2 + c^2 + 2\vec{u}\cdot\vec{c})\right\rangle\right] = \frac{\rho}{m}\vec{F}\cdot\vec{u}.$$

From the definition $\varepsilon = \rho\left\langle c^2\right\rangle/2$, we have

$$\frac{\partial}{\partial t}\left[\frac{\rho}{2}u^2 + \varepsilon\right] + \frac{\partial}{\partial\vec{q}}\cdot\left[\frac{\rho}{2}\left(\vec{u}u^2 + \vec{u}\left\langle c^2\right\rangle + \left\langle\vec{c}c^2\right\rangle + 2\vec{u}\cdot\left\langle\vec{c}\vec{c}\right\rangle\right)\right] = \frac{\rho}{m}\vec{F}\cdot\vec{u}.$$

Finally, by substituting $\vec{h} \equiv \rho \left\langle \vec{c}\, c^2 \right\rangle / 2$ and $P_{\alpha\beta} = \rho \left\langle c_\alpha c_\beta \right\rangle$, we get

$$\frac{\partial}{\partial t}\left[\frac{\rho}{2}u^2 + \varepsilon\right] + \frac{\partial}{\partial \vec{q}} \cdot \left[\vec{u}\left(\frac{\rho}{2}u^2 + \varepsilon\right) + \vec{h}\right] + \frac{\partial}{\partial q_\alpha}(u_\beta P_{\alpha\beta}) = \frac{\rho}{m}\vec{F} \cdot \vec{u}.$$

(g) Starting with a one particle density

$$f^0(\vec{p}, \vec{q}, t) = n(\vec{q}, t)\exp\left[-\frac{p^2}{2mk_B T(\vec{q}, t)}\right]\frac{1}{2\pi mk_B T(\vec{q}, t)},$$

reflecting local equilibrium conditions, calculate $\vec{u}$, $\vec{h}$, and $P_{\alpha\beta}$. Hence obtain the zeroth order hydrodynamic equations.

• There are only two quantities, 1 and $p^2/2m$, conserved in collisions. Let us start with the one particle density

$$f^0(\vec{p}, \vec{q}, t) = n(\vec{q}, t)\exp\left[-\frac{p^2}{2mk_B T(\vec{q}, t)}\right]\frac{1}{2\pi mk_B T(\vec{q}, t)}.$$

Then

$$\vec{u} = \left\langle \frac{\vec{p}}{m} \right\rangle_0 = 0, \qquad \text{and} \qquad \vec{h} = \left\langle \frac{\vec{p}}{m}\frac{p^2}{m} \right\rangle_0 \frac{\rho}{2} = 0,$$

since both are odd functions of $\vec{p}$, while f^o is an even function of $\vec{p}$, while

$$P_{\alpha\beta} = \rho \left\langle c_\alpha c_\beta \right\rangle = \frac{n}{m}\left\langle p_\alpha p_\beta \right\rangle = \frac{n}{m}\delta\alpha\beta \cdot mk_B T = nk_B T\delta_{\alpha\beta}.$$

Substituting these expressions into the results for (c) and (d), we obtain the zeroth–order hydrodynamic equations

$$\begin{cases} \dfrac{\partial \rho}{\partial t} = 0, \\[2mm] \dfrac{\partial}{\partial t}\varepsilon = \dfrac{\partial}{\partial t}\dfrac{\rho}{2}\left\langle c^2 \right\rangle = 0. \end{cases}$$

The above equations imply that ρ and ε are independent of time, i.e.

$$\rho = n(\vec{q}), \qquad \text{and} \qquad \varepsilon = k_B T(\vec{q}),$$

or

$$f^0 = \frac{n(\vec{q})}{2\pi mk_B T(\vec{q})}\exp\left[-\frac{p^2}{2mk_B T(\vec{q})}\right].$$

(h) Show that in the single collision time approximation to the collision term in the Bolzmann equation, the first order solution is

$$f^1(\vec{p}, \vec{q}, t) = f^0(\vec{p}, \vec{q}, t) \left[1 - \tau \frac{\vec{p}}{m} \cdot \left(\frac{\partial \ln \rho}{\partial \vec{q}} - \frac{\partial \ln T}{\partial \vec{q}} + \frac{p^2}{2mk_BT^2} \frac{\partial T}{\partial \vec{q}} - \frac{\vec{F}}{k_BT} \right) \right].$$

• The single collision time approximation is

$$C[f] = \frac{f^0 - f}{\tau}.$$

The first order solution to Boltzmann equation

$$f = f^0 (1 + g),$$

is obtained from

$$\mathcal{L}[f^0] = -\frac{f^0 g}{\tau},$$

as

$$g = -\tau \frac{1}{f^0} \mathcal{L}[f^0] = -\tau \left[\frac{\partial}{\partial t} \ln f^0 + \frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{q}} \ln f^0 + \vec{F} \cdot \frac{\partial}{\partial \vec{p}} \ln f^0 \right].$$

Noting that

$$\ln f^0 = -\frac{p^2}{2mk_BT} + \ln n - \ln T - \ln(2\pi mk_B),$$

where n and T are independent of t, we have $\partial \ln f^0 / \partial t = 0$, and

$$g = -\tau \left\{ \vec{F} \cdot \left(\frac{-\vec{p}}{mk_BT} \right) + \frac{\vec{p}}{m} \cdot \left[\frac{1}{n} \frac{\partial n}{\partial \vec{q}} - \frac{1}{T} \frac{\partial T}{\partial \vec{q}} + \frac{p^2}{2mk_BT^2} \frac{\partial T}{\partial \vec{q}} \right] \right\}$$

$$= -\tau \left\{ \frac{\vec{p}}{m} \cdot \left(\frac{1}{\rho} \frac{\partial \rho}{\partial \vec{q}} - \frac{1}{T} \frac{\partial T}{\partial \vec{q}} + \frac{p^2}{2mk_BT^2} \frac{\partial T}{\partial \vec{q}} - \frac{\vec{F}}{k_BT} \right) \right\}.$$

(i) Show that using the first order expression for f, we obtain

$$\rho \vec{u} = n\tau \left[\vec{F} - k_BT \nabla \ln (\rho T) \right].$$

• Clearly $\int d^2q f^0 (1 + g) = \int d^2q f^0 = n$, and

$$u_\alpha = \left\langle \frac{p_\alpha}{m} \right\rangle = \frac{1}{n} \int d^2p \frac{p_\alpha}{m} f^0 (1 + g)$$

$$= \frac{1}{n} \int d^2p \frac{p_\alpha}{m} \left[-\tau \frac{p_\beta}{m} \left(\frac{\partial \ln \rho}{\partial q_\beta} - \frac{\partial \ln T}{\partial q_\beta} - \frac{F_\beta}{k_BT} + \frac{p^2}{2mk_BT^2} \frac{\partial T}{\partial q_\beta} \right) \right] f^0.$$

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Wick's theorem can be used to check that

$$\langle p_\alpha p_\beta \rangle_0 = \delta_{\alpha\beta} m k_B T,$$

$$\langle p^2 p_\alpha p_\beta \rangle_0 = (m k_B T)^2 \left[2\delta_{\alpha\beta} + 2\delta_{\alpha\beta} \right] = 4\delta_{\alpha\beta}(m k_B T)^2,$$

resulting in

$$u_\alpha = -\frac{n\tau}{\rho} \left[\delta_{\alpha\beta} k_B T \left(\frac{\partial}{\partial q_\beta} \ln \left(\frac{\rho}{T} \right) - \frac{1}{k_B T} F_\beta \right) + 2 k_B \frac{\partial T}{\partial q_\beta} \delta_{\alpha\beta} \right].$$

Rearranging these terms yields

$$\rho u_\alpha = n\tau \left[F_\alpha - k_B T \frac{\partial}{\partial q_\alpha} \ln\left(\rho T \right) \right].$$

(j) From the above equation, calculate the velocity response function $\chi_{\alpha\beta} = \partial u_\alpha / \partial F_\beta$.

- The velocity response function is now calculated easily as

$$\chi_{\alpha\beta} = \frac{\partial u_\alpha}{\partial F_\beta} = \frac{n\tau}{\rho} \delta_{\alpha\beta}.$$

(k) Calculate $P_{\alpha\beta}$, and $\vec{h}$, and hence write down the first order hydrodynamic equations.

- The first order expressions for pressure tensor and heat flux are

$$P_{\alpha\beta} = \frac{\rho}{m^2} \langle p_\alpha p_\beta \rangle = \delta_{\alpha\beta} n k_B T, \qquad \text{and} \qquad \delta^1 P_{\alpha\beta} = 0,$$

$$h_\alpha = \frac{\rho}{2m^3} \langle p_\alpha p^2 \rangle = -\frac{\tau\rho}{2m^3} \left\langle p_\alpha p^2 \frac{p_i}{m} \left(a_i + b_i p^2 \right) \right\rangle_0.$$

The latter is calculated from Wick's theorem results

$$\langle p_i p_\alpha p^2 \rangle = 4\delta_{\alpha i} \left(m k_B T \right)^2, \qquad \text{and}$$

$$\langle p_i p_\alpha p^2 p^2 \rangle = (m k_B T)^3 \left[\delta_{\alpha i}(4+4) + 4 \times 2\delta\alpha i + 4 \times 2\delta_{\alpha i} \right] = 24\delta_{\alpha i},$$

as

$$h_\alpha = -\frac{\rho\tau}{2m^3} \left[(m k_B T)^2 \left(\frac{\partial}{\partial q_\alpha} \ln \frac{\rho}{T} - \vec{F} \right) + \frac{24(m k_B T)^3}{2 m k_b T} \frac{\partial}{\partial q_\alpha} \ln T \right]$$

$$= -12 n k_B^2 T \tau \frac{\partial T}{\partial q_\alpha}.$$

Substitute these expressions for $P_{\alpha\beta}$ and h_α into the equation obtained in (e)

$$\frac{\partial}{\partial t} \left[\frac{\rho}{2} u^2 + \epsilon \right] + \frac{\partial}{\partial \vec{q}} \cdot \left[\vec{u} \left(\frac{\rho}{2} u^2 + \epsilon \right) - 11 n k_B^2 T \tau \frac{\partial T}{\partial \vec{q}} \right] + \frac{\partial}{\partial \vec{q}} \left(\vec{u} \, n k_B T \right) = \frac{\rho}{m} \vec{F} \cdot \vec{u}.$$

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7. *Thermal conductivity:* Consider a classical gas between two plates separated by a distance w. One plate at $y = 0$ is maintained at a temperature T_1, while the other plate at $y = w$ is at a different temperature T_2. The gas velocity is zero, so that the initial zeroth order approximation to the one particle density is,

$$f_1^0(\vec{p}, x, y, z) = \frac{n(y)}{[2\pi m k_B T(y)]^{3/2}} \exp\left[-\frac{\vec{p}\cdot\vec{p}}{2m k_B T(y)}\right].$$

(a) What is the necessary relation between $n(y)$ and $T(y)$ to ensure that the gas velocity $\vec{u}$ remains zero? (Use this relation between $n(y)$ and $T(y)$ in the remainder of this problem.)

• Since there is no external force acting on the gas between plates, the gas can only flow locally if there are variations in pressure. Since the local pressure is $P(y) = n(y)k_B T(y)$, the condition for the fluid to be stationary is

$$n(y)T(y) = \text{constant}.$$

(b) Using Wick's theorem, or otherwise, show that

$$\langle p^2 \rangle^0 \equiv \langle p_\alpha p_\alpha \rangle^0 = 3\,(m k_B T), \quad \text{and} \quad \langle p^4 \rangle^0 \equiv \langle p_\alpha p_\alpha p_\beta p_\beta \rangle^0 = 15\,(m k_B T)^2,$$

where $\langle \mathcal{O} \rangle^0$ indicates local averages with the Gaussian weight f_1^0. Use the result $\langle p^6 \rangle^0 = 105(m k_B T)^3$ in conjunction with symmetry arguments to conclude

$$\langle p_y^2 p^4 \rangle^0 = 35\,(m k_B T)^3.$$

• The Gaussian weight has a covariance $\langle p_\alpha p_\beta \rangle^0 = \delta_{\alpha\beta}(m k_B T)$. Using Wick's theorem gives

$$\langle p^2 \rangle^0 = \langle p_\alpha p_\alpha \rangle^0 = (m k_B T)\,\delta_{\alpha\alpha} = 3\,(m k_B T).$$

Similarly

$$\langle p^4 \rangle^0 = \langle p_\alpha p_\alpha p_\beta p_\beta \rangle^0 = (m k_B T)^2\,(\delta_{\alpha\alpha} + 2\delta_{\alpha\beta}\delta_{\alpha\beta}) = 15\,(m k_B T)^2.$$

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The symmetry along the three directions implies

$$\langle p_x^2 p^4 \rangle^0 = \langle p_y^2 p^4 \rangle^0 = \langle p_z^2 p^4 \rangle^0 = \frac{1}{3} \langle p^2 p^4 \rangle^0 = \frac{1}{3} \times 105 \, (mk_B T)^3 = 35 \, (mk_B T)^3 \, .$$

(c) The zeroth order approximation does not lead to relaxation of temperature/density variations related as in part (a). Find a better (time independent) approximation $f_1^1(\vec{p}, y)$, by linearizing the Boltzmann equation in the single collision time approximation, to

$$\mathcal{L}\left[f_1^1\right] \approx \left[\frac{\partial}{\partial t} + \frac{p_y}{m}\frac{\partial}{\partial y}\right] f_1^0 \approx -\frac{f_1^1 - f_1^0}{\tau_K},$$

where τ_K is of the order of the mean time between collisions.

• Since there are only variations in y, we have

$$\left[\frac{\partial}{\partial t} + \frac{p_y}{m}\frac{\partial}{\partial y}\right] f_1^0 = f_1^0 \frac{p_y}{m} \partial_y \ln f_1^0 = f_1^0 \frac{p_y}{m} \partial_y \left[\ln n - \frac{3}{2}\ln T - \frac{p^2}{2mk_B T} - \frac{3}{2}\ln(2\pi mk_B)\right]$$

$$= f_1^0 \frac{p_y}{m}\left[\frac{\partial_y n}{n} - \frac{3}{2}\frac{\partial_y T}{T} + \frac{p^2}{2mk_B T}\frac{\partial T}{T}\right] = f_1^0 \frac{p_y}{m}\left[-\frac{5}{2} + \frac{p^2}{2mk_B T}\right]\frac{\partial_y T}{T},$$

where in the last equality we have used $nT = \text{constant}$ to get $\partial_y n/n = -\partial_y T/T$. Hence the first order result is

$$f_1^1(\vec{p}, y) = f_1^0(\vec{p}, y)\left[1 - \tau_K \frac{p_y}{m}\left(\frac{p^2}{2mk_B T} - \frac{5}{2}\right)\frac{\partial_y T}{T}\right].$$

(d) Use f_1^1, along with the averages obtained in part (b), to calculate h_y, the y component of the heat transfer vector, and hence find K, the coefficient of thermal conductivity.

• Since the velocity $\vec{u}$ is zero, the heat transfer vector is

$$h_y = n\left\langle c_y \frac{mc^2}{2}\right\rangle^1 = \frac{n}{2m^2}\langle p_y p^2\rangle^1 \, .$$

In the zeroth order Gaussian weight all odd moments of p have zero average. The corrections in f_1^1, however, give a non-zero heat transfer

$$h_y = -\tau_K \frac{n}{2m^2}\frac{\partial_y T}{T}\left\langle \frac{p_y}{m}\left(\frac{p^2}{2mk_B T} - \frac{5}{2}\right)p_y p^2\right\rangle^0 \, .$$

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Note that we need the Gaussian averages of $\langle p_y^2 p^4 \rangle^0$ and $\langle p_y^2 p^2 \rangle^0$. From the results of part (b), these averages are equal to $35(mk_BT)^3$ and $5(mk_BT)^2$, respectively. Hence

$$h_y = -\tau_K \frac{n}{2m^3} \frac{\partial_y T}{T} (mk_BT)^2 \left(\frac{35}{2} - \frac{5 \times 5}{2} \right) = -\frac{5}{2} \frac{n\tau_K k_B^2 T}{m} \partial_y T.$$

The coefficient of thermal conductivity relates the heat transferred to the temperature gradient by $\vec{h} = -K\nabla T$, and hence we can identify

$$K = \frac{5}{2} \frac{n\tau_K k_B^2 T}{m}.$$

(e) What is the temperature profile, $T(y)$, of the gas in steady state?

• Since $\partial_t T$ is proportional to $-\partial_y h_y$, there will be no time variation if h_y is a constant. But $h_y = -K\partial_y T$, where K, which is proportional to the product nT, is a constant in the situation under investigation. Hence $\partial_y T$ must be constant, and $T(y)$ varies linearly between the two plates. Subject to the boundary conditions of $T(0) = T_1$, and $T(w) = T_2$, this gives

$$T(y) = T_1 + \frac{T_2 - T_1}{w} y.$$

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8. *Zeroth-order hydrodynamics:* The hydrodynamic equations resulting from the conservation of particle number, momentum, and energy in collisions are (in a uniform box):

$$\begin{cases} \partial_t n + \partial_\alpha (nu_\alpha) = 0 \\[2mm] \partial_t u_\alpha + u_\beta \partial_\beta u_\alpha = -\dfrac{1}{mn} \partial_\beta P_{\alpha\beta} \\[2mm] \partial_t \varepsilon + u_\alpha \partial_\alpha \varepsilon = -\dfrac{1}{n} \partial_\alpha h_\alpha - \dfrac{1}{n} P_{\alpha\beta} u_{\alpha\beta} \end{cases},$$

where n is the local density, $\vec{u} = \langle \vec{p}/m \rangle$, $u_{\alpha\beta} = (\partial_\alpha u_\beta + \partial_\beta u_\alpha)/2$, and $\varepsilon = \langle mc^2/2 \rangle$, with $\vec{c} = \vec{p}/m - \vec{u}$.

(a) For the zeroth order density

$$f_1^0(\vec{p}, \vec{q}, t) = \frac{n(\vec{q}, t)}{(2\pi mk_BT(\vec{q}, t))^{3/2}} \exp \left[-\frac{(\vec{p} - m\vec{u}(\vec{q}, t))^2}{2mk_BT(\vec{q}, t)} \right],$$

calculate the pressure tensor $P_{\alpha\beta}^0 = mn \langle c_\alpha c_\beta \rangle^0$, and the heat flux $h_\alpha^0 = nm \langle c_\alpha c^2/2 \rangle^0$.

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- The PDF for $\vec{c}$ is proportional to the Gaussian $\exp\left(-mc^2/(2k_BT)\right)$, from which we immediately get

$$\langle c_\alpha c_\beta\rangle^0 = \frac{k_BT}{m}\delta_{\alpha\beta} \implies P^0_{\alpha\beta} = nk_BT\delta_{\alpha\beta}, \quad \text{and} \quad \varepsilon = \frac{3}{2}k_BT.$$

All odd expectation values of the symmetric weight are zero, specifically $\langle \vec{c}\rangle = 0$, and $\left\langle \vec{h}^0\right\rangle = 0$.

(b) Obtain the zeroth order hydrodynamic equations governing the evolution of $n(\vec{q}, t)$, $\vec{u}(\vec{q}, t)$, and $T(\vec{q}, t)$.

- Substituting $P^0_{\alpha\beta} = nk_BT\delta_{\alpha\beta}$, $\varepsilon = 3k_BT/2$, and $\left\langle \vec{h}^0\right\rangle = 0$ in the hydrodynamic equations gives:

$$\begin{cases} \partial_t n + u_\alpha\partial_\alpha n = -n\partial_\alpha u_\alpha \\[2mm] \partial_t u_\alpha + u_\beta\partial_\beta u_\alpha = -\dfrac{k_B}{mn}\partial_\alpha\left(nT\right) \\[2mm] \dfrac{3}{2}\left(\partial_t T + u_\alpha\partial_\alpha T\right) = -T\partial_\alpha u_\alpha \end{cases}.$$

(c) Show that the above equations imply $D_t\ln\left(nT^{-3/2}\right) = 0$, where $D_t = \partial_t + u_\beta\partial_\beta$ is the material derivative along streamlines.

- Using $D_t = \partial_t + u_\beta\partial_\beta$, the above equations can be written as

$$\begin{cases} D_t\ln n = -\partial_\alpha u_\alpha \\[2mm] D_t u_\alpha = -\dfrac{k_B}{mn}\partial_\alpha\left(nT\right) \\[2mm] \dfrac{3}{2}D_t\ln T = -\partial_\alpha u_\alpha \end{cases}.$$

Eliminating $\partial_\alpha u_\alpha$ between the first and third equations gives the required result of $D_t\ln\left(nT^{-3/2}\right) = 0$.

(d) Write down the expression for the function $\mathrm{H}^0(t) = \int d^3\vec{q}d^3\vec{p}f^0_1(\vec{p}, \vec{q}, t)\ln f^0_1(\vec{p}, \vec{q}, t)$, after performing the integrations over $\vec{p}$, in terms of $n(\vec{q}, t)$, $\vec{u}(\vec{q}, t)$, and $T(\vec{q}, t)$.

- Using the expression for f^0_1,

$$\mathrm{H}^0(t) = \int d^3\vec{q}d^3\vec{p}\frac{n}{(2\pi mk_BT)^{3/2}}\exp\left[-\frac{(\vec{p} - m\vec{u})^2}{2mk_BT}\right]$$

$$\times\left[\ln\left(nT^{-3/2}\right) - \frac{3}{2}\ln\left(2\pi mk_B\right) - \frac{(\vec{p} - m\vec{u})^2}{2mk_BT}\right].$$

The Gaussian averages over $\vec{p}$ are easily performed to yield

$$H^0(t) = \int d^3\vec{q}\, n \left[\ln\left(nT^{-3/2}\right) - \frac{3}{2}\ln\left(2\pi mk_B\right) - \frac{3}{2} \right].$$

(e) Using the hydrodynamic equations in (b) calculate dH^0/dt.

• Taking the time derivative inside the integral gives

$$\frac{dH^0}{dT} = \int d^3\vec{q} \left[\partial_t n \ln\left(nT^{-3/2}\right) + n\partial_t \ln\left(nT^{-3/2}\right) \right].$$

Use the results of parts (b) and (c) to substitute for $\partial_t n$ and $\partial_t \ln\left(nT^{-3/2}\right)$, to get

$$\frac{dH^0}{dT} = -\int d^3\vec{q} \left[\ln\left(nT^{-3/2}\right)\partial_\alpha\left(nu_\alpha\right) + nu_\alpha\partial_\alpha \ln\left(nT^{-3/2}\right) \right]$$

$$= -\int d^3\vec{q}\,\partial_\alpha \left[nu_\alpha \ln\left(nT^{-3/2}\right) \right] = 0,$$

since the integral of a complete derivative is zero.

(f) Discuss the implications of the result in (e) for approach to equilibrium.

• The expression for $-H^0$ is related to the entropy of the gas. The result in (f) implies that the entropy of the gas does not change if its n $\vec{u}$, and T vary according to the zeroth order equations. The corrections due to first order hydrodynamics are necessary in order to describe the increase in entropy.

<div align="center">********</div>

9. *Viscosity:* Consider a classical gas between two plates separated by a distance w. One plate at $y = 0$ is stationary, while the other at $y = w$ moves with a constant velocity $v_x = u$. A zeroth order approximation to the one particle density is,

$$f_1^0(\vec{p}, \vec{q}) = \frac{n}{(2\pi mk_BT)^{3/2}} \exp\left[-\frac{1}{2mk_BT} \left((p_x - m\alpha y)^2 + p_y^2 + p_z^2 \right) \right],$$

obtained from the *uniform* Maxwell–Boltzmann distribution by substituting the average value of the velocity at each point. ($\alpha = u/w$ is the velocity gradient.)

(a) The above approximation does not satisfy the Boltzmann equation as the collision term vanishes, while $df_1^0/dt \neq 0$. Find a better approximation, $f_1^1(\vec{p})$, by linearizing the Boltzmann equation, in the single collision time approximation, to

$$\mathcal{L}\left[f_1^1\right] \approx \left[\frac{\partial}{\partial t} + \frac{\vec{p}}{m}\cdot\frac{\partial}{\partial\vec{q}} \right] f_1^0 \approx -\frac{f_1^1 - f_1^0}{\tau_\times},$$

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where $\tau_\times$ is a characteristic mean time between collisions.

- We have

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m}\cdot\frac{\partial}{\partial\vec{q}}\right)f_1^0 = \frac{\alpha}{mk_BT}p_y(p_x - m\alpha y)f_1^0,$$

whence

$$f_1^1 = f_1^0\left\{1 - \tau_x\frac{\alpha}{mk_BT}p_y(p_x - m\alpha y)\right\}.$$

(b) Calculate the net transfer Π_{xy} of the x component of the momentum, of particles passing through a plane at y, per unit area and in unit time.

- The transfer of x-momentum in the y direction, across a plane at y, per unit area and per unit time, is calculated as

$$\Pi_{xy} = \int_{p_y>0} d^3p\frac{p_y}{m}p_x f_1^1(y) - \int_{p_y<0} d^3p\frac{(-p_y)}{m}p_x f_1^1(y)$$

$$= \int d^3p\frac{p_y}{m}p_x f_1^1(y)$$

$$= \int d^3p\frac{p_y}{m}p_x\left(-\frac{\tau_x\alpha}{mk_BT}\right)p_y(p_x - m\alpha y)f_1^0$$

$$= -\frac{\tau_x\alpha n}{m^2k_BT}\left\{\int dp_x(p_x - m\alpha y)^2\frac{\exp\left(-\frac{(p_x-m\alpha y)^2}{2mk_BT}\right)}{\sqrt{2\pi mk_BT}}\right\}\cdot\left\{\int dp_y p_y^2\frac{\exp\left(-\frac{p_y^2}{2mk_BT}\right)}{\sqrt{2\pi mk_BT}}\right\}$$

$$= -\frac{\tau_x\alpha n}{m^2k_BT}(mk_BT)^2 = -\alpha n\tau_x k_BT.$$

(c) Note that the answer to (b) is independent of y, indicating a uniform transverse force $F_x = -\Pi_{xy}$, exerted by the gas on each plate. Find the coefficient of viscosity, defined by $\eta = F_x/\alpha$.

- From part (b),

$$\eta = \frac{F_x}{a} = n\tau_x k_BT.$$

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10. *Light and matter:* In this problem we use kinetic theory to explore the equilibrium between atoms and radiation.

(a) The atoms are assumed to be either in their ground state a_0, or in an excited state a_1, which has a higher energy ε. By considering the atoms as a collection of N fixed two-state

systems of energy E (i.e. ignoring their coordinates and momenta), calculate the ratio n_1/n_0 of densities of atoms in the two states as a function of temperature T.

• The energy and temperature of a two-state system are related by

$$E = \frac{N\epsilon}{1 + \exp\left(\epsilon/k_B T\right)},$$

leading to

$$n_0 = \frac{N - E/\epsilon}{V} = \frac{N}{V}\frac{\exp\left(\epsilon/k_B T\right)}{1 + \exp\left(\epsilon/k_B T\right)}, \quad \text{and} \quad n_1 = \frac{E/\epsilon}{V} = \frac{N}{V}\frac{1}{1 + \exp\left(\epsilon/k_B T\right)},$$

so that

$$\frac{n_1}{n_0} = \exp\left(-\frac{\epsilon}{k_B T}\right).$$

Consider photons γ of frequency $\omega = \varepsilon/\hbar$ and momentum $|\vec{p}| = \hbar\omega/c$, which can interact with the atoms through the following processes:

(i) *Spontaneous emission:* $a_1 \rightarrow a_0 + \gamma$.

(ii) *Adsorption:* $a_0 + \gamma \rightarrow a_1$.

(iii) *Stimulated emission:* $a_1 + \gamma \rightarrow a_0 + \gamma + \gamma$.

Assume that spontaneous emission occurs with a probability $\sigma_{\rm sp}$, and that adsorption and stimulated emission have constant (angle-independent) differential cross-sections of $\sigma_{\rm ad}/4\pi$ and $\sigma_{\rm st}/4\pi$, respectively.

(b) Write down the Boltzmann equation governing the density f of the photon gas, treating the atoms as fixed scatterers of densities n_0 and n_1.

• The Boltzmann equation for photons in the presence of fixed scatterers reads

$$\frac{\partial f}{\partial t} + \vec{p} \cdot \frac{\partial f}{\partial \vec{q}} = -\sigma_{\rm ad}n_0 cf + \sigma_{\rm st}n_1 cf + \sigma_{\rm sp}n_1.$$

(c) Find the equilibrium density $f_{\rm eq.}$ for the photons of the above frequency.

• In uniform equilibrium, the left-hand side vanishes, leaving

$$-\sigma_{\rm ad}n_0 cf_{\rm eq.} + \sigma_{\rm st}n_1 cf_{\rm eq.} + \sigma_{\rm sp}n_1 = 0,$$

i.e.

$$f_{\rm eq.} = \frac{1}{c}\frac{\sigma_{\rm sp}}{\sigma_{\rm ad}n_0/n_1 - \sigma_{\rm st}} = \frac{1}{c}\frac{\sigma_{\rm sp}}{\sigma_{\rm ad}\exp\left(\epsilon/k_B T\right) - \sigma_{\rm st}}.$$

(d) According to Planck's law, the density of photons at a temperature T depends on their frequency ω as $f_{\text{eq.}} = [\exp(\hbar\omega/k_B T) - 1]^{-1}/h^3$. What does this imply about the above cross sections?

• The result of part (c) agrees with Planck's law if

$$\sigma_{\text{ad}} = \sigma_{\text{st}}, \quad \text{and} \quad \sigma_{\text{sp}} = \frac{c}{h^3}\sigma_{\text{st}},$$

a conclusion first reached by Einstein, and verified later with explicit quantum mechanical calculations of cross-sections.

(e) Consider a situation in which light shines along the x axis on a collection of atoms whose boundary coincides with the $x = 0$ plane, as illustrated in the figure.
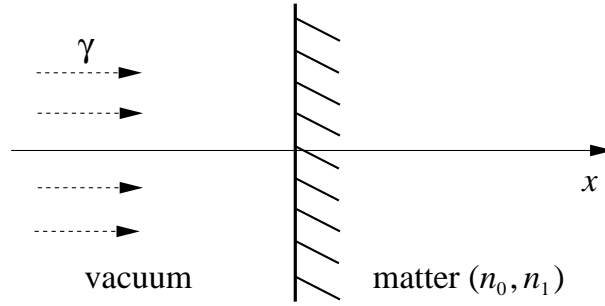
Clearly, f will depend on x (and p_x), but will be independent of y and z. Adapt the Boltzmann equation you propose in part (b) to the case of a uniform incoming flux of photons with momentum $\vec{p} = \hbar\omega\hat{x}/c$. What is the *penetration length* across which the incoming flux decays?

• In this situation, the Boltzmann equation reduces to

$$p_x \frac{\partial f}{\partial x} = \sigma_{\text{st}}c\left[(n_1 - n_0)f + \frac{n_1}{h^3}\right]\theta(x).$$

To the uniform solution obtained before, one can add an exponentially decaying term for $x > 0$, i.e.

$$f(p_x, x > 0) = A(p_x)e^{-ax/p_x} + f_{\text{eq.}}(p_x).$$

The constant $A(p_x)$ can be determined by matching to solution for $x < 0$ at $x = 0$, and is related to the incoming flux. The penetration depth d is the inverse of the decay parameter, and given by

$$d = \frac{p_x}{a}, \quad \text{with} \quad a = \sigma_{\text{st}}c(n_0 - n_1) > 0.$$

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11. *Equilibrium density:* Consider a gas of N particles of mass m, in an external potential $U(\vec{q})$. Assume that the one body density $\rho_1\,(\vec{p}, \vec{q}, t)$, satisfies the Boltzmann equation. For a stationary solution, $\partial\rho_1/\partial t = 0$, it is *sufficient* from Liouville's theorem for ρ_1 to satisfy $\rho_1 \propto \exp\left[-\beta\left(p^2/2m + U(\vec{q})\right)\right]$. Prove that this condition is also *necessary* by using the H-theorem as follows.

(a) Find $\rho_1\,(\vec{p}, \vec{q})$ that minimizes H $= N \int d^3\vec{p}d^3\vec{q}\rho_1\,(\vec{p}, \vec{q})\ln\rho_1(\vec{p}, \vec{q})$, subject to the constraint that the total energy $E = \langle\mathcal{H}\rangle$ is constant. (Hint: Use the method of Lagrange multipliers to impose the constraint.)

• Using Lagrange multipliers to impose the constraints, $\langle\mathcal{H}\rangle = E$ and $\int d^3\vec{p}d^3\vec{q}\,\rho_1 = 1$, minimizing H with the given constraints reduces to minimizing,

$$N \int d^3\vec{p}d^3\vec{q}(\rho_1 \ln \rho_1 + \beta\rho_1\mathcal{H} + \alpha\rho_1) - \beta E - \alpha N.$$

Differentiating with respect to α, β, and the function ρ_1 we get,

$$N \int d^3\vec{p}d^3\vec{q}\,\rho_1 = N \quad\rightarrow\quad \int d^3\vec{p}d^3\vec{q}\,\rho_1 = 1,$$
$$\int d^3\vec{p}d^3\vec{q}\,\rho_1\mathcal{H} = E \quad\rightarrow\quad \int d^3\vec{p}d^3\vec{q}\,\rho_1\mathcal{H} = E/N,$$
$$\ln\rho_1 + \beta\mathcal{H} + \alpha = 0 \quad\rightarrow\quad \rho_1 = \exp(-\beta\mathcal{H} - \alpha),$$

respectively. Hence we conclude,

$$\rho_1 = \frac{\exp(-\beta\mathcal{H})}{\int d^3\vec{p}d^3\vec{q}\exp(-\beta\mathcal{H})},$$

where β is determined by,

$$\frac{\int d^3\vec{p}d^3\vec{q}\mathcal{H}\exp(-\beta\mathcal{H})}{\int d^3\vec{p}d^3\vec{q}\exp(-\beta\mathcal{H})} = \frac{E}{N}.$$

(b) For a mixture of two gases (particles of masses m_a and m_b) find the distributions $\rho_1^{(a)}$ and $\rho_1^{(b)}$ that minimize H $=$ H$^{(a)}$ $+$ H$^{(b)}$ subject to the constraint of constant total energy. Hence show that the kinetic energy per particle can serve as an empirical temperature.

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- If we have N_a and N_b of each particle type with total energy E, then H is minimized with the total energy constraint by extremizing,

$$\int d^3\vec{p}d^3\vec{q}(N_a\rho_1^{(a)}\ln\rho_1^{(a)} + N_b\rho_1^{(b)}\ln\rho_1^{(b)} + \beta(N_a\mathcal{H}_a\rho_1^{(a)} + N_b\mathcal{H}_b\rho_1^{(b)})$$
$$+N_a\alpha\rho_1^{(a)} + N_b\alpha'\rho_1^{(b)}) - \beta E - \alpha N_a - \alpha' N_b$$

Differentiating this expression with respect to α, α', β, $\rho_1^{(a)}$, and $\rho_1^{(b)}$, we get,

$$\int d^3\vec{p}d^3\vec{q}\,\rho_1^{(a)} = 1,$$
$$\int d^3\vec{p}d^3\vec{q}\,\rho_1^{(b)} = 1,$$
$$\int d^3\vec{p}d^3\vec{q}\left(N_a\mathcal{H}_a\rho_1^{(a)} + N_b\mathcal{H}_b\rho_1^{(b)}\right) = E,$$
$$\ln\rho_1^{(a)} + \beta\mathcal{H}_a + \alpha = 0,$$
$$\ln\rho_1^{(b)} + \beta\mathcal{H}_b + \alpha' = 0.$$

So we get,

$$\rho_1^{(a)} = \frac{\exp(-\beta\mathcal{H}_a)}{\int d^3\vec{p}d^3\vec{q}\exp(-\beta\mathcal{H}_a)},$$
$$\rho_2^{(a)} = \frac{\exp(-\beta\mathcal{H}_b)}{\int d^3\vec{p}d^3\vec{q}\exp(-\beta\mathcal{H}_b)}.$$

where β is obtained by,

$$N_a\frac{\int d^3\vec{p}d^3\vec{q}\mathcal{H}_a\exp(-\beta\mathcal{H}_a)}{\int d^3\vec{p}d^3\vec{q}\exp(-\beta\mathcal{H}_a)} + N_b\frac{\int d^3\vec{p}d^3\vec{q}\mathcal{H}_b\exp(-\beta\mathcal{H}_b)}{\int d^3\vec{p}d^3\vec{q}\exp(-\beta\mathcal{H}_b)} = E.$$

Note that β is a value defined for both gases a and b, and hence can serve as an empirical temperature.

For the specific case of

$$\mathcal{H}_a = \frac{p^2}{2m_a} + U_a(\vec{q}), \quad \mathcal{H}_b = \frac{p^2}{2m_a} + U_b(\vec{q}),$$

the kinetic energy per particle in a distribution with equal β is also equal, since

$$\begin{aligned}
\frac{\int d^3\vec{p}d^3\vec{q}\frac{p^2}{2m_a}\exp\left[-\beta(p^2/2m_a + U_a(\vec{q}))\right]}{\int d^3\vec{p}d^3\vec{q}\exp(-\beta\mathcal{H}_a)} &= \frac{\int d^3\vec{q}\exp(-\beta U_a)\int d^3\vec{p}\frac{p^2}{2m_a}\exp(-\beta p^2/2m_a)}{\int d^3\vec{q}\exp(-\beta U_a)\int d^3\vec{p}\exp(-\beta p^2/2m_a)} \\
&= \frac{4\pi\int_0^\infty dp\frac{p^4}{2m_a}\exp(-\beta p^2/2m_a)}{4\pi\int_0^\infty dp\,p^2\exp(-\beta p^2/2m_a)} \\
&= \frac{1}{\beta}\frac{\int_0^\infty dt\,t^4 e^{-t^2}}{\int_0^\infty dt\,t^2 e^{-t^2}} = \frac{3}{2\beta}
\end{aligned}$$

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So we see that the kinetic energy per particle for the gas can also serve as an empirical temperature in this case.

<p style="text-align:center">********</p>

12. *Moments of momentum:* Consider a gas of N classical particles of mass m in thermal equilibrium at a temperature T, in a box of volume V.

(a) Write down the equilibrium one particle density $f_{\text{eq.}}(\vec{p}, \vec{q})$, for coordinate $\vec{q}$, and momentum $\vec{p}$.

• The equilibrium Maxwell-Boltzmann distribution reads

$$f(\vec{p}, \vec{q}) = \frac{n}{(2\pi m k_B T)^{3/2}} \exp\left(-\frac{p^2}{2m k_B T}\right).$$

(b) Calculate the joint characteristic function, $\left\langle \exp\left(-i\vec{k}\cdot\vec{p}\right)\right\rangle$, for momentum.

• Performing the Gaussian average yields

$$\tilde{p}\left(\vec{k}\right) = \left\langle e^{-i\vec{k}\cdot\vec{p}}\right\rangle = \exp\left(-\frac{m k_B T}{2} k^2\right).$$

(c) Find all the joint cumulants $\langle p_x^\ell p_y^m p_z^n \rangle_c$.

• The cumulants are calculated from the characteristic function, as

$$\langle p_x^\ell p_y^m p_z^n \rangle_c = \left[\frac{\partial}{\partial(-ik_x)}\right]^\ell \left[\frac{\partial}{\partial(-ik_y)}\right]^m \left[\frac{\partial}{\partial(-ik_z)}\right]^n \ln\tilde{p}\left(\vec{k}\right)\Bigg|_{\vec{k}=0}$$

$$= m k_B T \left(\delta_{\ell 2}\delta_{m0}\delta_{n0} + \delta_{\ell 0}\delta_{m2}\delta_{n0} + \delta_{\ell 0}\delta_{m0}\delta_{n2}\right),$$

i.e., there are only second cumulants; all other cumulants are zero.

(d) Calculate the joint moment $\langle p_\alpha p_\beta (\vec{p}\cdot\vec{p})\rangle$.

• Using Wick's theorem

$$\langle p_\alpha p_\beta (\vec{p}\cdot\vec{p})\rangle = \langle p_\alpha p_\beta p_\gamma p_\gamma\rangle$$

$$= \langle p_\alpha p_\beta\rangle \langle p_\gamma p_\gamma\rangle + 2 \langle p_\alpha p_\gamma\rangle \langle p_\beta p_\gamma\rangle$$

$$= (m k_B T)^2 \delta_{\alpha\beta}\delta_{\gamma\gamma} + 2 (m k_B T)^2 \delta_{\alpha\gamma}\delta_{\beta\gamma}$$

$$= 5 (m k_B T)^2 \delta_{\alpha\beta}.$$

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Alternatively, directly from the characteristic function,

$$
\begin{aligned}
\langle p_\alpha p_\beta \left(\vec{p} \cdot \vec{p} \right) \rangle &= \frac{\partial}{\partial \left(-ik_\alpha \right)} \frac{\partial}{\partial \left(-ik_\beta \right)} \frac{\partial}{\partial \left(-ik_\gamma \right)} \frac{\partial}{\partial \left(-ik_\gamma \right)} \tilde{p} \left(\vec{k} \right) \Big|_{\vec{k}=0} \\
&= \frac{\partial}{\partial \left(-ik_\alpha \right)} \frac{\partial}{\partial \left(-ik_\beta \right)} \left[3mk_B - (mk_B T)^2 \, \vec{k}^2 \right] e^{-\frac{mk_B T}{2} \vec{k}^2} \Big|_{\vec{k}=0} \\
&= 5 \left(mk_B T \right)^2 \delta_{\alpha\beta}.
\end{aligned}
$$

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13. *Generalized ideal gas:* Consider a gas of N particles confined to a box of volume V in d-dimensions. The energy, ϵ, and momentum, $\mathbf{p}$, of each particle are related by $\epsilon = p^s$, where $p = |\mathbf{p}|$. (For classical particles $s = 2$, while for highly relativistic ones $s = 1$.) Let $f(v)dv$ denote the probability of finding particles with speeds between v and $v + dv$, and $n = N/V$.

(a) Calculate the number of impacts of gas molecules per unit area of the wall of the box, and per unit time as follows:

(i) Show that the number of particles hitting area A in a time dt arriving from a specific direction $\vec{\Omega}$, with a speed v, is proportional to $\quad A \cdot vdt \cos\theta \cdot nf(v)dv \quad$, where θ is the angle between the direction $\vec{\Omega}$ and the normal to the wall.

(ii) Summing over all directions $\vec{\Omega}$ with the same polar angle θ, demonstrate that

$$
dN(\theta, v) = A \cdot vdt \cos\theta \cdot nf(v)dv \cdot \frac{S_{d-1} \sin^{d-2}\theta \, d\theta}{S_d} \quad,
$$

where $S_d = 2\pi^{d/2}/(d/2 - 1)!$ is the total solid angle in d dimensions.

(iii) By averaging over v and θ show that

$$
\frac{N}{A \, dt} = \frac{S_{d-1}}{(d-1)S_d} \cdot n\bar{v} \,, \quad \text{where} \quad \bar{v} = \int vf(v)dv \quad \text{is the average speed.}
$$

(b) Each (elastic) collision transfers a momentum $2p\cos\theta$ to the wall. By examining the net force on an element of area prove that the pressure P equals $\frac{s}{d} \cdot \frac{E}{V}$, where E is the average (kinetic) energy. (Note that the velocity $\mathbf{v}$ is not $\mathbf{p}/m$ but $\partial\epsilon/\partial\mathbf{p}$.) Hint: Clearly upon averaging over all directions $\langle \cos^2\theta \rangle = 1/d$.

(c) Using thermodynamics and the result in (b) show that along an adiabatic curve PV^γ is constant, and calculate γ.

(d) According to the equipartition theorem, each degree of freedom which appears quadratically in the energy has an energy $k_B T/2$. Calculate the value of γ if each gas particle has ℓ such quadratic degrees of freedom in addition to its translational motion. What values of γ are expected for helium and hydrogen at room temperature?

(e) Consider the following experiment to test whether the motion of ants is random. 250 ants are placed inside a $10cm \times 10cm$ box. They cannot climb the wall, but can escape through an opening of size $5mm$ in the wall. If the motion of ants is indeed random, and they move with an average speed of $2mms^{-1}$, how may are expected to escape the box in the first 30 seconds?

<div align="center">********</div>

14. *Effusion:* A box contains a perfect gas at temperature T and density n.

(a) What is the one-particle density, $\rho_1(\vec{v})$, for particles with velocity $\vec{v}$?

A small hole is opened in the wall of the box for a short time to allow some particles to escape into a previously empty container.

(b) During the time that the hole is open what is the flux (number of particles per unit time and per unit area) of particles into the container? (Ignore the possibility of any particles returning to the box.)

(c) Show that the average kinetic energy of escaping particles is $2k_B T$. (Hint: calculate contributions to kinetic energy of velocity components parallel and perpendicular to the wall separately.)

(d) The hole is closed and the container (now thermally insulated) is allowed to reach equilibrium. What is the final temperature of the gas in the container?

(e) A vessel partially filled with mercury (atomic weight 201), and closed except for a hole of area $0.1mm^2$ above the liquid level, is kept at $0^0 C$ in a continuously evacuated enclosure. After 30 days it is found that $24mg$ of mercury has been lost. What is the vapor pressure of mercury at $0^0 C$?

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15. *Adsorbed particles:* Consider a gas of classical particles of mass m in thermal equilibrium at a temperature T, and with a density n. A clean metal surface is introduced into the gas. Particles hitting this surface with normal velocity less than v_t are reflected back into the gas, while particles with normal velocity greater than v_t are absorbed by it.

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(a) Find the average number of particles hitting one side of the surface per unit area and per unit time.

(b) Find the average number of particles absorbed by one side of the surface per unit area and per unit time.

<div align="center">********</div>

16. *Electron emission:* When a metal is heated in vacuum, electrons are emitted from its surface. The metal is modeled as a classical gas of noninteracting electrons held in the solid by an abrupt potential well of depth ϕ (the work function) relative to the vacuum.

(a) What is the relationship between the initial and final velocities of an escaping electron?

(b) In thermal equilibrium at temperature T, what is the probability density function for the velocity of electrons?

(c) If the number density of electrons is n, calculate the current density of thermally emitted electrons.

<div align="center">********</div>

1. *Classical harmonic oscillators:*   Consider N harmonic oscillators with coordinates and momenta $\{q_i, p_i\}$, and subject to a Hamiltonian

$$\mathcal{H}(\{q_i, p_i\}) = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + \frac{m\omega^2 q_i^2}{2} \right].$$

(a) Calculate the entropy S, as a function of the total energy E.

(Hint: By appropriate change of scale, the surface of constant energy can be deformed into a sphere. You may then ignore the difference between the surface area and volume for $N \gg 1$. A more elegant method is to implement this deformation through a canonical transformation.)

• The volume of accessible phase space for a given total energy is proportional to

$$\Omega = \frac{1}{h^N} \int_{\mathcal{H}=E} dq_1 dq_2 \cdots dq_N dp_1 dp_2 \cdots dp_N,$$

where the integration is carried out under the condition of constant energy,

$$E = \mathcal{H}\left(\{q_i, p_i\}\right) = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + \frac{m\omega^2 q_i^2}{2} \right].$$

Note that Planck's constant h, is included as a measure of phase space volume, so as to make the final result dimensionless.

The surface of constant energy is an ellipsoid in $2N$ dimensions, whose area is difficult to calculate. However, for $N \to \infty$ the difference between volume and area is subleading in N, and we shall instead calculate the volume of the ellipsoid, replacing the constraint $\mathcal{H} = E$ by $\mathcal{H} \leq E$. The ellipsoid can be distorted into a sphere by a canonical transformation, changing coordinates to

$$q_i' \equiv \sqrt{m\omega} q_i, \qquad \text{and} \qquad p_i' \equiv \frac{p_i}{\sqrt{m\omega}}.$$

The Hamiltonian in this coordinate system is

$$E = \mathcal{H}\left(\{q_i', p_i'\}\right) = \frac{\omega}{2} \sum_{i=1}^{N} \left(p_i'^2 + q_i'^2 \right).$$

Since the canonical transformation preserves volume in phase space (the Jacobian is unity), we have

$$\Omega \approx \frac{1}{h^N} \int_{\mathcal{H} \leq E} dq_1' \cdots dq_N' dp_1' \cdots dp_N',$$

where the integral is now over the $2N$-dimensional (hyper-) sphere of radius $R = \sqrt{2E/\omega}$. As the volume of a d-dimensional sphere of radius R is $S_d R^d/d$, we obtain

$$\Omega \approx \frac{2\pi^N}{(N-1)!} \cdot \frac{1}{2N} \left(\frac{2E}{h\omega} \right)^N = \left(\frac{2\pi E}{h\omega} \right)^N \frac{1}{N!}.$$

The entropy is now given by

$$S \equiv k_B \ln \Omega \approx N k_B \ln \left(\frac{2\pi e E}{N h \omega} \right).$$

(b) Calculate the energy E, and heat capacity C, as functions of temperature T, and N.

• From the expression for temperature,

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} \bigg|_N \approx \frac{N k_B}{E},$$

we obtain the energy

$$E = N k_B T,$$

and the heat capacity

$$C = N k_B.$$

(c) Find the joint probability density $P(p, q)$ for a single oscillator. Hence calculate the mean kinetic energy, and mean potential energy for each oscillator.

• The single particle distribution function is calculated by summing over the undesired coordinates and momenta of the other $N - 1$ particles. Keeping track of the units of h used to make phase space dimensionless, gives

$$p(p_1, q_1) dp_1 dq_1 = \frac{\int_{(\mathcal{H} \leq E_{N-1})} \frac{1}{h^{N-1}} dq_2 \cdots dq_N dp_2 \cdots dp_N}{\int_{(\mathcal{H} \leq E)} \frac{1}{h^N} dq_1 dq_2 \cdots dq_N dp_1 dp_2 \cdots dp_N} \times \frac{dp_1 dq_1}{h},$$

where $E_{N-1} = E - p_1^2/2m - m\omega^2 q_1^2/2$. Using the results from part (a),

$$p(p_1, q_1) = \frac{\Omega(N-1, E_{N-1})}{h\Omega(N, E)}$$

$$= \frac{\left(\frac{2}{h\omega}\right)^{N-1} \frac{\pi^{N-1}}{(N-1)!} \left(E - \frac{p_1^2}{2m} - \frac{m\omega^2}{2}q_1^2\right)^{N-1}}{h\left(\frac{2}{h\omega}\right)^N \frac{\pi^N}{N!} E^N}$$

$$= \frac{\omega}{2\pi} \frac{N}{E} \left(1 - \frac{\frac{p_1^2}{2m} + \frac{m\omega^2}{2}q_1^2}{E}\right)^{N-1}.$$

Using the approximation $(N-1) \sim N$, for $N \gg 1$, and setting $E = Nk_BT$, we have

$$p(p_1, q_1) = \frac{\omega}{2\pi} \frac{N}{Nk_BT} \left(1 - \frac{\frac{p_1^2}{2m} + \frac{m\omega^2}{2}q_1^2}{Nk_BT}\right)^N$$

$$\approx \frac{\omega}{2\pi k_BT} \exp\left(-\frac{\frac{p_1^2}{2m} + \frac{m\omega^2}{2}q_1^2}{k_BT}\right).$$

Let us denote (p_1, q_1) by (p, q), then

$$p(p, q) = \frac{\omega}{2\pi k_BT} \exp\left(-\frac{p^2}{2mk_BT} - \frac{m\omega^2 q^2}{2k_BT}\right),$$

is a properly normalized product of two Gaussians. The mean kinetic energy is

$$\left\langle \frac{p^2}{2m} \right\rangle = \int p(p, q) \frac{p^2}{2m} dq dp = \frac{k_BT}{2},$$

while the mean potential energy is also

$$\left\langle \frac{m\omega^2 q^2}{2} \right\rangle = \int p(p, q) \frac{m\omega^2 q^2}{2} dq dp = \frac{k_BT}{2}.$$

$$********$$

2. *Quantum harmonic oscillators*: Consider N independent quantum oscillators subject to a Hamiltonian

$$\mathcal{H}(\{n_i\}) = \sum_{i=1}^{N} \hbar\omega \left(n_i + \frac{1}{2}\right),$$

where $n_i = 0, 1, 2, \cdots$, is the quantum occupation number for the ith oscillator.

(a) Calculate the entropy S, as a function of the total energy E.

(Hint: $\Omega(E)$ can be regarded as the number of ways of rearranging $M = \sum_i n_i$ balls, and $N - 1$ partitions along a line.)

- The total energy of the set of oscillators is

$$E = \hbar\omega \left(\sum_{i=1}^{N} n_i + \frac{N}{2} \right).$$

Let us set the sum over the individual quantum numbers to

$$M \equiv \sum_{i=1}^{N} n_i = \frac{E}{\hbar\omega} - \frac{N}{2}.$$

The number of configurations $\{n_i\}$ for a given energy (thus for a given value of M) is equal to the possible number of ways of distributing M energy units into N slots, or of partitioning M particles using $N - 1$ walls. This argument gives to the number of states as

$$\Omega = \frac{(M + N - 1)!}{M! \, (N - 1)!},$$

and a corresponding entropy

$$S = k_B \ln \Omega \approx k_B \left[(M + N - 1) \ln \left(\frac{M + N - 1}{e} \right) - M \ln \frac{M}{e} - (N - 1) \ln \left(\frac{N - 1}{e} \right) \right].$$

(b) Calculate the energy E, and heat capacity C, as functions of temperature T, and N.
- The temperature is calculated by

$$\frac{1}{T} \equiv \left. \frac{\partial S}{\partial E} \right|_N \approx \frac{k_B}{\hbar\omega} \ln \left(\frac{M + N - 1}{M} \right) = \frac{k_B}{\hbar\omega} \ln \left(\frac{\frac{E}{\hbar\omega} + \frac{N}{2} - 1}{\frac{E}{\hbar\omega} - \frac{N}{2}} \right) \approx \frac{k_B}{\hbar\omega} \ln \left(\frac{E + \frac{N}{2}\hbar\omega}{E - \frac{N}{2}\hbar\omega} \right).$$

By inverting this equation, we get the energy

$$E = \frac{N}{2} \hbar\omega \frac{\exp(\hbar\omega/k_B T) + 1}{\exp(\hbar\omega/k_B T) - 1} = N\hbar\omega \left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega/k_B T) - 1} \right],$$

and a corresponding heat capacity

$$C \equiv \left. \frac{\partial E}{\partial T} \right|_N = N k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2}.$$

(c) Find the probability $p(n)$ that a particular oscillator is in its nth quantum level.

• The probability that a particular oscillator is in its *nth* quantum level is given by summing the joint probability over states for all the other oscillators, i.e.

$$p(n) = \sum_{\{n_{i \neq 1}\}} p(n_i) = \frac{\sum_{(E-(n+1/2)\hbar\omega)} 1}{\sum_{(E)} 1} = \frac{\Omega\left(N-1, E-(n+\frac{1}{2})\hbar\omega\right)}{\Omega(N,E)}$$

$$= \frac{[(M-n)+N-2]!}{(M-n)! \cdot (N-2)!} \cdot \frac{M! \cdot (N-1)!}{(M+N-1)!}$$

$$\approx \frac{M(M-1)\cdots(M-n+1) \cdot N}{(M+N-1)(M+N-2)\cdots(M+N-n-1)}$$

$$\approx N(M+N)^{-n-1}M^n,$$

where the approximations used are of the from $(I-1) \approx I$, for $I \gg 1$. Hence,

$$p(n) = N\left(\frac{E}{\hbar\omega} - \frac{N}{2} + N\right)^{-n-1}\left(\frac{E}{\hbar\omega} - \frac{N}{2}\right)^n$$

$$= \frac{N}{\frac{E}{\hbar\omega} + \frac{N}{2}}\left(\frac{\frac{E}{\hbar\omega} - \frac{N}{2}}{\frac{E}{\hbar\omega} + \frac{N}{2}}\right)^n,$$

which using

$$\frac{1}{T} = \frac{k_B}{\hbar\omega}\ln\left(\frac{E + \frac{N\hbar\omega}{2}}{E - \frac{N\hbar\omega}{2}}\right), \quad \Longrightarrow \quad \left(\frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{\frac{E}{\hbar\omega} - \frac{N}{2}}\right)^n = \exp\left(-\frac{n\hbar\omega}{k_B T}\right),$$

leads to the probability

$$p(n) = \exp\left(-n\frac{\hbar\omega}{k_B T}\right)\left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right].$$

(d) Comment on the difference between heat capacities for classical and quantum oscillators.

• As found in part (b),

$$C_{quantum} = Nk_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^2}.$$

In the high temperature limit, $\hbar\omega/(k_B T) \ll 1$, using the approximation $e^x \approx 1 + x$ for $x \ll 1$, gives

$$C_{quantum} = Nk_B = C_{classical}.$$

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At low temperatures, the quantized nature of the energy levels of the quantum oscillators becomes noticeable. In the limit $T \to 0$, there is an energy gap between the ground state and the first excited state. This results in a heat capacity that goes to zero exponentially, as can be seen from the limit $\hbar\omega/(k_B T) \gg 1$,

$$C_{quantum} = N k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \exp \left(-\frac{\hbar\omega}{k_B T} \right).$$

****

3. *Relativistic particles:* N *indistinguishable* relativistic particles move in *one dimension* subject to a Hamiltonian

$$\mathcal{H} \left(\{p_i, q_i\} \right) = \sum_{i=1}^{N} \left[c|p_i| + U(q_i) \right],$$

with $U(q_i) = 0$ for $0 \leq q_i \leq L$, and $U(q_i) = \infty$ otherwise. Consider a *microcanonical* ensemble of total energy E.

(a) Compute the contribution of the coordinates q_i to the available volume in phase space $\Omega(E, L, N)$.

• Each of N coordinates explores a length L, for an overall contribution of $L^N/N!$. Division by $N!$ ensures no over-counting of phase space for indistinguishable particles.

(b) Compute the contribution of the momenta p_i to $\Omega(E, L, N)$.

(Hint: The volume of the hyper-pyramid defined by $\sum_{i=1}^{d} x_i \leq R$, and $x_i \geq 0$, in d dimensions is $R^d/d!$.)

• The N momenta satisfy the constraint $\sum_{i=1}^{N} |p_i| = E/c$. *For a particular choice of the signs of* $\{p_i\}$, this constraint describes the surface of a hyper-pyramid in N dimensions. If we ignore the difference between the surface area and volume in the large N limit, we can calculate the volume in momentum space from the expression given in the hint as

$$\Omega_{\mathbf{p}} = 2^N \cdot \frac{1}{N!} \cdot \left(\frac{E}{c} \right)^N.$$

The factor of 2^N takes into account the two possible signs for each p_i. The surface area of the pyramid is given by $\sqrt{d}R^{d-1}/(d-1)!$; the additional factor of $\sqrt{d}$ with respect to

$dvolume/dR$ is the ratio of the normal to the base to the side of the pyramid. Thus, the volume of a shell of energy uncertainly Δ_E, is

$$\Omega'_{\mathbf{p}} = 2^N \cdot \frac{\sqrt{N}}{(N-1)!} \cdot \left(\frac{E}{c}\right)^{N-1} \cdot \frac{\Delta_E}{c}.$$

We can use the two expressions interchangeably, as their difference is subleading in N.

(c) Compute the entropy $S(E, L, N)$.

• Taking into account quantum modifications due to anisotropy, and phase space measure, we have

$$\Omega(E, L, N) = \frac{1}{h^N} \cdot \frac{L^N}{N!} \cdot 2^N \cdot \frac{\sqrt{N}}{(N-1)!} \cdot \left(\frac{E}{c}\right)^{N-1} \cdot \frac{\Delta_E}{c}.$$

Ignoring subleading terms in the large N limit, the entropy is given by

$$S(E, L, N) = Nk_B \ln\left(\frac{2e^2}{hc} \cdot \frac{L}{N} \cdot \frac{E}{N}\right).$$

(d) Calculate the one dimensional pressure P.

• From $dE = TdS - PdV + \mu dN$, the pressure is given by

$$P = T \left.\frac{\partial S}{\partial L}\right|_{E,N} = \frac{Nk_B T}{L}.$$

(e) Obtain the heat capacities C_L and C_P.

• Temperature and energy are related by

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{L,N} = \frac{Nk_B}{E}, \quad \Longrightarrow \quad E = Nk_B T, \quad \Longrightarrow \quad C_L = \left.\frac{\partial E}{\partial T}\right|_{L,N} = Nk_B.$$

Including the work done against external pressure, and using the equation of state,

$$C_P = \left.\frac{\partial E}{\partial T}\right|_{P,N} + P \left.\frac{\partial L}{\partial T}\right|_{P,N} = 2Nk_B.$$

(f) What is the probability $p(p_1)$ of finding a particle with momentum p_1?

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- Having fixed p_1 for the first particle, the remaining $N - 1$ particles are left to share an energy of $(E - c|p_1|)$. Since we are not interested in the coordinates, we can get the probability from the ratio of phase spaces for the momenta, i.e.

$$
\begin{aligned}
p(p_1) &= \frac{\Omega_{\mathbf{p}}\left(E - c|p_1|, N - 1\right)}{\Omega_{\mathbf{p}}(E, N)} \\
&= \left[\frac{2^{N-1}}{(N-1)!} \cdot \left(\frac{E - c|p_1|}{c}\right)^{N-1}\right] \times \left[\frac{N!}{2^N} \cdot \left(\frac{c}{E}\right)^N\right] \\
&\approx \frac{cN}{2E} \cdot \left(1 - \frac{c|p_1|}{E}\right)^N \approx \frac{cN}{2E} \cdot \exp\left(-\frac{cN|p_1|}{E}\right).
\end{aligned}
$$

Substituting $E = Nk_BT$, we obtain the (property normalized) Boltzmann weight

$$
p(p_1) = \frac{c}{2k_BT} \cdot \exp\left(-\frac{c|p_1|}{k_BT}\right).
$$

****

4. *Hard sphere gas:* Consider a gas of N hard spheres in a box. A single sphere occupies volume ω, while its center of mass can explore a volume V (if the box is otherwise empty). There are no other interactions between the spheres, except for the constraints of hard-core exclusion.

(a) Calculate the entropy S, as a function of the total energy E.

(Hint: $(V - a\omega)(V - (N - a)\omega) \approx (V - N\omega/2)^2$.)

- The available phase space for N identical particles is given by

$$
\Omega = \frac{1}{N!h^{3N}} \int_{H=E} d^3\vec{q}_1 \cdots d^3\vec{q}_N d^3\vec{p}_1 \cdots d^3\vec{p}_N,
$$

where the integration is carried out under the condition,

$$
E = \mathcal{H}(\vec{q}_i, \vec{p}_i) = \sum_{i=1}^{N} \frac{p_i^2}{2m}, \qquad \text{or} \qquad \sum_{i=1}^{N} p_i^2 = 2mE.
$$

The momentum integrals are now performed as in an ideal gas, yielding

$$
\Omega = \frac{(2mE)^{3N/2-1}}{N!h^{3N}} \cdot \frac{2\pi^{3N}}{\left(\frac{3N}{2} - 1\right)!} \cdot \int d^3\vec{q}_1 \cdots d^3\vec{q}_N.
$$

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The joint integral over the spacial coordinates with excluded volume constraints is best performed by introducing particles one at a time. The first particle can explore a volume V, the second $V - \omega$, the third $V - 2\omega$, etc., resulting in

$$\int d^3\vec{q}_1 \cdots d^3\vec{q}_N = V(V - \omega)(V - 2\omega) \cdots (V - (N-1)\omega).$$

Using the approximation $(V - a\omega)(V - (N-a)\omega) \approx (V - N\omega/2)^2$, we obtain

$$\int d^3\vec{q}_1 \cdots d^3\vec{q}_N \approx \left(V - \frac{N\omega}{2} \right)^N.$$

Thus the entropy of the system is

$$S = k_B \ln \Omega \approx N k_B \ln \left[\frac{e}{N} \left(V - \frac{N\omega}{2} \right) \left(\frac{4\pi m E e}{3N h^2} \right)^{3/2} \right].$$

(b) Calculate the equation of state of this gas.

• We can obtain the equation of state by calculating the expression for the pressure of the gas,

$$\frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{E,N} \approx \frac{N k_B}{V - \frac{N\omega}{2}},$$

which is easily re-arranged to,

$$P \left(V - \frac{N\omega}{2} \right) = N k_B T.$$

Note that the joint effective excluded volume that appears in the above expressions is one half of the total volume excluded by N particles.

(c) Show that the isothermal compressibility, $\kappa_T = -V^{-1} \left. \partial V / \partial P \right|_T$, is always positive.

• The isothermal compressibility is calculated from

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{T,N} = \frac{N k_B T}{P^2 V} > 0,$$

and is explicitly positive, as required by stability constraints.

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5. *Non-harmonic gas:*   Let us reexamine the generalized ideal gas introduced in the previous section, using statistical mechanics rather than kinetic theory. Consider a gas of N non-interacting atoms in a d-dimensional box of "volume" V, with a kinetic energy

$$\mathcal{H} = \sum_{i=1}^{N} A \left| \vec{p}_i \right|^s,$$

where $\vec{p}_i$ is the momentum of the ith particle.

(a) Calculate the classical partition function $Z(N, T)$ at a temperature T. (*You don't have to keep track of numerical constants in the integration.*)

• The partition function is given by

$$Z(N, T, V) = \frac{1}{N! h^{dN}} \int \cdots \int d^d \vec{q}_1 \cdots d^d \vec{q}_N d^d \vec{p}_1 \cdots d^d \vec{p}_N \exp \left[-\beta \sum_{i=1}^{N} A \left| \vec{p}_i \right|^s \right]$$

$$= \frac{1}{N! h^{dN}} \left[\int \int d^d \vec{q} d^d \vec{p} \exp \left(-\beta A \left| \vec{p} \right|^s \right) \right]^N.$$

Ignoring hard core exclusion, each atom contributes a d–dimensional volume V to the integral over the spatial degrees of freedom, and

$$Z(N, T, V) = \frac{V^N}{N! h^{dN}} \left[\int d^d \vec{p} \exp \left(-\beta A \left| \vec{p} \right|^s \right) \right]^N.$$

Observing that the integrand depends only on the magnitude $|\vec{p}| = p$, we can evaluate the integral in spherical coordinates using $\int d^d \vec{p} = S_d \int dp\, p^{d-1}$, where S_d denotes the surface area of a unit sphere in d–dimensions, as

$$Z(N, T, V) = \frac{V^N}{N! h^{dN}} \left[S_d \int_0^\infty dp\, p^{d-1} \exp \left(-\beta A p^s \right) \right]^N.$$

Introducing the variable $x \equiv (\beta A)^{1/s} p$, we have

$$Z(N, T, V) = \frac{V^N S_d^N}{N! h^{dN}} \left(\frac{A}{k_B T} \right)^{-dN/s} \left[\int_0^\infty dx\, x^{d-1} \exp(-x^s) \right]^N$$

$$= C^N(d, s) \frac{1}{N!} \left(\frac{V S_d}{h^d} \right)^N \left(\frac{A}{k_B T} \right)^{-dN/s},$$

where C denotes the numerical value of the integral. (We assume that A and s are both real and positive. These conditions ensure that energy increases with increasing $|\vec{p}|$.) The integral is in fact equal to

$$C(d, s) = \int_0^\infty dx\, x^{d-1} \exp(-x^s) dx = \frac{1}{s} \Gamma \left(\frac{d}{s} \right),$$

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and the partition function is

$$Z = \frac{1}{N!} \left(\frac{V S_d}{h^d s} \right)^N \left(\frac{A}{k_B T} \right)^{-dN/s} \left[\Gamma \left(\frac{d}{s} \right) \right]^N.$$

(b) Calculate the pressure and the internal energy of this gas. (Note how the usual equipartition theorem is modified for non-quadratic degrees of freedom.)

● To calculate the pressure and internal energy, note that the Helmholtz free energy is

$$F = E - TS = -k_B T \ln Z,$$

and that

$$P = -\frac{\partial F}{\partial V}\bigg|_T, \qquad \text{while} \qquad E = -\frac{\partial \ln Z}{\partial \beta}\bigg|_V.$$

First calculating the pressure:

$$P = -\frac{\partial F}{\partial V}\bigg|_T = k_B T \frac{\partial \ln Z}{\partial V}\bigg|_T = \frac{N k_B T}{V}.$$

Now calculating the internal energy:

$$E = -\frac{\partial \ln Z}{\partial \beta}\bigg|_V = -\frac{\partial}{\partial \beta}\left[-\frac{dN}{s} \ln \left(\frac{A}{k_B T} \right) \right] = \frac{d}{s} N k_B T.$$

Note that for each degree of freedom with energy $A|\vec{p}_i|^s$, we have the average value, $\langle A|\vec{p}_i|^s \rangle = \frac{d}{s} k_B T$. This evaluates to $\frac{3}{2} k_B T$ for the 3–dimensional ideal gas.

(c) Now consider a diatomic gas of N molecules, each with energy

$$\mathcal{H}_i = A \left(\left| \vec{p}_i^{\,(1)} \right|^s + \left| \vec{p}_i^{\,(2)} \right|^s \right) + K \left| \vec{q}_i^{\,(1)} - \vec{q}_i^{\,(2)} \right|^t,$$

where the superscripts refer to the two particles in the molecule. (Note that this unrealistic potential allows the two atoms to occupy the same point.) Calculate the expectation value $\left\langle \left| \vec{q}_i^{\,(1)} - \vec{q}_i^{\,(2)} \right|^t \right\rangle$, at temperature T.

● Now consider N diatomic molecules, with

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i, \qquad \text{where} \qquad \mathcal{H}_i = A \left(\left| \vec{p}_i^{\,(1)} \right|^s + \left| \vec{p}_i^{\,(2)} \right|^s \right) + K \left| \vec{q}_i^{\,(1)} - \vec{q}_i^{\,(2)} \right|^t.$$

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The expectation value

$$\left\langle \left| \vec{q}_i^{(1)} - \vec{q}_i^{(2)} \right|^t \right\rangle = \frac{\frac{1}{N!} \int \prod_{i=1}^N d^d \vec{q}_i^{(1)} d^d \vec{q}_i^{(2)} d^d \vec{p}_i^{(1)} d^d \vec{p}_i^{(2)} \left| \vec{q}_i^{(1)} - \vec{q}_i^{(2)} \right|^t \exp\left[-\beta \sum_i \mathcal{H}_i\right]}{\frac{1}{N!} \int \prod_{i=1}^N d^d \vec{q}_i^{(1)} d^d \vec{q}_i^{(2)} d^d \vec{p}_i^{(1)} d^d \vec{p}_i^{(2)} \exp\left[-\beta \sum_i \mathcal{H}_i\right]},$$

is easily calculated by changing variables to

$$\vec{x} \equiv \vec{q}^{(1)} - \vec{q}^{(2)}, \qquad \text{and} \qquad \vec{y} \equiv \frac{\vec{q}^{(1)} + \vec{q}^{(2)}}{2},$$

as (note that the Jacobian of the transformation is unity)

$$\left\langle \left| \vec{q}^{(1)} - \vec{q}^{(2)} \right|^t \right\rangle = \frac{\int d^d \vec{x} d^d \vec{y} \cdot |\vec{x}|^t \cdot \exp\left[-\beta K |\vec{x}|^t\right]}{\int d^d \vec{x} d^d \vec{y} \cdot \exp\left[-\beta K |\vec{x}|^t\right]}$$

$$= \frac{\int d^d \vec{x} \cdot |\vec{x}|^t \cdot \exp\left[-\beta K |\vec{x}|^t\right]}{\int d^d \vec{x} \cdot \exp\left[-\beta K |\vec{x}|^t\right]}.$$

Further simplifying the algebra by introducing the variable $\vec{z} \equiv (\beta K)^{1/t} \vec{x}$, leads to

$$\left\langle \left| \vec{q}^{(1)} - \vec{q}^{(2)} \right|^t \right\rangle = \frac{(\beta K)^{-t/t} \int d^d \vec{z} \cdot |\vec{z}|^t \cdot \exp\left[-|\vec{z}|^t\right]}{\int d^d \vec{z} \cdot \exp\left[-|\vec{z}|^t\right]} = \frac{d}{t} \cdot \frac{k_B T}{K}.$$

Here we have assumed that the volume is large enough, so that the range of integration over the relative coordinate can be extended from 0 to ∞.

Alternatively, note that for the degree of freedom $\vec{x} = \vec{q}^{(1)} - \vec{q}^{(2)}$, the energy is $K|\vec{x}|^t$. Thus, from part (b) we know that

$$\left\langle K|\vec{x}|^t \right\rangle = \frac{d}{t} \cdot \frac{k_B T}{K},$$

i.e.

$$\left\langle |\vec{x}|^t \right\rangle = \left\langle \left| \vec{q}^{(1)} - \vec{q}^{(2)} \right|^t \right\rangle = \frac{d}{t} \cdot \frac{k_B T}{K}.$$

And yet another way of calculating the expectation value is from

$$\sum_{i=1}^N \left\langle \left| \vec{q}_i^{(1)} - \vec{q}_i^{(2)} \right|^t \right\rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial K} = \frac{Nd}{t} \cdot \frac{k_B T}{K},$$

(note that the relevant part of Z is calculated in part (d) below).

(d) Calculate the heat capacity ratio ratio $\gamma = C_P/C_V$, for the above diatomic gas.

- For the ideal gas, the internal energy depends only on temperature T. The gas in part (c) is ideal in the sense that there are no molecule–molecule interactions. Therefore,

$$C_V = \left.\frac{dQ}{dT}\right|_V = \left.\frac{dE + PdV}{dT}\right|_V = \frac{dE(T)}{dT},$$

and

$$C_P = \left.\frac{dQ}{dT}\right|_P = \left.\frac{dE + PdV}{dT}\right|_P = \frac{dE(T)}{dT} + P\left.\frac{\partial V(T)}{\partial T}\right|_P.$$

Since $PV = Nk_BT$,

$$C_P = \frac{dE(T)}{dT} + Nk_B.$$

We now calculate the partition function

$$Z = \frac{1}{N!h^{dN}} \int \prod_{i=1}^{N} d^d\vec{q}_i^{(1)} d^d\vec{q}_i^{(2)} d^d\vec{p}_i^{(1)} d^d\vec{p}_i^{(2)} \exp\left[-\beta \sum_i \mathcal{H}_i\right]$$

$$= \frac{1}{N!h^{dN}} z_1^N,$$

where

$$z_1 = \int d^d\vec{q}^{(1)} d^d\vec{q}^{(2)} d^d\vec{p}^{(1)} d^d\vec{p}^{(2)} \exp\left[-\beta \cdot \left(A\left|\vec{p}^{(1)}\right|^s + A\left|\vec{p}^{(2)}\right|^s + K\left|\vec{q}^{(1)} - \vec{q}^{(2)}\right|^t\right)\right]$$

$$= \left[\int d^d\vec{q}^{(1)} d^d\vec{q}^{(2)} \exp\left(-\beta K\left|\vec{q}^{(1)} - \vec{q}^{(2)}\right|^t\right)\right] \cdot \left[\int d^d\vec{p}^{(1)} \exp\left(-\beta A\left|\vec{p}^{(1)}\right|^s\right)\right]^2.$$

Introducing the variables, $\vec{x}$, $\vec{y}$, and $\vec{z}$, as in part (c),

$$Z \propto \frac{V^N}{N!} \left[(\beta K)^{-d/t} \int_0^\infty z^{d-1} \exp(-z^t)dz\right]^N \cdot \left[\int_0^\infty p^{d-1} \exp(-\beta A p^s)dp\right]^{2N}$$

$$= \frac{V^N}{N!} \left[(\beta K)^{-d/t}\frac{1}{t}\Gamma\left(\frac{d}{t}\right)\right]^N \cdot \left[\frac{1}{s}(\beta A)^{-d/s}\Gamma\left(\frac{d}{s}\right)\right]^{2N}$$

$$\propto \frac{V^N}{N!} (\beta K)^{-dN/t} (\beta A)^{-2Nd/s}.$$

Now we can calculate the internal energy as

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{d}{t}Nk_BT + \frac{2d}{s}Nk_BT = dNk_BT\left(\frac{1}{t} + \frac{2}{s}\right).$$

From this result, the heat capacities are obtained as

$$C_P = \left.\frac{\partial E}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P = Nk_B\left(\frac{2d}{s} + \frac{d}{t} + 1\right),$$

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = dNk_B\left(\frac{2}{s} + \frac{1}{t}\right).$$

resulting in the ratio

$$\gamma = \frac{C_P}{C_V} = \frac{2d/s + d/t + 1}{2d/s + d/t} = 1 + \frac{st}{d(2t + s)}.$$

****

6. *Surfactant adsorption:* A dilute solution of surfactants can be regarded as an ideal three dimensional gas. As surfactant molecules can reduce their energy by contact with air, a fraction of them migrate to the surface where they can be treated as a two dimensional ideal gas. Surfactants are similarly adsorbed by other porous media such as polymers and gels with an affinity for them.

(a) Consider an ideal gas of classical particles of mass m in d dimensions, moving in a *uniform* attractive potential of strength ε_d. By calculating the partition function, or otherwise, show that the chemical potential at a temperature T and particle density n_d, is given by

$$\mu_d = -\varepsilon_d + k_B T \ln\left[n_d \lambda(T)^d\right], \quad \text{where} \quad \lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}.$$

• The partition function of a d-dimensional ideal gas is given by

$$Z_d = \frac{1}{N_d! h^{dN_d}} \int \cdots \int \prod_{i=1}^{N_d} d^d \vec{q}_i d^d \vec{p}_i \exp\left\{-\beta \left[N_d \varepsilon_d + \sum_{i=1}^{N_d} \left(\frac{\vec{p}_i^{\,2}}{2m}\right)\right]\right\}$$

$$= \frac{1}{N_d!} \left(\frac{V_d}{\lambda^d}\right)^{N_d} e^{-\beta N_d \varepsilon_d},$$

where

$$\lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}}.$$

The chemical potential is calculated from the Helmholtz free energy as

$$\mu_d = \left.\frac{\partial F}{\partial N}\right|_{V,T} = -k_B T \left.\frac{\partial \ln Z_d}{\partial N_d}\right|_{V,T}$$

$$= -\varepsilon_d + k_B T \ln\left(\frac{V_d}{N_d \lambda^d}\right).$$

(b) If a surfactant lowers its energy by ε_0 in moving from the solution to the surface, calculate the concentration of floating surfactants as a function of the solution concentration $n \, (= n_3)$, at a temperature T.

• The density of particles can also be calculated from the grand canonical partition function, which for particles in a d–dimensional space is

$$\Xi(\mu, V_d, T) = \sum_{N_d=0}^{\infty} Z(N_d, V_d, T) e^{\beta N_d \mu}$$

$$= \sum_{N_d=0}^{\infty} \frac{1}{N_d!} \left(\frac{V_d}{\lambda^d}\right)^{N_d} e^{-\beta N_d \varepsilon_d} e^{\beta N_d \mu} = \exp\left[\left(\frac{V_d}{\lambda^d}\right) \cdot e^{\beta(\mu - \varepsilon_d)}\right].$$

The average number of particles absorbed in the space is

$$\langle N_d \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \Xi = \frac{1}{\beta} \frac{\partial}{\partial \mu} \left[\left(\frac{V_d}{\lambda^d}\right) \cdot e^{\beta(\mu - \varepsilon_d)}\right] = \left(\frac{V_d}{\lambda^d}\right) \cdot e^{\beta(\mu - \varepsilon_d)}.$$

We are interested in the coexistence of surfactants between a $d = 3$ dimensional solution, and its $d = 2$ dimensional surface. Dividing the expressions for $\langle N_3 \rangle$ and $\langle N_2 \rangle$, and taking into account $\varepsilon_0 = \varepsilon_3 - \varepsilon_2$, gives

$$\frac{\langle N_2 \rangle}{\langle N_3 \rangle} = \frac{A\lambda}{V} e^{\beta \varepsilon_0},$$

which implies that

$$n_2 = \frac{\langle N_2 \rangle}{A} = n\lambda e^{\beta \varepsilon_0}.$$

(c) Gels are formed by cross-linking linear polymers. It has been suggested that the porous gel should be regarded as *fractal*, and the surfactants adsorbed on its surface treated as a gas in d_f dimensional space, with a non-integer d_f. Can this assertion be tested by comparing the relative adsorption of surfactants to a gel, and to the individual polymers (presumably one dimensional) before cross-linking, as a function of temperature?

• Using the result found in part (b), but regarding the gel as a d_f–dimensional container, the adsorbed particle density is

$$\langle n_{\text{gel}} \rangle = n\lambda^{3-d_f} \exp\left[\beta(\varepsilon_3 - \varepsilon_{\text{gel}})\right].$$

Thus by studying the adsorption of particles as a function of temperature one can determine the fractal dimensionality, d_f, of the surface. The largest contribution comes from the

difference in energies. If this leading part is accurately determined, there is a subleading dependence via λ^{3-d_f} which depends on d_f.

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7. *Molecular adsorption:* N diatomic molecules are stuck on a metal surface of square symmetry. Each molecule can either lie flat on the surface in which case it must be aligned to one of two directions, x and y, or it can stand up along the z direction. There is an energy cost of $\varepsilon > 0$ associated with a molecule standing up, and zero energy for molecules lying flat along x or y directions.

(a) How many microstates have the smallest value of energy? What is the largest microstate energy?

• The ground state energy of $E = E_{min} = 0$ is obtained for 2^N configurations. The largest microstate energy is $N\epsilon$ is unique.

(b) For *microcanonical* macrostates of energy E, calculate the number of states $\Omega(E, N)$, and the entropy $S(E, N)$.

• Let $N_z = E/\epsilon$. Expressing Ω as the number of ways to choose the N_g excited molecules, multiplied by the number of possible configurations

$$\Omega(E, N) = \frac{N!}{N_z!(N - N_z)!} \cdot 2^{N - N_z},$$

and

$$S(E, N) = S_{two-level\ system} + k_b(N - N_z)\ln 2$$
$$= -Nk_B\left\{\frac{E}{N\epsilon}\ln\frac{E}{N\epsilon} + (1 - \frac{E}{N\epsilon})\ln(1 - \frac{E}{N\epsilon})\right\} + k_b(N - \frac{E}{\epsilon})\ln 2.$$

(c) Calculate the heat capacity $C(T)$ and sketch it.

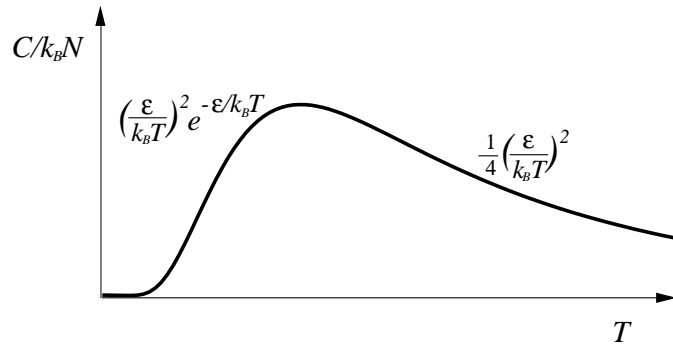• The temperature dependence of the energy is obtained from the relation

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_N = -\frac{k_B}{\epsilon}\ln(\frac{E}{N\epsilon - E}) - \frac{k_B}{\epsilon}\ln 2,$$

whence

$$E = \frac{N\epsilon}{\exp(\frac{\epsilon}{k_B}(\frac{1}{T} + \frac{k_B}{\epsilon}\ln 2)) + 1} = \frac{N\epsilon}{2\exp(\frac{\epsilon}{k_BT}) + 1},$$

and

$$C = \frac{dE}{dT} = Nk_B(\frac{\epsilon}{k_BT})^2\frac{2\exp(\frac{\epsilon}{k_BT})}{(1 + 2\exp(\frac{\epsilon}{k_BT}))^2}.$$

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The curve is labeled $C/k_B N$ on the vertical axis and T on the horizontal axis, with annotations $\left(\frac{\varepsilon}{k_B T}\right)^2 e^{-\varepsilon/k_B T}$ and $\frac{1}{4}\left(\frac{\varepsilon}{k_B T}\right)^2$.

(d) What is the probability that a specific molecule is standing up?

• The probability that a specific molecule is standing up is

$$p(\vec{r}_1 = \hat{z}) = \frac{\Omega(E - \epsilon, N - 1)}{\Omega(E, N)}$$

$$= \frac{(N-1)!}{(N_z - 1)!((N-1) - (N_z - 1))!} 2^{(N-1)-(N_z-1)} \frac{N_z!(N - N_z)!}{N!} \frac{1}{2^{N-N_z}}$$

$$= \frac{N_z}{N} = \frac{E}{N\epsilon}$$

$$= \frac{1}{2 \exp \frac{\epsilon}{k_B T} + 1}.$$

(e) What is the largest possible value of the internal energy at any positive temperature?

• Since $\frac{dE}{dT} > 0$ for all $T > 0$, the energy is largest for $\to \infty$, i.e.

$$E_{max} = \frac{N\epsilon}{3}.$$

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8. *Curie susceptibility:* Consider N non-interacting quantized spins in a magnetic field $\vec{B} = B\hat{z}$, and at a temperature T. The work done by the field is given by BM_z, with a magnetization $M_z = \mu \sum_{i=1}^{N} m_i$. For each spin, m_i takes only the $2s + 1$ values $-s, -s + 1, \cdots, s - 1, s$.

(a) Calculate the Gibbs partition function $\mathcal{Z}(T, B)$. (Note that the ensemble corresponding to the macrostate (T, B) includes magnetic work.)

• The Gibbs partition function is

$$\mathcal{Z} = \sum_{\{m_i\}} \exp\left(\beta \vec{B} \cdot \vec{M}\right) = \sum_{\{m_i\}} \exp\left(\beta B\mu \sum_{i=1}^{N} m_i\right) = \left[\sum_{m_i=-s}^{m_i=s} \exp(\beta\mu B \cdot m_i)\right]^N.$$

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Thus we obtain the series

$$\mathcal{Z} = [\exp(-\beta B\mu s) + \exp(-\beta B\mu(s-1)) + \cdots + \exp(\beta B\mu(s-1)) + \exp(\beta B\mu s)]^N.$$

In general, to evaluate a geometrical series of the form

$$S = x^{-s} + x^{-(s-1)} + \cdots + x^{s-1} + x^s,$$

increase the order of the series by one,

$$Sx = x^{-s+1} + \cdots + x^s + x^{s+1},$$

and subtract from the original series:

$$(1-x)S = x^{-s} - x^{s+1}, \quad \Longrightarrow \quad S = \frac{x^{-s} - x^{s+1}}{1-x}.$$

(Note that the same result is obtained whether s is an integer or half–integer quantity.)
Using this expression, we get

$$\mathcal{Z} = \left(\frac{\exp(-\beta B\mu s) - \exp(\beta B\mu(s+1))}{1 - \exp(\beta B\mu)}\right)^N$$

$$= \left(\frac{\exp(-\beta B\mu(s+1/2)) - \exp(-\beta B\mu(s+1/2))}{\exp(-\beta B\mu/2) - \exp(-\beta B\mu/2)}\right)^N.$$

Substituting in the proper trigonometric identity,

$$\mathcal{Z} = \left[\frac{\sinh\left(\beta\mu B(s+1/2)\right)}{\sinh(\beta\mu B/2)}\right]^N.$$

(b) Calculate the Gibbs free energy $G(T, B)$, and show that for small B,

$$G(B) = G(0) - \frac{N\mu^2 s(s+1)B^2}{6k_B T} + \mathcal{O}(B^4).$$

- The Gibbs free energy is

$$G = E - BM = -k_B T \ln \mathcal{Z}$$

$$= -Nk_B T \ln[\sinh(\beta\mu B(s+1/2))] + Nk_B T \ln[\sinh(\beta\mu B/2)].$$

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Using an approximation of $\sinh\theta$ for small θ,

$$\sinh\theta = \frac{1}{2}\left(e^\theta - e^{-\theta}\right) \approx \frac{1}{2}\left(2\theta + 2\frac{\theta^3}{3!}\right) + \mathcal{O}(\theta^5), \qquad \text{for} \qquad \theta \ll 1,$$

we find (setting $\alpha = \beta\mu B$),

$$G \approx -Nk_BT\left\{\ln\left[\alpha\left(s+\frac{1}{2}\right)\left(1+\frac{\alpha^2}{6}\left(s+\frac{1}{2}\right)^2\right)\right] - \ln\left[\frac{\alpha}{2}\left(1+\frac{\alpha^2}{24}\right)\right] + \mathcal{O}(\alpha^4)\right\}.$$

Using the expansion $\ln(1+x) = x - x^2/2 + x^3/3 - \cdots$, we find

$$G \approx -Nk_BT\left[\ln(2s+1) + \frac{1}{6}\left(\alpha(s+1/2)\right)^2 - \frac{1}{6}\left(\alpha/2\right)^2 + \mathcal{O}(\alpha^4)\right]$$

$$\approx -Nk_BT\ln(2s+1) - Nk_BT\alpha^2\frac{(s^2+s)}{6}$$

$$= G_0 - \frac{N\mu^2B^2s(s+1)}{6k_BT} + \mathcal{O}(B^4).$$

(c) Calculate the zero field susceptibility $\chi = \partial M_z/\partial B|_{B=0}$, and show that is satisfies *Curie's law*

$$\chi = c/T.$$

● The magnetic susceptibility, $\chi = \partial M_z/\partial B$, is obtained by noting that the average magnetization is

$$\langle M_z\rangle = k_BT\frac{\partial\ln\mathcal{Z}}{\partial B} = -\frac{\partial G}{\partial B}.$$

Thus

$$\chi = \frac{\partial\langle M_z\rangle}{\partial B} = -\frac{\partial}{\partial B}\frac{\partial G}{\partial B} = \frac{N\mu^2ts(s+1)}{3k_BT},$$

which obeys *Curie's law*, $\chi = c/T$, with $c = N\mu^2s(s+1)/3k_B$.

(d) Show that $C_B - C_M = cB^2/T^2$ where C_B and C_M are heat capacities at constant B and M respectively.

$$********$$

9. *Langmuir isotherms:* An ideal gas of particles is in contact with the surface of a catalyst.

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(a) Show that the chemical potential of the gas particles is related to their temperature and pressure via $\mu = k_B T \left[\ln \left(P/T^{5/2} \right) + A_0 \right]$, where A_0 is a constant.

- For convenience, we begin by defining the characteristic length,

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}},$$

in terms of which the free energy of ideal gas is given by,

$$F = -N k_B T \ln \left(\frac{Ve}{N\lambda^3} \right).$$

Then using the equation of state of ideal gas we get,

$$\mu = \frac{\partial F}{\partial N} = -k_B T \ln \left(\frac{V}{N\lambda^3} \right) = -k_B T \ln \left(\frac{k_B T}{P\lambda^3} \right)$$
$$= k_B T \left[\ln(PT^{-5/2}) + \ln \left(\frac{h^3}{k_B^{5/2} 2^{3/2} \pi^{3/2} m^{3/2}} \right) \right].$$

(b) If there are $\mathcal{N}$ distinct adsorption sites on the surface, and each adsorbed particle gains an energy ϵ upon adsorption, calculate the grand partition function for the two dimensional gas with a chemical potential μ.

- We have,

$$Q(T, \mu) = \sum_{n=0}^{\mathcal{N}} \binom{\mathcal{N}}{n} e^{n\beta\mu} e^{-n\beta\epsilon} = \left(1 + e^{\beta(\mu - \epsilon)} \right)^{\mathcal{N}}.$$

(c) In equilibrium, the gas and surface particles are at the same temperature and chemical potential. Show that the fraction of occupied surface sites is then given by $f(T, P) = P/\left(P + P_0(T)\right)$. Find $P_0(T)$.

- Since the average number of absorption sites occupied is,

$$\langle N \rangle = k_B T \frac{\partial \ln Q}{\partial \mu} = \mathcal{N} \frac{e^{\beta(\mu - \epsilon)}}{1 + e^{\beta(\mu - \epsilon)}},$$

and the fraction of occupied sites is given by,

$$f(T, P) = \frac{e^{\beta(\mu - \epsilon)}}{1 + e^{\beta(\mu - \epsilon)}}.$$

Since the gas and surface particles have the same temperature and chemical potential, the realtion in (a), namely,

$$e^{\beta\mu} = \frac{P\lambda^3}{k_B T}$$

holds. Plugging this into the formula for f we obtain,

$$f(T, P) = \frac{P}{P + P_0(T)}, \quad \text{with} \quad P_0(T) = \frac{k_B T}{\lambda^3} e^{\beta\epsilon}.$$

(d) In the grand canonical ensemble, the particle number N is a random variable. Calculate its characteristic function $\langle \exp(-ikN) \rangle$ in terms of $\mathcal{Q}(\beta\mu)$, and hence show that

$$\langle N^m \rangle_c = -(k_B T)^{m-1} \frac{\partial^m \mathcal{G}}{\partial \mu^m}\bigg|_T,$$

where $\mathcal{G}$ is the grand potential.

- Note that in calculating $\mathcal{Q}(\beta\mu)$ the term for N particles is proportional to $e^{\beta\mu N}$. In calculating the average of e^{-ikN}, we just replace the initial factor with $e^{(\beta\mu-ik)N}$, and hence

$$\langle e^{-ikN} \rangle = \frac{\mathcal{Q}(\beta\mu - ik)}{\mathcal{Q}(\beta\mu)}.$$

For the cumulant generating function, we get

$$\ln \langle e^{-ikN} \rangle = \ln \mathcal{Q}(\beta\mu - ik) - \ln \mathcal{Q}(\beta\mu) = -\beta\mathcal{G}(\beta\mu - ik) + \beta\mathcal{G}(\beta\mu).$$

Hence,

$$\langle N^m \rangle_c = \frac{\partial^m}{\partial(-ik)^m}(-\beta\mathcal{G}(\beta\mu - ik))|_T$$

$$= -\beta \frac{\partial^m \mathcal{G}}{\partial(\beta\mu)^m}\bigg|_T = -\beta^{1-m} \frac{\partial^m \mathcal{G}}{\partial \mu^m}\bigg|_T$$

$$= -(k_B T)^{m-1} \frac{\partial^m \mathcal{G}}{\partial \mu^m}\bigg|_T.$$

(e) Using the characteristic function, show that

$$\langle N^2 \rangle_c = k_B T \frac{\partial \langle N \rangle}{\partial \mu}\bigg|_T.$$

●
$$\langle N^2 \rangle_c = -k_B T \left. \frac{\partial^2 \mathcal{G}}{\partial \mu^2} \right|_T = k_B T \left. \frac{\partial \langle N \rangle}{\partial \mu} \right|_T .$$

(f) Show that fluctuations in the number of adsorbed particles satisfy

$$\frac{\langle N^2 \rangle_c}{\langle N \rangle_c^2} = \frac{1-f}{\mathcal{N}f}.$$

• By definition of f,

$$\langle N \rangle_c = -\left. \frac{\partial \mathcal{G}}{\partial \mu} \right|_T = \mathcal{N}f,$$

and since,

$$\left. \frac{\partial f}{\partial \mu} \right|_T = \left. \frac{\partial}{\partial \mu} \frac{e^{-\beta\epsilon}}{e^{-\beta\mu} + e^{-\beta\epsilon}} \right|_T = \frac{\beta e^{-\beta\mu} e^{-\beta\epsilon}}{(e^{-\beta\mu} + e^{-\beta\epsilon})^2} = \beta f(1-f),$$

we get,

$$\langle N^2 \rangle_c = \frac{1}{\beta} \frac{\partial N}{\partial \mu} = \frac{1}{\beta} \mathcal{N} \frac{\partial f}{\partial \mu} = \mathcal{N}f(1-f),$$

leading to the equality,

$$\frac{\langle N^2 \rangle_c}{\langle N \rangle_c^2} = \frac{1-f}{\mathcal{N}f}.$$

****

10. *Molecular oxygen* has a net magnetic spin, $\vec{S}$, of unity, i.e. S^z is quantized to -1, 0, or +1. The Hamiltonian for an ideal gas of N such molecules in a magnetic field $\vec{B} \parallel \hat{z}$ is

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{\vec{p_i}^{\,2}}{2m} - \mu B S_i^z \right],$$

where $\{\vec{p_i}\}$ are the center of mass momenta of the molecules. The corresponding coordinates $\{\vec{q_i}\}$ are confined to a volume V. (Ignore all other degrees of freedom.)

(a) Treating $\{\vec{p_i}, \vec{q_i}\}$ classically, but the spin degrees of freedom as quantized, calculate the partition function, $\tilde{Z}(T, N, V, B)$.

●
$$Z = \sum_{\mu_s} e^{-\beta \mathcal{H}(\mu_s)} = \sum_{\mu_s} e^{-\beta \sum (\vec{p_i}^2/2m - \mu B S_i^z)} = \frac{1}{N!} \left(\frac{V}{\lambda^3} (e^{\beta\mu B} + 1 + e^{-\beta\mu B}) \right)^N,$$

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where,

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

(b) What are the probabilities for S_i^z of a specific molecule to take on values of -1, 0, +1 at a temperature T?

• The probabilities for S_i^z of a given molecule to take values -1, 0, +1, are,

$$\frac{e^{-\beta\mu B}}{2\cosh\beta\mu B + 1}, \qquad \frac{1}{2\cosh\beta\mu B + 1}, \qquad \frac{e^{\beta\mu B}}{2\cosh\beta\mu B + 1},$$

respectively.

(c) Find the average magnetic dipole moment, $\langle M \rangle /V$, where $M = \mu \sum_{i=1}^{N} S_i^z$.

•

$$\langle M \rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial B} = \frac{1}{\beta}\frac{\partial N \ln(2\cosh\beta\mu B + 1)}{\partial B}$$

$$= N\mu \left(\frac{2\sinh\beta\mu B}{2\cosh\beta\mu B + 1}\right).$$

(d) Calculate the zero field susceptibility $\chi = \partial <M> /\partial B|_{B=0}$.

•

$$\chi = N\beta\mu^2 \left. \frac{2\cosh\beta\mu B(2\cosh\beta\mu B + 1) - 4\sinh\beta\mu B\sinh\beta\mu B}{(2\cosh\beta\mu B + 1)^2}\right|_{B=0} = \frac{2}{3}N\beta\mu^2.$$

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11. *Molecular oxygen* has a net magnetic spin, $\vec{S}$, of unity, i.e. S^z is quantized to -1, 0, or +1. The Hamiltonian for an ideal gas of N such molecules in a magnetic field $\vec{B} \parallel \hat{z}$ is

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{\vec{p_i}^{\,2}}{2m} - \mu B S_i^z\right],$$

where $\{\vec{p_i}\}$ are the center of mass momenta of the molecules. The corresponding coordinates $\{\vec{q_i}\}$ are confined to a volume V. (Ignore all other degrees of freedom.)

(a) Treating $\{\vec{p_i}, \vec{q_i}\}$ classically, but the spin degrees of freedom as quantized, calculate the partition function, $\tilde{Z}(T, N, V, B)$.

•

$$Z = \sum_{\mu_s} e^{-\beta\mathcal{H}(\mu_s)} = \sum_{\mu_s} e^{-\beta\sum(\vec{p_i}^2/2m - \mu B S_i^z)} = \frac{1}{N!}\left(\frac{V}{\lambda^3}(e^{\beta\mu B} + 1 + e^{-\beta\mu B})\right)^N,$$

where,

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

(b) What are the probabilities for S_i^z of a specific molecule to take on values of -1, 0, +1 at a temperature T?

- The probabilities for S_i^z of a given molecule to take values -1, 0, +1, are,

$$\frac{e^{-\beta\mu B}}{2\cosh\beta\mu B + 1}, \qquad \frac{1}{2\cosh\beta\mu B + 1}, \qquad \frac{e^{\beta\mu B}}{2\cosh\beta\mu B + 1},$$

respectively.

(c) Find the average magnetic dipole moment, $\langle M \rangle /V$, where $M = \mu\sum_{i=1}^{N} S_i^z$.

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$$\langle M \rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial B} = \frac{1}{\beta}\frac{\partial N \ln(2\cosh\beta\mu B + 1)}{\partial B}$$
$$= N\mu\left(\frac{2\sinh\beta\mu B}{2\cosh\beta\mu B + 1}\right).$$

(d) Calculate the zero field susceptibility $\chi = \partial <M> /\partial B|_{B=0}$.

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$$\chi = N\beta\mu^2 \left.\frac{2\cosh\beta\mu B(2\cosh\beta\mu B + 1) - 4\sinh\beta\mu B\sinh\beta\mu B}{(2\cosh\beta\mu B + 1)^2}\right|_{B=0} = \frac{2}{3}N\beta\mu^2.$$

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12. *Polar rods:* Consider rod shaped molecules with moment of inertia I, and a dipole moment μ. The contribution of the rotational degrees of freedom to the Hamiltonian is given by

$$\mathcal{H}_{\text{rot.}} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) - \mu E \cos\theta \quad,$$

where E is an external electric field. ($\phi \in [0, 2\pi]$, $\theta \in [0, \pi]$ are the azimuthal and polar angles, and p_ϕ, p_θ are their conjugate momenta.)

(a) Calculate the contribution of the rotational degrees of freedom of each dipole to the *classical* partition function.

- The classical partition function is obtained by integrating over the angles θ and ϕ, and the corresponding momenta as

$$Z_{\rm rot} = \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_{-\infty}^\infty dp_\theta dp_\phi \exp\left[-\frac{\beta}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) + \beta\mu\cos\theta\right].$$

The Gaussian integrations over momenta are easily carried out, and after the change of variables to $x = \cos\theta$, we find

$$Z_{\rm rot} = \left(\frac{2\pi I}{\beta h^2}\right)(2\pi)\int_{-1}^{+1} dx\, e^{\beta\mu E x} = \left(\frac{8\pi^2 I}{\beta h^2}\right)\frac{\sinh(\beta\mu E)}{\beta\mu E}.$$

(b) Obtain the mean polarization $P = \langle\mu\cos\theta\rangle$, of each dipole.
- From the form of the partition function, we note that

$$P = \langle\mu\cos\theta\rangle = \frac{\partial \ln Z_{\rm rot}}{\partial\beta E} = \mu\left[\coth(\beta\mu E) - \frac{1}{\beta\mu E}\right].$$

(c) Find the *zero–field* polarizability

$$\chi_T = \left.\frac{\partial P}{\partial E}\right|_{E=0} \quad .$$

- The susceptibility is

$$\chi_T = \frac{\partial P}{\partial E} = \beta\mu^2\left[-\frac{1}{\sinh^2(\beta\mu E)} + \frac{1}{(\beta\mu E)^2}\right] = \frac{1}{3}\frac{\mu^2}{k_B T} \qquad \text{for } E = 0 \;.$$

(d) Calculate the rotational energy per particle (at finite E), and comment on its high and low temperature limits.
- The energy stored in this degree of freedom is

$$\langle E_{\rm rot}\rangle = -\frac{\partial \ln Z_{\rm rot}}{\partial\beta} = 2k_B T - \mu E\coth(\beta\mu E).$$

At high temperature $\langle E_{\rm rot}\rangle \approx k_B T$ coming entirely from the kinetic energies. At temperatures $k_B T \ll \mu E$, the polarization is saturated, and $\langle E_{\rm rot}\rangle \approx -\mu E + 2k_B T$.

(e) Sketch the rotational heat capacity per dipole.
- The classical heat capacity is $2k_B$ at low temperatures, and decreases to $1k_B$ at high temperatures, with a 'knee' at $k_B T \approx \mu E$.

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Problems for Chapter V - Interacting Particles

1. *Debye–Hückel theory and ring diagrams:* The virial expansion gives the gas pressure as an *analytic* expansion in the density $n = N/V$. Long range interactions can result in *non-analytic* corrections to the ideal gas equation of state. A classic example is the Coulomb interaction in plasmas, whose treatment by Debye–Hückel theory is equivalent to summing all the *ring diagrams* in a cumulant expansion.

For simplicity consider a gas of N electrons moving in a uniform background of positive charge density Ne/V to ensure overall charge neutrality. The Coulomb interaction takes the form

$$\mathcal{U}_Q = \sum_{i<j} \mathcal{V}(\vec{q}_i - \vec{q}_j), \quad \text{with} \quad \mathcal{V}(\vec{q}) = \frac{e^2}{4\pi|\vec{q}|} - c.$$

The constant c results from the background and ensures that the first order correction vanishes, i.e. $\int d^3\vec{q}\,\mathcal{V}(\vec{q}) = 0$.

(a) Show that the Fourier transform of $\mathcal{V}(\vec{q})$ takes the form

$$\tilde{\mathcal{V}}(\vec{\omega}) = \begin{cases} e^2/\omega^2 & \text{for } \vec{\omega} \neq 0 \\ 0 & \text{for } \vec{\omega} = 0 \end{cases}.$$

- The Fourier transform of $\mathcal{V}(\vec{q})$ is singular at the origin, and can be defined explicitly as

$$\tilde{\mathcal{V}}(\vec{\omega}) = \lim_{\varepsilon \to 0} \int d^3\vec{q}\,\mathcal{V}(\vec{q})e^{i\vec{\omega}\cdot\vec{q}-\varepsilon q}.$$

The result at $\vec{\omega} = 0$ follows immediately from the definition of c. For $\vec{\omega} \neq 0$,

$$\tilde{\mathcal{V}}(\vec{\omega}) = \lim_{\varepsilon \to 0} \int d^3\vec{q}\left(\frac{e^2}{4\pi q} - c\right)e^{i\vec{\omega}\cdot\vec{q}-\varepsilon q} = \lim_{\varepsilon \to 0} \int d^3\vec{q}\left(\frac{e^2}{4\pi q}\right)e^{i\vec{\omega}\cdot\vec{q}-\varepsilon q}$$

$$= \lim_{\varepsilon \to 0}\left[2\pi \int_0^\pi \sin\theta d\theta \int_0^\infty q^2 dq\left(\frac{e^2}{4\pi q}\right)e^{i\omega q\cos\theta - \varepsilon q}\right]$$

$$= -\frac{e^2}{2}\int_0^\infty \frac{e^{i\omega q-\varepsilon q} - e^{-i\omega q-\varepsilon q}}{i\omega}dq$$

$$= \lim_{\varepsilon \to 0}\frac{e^2}{2i\omega}\left(\frac{1}{i\omega - \varepsilon} + \frac{1}{i\omega + \varepsilon}\right) = \lim_{\varepsilon \to 0}\left(\frac{e^2}{\omega^2 + \varepsilon^2}\right) = \frac{e^2}{\omega^2}.$$

(b) In the cumulant expansion for $\left\langle \mathcal{U}_Q^\ell \right\rangle_c^0$, we shall retain only the diagrams forming a ring; which are proportional to

$$R_\ell = \int \frac{d^3\vec{q}_1}{V} \cdots \frac{d^3\vec{q}_\ell}{V}\,\mathcal{V}(\vec{q}_1 - \vec{q}_2)\mathcal{V}(\vec{q}_2 - \vec{q}_3)\cdots\mathcal{V}(\vec{q}_\ell - \vec{q}_1).$$

Use properties of Fourier transforms to show that

$$R_\ell = \frac{1}{V^{\ell-1}} \int \frac{d^3\vec{\omega}}{(2\pi)^3} \, \tilde{\mathcal{V}}(\vec{\omega})^\ell.$$

• In the cumulant expansion for $\left\langle \mathcal{U}_Q^\ell \right\rangle_c^0$, we retain only the diagrams forming a ring. The contribution of these diagrams to the partition function is

$$R_\ell = \int \frac{d^3\vec{q}_1}{V} \frac{d^3\vec{q}_2}{V} \cdots \frac{d^3\vec{q}_\ell}{V} \mathcal{V}(\vec{q}_1 - \vec{q}_2) \mathcal{V}(\vec{q}_2 - \vec{q}_3) \cdots \mathcal{V}(\vec{q}_\ell - \vec{q}_1)$$

$$= \frac{1}{V^\ell} \int \cdots \int d^3\vec{x}_1 d^3\vec{x}_2 \cdots d^3\vec{x}_{\ell-1} d^3\vec{q}_\ell \mathcal{V}(\vec{x}_1) \mathcal{V}(\vec{x}_2) \cdots \mathcal{V}(\vec{x}_{\ell-1}) \mathcal{V}\left(-\sum_{i=1}^{\ell-1} \vec{x}_i \right),$$

where we introduced the new set of variables $\{\vec{x}_i \equiv \vec{q}_i - \vec{q}_{i+1}\}$, for $i = 1, 2, \cdots, \ell-1$. Note that since the integrand is independent of $\vec{q}_\ell$,

$$R_\ell = \frac{1}{V^{\ell-1}} \int \cdots \int d^3\vec{x}_1 d^3\vec{x}_2 \cdots d^3\vec{x}_{\ell-1} \mathcal{V}(\vec{x}_1) \mathcal{V}(\vec{x}_2) \cdots \mathcal{V}\left(-\sum_{i=1}^{\ell-1} \vec{x}_i \right).$$

Using the inverse Fourier transform

$$\mathcal{V}(\vec{q}) = \frac{1}{(2\pi)^3} \int d^3\vec{\omega} \cdot \tilde{\mathcal{V}}(\vec{\omega}) e^{-i\vec{q} \cdot \vec{\omega}},$$

the integral becomes

$$R_\ell = \frac{1}{(2\pi)^{3\ell} V^{\ell-1}} \int \cdots \int d^3\vec{x}_1 \cdots d^3\vec{x}_{\ell-1} \tilde{\mathcal{V}}(\vec{\omega}_1) e^{-i\vec{\omega}_1 \cdot \vec{x}_1} \tilde{\mathcal{V}}(\vec{\omega}_2) e^{-i\vec{\omega}_2 \cdot \vec{x}_2}$$

$$\cdots \tilde{\mathcal{V}}(\vec{\omega}_\ell) \exp\left(-i \sum_{k=1}^{\ell-1} \vec{\omega}_\ell \cdot \vec{x}_k \right) d^3\vec{\omega}_1 \cdots d^3\vec{\omega}_\ell.$$

Since

$$\int \frac{d^3\vec{q}}{(2\pi)^3} e^{-i\vec{\omega} \cdot \vec{q}} = \delta^3(\vec{\omega}),$$

we have

$$R_\ell = \frac{1}{(2\pi)^3 V^{\ell-1}} \int \cdots \int \left(\prod_{k=1}^{\ell-1} \delta(\vec{\omega}_k - \vec{\omega}_\ell) \tilde{\mathcal{V}}(\vec{\omega}_k) d^3\vec{\omega}_k \right) d^3\vec{\omega}_\ell,$$

resulting finally in

$$R_\ell = \frac{1}{V^{\ell-1}} \int \frac{d^3\vec{\omega}}{(2\pi)^3} \tilde{\mathcal{V}}(\vec{\omega})^\ell.$$

(c) Show that the number of ring graphs generated in $\left\langle \mathcal{U}_Q^\ell \right\rangle_c^0$ is

$$S_\ell = \frac{N!}{(N-\ell)!} \times \frac{(\ell-1)!}{2} \approx \frac{(\ell-1)!}{2} N^\ell.$$

• The number of rings graphs generated in $\left\langle \mathcal{U}_Q^\ell \right\rangle_c^0$ is given by the product of the number of ways to choose ℓ particles out of a total of N,

$$\frac{N!}{(N-\ell)!}.$$

multiplied by the number of ways to arrange the ℓ particles in a ring

$$\frac{\ell!}{2\ell}.$$

The numerator is the number of ways of distributing the ℓ labels on the ℓ points of the ring. This overcounts by the number of equivalent arrangements that appear in the denominator. The factor of $1/2$ comes from the equivalence of clockwise and counterclockwise arrangements (reflection), and there are ℓ equivalent choices for the starting point of the ring (rotations). Hence

$$S_\ell = \frac{N!}{(N-\ell)!} \times \frac{\ell!}{2\ell} = \frac{N!}{(N-\ell)!} \times \frac{(\ell-1)!}{2}.$$

For $N \gg \ell$, we can approximate $N(N-1)\cdots(N-\ell+1) \approx N^\ell$, and

$$S_\ell \approx \frac{(\ell-1)!}{2} N^\ell.$$

Another way to justify this result is by induction: A ring of length $\ell+1$ can be created from a ring of ℓ links by inserting an additional point in between any of the existing ℓ nodes. Hence $S_{\ell+1} = S_\ell \times (N-\ell-1) \times \ell$, leading to the above result, when starting with $S_2 = N(N-1)/2$.

(d) Show that the contribution of the ring diagrams can be summed as

$$\ln Z_{\text{rings}} = \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{(-\beta)^\ell}{\ell!} S_\ell R_\ell$$

$$\approx \ln Z_0 + \frac{V}{2} \int_0^\infty \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \left[\left(\frac{\kappa}{\omega}\right)^2 - \ln\left(1 + \frac{\kappa^2}{\omega^2}\right) \right],$$

where $\kappa = \sqrt{\beta e^2 N/V}$ is the inverse Debye screening length.

(*Hint:* Use $\ln(1+x) = -\sum_{\ell=1}^{\infty}(-x)^{\ell}/\ell$.)

- The contribution of the ring diagrams is summed as

$$
\begin{aligned}
\ln Z_{\text{rings}} &= \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{(-\beta)^{\ell}}{\ell!} S_{\ell} R_{\ell} \\
&= \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{(-\beta)^{\ell}}{\ell!} \frac{(\ell-1)!}{2} N^{\ell} \frac{1}{V^{\ell-1}} \int \frac{d^3\vec{\omega}}{(2\pi)^3} \tilde{\mathcal{V}}(\vec{\omega})^{\ell} \\
&= \ln Z_0 + \frac{V}{2} \int_0^{\infty} \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \sum_{\ell=2}^{\infty} \frac{1}{\ell} \left(-\frac{\beta N}{V}\tilde{\mathcal{V}}(\omega) \right)^{\ell} \\
&= \ln Z_0 + \frac{V}{2} \int_0^{\infty} \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \sum_{\ell=2}^{\infty} \frac{1}{\ell} \left(-\frac{\beta N e^2}{V \omega^2} \right)^{\ell} \\
&= \ln Z_0 + \frac{V}{2} \int_0^{\infty} \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \left[\frac{\beta N e^2}{V \omega^2} - \ln\left(1 + \frac{\beta N e^2}{V \omega^2}\right) \right],
\end{aligned}
$$

where we have used $\ln(1+x) = -\sum_{\ell=1}^{\infty}(-x)^{\ell}/\ell$. Finally, substituting $\kappa = \sqrt{\beta e^2 N/V}$, leads to

$$
\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{2} \int_0^{\infty} \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \left[\left(\frac{\kappa}{\omega}\right)^2 - \ln\left(1 + \frac{\kappa^2}{\omega^2}\right) \right].
$$

(e) The integral in the previous part can be simplified by changing variables to $x = \kappa/\omega$, and performing integration by parts. Show that the final result is

$$
\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{12\pi} \kappa^3 \quad .
$$

- Changing variables to $x = \kappa/\omega$, and integrating the integrand by parts, gives

$$
\begin{aligned}
\int_0^{\infty} \omega^2 d\omega \left[\left(\frac{\kappa}{\omega}\right)^2 - \ln\left(1 + \frac{\kappa^2}{\omega^2}\right) \right] &= \kappa^3 \int_0^{\infty} \frac{dx}{x^4} \left[x^2 - \ln(1+x^2) \right] \\
&= \frac{\kappa^3}{3} \int_0^{\infty} \frac{dx}{x^3} \left[2x - \frac{2x}{1+x^2} \right] = \frac{2\kappa^3}{3} \int_0^{\infty} \frac{dx}{1+x^2} = \frac{\pi\kappa^3}{3},
\end{aligned}
$$

resulting in

$$
\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{4\pi^2} \cdot \frac{\pi\kappa^3}{3} = \ln Z_0 + \frac{V}{12\pi}\kappa^3.
$$

(f) Calculate the correction to pressure from the above ring diagrams.

- The correction to the ideal gas pressure due to the Debye–Hückel approximation is

$$P = k_B T \left(\left. \frac{\partial \ln Z_{\text{rings}}}{\partial V} \right|_{T,N} \right)$$

$$= P_0 + k_B T \left. \frac{\partial}{\partial V} \left(\frac{V \kappa^3}{12\pi} \right) \right|_{T,N} = P_0 - \frac{k_B T}{24\pi} \kappa^3$$

$$= P_0 - \frac{k_B T}{24\pi} \left(\frac{e^2 N}{k_B T V} \right)^{3/2}.$$

Note that the correction to the ideal gas behavior is non-analytic, and cannot be expressed by a virial series. This is due to the long range nature of the Coulomb interaction.

(g) We can introduce an effective potential $\overline{V}(\vec{q} - \vec{q}')$ between two particles by integrating over the coordinates of all the other particles. This is equivalent to an expectation value that can be calculated perturbatively in a cumulant expansion. If we include only the loop-less diagrams (the analog of the rings) between the particles, we have

$$\overline{V}(\vec{q} - \vec{q}') = V(\vec{q} - \vec{q}') + \sum_{\ell=1}^{\infty} (-\beta N)^\ell \int \frac{d^3 \vec{q}_1}{V} \cdots \frac{d^3 \vec{q}_\ell}{V} \, \mathcal{V}(\vec{q} - \vec{q}_1) \mathcal{V}(\vec{q}_1 - \vec{q}_2) \cdots \mathcal{V}(\vec{q}_\ell - \vec{q}').$$

Show that this sum leads to the screened Coulomb interaction $\overline{V}(\vec{q}) = \exp(-\kappa|\vec{q}|)/(4\pi|\vec{q}|)$.

- Introducing the effective potential $\overline{\mathcal{V}}(\vec{q} - \vec{q}')$, and summing over the loop–less diagrams gives

$$\overline{\mathcal{V}}(\vec{q} - \vec{q}') = \mathcal{V}(\vec{q} - \vec{q}') + \sum_{\ell=1}^{\infty} (-\beta N)^\ell \int \frac{d^3 \vec{q}_1}{V} \cdots \frac{d^3 \vec{q}_\ell}{V} \mathcal{V}(\vec{q} - \vec{q}_1) \mathcal{V}(\vec{q}_1 - \vec{q}_2) \cdots \mathcal{V}(\vec{q}_\ell - \vec{q}')$$

$$= \mathcal{V}(\vec{q} - \vec{q}') - \beta N \int \frac{d^3 \vec{q}_1}{V} \mathcal{V}(\vec{q} - \vec{q}_1) \mathcal{V}(\vec{q}_1 - \vec{q}')$$

$$+ (\beta N)^2 \int \frac{d^3 \vec{q}_1}{V} \frac{d^3 \vec{q}_2}{V} \mathcal{V}(\vec{q} - \vec{q}_1) \mathcal{V}(\vec{q}_1 - \vec{q}_2) \mathcal{V}(\vec{q}_2 - \vec{q}') - \cdots.$$

Using the changes of notation

$$\vec{x}_1 \equiv \vec{q}, \quad \vec{x}_2 \equiv \vec{q}', \quad \vec{x}_3 \equiv \vec{q}_1, \quad \vec{x}_4 \equiv \vec{q}_2, \quad \cdots \quad \vec{x}_\ell \equiv \vec{q}_\ell,$$

$$\mathcal{V}_{12} \equiv \mathcal{V}(\vec{x}_1 - \vec{x}_2), \quad \text{and} \quad n \equiv N/V,$$

we can write

$$\overline{\mathcal{V}}_{12} = \mathcal{V}_{12} - \beta n \int d^3 \vec{x}_3 \mathcal{V}_{13} \mathcal{V}_{32} + (\beta n)^2 \int d^3 \vec{x}_3 d^3 \vec{x}_4 \mathcal{V}_{13} \mathcal{V}_{34} \mathcal{V}_{42} - \cdots.$$

Using the inverse Fourier transform (as in part (a)), and the notation $\vec{x}_{ij} \equiv \vec{x}_i - \vec{x}_j$,

$$\overline{\mathcal{V}}_{12} = \mathcal{V}_{12} - \beta n \int \frac{d^3\vec{x}_3}{(2\pi)^6} \tilde{\mathcal{V}}(\vec{\omega}_{13}) \tilde{\mathcal{V}}(\vec{\omega}_{32}) e^{-i(\vec{x}_{13}\cdot\vec{\omega}_{13} + \vec{x}_{32}\cdot\vec{\omega}_{32})} d^3\vec{\omega}_{13} d^3\vec{\omega}_{32} + \cdots,$$

and employing the delta function, as in part (a)

$$\overline{\mathcal{V}}_{12} = \mathcal{V}_{12} - \beta n \int \frac{d^3\vec{\omega}_{13} d^3\vec{\omega}_{32}}{(2\pi)^3} \delta^3\left(\vec{\omega}_{13} - \vec{\omega}_{32}\right) \tilde{\mathcal{V}}(\vec{\omega}_{13}) \tilde{\mathcal{V}}(\vec{\omega}_{32}) \exp[\vec{x}_1 \cdot \vec{\omega}_{13} - \vec{x}_2 \cdot \vec{\omega}_{32}] + \cdots$$

$$= \mathcal{V}_{12} - \beta n \int \frac{d^3\vec{\omega}}{(2\pi)^3} \left[\tilde{\mathcal{V}}(\vec{\omega})\right]^2 \exp[\vec{\omega} \cdot \vec{x}_{12}] + \cdots.$$

Generalizing this result and dropping the subscript such that $\vec{x} \equiv \vec{x}_{12}$,

$$\overline{\mathcal{V}}_{12} = \mathcal{V}_{12} + \sum_{\ell=1}^{\infty} \frac{(-\beta n)^\ell}{(2\pi)^3} \int \left[\tilde{\mathcal{V}}(\vec{\omega})\right]^{\ell+1} e^{i\vec{x}\cdot\vec{\omega}} d^3\vec{\omega}.$$

Finally, including the Fourier transform of the direct potential (first term), gives

$$\overline{\mathcal{V}}_{12} = \sum_{\ell=0}^{\infty} \int \frac{d^3\vec{\omega}}{(2\pi)^3} (-\beta n)^\ell \frac{e^{2\ell+2}}{\omega^{2\ell+2}} e^{i\vec{x}\cdot\vec{\omega}} = \sum_{\ell=0}^{\infty} \int \frac{d^3\vec{\omega}}{(2\pi)^3} \frac{(-1)^\ell e^2 \kappa^{2\ell}}{\omega^{2\ell+2}} e^{ix\omega\cos\theta}$$

$$= \int_0^\infty d\omega \sum_{\ell=0}^{\infty} \frac{(-1)^\ell e^2}{2\pi^2} \left(\frac{\kappa}{\omega}\right)^{2\ell} \int_{-1}^{1} e^{ix\omega\cos\theta} d\cos\theta$$

$$= \int_0^\infty d\omega \frac{e^2}{2\pi^2} \frac{2\sin x\omega}{x\omega} \sum_{\ell=0}^{\infty} (-1)^\ell \left(\frac{\kappa}{\omega}\right)^{2\ell}.$$

Setting $y \equiv \omega/\kappa$, gives

$$\overline{\mathcal{V}}_{12} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{e^2}{2\pi^2} \kappa \frac{e^{ix\kappa y} - e^{-ix\kappa y}}{2ix\kappa y} \frac{-1}{y^2+1} dy.$$

Intergrating in the complex plane, via the residue theorem, gives

$$\overline{\mathcal{V}}_{12} = \frac{e^2}{4\pi^2} \left(\frac{e^{-\kappa x}}{2x} + \frac{e^{-\kappa x}}{2x}\right) \cdot \pi = \frac{e^2 e^{-\kappa x}}{4\pi x}.$$

Recalling our original notation, $x = |\vec{q} - \vec{q}'| \equiv |\vec{q}|$, we obtain the screened Coulomb potential

$$\overline{\mathcal{V}}(\vec{q}) = \frac{e^2}{4\pi} \frac{e^{-\kappa|\vec{q}|}}{|\vec{q}|}.$$

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2. *Virial coefficients:* Consider a gas of particles in d-dimensional space interacting through a pair-wise central potential, $\mathcal{V}(r)$, where

$$\mathcal{V}(r) = \begin{cases} +\infty & \text{for } 0 < r < a, \\ -\varepsilon & \text{for } a < r < b, \\ 0 & \text{for } b < r < \infty. \end{cases}$$

(a) Calculate the second virial coefficient $B_2(T)$, and comment on its high and low temperature behaviors.

• The second virial coefficient is obtained from

$$B_2 \equiv -\frac{1}{2} \int d^d r_{12} \left\{ \exp[-\beta\mathcal{V}(r_{12})] - 1 \right\},$$

where $r_{12} \equiv |\vec{r}_1 - \vec{r}_2|$, as

$$B_2 = -\frac{1}{2} \left[\int_0^a d^d r_{12}(-1) + \int_a^b d^d r_{12} \left(e^{\beta\varepsilon} - 1 \right) \right]$$

$$= -\frac{1}{2} \left\{ V_d(a)(-1) + [V_d(b) - V_d(a)] \cdot [\exp(\beta\varepsilon) - 1] \right\},$$

where

$$V_d(r) = \frac{S_d}{d} r^d = \frac{2\pi^{d/2}}{d\,(d/2 - 1)!} r^d,$$

is the volume of a d–dimensional sphere of radius r. Thus,

$$B_2(T) = \frac{1}{2} V_d(b) - \frac{1}{2} \exp(\beta\varepsilon) \left[V_d(b) - V_d(a) \right].$$

For high temperatures $\exp(\beta\varepsilon) \approx 1 + \beta\varepsilon$, and

$$B_2(T) \approx \frac{1}{2} V_d(a) - \frac{\beta\varepsilon}{2} \left[V_d(b) - V_d(a) \right].$$

At the highest temperatures, $\beta\varepsilon \ll 1$, the hard-core part of the potential is dominant, and

$$B_2(T) \approx \frac{1}{2} V_d(a).$$

For low temperatures $\beta \gg 1$, the attractive component takes over, and

$$B_2 = -\frac{1}{2} \left\{ V_d(a)(-1) + [V_d(b) - V_d(a)] \cdot [\exp(\beta\varepsilon) - 1] \right\}$$

$$\approx -\frac{1}{2} \left[V_d(b) - V_d(a) \right] \exp(\beta\varepsilon),$$

resulting in $B_2 < 0$.

(b) Calculate the first correction to isothermal compressibility

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_{T,N}.$$

• The isothermal compressibility is defined by

$$\kappa_T \equiv -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_{T,N}.$$

From the expansion

$$\frac{P}{k_B T} = \frac{N}{V} + \frac{N^2}{V^2}B_2,$$

for constant temperature and particle number, we get

$$\frac{1}{k_B T}dP = -\frac{N}{V^2}dV - 2B_2\frac{N^2}{V^3}dV.$$

Thus

$$\frac{\partial V}{\partial P}\bigg|_{T,N} = -\frac{1}{k_B T}\frac{1}{N/V^2 + 2B_2 N^2/V^3} = -\frac{V^2}{Nk_B T}\left(\frac{1}{1 + 2B_2 N/V}\right),$$

and

$$\kappa_T = \frac{V}{Nk_B T}\left(\frac{1}{1 + 2B_2 N/V}\right) \approx \frac{V}{Nk_B T}\left(1 - 2B_2\frac{N}{V}\right).$$

(c) In the high temperature limit, reorganize the equation of state into the van der Waals form, and identify the van der Waals parameters.

• Including the correction introduced by the second virial coefficient, the equation of state becomes

$$\frac{PV}{Nk_B T} = 1 + \frac{N}{V}B_2(T).$$

Using the expression for B_2 in the high temperature limit,

$$\frac{PV}{Nk_B T} = 1 + \frac{N}{2V}\left\{V_d(a) - \beta\varepsilon[V_d(b) - V_d(a)]\right\},$$

and

$$P + \frac{N^2}{2V^2}\varepsilon[V_d(b) - V_d(a)] = k_B T\frac{N}{V}\left(1 + \frac{N}{2V}V_d(a)\right).$$

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Using the variable $n = N/V$, and noting that for low concentrations

$$1 + \frac{n}{2} V_d(a) \approx \left(1 - \frac{n}{2} V_d(a)\right)^{-1} = V \left(V - \frac{N}{2} V_d(a)\right)^{-1},$$

the equation of state becomes

$$\left(P + \frac{n^2 \varepsilon}{2} \left[V_d(b) - V_d(a)\right]\right) \cdot \left(V - \frac{N}{2} V_d(a)\right) = N k_B T.$$

This can be recast in the usual van der Waals form

$$(P - an^2) \cdot (V - Nb) = N k_B T,$$

with

$$a = \frac{\varepsilon}{2} \left[V_d(b) - V_d(a)\right], \qquad \text{and} \qquad b = \frac{1}{2} V_d(a).$$

(d) For $b = a$ (a hard sphere), and $d = 1$, calculate the third virial coefficient $B_3(T)$.

• By definition, the third virial coefficient is

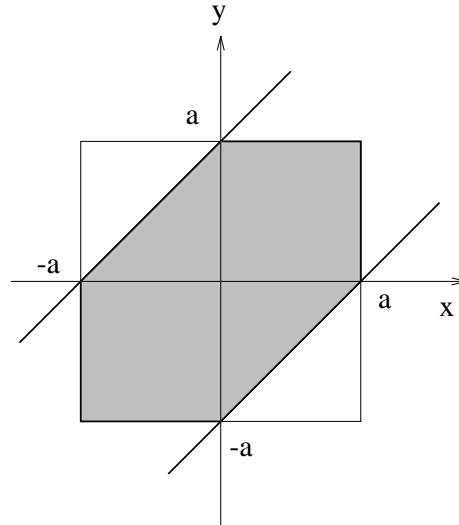$$B_3 = -\frac{1}{3} \int d^d r d^d r' f(r) f(r') f(r - r'),$$

where, for a hard core gas

$$f(r) \equiv \exp\left(-\frac{\mathcal{V}(r)}{k_B T}\right) - 1 = \begin{cases} -1 & \text{for} & 0 < r < a, \\ 0 & \text{for} & a < r < \infty \end{cases}.$$

In one–dimension, the only contributions come from $0 < r$, and $r' < a$, where $f(r) = f(r') = -1$. Using the notations $|x| \equiv r$, $|y| \equiv r'$ (i.e. $-a < x$, and $y < a$),

$$B_3 = -\frac{1}{3} \int_{-a}^{a} dx \int_{-a}^{a} dy \cdot f(x - y) = \frac{1}{3} \int \int_{-a<x,y<a,-a<x-y<a} (-1) = \frac{1}{3} \frac{6}{8} (2a)^2 = a^2,$$

where the relevant integration area is plotted below.

3. *Dieterici's equation:* A gas obeys Dieterici's equation of state:
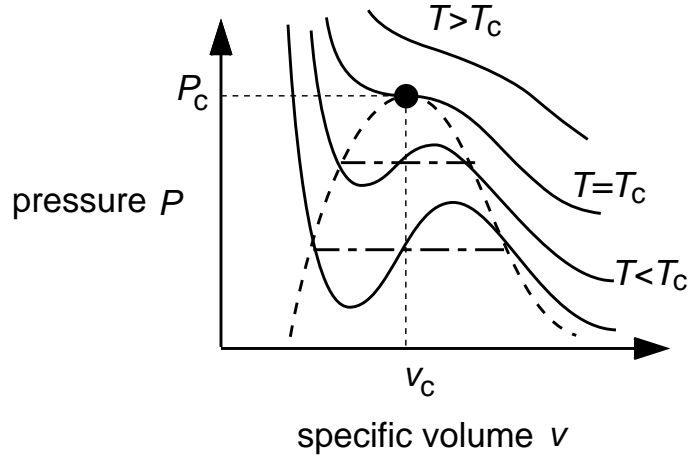
$$P(v - b) = k_B T \exp\left(-\frac{a}{k_B T v}\right),$$

where $v = V/N$.

(a) Find the ratio $Pv/k_B T$ at the critical point.

• The critical point is the point of inflection, described by

$$\left.\frac{\partial P}{\partial v}\right|_{T_c, N} = 0, \qquad \text{and} \qquad \left.\frac{\partial^2 P}{\partial v^2}\right|_{T_c, N} = 0.$$

The first derivative of P is

$$\left.\frac{\partial P}{\partial v}\right|_{T_c, N} = \frac{\partial}{\partial v}\left[\frac{k_B T}{v - b}\exp\left(-\frac{a}{k_B T v}\right)\right] = \frac{k_B T}{v - b}\exp\left(-\frac{a}{k_B T v}\right)\left(\frac{a}{k_B T v^2} - \frac{1}{v - b}\right)$$

$$= P\left(\frac{a}{k_B T v^2} - \frac{1}{v - b}\right),$$

while a second derivative gives

$$\left.\frac{\partial^2 P}{\partial v^2}\right|_{T_c, N} = \frac{\partial}{\partial v}\left[P\left(\frac{a}{k_B T v^2} - \frac{1}{v - b}\right)\right]$$

$$= \frac{\partial P}{\partial v}\left(\frac{a}{k_B T v^2} - \frac{1}{v - b}\right) - P\left(\frac{2a}{k_B T v^3} - \frac{1}{(v - b)^2}\right).$$

Therefore v_c and T_c are determined by

$$\frac{a}{k_B T_c v_c^2} - \frac{1}{v_c - b} = 0, \qquad \text{and} \qquad \frac{2a}{k_B T_c v_c^3} - \frac{1}{(v_c - b)^2} = 0,$$

with the solutions

$$v_c = 2b, \qquad \text{and} \qquad k_B T_c = \frac{a}{4b}.$$

The critical pressure is

$$P_c = \frac{k_B T_c}{v_c - b} \exp\left(-\frac{a}{k_B T_c v_c}\right) = \frac{a}{4b^2} e^{-2},$$

resulting in the ratio

$$\frac{P_c v_c}{k_B T_c} = 2e^{-2} \approx 0.27.$$

Note that for the van der Waals gas

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} = 0.375,$$

while for some actual gases

$$\left(\frac{P_c v_c}{k_B T_c}\right)_{\text{water}} = 0.230, \qquad \text{and} \qquad \left(\frac{P_c v_c}{k_B T_c}\right)_{\text{Argon}} = 0.291.$$

(b) Calculate the isothermal compressibility κ_T for $v = v_c$ as a function of $T - T_c$.

- The isothermal compressibility is defined by

$$\kappa_T \equiv -\frac{1}{v} \left.\frac{\partial v}{\partial P}\right|_{T,N},$$

and from part (a), given by

$$\left.\frac{\partial P}{\partial v}\right|_{T_c,N} = P\left(\frac{a}{k_B T v^2} - \frac{1}{v - b}\right).$$

Expanding this expression, at $v = v_c$, in terms of $t \equiv k_B T - k_B T_c$ (for $T > T_c$), yields

$$\left.\frac{\partial P}{\partial v}\right|_{T_c,N} \approx P_c\left(\frac{a}{(a/4b + t)\, 4b^2} - \frac{1}{b}\right) \approx -\frac{P_c}{b}\frac{4bt}{a} = -\frac{2P_c}{v_c k_B T_c}t,$$

and thus

$$\kappa_T = \frac{k_B T_c}{2P_c}\frac{1}{t} = \frac{be^2}{2k_B(T - T_c)}.$$

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Note that expanding any analytic equation of state will yield the same simple pole for the divergence of the compressibility.

(c) On the critical isotherm expand the pressure to the lowest non-zero order in $(v - v_c)$.

• Perform a Taylor–series expansion along the critical isotherm $T = T_c$, as

$$P(v, T_c) = P_c + \left.\frac{\partial P}{\partial v}\right|_{T_c,v_c} (v - v_c) + \frac{1}{2!} \left.\frac{\partial^2 P}{\partial v^2}\right|_{T_c,v_c} (v - v_c)^2 + \frac{1}{3!} \left.\frac{\partial^3 P}{\partial v^3}\right|_{T_c,v_c} (v - v_c)^3 + \cdots.$$

The first two terms are zero at the critical point, and

$$
\begin{aligned}
\left.\frac{\partial^3 P}{\partial v^3}\right|_{T_c,v_c} &= -P_c \frac{\partial}{\partial v} \left(\frac{2a}{k_B T_c v^3} - \frac{1}{(v - b)^2} \right) \\
&= -P_c \left(\frac{6a}{k_B T_c v_c^4} - \frac{2}{(v_c - b)^3} \right) \\
&= -\frac{P_c}{2b^3}.
\end{aligned}
$$

Substituting this into the Taylor expansion for $P(v, T_c)$, results in

$$P(v, T_c) = P_c \left(1 - \frac{(v - v_c)^3}{12b^3} \right),$$

which is equivalent to

$$\frac{P}{P_c} - 1 = -\frac{2}{3} \left(\frac{v}{v_c} - 1 \right)^3.$$

****

4. *Two dimensional Coulomb gas:* Consider a classical mixture of N positive, and N negative charged particles in a *two dimensional* box of area $A = L \times L$. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{2N} \frac{\vec{p}_i{}^2}{2m} - \sum_{i<j}^{2N} c_i c_j \ln |\vec{q}_i - \vec{q}_j| \quad,$$

where $c_i = +c_0$ for $i = 1, \cdots N$, and $c_i = -c_0$ for $i = N + 1, \cdots 2N$, denote the charges of the particles; $\{\vec{q}_i\}$ and $\{\vec{p}_i\}$ their coordinates and momenta respectively.

(a) Note that in the interaction term each pair appears only once, and that there is no self interaction $i = j$. How many pairs have repulsive interactions, and how many have attractive interactions?

- There are N positively charged particles, and N negatively charged particles. Hence there are $N \cdot N = N^2$ pairs of opposite charges, and $n_{\text{attractive}} = N^2$. For like charges, we can choose pairs from the N particles of positive charge, or from the N particles with negative charges. Hence the number of pairs of like pairs is

$$n_{\text{repulsive}} = 2 \times \binom{N}{2} = 2 \times \frac{N!}{2!(N-2)!} = N(N-1).$$

(b) Write down the expression for the partition function $Z(N, T, A)$ in terms of integrals over $\{\vec{q}_i\}$ and $\{\vec{p}_i\}$. Perform the integrals over the momenta, and rewrite the contribution of the coordinates as a product involving powers of $\{\vec{q}_i\}$, using the identity $e^{\ln x} = x$.

- The partition function is

$$Z(N, T, A) = \frac{1}{(N!)^2 h^{4N}} \int \prod_{i=1}^{2N} d^2\vec{q}_i d^2\vec{p}_i \exp\left[-\beta \sum_{i=1}^{2N} \frac{p_i^2}{2m} + \beta \sum_{i<j} c_i c_j \ln |\vec{q}_i - \vec{q}_j| \right]$$

$$= \frac{1}{\lambda^{4N}(N!)^2} \int \prod_{i=1}^{2N} d^2\vec{q}_i \exp\left[\beta \ln |\vec{q}_i - \vec{q}_j|^{c_i c_j} \right],$$

where $\lambda = h/\sqrt{2\pi m k_B T}$. Further simplifying the expression for the partition function

$$Z(N, T, A) = \frac{1}{\lambda^{4N}(N!)^2} \int \prod_{i=1}^{2N} d^2\vec{q}_i \prod_{i<j} |\vec{q}_i - \vec{q}_j|^{\beta c_i c_j},$$

where we have used the fact that $e^{\ln x} = x$.

(c) Although it is not possible to perform the integrals over $\{\vec{q}_i\}$ exactly, the dependence of Z on A can be obtained by the simple rescaling of coordinates, $\vec{q}_i{}' = \vec{q}_i/L$. Use the results in parts (a) and (b) to show that $Z \propto A^{2N - \beta c_0^2 N/2}$.

- The only length scale appearing in the problem is set by the system size L. Rescaling the expression using $\vec{q}_i{}' = \vec{q}_i/L$, then yields

$$Z(N, T, A) = \frac{1}{\lambda^{4N}(N!)^2} \int \prod_{i=1}^{2N} \left(L^2 d^2\vec{q}_i{}' \right) \prod_{i<j} L^{\beta c_i c_j} |\vec{q}_i{}' - \vec{q}_j{}'|^{\beta c_i c_j}.$$

Note that there are N^2 terms for which the interaction is attractive ($\beta c_i c_j = -\beta c_0^2$), and $N(N-1)$ terms for which the interaction is repulsive ($\beta c_i c_j = \beta c_0^2$). Thus

$$Z(N, T, A) = L^{4N} \cdot L^{\beta c_0^2 N(N-1)} \cdot L^{-\beta c_0^2 N^2} \frac{1}{\lambda^{4N}(N!)^2} \int \prod_{i=1}^{2N} d^2\vec{q}_i{}' \prod_{i<j} |\vec{q}_i{}' - \vec{q}_j{}'|^{\beta c_i c_j}$$

$$= L^{4N - \beta N c_0^2} Z_0(N, T, A' = L'^2 = 1) \propto A^{2N - \beta c_0^2 N/2},$$

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since $A = L^2$.

(d) Calculate the two dimensional pressure of this gas, and comment on its behavior at high and low temperatures.

• The pressure is then calculated from

$$P = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial A}\bigg|_{N,T} = k_B T \frac{\partial}{\partial A} \ln\left(A^{2N - \beta c_0^2 N/2} Z_0\right)$$

$$= k_B T \left(2N - \beta c_0^2 N/2\right) \frac{\partial}{\partial A} \ln A = \frac{2N k_B T}{A} - \frac{N c_0^2}{2A}.$$

At high temperatures,

$$P = \frac{2N k_B T}{A},$$

which is the ideal gas behavior for $2N$ particles. The pressure becomes negative at temperature below

$$T_c^0 = \frac{c_0^2}{4k_B},$$

which is unphysical, indicating the collapse of the particles due to their attractions.

(e) The unphysical behavior at low temperatures is avoided by adding a hard–core which prevents the coordinates of any two particles from coming closer than a distance a. The appearance of two length scales a and L, makes the scaling analysis of part (c) questionable. By examining the partition function for $N = 1$, obtain an estimate for the temperature T_c at which the short distance scale a becomes important in calculating the partition function, invalidating the result of the previous part. What are the phases of this system at low and high temperatures?

• A complete collapse of the system (to a single point) can be avoided by adding a hard core repulsion which prevents any two particles from coming closer than a distance a. The partition function for two particles (i.e. $N = 1$) is now given by

$$Z(N = 1, T, A) = \frac{1}{\lambda^4} \int d^2\vec{q}_1 d^2\vec{q}_2 \cdot |\vec{q}_1 - \vec{q}_2|^{-\beta c_0^2}.$$

To evaluate this integral, first change to center of mass and relative coordinates

$$\begin{cases} \vec{Q} = \frac{1}{2}(\vec{q}_1 + \vec{q}_2), \\ \vec{q} = \vec{q}_1 - \vec{q}_2. \end{cases}$$

Integrating over the center of mass gives

$$Z(N = 1, T, A) = \frac{A}{\lambda^4} \int d^2\vec{q} \, q^{-\beta c_0^2} \approx \frac{2\pi A}{\lambda^4} \int_a^L dq \cdot q^{1-\beta c_0^2}$$

$$= \frac{2\pi A}{\lambda^4} \left. \frac{q^{2-\beta c_0^2}}{2 - \beta c_0^2} \right|_a^L = \frac{2\pi A}{\lambda^4} \frac{L^{2-\beta c_0^2} - a^{2-\beta c_0^2}}{2 - \beta c_0^2}.$$

If $2 - \beta c_0^2 < 0$, as $L \to \infty$,

$$Z \approx \frac{2\pi A}{\lambda^4} \frac{a^{2-\beta c_0^2}}{2 - \beta c_0^2},$$

is controlled by the short distance cutoff a; while if $2 - \beta c_0^2 > 0$, the integral is controlled by the system size L, as assumed in part (c). Hence the critical temperature can be estimated by $\beta c_0^2 = 2$, giving

$$T_c = \frac{c_0^2}{2k_B},$$

which is larger than T_c^0 by a factor of 2. Thus the unphysical collapse at low temperatures is preempted at the higher temperature where the hard cores become important. The high temperature phase $(T > T_c)$ is a dissociated plasma; while the low temperature phase is a gas of paired dipoles.

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5. *Exact solutions for a one dimensional gas:* In statistical mechanics, there are very few systems of interacting particles that can be solved *exactly*. Such exact solutions are very important as they provide a check for the reliability of various approximations. A one dimensional gas with short-range interactions is one such solvable case.

(a) Show that for a potential with a hard core that screens the interactions from further neighbors, the Hamiltonian for N particles can be written as

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=2}^{N} \mathcal{V}(x_i - x_{i-1}).$$

The (indistinguishable) particles are labelled with coordinates $\{x_i\}$ such that

$$0 \le x_1 \le x_2 \le \cdots \le x_N \le L,$$

where L is the length of the box confining the particles.

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- Each particle i interacts only with adjacent particles $i - 1$ and $i + 1$, as the hard cores from these nearest neighbors screen the interactions with any other particle. Thus we need only consider nearest neighbor interactions, and, included the kinetic energies, the Hamiltonian is given by

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=2}^{N} \mathcal{V}(x_i - x_{i-1}), \qquad \text{for} \qquad 0 \le x_1 \le x_2 \le \cdots x_N \le L.$$

(b) Write the expression for the partition function $Z(T, N, L)$. Change variables to $\delta_1 = x_1$, $\delta_2 = x_2 - x_1$, $\cdots$, $\delta_N = x_N - x_{N-1}$, and carefully indicate the allowed ranges of integration and the constraints.

- The partition function is

$$Z(T, N, L) = \frac{1}{h^N} \int_0^L dx_1 \int_{x_1}^L dx_2 \cdots \int_{x_{N-1}}^L dx_N \exp\left[-\beta \sum_{i=2}^{N} \mathcal{V}(x_i - x_{i-1})\right]$$

$$\cdot \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_N \exp\left[-\beta \sum_{i=1}^{N} N \frac{p_i^2}{2m}\right]$$

$$= \frac{1}{\lambda^N} \int_0^L dx_1 \int_{x_1}^L dx_2 \cdots \int_{x_{N-1}}^L dx_N \exp\left[-\beta \sum_{i=2}^{N} \mathcal{V}(x_i - x_{i-1})\right],$$

where $\lambda = h/\sqrt{2\pi m k_B T}$. (Note that there is no $N!$ factor, as the ordering of the particles is specified.) Introducing a new set of variables

$$\delta_1 = x_1, \quad \delta_2 = x_2 - x_1, \quad \cdots \quad \delta_n = x_N - x_{N-1},$$

or equivalently

$$x_1 = \delta_1, \quad x_2 = \delta_1 + \delta_2, \quad \cdots \quad x_N = \sum_{i=1}^{N} \delta_i,$$

the integration becomes

$$Z(T, N, L) = \frac{1}{\lambda^N} \int_0^L d\delta_1 \int_0^{L - \delta_1} d\delta_2 \int_0^{L - (\delta_1 + \delta_2)} d\delta_3 \cdots \int_0^{L - \sum_{i=1}^{N} \delta_i} d\delta_N e^{-\beta \sum_{i=2}^{N} \mathcal{V}(\delta_i)}.$$

This integration can also be expressed as

$$Z(T, N, L) = \frac{1}{\lambda^N} \left[\int d\delta_1 d\delta_2 \cdots d\delta_N\right]' \exp\left[-\beta \sum_{i=2}^{N} \mathcal{V}(\delta_i)\right],$$

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with the constraint

$$0 \leq \sum_{i=1}^{N} \delta_i \leq L.$$

This constraint can be put into the equation explicitly with the use of the step function

$$\Theta(x) = \begin{cases} 0 & \text{for} & x < 0 \\ 1 & \text{for} & x \geq 0 \end{cases},$$

as

$$Z(T, N, L) = \frac{1}{\lambda^N} \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \exp\left[-\beta \sum_{i=2}^{N} \mathcal{V}(\delta_i)\right] \Theta\left(L - \sum_{i=1}^{N} \delta_i\right).$$

(c) Consider the Gibbs partition function obtained from the Laplace transformation

$$\mathcal{Z}(T, N, P) = \int_0^\infty dL \exp(-\beta P L) Z(T, N, L),$$

and by extremizing the integrand find the standard formula for P in the canonical ensemble.

• The Gibbs partition function is

$$\mathcal{Z}(T, N, P) = \int_0^\infty dL \exp(-\beta P L) Z(T, N, L).$$

The saddle point is obtained by extremizing the integrand with respect to L,

$$\frac{\partial}{\partial L} \exp(-\beta P L) Z(T, N, L) \Big|_{T,N} = 0,$$

which implies that

$$\beta P = \frac{\partial}{\partial L} \ln Z(T, N, L) \Big|_{T,N}, \qquad \implies \qquad P = k_B T \frac{\partial \ln Z}{\partial L} \Big|_{T,N}.$$

From thermodynamics, for a one–dimensional gas we have

$$dF = -SdT - PdL, \qquad \implies \qquad P = -\frac{\partial F}{\partial L} \Big|_{T,N}.$$

Further noting that

$$F = -k_B T \ln Z,$$

again results in

$$P_{\text{canonical}} = k_B T \left. \frac{\partial \ln Z}{\partial L} \right|_{T,N}.$$

(d) Change variables from L to $\delta_{N+1} = L - \sum_{i=1}^{N} \delta_i$, and find the expression for $\mathcal{Z}(T, N, P)$ as a product over one-dimensional integrals over each δ_i.

• The expression for the partition function given above is

$$Z(T, N, L) = \frac{1}{\lambda^N} \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \exp\left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i)\right] \Theta\left(L - \sum_{i=1}^N \delta_i\right).$$

The Laplace transform of this equation is

$$\mathcal{Z}(T, N, P) = \frac{1}{\lambda^N} \int_0^\infty dL \exp(-\beta PL) \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N$$

$$\cdot \exp\left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i)\right] \Theta\left(L - \sum_{i=1}^N \delta_i\right)$$

$$= \frac{1}{\lambda^N \beta P} \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \exp\left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i)\right] \exp\left[-\beta P \left(\sum_{i=1}^N \delta_1\right)\right]$$

$$= \frac{1}{\lambda^N (\beta P)^2} \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \exp\left\{-\sum_{i=2}^N [\beta \mathcal{V}(\delta_i) + \beta P \delta_i]\right\}.$$

Since the integrals for different $\delta_i's$ are equivalent, we obtain

$$\mathcal{Z}(T, N, P) = \frac{1}{\lambda^N (\beta P)^2} \left\{\int_0^\infty d\delta \exp\left[-\beta \left(\mathcal{V}(\delta) + P\delta\right)\right]\right\}^{N-1}.$$

This expression can also be obtained directly, without use of the step function as follows.

$$\mathcal{Z}(T, N, P) = \frac{1}{\lambda^N} \int_0^L d\delta_1 \int_0^{L-\delta_1} d\delta_2 \int_0^{L-(\delta_1+\delta_2)} d\delta_3 \cdots \int_0^{L-\sum_{i=1}^N \delta_i} d\delta_N$$

$$\cdot \int_0^\infty dL \exp\left[-\beta PL - \beta \left(\sum_{i=2}^N \mathcal{V}(\delta)\right)\right]$$

$$= \frac{1}{\lambda^N} \int_0^L d\delta_1 \int_0^{L-\delta_1} d\delta_2 \cdots \int_0^{L-\sum_{i=1}^N \delta_i} d\delta_N \int_{-\sum_{i=1}^N \delta_i}^\infty d\left(L - \sum_{i=1}^N \delta_i\right)$$

$$\cdot \exp\left\{-\beta P\left[\sum_{i=1}^N \delta_i + \left(L - \sum_{i=1}^N \delta_i\right)\right] - \beta \left(\sum_{i=2}^N \mathcal{V}(\delta_i)\right)\right\}.$$

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Change variables to $\delta_{N+1} \equiv L - \sum_{i=1}^{N} \delta_i$, and note that each of the $\delta's$ indicates the distance between neighboring particles. The size of the gas L, has been extended to any value, hence each δ can be varied independently from 0 to ∞. Thus the Gibbs partition function is

$$
\mathcal{Z}(T, N, P) = \frac{1}{\lambda^N} \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \int_0^\infty d\delta_{N+1}
$$

$$
\cdot \exp\left[-\beta P \left(\sum_{i=1}^{N+1} \delta_i \right) - \beta \left(\sum_{i=2}^{N} \mathcal{V}(\delta_i) \right) \right]
$$

$$
= \frac{1}{\lambda^N} \left(\int_0^\infty d\delta \cdot \exp\left[-\beta\mathcal{V}(\delta) - \beta P \delta \right] \right)^{N-1} \int_0^\infty d\delta_1 \exp(-\beta P \delta_1)
$$

$$
\cdot \int_0^\infty d\delta_{N+1} \exp(-\beta P \delta_{N+1})
$$

$$
= \frac{1}{\lambda^N (\beta P)^2} \left\{ \int_0^\infty d\delta \exp\left[-\beta \left(\mathcal{V}(\delta) + P \delta \right) \right] \right\}^{N-1}.
$$

(e) At a fixed pressure P, find expressions for the mean length $L(T, N, P)$, and the density $n = N/L(T, N, P)$ (involving ratios of integrals which should be easy to interpret).

- The mean length is

$$
L(T, N, P) = -k_B T \left. \frac{\partial}{\partial(\beta P)} \ln \mathcal{Z}(T, N, P) \right|_{T,N}
$$

$$
= \frac{2}{\beta P} + (N-1) \frac{\int_0^\infty d\delta \cdot \delta \cdot \exp\left[-\beta\mathcal{V}(\delta) - \beta P \delta \right]}{\int_0^\infty d\delta \cdot \exp\left[-\beta\mathcal{V}(\delta) - \beta P \delta \right]},
$$

and the density n is given by

$$
n = \frac{N}{L(T, N, P)} = N \left\{ \frac{2k_B T}{P} + (N-1) \frac{\int_0^\infty d\delta \cdot \delta \cdot \exp\left[-\beta \left(\mathcal{V}(\delta) - P \delta \right) \right]}{\int_0^\infty d\delta \cdot \exp\left[-\beta \left(\mathcal{V}(\delta) - P \delta \right) \right]} \right\}^{-1}.
$$

Note that for an ideal gas $\mathcal{V}_{\text{i.g.}}(\delta) = 0$, and

$$
L_{\text{i.g.}}(T, N, P) = \frac{(N+1)k_B T}{P},
$$

leading to

$$
n(p)_{\text{i.g.}} = \frac{N}{N+1} \frac{P}{k_B T}.
$$

Since the expression for $n(T, P)$ in part (e) is continuous and non-singular for any choice of potential, there is in fact no condensation transition for the one-dimensional gas. By contrast, the approximate van der Waals equation (or the mean-field treatment) incorrectly predicts such a transition.

(f) For a hard sphere gas, with minimum separation a between particles, calculate the equation of state $P(T, n)$. Compare the excluded volume factor with the approximate result obtained in earlier problems, and also obtain the general virial coefficient $B_\ell(T)$.

- For a hard sphere gas

$$\delta_i \geq a, \qquad \text{for} \qquad i = 2, 3, \cdots, N,$$

the Gibbs partition function is

$$\mathcal{Z}(T, N, P) = \frac{1}{\lambda^N (\beta P)^2} \left[\int_a^\infty d\delta \exp\left(-\beta \mathcal{V}(\delta) - \beta P \delta\right) \right]^{N-1}$$

$$= \frac{1}{\lambda^N (\beta P)^2} \left[\int_a^\infty d\delta \exp\left(-\beta P \delta\right) \right]^{N-1}$$

$$= \frac{1}{\lambda^N} \left(\frac{1}{\beta P} \right)^{N+1} \exp\left(-\beta P a\right)^{N-1}.$$

From the partition function, we can calculate the mean length

$$L = -k_B T \left. \frac{\partial \ln \mathcal{Z}}{\partial P} \right|_{T,N} = \frac{(N+1)k_B T}{P} + (N-1)a,$$

which after rearrangement yields

$$\beta P = \frac{(N+1)}{L - (N-1)a} = \frac{n + 1/L}{1 - (n - 1/L)a} \approx (n + 1/l)(1 + (n - 1/L)a + (n - 1/L)^2 a^2 + \cdots).$$

For $N \gg 1$, $n \gg 1/L$, and

$$\beta P \approx n(1 + na + n^2 a^2 + \cdots) = n + an^2 + a^2 n^3 + \cdots,$$

which gives the virial coefficients

$$B_\ell(T) = a^{\ell-1}.$$

The value of $B_3 = a^2$ agrees with the result obtained in an earlier problem. Also note that the exact 'excluded volume' is $(N-1)a$, as opposed to the estimate of $Na/2$ used in deriving the van der Waals equation.

6. *The Manning transition:* When ionic polymers (polyelectrolytes) such as DNA are immersed in water, the negatively charged *counter-ions* go into solution, leaving behind a positively charged polymer. Because of the electrostatic repulsion of the charges left behind, the polymer stretches out into a cylinder of radius a, as illustrated in the figure. While thermal fluctuations tend to make the ions wander about in the solvent, electrostatic attractions favor their return and condensation on the polymer. If the number of counter-ions is N, they interact with the N positive charges left behind on the rod through the potential $\phi(r) = -2(Ne/L)\ln(r/L)$, where r is the radial coordinate in a cylindrical geometry. If we ignore the Coulomb repulsion between counter-ions, they can be described by the classical Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m} + 2e^2 n\ln\left(\frac{r}{L}\right)\right],$$

where $n = N/L$.
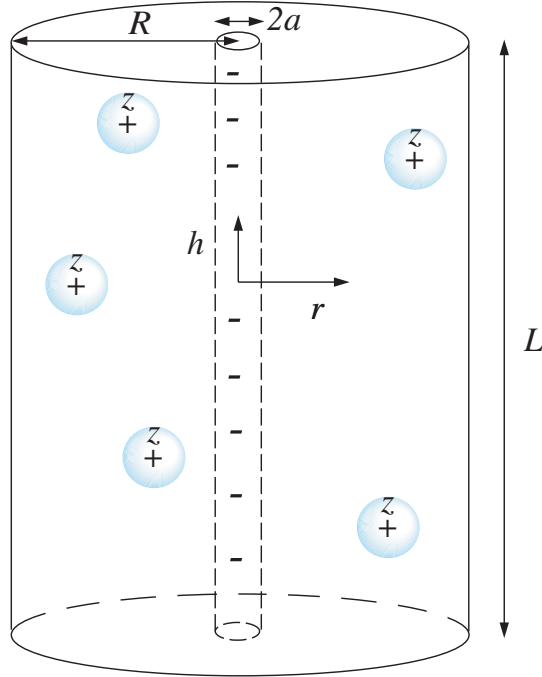
(a) For a cylindrical container of radius R, calculate the canonical partition function Z in terms of temperature T, density n, and radii R and a.

• The canonical partition function is

$$Z = \int \frac{\prod_i d^3p_i d^3q_i}{N!h^{3N}} \exp\left\{-\beta \sum_{i=1}^{N}\left[\frac{p_i^2}{2m} + 2e^2 n \ln\left(\frac{r}{L}\right)\right]\right\}$$

$$= \left(\frac{2\pi Le}{N\lambda^3}\right)^N L^{N\cdot\beta 2e^2 n}\left[\int_a^R rdr \cdot r^{-2e^2 n/k_B T}\right]^N$$

$$= \left(\frac{2\pi e}{n\lambda^3}\right)^N L^{2Ne^2 n\beta}\left[\frac{R^{2\left(1-e^2 n/k_B T\right)} - a^{2\left(1-e^2 n/k_B T\right)}}{2\left(1 - e^2 n/k_B T\right)}\right]^N.$$

(b) Calculate the probability distribution function $p(r)$ for the radial position of a counter-ion, and its first moment $\langle r \rangle$, the average radial position of a counter-ion.

• Integrating out the unspecified N momenta and $N - 1$ positions from the canonical distribution, one obtains the distribution function

$$p(r) = \frac{re^{-\left(2e^2 n/k_B T\right)\ln(r/L)}}{\int_a^R dr re^{-(2e^2 n/k_B T)\ln(r/L)}} = 2\left(1 - \frac{e^2 n}{k_B T}\right)\frac{r^{1-2e^2 n/k_B T}}{R^{2(1-e^2 n/k_B T)} - a^{2(1-e^2 n/k_B T)}}.$$

(Note the normalization condition $\int_a^R dr p(r) = 1$.) The average position is then

$$\langle r \rangle = \int_a^R rp(r)\,dr = \left(\frac{2k_B T - 2e^2 n}{3k_B T - 2e^2 n}\right)\left(\frac{R^{3-2e^2 n/k_B T} - a^{3-2e^2 n/k_B T}}{R^{2-2e^2 n/k_B T} - a^{2-2e^2 n/k_B T}}\right).$$

(c) The behavior of the results calculated above in the limit $R \gg a$ is very different at high and low temperatures. Identify the transition temperature, and characterize the nature of the two phases. In particular, how does $\langle r \rangle$ depend on R and a in each case?

• Consider first low temperatures, such that $e^2 n/k_B T > 1$. In the $R \gg a$ limit, the distribution function becomes

$$p(r) = 2\left(1 - \frac{e^2 n}{k_B T}\right)\frac{r^{1-2e^2 n/k_B T}}{a^{2(1-e^2 n/k_B T)}},$$

and $\langle r \rangle \propto a$. To see this, either examine the above calculated average $\langle r \rangle$ in the $R \gg a$ limit, or notice that

$$p(r)\,dr = 2\left(1 - \frac{e^2 n}{k_B T}\right)x^{1-2e^2 n/k_B T}dx,$$

where $x = r/a$, immediately implying $\langle r \rangle \propto a$ (as $\int_1^\infty dx x^{1-2e^2 n/k_B T} < \infty$ if $e^2 n/k_B T > 1$). On the other hand, at high temperatures ($e^2 n/k_B T < 1$), the distribution function reduces to

$$p(r) = 2\left(1 - \frac{e^2 n}{k_B T}\right)\frac{r^{1-2e^2 n/k_B T}}{R^{2(1-e^2 n/k_B T)}},$$

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and $\langle r \rangle \propto R$, from similar arguments. Thus, at temperature $T_c = e^2 n / k_B$ there is a transition from a "condensed" phase, in which the counter-ions are stuck on the polymer, to a "gas" phase, in which the counter-ions fluctuate in water at typical distances from the polymer which are determined by the container size.

(d) Calculate the pressure exerted by the counter-ions on the wall of the container, at $r = R$, in the limit $R \gg a$, at all temperatures.

• The work done by the counter-ions to expand the container from a radius R to a radius $R + dR$ is

$$dW = dF = (\text{force}) \, dR = -P \, (2\pi R L) \, dR,$$

leading to

$$P = -\frac{1}{2\pi R L} \frac{\partial F}{\partial R} = \frac{k_B T}{2\pi R L} \frac{\partial \ln Z}{\partial R}.$$

At low temperatures, $T < T_c$, the pressure vanishes, since the partition function is independent of R in the limit $R \gg a$. At $T > T_c$, the above expression results in

$$P = \frac{k_B T}{2\pi R L} 2N \left(1 - \frac{e^2 n}{k_B T} \right) \frac{1}{R},$$

i.e.

$$PV = N k_B T \left(1 - \frac{e^2 n}{k_B T} \right).$$

(e) The character of the transition examined in part (d) is modified if the Coulomb interactions between counter-ions are taken into account. An approximate approach to the interacting problem is to allow a fraction N_1 of counter-ions to condense along the polymer rod, while the remaining $N_2 = N - N_1$ fluctuate in the solvent. The free counter-ions are again treated as non-interacting particles, governed by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + 2e^2 n_2 \ln \left(\frac{r}{L} \right) \right],$$

where $n_2 = N_2 / L$. *Guess* the equilibrium number of non-interacting ions, N_2^*, and justify your guess by discussing the response of the system to slight deviations from N_2^*. (This is a qualitative question for which no new calculations are needed.)

• Consider a deviation (n_2) from $n_2^* \equiv N_2^* / V \equiv k_B T / e^2$, occuring at a temperature lower than T_c (*i.e.* $e^2 n / k_B T > 1$). If $n_2 > n_2^*$, the counter-ions have a tendency to condensate (since $e^2 n / k_B T > 1$), thus decreasing n_2. On the other hand, if $n_2 > n_2^*$, the counter-ions tend to "evaporate" (since $e^2 n / k_B T < 1$). In both cases, the system drives the density n_2

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to the (equilibrium) value of $n_2^* = k_B T/e^2$. If the temperature is higher than T_c, clearly $n_2^* = n$ and there is no condensation.

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7. *Hard rods:* A collection of N asymmetric molecules in two dimensions may be modeled as a gas of rods, each of length $2l$ and lying in a plane. A rod can move by translation of its center of mass and rotation about latter, as long as it does not encounter another rod. Without treating the hard-core interaction exactly, we can incorporate it approximately by assuming that the rotational motion of each rod is restricted (by the other rods) to an angle θ, which in turn introduces an excluded volume $\Omega(\theta)$ (associated with each rod). The value of θ is then calculated self consistently by maximizing the entropy at a given density $n = N/V$, where V is the total accessible area.
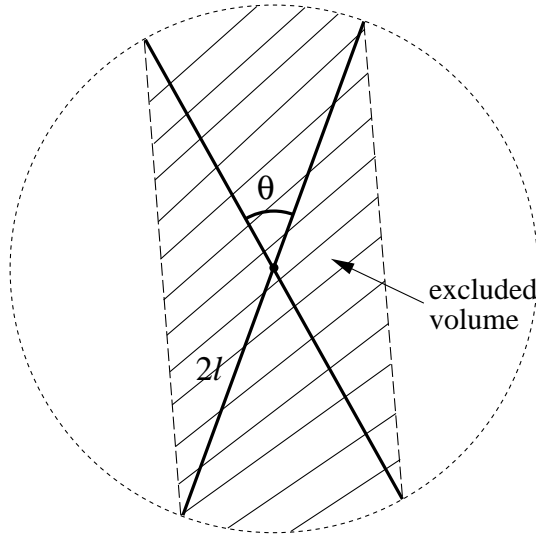
(a) Write down the entropy of such a collection of rods in terms of N, n, Ω, and $A(\theta)$, the phase space volume associated to the rotational freedom of a *single* rod. (You may ignore the momentum contributions throughout, and consider the large N limit.)

• Including both forms of entropy, translational and rotational, leads to

$$S = k_B \ln \left[\frac{1}{N!} \left(V - \frac{N\Omega(\theta)}{2} \right)^N A(\theta)^N \right] \approx N k_B \left[\ln \left(n^{-1} - \frac{\Omega(\theta)}{2} \right) + 1 + \ln A(\theta) \right].$$

(b) Extremizing the entropy as a function of θ, relate the density to Ω, A, and their derivatives Ω', A'; express your result in the form $n = f(\Omega, A, \Omega', A')$.

• The extremum condition $\partial S/\partial\theta = 0$ is equivalent to

$$\frac{\Omega'}{2n^{-1} - \Omega} = \frac{A'}{A},$$

where primes indicate derivatives with respect to θ. Solving for the density gives

$$n = \frac{2A'}{\Omega A' + \Omega' A}.$$

(c) Express the excluded volume Ω in terms of θ and sketch f as a function of $\theta \in [0, \pi]$, assuming $A \propto \theta$.
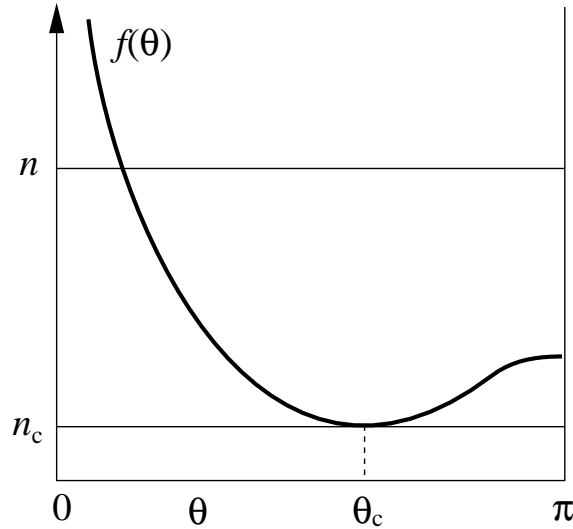
• Elementary geometry yields

$$\Omega = l^2 \left(\theta + \sin\theta\right),$$

so that the equilibrium condition becomes

$$n = f\left(\theta\right) = \frac{2}{l^2}\left[\theta\left(2 + \cos\theta\right) + \sin\theta\right]^{-1},$$

with the function $f(\theta)$ plotted below:

(d) Describe the equilibrium state at high densities. Can you identify a phase transition as the density is decreased? Draw the corresponding critical density n_c on your sketch. What is the critical angle θ_c at the transition? You don't need to calculate θ_c explicitly, but give an (implicit) relation defining it. What value does θ adopt at $n < n_c$?

• At high densities, $\theta \ll 1$ and the equilibrium condition reduces to

$$N \approx \frac{V}{2\theta l^2};$$

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the angle θ is as open as allowed by the close packing. The equilibrium value of θ increases as the density is decreased, up to its "optimal" value θ_c at n_c, and $\theta(n < n_c) = \theta_c$. The transition occurs at the minimum of $f(\theta)$, whence θ_c satisfies

$$\frac{d}{d\theta}\left[\theta(2 + \cos\theta) + \sin\theta\right] = 0,$$

i.e.

$$2(1 + \cos\theta_c) = \theta_c \sin\theta_c.$$

Actually, the above argument tracks the stability of a local maximum in entropy (as density is varied) which becomes unstable at θ_c. There is another entropy maximum at $\theta = \pi$, corresponding to freely rotating rods, which becomes more advantageous (i.e. the global equilibrium state) at a density slightly below θ_c.

****

8. *Surfactant condensation:* N surfactant molecules are added to the surface of water over an area A. They are subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p_i}^{\,2}}{2m} + \frac{1}{2}\sum_{i,j}\mathcal{V}(\vec{r_i} - \vec{r_j}),$$

where $\vec{r_i}$ and $\vec{p_i}$ are two dimensional vectors indicating the position and momentum of particle i. (This simple form ignores the couplings to the fluid itself. The actual kientic and potential energies are more complicated.)

(a) Write down the expression for the partition function $Z(N, T, A)$ in terms of integrals over $\vec{r_i}$ and $\vec{p_i}$, and perform the integrals over the momenta.

• The partition function is obtained by integrating the Boltzmann weight over phase space, as

$$Z(N, T, A) = \int \frac{\prod_{i=1}^{N} d^2\vec{p_i}\,d^2\vec{q_i}}{N!h^{2N}}\exp\left[-\beta\sum_{i=1}^{N}\frac{p_i^2}{2m} - \beta\sum_{i<j}\mathcal{V}(\vec{q_i} - \vec{q_j})\right],$$

with $\beta = 1/(k_B T)$. The integrals over momenta are simple Gaussians, yielding

$$Z(N, T, A) = \frac{1}{N!}\frac{1}{\lambda^{2N}}\int\prod_{i=1}^{N}d^2\vec{q_i}\exp\left[-\beta\sum_{i<j}\mathcal{V}(\vec{q_i} - \vec{q_j})\right],$$

where as usual $\lambda = h/\sqrt{2\pi m k_B T}$ denotes the thermal wavelength.

The inter–particle potential $\mathcal{V}(\vec{r})$ is infinite for separations $|\vec{r}| < a$, and attractive for $|\vec{r}| > a$ such that $\int_a^\infty 2\pi r dr \mathcal{V}(r) = -u_0$.

(b) Estimate the total non–excluded area available in the positional phase space of the system of N particles.

• To estimate the joint phase space of particles with excluded areas, add them to the system one by one. The first one can occupy the whole area A, while the second can explore only $A - 2\Omega$, where $\Omega = \pi a^2$. Neglecting three body effects (i.e. in the dilute limit), the area available to the third particle is $(A - 2\Omega)$, and similarly $(A - n\Omega)$ for the n-th particle. Hence the joint excluded volume in this dilute limit is

$$A(A - \Omega)(A - 2\Omega) \cdots (A - (N - 1)\Omega) \approx (A - N\Omega/2)^N,$$

where the last approximation is obtained by pairing terms m and $(N - m)$, and ignoring order of Ω^2 contributions to their product.

(c) Estimate the total *potential* energy of the system, within a *uniform density approximation* $n = N/A$. Using this potential energy for all configurations allowed in the previous part, write down an approximation for Z.

• Assuming a *uniform density* $n = N/A$, an average attractive potential energy, $\bar{U}$, is estimated as

$$\bar{U} = \frac{1}{2} \sum_{i,j} \mathcal{V}_{\text{attr.}}(\vec{q}_i - \vec{q}_j) = \frac{1}{2} \int d^2\vec{r}_1 d^2\vec{r}_2 \, n(\vec{r}_1) n(\vec{r}_2) \mathcal{V}_{\text{attr.}}(\vec{r}_1 - \vec{r}_2)$$

$$\approx \frac{n^2}{2} A \int d^2\vec{r} \, \mathcal{V}_{\text{attr.}}(\vec{r}) \equiv -\frac{N^2}{2A} u_0.$$

Combining the previous results gives

$$Z(N, T, A) \approx \frac{1}{N!} \frac{1}{\lambda^{2N}} (A - N\Omega/2)^N \exp\left[\frac{\beta u_0 N^2}{2A}\right].$$

(d) The surface tension of water without surfactants is σ_0, approximately independent of temperature. Calculate the surface tension $\sigma(n, T)$ in the presence of surfactants.

• Since the work done is changing the surface area is $dW = \sigma dA$, we have $dF = -TdS + \sigma dA + \mu dN$, where $F = -k_B T \ln Z$ is the free energy. Hence, the contribution of the surfactants to the surface tension of the film is

$$\sigma_s = -\frac{\partial \ln Z}{\partial A}\bigg|_{T,N} = -\frac{N k_B T}{A - N\Omega/2} + \frac{u_0 N^2}{2A^2},$$

which is a two-dimensional variant of the familiar van der Waals equation. Adding the (constant) contribution in the absence of surfactants gives

$$\sigma(n, T) = \sigma_0 - \left.\frac{\partial \ln Z}{\partial A}\right|_{T,N} = -\frac{Nk_BT}{A - N\Omega/2} + \frac{u_0 N^2}{2A^2}.$$

(e) Show that below a certain temperature, T_c, the expression for σ is manifestly incorrect. What do you think happens at low temperatures?

• Thermodynamic stability requires $\delta\sigma\delta A \geq 0$, i.e. σ must be a monotonically increasing function of A at any temperature. This is the case at high temperatures where the first term in the equation for σ_s dominates, but breaks down at low temperatures when the term from the attractive interactions becomes significant. The critical temperature is obtained by the usual conditions of $\partial\sigma_s/\partial A = \partial^2\sigma_s/\partial A^2 = 0$, i.e. from

$$\begin{cases} \left.\dfrac{\partial\sigma_s}{\partial A}\right|_T = \dfrac{Nk_BT}{(A - N\Omega/2)^2} - \dfrac{u_0 N^2}{A^3} = 0 \\ \left.\dfrac{\partial^2\sigma_s}{\partial A^2}\right|_T = -\dfrac{2Nk_BT}{(A - N\Omega/2)^3} + \dfrac{3u_0 N^2}{A^4} = 0 \end{cases},$$

The two equations are simultaneously satisfied for $A_c = 3N\Omega/2$, at a temperature

$$T_c = \frac{8u_0}{27k_B\Omega}.$$

As in the van der Waals gas, at temperatures below T_c, the surfactants separate into a high density (liquid) and a low density (gas) phase.

(f) Compute the heat capacities, C_A and write down an expression for C_σ without explicit evaluation, due to the surfactants.

• The contribution of the surfactants to the energy of the film is given by

$$E_s = -\frac{\partial \ln Z}{\partial \beta} = 2N \times \frac{k_BT}{2} - \frac{u_0 N^2}{2A}.$$

The first term is due to the kinetic energy of the surfactants, while the second arises from their (mean-field) attraction. The heat capacities are then calculated as

$$C_A = \left.\frac{dQ}{dT}\right|_A = \left.\frac{\partial E}{\partial T}\right|_A = Nk_B,$$

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and

$$C_\sigma = \left.\frac{dQ}{dT}\right|_\sigma = \left.\frac{\partial E}{\partial T}\right|_\sigma - \sigma\left.\frac{\partial A}{\partial T}\right|_\sigma.$$

****

9. *Critical point behavior:* The pressure P of a gas is related to its density $n = N/V$, and temperature T by the truncated expansion

$$P = k_B T n - \frac{b}{2}n^2 + \frac{c}{6}n^3 \quad,$$

where b and c are assumed to be *positive* temperature independent constants.

(a) Locate the critical temperature T_c below which this equation must be invalid, and the corresponding density n_c and pressure P_c of the critical point. Hence find the ratio $k_B T_c n_c/P_c$.

• Mechanical stability of the gas requires that any spontaneous change in volume should be opposed by a compensating change in pressure. This corresponds to $\delta P \delta V < 0$, and since $\delta n = -(N/V^2)\delta V$, any equation of state must have a pressure that is an increasing function of density. The transition point between pressure isotherms that are monotonically increasing functions of n, and those that are not (hence manifestly incorrect) is obtained by the usual conditions of $dP/dn = 0$ and $d^2P/dn^2 = 0$. Starting from the cubic equation of state, we thus obtain

$$\begin{aligned}\frac{dP}{dn} &= k_B T_c - bn_c + \frac{c}{2}n_c^2 = 0 \\ \frac{d^2 P}{dn^2} &= -b + cn_c = 0\end{aligned}.$$

From the second equation we obtain $n_c = b/c$, which substituted in the first equation gives $k_B T_c = b^2/(2c)$. From the equation of state we then find $P_c = b^3/(6c^2)$, and the dimensionless ratio of

$$\frac{k_B T_c n_c}{P_c} = 3.$$

(b) Calculate the isothermal compressibility $\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$, and sketch its behavior as a function of T for $n = n_c$.

• Using $V = N/n$, we get

$$\kappa_T(n) = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T = \frac{1}{n}\left.\frac{\partial P}{\partial n}\right|_T^{-1} = \left[n\left(k_B T - bn + cn^2/2\right)\right]^{-1}.$$

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For $n = n_c$, $\kappa_T(n_c) \propto (T - T_c)^{-1}$, and diverges at T_c.

(c) On the critical isotherm give an expression for $(P - P_c)$ as a function of $(n - n_c)$.

• Using the coordinates of the critical point computed above, we find

$$
\begin{aligned}
P - P_c &= -\frac{b^3}{6c^2} + \frac{b^2}{2c}n - \frac{b}{2}n^2 + \frac{c}{6}n^3 \\
&= \frac{c}{6}\left(n^3 - 3\frac{b}{c}n^2 + 3\frac{b^2}{c^2}n - \frac{b^3}{c^3}\right) \\
&= \frac{c}{6}\left(n - n_c\right)^3.
\end{aligned}
$$

(d) The instability in the isotherms for $T < T_c$ is avoided by phase separation into a liquid of density n_+ and gas of density n_-. For temperatures close to T_c, these densities behave as $n_\pm \approx n_c\,(1 \pm \delta)$. Using a Maxwell construction, or otherwise, find an implicit equation for $\delta(T)$, and indicate its behavior for $(T_c - T) \to 0$. (Hint: Along an isotherm, variations of chemical potential obey $d\mu = dP/n$.)

• According to the Gibbs–Duhem relation, the variations of the intensive variables are related by $SdT - VdP + Nd\mu = 0$, and thus along an isotherm $(dT = 0)$ $d\mu = dP/n = \partial P/\partial n|_T dn/n$. Since the liquid and gas states are in coexistence they should have the same chemical potential. Integrating the above expression for $d\mu$ from n_- to n_+ leads to the so-called Maxwell construction, which reads

$$
0 = \mu(n_+) - \mu(n_-) = \int_{n_-}^{n_+} \frac{dP}{n} = \int_{n_c(1-\delta)}^{n_c(1+\delta)} dn \left(\frac{k_B T - bn + cn^2/2}{n}\right).
$$

Performing the integrals gives the equation

$$
0 = k_B T \ln\left(\frac{1+\delta}{1-\delta}\right) - bn_c(2\delta) + \frac{c}{4}n_c^2\left[(1+\delta)^2 - (1-\delta)^2\right] = k_B T \ln\left(\frac{1+\delta}{1-\delta}\right) - 2k_B T_c\delta,
$$

where for the find expression, we have used $n_c = b/c$ and $k_B T_c = b^2/(2c)$. The implicit equation for δ is thus

$$
\delta = \frac{T}{2T_c}\ln\left(\frac{1+\delta}{1-\delta}\right) \approx \frac{T}{T_c}\left(\delta - \delta^3 + \cdots\right).
$$

The leading behavior as $(T_c - T) \to 0$ is obtained by keeping up to the cubic term, and given by

$$
\delta \approx \sqrt{1 - \frac{T_c}{T}}.
$$

10. *The binary alloy:* A binary alloy (as in β brass) consists of N_A atoms of type A, and N_B atoms of type B. The atoms form a simple cubic lattice, each interacting only with its six nearest neighbors. Assume an attractive energy of $-J$ $(J > 0)$ between like neighbors $A - A$ and $B - B$, but a repulsive energy of $+J$ for an $A - B$ pair.

(a) What is the minimum energy configuration, or the state of the system at zero temperature?

• The minimum energy configuration has as little A-B bonds as possible. Thus, at zero temperature atoms A and B *phase separate*, e.g. as indicated below.
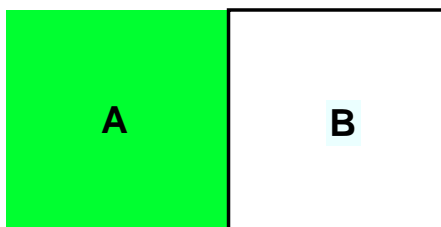
(b) Estimate the total interaction energy assuming that the atoms are randomly distributed among the N sites; i.e. each site is occupied independently with probabilities $p_A = N_A/N$ and $p_B = N_B/N$.

• In a mixed state, the average energy is obtained from

$$E = (\text{number of bonds}) \times (\text{average bond energy})$$
$$= 3N \cdot \left(-Jp_A^2 - Jp_B^2 + Jp_Ap_B\right)$$
$$= -3JN \left(\frac{N_A - N_B}{N}\right)^2.$$

(c) Estimate the mixing entropy of the alloy with the same approximation. Assume $N_A, N_B \gg 1$.

• From the number of ways of randomly mixing N_A and N_B particles, we obtain the mixing entropy of

$$S = k_B \ln \left(\frac{N!}{N_A!N_B!}\right).$$

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Using Stirling's approximation for large N ($\ln N! \approx N \ln N - N$), the above expression can be written as

$$S \approx k_B \left(N \ln N - N_A \ln N_A - N_B \ln N_B \right) = -N k_B \left(p_A \ln p_A + p_B \ln p_B \right).$$

(d) Using the above, obtain a free energy function $F(x)$, where $x = (N_A - N_B)/N$. Expand $F(x)$ to the fourth order in x, and show that the requirement of convexity of F breaks down below a critical temperature T_c. For the remainder of this problem use the expansion obtained in (d) in place of the full function $F(x)$.

- In terms of $x = p_A - p_B$, the free energy can be written as

$$F = E - TS$$
$$= -3JNx^2 + k_B T \left\{ \left(\frac{1+x}{2} \right) \ln \left(\frac{1+x}{2} \right) + \left(\frac{1-x}{2} \right) \ln \left(\frac{1-x}{2} \right) \right\}.$$

Expanding about $x = 0$ to fourth order, gives

$$F \simeq -N k_B T \ln 2 + N \left(\frac{k_B T}{2} - 3J \right) x^2 + \frac{N k_B T}{12} x^4.$$

Clearly, the second derivative of F,

$$\frac{\partial^2 F}{\partial x^2} = N \left(k_B T - 6J \right) + N k_B T x^2,$$

becomes negative for T small enough. Upon decreasing the temperature, F becomes concave first at $x = 0$, at a critical temperature $T_c = 6J/k_B$.
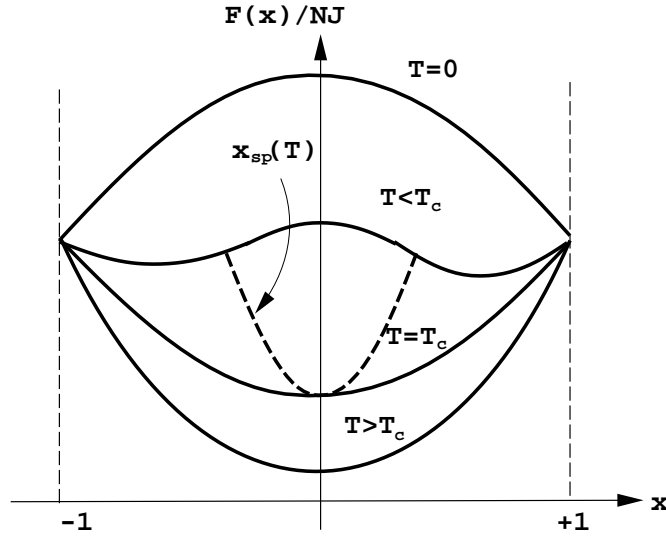
(e) Sketch $F(x)$ for $T > T_c$, $T = T_c$, and $T < T_c$. For $T < T_c$ there is a range of compositions $x < |x_{sp}(T)|$ where $F(x)$ is not convex and hence the composition is locally unstable. Find $x_{sp}(T)$.

- The function $F(x)$ is concave if $\partial^2 F/\partial x^2 < 0$, i.e. if

$$x^2 < \left(\frac{6J}{k_B T} - 1 \right).$$

This occurs for $T < T_c$, at the spinodal line given by

$$x_{sp}(T) = \sqrt{\frac{6J}{k_B T} - 1},$$

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as indicated by the dashed line in the figure below.

(f) The alloy globally minimizes its free energy by separating into A rich and B rich phases of compositions $\pm x_{eq}(T)$, where $x_{eq}(T)$ minimizes the function $F(x)$. Find $x_{eq}(T)$.

• Setting the first derivative of $dF\left(x\right)/dx = Nx\left\{(k_BT - 6J) + k_BTx^2/3\right\}$, to zero yields the equilibrium value of

$$x_{eq}\left(T\right) = \begin{cases} \pm\sqrt{3}\sqrt{\dfrac{6J}{k_BT} - 1} & \text{for } T < T_c \\ 0 & \text{for } T > T_c \end{cases} .$$

(g) In the (T, x) plane sketch the phase separation boundary $\pm x_{eq}(T)$; and the so called spinodal line $\pm x_{sp}(T)$. (The spinodal line indicates onset of metastability and hysteresis effects.)

• The spinodal and equilibrium curves are indicated in the figure above. In the interval between the two curves, the system is locally stable, but globally unstable. The formation of ordered regions in this regime requires nucleation, and is very slow. The dashed area is locally unstable, and the system easily phase separates to regions rich in A and B.

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T

T_c

$x_{sp}(T)$

$x_{eq}(T)$

unstable

meta-
stable

meta-
stable

ÿ1

1   x
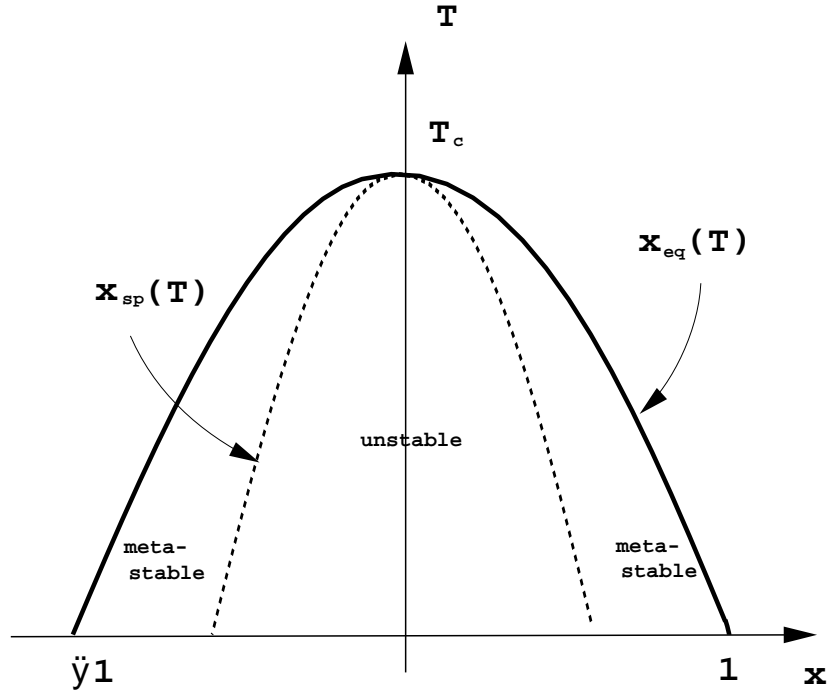
Problems for Chapter VI - Quantum Statistical Mechanics

1. *One dimensional chain:* A chain of $N+1$ particles of mass m is connected by N massless springs of spring constant K and relaxed length a. The first and last particles are held fixed at the equilibrium separation of Na. Let us denote the longitudinal displacements of the particles from their equilibrium positions by $\{u_i\}$, with $u_0 = u_N = 0$ since the end particles are fixed. The Hamiltonian governing $\{u_i\}$, and the conjugate momenta $\{p_i\}$, is

$$\mathcal{H} = \sum_{i=1}^{N-1} \frac{p_i^2}{2m} + \frac{K}{2} \left[u_1^2 + \sum_{i=1}^{N-2} (u_{i+1} - u_i)^2 + u_{N-1}^2 \right].$$

(a) Using the appropriate (sine) Fourier transforms, find the normal modes $\{\tilde{u}_k\}$, and the corresponding frequencies $\{\omega_k\}$.

• From the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N-1} \frac{p_i^2}{2m} + \frac{K}{2} \left[u_1^2 + \sum_{i=2}^{N-1} (u_i - u_{i-1})^2 + u_{N-1}^2 \right],$$

the classical equations of motion are obtained as

$$m\frac{d^2 u_j}{dt^2} = -K(u_j - u_{j-1}) - K(u_j - u_{j+1}) = K(u_{j-1} - 2u_j + u_{j+1}),$$

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for $j = 1, 2, \cdots, N-1$, and with $u_0 = u_N = 0$. In a normal mode, the particles oscillate in phase. The usual procedure is to obtain the modes, and corresponding frequencies, by diagonalizing the matrix of coefficeints coupling the displacements on the right hand side of the equation of motion. For any linear system, we have $m d^2 u_i / dt^2 = \mathcal{K}_{ij} u_j$, and we must diagonalize $\mathcal{K}_{ij}$. In the above example, $\mathcal{K}_{ij}$ is only a function of the difference $i - j$. This is a consequence of translational symmetry, and allows us to diagonalize the matrix using Fourier modes. Due to the boundary conditions in this case, the appropriate transformation involves the sine, and the motion of the j-th particle in a normal mode is given by

$$\tilde{u}_{k(n)}(j) = \sqrt{\frac{2}{N}} e^{\pm i \omega_n t} \sin\left(k(n) \cdot j\right).$$

The origin of time is arbitrary, but to ensure that $u_N = 0$, we must set

$$k(n) \equiv \frac{n\pi}{N}, \qquad \text{for} \qquad n = 1, 2, \cdots, N-1.$$

Larger values of n give wave-vectors that are simply shifted by a multiple of π, and hence coincide with one of the above normal modes. The number of normal modes thus equals the number of original displacement variables, as required. Furthermore, the amplitudes are chosen such that the normal modes are also orthonormal, i.e.

$$\sum_{j=1}^{N-1} \tilde{u}_{k(n)}(j) \cdot \tilde{u}_{k(m)}(j) = \delta_{n,m}.$$

By substituting the normal modes into the equations of motion we obtain the dispersion relation

$$\omega_n^2 = 2\omega_0^2 \left[1 - \cos\left(\frac{n\pi}{N}\right)\right] = \omega_0^2 \sin^2\left(\frac{n\pi}{2N}\right),$$

where $\omega_0 \equiv \sqrt{K/m}$.

The potential energy for each normal mode is given by

$$U_n = \frac{K}{2} \sum_{i=1}^{N} |u_i - u_{i-1}|^2 = \frac{K}{N} \sum_{i=1}^{N} \left\{ \sin\left(\frac{n\pi}{N} i\right) - \sin\left[\frac{n\pi}{N}(i-1)\right] \right\}^2$$

$$= \frac{4K}{N} \sin^2\left(\frac{n\pi}{2N}\right) \sum_{i=1}^{N} \cos^2\left[\frac{n\pi}{N}\left(i - \frac{1}{2}\right)\right].$$

Noting that

$$\sum_{i=1}^{N} \cos^2\left[\frac{n\pi}{N}\left(i - \frac{1}{2}\right)\right] = \frac{1}{2} \sum_{i=1}^{N} \left\{1 + \cos\left[\frac{n\pi}{N}(2i - 1)\right]\right\} = \frac{N}{2},$$

we have

$$U_{k(n)} = 2K \sin^2\left(\frac{n\pi}{2N}\right).$$

(b) Express the Hamiltonian in terms of the amplitudes of normal modes $\{\tilde{u}_k\}$, and evaluate the *classical* partition function. (You may integrate the $\{u_i\}$ from $-\infty$ to $+\infty$).

• Before evaluating the classical partition function, lets evaluate the potential energy by first expanding the displacement using the basis of normal modes, as

$$u_j = \sum_{n=1}^{N-1} a_n \cdot \tilde{u}_{k(n)}(j).$$

The expression for the total potential energy is

$$U = \frac{K}{2} \sum_{i=1}^{N} (u_i - u_{i-1})^2 = \frac{K}{2} \sum_{i=1}^{N} \left\{ \sum_{n=1}^{N-1} a_n \left[\tilde{u}_{k(n)}(j) - \tilde{u}_{k(n)}(j-1) \right] \right\}^2.$$

Since

$$\sum_{j=1}^{N-1} \tilde{u}_{k(n)}(j) \cdot \tilde{u}_{k(m)}(j-1) = \frac{1}{N} \delta_{n,m} \sum_{j=1}^{N-1} \left\{ -\cos\left[k(n)(2j-1) \right] + \cos k(n) \right\} = \delta_{n,m} \cos k(n),$$

the total potential energy has the equivalent forms

$$U = \frac{K}{2} \sum_{i=1}^{N} (u_i - u_{i-1})^2 = K \sum_{n=1}^{N-1} a_n^2 \left(1 - \cos k(n) \right),$$

$$= \sum_{i=1}^{N-1} a_{k(n)}^2 \varepsilon_{k(n)}^2 = 2K \sum_{i=1}^{N-1} a_{k(n)}^2 \sin^2\left(\frac{n\pi}{2N}\right).$$

The next step is to change the coordinates of phase space from u_j to a_n. The Jacobian associated with this change of variables is unity, and the classical partition function is now obtained from

$$Z = \frac{1}{\lambda^{N-1}} \int_{-\infty}^{\infty} da_1 \cdots \int_{-\infty}^{\infty} da_{N-1} \exp\left[-2\beta K \sum_{n=1}^{N-1} a_n^2 \sin^2\left(\frac{n\pi}{2N}\right) \right],$$

where $\lambda = h/\sqrt{2\pi m k_B T}$ corresponds to the contribution to the partition function from each momentum coordinate. Performing the Gaussian integrals, we obtain

$$Z = \frac{1}{\lambda^{N-1}} \prod_{n=1}^{N-1} \left\{ \int_{-\infty}^{\infty} da_n \exp\left[-2\beta K a_n^2 \sin^2\left(\frac{n\pi}{2N}\right) \right] \right\},$$

$$= \frac{1}{\lambda^{N-1}} \left(\frac{\pi k_B T}{2K}\right)^{\frac{N-1}{2}} \prod_{n=1}^{N-1} \left[\sin\left(\frac{n\pi}{2N}\right) \right]^{-1}.$$

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(c) First evaluate $\left\langle |\tilde{u}_k|^2 \right\rangle$, and use the result to calculate $\left\langle u_i^2 \right\rangle$. Plot the resulting squared displacement of each particle as a function of its equilibrium position.

• The average squared amplitude of each normal mode is

$$\left\langle a_n^2 \right\rangle = \frac{\int_{-\infty}^{\infty} da_n (a_n^2) \exp\left[-2\beta K a_n^2 \sin^2\left(\frac{n\pi}{2N}\right)\right]}{\int_{-\infty}^{\infty} da_n \exp\left[-2\beta K a_n^2 \sin^2\left(\frac{n\pi}{2N}\right)\right]}$$

$$= \left[4\beta K \sin^2\left(\frac{n\pi}{2N}\right)\right]^{-1} = \frac{k_B T}{4K} \frac{1}{\sin^2\left(\frac{n\pi}{2N}\right)}.$$

The variation of the displacement is then given by

$$\left\langle u_j^2 \right\rangle = \left\langle \left[\sum_{n=1}^{N-1} a_n \tilde{u}_n(j)\right]^2 \right\rangle = \sum_{n=1}^{N-1} \left\langle a_n^2 \right\rangle \tilde{u}_n^2(j)$$

$$= \frac{2}{N} \sum_{n=1}^{N-1} \left\langle a_n^2 \right\rangle \sin^2\left(\frac{n\pi}{N} j\right) = \frac{k_B T}{2KN} \sum_{n=1}^{N-1} \frac{\sin^2\left(\frac{n\pi}{N} j\right)}{\sin^2\left(\frac{n\pi}{2N}\right)}.$$

The evaluation of the above sum is considerably simplified by considering the combination

$$\left\langle u_{j+1}^2 \right\rangle + \left\langle u_{j-1}^2 \right\rangle - 2\left\langle u_j^2 \right\rangle = \frac{k_B T}{2KN} \sum_{n=1}^{N-1} \frac{2\cos\left[\frac{2n\pi}{N} j\right] - \cos\left[\frac{2n\pi}{N}(j+1)\right] - \cos\left[\frac{2n\pi}{N}(j-1)\right]}{1 - \cos\left(\frac{n\pi}{N}\right)}$$

$$= \frac{k_B T}{2KN} \sum_{n=1}^{N-1} \frac{2\cos\left(\frac{2n\pi}{N} j\right)\left[1 - \cos\left(\frac{n\pi}{N}\right)\right]}{1 - \cos\left(\frac{n\pi}{N}\right)} = -\frac{k_B T}{KN},$$

where we have used $\sum_{n=1}^{N-1} \cos(\pi n/N) = -1$. It is easy to check that subject to the boundary conditions of $\left\langle u_0^2 \right\rangle = \left\langle u_N^2 \right\rangle = 0$, the solution to the above recursion relation is

$$\left\langle u_j^2 \right\rangle = \frac{k_B T}{K} \frac{j(N-j)}{N}.$$

(d) How are the results modified if only the first particle is fixed $(u_0 = 0)$, while the other end is free $(u_N \neq 0)$? (Note that this is a much simpler problem as the partition function can be evaluated by changing variables to the $N-1$ spring extensions.)

• When the last particle is free, the overall potential energy is the sum of the contributions of each spring, i.e. $U = K \sum_{j=1}^{N-1} (u_j - u_{j-1})^2/2$. Thus each extension can be treated independently, and we introduce a new set of independent variables $\Delta u_j \equiv u_j - u_{j-1}$. (In
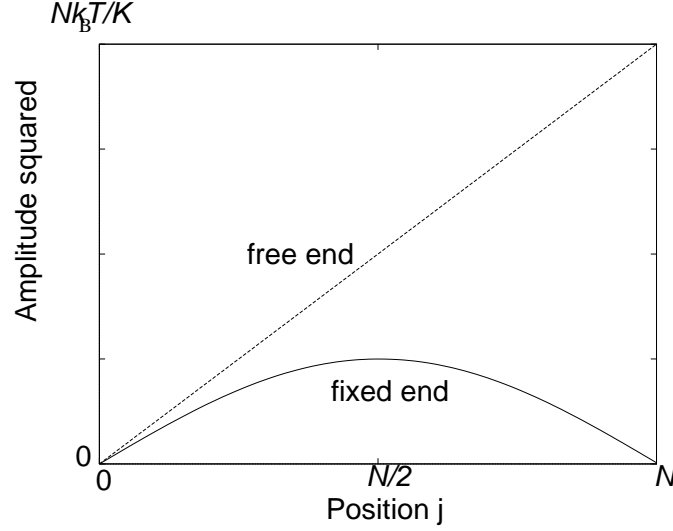
the previous case, where the two ends are fixed, these variables were not independent.) The partition function can be calculated separately for each spring as

$$Z = \frac{1}{\lambda^{N-1}} \int_{-\infty}^{\infty} du_1 \cdots \int_{-\infty}^{\infty} du_{N-1} \exp\left[-\frac{K}{2k_B T} \sum_{j=1}^{N-1} (u_j - u_{j-1})^2\right]$$

$$= \frac{1}{\lambda^{N-1}} \int_{-\infty}^{\infty} d\Delta u_1 \cdots \int_{-\infty}^{\infty} d\Delta u_{N-1} \exp\left[-\frac{K}{2k_B T} \sum_{j=1}^{N-1} \Delta u_j^2\right] = \left(\frac{2\pi k_B T}{\lambda^2 K}\right)^{(N-1)/2}.$$

For each spring extension, we have

$$\left\langle \Delta u_j^2 \right\rangle = \left\langle (u_j - u_{j-1})^2 \right\rangle = \frac{k_B T}{K}.$$

The displacement

$$u_j = \sum_{i=1}^{j} \Delta u_i,$$

is a sum of *independent* random variables, leading to the variance

$$\left\langle u_j^2 \right\rangle = \left\langle \left(\sum_{i=1}^{j} \Delta u_i\right)^2 \right\rangle = \sum_{i=1}^{j} (\Delta u_i)^2 = \frac{k_B T}{K} j.$$

The results for displacements of open and closed chains are compared in the above figure.

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2. *Black hole thermodynamics:* According to Bekenstein and Hawking, the entropy of a black hole is proportional to its area A, and given by

$$S = \frac{k_B c^3}{4G\hbar} A \quad .$$

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(a) Calculate the escape velocity at a radius R from a mass M using classical mechanics. Find the relationship between the radius and mass of a black hole by setting this escape velocity to the speed of light c. (Relativistic calculations do not modify this result which was originally obtained by Laplace.)

• The classical escape velocity is obtained by equating the gravitational energy and the kinetic energy on the surface as,

$$G\frac{Mm}{R} = \frac{mv_E^2}{2},$$

leading to

$$v_E = \sqrt{\frac{2GM}{r}}.$$

Setting the escape velocity to the speed of light, we find

$$R = \frac{2G}{c^2}M.$$

For a mass larger than given by this ratio (i.e. $M > c^2 R/2G$), nothing will escape from distances closer than R.

(b) Does entropy increase or decrease when two black holes collapse into one? What is the entropy change for the universe (in equivalent number of bits of information), when two solar mass black holes ($M_\odot \approx 2 \times 10^{30} kg$) coalesce?

• When two black holes of mass M collapse into one, the entropy change is

$$\Delta S = S_2 - 2S_1 = \frac{k_B c^3}{4G\hbar}\left(A_2 - 2A_1\right) = \frac{k_B c^3}{4G\hbar}4\pi\left(R_2^2 - 2R_1^2\right)$$

$$= \frac{\pi k_B c^3}{G\hbar}\left[\left(\frac{2G}{c^2}2M\right)^2 - 2\left(\frac{2G}{c^2}M\right)^2\right] = \frac{8\pi G k_B M^2}{c\hbar} > 0.$$

Thus the merging of black holes increases the entropy of the universe.

Consider the coalescence of two solar mass black holes. The entropy change is

$$\Delta S = \frac{8\pi G k_B M_\odot^2}{c\hbar}$$

$$\approx \frac{8\pi \cdot 6.7 \times 10^{-11}(N \cdot m^2/kg^2) \cdot 1.38 \times 10^{-23}(J/K) \cdot (2 \times 10^{30})^2 kg^2}{3 \times 10^8(m/s) \cdot 1.05 \times 10^{-34}(J \cdot s)}$$

$$\approx 3 \times 10^{54}(J/K).$$

In units of bits, the information lost is

$$N_I = \frac{\Delta S \ln 2}{k_B} = 1.5 \times 10^{77}.$$

(c) The internal energy of the black hole is given by the Einstein relation, $E = Mc^2$. Find the temperature of the black hole in terms of its mass.

● Using the thermodynamic definition of temperature $\frac{1}{T} = \frac{\partial S}{\partial E}$, and the Einstein relation $E = Mc^2$,

$$\frac{1}{T} = \frac{1}{c^2}\frac{\partial}{\partial M}\left[\frac{k_B c^3}{4G\hbar}4\pi\left(\frac{2G}{c^2}M\right)^2\right] = \frac{8\pi k_B G}{\hbar c^3}M, \qquad \Longrightarrow \qquad T = \frac{\hbar c^3}{8\pi k_B G}\frac{1}{M}.$$

(d) A "black hole" actually emits thermal radiation due to pair creation processes on its event horizon. Find the rate of energy loss due to such radiation.

● The (quantum) vacuum undergoes fluctuations in which particle–antiparticle pairs are constantly created and destroyed. Near the boundary of a black hole, sometimes one member of a pair falls into the black hole while the other escapes. This is a hand-waving explanation for the emission of radiation from black holes. The decrease in energy E of a black body of area A at temperature T is given by the Stefan-Boltzmann law,

$$\frac{1}{A}\frac{\partial E}{\partial t} = -\sigma T^4, \quad \text{where} \quad \sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}.$$

(e) Find the amount of time it takes an isolated black hole to evaporate. How long is this time for a black hole of solar mass?

● Using the result in part (d) we can calculate the time it takes a black hole to evaporate. For a black hole

$$A = 4\pi R^2 = 4\pi\left(\frac{2G}{c^2}M\right)^2 = \frac{16\pi G^2}{c^4}M^2, \quad E = Mc^2, \quad \text{and} \quad T = \frac{\hbar c^3}{8\pi k_B G}\frac{1}{M}.$$

Hence

$$\frac{d}{dt}\left(Mc^2\right) = -\frac{\pi^2 k_B^4}{60\hbar^3 c^2}\left(\frac{16\pi G^2}{c^4}M^2\right)\left(\frac{\hbar c^3}{8\pi k_B G}\frac{1}{M}\right)^4,$$

which implies that

$$M^2\frac{dM}{dt} = -\frac{\hbar c^4}{15360 G^2} \equiv -b.$$

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This can be solved to give
$$M(t) = \left(M_0^3 - 3bt \right)^{1/3} .$$

The mass goes to zero, and the black hole evaporates after a time
$$\tau = \frac{M_0^3}{3b} = \frac{5120 G^2 M \odot^3}{\hbar c^4} \approx 2.2 \times 10^{74} s,$$

which is considerably longer than the current age of the universe (approximately $\times 10^{18} s$).

(f) What is the mass of a black hole that is in thermal equilibrium with the current cosmic background radiation at $T = 2.7$K?

• The temperature and mass of a black hole are related by $M = \hbar c^3/(8\pi k_B G T)$. For a black hole in thermal equilibrium with the current cosmic background radiation at $T = 2.7°K$,

$$M \approx \frac{1.05 \times 10^{-34}(J \cdot s)(3 \times 10^8)^3(m/s)^3}{8\pi \cdot 1.38 \times 10^{-23}(J/K) \cdot 6.7 \times 10^{-11}(N \cdot m^2/kg^2) \cdot 2.7°K} \approx 4.5 \times 10^{22} kg.$$

(g) Consider a spherical volume of space of radius R. According to the recently formulated *Holographic Principle* there is a maximum to the amount of entropy that this volume of space can have, independent of its contents! What is this maximal entropy?

• The mass inside the spherical volume of radius R must be less than the mass that would make a black hole that fills this volume. Bring in additional mass (from infinity) inside the volume, so as to make a volume-filling balck hole. Clearly the entropy of the system will increase in the process, and the final entropy, which is the entropy of the black hole is larger than the initial entropy in the volume, leading to the inequality

$$S \le S_{BH} = \frac{k_B c^3}{4G\hbar} A,$$

where $A = 4\pi R^2$ is the area enclosing the volume. The surprising observation is that the upper bound on the entropy is proportional to area, whereas for any system of particles we expect the entropy to be proportional to N. This should remain valid even at very high temperatures when interactions are unimportant. The 'holographic principle' is an allusion to the observation that it appears as if the degrees of freedom are living on the surface of the system, rather than its volume. It was formulated in the context of string theory which attempts to construct a consistent theory of quantum gravity, which replaces particles as degrees of freedom, with strings.

3. *Quantum harmonic oscillator:* Consider a single harmonic oscillator with the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}, \quad \text{with} \quad p = \frac{\hbar}{i}\frac{d}{dq} \quad .$$

(a) Find the partition function Z, at a temperature T, and calculate the energy $\langle \mathcal{H} \rangle$.

• The partition function Z, at a temperature T, is given by

$$Z = \operatorname{tr}\rho = \sum_n e^{-\beta E_n}.$$

As the energy levels for a harmonic oscillator are given by

$$\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right),$$

the partition function is

$$Z = \sum_n \exp\left[-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right] = e^{-\beta\hbar\omega/2} + e^{-3\beta\hbar\omega/2} + \cdots$$

$$= \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2\sinh\left(\beta\hbar\omega/2\right)}.$$

The expectation value of the energy is

$$\langle \mathcal{H} \rangle = -\frac{\partial \ln Z}{\partial \beta} = \left(\frac{\hbar\omega}{2}\right)\frac{\cosh(\beta\hbar\omega/2)}{\sinh(\beta\hbar\omega/2)} = \left(\frac{\hbar\omega}{2}\right)\frac{1}{\tanh(\beta\hbar\omega/2)}.$$

(b) Write down the formal expression for the canonical density matrix ρ in terms of the eigenstates ($\{|n\rangle\}$), and energy levels ($\{\epsilon_n\}$) of $\mathcal{H}$.

• Using the formal representation of the energy eigenstates, the density matrix ρ is

$$\rho = 2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\left(\sum_n |n> \exp\left[-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right] <n|\right).$$

In the coordinate representation, the eigenfunctions are in fact given by

$$\langle n|q \rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{H_n(\xi)}{\sqrt{2^n n!}}\exp\left(-\frac{\xi^2}{2}\right),$$

where
$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}} q,$$

with
$$H_n(\xi) = (-1)^n \exp(\xi^2) \left(\frac{d}{d\xi}\right)^n \exp(-\xi^2)$$
$$= \frac{\exp(\xi^2)}{\pi} \int_{-\infty}^{\infty} (-2iu)^n \exp(-u^2 + 2i\xi u) du.$$

For example,
$$H_0(\xi) = 1, \quad \text{and} \quad H_1(\xi) = -\exp(\xi^2)\frac{d}{d\xi}\exp(-\xi^2) = 2\xi,$$

result in the eigenstates
$$\langle 0|q\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}q^2\right),$$

and
$$\langle 1|q\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} q \cdot \exp\left(-\frac{m\omega}{2\hbar}q^2\right).$$

Using the above expressions, the matrix elements are obtained as
$$\langle q'|\rho|q\rangle = \sum_{n,n'} \langle q'|n'\rangle \langle n'|\rho|n\rangle \langle n|q\rangle = \frac{\sum_n \exp\left[-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right] \cdot \langle q'|n\rangle \langle n|q\rangle}{\sum_n \exp\left[-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right]}$$
$$= 2\sinh\left(\frac{\beta\hbar\omega}{2}\right) \cdot \sum_n \exp\left[-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right] \cdot \langle q'|n\rangle \langle n|q\rangle.$$

(c) Show that for a general operator $A(x)$,
$$\frac{\partial}{\partial x}\exp\left[A(x)\right] \neq \frac{\partial A}{\partial x}\exp\left[A(x)\right], \quad \text{unless} \quad \left[A, \frac{\partial A}{\partial x}\right] = 0,$$

while in all cases
$$\frac{\partial}{\partial x}\operatorname{tr}\left\{\exp\left[A(x)\right]\right\} = \operatorname{tr}\left\{\frac{\partial A}{\partial x}\exp\left[A(x)\right]\right\}.$$

• By definition
$$e^A = \sum_{n=0}^{\infty} \frac{1}{n!}A^n,$$

and

$$\frac{\partial e^A}{\partial x} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial A^n}{\partial x}.$$

But for a product of n operators,

$$\frac{\partial}{\partial x}(A \cdot A \cdots A) = \frac{\partial A}{\partial x} \cdot A \cdots A + A \cdot \frac{\partial A}{\partial x} \cdots A + \cdots + A \cdot A \cdots \frac{\partial A}{\partial x}.$$

The $\frac{\partial A}{\partial x}$ can be moved through the $A's$ surrounding it only if $\left[A, \frac{\partial A}{\partial x}\right] = 0$, in which case

$$\frac{\partial A}{\partial x} = n \frac{\partial A}{\partial x} A^{n-1}, \qquad \text{and} \qquad \frac{\partial e^A}{\partial x} = \frac{\partial A}{\partial x} e^A.$$

However, as we can always reorder operators inside a trace, i.e. $\text{tr}(BC) = \text{tr}(CB)$, and

$$\text{tr}\left(A \cdots A \cdots \frac{\partial A}{\partial x} \cdots A\right) = \text{tr}\left(\frac{\partial A}{\partial x} \cdot A^{n-1}\right),$$

and the identity

$$\frac{\partial}{\partial x} \text{tr}\left(e^A\right) = \text{tr}\left(\frac{\partial A}{\partial x} \cdot e^A\right),$$

can always be satisfied, independent of any constraint on $\left[A, \frac{\partial A}{\partial x}\right]$.

(d) Note that the partition function calculated in part (a) does not depend on the mass m, i.e. $\partial Z / \partial m = 0$. Use this information, along with the result in part (c), to show that

$$\left\langle \frac{p^2}{2m} \right\rangle = \left\langle \frac{m\omega^2 q^2}{2} \right\rangle.$$

• The expectation values of the kinetic and potential energy are given by

$$\left\langle \frac{p^2}{2m} \right\rangle = \text{tr}\left(\frac{p^2}{2m}\rho\right), \qquad \text{and} \qquad \left\langle \frac{m\omega^2 q^2}{2} \right\rangle = \text{tr}\left(\frac{m\omega^2 q^2}{2}\rho\right).$$

Noting that the expression for the partition function derived in part (a) is independent of mass, we know that $\partial Z / \partial m = 0$. Starting with $Z = \text{tr}\left(e^{-\beta\mathcal{H}}\right)$, and differentiating

$$\frac{\partial Z}{\partial m} = \frac{\partial}{\partial m} \text{tr}\left(e^{-\beta\mathcal{H}}\right) = \text{tr}\left[\frac{\partial}{\partial m}(-\beta\mathcal{H})e^{-\beta\mathcal{H}}\right] = 0,$$

where we have used the result in part (c). Differentiating the Hamiltonian, we find that

$$\text{tr}\left[\beta \frac{p^2}{2m^2} e^{-\beta\mathcal{H}}\right] + \text{tr}\left[-\beta \frac{m\omega^2 q^2}{2} e^{-\beta\mathcal{H}}\right] = 0.$$

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Equivalently,

$$\text{tr}\left[\frac{p^2}{2m}e^{-\beta\mathcal{H}}\right] = \text{tr}\left[\frac{m\omega^2q^2}{2}e^{-\beta\mathcal{H}}\right],$$

which shows that the expectation values of kinetic and potential energies are equal.

(e) Using the results in parts (d) and (a), or otherwise, calculate $\langle q^2\rangle$. How are the results in Problem #1 modified at low temperatures by inclusion of quantum mechanical effects.

• In part (a) it was found that $\langle\mathcal{H}\rangle = (\hbar\omega/2)\,(\tanh(\beta\hbar\omega/2))^{-1}$. Note that $\langle\mathcal{H}\rangle = \langle p^2/2m\rangle + \langle m\omega^2q^2/2\rangle$, and that in part (d) it was determined that the contribution from the kinetic and potential energy terms are equal. Hence,

$$\langle m\omega^2q^2/2\rangle = \frac{1}{2}\,(\hbar\omega/2)\,(\tanh(\beta\hbar\omega/2))^{-1}.$$

Solving for $\langle q^2\rangle$,

$$\langle q^2\rangle = \frac{\hbar}{2m\omega}\,(\tanh(\beta\hbar\omega/2))^{-1} = \frac{\hbar}{2m\omega}\,\coth(\beta\hbar\omega/2).$$

While the classical result $\langle q^2\rangle = k_BT/m\omega^2$, vanishes as $T \to 0$, the quantum result saturates at $T = 0$ to a constant value of $\langle q^2\rangle = \hbar/(2m\omega)$. The amplitude of the displacement curves in Problem #1 are effected by exactly the same saturation factors.

(f) In a coordinate representation, calculate $\langle q'|\rho|q\rangle$ in the high temperature limit. One approach is to use the result

$$\exp(\beta A)\exp(\beta B) = \exp\left[\beta(A+B) + \beta^2[A,B]/2 + \mathcal{O}(\beta^3)\right].$$

• Using the general operator identity

$$\exp(\beta A)\exp(\beta B) = \exp\left[\beta(A+B) + \beta^2[A,B]/2 + \mathcal{O}(\beta^3)\right],$$

the Boltzmann operator can be decomposed in the high temperature limit into those for kinetic and potential energy; to the lowest order as

$$\exp\left(-\beta\frac{p^2}{2m} - \beta\frac{m\omega^2q^2}{2}\right) \approx \exp(-\beta p^2/2m)\cdot\exp(-\beta m\omega^2q^2/2).$$

The first term is the Boltzmann operator for an ideal gas. The second term contains an operator diagonalized by $|q>$. The density matrix element

$$< q'|\rho|q > =< q'|\exp(-\beta p^2/2m)\exp(-\beta m\omega^2 q^2/2)|q >$$
$$= \int dp' < q'|\exp(-\beta p^2/2m)|p' >< p'|\exp(-\beta m\omega^2 q^2/2)|q >$$
$$= \int dp' < q'|p' >< p'|q > \exp(-\beta p'^2/2m)\exp(-\beta q^2 m\omega^2/2).$$

Using the free particle basis $< q'|p' >= \frac{1}{\sqrt{2\pi\hbar}}e^{-iq\cdot p/\hbar}$,

$$< q'|\rho|q >= \frac{1}{2\pi\hbar}\int dp' e^{ip'(q-q')/\hbar}e^{-\beta p'^2/2m}e^{-\beta q^2 m\omega^2/2}$$

$$= e^{-\beta q^2 m\omega^2/2}\frac{1}{2\pi\hbar}\int dp'\exp\left[-\left(p'\sqrt{\frac{\beta}{2m}}+\frac{i}{2\hbar}\sqrt{\frac{2m}{\beta}}(q-q')\right)^2\right]\exp\left(-\frac{1}{4}\frac{2m}{\beta\hbar^2}(q-q')^2\right),$$

where we completed the square. Hence

$$< q'|\rho|q >= \frac{1}{2\pi\hbar}e^{-\beta q^2 m\omega^2/2}\sqrt{2\pi mk_BT}\exp\left[-\frac{mk_BT}{2\hbar^2}(q-q')^2\right].$$

The proper normalization in the high temperature limit is

$$Z = \int dq < q|e^{-\beta p^2/2m}\cdot e^{-\beta m\omega^2 q^2/2}|q >$$
$$= \int dq \int dp' < q|e^{-\beta p^2/2m}|p' >< p'|e^{-\beta m\omega^2 q^2/2}|q >$$
$$= \int dq \int dp |< q|p >|^2 e^{-\beta p'^2/2m}e^{-\beta m\omega^2 q^2/2} = \frac{k_BT}{\hbar\omega}.$$

Hence the properly normalized matrix element in the high temperature limit is

$$< q'|\rho|q >_{\lim T\to\infty}= \sqrt{\frac{m\omega^2}{2\pi k_BT}}\exp\left(-\frac{m\omega^2}{2k_BT}q^2\right)\exp\left[-\frac{mk_BT}{2\hbar^2}(q-q')^2\right].$$

(g) At low temperatures, ρ is dominated by low energy states. Use the ground state wave-function to evaluate the limiting behavior of $\langle q'|\rho|q\rangle$ as $T\to 0$.

• In the low temperature limit, we retain only the first terms in the summation

$$\rho_{\lim T\to 0} \approx \frac{|0 > e^{-\beta\hbar\omega/2} < 0| + |1 > e^{-3\beta\hbar\omega/2} < 1| + \cdots}{e^{-\beta\hbar\omega/2} + e^{-3\beta\hbar\omega/2}}.$$

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Retaining only the term for the ground state in the numerator, but evaluating the geometric series in the denominator,

$$< q'|\rho|q >_{\lim T \to 0} \approx < q'|0 >< 0|q > e^{-\beta\hbar\omega/2} \cdot \left(e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2} \right).$$

Using the expression for $< q|0 >$ given in part (b),

$$< q'|\rho|q >_{\lim T \to 0} \approx \sqrt{\frac{m\omega}{\pi\hbar}} \exp\left[-\frac{m\omega}{2\hbar} \left(q^2 + q'^2 \right) \right] \left(1 - e^{-\beta\hbar\omega} \right).$$

(h) Calculate the exact expression for $\langle q'|\rho|q \rangle$.

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4. *Relativistic Coulomb gas:* Consider a *quantum* system of N positive, and N negative charged relativistic particles in box of volume $V = L^3$. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{2N} c|\vec{p}_i| + \sum_{i<j}^{2N} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|} \quad ,$$

where $e_i = +e_0$ for $i = 1, \cdots N$, and $e_i = -e_0$ for $i = N + 1, \cdots 2N$, denote the charges of the particles; $\{\vec{r}_i\}$ and $\{\vec{p}_i\}$ their coordinates and momenta respectively. While this is too complicated a system to solve, we can nonetheless obtain some exact results.

(a) Write down the Schrödinger equation for the eigenvalues $\varepsilon_n(L)$, and (in coordinate space) eigenfunctions $\Psi_n(\{\vec{r}_i\})$. State the constraints imposed on $\Psi_n(\{\vec{r}_i\})$ if the particles are bosons or fermions?

• In the coordinate representation $\vec{p}_i$ is replaced by $-i\hbar\nabla_i$, leading to the Schrödinger equation

$$\left[\sum_{i=1}^{2N} c| -i\hbar\nabla_i | + \sum_{i<j}^{2N} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|} \right] \Psi_n(\{\vec{r}_i\}) = \varepsilon_n(L)\Psi_n(\{\vec{r}_i\}).$$

There are N identical particles of charge $+e_0$, and N identical particles of charge $-e_0$. We can examine the effect of permutation operators P_+ and P_- on these two sets. The symmetry constraints can be written compactly as

$$P_+ P_- \Psi_n(\{\vec{r}_i\}) = \eta_+^{P_+} \cdot \eta_-^{P_-} \Psi_n(\{\vec{r}_i\}),$$

where $\eta = +1$ for bosons, $\eta = -1$ for fermions, and $(-1)^P$ denotes the parity of the permutation. Note that there is no constraint associated with exchange of particles with opposite charge.

(b) By a change of scale $\vec{r}_i\,' = \vec{r}_i/L$, show that the eigenvalues satisfy a scaling relation $\varepsilon_n(L) = \varepsilon_n(1)/L$.

• After the change of scale $\vec{r}_i\,' = \vec{r}_i/L$ (and corresponding change in the derivative $\nabla_i\,' = L\nabla_i$), the above Schrödinger equation becomes

$$\left[\sum_{i=1}^{2N} c \left| -i\hbar \frac{\nabla_i\,'}{L} \right| + \sum_{i<j}^{2N} \frac{e_i e_j}{L\,|\vec{r}_i\,' - \vec{r}_j\,'|} \right] \Psi_n\left(\left\{ \frac{\vec{r}_i\,'}{L} \right\} \right) = \varepsilon_n(L)\Psi_n\left(\left\{ \frac{\vec{r}_i\,'}{L} \right\} \right).$$

The coordinates in the above equation are confined to a box of unit size. We can regard it as the Schrödinger equation in such a box, with wave-functions $\Psi_n'(\{\vec{r}_i\}) = \Psi_n\left(\{\vec{r}_i\,'/L\}\right)$. The corresponding eigenvalues are $\varepsilon_n(1) = L\varepsilon_n(L)$ (obtained after multiplying both sides of the above equation by L We thus obtain the scaling relation

$$\varepsilon_n(L) = \frac{\varepsilon_n(1)}{L}.$$

(c) Using the formal expression for the partition function $Z(N, V, T)$, in terms of the eigenvalues $\{\varepsilon_n(L)\}$, show that Z does not depend on T and V separately, but only on a specific scaling combination of them.

• The formal expression for the partition function is

$$Z(N, V, T) = \mathrm{tr}\left(e^{-\beta \mathcal{H}} \right) = \sum_n \exp\left(-\frac{\varepsilon_n(L)}{k_B T} \right)$$

$$= \sum_n \exp\left(-\frac{\varepsilon_n(1)}{k_B T L} \right),$$

where we have used the scaling form of the energy levels. Clearly, in the above sum T and L always occur in the combination TL. Since $V = L^3$, the appropriate scaling variable is VT^3, and

$$Z(N, V, T) = \mathcal{Z}(N, VT^3).$$

(d) Relate the energy E, and pressure P of the gas to variations of the partition function. Prove the exact result $E = 3PV$.

- The average energy in the canonical ensemble is given by

$$E = -\frac{\partial \ln Z}{\partial \beta} = k_B T^2 \frac{\partial \ln Z}{\partial T} = k_B T^2 (3VT^2) \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)} = 3k_B VT^4 \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)}.$$

The free energy is $F = -k_B T \ln Z$, and its variations are $dF = -SdT - PdV + \mu dN$. Hence the gas pressure is given by

$$P = -\frac{\partial F}{\partial V} = k_B T \frac{\partial \ln Z}{\partial V} = k_B T^4 \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)}.$$

The ratio of the above expressions gives the exact identity $E = 3PV$.

(e) The Coulomb interaction between charges in in d-dimensional space falls off with separation as $e_i e_j / |\vec{r}_i - \vec{r}_j|^{d-2}$. (In $d = 2$ there is a logarithmic interaction.) In what dimension d can you construct an exact relation between E and P for *non-relativistic* particles (kinetic energy $\sum_i \vec{p}_i^2/2m$)? What is the corresponding exact relation between energy and pressure?

- The above exact result is a consequence of the simple scaling law relating the energy eigenvalues $\varepsilon_n(L)$ to the system size. We could obtain the scaling form in part (b) since the kinetic and potential energies scaled in the same way. The kinetic energy for *non-relativistic* particles $\sum_i \vec{p}_i^2/2m = -\sum_i \hbar^2 \nabla_i^2/2m$, scales as $1/L^2$ under the change of scale $\vec{r}_i{}' = \vec{r}_i/L$, while the interaction energy $\sum_{i<j}^{2N} e_i e_j / |\vec{r}_i - \vec{r}_j|^{d-2}$ in d space dimensions scales as $1/L^{d-2}$. The two forms will scale the same way in $d = 4$ dimensions, leading to

$$\varepsilon_n(L) = \frac{\varepsilon_n(1)}{L^2}.$$

The partition function now has the scaling form

$$Z(N, V = L^4, T) = \mathcal{Z}\left(N, (TL^2)^2\right) = \mathcal{Z}\left(N, VT^2\right).$$

Following steps in the previous part, we obtain the exact relationship $E = 2PV$.

(f) Why are the above 'exact' scaling laws not expected to hold in dense (liquid or solid) Coulomb mixtures?

- The scaling results were obtained based on the assumption of the existence of a single scaling length L, relevant to the statistical mechanics of the problem. This is a good approximation in a gas phase. In a dense (liquid or solid) phase, the short-range repulsion between particles is expected to be important, and the particle size a is another relevant

length scale which will enter in the solution to the Schrödinger equation, and invalidate the scaling results.

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5. *The virial theorem* is a consequence of the invariance of the phase space for a system of N (classical or quantum) particles under canonical transformations, such as a change of scale. In the following, consider N particles with coordinates $\{\vec{q}_i\}$, and conjugate momenta $\{\vec{p}_i\}$ (with $i = 1, \cdots, N$), and subject to a Hamiltonian $\mathcal{H}(\{\vec{p}_i\}, \{\vec{q}_i\})$.

(a) *Classical version*: Write down the expression for the classical partition function, $Z \equiv Z[\mathcal{H}]$. Show that it is invariant under the rescaling $\vec{q}_1 \rightarrow \lambda \vec{q}_1$, $\vec{p}_1 \rightarrow \vec{p}_1/\lambda$ of a pair of conjugate variables, i.e. $Z[\mathcal{H}_\lambda]$ is independent of λ, where $\mathcal{H}_\lambda$ is the Hamiltonian obtained after the above rescaling.

• The classical partition function is obtained by appropriate integrations over phase space as

$$Z = \frac{1}{N! h^{3N}} \int \left(\prod_i d^3 p_i d^3 q_i\right) e^{-\beta \mathcal{H}}.$$

The rescaled Hamiltonian $\mathcal{H}_\lambda = \mathcal{H}(\vec{p}_1/\lambda, \{\vec{p}_{i \neq 1}\}, \lambda \vec{q}_1, \{\vec{q}_{i \neq 1}\})$ leads to a rescaled partition function

$$Z[\mathcal{H}_\lambda] = \frac{1}{N! h^{3N}} \int \left(\prod_i d^3 p_i d^3 q_i\right) e^{-\beta \mathcal{H}_\lambda},$$

which reduces to

$$Z[\mathcal{H}_\lambda] = \frac{1}{N! h^{3N}} \int (\lambda^3 d^3 p_1')(\lambda^{-3} d^3 q_1') \left(\prod_i d^3 p_i d^3 q_i\right) e^{-\beta \mathcal{H}} = Z,$$

under the change of variables $\vec{q}_1{}' = \lambda \vec{q}_1$, $\vec{p}_1{}' = \vec{p}_1/\lambda$.

(b) *Quantum mechanical version*: Write down the expression for the quantum partition function. Show that it is also invariant under the rescalings $\vec{q}_1 \rightarrow \lambda \vec{q}_1$, $\vec{p}_1 \rightarrow \vec{p}_1/\lambda$, where $\vec{p}_i$ and $\vec{q}_i$ are now quantum mechanical operators. (Hint: start with the time-independent Schrödinger equation.)

• Using the energy basis

$$Z = \text{tr}\left(e^{-\beta \mathcal{H}}\right) = \sum_n e^{-\beta E_n},$$

where E_n are the energy eigenstates of the system, obtained from the Schrödinger equation

$$\mathcal{H}(\{\vec{p}_i\}, \{\vec{q}_i\}) |\psi_n\rangle = E_n |\psi_n\rangle,$$

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where $|\psi_n\rangle$ are the eigenstates. After the rescaling transformation, the corresponding equation is

$$\mathcal{H}\left(\vec{p}_1/\lambda, \{\vec{p}_{i\neq1}\}, \lambda\vec{q}_1, \{\vec{q}_{i\neq1}\}\right)\left|\psi_n^{(\lambda)}\right\rangle = E_n^{(\lambda)}\left|\psi_n^{(\lambda)}\right\rangle.$$

In the coordinate representation, the momentum operator is $\vec{p}_i = -i\hbar\partial/\partial\vec{q}_i$, and therefore $\psi_\lambda\left(\{\vec{q}_i\}\right) = \psi\left(\{\lambda\vec{q}_i\}\right)$ is a solution of the rescaled equation with eigenvalue $E_n^{(\lambda)} = E_n$. Since the eigen-energies are invariant under the transformation, so is the partition function which is simply the sum of corresponding exponentials.

(c) Now assume a Hamiltonian of the form

$$\mathcal{H} = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + V\left(\{\vec{q}_i\}\right).$$

Use the result that $Z\left[\mathcal{H}_\lambda\right]$ is independent of λ to prove the *virial* relation

$$\left\langle\frac{\vec{p}_1^{\,2}}{m}\right\rangle = \left\langle\frac{\partial V}{\partial\vec{q}_1}\cdot\vec{q}_1\right\rangle,$$

where the brackets denote thermal averages.

• Differentiating the free energy with respect to λ at $\lambda = 1$, we obtain

$$0 = \left.\frac{\partial\ln Z_\lambda}{\partial\lambda}\right|_{\lambda=1} = -\beta\left\langle\left.\frac{\partial\mathcal{H}_\lambda}{\partial\lambda}\right|_{\lambda=1}\right\rangle = -\beta\left\langle-\frac{\vec{p}_1^{\,2}}{m} + \frac{\partial V}{\partial\vec{q}_1}\cdot\vec{q}_1\right\rangle,$$

i.e.,

$$\left\langle\frac{\vec{p}_1^{\,2}}{m}\right\rangle = \left\langle\frac{\partial V}{\partial\vec{q}_1}\cdot\vec{q}_1\right\rangle.$$

(d) The above relation is sometimes used to estimate the mass of distant galaxies. The stars on the outer boundary of the G-8.333 galaxy have been measured to move with velocity $v \approx 200$ km/s. Give a numerical estimate of the ratio of the G-8.333's mass to its size.

• The virial relation applied to a gravitational system gives

$$\langle mv^2\rangle = \left\langle\frac{GMm}{R}\right\rangle.$$

Assuming that the kinetic and potential energies of the starts in the galaxy have reached some form of equilibrium gives

$$\frac{M}{R} \approx \frac{v^2}{G} \approx 6\times10^{20}\text{kg/m}.$$

6. *Electron spin:* The Hamiltonian for an electron in a magnetic field $\vec{B}$ is

$$\mathcal{H} = -\mu_B \vec{\sigma}.\vec{B}, \quad \text{where} \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

are the Pauli spin operators, and μ_B is the Bohr magneton.

(a) In the quantum canonical ensemble evaluate the density matrix if $\vec{B}$ is along the z direction.

● By definition,

$$\rho = \frac{\exp(-\beta\mathcal{H})}{\text{tr} \exp(-\beta\mathcal{H})}.$$

Noting that for any $i = 1, 2, 3$, $\sigma_i^2 = I$, we get,

$$\exp(a\sigma_i) = (1 + \frac{1}{2!}a^2 + \frac{1}{4!}a^4 + \cdots)I + (a + \frac{1}{3!}a^3 + \frac{1}{5!}a^5 + \cdots)\sigma_i = \cosh a I + \sinh a \sigma_i,$$

and thus

$$\text{tr} \exp(a\sigma_i) = \text{tr}(\cosh a I + \sinh a \sigma_i) = 2 \cosh a,$$

as the Pauli matrices are traceless. Hence in the case $\vec{B} = B\hat{z}$,

$$\rho = \frac{\exp(\beta\mu_B\sigma_z B)}{2\cosh(\beta\mu_B B)}$$
$$= \frac{\cosh(\beta\mu_B B)I + \sinh(\beta\mu_B B)\sigma_z}{2\cosh(\beta\mu_B B)} = \frac{1}{2\cosh(\beta\mu_B B)} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}.$$

(b) Repeat the calculation assuming that $\vec{B}$ points along the x-direction.

● For $\vec{B} = B\hat{x}$,

$$\rho = \frac{\exp(-\beta\mathcal{H})}{\text{tr} \exp(-\beta\mathcal{H})} = \frac{\exp(\beta\mu_B\sigma_x B)}{2\cosh(\beta\mu_B B)}$$
$$= \frac{\cosh(\beta\mu_B B)I + \sinh(\beta\mu_B B)\sigma_x}{2\cosh(\beta\mu_B B)} = \begin{pmatrix} 1/2 & \tanh(\beta\mu_B B)/2 \\ \tanh(\beta\mu_B B)/2 & 1/2 \end{pmatrix}.$$

(c) Calculate the average energy in each of the above cases.

● Note that

$$\text{tr} \sigma_i \exp(a\sigma_i) = \text{tr}(\cosh a \sigma_i + \sinh a I) = 2 \sinh a,$$

so that for $\mathcal{H} = -\mu_B B \sigma_i$,

$$\frac{\text{tr}\,\mathcal{H}\rho}{\text{tr}\,\rho} = \frac{\text{tr}[-\mu_B B \sigma_i \exp(\beta\mu_B\sigma_i B)]}{\text{tr}[\exp(\beta\mu_B\sigma_i B)]}$$

$$= \frac{-2\mu_B B \sinh(\beta\mu_B B)}{2\cosh(\beta\mu_B B)} = -\mu_B B \tanh(\beta\mu_B B),$$

independent of the direction of $\vec{B}$.

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7. *Quantum rotor:* Consider a rotor in two dimensions with

$$\mathcal{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\theta^2}, \quad \text{and} \quad 0 \leq \theta < 2\pi.$$

(a) Find the eigenstates and energy levels of the system.

• Solving,

$$-\frac{\hbar^2}{2I}\frac{d^2}{d\theta^2}\psi(\theta) = E\psi(\theta)$$

we get,

$$\psi(\theta) = \frac{1}{\sqrt{2\pi}}\exp\left(\pm i\sqrt{\frac{2IE}{\hbar^2}}\theta\right).$$

Imposing $\psi(\theta) = \psi(\theta + 2\pi)$, we finally obtain,

$$\psi_n(\theta) = \frac{1}{\sqrt{2\pi}}\exp(in\theta), \quad E_n = \frac{\hbar^2 n^2}{2I}, \quad n: \text{integer.}$$

(b) Write the expression for the density matrix $\langle\theta'|\rho|\theta\rangle$ in a canonical ensemble of temperature T, and evaluate its low and high temperature limits.

• Defining, $Z = \text{tr}\,e^{-\beta\mathcal{H}}$,

$$\rho = \frac{1}{Z}\sum_n |n\rangle e^{-\beta\hbar^2 n^2/2I} \langle n| \quad ,$$

and,

$$\langle\theta'|\rho|\theta\rangle = \frac{1}{2\pi}\frac{\sum_n e^{in(\theta-\theta')}e^{-\beta\hbar^2 n^2/2I}}{\sum_n e^{-\beta\hbar^2 n^2/2I}}.$$

In the low temperature limit ($\hbar^2\beta/2I \gg 1$) the ground state dominates. In other words, since $e^{-\beta\hbar^2/2I} \ll 1$, to leading order the contributions come from the states with $n = 0$ and $n = \pm 1$, resulting in

$$\langle\theta'|\rho|\theta\rangle \approx \frac{1}{2\pi} \frac{\left[1 + 2e^{-2\hbar^2/2I}\cos(\theta - \theta') + \cdots\right]}{\left[1 + 2e^{-2\hbar^2/2I} + \cdots\right]} \approx \frac{1}{2\pi}\left[1 - 4e^{-2\hbar^2/2I}\sin^2\frac{\theta - \theta'}{2} + \cdots\right].$$

In the high temperature limit ($\hbar^2\beta/2I \ll 1$), by taking $x = n\sqrt{\hbar^2\beta/2I}$ we may write,

$$\sum_n e^{-\beta\hbar^2 n^2/2I} \to \sqrt{\frac{2I}{\hbar^2\beta}}\int dx e^{-x^2},$$

$$\sum_n e^{in(\theta - \theta')}e^{-\beta\hbar^2 n^2/2I} \to \sqrt{\frac{2I}{\hbar^2\beta}}\int dx e^{-x^2}e^{i\sqrt{\frac{2I}{\hbar^2\beta}}(\theta - \theta')x}$$

$$= \sqrt{\frac{2I}{\hbar^2\beta}}e^{-I(\theta - \theta')^2/2\beta\hbar^2}\int dx e^{-x^2},$$

and,

$$\langle\theta'|\rho|\theta\rangle \approx \frac{1}{2\pi}e^{-\frac{I(\theta - \theta')^2}{2\beta\hbar^2}}.$$

Note that this expression is valid as long as $(\theta - \theta') \sim \sqrt{\hbar^2\beta/2I} \ll 1$, since this is our scale of coarse graining. That's why the ρ matrix element for $\theta - \theta' = 2\pi$ is different from that for $\theta - \theta' = 0$ in this approximation; it simply doesn't apply for $\Delta\theta \sim 1$.

****

8. *Quantum mechanical entropy:* A quantum mechanical system (defined by a Hamiltonian $\mathcal{H}$), at temperature T, is described by a density matrix $\rho(t)$, which has an associated entropy $S(t) = -\text{tr}\rho(t)\ln\rho(t)$.

(a) Write down the time evolution equation for the density matrix, and calculate dS/dt.

• The time evolution of the density operator is given by the Heisenberg equation

$$\frac{\partial\rho}{\partial t} = i\hbar\left[\rho, \mathcal{H}\right],$$

leading to

$$\frac{dS}{dt} = i\hbar\text{tr}\left\{(1 + \rho)\left[\rho, \mathcal{H}\right]\right\} = i\hbar\left\{\text{tr}(\rho\mathcal{H}) - \text{tr}(\mathcal{H}\rho) + \text{tr}(\rho^{\in}\mathcal{H}) - \text{tr}(\rho\mathcal{H}\rho)\right\} = 0,$$

since the trace of a product is invariant under cyclic permutations.

(b) Using the method of Lagrange multipliers, find the density operator ρ_{max} which maximizes the functional $S[\rho]$, subject to the constraint of fixed average energy $\langle \mathcal{H} \rangle = \text{tr}\rho\mathcal{H} = E$.

• In order to satisfy the two constraints, normalization and constant average energy, written respectively as

$$\text{tr}\rho = 1 \quad \text{and} \quad \langle \mathcal{H} \rangle = \text{tr}\rho\mathcal{H} = E,$$

we construct the functional

$$S(t) = \text{tr}\rho\left[-\ln\rho - \alpha - \beta\mathcal{H}\right] + \alpha + \beta E,$$

where α and β are Lagrange multipliers. Extremizing the above expression with respect to ρ results in

$$\left.\frac{\partial S}{\partial \rho}\right|_{\rho=\rho_{\text{max}}} = -\ln\rho_{\text{max}} - \alpha - \beta\mathcal{H} - 1 = 0.$$

The solution to this equation is

$$\ln\rho_{\text{max}} = -(\alpha + 1) - \beta\mathcal{H},$$

which can be rewritten as

$$\rho_{\text{max}} = C\exp\left(-\beta\mathcal{H}\right), \quad \text{where} \quad C = e^{-(\alpha+1)}.$$

(c) Show that the solution to part (b) is stationary, i.e. $\partial\rho_{\text{max}}/\partial t = 0$.

• The density obtained in part (b) is stationary, as the commutator of $\mathcal{H}$ with any function of $\mathcal{H}$ vanishes, implying, in particular,

$$\frac{\partial\rho_{\text{max}}}{\partial t} = 0.$$

****

9. *Ortho/para–hydrogen:* Hydrogen molecules can exist in ortho and para states.

(a) The two electrons of H_2 in para-hydrogen form a singlet (antisymmetric) state. The orbital angular momentum can thus only take even values; i.e.

$$\mathcal{H}_p = \frac{\hbar^2}{2I}\ell(\ell+1),$$

where $\ell = 0, 2, 4, \cdots$. Calculate the rotational partition function of para-hydrogen, and evaluate its low and high temperature limits.

- Since there are $2\ell + 1$ states for each ℓ,

$$Z_p = \sum_{\ell \,:\, even} (2\ell+1)e^{-\beta\hbar^2\ell(\ell+1)/2I} = \sum_{n=0}^{\infty}(4n+1)e^{-\beta\hbar^2 n(2n+1)/I}.$$

In the low temperature limit, only the first few terms matter, and to leading order

$$Z_p \approx 1 + 5e^{-3\beta\hbar^2/I}.$$

In the high temperature limit,

$$Z_p = \sum_{n=0}^{\infty}(4n+1)e^{-\beta\hbar^2 n(2n+1)/I} \approx \frac{I}{\beta\hbar^2}\sum_{n=0}^{\infty} e^{-2\left(\sqrt{\frac{\beta}{I}}\hbar n\right)^2} 4\left(\sqrt{\frac{\beta}{I}}\hbar n\right)\left(\sqrt{\frac{\beta}{I}}\hbar\right)$$

$$= \frac{I}{\beta\hbar^2}\int_0^{\infty} 4xe^{-2x^2}\,dx = \frac{I}{\beta\hbar^2}.$$

(b) In ortho-hydrogen the electrons are in a triply degenerate symmetric state, hence

$$\mathcal{H}_o = \frac{\hbar^2}{2I}\ell(\ell+1),$$

with $\ell = 1, 3, 5, \cdots$. Calculate the rotational partition function of ortho-hydrogen, and evaluate its low and high temperature limits.

- Since there are $2\ell + 1$ states for each ℓ, and a 3-fold degeneracy in the spin state,

$$Z_o = 3\sum_{\ell \,:\, odd} (2\ell+1)e^{-\beta\hbar^2\ell(\ell+1)/2I} = 3\sum_{n=0}^{\infty}(4n+3)e^{-\beta\hbar^2(n+1)(2n+1)/I}.$$

In the low temperature limit, only the first few terms matter, and to leading order

$$Z_o \approx 9e^{-\beta\hbar^2/I}.$$

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In the high temperature limit,

$$Z_o = \sum_{n=0}^{\infty}(4n+3)e^{-\beta\hbar^2(n+1)(2n+1)/I} \approx \frac{3I}{\beta\hbar^2}\sum_{n=0}^{\infty}e^{-2\left(\sqrt{\frac{\beta}{I}}\hbar n\right)^2}4\left(\sqrt{\frac{\beta}{I}}\hbar n\right)\left(\sqrt{\frac{\beta}{I}}\hbar\right)$$

$$= \frac{3I}{\beta\hbar^2}\int_0^{\infty}4xe^{-2x^2}dx = \frac{3I}{\beta\hbar^2}.$$

(c) For an equilibrium gas of N hydrogen molecules calculate the partition function.

(Hint: Sum over contributions from mixtures of N_p para- and $N_o = N-N_p$ ortho-hydrogen particles. Ignore vibrational degrees of freedom.)

-
$$Z = \sum_{N_p}\frac{1}{(N-N_p)!N_p!}Z_p^{N_p}Z_o^{N-N_p} = \frac{1}{N!}(Z_o + Z_p)^N,$$

which is what we should expect.

(d) Write down the expression for the rotational contribution to the internal energy $\langle E_{\rm rot.}\rangle$, and comment on its low and high temperature limits.

Actually, due to small transition rates between ortho- and para-hydrogen, in most circumstances the mixture is not in equilibrium.

-
$$\langle E_{rot}\rangle = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln(Z_0 + Z_p)}{\partial \beta}.$$

In the low energy limit,

$$Z_0 + Z_p \approx 1 + 9e^{-\beta\hbar^2/I},$$

giving up to leading order,

$$\langle E_{rot}\rangle \approx \frac{9N\hbar^2}{I}e^{-\beta\hbar^2/I}.$$

In the high energy limit,

$$Z_0 + Z_p \approx \frac{4I}{\beta\hbar^2},$$

giving,

$$\langle E_{rot}\rangle \approx Nk_BT,$$

which is what we expect since we have 2 rotational degrees of freedom.

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10. *van Leeuwen's theorem:* Consider a gas of charged particles subject to a general Hamiltonian of the form

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\ 2}}{2m} + U(\vec{q}_1, \cdots, \vec{q}_N).$$

In an external magnetic field, $\vec{B}$, the canonical momenta, $\vec{p}_n$, are replaced with $\vec{p}_n - e\vec{A}$, where $\vec{A}$ is the vector potential, $\vec{B} = \vec{\nabla} \times \vec{A}$. Show that if quantum effects are ignored, the thermodynamics of the problem is independent of $\vec{B}$.

- Ignoring quantum effects and taking the coarse graining scale to be h,

$$Z = \sum_{\mu_s} e^{-\beta \mathcal{H}(\mu_s)} = \int \prod_{n=1}^{N} \frac{d^3\vec{p}_n d^3\vec{q}_n}{h^3} e^{-\beta[\sum_{i=1}^{N} \frac{\vec{p}_i^{\ 2}}{2m} + U(\vec{q}_1, \cdots, \vec{q}_N)]}.$$

Now with a magnetic field,

$$Z(\vec{B}) = \sum_{\mu_s} e^{-\beta \mathcal{H}(\mu_s)} = \int \prod_{n=1}^{N} \frac{d^3\vec{p}_n d^3\vec{q}_n}{h^3} e^{-\beta[\sum_{i=1}^{N} \frac{(\vec{p}_i - e\vec{A})^2}{2m} + U(\vec{q}_1, \cdots, \vec{q}_N)]}$$

$$= \int \prod_{n=1}^{N} \frac{d^3\vec{p'}_n d^3\vec{q}_n}{h^3} e^{-\beta[\sum_{i=1}^{N} \frac{\vec{p'}_i^{\ 2}}{2m} + U(\vec{q}_1, \cdots, \vec{q}_N)]},$$

for $\vec{B} = \vec{\nabla} \times \vec{A}$, where we have defined $\vec{p'} = \vec{p} - e\vec{A}$. Hence we see that classically,

$$Z(\vec{B}) = Z(\vec{0}),$$

so the thermodynamics of the problem is independent of $\vec{B}$.

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Problems for Chapter VII - Ideal Quantum Gases

1. *Identical particle pair:* Let $Z_1(m)$ denote the partition function for a single quantum particle of mass m in a volume V.

(a) Calculate the partition function of two such particles, if they are bosons, and also if they are (spinless) fermions.

• A two particle wave function is constructed from one particle states k_1, and k_2. Depending on the statistics of the two particles, we have

Bosons:
$$|k_1, k_2\rangle_B = \begin{cases} \left(|k_1\rangle|k_2\rangle + |k_2\rangle|k_1\rangle\right)/\sqrt{2} & \text{for } k_1 \neq k_2 \\ |k_1\rangle|k_2\rangle & \text{for } k_1 = k_2 \end{cases},$$

Fermions:
$$|k_1, k_2\rangle_F = \begin{cases} \left(|k_1\rangle|k_2\rangle - |k_2\rangle|k_1\rangle\right)/\sqrt{2} & \text{for } k_1 \neq k_2 \\ \text{no state} & \text{for } k_1 = k_2 \end{cases}.$$

For the Boson system, the partition function is given by

$$
\begin{aligned}
Z_2^B = \text{tr}\left(e^{-\beta H}\right) &= \sum_{k_1, k_2} \langle k_1, k_2|e^{-\beta H}|k_1, k_2\rangle_B \\
&= \sum_{k_1 > k_2} \frac{\langle k_1|\langle k_2| + \langle k_2|\langle k_1|}{\sqrt{2}} e^{-\beta H} \frac{|k_1\rangle|k_2\rangle + |k_2\rangle|k_1\rangle}{\sqrt{2}} + \sum_k \langle k|\langle k|e^{-\beta H}|k\rangle|k\rangle \\
&= \sum_{k_1 > k_2} \exp\left[-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)\right] + \sum_k \exp\left(-\frac{2\beta\hbar^2 k^2}{2m}\right) \\
&= \frac{1}{2}\sum_{k_1, k_2} \exp\left[-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)\right] + \frac{1}{2}\sum_k \exp\left(-\frac{\beta\hbar^2 k^2}{m}\right),
\end{aligned}
$$

and thus
$$Z_2^B = \frac{1}{2}\left[Z_1^2(m) + Z_1\left(\frac{m}{2}\right)\right].$$

For the Fermion system,

$$
\begin{aligned}
Z_2^F = \text{tr}\left(e^{-\beta H}\right) &= \sum_{k_1, k_2} \langle k_1, k_2|e^{-\beta H}|k_1, k_2\rangle_F \\
&= \sum_{k_1 > k_2} \frac{\langle k_1|\langle k_2| - \langle k_2|\langle k_1|}{\sqrt{2}} e^{-\beta H} \frac{|k_1\rangle|k_2\rangle - |k_2\rangle|k_1\rangle}{\sqrt{2}} \\
&= \frac{1}{2}\sum_{k_1, k_2} \exp\left[-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)\right] - \frac{1}{2}\sum_k \exp\left(-\frac{\beta\hbar^2 k^2}{m}\right),
\end{aligned}
$$

and thus

$$Z_2^F = \frac{1}{2}\left[Z_1^2(m) - Z_1\left(\frac{m}{2}\right)\right].$$

Note that *classical Boltzmann particles* have a partition function

$$Z_2^{classical} = \frac{1}{2}Z_1(m)^2.$$

(b) Use the classical approximation $Z_1(m) = V/\lambda^3$ with $\lambda = h/\sqrt{2\pi m k_B T}$. Calculate the corrections to the energy E, and the heat capacity C, due to Bose or Fermi statistics.

• If the system is non-degenerate, the correction term is much smaller than the classical term, and

$$\ln Z_2^\pm = \ln\left\{\left[Z_1(m)^2 \pm Z_1(m/2)\right]/2\right\}$$

$$= 2\ln Z_1(m) + \ln\left\{1 \pm \frac{Z_1(m/2)}{Z_1(m)^2}\right\} - \ln 2$$

$$\approx 2\ln Z_1(m) \pm \frac{Z_1(m/2)}{Z_1(m)^2} - \ln 2.$$

Using

$$Z_1(m) = \frac{V}{\lambda(m)^3}, \quad \text{where} \quad \lambda(m) \equiv \frac{h}{\sqrt{2\pi m k_B T}},$$

we can write

$$\ln Z_2^\pm \approx \ln Z_2^{Classical} \pm \frac{\lambda(m)^3}{V}\left(\frac{\lambda(m)}{\lambda(m/2)}\right)^3 = \ln Z_2^{Classical} \pm 2^{-3/2}\frac{\lambda(m)^3}{V},$$

$$\implies \quad \Delta\ln Z_2^\pm = \pm 2^{-3/2}\frac{h^3}{V(2\pi m k_B T)^{3/2}} = \pm 2^{-3/2}\frac{h^3\beta^{3/2}}{V(2\pi m)^{3/2}}.$$

Thus the energy differences are

$$\Delta E^\pm = -\frac{\partial}{\partial\beta}\Delta\ln Z_2 = \mp\frac{3}{2^{5/2}}\frac{h^3\beta^{3/2}}{V(2\pi m)^{3/2}} = \mp\frac{3}{2^{5/2}}k_B T\left(\frac{\lambda^3}{V}\right),$$

resulting in heat capacity differences of

$$\Delta C_V^\pm = \frac{\partial\Delta E}{\partial T}\bigg|_V = \pm\frac{3}{2^{7/2}}\frac{h^3 k_B}{V(2\pi m k_B T)^{3/2}} = \pm\frac{3}{2^{7/2}}k_B\left(\frac{\lambda^3}{V}\right).$$

This approximation holds only when the thermal volume is much smaller than the volume of the gas where the ratio constitutes a small correction.

(c) At what temperature does the approximation used above break down?

- The approximation is invalid if the correction terms are comparable to the first term. This occurs when the thermal wavelength becomes comparable to the size of the box, i.e. for

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} \geq L \sim V^{1/3}, \quad \text{or} \quad T \leq \frac{h^2}{2\pi m k_B L^2}.$$

****

2. *Generalized ideal gas:* Consider a gas of non-interacting identical (spinless) quantum particles with an energy spectrum $\varepsilon = |\vec{p}/\hbar|^s$, contained in a box of "volume" V in d-dimensions.

(a) Calculate the grand potential $\mathcal{G}_\eta = -k_B T \ln \mathcal{Q}_\eta$, and the density $n = N/V$, at a chemical potential μ. Express your answers in terms of s, d, and $f_m^\eta(z)$, where $z = e^{\beta\mu}$, and

$$f_m^\eta(z) = \frac{1}{\Gamma(m)} \int_0^\infty \frac{dx\, x^{m-1}}{z^{-1} e^x - \eta}.$$

(Hint: Use integration by parts on the expression for $\ln \mathcal{Q}_\eta$.)

- The grand partition function is given by

Fermions:

$$Q_F = \sum_{N=0}^\infty e^{\beta\mu N} \sum_{\{n_\nu\}} e^{-\beta \sum_\nu n_\nu \varepsilon_\nu} = \prod_\nu \sum_{n_\nu=0}^1 e^{\beta(\mu-\varepsilon_\nu)n_\nu} = \prod_\nu \left[1 + e^{\beta(\mu-\varepsilon_\nu)} \right].$$

Bosons:

$$Q_B = \sum_{N=0}^\infty e^{\beta\mu N} \sum_{\{n_\nu\}} e^{-\beta \sum_\nu n_\nu \varepsilon_\nu} = \prod_\nu \sum_{\{n_\nu\}} e^{\beta(\mu-\varepsilon_\nu)n_\nu} = \prod_\nu \left[1 - e^{\beta(\mu-\varepsilon_\nu)} \right]^{-1}.$$

Hence we obtain

$$\ln Q_\eta = -\eta \sum_\nu \ln \left[1 - \eta e^{\beta(\mu-\varepsilon_\nu)} \right],$$

where $\eta = +1$ for bosons, and $\eta = -1$ for fermions.

Changing the summation into an integration in d-dimensions yields

$$\sum_\nu \quad \rightarrow \quad \int d^d n \quad \rightarrow \quad \frac{V}{(2\pi)^d} \int d^d k = \frac{V S_d}{(2\pi)^d} \int k^{d-1} dk,$$

where

$$S_d = \frac{2\pi^{d/2}}{(d/2 - 1)!}.$$

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Then

$$\ln Q_\eta = -\eta \frac{VS_d}{(2\pi)^d} \int k^{d-1} dk \ln \left[1 - \eta e^{\beta(\mu-\varepsilon_\nu)}\right]$$

$$= -\eta \frac{VS_d}{(2\pi)^d} \int k^{d-1} dk \ln \left[1 - \eta z e^{-\beta k^s}\right],$$

where

$$z \equiv e^{\beta\mu}.$$

Introducing a new variable

$$x \equiv \beta k^s, \quad \rightarrow \quad k = \left(\frac{x}{\beta}\right)^{1/s}, \quad \text{and} \quad dk = \frac{1}{s}\left(\frac{x}{\beta}\right)^{1/s-1}\frac{dx}{\beta},$$

results in

$$\ln Q_\eta = -\eta \frac{VS_d}{(2\pi)^d}\frac{\beta^{-d/s}}{s} \int dx\, x^{d/s-1} \ln\left(1 - \eta z e^{-x}\right).$$

Integrating by parts,

$$\ln Q_\eta = \frac{VS_d}{(2\pi)^d}\frac{\beta^{-d/s}}{d} \int dx\, x^{d/s} \frac{z e^{-x}}{1 - \eta z e^{-x}} = \frac{VS_d}{(2\pi)^d}\frac{\beta^{-d/s}}{d} \int dx\, \frac{x^{d/s}}{z^{-1}e^x - \eta}.$$

Finally,

$$\ln Q_\eta = \frac{VS_d}{(2\pi)^d}\beta^{-d/s}\Gamma\left(\frac{d}{s}+1\right) \cdot f^\eta_{d/s+1}(z),$$

where

$$f^\eta_n(z) \equiv \frac{1}{\Gamma(n)} \int dx\, \frac{x^{n-1}}{z^{-1}e^x - \eta}.$$

Using similar notation, the total particle number is obtained as

$$N = \frac{\partial}{\partial(\beta\mu)} \ln Q_\eta \bigg|_\beta = -\eta \frac{VS_d}{(2\pi)^d}\frac{\beta^{d/s}}{s}\frac{\partial}{\partial(\beta\mu)} \int dx\, x^{d/s-1} \ln\left(1 - \eta z e^{-x}\right)$$

$$= \frac{VS_d}{(2\pi)^d}\frac{\beta^{d/s}}{s} \int dx\, \frac{x^{d/s-1} z e^{-x}}{1 - \eta z e^{-x}} = \frac{VS_d}{(2\pi)^d}\frac{\beta^{d/s}}{s} z \int dx\, \frac{x^{d/s-1}}{z^{-1}e^{-x} - \eta},$$

and thus

$$n = \frac{N}{V} = \frac{S_d}{(2\pi)^d s}(k_B T)^{d/s}\,\Gamma\left(\frac{d}{s}\right) \cdot f^\eta_{d/s}(z).$$

(b) Find the ratio PV/E, and compare it to the classical result obtained previously.

• The gas pressure is given by

$$PV = -k_B T \ln Q_\eta = \frac{VS_d}{(2\pi)^d}\frac{(k_B T)^{d/s+1}}{d}\Gamma\left(\frac{d}{s}+1\right) \cdot f_{d/s+1}(z).$$

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Note that since $\ln Q_\eta \propto \beta^{-d/s}$,

$$E = -\frac{\partial}{\partial \beta} \ln Q_\eta \bigg|_z = -\frac{d}{s} \frac{\ln Q_\eta}{\beta} = -\frac{d}{s} k_B T \ln Q_\eta, \implies \frac{PV}{E} = \frac{s}{d},$$

which is the same result obtained classically.

(c) *For fermions*, calculate the dependence of E/N, and P, on the density $n = N/V$, at zero temperature. (Hint: $f_m(z) \to (\ln z)^m/m!$ as $z \to \infty$.)

• For fermions at low T,

$$\frac{1}{e^{\beta(\varepsilon - \varepsilon_F)} + 1} \approx \theta(\varepsilon - \varepsilon_F), \implies f_n(z) \approx \frac{(\beta \varepsilon_F)^n}{n\Gamma(n)},$$

resulting in

$$E \approx \frac{VS_d}{(2\pi)^d} \frac{\varepsilon_F^{d/s+1}}{d}, \quad PV \approx \frac{VS_d}{(2\pi)^d} \frac{\varepsilon_F^{d/s+1}}{s}, \quad n \approx \frac{S_d}{(2\pi)^d} \frac{\varepsilon_F^{d/s}}{s}.$$

Hence, we obtain

$$\frac{E}{N} \approx \frac{1}{n} \cdot \frac{S_d}{(2\pi)^d} \frac{\varepsilon_F^{d/s+1}}{d} \approx \frac{s}{d} \varepsilon_F \propto n^{s/d}, \quad \text{and}$$
$$P \propto \varepsilon_F^{d/s+1} \propto n^{s/d+1}.$$

(d) *For bosons*, find the dimension $d_\ell(s)$, below which there is no Bose condensation. Is there condensation for $s = 2$ at $d = 2$?

• To see if Bose-Einstein condensation occurs, check whether a density n can be found such that $z = z_{max} = 1$. Since $f_{d/s}^+(z)$ is a monotonic function of z for $0 \leq z \leq 1$, the maximum value for the right hand side of the equation for $n = N/V$, given in part (a) is

$$\frac{S_d}{(2\pi)^d s} (k_B T)^{d/s} \Gamma\left(\frac{d}{s}\right) f_{d/s}^+(1).$$

If this value is larger than n, we can always find $z < 1$ that satisfies the above equation. If this value is smaller than n, then the remaining portion of the particles should condense into the ground state. Thus the question is whether $f_{d/s}^+(1)$ diverges at $z = 1$, where

$$f_{d/s}^+(z_{max} = 1) = \frac{1}{\Gamma(d/s)} \int dx \frac{x^{d/s-1}}{e^x - 1}.$$

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The integrand may diverge near $x = 0$; the contribution for $x \sim 0$ is

$$\int_0^\varepsilon dx \, \frac{x^{d/s-1}}{e^x - 1} \simeq \int_0^\varepsilon dx \, x^{d/s-2},$$

which converges for $d/s - 2 > -1$, or $d > s$. Therefore, Bose-Einstein condensation occurs for $d > s$. For a two dimensional gas, $d = s = 2$, the integral diverges logarithmically, and hence Bose-Einstein condensation does not occur.

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3. *Pauli paramagnetism:* Calculate the contribution of electron spin to its magnetic susceptibility as follows. Consider non-interacting electrons, each subject to a Hamiltonian

$$\mathcal{H}_1 = \frac{\vec{p}^2}{2m} - \mu_0 \vec{\sigma} \cdot \vec{B} \quad,$$

where $\mu_0 = e\hbar/2mc$, and the eigenvalues of $\vec{\sigma} \cdot \vec{B}$ are $\pm B$.

(The orbital effect, $\vec{p} \to \vec{p} - e\vec{A}$, has been ignored.)

(a) Calculate the grand potential $\mathcal{G}_- = -k_B T \ln \mathcal{Q}_-$, at a chemical potential μ.

• The energy of the electron gas is given by

$$E \equiv \sum_p E_p(n_p^+, n_p^-),$$

where $n_p^\pm$ ($= 0$ or 1), denote the number of particles having $\pm$ spins and momentum p, and

$$E_p(n_p^+, n_p^-) \equiv \left(\frac{p^2}{2m} - \mu_0 B \right) n_p^+ + \left(\frac{p^2}{2m} + \mu_0 B \right) n_p^-$$

$$= (n_p^+ + n_p^-)\frac{p^2}{2m} - (n_p^+ - n_p^-)\mu_0 B.$$

The grand partition function of the system is

$$Q = \sum_{N=0}^{\infty} \exp(-\beta \mu N) \overset{N = \sum (n_p^+ + n_p^-)}{\sum_{\{n_p^+, n_p^-\}}} \exp\left[-\beta E_p(n_p^+, n_p^-) \right]$$

$$= \sum_{\{n_p^+, n_p^-\}} \exp\left[\beta \mu \left(n_p^+ + n_p^- \right) - \beta E_p \left(n_p^+, n_p^- \right) \right]$$

$$= \prod_p \sum_{\{n_p^+, n_p^-\}} \exp\left\{ \beta \left[\left(\mu - \mu_0 B - \frac{p^2}{2m} \right) n_p^+ + \left(\mu + \mu_0 B - \frac{p^2}{2m} \right) n_p^- \right] \right\}$$

$$= \prod_p \left\{ 1 + \exp\left[\beta \left(\mu - \mu_0 B - \frac{p^2}{2m} \right) \right] \right\} \cdot \left\{ 1 + \exp\left[\beta \left(\mu + \mu_0 B - \frac{p^2}{2m} \right) \right] \right\}$$

$$= Q_0 \left(\mu + \mu_0 B \right) \cdot Q_0 \left(\mu - \mu_0 B \right),$$

where

$$Q_0(\mu) \equiv \prod_p \left\{ 1 + \exp\left[\beta\left(\mu - \frac{p^2}{2m} \right) \right] \right\}.$$

Thus

$$\ln Q = \ln\left\{ Q_0(\mu + \mu_0 B) \right\} + \ln\left\{ Q_0(\mu - \mu_0 B) \right\}.$$

Each contribution is given by

$$\ln Q_0(\mu) = \sum_p \ln\left(1 + \exp\left[\beta(\mu - \frac{p^2}{2m}) \right] \right) = \frac{V}{(2\pi\hbar)^3} \int d^3p \, \ln\left(1 + ze^{-\beta\frac{p^2}{2m}} \right)$$

$$= \frac{V}{h^3} \frac{4\pi m}{\beta} \sqrt{\frac{2m}{\beta}} \int dx \, \sqrt{x} \ln(1 + ze^{-x}), \quad \text{where} \quad z \equiv e^{\beta\mu},$$

and integrating by parts yields

$$\ln Q_0(\mu) = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{2}{\sqrt{\pi}} \frac{2}{3} \int dx \, \frac{x^{3/2}}{z^{-1} e^x + 1} = \frac{V}{\lambda^3} f_{5/2}^-(z).$$

The total grand free energy is obtained from

$$\ln Q(\mu) = \frac{V}{\lambda^3} \left[f_{5/2}^-\left(ze^{\beta\mu_0 B} \right) + f_{5/2}^-\left(ze^{-\beta\mu_0 B} \right) \right],$$

as

$$G = -k_B T \ln Q(\mu) = -k_B T \frac{V}{\lambda^3} \left[f_{5/2}^-\left(ze^{\beta\mu_0 B} \right) + f_{5/2}^-\left(ze^{-\beta\mu_0 B} \right) \right].$$

(b) Calculate the densities $n_+ = N_+/V$, and $n_- = N_-/V$, of electrons pointing parallel and antiparallel to the field.

- *The number densities* of electrons with up or down spins is given by

$$\frac{N_\pm}{V} = z \frac{\partial}{\partial z} \ln Q_\pm = \frac{V}{\lambda^3} f_{3/2}^-\left(ze^{\pm\beta\mu_0 B} \right),$$

where we used

$$z \frac{\partial}{\partial z} f_n^-(z) = f_{n-1}^-(z).$$

The total number of electrons is the sum of these, i.e.

$$N = N_+ + N_- = \frac{V}{\lambda^3} \left[f_{3/2}^-(ze^{\beta\mu_0 B}) + f_{3/2}^-(ze^{-\beta\mu_0 B}) \right].$$

(c) Obtain the expression for the magnetization $M = \mu_0(N_+ - N_-)$, and expand the result for small B.

● *The magnetization* is related to the difference between numbers of spin up and down electrons as

$$M = \mu_0(N_+ - N_-) = \mu_0 \frac{V}{\lambda^3} \left[f_{3/2}^- \left(z e^{\beta \mu_0 B} \right) - f_{3/2}^- \left(z e^{-\beta \mu_0 B} \right) \right].$$

Expanding the results for small B, gives

$$f_{3/2}^- \left(z e^{\pm \beta \mu_0 B} \right) \approx f_{3/2}^- \left[z \left(1 \pm \beta \mu_0 B \right) \right] \approx f_{3/2}^-(z) \pm z \cdot \beta \mu_0 B \frac{\partial}{\partial z} f_{3/2}^-(z),$$

which results in

$$M = \mu_0 \frac{V}{\lambda^3} (2 \beta \mu_0 B) \cdot f_{1/2}^-(z) = \frac{2 \mu_0^2}{k_B T} \frac{V}{\lambda^3} \cdot B \cdot f_{1/2}^-(z).$$

(d) Sketch the zero field susceptibility $\chi(T) = \partial M / \partial B |_{B=0}$, and indicate its behavior at low and high temperatures.

● The magnetic susceptibility is

$$\chi \equiv \left. \frac{\partial M}{\partial B} \right|_{B=0} = \frac{2 \mu_0^2}{k_B T} \frac{V}{\lambda^3} \cdot f_{1/2}^-(z),$$

with z given by,

$$N = 2 \frac{V}{\lambda^3} \cdot f_{3/2}^-(z).$$

In the low temperature limit, $(\ln z = \beta \mu \to \infty)$

$$f_n^-(z) = \frac{1}{\Gamma(n)} \int_0^\infty dx \, \frac{x^{n-1}}{1 + e^{x - \ln(z)}} \underset{T \to 0}{\approx} \frac{1}{\Gamma(n)} \int_0^{\ln(z)} dx \, x^{n-1} = \frac{[\ln(z)]^n}{n \Gamma(n)},$$

$$N = 2 \frac{V}{\lambda^3} \cdot \frac{4(\ln z)^{3/2}}{3 \sqrt{\pi}}, \quad \Longrightarrow \quad \ln z = \left(\frac{3N \sqrt{\pi}}{8V} \lambda^3 \right)^{2/3},$$

$$\chi = \frac{4 \mu_0^2 V}{\sqrt{\pi} k_B T \lambda^3} \cdot \left(\frac{3N \sqrt{\pi}}{8V} \lambda^3 \right)^{1/3} = \frac{2 \mu_o^2 V}{k_B T \lambda^2} \cdot \left(\frac{3N}{\pi V} \right)^{1/3} = \frac{4 \pi m \mu_0^2 V}{h^2} \cdot \left(\frac{3N}{\pi V} \right)^{1/3}.$$

Their ratio of the last two expressions gives

$$\left. \frac{\chi}{N} \right|_{T \to 0} = \frac{\mu_0^2}{k_B T} \frac{f_{1/2}^-}{f_{3/2}^-} = \frac{3 \mu_0^2}{2 k_B T} \frac{1}{\ln(z)} = \frac{3 \mu_0^2}{2 k_B T} \frac{1}{\beta \varepsilon_F} = \frac{3 \mu_0^2}{2 k_B T_F}.$$

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In the high temperature limit ($z \to 0$),

$$f_n(z) \underset{z \to 0}{\to} \frac{z}{\Gamma(n)} \int_0^\infty dx\, x^{n-1} e^{-x} = z,$$

and thus

$$N \underset{\beta \to 0}{\to} \frac{2V}{\lambda^3} \cdot z, \quad \implies \quad z \approx \frac{N}{2V} \cdot \lambda^3 = \frac{N}{2V} \cdot \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \to 0,$$

which is consistent with $\beta \to 0$. Using this result,

$$\chi \approx \frac{2\mu_0^2 V}{k_B T \lambda^3} \cdot z = \frac{N\mu_0^2}{k_B T}.$$

The result

$$\left(\frac{\chi}{N} \right)_{T \to \infty} = \frac{\mu_0^2}{k_B T},$$

is known as the *Curie susceptibility*.
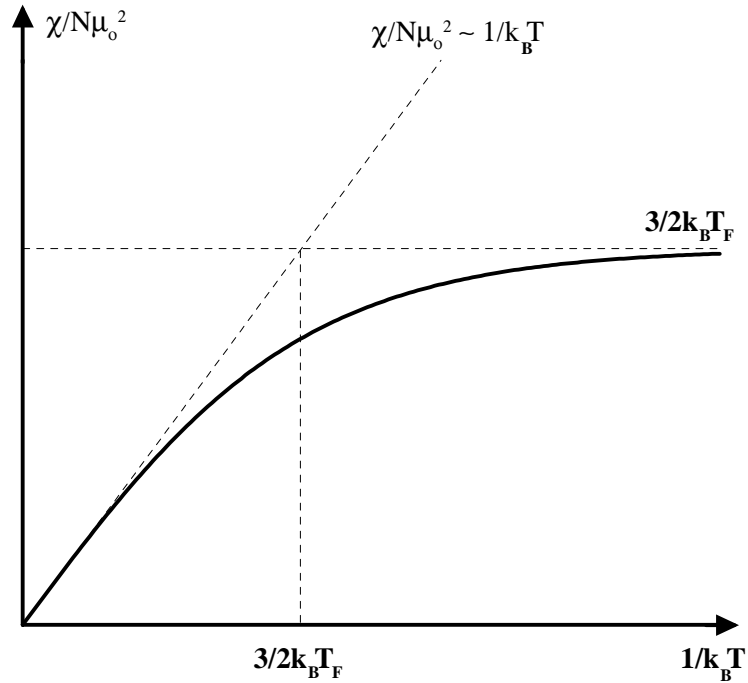
(e) Estimate the magnitude of χ/N for a typical metal at room temperature.

- Since $T_{Room} \ll T_F \approx 10^4 K$, we can take the low T limit for χ (see(d)), and

$$\frac{\chi}{N} = \frac{3\mu_0^2}{2k_B T_F} \approx \frac{3 \times (9.3 \times 10^{-24})^2}{2 \times 1.38 \times 10^{-23}} \approx 9.4 \times 10^{-24} \text{J/T}^2,$$

where we used

$$\mu_0 = \frac{eh}{2mc} \simeq 9.3 \times 10^{-24} \text{ J/T}.$$

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4. *Freezing of He^3:*   At low temperatures He^3 can be converted from liquid to solid by application of pressure. A peculiar feature of its phase boundary is that $(dP/dT)_{\text{melting}}$ is negative at temperatures below $0.3\,$K $[(dP/dT)_m \approx -30\text{atm K}^{-1}$ at $T \approx 0.1\,$K$]$. We will use a simple model of liquid and solid phases of He^3 to account for this feature.

(a) In the solid phase, the He^3 atoms form a crystal lattice. Each atom has nuclear spin of $1/2$. Ignoring the interaction between spins, what is the entropy per particle s_s, due to the spin degrees of freedom?

• Entropy of solid He^3 comes from the nuclear spin degeneracies, and is given by

$$s_s = \frac{S_s}{N} = \frac{k_B \ln(2^N)}{N} = k_B \ln 2.$$

(b) Liquid He^3 is modelled as an ideal Fermi gas, with a volume of 46Å^3 per atom. What is its Fermi temperature T_F, in degrees Kelvin?

• The Fermi temperature for liquid ^{3}He may be obtained from its density as

$$T_F = \frac{\varepsilon_F}{k_B} = \frac{h^2}{2mk_B} \left(\frac{3N}{8\pi V}\right)^{2/3}$$

$$\approx \frac{(6.7 \times 10^{-34})^2}{2 \cdot (6.8 \times 10^{-27})(1.38 \times 10^{-23})} \left(\frac{3}{8\pi \times 46 \times 10^{-30}}\right)^{2/3} \approx 9.2\,\text{K}.$$

(c) How does the heat capacity of liquid He^3 behave at low temperatures? Write down an expression for C_V in terms of N, T, k_B, T_F, *up to a numerical constant*, that is valid for $T \ll T_F$.

• The heat capacity comes from the excited states at the fermi surface, and is given by

$$C_V = k_B \frac{\pi^2}{6} k_B T \; D(\varepsilon_F) = \frac{\pi^2}{6} k_B^2 T \frac{3N}{2k_B T_F} = \frac{\pi^2}{4} N k_B \frac{T}{T_F}.$$

(d) Using the result in (c), calculate the entropy per particle s_ℓ, in the liquid at low temperatures. For $T \ll T_F$, which phase (solid or liquid) has the higher entropy?

• The entropy can be obtained from the heat capacity as

$$C_V = \frac{TdS}{dT}, \quad \Rightarrow \quad s_\ell = \frac{1}{N} \int_0^T \frac{C_V \, dT}{T} = \frac{\pi^2}{4} k_B \frac{T}{T_F}.$$

As $T \to 0$, $s_\ell \to 0$, while s_s remains finite. This is an unusual situation in which the solid has more entropy than the liquid! (The finite entropy is due to treating the nuclear spins as independent. There is actually a weak coupling between spins which causes magnetic ordering at a much lower temperature, removing the finite entropy.)

(e) By equating chemical potentials, or by any other technique, prove the Clausius–Clapeyron equation $(dP/dT)_{\text{melting}} = (s_\ell - s_s)/(v_\ell - v_s)$, where v_ℓ and v_s are the volumes per particle in the liquid and solid phases respectively.

• The Clausius-Clapeyron equation can be obtained by equating the chemical potentials at the phase boundary,

$$\mu_\ell(T, P) = \mu_s(T, P), \quad \text{and} \quad \mu_\ell(T + \Delta T, P + \Delta P) = \mu_s(T + \Delta T, P + \Delta P).$$

Expanding the second equation, and using the thermodynamic identities

$$\left(\frac{\partial \mu}{\partial T} \right)_P = -\frac{S}{N}, \text{ and } \left(\frac{\partial \mu}{\partial P} \right)_T = \frac{V}{N},$$

results in

$$\left(\frac{\partial P}{\partial T} \right)_{\text{melting}} = \frac{s_\ell - s_s}{v_\ell - v_s}.$$

(f) It is found experimentally that $v_\ell - v_s = 3\text{Å}^3$ per atom. Using this information, plus the results obtained in previous parts, estimate $(dP/dT)_{\text{melting}}$ at $T \ll T_F$.

• The negative slope of the phase boundary results from the solid having more entropy than the liquid, and can be calculated from the Clausius-Clapeyron relation

$$\left(\frac{\partial P}{\partial T} \right)_{\text{melting}} = \frac{s_\ell - s_s}{v_\ell - v_s} \approx k_B \frac{\frac{\pi^2}{4} \left(\frac{T}{T_F} \right) - \ln 2}{v_\ell - v_s}.$$

Using the values, $T = 0.1 \, \text{K}$, $T_F = 9.2 \, \text{J K}$, and $v_\ell - v_s = 3 \, \text{Å}^3$, we estimate

$$\left(\frac{\partial P}{\partial T} \right)_{\text{melting}} \approx -2.7 \times 10^6 \text{Pa} \, ^\circ\text{K}^{-1},$$

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in reasonable agreement with the observations.

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5. *Non-interacting fermions:* Consider a grand canonical ensemble of non-interacting *fermions* with chemical potential μ. The one–particle states are labelled by a wavevector $\vec{k}$, and have energies $\mathcal{E}(\vec{k})$.

(a) What is the joint probability $P(\{n_{\vec{k}}\})$, of finding a set of occupation numbers $\{n_{\vec{k}}\}$, of the one–particle states?

• In the grand canonical ensemble with chemical potential μ, the joint probability of finding a set of occupation numbers $\{n_{\vec{k}}\}$, for one–particle states of energies $\mathcal{E}(\vec{k})$ is given by the Fermi distribution

$$P(\{n_{\vec{k}}\}) = \prod_{\vec{k}} \frac{\exp\left[\beta(\mu - \mathcal{E}(\vec{k}))n_{\vec{k}}\right]}{1 + \exp\left[\beta(\mu - \mathcal{E}(\vec{k}))\right]}, \qquad \text{where} \quad n_{\vec{k}} = 0 \text{ or } 1, \quad \text{for each } \vec{k}.$$

(b) Express your answer to part (a) in terms of the average occupation numbers $\left\{\langle n_{\vec{k}}\rangle_{-}\right\}$.

• The average occupation numbers are given by

$$\langle n_{\vec{k}}\rangle_{-} = \frac{\exp\left[\beta(\mu - \mathcal{E}(\vec{k}))\right]}{1 + \exp\left[\beta(\mu - \mathcal{E}(\vec{k}))\right]},$$

from which we obtain

$$\exp\left[\beta(\mu - \mathcal{E}(\vec{k}))\right] = \frac{\langle n_{\vec{k}}\rangle_{-}}{1 - \langle n_{\vec{k}}\rangle_{-}}.$$

This enables us to write the joint probability as

$$P(\{n_{\vec{k}}\}) = \prod_{\vec{k}} \left[\left(\langle n_{\vec{k}}\rangle_{-}\right)^{n_{\vec{k}}} \left(1 - \langle n_{\vec{k}}\rangle_{-}\right)^{1-n_{\vec{k}}}\right].$$

(c) A random variable has a set of ℓ discrete outcomes with probabilities p_n, where $n = 1, 2, \cdots, \ell$. What is the entropy of this probability distribution? What is the maximum possible entropy?

• A random variable has a set of ℓ discrete outcomes with probabilities p_n. The entropy of this probability distribution is calculated from

$$S = -k_B \sum_{n=1}^{\ell} p_n \ln p_n \quad .$$

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The maximum entropy is obtained if all probabilities are equal, $p_n = 1/\ell$, and given by $S_{max} = k_B \ln \ell$.

(d) Calculate the entropy of the probability distribution for fermion occupation numbers in part (b), and comment on its zero temperature limit.

• Since the occupation numbers of different one-particle states are independent, the corresponding entropies are additive, and given by

$$S = -k_B \sum_{\vec{k}} \left[\langle n_{\vec{k}} \rangle_- \ln \langle n_{\vec{k}} \rangle_- + \left(1 - \langle n_{\vec{k}} \rangle_- \right) \ln \left(1 - \langle n_{\vec{k}} \rangle_- \right) \right].$$

In the zero temperature limit all occupation numbers are either 0 or 1. In either case the contribution to entropy is zero, and the fermi system at $T = 0$ has zero entropy.

(e) Calculate the variance of the total number of particles $\langle N^2 \rangle_c$, and comment on its zero temperature behavior.

• The total number of particles is given by $N = \sum_{\vec{k}} n_{\vec{k}}$. Since the occupation numbers are independent

$$\langle N^2 \rangle_c = \sum_{\vec{k}} \langle n_{\vec{k}}^2 \rangle_c = \sum_{\vec{k}} \left(\langle n_{\vec{k}}^2 \rangle_- - \langle n_{\vec{k}} \rangle_-^2 \right) = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle_- \left(1 - \langle n_{\vec{k}} \rangle_- \right),$$

since $\langle n_{\vec{k}}^2 \rangle_- = \langle n_{\vec{k}} \rangle_-$. Again, since at $T = 0$, $\langle n_{\vec{k}} \rangle_- = 0$ or 1, the variance $\langle N^2 \rangle_c$ vanishes.

(f) The number fluctuations of a gas is related to its compressibility κ_T, and number density $n = N/V$, by

$$\langle N^2 \rangle_c = N n k_B T \kappa_T \quad .$$

Give a *numerical estimate* of the compressibility of the fermi gas in a metal at $T = 0$ in units of $\AA^3 eV^{-1}$.

• To obtain the compressibility from $\langle N^2 \rangle_c = N n k_B T \kappa_T$, we need to examine the behavior at small but finite temperatures. At small but finite T, a small fraction of states around the fermi energy have occupation numbers around $1/2$. The number of such states is roughly $N k_B T / \varepsilon_F$, and hence we can estimate the variance as

$$\langle N^2 \rangle_c = N n k_B T \kappa_T \approx \frac{1}{4} \times \frac{N k_B T}{\varepsilon_F}.$$

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The compressibility is then approximates as

$$\kappa_T \approx \frac{1}{4n\varepsilon_F},$$

where $n = N/V$ is the density. For electrons in a typical metal $n \approx 10^{29} m^{-3} \approx 0.1 \mathring{A}^3$, and $\varepsilon_F \approx 5eV \approx 5 \times 10^4 \,^\circ K$, resulting in

$$\kappa_T \approx 0.5 \mathring{A}^3 eV^{-1}.$$

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6. *Stoner ferromagnetism:* The conduction electrons in a metal can be treated as a gas of fermions of spin $1/2$ (with up/down degeneracy), and density $n = N/V$. The Coulomb repulsion favors wave functions which are antisymmetric in position coordinates, thus keeping the electrons apart. Because of the full (position *and* spin) antisymmetry of fermionic wave functions, this interaction may be approximated by an effective spin-spin coupling which favors states with parallel spins. In this simple approximation, the net effect is described by an interaction energy

$$U = \alpha \frac{N_+ N_-}{V},$$

where N_+ and $N_- = N - N_+$ are the numbers of electrons with up and down spins, and V is the volume. (The parameter α is related to the scattering length a by $\alpha = 4\pi\hbar^2 a/m$.)

(a) The ground state has two fermi seas filled by the spin up and spin down electrons. Express the corresponding fermi wavevectors $k_{F\pm}$ in terms of the densities $n_\pm = N_\pm/V$.

● In the ground state, all available wavevectors are filled up in a sphere. Using the appropriate density of states, the corresponding radii of $k_{F\pm}$ are calculated as

$$N_\pm = V \int_{k < k_{F\pm}} \frac{d^3k}{(2\pi)^3} = V \int_0^{k_{F\pm}} \frac{4\pi}{(2\pi)^3} k^2 dk = \frac{V k_{F\pm}^3}{6\pi^2},$$

leading to

$$k_{F\pm} = \left(6\pi^2 n_\pm\right)^{1/3}.$$

(b) Calculate the kinetic energy density of the ground state as a function of the densities $n_\pm$, and fundamental constants.

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- For each Fermi sea, the kinetic energy is given by

$$E_{\text{kin}.\pm} = V \int_{k < k_{\text{F}\pm}} \frac{\hbar^2 k^2}{2m} \frac{d^3 k}{(2\pi)^3} = V \frac{\hbar^2}{2m} \frac{4\pi}{(2\pi)^3} \frac{k_{\text{F}\pm}^5}{5},$$

where m is the mass of the electron. The total kinetic energy density is thus equal to

$$\frac{E_{\text{kin}}}{V} = \frac{\hbar^2}{2m} \frac{1}{10\pi^2} \left(k_{F+}^5 + k_{F-}^5\right) = \frac{\hbar^2}{2m} \frac{3}{5} \left(6\pi^2\right)^{2/3} \left(n_+^{5/3} + n_-^{5/3}\right).$$

(c) Assuming small deviations $n_\pm = n/2 \pm \delta$ from the symmetric state, expand the kinetic energy to *fourth order in* δ.

- Using the expansion

$$(x + \delta)^{5/3} = x^{5/3} + \frac{5}{3} x^{2/3} \delta + \frac{10}{9} x^{-1/3} \frac{\delta^2}{2} - \frac{10}{27} x^{-4/3} \frac{\delta^3}{6} + \frac{40}{81} x^{-7/3} \frac{\delta^4}{24} + \mathcal{O}(\delta^5),$$

the kinetic energy calculated in the previous part can be written as

$$\frac{E_{kin}}{V} = \frac{\hbar^2}{2m} \frac{6}{5} \left(6\pi^2\right)^{2/3} \left[\left(\frac{n}{2}\right)^{5/3} + \frac{5}{9} \left(\frac{n}{2}\right)^{-1/3} \delta^2 + \frac{5}{243} \left(\frac{n}{2}\right)^{-7/3} \delta^4 + \mathcal{O}(\delta^6)\right].$$

(d) Express the spin-spin interaction density U/V in terms of n and δ. Find the critical value of α_c, such that for $\alpha > \alpha_c$ the electron gas can lower its total energy by spontaneously developing a magnetization. (This is known as the *Stoner instability.*)

- The interaction energy density is

$$\frac{U}{V} = \alpha n_+ n_- = \alpha \left(\frac{n}{2} + \delta\right) \left(\frac{n}{2} - \delta\right) = \alpha \frac{n^2}{4} - \alpha \delta^2.$$

The total energy density has the form

$$\frac{E}{V} = \frac{E_0 + \alpha n^2/4}{V} + \left[\frac{4}{3} \left(3\pi^2\right)^{2/3} \frac{\hbar^2}{2m} n^{-1/3} - \alpha\right] \delta^2 + \mathcal{O}\left(\delta^4\right).$$

When the second order term in δ is negative, the electron gas has lower energy for finite δ, i.e. it acquires a spontaneous magnetization. This occurs for

$$\alpha > \alpha_c = \frac{4}{3} \left(3\pi^2\right)^{2/3} \frac{\hbar^2}{2m} n^{-1/3}.$$

(e) Explain qualitatively, and sketch the behavior of the spontaneous magnetization as a function of α.

• For $\alpha > \alpha_c$, the optimal value of δ is obtained by minimizing the energy density. Since the coefficient of the fourth order term is positive, and the optimal δ goes to zero continuously as $\alpha \to \alpha_c$; the minimum energy is obtained for a value of $\delta^2 \propto (\alpha - \alpha_c)$. The magnetization is proportional to δ, and hence grows in the vicinity of α_c as $\sqrt{\alpha - \alpha_c}$, as sketched below.

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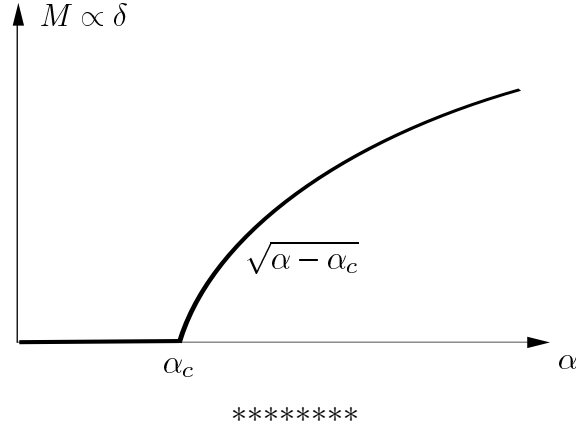
7. *Boson magnetism:* Consider a gas of non-interacting spin 1 bosons, each subject to a Hamiltonian

$$\mathcal{H}_1(\vec{p}, s_z) = \frac{\vec{p}^{\,2}}{2m} - \mu_0 s_z B \quad ,$$

where $\mu_0 = e\hbar/mc$, and s_z takes *three* possible values of (-1, 0, +1). (The orbital effect, $\vec{p} \to \vec{p} - e\vec{A}$, has been ignored.)

(a) In a grand canonical ensemble of chemical potential μ, what are the average occupation numbers $\left\{ \langle n_+(\vec{k}) \rangle, \langle n_0(\vec{k}) \rangle, \langle n_-(\vec{k}) \rangle \right\}$, of one-particle states of wavenumber $\vec{k} = \vec{p}/\hbar$?

• Average occupation numbers of the one-particle states in the grand canonical ensemble of chemical potential μ, are given by the Bose-Einstein distribution

$$n_s(\vec{k}) = \frac{1}{e^{\beta[\mathcal{H}(s)-\mu]} - 1}, \qquad (\text{for } s = -1, 0, 1)$$

$$= \frac{1}{\exp\left[\beta\left(\frac{p^2}{2m} - \mu_0 s B\right) - \beta\mu\right] - 1}$$

(b) Calculate the average total numbers $\{N_+, N_0, N_-\}$, of bosons with the three possible values of s_z in terms of the functions $f_m^+(z)$.

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- The total numbers of particles with spin s are given by

$$N_s = \sum_{\{\vec{k}\}} n_s(\vec{k}), \quad \Longrightarrow \quad N_s = \frac{V}{(2\pi)^3} \int d^3k \frac{1}{\exp\left[\beta\left(\frac{p^2}{2m} - \mu_0 sB\right) - \beta\mu\right] - 1}.$$

After a change of variables, $k \equiv x^{1/2} \sqrt{2mk_BT}/h$, we get

$$N_s = \frac{V}{\lambda^3} f_{3/2}^+ \left(ze^{\beta\mu_0 sB}\right),$$

where

$$f_m^+(z) \equiv \frac{1}{\Gamma(m)} \int_0^\infty \frac{dx\, x^{m-1}}{z^{-1}e^x - 1}, \qquad \lambda \equiv \frac{h}{\sqrt{2\pi mk_BT}}, \qquad z \equiv e^{\beta\mu}.$$

(c) Write down the expression for the magnetization $M(T, \mu) = \mu_0(N_+ - N_-)$, and by expanding the result for small B find the *zero field susceptibility* $\chi(T, \mu) = \partial M/\partial B|_{B=0}$.

- The magnetization is obtained from

$$M(T, \mu) = \mu_0 \left(N_+ - N_-\right)$$
$$= \mu_0 \frac{V}{\lambda^3} \left[f_{3/2}^+ \left(ze^{\beta\mu_0 B}\right) - f_{3/2}^+ \left(ze^{-\beta\mu_0 sB}\right)\right].$$

Expanding the result for small B gives

$$f_{3/2}^+ \left(ze^{\pm\beta\mu_0 B}\right) \approx f_{3/2}^+ \left(z[1 \pm \beta\mu_0 B]\right) \approx f_{3/2}^+(z) \pm z \cdot \beta\mu_0 B \frac{\partial}{\partial z} f_{3/2}^+(z).$$

Using $zdf_m^+(z)/dz = f_{m-1}^+(z)$, we obtain

$$M = \mu_0 \frac{V}{\lambda^3} (2\beta\mu_0 B) \cdot f_{1/2}^+(z) = \frac{2\mu_0^2}{k_BT} \frac{V}{\lambda^3} \cdot B \cdot f_{1/2}^+(z),$$

and

$$\chi \equiv \left.\frac{\partial M}{\partial B}\right|_{B=0} = \frac{2\mu_0^2}{k_BT} \frac{V}{\lambda^3} \cdot f_{1/2}^+(z).$$

To find the behavior of $\chi(T, n)$, where $n = N/V$ is the total density, proceed as follows:

(d) For $B = 0$, find the high temperature expansion for $z(\beta, n) = e^{\beta\mu}$, correct to second order in n. Hence obtain the first correction from quantum statistics to $\chi(T, n)$ at high temperatures.

- In the high temperature limit, z is small. Use the Taylor expansion for $f_m^+(z)$ to write the total density $n(B = 0)$, as

$$n(B = 0) = \left.\frac{N_+ + N_0 + N_-}{V}\right|_{B=0} = \frac{3}{\lambda^3} f_{3/2}^+(z)$$

$$\approx \frac{3}{\lambda^3}\left(z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots\right).$$

Inverting the above equation gives

$$z = \left(\frac{n\lambda^3}{3}\right) - \frac{1}{2^{3/2}}\left(\frac{n\lambda^3}{3}\right)^2 + \cdots.$$

The susceptibility is then calculated as

$$\chi = \frac{2\mu_0^2}{k_B T}\frac{V}{\lambda^3} \cdot f_{1/2}^+(z),$$

$$\chi/N = \frac{2\mu_0^2}{k_B T}\frac{1}{n\lambda^3}\left(z + \frac{z^2}{2^{1/2}} + \cdots\right)$$

$$= \frac{2\mu_0^2}{3k_B T}\left[1 + \left(-\frac{1}{2^{3/2}} + \frac{1}{2^{1/2}}\right)\left(\frac{n\lambda^3}{3}\right) + O\left(n^2\right)\right].$$

(e) Find the temperature $T_c(n, B = 0)$, of Bose–Einstein condensation. What happens to $\chi(T, n)$ on approaching $T_c(n)$ from the high temperature side?

- Bose-Einstein condensation occurs when $z = 1$, at a density

$$n = \frac{3}{\lambda^3} f_{3/2}^+(1),$$

or a temperature

$$T_c(n) = \frac{h^2}{2\pi m k_B}\left(\frac{n}{3\,\zeta_{3/2}}\right)^{2/3},$$

where $\zeta_{3/2} \equiv f_{3/2}^+(1) \approx 2.61$. Since $\lim_{z\to 1} f_{1/2}^+(z) = \infty$, the susceptibility $\chi(T, n)$ diverges on approaching $T_c(n)$ from the high temperature side.

(f) What is the chemical potential μ for $T < T_c(n)$, at a small but finite value of B? Which one-particle state has a macroscopic occupation number?

- Since $n_s(\vec{k}, B) = \left[z^{-1}e^{\beta\mathcal{E}_s(\vec{k},B)} - 1\right]^{-1}$ is a positive number for all $\vec{k}$ and s_z, μ is bounded above by the minimum possible energy, i.e.

$$\text{for} \quad T < T_c, \quad \text{and} \quad B \text{ finite}, \quad ze^{\beta\mu_0 B} = 1, \quad \Longrightarrow \quad \mu = -\mu_0 B.$$

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Hence the macroscopically occupied one particle state has $\vec{k} = 0$, *and* $s_z = +1$.

(g) Using the result in (f), find the spontaneous magnetization,

$$\overline{M}(T, n) = \lim_{B \to 0} M(T, n, B).$$

• Contribution of the excited states to the magnetization vanishes as $B \to 0$. Therefore the total magnetization for $T < T_c$ is due to the macroscopic occupation of the $(k = 0, s_z = +1)$ state, and

$$\overline{M}(T, n) = \mu_0 \, V \, n_+(k = 0)$$

$$= \mu_0 \, V \left(n - n_{excited} \right) = \mu_0 \left(N - \frac{3 \, V}{\lambda^3} \zeta_{3/2} \right).$$

$$********$$

8. *Dirac fermions* are non-interacting particles of spin $1/2$. The one-particle states come in pairs of positive and negative energies,

$$\mathcal{E}_\pm(\vec{k}) = \pm \sqrt{m^2 c^4 + \hbar^2 k^2 c^2} \quad ,$$

independent of spin.

(a) For *any* fermionic system of chemical potential μ, show that the probability of finding an occupied state of energy $\mu + \delta$ is the same as that of finding an unoccupied state of energy $\mu - \delta$. (δ is any constant energy.)

• According to Fermi statistics, the probability of occupation of a state of of energy $\mathcal{E}$ is

$$p\left[n(\mathcal{E})\right] = \frac{e^{\beta(\mu - \mathcal{E})n}}{1 + e^{\beta(\mu - \mathcal{E})}}, \qquad \text{for} \quad n = 0, 1.$$

For a state of energy $\mu + \delta$,

$$p\left[n(\mu + \delta)\right] = \frac{e^{\beta\delta n}}{1 + e^{\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu + \delta) = 1\right] = \frac{e^{\beta\delta}}{1 + e^{\beta\delta}} = \frac{1}{1 + e^{-\beta\delta}}.$$

Similarly, for a state of energy $\mu - \delta$,

$$p\left[n(\mu - \delta)\right] = \frac{e^{-\beta\delta n}}{1 + e^{-\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu - \delta) = 0\right] = \frac{1}{1 + e^{-\beta\delta}} = p\left[n(\mu + \delta) = 1\right],$$

i.e. the probability of finding an occupied state of energy $\mu + \delta$ is the same as that of finding an unoccupied state of energy $\mu - \delta$.

(b) At zero temperature all negative energy Dirac states are occupied and all positive energy ones are empty, i.e. $\mu(T = 0) = 0$. Using the result in (a) find the chemical potential at finite temperatures T.

• The above result implies that for $\mu = 0$, $\langle n(\mathcal{E}) \rangle + \langle n - \mathcal{E}) \rangle$ is unchanged for an temperature; any particle leaving an occupied negative energy state goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if μ stays at zero. Thus, the particle–hole symmetry enfrces $\mu(T) = 0$.

(c) Show that the mean excitation energy of this system at finite temperature satisfies

$$E(T) - E(0) = 4V \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1} \quad .$$

• Using the label +(-) for the positive (energy) states, the excitation energy is calculated as

$$E(T) - E(0) = \sum_{k,s_z} \left[\langle n_+(k) \rangle \mathcal{E}_+(k) - (1 - \langle n_-(k) \rangle) \mathcal{E}_-(k) \right]$$

$$= 2\sum_k 2 \langle n_+(k) \rangle \mathcal{E}_+(k) = 4V \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1}.$$

(d) Evaluate the integral in part (c) for *massless Dirac particles* (i.e. for $m = 0$).
• For $m = 0$, $\mathcal{E}_+(k) = \hbar c|k|$, and

$$E(T) - E(0) = 4V \int_0^\infty \frac{4\pi k^2 dk}{8\pi^3} \frac{\hbar c k}{e^{\beta\hbar c k} + 1} = \qquad (\text{set } \beta\hbar ck = x)$$

$$= \frac{2V}{\pi^2} k_B T \left(\frac{k_B T}{\hbar c}\right)^3 \int_0^\infty dx \frac{x^3}{e^x + 1}$$

$$= \frac{7\pi^2}{60} V k_B T \left(\frac{k_B T}{\hbar c}\right)^3 .$$

For the final expression, we have noted that the needed integral is $3! f_4^-(1)$, and used the given value of $f_4^-(1) = 7\pi^4/720$.

(e) Calculate the heat capacity, C_V, of such massless Dirac particles.

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• The heat capacity can now be evaluated as

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{7\pi^2}{15} V k_B \left(\frac{k_B T}{\hbar c} \right)^3 .$$

(f) Describe the qualitative dependence of the heat capacity at low temperature if the particles are massive.

• When $m \neq 0$, there is an energy gap between occupied and empty states, and we thus expect an exponentially activated energy, and hence heat capacity. For the low energy excitations,

$$\mathcal{E}_+(k) \approx mc^2 + \frac{\hbar^2 k^2}{2m} + \cdots ,$$

and thus

$$E(T) - E(0) \approx \frac{2V}{\pi^2} mc^2 e^{-\beta mc^2} \frac{4\pi\sqrt{\pi}}{\lambda^3} \int_0^\infty dx x^2 e^{-x}$$

$$= \frac{48}{\sqrt{\pi}} \frac{V}{\lambda^3} mc^2 e^{-\beta mc^2} .$$

The corresponding heat capacity, to leading order thus behaves as

$$C(T) \propto k_B \frac{V}{\lambda^3} \left(\beta mc^2 \right)^2 e^{-\beta mc^2} .$$

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9. *Numerical estimates:* The following table provides typical values for the Fermi energy and Fermi temperature for (i) Electrons in a typical metal; (ii) Nucleons in a heavy nucleus; and (iii) He^3 atoms in liquid He^3 (atomic volume $= 46.2 \mathring{A}^3$ per atom).

	$n(1/\text{m}^3)$	$m(\text{Kg})$	$\varepsilon_F(\text{eV})$	$T_F(\text{K})$
electron	10^{29}	9×10^{-31}	4.4	5×10^4
nucleons	10^{44}	1.6×10^{-27}	1.0×10^8	1.1×10^{12}
liquid He^3	2.6×10^{28}	4.6×10^{-27}	$\times 10^{-3}$	10^1

(a) Estimate the ratio of the electron and phonon heat capacities at room temperature for a typical metal.

• For an electron gas, $T_F \approx 5 \times 10^4 \text{K}$,

$$T_F \gg T_{\text{room}}, \quad \Longrightarrow \quad \frac{C_{\text{electron}}}{N k_B} \approx \frac{\pi^2}{2} \cdot \frac{T}{T_F} \approx 0.025 .$$

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For the phonon gas in iron, the Debye temperature is $T_D \approx 470$K, and hence

$$\frac{C_{\text{phonon}}}{Nk_B} \approx 3 \left[1 - \frac{1}{20} \left(\frac{T}{T_D} \right)^2 + \dots \right] \approx 3,$$

resulting in

$$\frac{C_{\text{electron}}}{C_{\text{phonon}}} \approx 8 \times 10^{-3}.$$

(b) Compare the thermal wavelength of a neutron at room temperature to the minimum wavelength of a phonon in a typical crystal.

• Thermal wavelengths are given by

$$\lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}}.$$

For a neutron at room temperature, using the values

$$m = 1.67 \times 10^{-27} \text{kg}, \quad T = 300\,\text{K},$$

$$k_B = 1.38 \times 10^{-23}\,\text{JK}^{-1}, \quad h = 6.67 \times 10^{-34}\,\text{Js},$$

we obtain $\lambda = 1\text{Å}$.

The typical wavelength of a phonon in a solid is $\lambda = 0.01\,m$, which is much longer than the neutron wavelength. The minimum wavelength is, however, of the order of atomic spacing $(3 - 5\,\text{Å})$, which is comparable to the neutron thermal wavelength.

(c) Estimate the degeneracy discriminant, $n\lambda^3$, for hydrogen, helium, and oxygen gases at room temperature and pressure. At what temperatures do quantum mechanical effects become important for these gases?

• Quantum mechanical effects become important if $n\lambda^3 \geq 1$. In the high temperature limit the ideal gas law is valid, and the degeneracy criterion can be reexpressed in terms of pressure $P = nk_B T$, as

$$n\lambda^3 = \frac{nh^3}{(2\pi m k_B T)^{3/2}} = \frac{P}{(k_B T)^{5/2}} \frac{h^3}{(2\pi m)^{3/2}} \ll 1.$$

It is convenient to express the answers starting with an imaginary gas of 'protons' at room temperature and pressure, for which

$$m_p = 1.7 \times 10^{-34}\text{Kg}, \qquad P = 1\,\text{atm.} = 10^5\,\text{Nm}^{-2},$$

$$\text{and} \quad (n\lambda^3)_{\text{proton}} = \frac{10^{-5}}{(4.1 \times 10^{-21})^{5/2}} \frac{(6.7 \times 10^{-34})^3}{(2\pi \cdot 1.7 \times 10^{-27})^{3/2}} = 2 \times 10^{-5}.$$

The quantum effects appear below $T = T_Q$, at which $n\lambda^3$ becomes order of unity. Using

$$n\lambda^3 = (n\lambda^3)_{\text{proton}} \left(\frac{m_p}{m}\right)^{3/2}, \quad \text{and} \quad T_Q = T_{\text{room}}(n\lambda^3)^{3/2},$$

we obtain the following table:

(d) Experiments on He^4 indicate that at temperatures below 1K, the heat capacity is given by $C_V = 20.4T^3 JKg^{-1}K^{-1}$. Find the low energy excitation spectrum, $\mathcal{E}(k)$, of He^4. (Hint: There is only one non-degenerate branch of such excitations.)

• A spectrum of low energy excitations scaling as

$$\mathcal{E}(k) \propto k^s,$$

in d-dimensional space, leads to a low temperature heat capacity that vanishes as

$$C \propto T^{d/s}.$$

Therefore, from $C_V = 20.4\,T^3 \text{JKg}^{-1}\text{K}^{-1}$ in $d = 3$, we can conclude $s = 1$, i.e. a spectrum of the form

$$\mathcal{E}(k) = \hbar c_s |\vec{k}|,$$

corresponding to sound waves of speed c_s. Inserting all the numerical factors, we have

$$C_V = \frac{12\pi^4 Nk_B}{5}\left(\frac{T}{\Theta}\right)^3, \quad \text{where} \quad \Theta = \frac{\hbar c_s}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}.$$

Hence, we obtain

$$\mathcal{E} = \hbar c_s k = k_B \left(\frac{2\pi^2 k_B V}{5}\frac{T^3}{C_V}\right)^{1/3} k = (2 \times 10^{-32}\text{Jm})\, k,$$

corresponding to a sound speed of $c_s \approx 2 \times 10^2 \text{ms}^{-1}$.

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10. *Solar interior:* According to astrophysical data, the plasma at the center of the sun has the following properties:

Temperature:	$T = 1.6 \times 10^7$ K
Hydrogen density:	$\rho_H = 6 \times 10^4$ kg m^{-3}
Helium density:	$\rho_{He} = 1 \times 10^5$ kg m^{-3}.

(a) Obtain the thermal wavelengths for electrons, protons, and α-particles (nuclei of He).

- The thermal wavelengths of electrons, protons, and α-particles in the sun are obtained from

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}},$$

and $T = 1.6 \times 10^7 \text{K}$, as

$$\lambda_{\text{electron}} \approx \frac{6.7 \times 10^{-34}\,\text{J/s}}{\sqrt{2\pi \times (9.1 \times 10^{-31}\,\text{Kg}) \cdot (1.4 \times 10^{-23}\,\text{J/K}) \cdot (1.6 \times 10^7\,\text{K})}} \approx 1.9 \times 10^{-11}\,\text{m},$$

$$\lambda_{\text{proton}} \approx \frac{6.7 \times 10^{-34}\,\text{J/s}}{\sqrt{2\pi \times (1.7 \times 10^{-27}\,\text{Kg}) \cdot (1.4 \times 10^{-23}\,\text{J/K}) \cdot (1.6 \times 10^7\,\text{K})}} \approx 4.3 \times 10^{-13}\,\text{m},$$

$$\text{and} \qquad \lambda_{\alpha-\text{particle}} = \frac{1}{2}\lambda_{\text{proton}} \approx 2.2 \times 10^{-13}\,\text{m}.$$

(b) Assuming that the gas is ideal, determine whether the electron, proton, or α-particle gases are degenerate in the quantum mechanical sense.

- The corresponding number densities are given by

$$\rho_H \approx 6 \times 10^4\,\text{kg/m}^3 \quad \implies \quad n_H \approx 3.5 \times 10^{31}\,\text{m}^{-3},$$

$$\rho_{He} \approx 1.0 \times 10^5\,\text{Kg/m}^3 \quad \implies \quad n_{He} = \frac{\rho_{He}}{4 m_H} \approx 1.5 \times 10^{31}\,\text{m}^{-3},$$

$$n_e = 2 n_{He} + n_H \approx 8.5 \times 10^{31}\,\text{m}^3.$$

The criterion for degeneracy is $n\lambda^3 \geq 1$, and

$$n_H \cdot \lambda_H^3 \approx 2.8 \times 10^{-6} \ll 1,$$

$$n_{He} \cdot \lambda_{He}^3 \approx 1.6 \times 10^{-7} \ll 1,$$

$$n_e \cdot \lambda_e^3 \approx 0.58 \sim 1.$$

Thus the electrons are weakly degenerate, and the nuclei are not.

(c) Estimate the total gas pressure due to these gas particles near the center of the sun.

- Since the nuclei are non-degenerate, and even the electrons are only weakly degenerate, their contributions to the overall pressure can be approximately calculated using the ideal gas law, as

$$P \approx (n_H + n_{he} + n_e) \cdot k_B T \approx 13.5 \times 10^{31}\,(\text{m}^{-3}) \cdot 1.38 \times 10^{-23}\,(\text{J/K}) \cdot 1.6 \times 10^7\,(\text{K})$$

$$\approx 3.0 \times 10^{16}\,\text{N/m}^2.$$

(d) Estimate the total radiation pressure close to the center of the sun. Is it matter, or radiation pressure, that prevents the gravitational collapse of the sun?

• The Radiation pressure at the center of the sun can be calculated using the black body formulas,

$$P = \frac{1}{3}\frac{U}{V}, \qquad \text{and} \qquad \frac{1}{4}\frac{U}{V}c = \frac{\pi^2 k^4}{60\hbar^3 c^3}T^4 = \sigma T^4,$$

as

$$P = \frac{4}{3c}\sigma T^4 = \frac{4 \cdot 5.7 \times 10^{-8}\,\text{W}/(\text{m}^2\text{K}^4) \cdot (1.6 \times 10^7\,\text{K})^4}{3 \cdot 3.0 \times 10^8\,\text{m/s}} \approx 1.7 \times 10^{13}\,\text{N/m}^2.$$

Thus at the pressure in the solar interior is dominated by the particles.

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11. *Bose condensation in d–dimensions:* Consider a gas of non-interacting (spinless) bosons with an energy spectrum $\epsilon = p^2/2m$, contained in a box of "volume" $V = L^d$ in d dimensions.

(a) Calculate the grand potential $\mathcal{G} = -k_B T \ln \mathcal{Q}$, and the density $n = N/V$, at a chemical potential μ. Express your answers in terms of d and $f_m^+(z)$, where $z = e^{\beta\mu}$, and

$$f_m^+(z) = \frac{1}{\Gamma(m)}\int_0^\infty \frac{x^{m-1}}{z^{-1}e^x - 1}dx.$$

(Hint: Use integration by parts on the expression for $\ln \mathcal{Q}$.)

• We have

$$\mathcal{Q} = \sum_{N=0}^{\infty} e^{N\beta\mu} \sum_{\{n_i\}}^{\sum_i n_i = N} \exp\left(-\beta\sum_i n_i\epsilon_i\right),$$

$$= \prod_i \sum_{\{n_i\}} e^{\beta(\mu-\epsilon_i)n_i} = \prod_i \frac{1}{1 - e^{\beta(\mu-\epsilon_i)}},$$

whence $\ln \mathcal{Q} = -\sum_i \ln\left(1 - e^{\beta(\mu-\epsilon_i)}\right)$. Replacing the summation $\sum_i$ with a d dimensional integration $\int V d^d k/(2\pi)^d = \left[VS_d/(2\pi)^d\right]\int k^{d-1}dk$, where $S_d = 2\pi^{d/2}/(d/2-1)!$, leads to

$$\ln \mathcal{Q} = -\frac{VS_d}{(2\pi)^d}\int k^{d-1}dk \ln\left(1 - ze^{-\beta\hbar^2 k^2/2m}\right).$$

The change of variable $x = \beta\hbar^2 k^2/2m$ ($\Rightarrow k = \sqrt{2mx/\beta}/\hbar$ and $dk = dx\sqrt{2m/\beta x}/2\hbar$) results in

$$\ln \mathcal{Q} = -\frac{VS_d}{(2\pi)^d}\frac{1}{2}\left(\frac{2m}{\hbar^2\beta}\right)^{d/2}\int x^{d/2-1}dx \ln\left(1 - ze^{-x}\right).$$

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Finally, integration by parts yields

$$\ln \mathcal{Q} = \frac{VS_d}{(2\pi)^d}\frac{1}{d}\left(\frac{2m}{\hbar^2\beta}\right)^{d/2}\int x^{d/2}dx\frac{ze^{-x}}{1-ze^{-x}} = V\frac{S_d}{d}\left(\frac{2m}{h^2\beta}\right)^{d/2}\int dx\frac{x^{d/2}}{z^{-1}e^x - 1},$$

i.e.

$$\mathcal{G} = -k_BT\ln\mathcal{Q} = -V\frac{S_d}{d}\left(\frac{2m}{h^2\beta}\right)^{d/2}k_BT\Gamma\left(\frac{d}{2}+1\right)f_{\frac{d}{2}+1}^+(z),$$

which can be simplified, using the property $\Gamma(x+1) = x\Gamma(x)$, to

$$\mathcal{G} = -\frac{V}{\lambda^d}k_BTf_{\frac{d}{2}+1}^+(z).$$

The average number of particles is calculated as

$$N = \frac{\partial}{\partial(\beta\mu)}\ln\mathcal{Q} = V\frac{S_d}{d}\left(\frac{2m}{h^2\beta}\right)^{d/2}\int x^{d/2-1}dx\frac{ze^{-x}}{1-ze^{-x}},$$

$$= V\frac{S_d}{2}\left(\frac{2m}{h^2\beta}\right)^{d/2}\Gamma\left(\frac{d}{2}\right)f_{\frac{d}{2}}^+(z) = \frac{V}{\lambda^d}f_{\frac{d}{2}}^+(z)$$

i.e.

$$n = \frac{1}{\lambda^d}f_{\frac{d}{2}}^+(z).$$

(b) Calculate the ratio PV/E, and compare it to the classical value.

• We have $PV = -\mathcal{G}$, while

$$E = -\frac{\partial}{\partial\beta}\ln\mathcal{Q} = +\frac{d}{2}\frac{\ln\mathcal{Q}}{\beta} = -\frac{d}{2}\mathcal{G}.$$

Thus $PV/E = 2/d$, identical to the classical value.

(c) Find the critical temperature, $T_c(n)$, for Bose-Einstein condensation.

• The critical temperature $T_c(n)$ is given by

$$n = \frac{1}{\lambda^d}f_{\frac{d}{2}}^+(1) = \frac{1}{\lambda^d}\zeta_{\frac{d}{2}},$$

for $d > 2$, *i.e.*

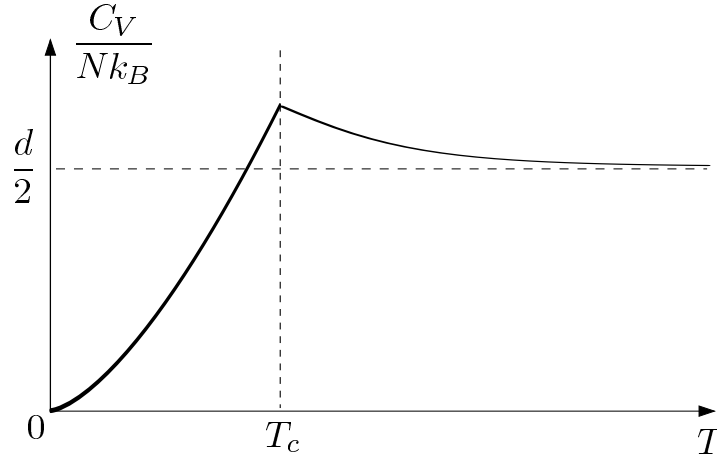$$T_c = \frac{h^2}{2mk_B}\left(\frac{n}{\zeta_{\frac{d}{2}}}\right)^{2/d}.$$

(d) Calculate the heat capacity $C(T)$ for $T < T_c(n)$.

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- At $T < T_c$, $z = 1$ and

$$C(T) = \left.\frac{\partial E}{\partial T}\right|_{z=1} = -\frac{d}{2}\left.\frac{\partial \mathcal{G}}{\partial T}\right|_{z=1} = -\frac{d}{2}\left(\frac{d}{2}+1\right)\frac{\mathcal{G}}{T} = \frac{d}{2}\left(\frac{d}{2}+1\right)\frac{V}{\lambda^d}k_B\zeta_{\frac{d}{2}+1}.$$

(e) Sketch the heat capacity at all temperatures.

-

(f) Find the ratio, $C_{\max}/C(T\to\infty)$, of the maximum heat capacity to its classical limit, and evaluate it in $d = 3$.

- As the maximum of the heat capacity occurs at the transition,

$$C_{\max} = C(T_c) = \frac{d}{2}\left(\frac{d}{2}+1\right)\frac{V}{\left(\zeta_{\frac{d}{2}}/n\right)}k_B f^+_{\frac{d}{2}+1}(1) = \frac{d}{2}Nk_B\left(\frac{d}{2}+1\right)\frac{\zeta_{\frac{d}{2}+1}}{\zeta_{\frac{d}{2}}}.$$

Thus

$$\frac{C_{\max}}{C(T\to\infty)} = \left(\frac{d}{2}+1\right)\frac{\zeta_{\frac{d}{2}+1}}{\zeta_{\frac{d}{2}}},$$

which evaluates to 1.283 in $d = 3$.

(g) How does the above calculated ratio behave as $d \to 2$? In what dimensions are your results valid? Explain.

- The maximum heat capacity, *as it stands above*, vanishes as $d \to 2$! Since $f^+_m(x \to 1) \to \infty$ if $m \leq 2$, the fugacuty z is always smaller than 1. Hence, there is no macroscopic occupation of the ground state, even at the lowest temperatures, *i.e.* no Bose-Einstein condensation in $d \leq 2$. The above results are thus only valid for $d \geq 2$.

12. *Exciton dissociation in a semiconductor:* Shining an intense laser beam on a semiconductor can create a metastable collection of electrons (charge $-e$, and effective mass m_e) and holes (charge $+e$, and effective mass m_h) in the bulk. The oppositely charged particles may pair up (as in a hydrogen atom) to form a gas of *excitons*, or they may dissociate into a plasma. We shall examine a much simplified model of this process.

(a) Calculate the free energy of a gas composed of N_e electrons and N_h holes, at temperature T, treating them as classical non-interacting particles of masses m_e and m_h.

• The canonical partition function of gas of non-interacting electrons and holes is the product of contributions from the electron gas, and from the hole gas, as

$$Z_{e-h} = Z_e Z_h = \frac{1}{N_e!} \left(\frac{V}{\lambda_e^3} \right)^{N_e} \cdot \frac{1}{N_h!} \left(\frac{V}{\lambda_h^3} \right)^{N_h},$$

where $\lambda_\alpha = h/\sqrt{2\pi m_\alpha k_B T}$ ($\alpha =$ e, h). Evaluating the factorials in Stirling's approximation, we obtain the free energy

$$F_{e-h} = -k_B T \ln Z_{e-h} = N_e k_B T \ln \left(\frac{N_e}{eV} \lambda_e^3 \right) + N_h k_B T \ln \left(\frac{N_h}{eV} \lambda_h^3 \right).$$

(b) By pairing into an excition, the electron hole pair lowers its energy by ε. [The binding energy of a hydrogen-like exciton is $\varepsilon \approx me^4/(2\hbar^2 \epsilon^2)$, where ϵ is the dielectric constant, and $m^{-1} = m_e^{-1} + m_h^{-1}$.] Calculate the free energy of a gas of N_p excitons, treating them as classical non-interacting particles of mass $m = m_e + m_h$.

• Similarly, the partition function of the exciton gas is calculated as

$$Z_p = \frac{1}{N_p!} \left(\frac{V}{\lambda_p^3} \right)^{N_p} e^{-\beta(-N_p \epsilon)},$$

leading to the free energy

$$F_p = N_p k_B T \ln \left(\frac{N_p}{eV} \lambda_p^3 \right) - N_p \epsilon,$$

where $\lambda_p = h/\sqrt{2\pi (m_e + m_h) k_B T}$.

(c) Calculate the chemical potentials μ_e, μ_h, and μ_p of the electron, hole, and exciton states, respectively.

- The chemical potentials are derived from the free energies, through

$$\mu_{\mathrm{e}} = \left. \frac{\partial F_{\mathrm{e-h}}}{\partial N_{\mathrm{e}}} \right|_{T,V} = k_B T \ln\left(n_{\mathrm{e}}\lambda_{\mathrm{e}}^3\right),$$

$$\mu_{\mathrm{h}} = \left. \frac{\partial F_{\mathrm{e-h}}}{\partial N_{\mathrm{h}}} \right|_{T,V} = k_B T \ln\left(n_{\mathrm{h}}\lambda_{\mathrm{h}}^3\right),$$

$$\mu_{\mathrm{p}} = \left. \frac{\partial F_{\mathrm{p}}}{\partial N_{\mathrm{p}}} \right|_{T,V} = k_B T \ln\left(n_{\mathrm{p}}\lambda_{\mathrm{p}}^3\right) - \epsilon,$$

where $n_\alpha = N_\alpha/V$ ($\alpha =$ e, h, p).

(d) Express the equilibrium condition between excitons and electron/holes in terms of their chemical potentials.

- The equilibrium condition is obtained by equating the chemical potentials of the electron and hole gas with that of the exciton gas, since the exciton results from the pairing of an electron *and* a hole,

$$\text{electron} + \text{hole} \rightleftharpoons \text{exciton}.$$

Thus, at equilibrium

$$\mu_{\mathrm{e}}\left(n_{\mathrm{e}}, T\right) + \mu_{\mathrm{h}}\left(n_{\mathrm{h}}, T\right) = \mu_{\mathrm{p}}\left(n_{\mathrm{p}}, T\right),$$

which is equivalent, after exponentiation, to

$$n_{\mathrm{e}}\lambda_{\mathrm{e}}^3 \cdot n_{\mathrm{h}}\lambda_{\mathrm{h}}^3 = n_{\mathrm{p}}\lambda_{\mathrm{p}}^3 e^{-\beta\epsilon}.$$

(e) At a high temperature T, find the density n_{p} of excitons, as a function of the total density of excitations $n \approx n_{\mathrm{e}} + n_{\mathrm{h}}$.

- The equilibrium condition yields

$$n_{\mathrm{p}} = n_{\mathrm{e}} n_{\mathrm{h}} \frac{\lambda_{\mathrm{e}}^3 \lambda_{\mathrm{h}}^3}{\lambda_{\mathrm{p}}^3} e^{\beta\epsilon}.$$

At high temperature, $n_{\mathrm{p}} \ll n_{\mathrm{e}} = n_{\mathrm{h}} \approx n/2$, and

$$n_{\mathrm{p}} = n_{\mathrm{e}} n_{\mathrm{h}} \frac{\lambda_{\mathrm{e}}^3 \lambda_{\mathrm{h}}^3}{\lambda_{\mathrm{p}}^3} e^{\beta\epsilon} = \left(\frac{n}{2}\right)^2 \frac{h^3}{(2\pi k_B T)^{3/2}} \left(\frac{m_{\mathrm{e}} + m_{\mathrm{h}}}{m_{\mathrm{e}} m_{\mathrm{h}}}\right)^{3/2} e^{\beta\epsilon}.$$

****

13. *Freezing of He⁴:* At low temperatures He⁴ can be converted from liquid to solid by application of pressure. An interesting feature of the phase boundary is that the melting pressure is reduced slightly from its $T = 0K$ value, by approximately 20Nm^{-2} at its minimum at $T = 0.8K$. We will use a simple model of liquid and solid phases of ⁴He to account for this feature.

(a) The important excitations in liquid ⁴He at $T < 1\text{K}$ are phonons of velocity c. Calculate the contribution of these modes to the heat capacity per particle C_V^ℓ/N, of the liquid.

• The dominant excitations in liquid ⁴He at $T < 1K$ are phonons of velocity c. The corresponding dispersion relation is $\varepsilon(k) = \hbar ck$. From the average number of phonons in mode $\vec{k}$, given by $\left\langle n(\vec{k}) \right\rangle = [\exp(\beta\hbar ck) - 1]^{-1}$, we obtain the net excitation energy as

$$
\begin{aligned}
E_{phonons} &= \sum_{\vec{k}} \frac{\hbar ck}{\exp(\beta\hbar ck) - 1} \\
&= V \times \int \frac{4\pi k^2 dk}{(2\pi)^3} \frac{\hbar ck}{\exp(\beta\hbar ck) - 1} \qquad \text{(change variables to } x = \beta\hbar ck) \\
&= \frac{V}{2\pi^2}\hbar c \left(\frac{k_B T}{\hbar c}\right)^4 \frac{6}{3!} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^2}{30} V\hbar c \left(\frac{k_B T}{\hbar c}\right)^4,
\end{aligned}
$$

where we have used

$$
\zeta_4 \equiv \frac{1}{3!} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{90}.
$$

The corresponding heat capacity is now obtained as

$$
C_V = \frac{dE}{dT} = \frac{2\pi^2}{15} V k_B \left(\frac{k_B T}{\hbar c}\right)^3,
$$

resulting in a heat capacity per particle for the liquid of

$$
\frac{C_V^\ell}{N} = \frac{2\pi^2}{15} k_B v_\ell \left(\frac{k_B T}{\hbar c}\right)^3.
$$

(b) Calculate the low temperature heat capacity per particle C_V^s/N, of solid ⁴He in terms of longitudinal and transverse sound velocities c_L, and c_T.

• The elementary excitations of the solid are also phonons, but there are now *two* transverse sound modes of velocity c_T, and *one* longitudinal sound mode of velocity c_L. The

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contributions of these modes are additive, each similar inform to the liquid result calculated above, resulting in the final expression for solid heat capacity of

$$\frac{C_V^s}{N} = \frac{2\pi^2}{15} k_B v_s \left(\frac{k_B T}{\hbar}\right)^3 \times \left(\frac{2}{c_T^3} + \frac{1}{c_L^3}\right).$$

(c) Using the above results calculate the entropy difference $(s_\ell - s_s)$, assuming a single sound velocity $c \approx c_L \approx c_T$, and approximately equal volumes per particle $v_\ell \approx v_s \approx v$. Which phase (solid or liquid) has the higher entropy?

- The entropies can be calculated from the heat capacities as

$$s_\ell(T) = \int_0^T \frac{C_V^\ell(T')dT'}{T'} = \frac{2\pi^2}{45} k_B v_\ell \left(\frac{k_B T}{\hbar c}\right)^3,$$

$$s_s(T) = \int_0^T \frac{C_V^s(T')dT'}{T'} = \frac{2\pi^2}{45} k_B v_s \left(\frac{k_B T}{\hbar}\right)^3 \times \left(\frac{2}{c_T^3} + \frac{1}{c_L^3}\right).$$

Assuming approximately equal sound speeds $c \approx c_L \approx c_T \approx 300 \text{ms}^{-1}$, and specific volumes $v_\ell \approx v_s \approx v = 46 \text{Å}^3$, we obtain the entropy difference

$$s_\ell - s_s \approx -\frac{4\pi^2}{45} k_B v \left(\frac{k_B T}{\hbar c}\right)^3.$$

The solid phase has more entropy than the liquid because it has two more phonon excitation bands.

(d) Assuming a small (temperature independent) volume difference $\delta v = v_\ell - v_s$, calculate the form of the melting curve. To explain the anomaly described at the beginning, which phase (solid or liquid) must have the higher density?

- Using the Clausius-Clapeyron equation, and the above calculation of the entropy difference, we get

$$\left(\frac{\partial P}{\partial T}\right)_{melting} = \frac{s_\ell - s_s}{v_\ell - v_s} = -\frac{4\pi^2}{45} k_B \frac{v}{\delta v} \left(\frac{k_B T}{\hbar c}\right)^3.$$

Integrating the above equation gives the melting curve

$$P_{melt}(T) = P(0) - \frac{\pi^2}{45} k_B \frac{v}{\delta v} \left(\frac{k_B T}{\hbar c}\right)^3 T.$$

To explain the reduction in pressure, we need $\delta v = v_\ell - v_s > 0$, i.e. the solid phase has the higher density, which is normal.

14. *Neutron star core:* Professor Rajagopal's group at MIT has proposed that a new phase of QCD matter may exist in the core of neutron stars. This phase can be viewed as a condensate of quarks in which the low energy excitations are approximately

$$\mathcal{E}(\vec{k})_\pm =\pm\ \hbar^2 \frac{\left(|\vec{k}|-k_F\right)^2}{2M}\quad .$$

The excitations are fermionic, with a degeneracy of $g = 2$ from spin.

(a) At zero temperature all negative energy states are occupied and all positive energy ones are empty, i.e. $\mu(T = 0) = 0$. By relating occupation numbers of states of energies $\mu + \delta$ and $\mu - \delta$, or otherwise, find the chemical potential at finite temperatures T.

• According to Fermi statistics, the probability of occupation of a state of of energy $\mathcal{E}$ is

$$p\left[n(\mathcal{E})\right] = \frac{e^{\beta(\mu-\mathcal{E})n}}{1+e^{\beta(\mu-\mathcal{E})}}, \qquad \text{for}\quad n = 0, 1.$$

For a state of energy $\mu + \delta$,

$$p\left[n(\mu+\delta)\right] = \frac{e^{\beta\delta n}}{1+e^{\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu+\delta) = 1\right] = \frac{e^{\beta\delta}}{1+e^{\beta\delta}} = \frac{1}{1+e^{-\beta\delta}}.$$

Similarly, for a state of energy $\mu - \delta$,

$$p\left[n(\mu-\delta)\right] = \frac{e^{-\beta\delta n}}{1+e^{-\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu-\delta) = 0\right] = \frac{1}{1+e^{-\beta\delta}} = p\left[n(\mu+\delta) = 1\right],$$

i.e. the probability of finding an occupied state of energy $\mu + \delta$ is the same as that of finding an unoccupied state of energy $\mu - \delta$. This implies that for $\mu = 0$, $\langle n(\mathcal{E})\rangle + \langle n(-\mathcal{E})\rangle$ is unchanged for an temperature; for every particle leaving an occupied negative energy state a particle goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if μ stays at zero. Thus, the particle–hole symmetry enforces $\mu(T) = 0$.

(b) Assuming a constant density of states near $k = k_F$, i.e. setting $d^3k \approx 4\pi k_F^2 dq$ with $q = |\vec{k}| - k_F$, show that the mean excitation energy of this system at finite temperature is

$$E(T) - E(0) \approx 2gV\frac{k_F^2}{\pi^2}\int_0^\infty dq\frac{\mathcal{E}_+(q)}{\exp\left(\beta\mathcal{E}_+(q)\right)+1}\quad .$$

• Using the label +(-) for the positive (energy) states, the excitation energy is calculated as

$$E(T) - E(0) = \sum_{k,s} \left[\langle n_+(k) \rangle \, \mathcal{E}_+(k) - (1 - \langle n_-(k) \rangle) \, \mathcal{E}_-(k) \right]$$

$$= g \sum_k 2 \langle n_+(k) \rangle \, \mathcal{E}_+(k) = 2gV \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1}.$$

The largest contribution to the integral comes for $|\vec{k}| \approx k_F$. and setting $q = (|\vec{k}| - k_F)$ and using $d^3k \approx 4\pi k_F^2 dq$, we obtain

$$E(T) - E(0) \approx 2gV \frac{4\pi k_F^2}{8\pi^3} 2 \int_0^\infty dq \frac{\mathcal{E}_+(q)}{\exp\left(\beta\mathcal{E}_+(q)\right) + 1} = 2gV \frac{k_F^2}{\pi^2} \int_0^\infty dq \frac{\mathcal{E}_+(q)}{\exp\left(\beta\mathcal{E}_+(q)\right) + 1} \quad .$$

(c) Give a closed form answer for the excitation energy by evaluating the above integral.

• For $\mathcal{E}_+(q) = \hbar^2 q^2/(2M)$, we have

$$E(T) - E(0) = 2gV \frac{k_F^2}{\pi^2} \int_0^\infty dq \frac{\hbar^2 q^2/2M}{e^{\beta\hbar^2 q^2/2M} + 1} = \qquad (\text{set } \beta\hbar^2 q^2/2M = x)$$

$$= \frac{gV k_F^2}{\pi^2} k_B T \left(\frac{2M k_B T}{\hbar^2} \right)^{1/2} \int_0^\infty dx \frac{x^{1/2}}{e^x + 1}$$

$$= \frac{gV k_F^2}{\pi^2} k_B T \left(\frac{2M k_B T}{\hbar^2} \right)^{1/2} \frac{\sqrt{\pi}}{2} \left(1 - \frac{1}{\sqrt{2}} \right) \zeta_{3/2} = \left(1 - \frac{1}{\sqrt{2}} \right) \frac{\zeta_{3/2}}{\pi} \frac{V k_F^2}{\lambda} k_B T.$$

For the final expression, we have used the value of $f_m^-(1)$, and introduced the thermal wavelength $\lambda = h/\sqrt{2\pi M k_B T}$.

(d) Calculate the heat capacity, C_V, of this system, and comment on its behavior at low temperature.

• Since $E \propto T^{3/2}$,

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{3}{2} \frac{E}{T} = \frac{3\zeta_{3/2}}{2\pi} \left(1 - \frac{1}{\sqrt{2}} \right) \frac{V k_F^2}{\lambda} k_B \propto \sqrt{T}.$$

This is similar to the behavior of a one dimensional system of bosons (since the density of states is constant in q as in $d = 1$). Of course, for any fermionic system the density of states close to the Fermi surface has this character. The difference with the usual Fermi systems is the quadratic nature of the excitations above the Fermi surface.

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15. *Non-interacting bosons:* Consider a grand canonical ensemble of non-interacting *bosons* with chemical potential μ. The one–particle states are labelled by a wavevector $\vec{q}$, and have energies $\mathcal{E}(\vec{q})$.

(a) What is the joint probability $P(\{n_{\vec{q}}\})$, of finding a set of occupation numbers $\{n_{\vec{q}}\}$, of the one–particle states, in terms of the fugacities $z_{\vec{q}} \equiv \exp\left[\beta(\mu - \mathcal{E}(\vec{q}))\right]$?

● In the grand canonical ensemble with chemical potential μ, the joint probability of finding a set of occupation numbers $\{n_{\vec{q}}\}$, for one–particle states of energies $\mathcal{E}(\vec{q})$ is given by the normalized bose distribution

$$P(\{n_{\vec{q}}\}) = \prod_{\vec{q}} \left\{1 - \exp\left[\beta(\mu - \mathcal{E}(\vec{q}))\right]\right\} \exp\left[\beta(\mu - \mathcal{E}(\vec{q}))n_{\vec{q}}\right]$$

$$= \prod_{\vec{q}} (1 - z_{\vec{q}})\, z_{\vec{q}}^{n_{\vec{q}}}, \quad \text{with} \quad n_{\vec{q}} = 0, 1, 2, \cdots, \quad \text{for each } \vec{q}.$$

(b) For a particular $\vec{q}$, calculate the characteristic function $\langle \exp\left[ikn_{\vec{q}}\right]\rangle$.

● Summing the geometric series with terms growing as $\left(z_{\vec{q}}e^{ik}\right)^{n_{\vec{q}}}$, gives

$$\langle \exp\left[ikn_{\vec{q}}\right]\rangle = \frac{1 - \exp\left[\beta(\mu - \mathcal{E}(\vec{q}))\right]}{1 - \exp\left[\beta(\mu - \mathcal{E}(\vec{q})) + ik\right]} = \frac{1 - z_{\vec{q}}}{1 - z_{\vec{q}}e^{ik}}.$$

(c) Using the result of part (b), **or otherwise**, give expressions for the mean and variance of $n_{\vec{q}}$. occupation number $\langle n_{\vec{q}}\rangle$.

● Cumulnats can be generated by expanding the logarithm of the characteristic function in powers of k. Using the expansion formula for $\ln(1 + x)$, we obtain

$$\ln \langle \exp\left[ikn_{\vec{q}}\right]\rangle = \ln\left(1 - z_{\vec{q}}\right) - \ln\left[1 - z_{\vec{q}}\left(1 + ik - k^2/2 + \cdots\right)\right]$$

$$= -\ln\left[1 - ik\frac{z_{\vec{q}}}{1 - z_{\vec{q}}} + \frac{k^2}{2}\frac{z_{\vec{q}}}{1 - z_{\vec{q}}} + \cdots\right]$$

$$= ik\frac{z_{\vec{q}}}{1 - z_{\vec{q}}} - \frac{k^2}{2}\left[\frac{z_{\vec{q}}}{1 - z_{\vec{q}}} + \left(\frac{z_{\vec{q}}}{1 - z_{\vec{q}}}\right)^2\right] + \cdots$$

$$= ik\frac{z_{\vec{q}}}{1 - z_{\vec{q}}} - \frac{k^2}{2}\frac{z_{\vec{q}}}{(1 - z_{\vec{q}})^2} + \cdots.$$

From the coefficients in the expansion, we can read off the mean and variance

$$\langle n_{\vec{q}}\rangle = \frac{z_{\vec{q}}}{1 - z_{\vec{q}}}, \quad \text{and} \quad \langle n_{\vec{q}}^2\rangle_c = \frac{z_{\vec{q}}}{(1 - z_{\vec{q}})^2}.$$

(d) Express the variance in part (c) in terms of the mean occupation number $\langle n_{\vec{q}} \rangle$.

• Inverting the relation relating $n_{\vec{q}}$ to $z_{\vec{q}}$, we obtain

$$z_{\vec{q}} = \frac{\langle n_{\vec{q}} \rangle}{1 + \langle n_{\vec{q}} \rangle}.$$

Substituting this value in the expression for the variance gives

$$\langle n_{\vec{q}}^2 \rangle_c = \frac{z_{\vec{q}}}{\left(1 - z_{\vec{q}}\right)^2} = \langle n_{\vec{q}} \rangle \left(1 + \langle n_{\vec{q}} \rangle\right).$$

(e) Express your answer to part (a) in terms of the occupation numbers $\{\langle n_{\vec{q}} \rangle\}$.

• Using the relation between $z_{\vec{q}}$ and $n_{\vec{q}}$, the joint probability can be reexpressed as

$$P(\{n_{\vec{q}}\}) = \prod_{\vec{q}} \left[\left(\langle n_{\vec{q}} \rangle\right)^{n_{\vec{q}}} \left(1 + \langle n_{\vec{q}} \rangle\right)^{-1-n_{\vec{q}}} \right].$$

(f) Calculate the entropy of the probability distribution for bosons, in terms of $\{\langle n_{\vec{q}} \rangle\}$, and comment on its zero temperature limit.

• Quite generally, the entropy of a probability distribution P is given by $S = -k_B \langle \ln P \rangle$. Since the occupation numbers of different one-particle states are independent, the corresponding entropies are additive, and given by

$$S = -k_B \sum_{\vec{q}} \left[\langle n_{\vec{q}} \rangle \ln \langle n_{\vec{q}} \rangle - \left(1 + \langle n_{\vec{q}} \rangle\right) \ln \left(1 + \langle n_{\vec{q}} \rangle\right) \right].$$

In the zero temperature limit all occupation numbers are either 0 (for excited states) or infinity (for the ground states). In either case the contribution to entropy is zero, and the system at $T = 0$ has zero entropy.

****

16. *Relativistic Bose gas in d dimensions:* Consider a gas of non-interacting (spinless) bosons with energy $\epsilon = c\,|\vec{p}|$, contained in a box of "volume" $V = L^d$ in d dimensions.

(a) Calculate the grand potential $\mathcal{G} = -k_B T \ln \mathcal{Q}$, and the density $n = N/V$, at a chemical potential μ. Express your answers in terms of d and $f_m^+(z)$, where $z = e^{\beta\mu}$, and

$$f_m^+(z) = \frac{1}{(m-1)!} \int_0^\infty \frac{x^{m-1}}{z^{-1}e^x - 1} dx.$$

(Hint: Use integration by parts on the expression for $\ln \mathcal{Q}$.)

- We have

$$
\mathcal{Q} = \sum_{N=0}^{\infty} e^{N\beta\mu} \sum_{\{n_i\}}^{\sum_i n_i = N} \exp\left(-\beta \sum_i n_i \epsilon_i\right),
$$

$$
= \prod_i \sum_{\{n_i\}} e^{\beta(\mu-\epsilon_i)n_i} = \prod_i \frac{1}{1 - e^{\beta(\mu-\epsilon_i)}}
$$

whence $\ln \mathcal{Q} = -\sum_i \ln\left(1 - e^{\beta(\mu-\epsilon_i)}\right)$. Replacing the summation $\sum_i$ with a d dimensional integration $\int_0^{\infty} V d^d k / (2\pi)^d = \left[V S_d / (2\pi)^d\right] \int_0^{\infty} k^{d-1} dk$, where $S_d = 2\pi^{d/2} / (d/2 - 1)!$, leads to

$$
\ln \mathcal{Q} = -\frac{V S_d}{(2\pi)^d} \int_0^{\infty} k^{d-1} dk \ln\left(1 - z e^{-\beta\hbar ck}\right).
$$

The change of variable $x = \beta\hbar ck$ results in

$$
\ln \mathcal{Q} = -\frac{V S_d}{(2\pi)^d} \left(\frac{k_B T}{\hbar c}\right)^d \int_0^{\infty} x^{d-1} dx \ln\left(1 - z e^{-x}\right).
$$

Finally, integration by parts yields

$$
\ln \mathcal{Q} = \frac{V S_d}{(2\pi)^d} \frac{1}{d} \left(\frac{k_B T}{\hbar c}\right)^d \int_0^{\infty} x^d dx \frac{z e^{-x}}{1 - z e^{-x}} = V \frac{S_d}{d} \left(\frac{k_B T}{hc}\right)^d \int_0^{\infty} dx \frac{x^d}{z^{-1} e^x - 1},
$$

leading to

$$
\mathcal{G} = -k_B T \ln \mathcal{Q} = -V \frac{S_d}{d} \left(\frac{k_B T}{hc}\right)^d k_B T d! f_{d+1}^+(z),
$$

which can be somewhat simplified to

$$
\mathcal{G} = -k_B T \frac{V}{\lambda_c^d} \frac{\pi^{d/2} d!}{(d/2)!} f_{d+1}^+(z),
$$

where $\lambda_c \equiv hc/(k_B T)$. The average number of particles is calculated as

$$
N = -\frac{\partial \mathcal{G}}{\partial \mu} = -\beta z \frac{\partial \mathcal{G}}{\partial z} = \frac{V}{\lambda_c^d} \frac{\pi^{d/2} d!}{(d/2)!} f_d^+(z),
$$

where we have used $z \partial f_{d+1}(z)/\partial z = f_d(z)$. Dividing by volume, the density is obtained as

$$
n = \frac{1}{\lambda_c^d} \frac{\pi^{d/2} d!}{(d/2)!} f_d^+(z).
$$

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(b) Calculate the gas pressure P, its energy E, and compare the ratio $E/(PV)$ to the classical value.

• We have $PV = -\mathcal{G}$, while

$$E = -\left.\frac{\partial \ln \mathcal{Q}}{\partial \beta}\right|_z = +d\frac{\ln \mathcal{Q}}{\beta} = -d\mathcal{G}.$$

Thus $E/(PV) = d$, identical to the classical value for a relativistic gas.

(c) Find the critical temperature, $T_c(n)$, for Bose-Einstein condensation, indicating the dimensions where there is a transition.

• The critical temperature $T_c(n)$ is given by

$$n = \frac{1}{\lambda_c^d}\frac{\pi^{d/2}d!}{(d/2)!}f_d^+(z=1) = \frac{1}{\lambda_c^d}\frac{\pi^{d/2}d!}{(d/2)!}\zeta_d.$$

This leads to
$$T_c = \frac{hc}{k_B}\left(\frac{n(d/2)!}{\pi^{d/2}d!\zeta_d}\right)^{1/d}.$$

However, ζ_d is finite only for $d > 1$, and thus a transition exists for all $d > 1$.

(d) What is the temperature dependence of the heat capacity $C(T)$ for $T < T_c(n)$?

• At $T < T_c$, $z = 1$ and $E = -d\mathcal{G} \propto T^{d+1}$, resulting in

$$C(T) = \left.\frac{\partial E}{\partial T}\right|_{z=1} = (d+1)\frac{E}{T} = -d(d+1)\frac{\mathcal{G}}{T} = d(d+1)\frac{V}{\lambda_c^d}k_B\frac{\pi^{d/2}d!}{(d/2)!}\zeta_{d+1} \propto T^d.$$

(e) Evaluate the dimensionless heat capacity $C(T)/(Nk_B)$ at the critical temperature $T = T_c$, and compare its value to the classical (high temperature) limit.

• We can divide the above formula of $C(T \leq Tc)$, and the one obtained earlier for $N(T \geq Tc)$, and evaluate the result at $T = T_c$ ($z = 1$) to obtain

$$\frac{C(T_c)}{Nk_B} = \frac{d(d+1)\zeta_{d+1}}{\zeta_d}.$$

In the absence of quantum effects, the heat capacity of a relativistic gas is $C/(Nk_B) = d$; this is the limiting value for the quantum gas at infinite temperature.

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17. *Graphene* is a single sheet of carbon atoms bonded into a *two dimensional* hexagonal lattice. It can be obtained by exfoliation (repeated peeling) of graphite. The band structure of graphene is such that the single particles excitations behave as relativistic *Dirac fermions*, with a spectrum that at low energies can be approximated by

$$\mathcal{E}_\pm(\vec{k}) = \pm\hbar v \left|\vec{k}\right| \quad .$$

There is spin degeneracy of $g = 2$, and $v \approx 10^6 \mathrm{ms}^{-1}$. Recent experiments on unusual transport properties of graphene were reported in *Nature* **438**, 197 (2005). In this problem, you shall calculate the heat capacity of this material.

(a) If at zero temperature all negative energy states are occupied and all positive energy ones are empty, find the chemical potential $\mu(T)$.

• According to Fermi statistics, the probability of occupation of a state of of energy $\mathcal{E}$ is

$$p\left[n(\mathcal{E})\right] = \frac{e^{\beta(\mu-\mathcal{E})n}}{1 + e^{\beta(\mu-\mathcal{E})}}, \qquad \text{for} \quad n = 0, 1.$$

For a state of energy $\mu + \delta$,

$$p\left[n(\mu+\delta)\right] = \frac{e^{\beta\delta n}}{1 + e^{\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu+\delta) = 1\right] = \frac{e^{\beta\delta}}{1 + e^{\beta\delta}} = \frac{1}{1 + e^{-\beta\delta}}.$$

Similarly, for a state of energy $\mu - \delta$,

$$p\left[n(\mu-\delta)\right] = \frac{e^{-\beta\delta n}}{1 + e^{-\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu-\delta) = 0\right] = \frac{1}{1 + e^{-\beta\delta}} = p\left[n(\mu+\delta) = 1\right],$$

i.e. the probability of finding an occupied state of energy $\mu + \delta$ is the same as that of finding an unoccupied state of energy $\mu - \delta$.

At zero temperature all negative energy Dirac states are occupied and all positive energy ones are empty, i.e. $\mu(T = 0) = 0$. The above result implies that for $\mu = 0$, $\langle n(\mathcal{E})\rangle + \langle n - \mathcal{E})\rangle$ is unchanged for all temperatures; any particle leaving an occupied negative energy state goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if μ stays at zero. Thus, the particle–hole symmetry enforces $\mu(T) = 0$.

(b) Show that the mean excitation energy of this system at finite temperature satisfies

$$E(T) - E(0) = 4A \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1} \quad .$$

• Using the label +(-) for the positive (energy) states, the excitation energy is calculated as

$$E(T) - E(0) = \sum_{k,s_z} \left[\langle n_+(k) \rangle \, \mathcal{E}_+(k) - (1 - \langle n_-(k) \rangle) \, \mathcal{E}_-(k) \right]$$

$$= 2 \sum_k 2 \langle n_+(k) \rangle \, \mathcal{E}_+(k) = 4A \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1}.$$

(c) Give a closed form answer for the excitation energy by evaluating the above integral.

• For $\mathcal{E}_+(k) = \hbar v |k|$, and

$$E(T) - E(0) = 4A \int_0^\infty \frac{2\pi k dk}{4\pi^2} \frac{\hbar v k}{e^{\beta\hbar v k} + 1} = \qquad (\text{set } \beta\hbar ck = x)$$

$$= \frac{2A}{\pi} k_B T \left(\frac{k_B T}{\hbar v} \right)^2 \int_0^\infty dx \frac{x^2}{e^x + 1}$$

$$= \frac{3\zeta_3}{\pi} A k_B T \left(\frac{k_B T}{\hbar v} \right)^2.$$

For the final expression, we have noted that the needed integral is $2! f_3^-(1)$, and used $f_3^-(1) = 3\zeta_3/4$.

$$E(T) - E(0) = A \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) - 1} \qquad .$$

(d) Calculate the heat capacity, C_V, of such massless Dirac particles.

• The heat capacity can now be evaluated as

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{9\zeta_3}{\pi} A k_B \left(\frac{k_B T}{\hbar v} \right)^2.$$

(e) Explain qualitatively the contribution of phonons (lattice vibrations) to the heat capacity of graphene. The typical sound velocity in graphite is of the order of $2 \times 10^4 \text{ms}^{-1}$. Is the low temperature heat capacity of graphene controlled by phonon or electron contributions?

• The single particle excitations for phonons also have a linear spectrum, with $\mathcal{E}_p = \hbar v_p |k|$ and correspond to $\mu = 0$. Thus qualitatively they give the same type of contribution to

energy and heat capacity. The difference is only in numerical pre-factors. The precise contribution from a single phonon branch is given by

$$E_p(T) - E_p(0) = A \int_0^\infty \frac{2\pi k dk}{4\pi^2} \frac{\hbar v_p k}{e^{\beta \hbar v_p k} - 1} = \qquad (\text{set } \beta \hbar c k = x)$$

$$= \frac{A}{2\pi} k_B T \left(\frac{k_B T}{\hbar v_p}\right)^2 \int_0^\infty dx \frac{x^2}{e^x - 1}$$

$$= \frac{\zeta_3}{\pi} A k_B T \left(\frac{k_B T}{\hbar v_p}\right)^2, \quad C_{V,p} = \frac{3\zeta_3}{\pi} A k_B \left(\frac{k_B T}{\hbar v_p}\right)^2.$$

We see that the ratio of electron to phonon heat capacities is proportional to $(v_p/v)^2$. Since the speed of Dirac fermions is considerably larger than that of phonons, their contribution to heat capacity of graphene is negligible.

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18. *Graphene bilayer:* The layers of graphite can be peeled apart through different exfoliation processes. Many such processes generate single sheets of carbon atoms, as well as bilayers in which the two sheets are weakly coupled. The hexagonal lattice of the single layer graphene, leads to a band structure that at low energies can be approximated by $\mathcal{E}_\pm^{1 \text{ layer}}(\vec{k}) = \pm t_\parallel (ak)$, as in relativistic Dirac *fermions*. (Here $k = \left|\vec{k}\right|$, a is a lattice spacing, and $t_\parallel$ is a typical in-plane hopping energy.) A weak hopping energy $t_\perp$ between the two sheets of the bilayer modifies the low energy excitations drastically, to

$$\mathcal{E}_\pm^{\text{bilayer}}(\vec{k}) = \pm \frac{t_\parallel^2}{2t_\perp}(ka)^2 \quad ,$$

i.e. resembling massive Dirac fermions. In addition to the spin degeneracy, there are two branches of such excitations per unit cell, for an overall degeneracy of $g = 4$.

(a) For the undoped material with one electron per site, at zero temperature all negative energy states are occupied and all positive energy ones are empty. Find the chemical potential $\mu(T)$.

• According to Fermi statistics, the probability of occupation of a state of of energy $\mathcal{E}$ is

$$p[n(\mathcal{E})] = \frac{e^{\beta(\mu - \mathcal{E})n}}{1 + e^{\beta(\mu - \mathcal{E})}}, \qquad \text{for} \quad n = 0, 1.$$

For a state of energy $\mu + \delta$,

$$p[n(\mu + \delta)] = \frac{e^{\beta \delta n}}{1 + e^{\beta \delta}}, \quad \Longrightarrow \quad p[n(\mu + \delta) = 1] = \frac{e^{\beta \delta}}{1 + e^{\beta \delta}} = \frac{1}{1 + e^{-\beta \delta}}.$$

Similarly, for a state of energy $\mu - \delta$,

$$p\left[n(\mu - \delta)\right] = \frac{e^{-\beta\delta n}}{1 + e^{-\beta\delta}}, \quad \implies \quad p\left[n(\mu - \delta) = 0\right] = \frac{1}{1 + e^{-\beta\delta}} = p\left[n(\mu + \delta) = 1\right],$$

i.e. the probability of finding an occupied state of energy $\mu + \delta$ is the same as that of finding an unoccupied state of energy $\mu - \delta$.

At zero temperature all negative energy Dirac states are occupied and all positive energy ones are empty, i.e. $\mu(T = 0) = 0$. The above result implies that for $\mu = 0$, $\langle n(\mathcal{E}) \rangle + \langle n - \mathcal{E}) \rangle$ is unchanged for all temperatures; any particle leaving an occupied negative energy state goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if μ stays at zero. Thus, the particle–hole symmetry enforces $\mu(T) = 0$.

(b) Show that the mean excitation energy of this system at finite temperature satisfies

$$E(T) - E(0) = 2gA \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1} \quad .$$

• Using the label +(-) for the positive (energy) states, the excitation energy is calculated as

$$E(T) - E(0) = \sum_{k,s_z,\alpha} \left[\langle n_+(k) \rangle \, \mathcal{E}_+(k) + (1 - \langle n_-(k) \rangle) \, \mathcal{E}_-(k)\right]$$

$$= g \sum_k 2 \langle n_+(k) \rangle \, \mathcal{E}_+(k) = 2gA \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1}.$$

(c) Give a closed form answer for the excitation energy *of the bilayer* by evaluating the above integral.

• Let $\mathcal{E}_+(k) = \alpha k^2$, with $\alpha = (t_\| a)^2/(2t_\perp)$, to get

$$E(T) - E(0) = 2gA \int_0^\infty \frac{2\pi k dk}{4\pi^2} \frac{\alpha k^2}{e^{\beta\alpha k^2} + 1} = \quad (\text{set } \beta\alpha k^2 = x)$$

$$= \frac{gA}{2\pi} k_B T \left(\frac{k_B T}{\alpha}\right) \int_0^\infty dx \frac{x}{e^x + 1}$$

$$= \frac{g\pi}{24} A k_B T \left(\frac{k_B T}{\alpha}\right) = \frac{\pi}{3} \frac{A}{a^2} \left(\frac{k_B T}{t_\|}\right)^2 t_\perp.$$

For the final expression, we have noted that the needed integral is $f_2^-(1)$, and used $f_2^-(1) = \zeta_2/2 = \pi^2/12$.

(d) Calculate the heat capacity, C_A, of such massive Dirac particles.

• The heat capacity can now be evaluated as

$$C_A = \left.\frac{\partial E}{\partial T}\right|_A = \frac{2\pi}{3}\frac{A}{a^2}k_B\left(\frac{k_BTt_\perp}{t_\parallel^2}\right).$$

(e) A sample contains an equal proportion of single and bilayers. Estimate (in terms of the hopping energies) the temperature below which the electronic heat capacity is dominated by the bilayers.

• As stated earlier, the monolayer excitations for phonons have a linear spectrum, with $\mathcal{E}^{1\ \mathrm{layer}} = \pm t_\parallel(ka)$. Their contribution to energy and heat capacity can be calculated as before. Including the various prefactors (which are not required for the solution), we have

$$E^{1\ \mathrm{layer}}(T) = 2gA\int_0^\infty \frac{2\pi kdk}{4\pi^2}\frac{t_\parallel ak}{e^{\beta t_\parallel ak}+1} = \qquad (\text{set } \beta t_\parallel ak = x)$$

$$= \frac{gA}{\pi}k_BT\left(\frac{k_BT}{t_\parallel a}\right)^2\int_0^\infty dx\frac{x^2}{e^x+1}$$

$$\propto \frac{A}{a^2}k_BT\left(\frac{k_BT}{t_\parallel}\right)^2, \quad C_A^{1\ \mathrm{layer}}\propto \frac{A}{a^2}k_B\left(\frac{k_BT}{t_\parallel}\right)^2.$$

The bilayer heat capacity, which is proportional to T is more important at lower temperatures. By comparing the two expressions, it is apparent that the electronic heat capacity per particle is larger in the bilayer for temperatures smaller than $T^* \approx t_\perp/k_B$.

(f) Explain qualitatively the contribution of phonons (lattice vibrations) to the heat capacity of graphene. The typical sound velocity in graphite is of the order of $2\times 10^4\mathrm{ms}^{-1}$. Is the low temperature heat capacity of (monolayer) graphene controlled by phonon or electron contributions?

• The single particle excitations for phonons also have a linear spectrum, with $\mathcal{E}_p = \hbar v_p|k|$ and correspond to $\mu = 0$. Thus qualitatively they give the same type of contribution to energy and heat capacity. The difference is only in numerical pre-factors. The precise contribution from a single phonon branch is given by

$$E_p(T) - E_p(0) = A\int_0^\infty \frac{2\pi kdk}{4\pi^2}\frac{\hbar v_p k}{e^{\beta\hbar v_p k}-1} = \qquad (\text{set } \beta\hbar ck = x)$$

$$= \frac{A}{2\pi}k_BT\left(\frac{k_BT}{\hbar v_p}\right)^2\int_0^\infty dx\frac{x^2}{e^x-1}$$

$$= \frac{\zeta_3}{\pi}Ak_BT\left(\frac{k_BT}{\hbar v_p}\right)^2, \quad C_{V,p} = \frac{3\zeta_3}{\pi}Ak_B\left(\frac{k_BT}{\hbar v_p}\right)^2.$$

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We see that the ratio of electron to phonon heat capacities is proportional to $(v_p/v)^2$. Since the speed of Dirac fermions is considerably larger than that of phonons, their contribution to heat capacity of graphene is negligible.

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