

## Solutions to sample quiz problems and assigned problems

### Sample Quiz Problems

**Quiz Problem 1.** Prove the expression for the Carnot efficiency for a perfectly reversible Carnot cycle using an ideal gas.

**Solution:** The ideal Carnot cycle consists of four segments as follows (1) An isothermal expansion during which heat  $Q_H$  is added to the system at temperature  $T_H$ ; (2) an adiabatic expansion during which the gas cools from temperature  $T_H$  to  $T_C$ ; (3) An isothermal compression during which heat  $Q_C$  is extracted from the system to a cold reservoir at temperature  $T_C$ ; (4) Adiabatic compression during which the temperature of the gas rises from  $T_C$  to  $T_H$ . The efficiency of the engine is given by  $\eta = W/Q_H$ , where  $W$  is the useful work done by the system and  $Q_H$  is the heat added to the system. This is a thermodynamic cycle provided it is carried out reversibly (i.e. kept very close to equilibrium), and then the internal energy is the same at the beginning and the end of the cycle. In that case,  $dU = 0$ , and  $W_{total} = Q_H - Q_C$ , so we can also write the efficiency as

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C \Delta S}{T_H \Delta S} = 1 - \frac{T_C}{T_H} \quad (1)$$

The introduction of Entropy by Clausius greatly simplified understanding of engines.

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**Quiz Problem 2.** Show that in the eigenfunction basis, the von Neuman entropy  $S = -k_B \text{tr}(\hat{\rho} \ln(\hat{\rho}))$  reduces to the Gibbs form  $S = -k_B \sum_i p_i \ln(p_i)$  where the sum is over all eigenstates.

**Solution.** See Eq. (20) of Lecture notes.

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**Quiz Problem 3.** Use Stirling's approximation to show that,

$$\ln\left(\binom{N}{n}\right) \approx -N[p \ln(p) + (1-p) \ln(1-p)], \quad \text{where } p = n/N \quad (2)$$

**Solution.** Using Stirling's approximation we have,

$$\ln\left(\binom{N}{n}\right) = \ln(N!) - \ln(n!) - \ln(N-n)! = N \ln(N) - N - n \ln(n) + n - (N-n) \ln(N-n) + (N-n) \quad (3)$$

which reduces to

$$\ln\left(\binom{N}{n}\right) = N \ln(N) - n \ln(n) - (N-n) \ln(N-n). \quad (4)$$

Defining  $p = n/N$  gives,

$$\ln\left(\binom{N}{n}\right) = N \ln(N) - pN \ln(pN) - N(1-p) \ln(N(1-p)) = -N[p \ln(p) + (1-p) \ln(1-p)] \quad (5)$$

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**Quiz Problem 4.** If  $S = -k_B N[p \ln(p) + (1-p) \ln(1-p)]$ , by doing a variation with respect to  $p$  find the value of  $p$  that gives the maximum entropy. Demonstrate that it is a maximum by showing that the second derivative with respect to  $p$  is negative.

**Solution.** Taking a derivative with respect to  $p$  gives,

$$\frac{\partial S}{\partial p} = -k_B N[\ln(p) - \ln(1-p)] \quad (6)$$

The extrema occur at values of  $p = p^*$  where this expression is zero, which yields  $p^* = 1/2$ . To determine whether this is a minimum or maximum, we take the second derivative to find that,

$$\frac{\partial^2 S}{\partial p^2} = -k_B N \left[ \frac{1}{p} + \frac{1}{1-p} \right]_{p=p^*} = -k_B N \quad (7)$$

Since the second derivative is negative the extremum at  $p^* = 1/2$  is a maximum. We have thus found the value of the probability at which the entropy is a maximum.

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**Quiz Problem 5.** Use the Master equation to prove the second law of thermodynamics, i.e. in a closed system  $dS/dt \geq 0$ .

**Solution.** see lecture notes page 10.

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**Quiz Problem 6.** Give three examples of systems where the ergodic hypothesis fails. Explain why it fails in these cases.

**Solution.** Non-interacting classical gas, as in the absence of interactions the system is non-chaotic. Coupled harmonic oscillators with no other interactions, as the normal modes do not share energy. Any system with spontaneous symmetry breaking at low temperature, e.g. magnetic systems. Once in the up magnetized state at low enough temperature the system stays in that state. Similarly once a crystal has formed from the gas phase at low temperature it almost never transforms to another crystal phase.

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**Quiz Problem 7.** Why is the ideal gas law still a good starting point for high temperature gases, even though a non-interacting gas is non-ergodic?

**Solution.** Even very small interactions can make the system chaotic. These interactions have little effect on the equilibrium thermodynamic behavior though they are critical to the transport properties.

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**Quiz Problem 8.** Using  $p_i = e^{-\beta E_i}/Z$  in the Gibbs form for the entropy, show that  $F = -k_B T \ln(Z)$ , where  $F = U - TS$  is the Helmholtz free energy. Here  $Z = \sum_i e^{-\beta E_i}$  is the canonical partition function.

**Solution.** The Gibbs formula for the entropy is

$$S = -k_B \sum_i p_i \ln(p_i). \quad (8)$$

Using the Boltzmann probability in the canonical ensemble  $p_i = \exp(-\beta E_i)/Z$ , we have,

$$S = -k_B \sum_i p_i \left[ \frac{-E_i}{k_B T} - \ln(Z) \right] = \frac{U}{T} + k_B \ln(Z) \quad \text{so} \quad U - TS = -k_B T \ln(Z), \quad (9)$$

where we used  $\sum_i p_i = 1$ ,  $U = \sum_i p_i E_i$

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**Quiz Problem 9.** If  $x = e^{-\beta(E_i - E_j)}$ , so that  $w_{ji} \rightarrow f(x)$ . Show that the Metropolis algorithm is given by  $f(x) = \min(x, 1)$ .

**Solution** With this notation, the Metropolis algorithm is: If  $x > 1$ ,  $w_{ji} = 1$ , and if  $x < 1$ ,  $w_{ji} = x$ . This can be put in one equation as  $w_{ji} = f(x) = \min(1, x)$ .

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**Quiz Problem 10.** If  $x = e^{-\beta(E_i - E_j)}$ , so that  $w_{ji} \rightarrow f(x)$ . Show that detailed balance is satisfied for any  $f(x)$  satisfying  $f(x)/f(1/x) = x$ . Moreover, show that  $f(x) = x/(1+x)$ , the heat bath algorithm, is one such solution.

**Solution** Since  $w_{ij} = 1/w_{ji}$ , if  $f(x) = w_{ji}$ , and if  $f(1/x) = w_{ij}$ , then detailed balance is satisfied provided  $f(x)/f(1/x) = x$ . For the heat bath case,

$$f(x)/f(1/x) = (x/1+x)/(1/x/(1+1/x)) = x \quad (10)$$


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**Quiz Problem 11.** For a monatomic interacting classical gas, with interactions that only depend on the particle co-ordinates, derive the Maxwell Boltzmann distribution of velocities and show that the average kinetic energy is given by  $\langle KE \rangle = 3Nk_B T/2$ .

**Solution.** See page 23 of the notes.

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**Quiz Problem 12.** Using the fact that  $\delta E^2 = \langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 C_V$  show that  $\delta E/E$  is proportional  $1/N^{1/2}$ .

**Solution.** See page 28 of the notes.

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**Quiz Problem 13.** Write down the central difference form of the second derivative. Using this expression for the acceleration, write down the basic form of the Verlet algorithm for Molecular dynamics.

**Solution.** See. page 21-22 of the notes.

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**Quiz Problem 14.** Given that the virial is defined to be  $G = \sum_k \vec{p}_k \cdot \vec{r}_k$ . Explain why the average of its time derivative is expected to be zero at long times.

**Solution.** The average of the time derivative of the virial gives,

$$\left\langle \frac{dG}{dt} \right\rangle = \frac{1}{\tau} \int_0^\tau \frac{dG}{dt} dt = (G(\tau) - G(0))/\tau$$

where the average is taken over the time interval  $\tau$ . Since  $G$  is bounded, as  $\tau$  goes to infinity, the average of the time derivative of  $G$  goes to zero.

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**Quiz Problem 15.** The ground state structure of Argon is a fcc crystal. If a MD simulation is carried out where a high temperature structure is quenched to a low temperature where the fcc structure is the equilibrium state. If the starting high temperature state in your MD simulation is a liquid phase, do you expect the simulation to find the correct fcc state? Explain.

**Solution.** For most particle systems it is difficult to find the low temperature ground state, so the fcc single crystal state is usually not found. In experiments a polycrystal is quite often found but it is harder to make single crystals. In MD simulations, the timescale is very short so unless special conditions are applied, the low temperature state is a frozen glass state.

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**Quiz Problem 16.** In a MC calculation of the ferromagnetic Ising model on a square lattice, you calculate the magnetization as a function of temperature as accurately as you can. However your simulations remain rounded at the critical point, instead of showing the behavior  $|T_c - T|^\beta$  expected in the thermodynamic limit. Explain the physical origins of the rounding that you observe. Your experimental colleague does a measurement of a model Ising magnet that consists of quantum dots with around 1000 spins in each quantum dot. She also observes a rounding of the behavior of the magnetization. Provide some reasons why her magnetization experiment also gives a rounded behavior near the critical point.

**Solution.** Three reasons for rounding of the transition are finite size effects, sample inhomogeneity and non-equilibrium effects. Non-equilibrium effects occur when the system is not fully equilibrated. In experiments all three effects occur, while in simulations the sample inhomogeneity effect is avoided.

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**Quiz Problem 17.** Derive the relation,

$$PV = Nk_B T + \frac{1}{3} \sum_k^{internal} \vec{r}_k \cdot \vec{F}_k \quad (11)$$

Explain the physical origin of each of the three terms. This relation is not always true for periodic boundary conditions, though rather fortuitously it is true for periodic boundaries provided the interaction potential is a pair potential.

**Solution.** See page 23-24 of the notes.

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**Quiz Problem 18.** Show that

$$(\delta E)^2 = k_B T^2 C_V \quad (12)$$

**Solution.** See page 28 of the notes.

### Solutions to assigned problems

**Problem 1.** Find the relation between pressure and volume for an ideal gas under going an adiabatic process.

**Solution:** In an adiabatic process no heat is added to the system, so  $dU + dW = 0$ , where  $dW = PdV$ . Combining the ideal gas law and the equipartition theorem, we have

$$dU = \alpha N k_B dT = \alpha d(PV) = \alpha(VdP + PdV) \quad (13)$$

where  $\alpha = DOF/2$ . Using the first law, we then have,

$$-PdV = \alpha(VdP + PdV) \quad \text{or} \quad \alpha \frac{dP}{P} = -(\alpha + 1) \frac{dV}{V} \quad (14)$$

Integrating gives,

$$\frac{P}{P_0} = \left(\frac{V_0}{V}\right)^{1+1/\alpha} \quad (15)$$

which may be written in its most common form,

$$PV^\gamma = \text{constant} \quad \text{where} \quad \gamma = \frac{\alpha + 1}{\alpha} \quad (16)$$

For a mono-atomic ideal gas in three dimensions there are three translational degrees of freedom, so  $DOF = 3$ ,  $\alpha = 3/2$ , and  $\gamma = 5/3$ .

**Problem 2:** Derive the ideal monatomic gas law using kinetic theory. You may use the equipartition result  $U = \frac{3}{2}Nk_B T$ .

**Solution:** The internal energy of an ideal gas is purely kinetic energy, so that,

$$U = \frac{3}{2}Nk_B T = \frac{1}{2} \sum_i m \langle [(v_x^i)^2 + (v_y^i)^2 + (v_z^i)^2] \rangle = \frac{1}{2}Nm \langle \vec{v}^2 \rangle \quad (17)$$

The pressure is calculated by considering a particle incident normally on a perfectly reflecting wall,

$$F_x = ma_x = m \frac{\Delta p_x}{\delta t} = \frac{2mv_x}{\delta t} \quad (18)$$

The time taken for the particle to strike the wall again is  $\delta t = 2L/v_x$ , so that

$$F_{wall} = \frac{2mv_x^2}{2L} \quad \text{so that} \quad P = \frac{\sum_i F_x^i}{A} = \frac{m \sum_i (v_x^i)^2}{AL} \quad (19)$$

Noting that  $V = AL$ , with  $\sum_i (v_x^i)^2 = \frac{1}{3} \langle \vec{v}^2 \rangle$  and combining (12) and (14) yields,

$$PV = m \sum_i (v_x^i)^2 = Nk_B T \quad (20)$$

**Problem 3.** Find the degeneracy  $\Omega(E, N)$  for  $N$  a spin 1/2 Ising system with Hamiltonian  $H = -h \sum_i S_i$ .

**Solution:** The energy of a spin state depends only on the number of up spins  $N_u$ , and the number of down spins  $N_d$ , but not their arrangement. We then have,

$$E = -\frac{h}{2}(N_u - N_d), \quad \text{with degeneracy} \quad \Omega(E) = \frac{N!}{N_u!N_d!} \quad (21)$$

We also have  $N = N_u + N_d$ , so that

$$E = -\frac{h}{2}(2N_u - N) \quad \text{or} \quad N_u = \frac{N}{2} - \frac{E}{h}, \quad N_d = \frac{E}{h} - \frac{N}{2} \quad (22)$$

Since entropy is the  $k_B \ln(\Omega(E))$ , we use Stirling's approximation to write,

$$\ln(\Omega(E)) = N \ln N - N - N_u \ln N_u + N_u - N_d \ln N_d + N_d = N \ln N - N_u \ln N_u - N_d \ln N_d \quad (23)$$

It is useful to introduce the fraction  $f = N_u/N$ , so that  $N_d/N = 1 - f$  and

$$\ln(\Omega) = N \ln N - fN \ln(fN) - (1-f)N \ln[(1-f)N] = N[f \ln(f) + (1-f) \ln(1-f)] \quad (24)$$

which shows that the entropy in this model is extensive. In terms of  $f$ ,  $E = (Nh/2)(2f - 1)$ . We define  $\epsilon = E/N$ , so that  $f = 1/2 - \epsilon/h$ . Finally the entropy is,

$$S = -k_B \ln(\Omega(E)) = -k_B N [(1/2 - \epsilon/h) \ln(1/2 - \epsilon/h) + (\epsilon/h - 1/2) \ln(\epsilon/h - 1/2)] \quad (25)$$

**Problem 4.** Consider a random walk on a one dimensional lattice where the probability of stepping to the right or to the left is  $1/2$ . Find the probability that after  $N$  steps the walker is at position  $x$  lattice units from the starting position. Use Stirling's approximation to show that for large  $N$  the probability distribution is a Gaussian in  $x$ . Find the average mean square distance the walker is from the origin as a function of  $N$ .

**Solution:** Let us define the number of steps that the student takes to be  $N = t/\delta t$ . The number of steps taken in the positive x-direction,  $n$ , and the number taken in the negative x-direction,  $m$ , must add up to  $N$ , so that,

$$N = n + m \quad (26)$$

The  $x$  position of the student at time  $t = N\delta t$  is given by  $x = d\delta x$ , where

$$d = (n - m). \quad (27)$$

But what is the probability that the student reaches this position at time  $t$ ?

$$P(d, N) = \frac{1}{2^N} \frac{N!}{m!n!} = \frac{1}{2^N} \frac{N!}{((N+d)/2)!((N-d)/2)!} \quad (28)$$

Stirling's approximation:

$$\text{Log}(n!) \approx n \ln(n) - n \quad (29)$$

We then have,

$$\begin{aligned} \text{Ln}(P(d, N)) &\approx -N \text{Ln}(2) + N \text{Ln}(N) - N \\ &\quad - \frac{N+d}{2} \text{Ln}((N+d)/2) + (N+d)/2 \\ &\quad - \left(\frac{N-d}{2}\right) \text{Log}((N-d)/2) + (N-d)/2 \end{aligned} \quad (30)$$

This reduces to,

$$\begin{aligned} \text{Ln}(P(d, N)) &\approx -N \text{Ln}(2) + N \text{Ln}(N) \\ &\quad - \frac{N+d}{2} [\text{Ln}(N) + \text{Ln}(1+d/N) - \text{Ln}(2)] \\ &\quad - \left(\frac{N-d}{2}\right) [\text{Ln}(N) + \text{Ln}(1-d/N) - \text{Ln}(2)] \end{aligned} \quad (31)$$

Defining  $y = d/N$  and expanding for small  $y$  yields,

$$\ln(P(d, N)) = -\frac{N}{2} [(1+y)\ln(1+y) + (1-y)\ln(1-y)] \approx -\frac{N}{2} [(1+y)(y - \frac{1}{2}y^2) + \dots + (1-y)(-y - \frac{1}{2}y^2) + \dots] \quad (32)$$

To leading order this yields

$$\ln(P(d, N)) \approx -Ny^2 = -\frac{d^2}{N} \quad (33)$$

or,

$$P(d, N) \approx e^{-d^2/N} \rightarrow e^{-x^2\delta t/(\delta x)^2 t}. \quad (34)$$

Comparing to the solutions to the continuum diffusion equation in one dimension, this shows that the diffusion constant is related to the stochastic parameters  $\delta x$  and  $\delta t$  through,

$$D \approx (\delta x)^2/\delta t. \quad (35)$$

From the probability distribution (28), it is easy to see that the average displacement of an ink particle is  $\langle x \rangle = 0$ , but the typical distance from the origin is  $(\langle x^2 \rangle - \langle x \rangle^2)^{1/2} \approx N^{1/2}\delta x$ .

**Problem 5.** Prove the central limit theorem for a set of  $N$  independent subsystems that each have an energy  $E_i$  drawn from a Gaussian distribution with standard deviation  $\sigma$ . You will need to use the integral,

$$\int_{-\infty}^{\infty} e^{-ax^2+bx} dx = \left(\frac{\pi}{a}\right)^{1/2} e^{\frac{b^2}{4a}} \quad (36)$$

**Solution:** Consider any intensive thermodynamic variable  $X_i$  (e.g.  $E/N$ ) that has a different value in each of  $N$  subsystems. Consider each subsystem to have the same volume and that each subsystem is statistically equivalent. Each subsystem is assumed to have a statistical behavior that is Gaussian distributed, so that,

$$P_1(X_i) = (2\pi\sigma^2)^{-1/2} e^{-\frac{X_i^2}{2\sigma^2}} \quad (37)$$

where we assumed that each subsystem has the same statistical variations, quantified by  $\sigma$ . We would like to calculate the statistical behavior of the quantity

$$\bar{X}_N = \frac{1}{N} \sum_{i=1}^N X_i \quad (38)$$

The statistical behavior of  $\bar{X}_N$  is given by,

$$P_N(\bar{X}_N) = (2\pi\sigma^2)^{-N/2} \int_{-\infty}^{\infty} \prod_i dX_i e^{-\frac{X_i^2}{2\sigma^2}} \delta\left(\sum_i X_i - N\bar{X}_N\right) \quad (39)$$

Using the delta function representation,

$$\delta(\alpha) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iy\alpha} dy \quad (40)$$

we find,

$$P_N(\bar{X}_N) = (2\pi\sigma^2)^{-N/2} \int_{-\infty}^{\infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \prod_i dX_i e^{-\frac{X_i^2}{2\sigma^2}} e^{iy(\sum_i X_i - N\bar{X}_N)} \quad (41)$$

which is equivalent to

$$P_N(\bar{X}_N) = (2\pi\sigma^2)^{-N/2} \int_{-\infty}^{\infty} \frac{dy}{2\pi} e^{-iyN\bar{X}_N} [I]^N \quad (42)$$

where

$$I = \int_{-\infty}^{\infty} dX e^{-\frac{X^2}{2\sigma^2}} e^{iyX} = (2\pi\sigma^2)^{1/2} e^{-\frac{\sigma^2 y^2}{2}} \quad (43)$$

Finally,

$$P_N(\bar{X}_N) = \int_{-\infty}^{\infty} \frac{dy}{2\pi} e^{-iyN\bar{X}_N} e^{-\frac{N\sigma^2 y^2}{2}} = \frac{1}{(2\pi N)^{1/2} \sigma} e^{-\frac{\bar{X}_N^2}{2\sigma_N^2}} \quad (44)$$

where  $\sigma_N = \sigma/N^{1/2}$

**Problem 6.** Find the entropy of mixing for a system consisting of  $m$  different atom types, with  $n_i$  of each atom type and with the total of atoms,  $N = \sum_i^m n_i$ .

*Solution:* The number of ways of arranging the system is given by the multinomial,

$$\Omega(\{n_i\}) = \frac{N!}{n_1!n_2!\dots n_m!} \quad (45)$$

Using Stirling's approximation we find,

$$\ln(\Omega) = N \ln N - N - \left[ \sum_i (n_i \ln(n_i) - n_i) \right] = N \ln N - N - \left[ \sum_i (N p_i \ln(N p_i) - N p_i) \right] \quad (46)$$

where  $p_i = n_i/N$ . Using  $\sum_i p_i = 1$  this simplifies to,

$$S = k_B \ln(\Omega) = -k_B N \sum_i p_i \ln(p_i) \quad (47)$$

which is the same form as the Gibbs entropy, though the interpretation of  $p_i$  is different here as it is not the probability of an individual many body state.

**Problem 7.** Derive Stirling's approximation  $\ln(N!) = N \ln(N) - N$ .

**Solution.** Expanding the logarithm of  $N!$  as a sum we write,

$$\ln(N!) = \sum_{i=1}^N \ln(i) \approx \int_1^N \ln(x) dx = [x \ln(x) - x]_1^N = N \ln(N) - N + 1 \quad (48)$$

In the large  $N$  limit the constant "one" is negligible.

**Problem 8.** Find the entropy of a system of  $N$  non-interacting gas particles in a box of volume  $V = L^d$ , where  $d$  is the dimension. Consider two cases: Where the particles are distinguishable; and where they are indistinguishable. Is the entropy extensive in both cases? Assume that all configuration of the particles have the same energy, so we can ignore the kinetic energy term.

*Solution*

In the case where all of the particles are distinguishable, the number of available configurations is  $V^N$  as each particle can be at any position in the volume. The entropy is then  $S = k_B N \ln(V)$ , which is not extensive. Gibbs realized that identical particles are not distinguishable so the naive calculation of the number of states  $V^N$  is not valid. Instead, we must order the co-ordinates to eliminate overcounting of indistinguishable particles.

Consider a set of particles with co-ordinates  $\vec{r}_1 \dots \vec{r}_N$ . If we order one component of these co-ordinates, say the x-component so that  $x_1 \geq x_2 \geq x_3 \dots \geq x_N$  then the co-ordinates of the particles are always different hence ensuring that there is no overcounting. The integration over the spatial co-ordinates then becomes,

$$\Omega = L^{d-1} \int_0^L dx_1 \int_0^{x_1} dx_2 \dots \int_0^{x_{N-1}} dx_N = L^{(d-1)N} \frac{L^N}{N!} = \frac{V^N}{N!} \quad (49)$$

The entropy of indistinguishable particles is then,

$$S = k_B N [\ln(V) - \ln(N) + 1] \rightarrow N k_B \ln(V/N) \quad (50)$$

which is extensive for  $V/N$  finite.

**Problem 9.** Prove the central limit theorem holds for any distribution provided it has a finite standard deviation. i.e. extend the solution to problem 5 to arbitrary distributions that have a finite second moment.

*Solution* We consider that the statistics of an extensive quantity  $X$  obeys a distribution  $g(X)$  that has mean  $X_\infty$  and standard deviation  $\sigma$ . Without loss of generality, we can set  $X_\infty = 0$  by a simple shift of  $X$ . The statistical behavior of  $\bar{X}_N$  is given by,

$$P_N(\bar{X}_N) = (2\pi\sigma^2)^{-N/2} \int_{-\infty}^{\infty} \prod_i dX_i g(x_i) \delta\left(\sum_i X_i - N\bar{X}_N\right) \quad (51)$$



Using the delta function representation,

$$\delta(\alpha) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iy\alpha} dy \quad (52)$$

we find,

$$P_N(\bar{X}_N) = (2\pi\sigma^2)^{-N/2} \int_{-\infty}^{\infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \prod_i dX_i g(X_i) e^{iy(\sum_i X_i - N\bar{X}_N)} \quad (53)$$

which is equivalent to

$$P_N(\bar{X}_N) = (2\pi\sigma^2)^{-N/2} \int_{-\infty}^{\infty} \frac{dy}{2\pi} e^{-iyN\bar{X}_N} [I]^N \quad (54)$$

where

$$I = \int_{-\infty}^{\infty} dX g(X) e^{iyX} \quad (55)$$

Now  $X$  is extensive, so the exponential is a rapidly oscillating function and the integral is dominated by the region near  $y = 0$ . We then expand the exponential to find,

$$I = \int_{-\infty}^{\infty} dX g(X) e^{iyX} \approx \int_{-\infty}^{\infty} dX g(X) (1 - iyX - \frac{1}{2}y^2X^2 + \dots) \quad (56)$$

Assuming that  $g(X)$  is symmetric, this reduces to,

$$I = \int_{-\infty}^{\infty} dX g(X) e^{iyX} \approx (1 - \frac{1}{2}y^2\sigma^2 + \dots) \approx e^{-\frac{1}{2}y^2\sigma^2} \quad (57)$$

Finally, this is of the same form as that of Problem 5 and hence the result there applies,

$$P_N(\bar{X}_N) = \int_{-\infty}^{\infty} \frac{dy}{2\pi} e^{-iyN\bar{X}_N} e^{-\frac{N\sigma^2 y^2}{2}} = \frac{1}{(2\pi N)^{1/2} \sigma} e^{-\bar{X}_N^2 / 2\sigma_N^2} \quad (58)$$

where  $\sigma_N = \sigma/N^{1/2}$

**Problem 10.** Which of the following is an exact differential? a)  $dU(x, y) = 2xdx + 3xydy$ ; b)  $dU(x, y) = (-1/y)dx + (x/y^2)dy$ ; c)  $dU(x, y) = -ydx + xdy$ ? For these three examples, set  $dU = 0$  and solve the differential equations to find  $y(x)$ . In cases where the differential is exact, find  $U(x, y)$ .

**Solution:**

a) We have

$$\frac{\partial U}{\partial x} = 2x; \quad \text{and} \quad \frac{\partial U}{\partial y} = 3xy \quad (59)$$

so that

$$\frac{\partial^2 U}{\partial x \partial y} = 1/y^2 \neq \frac{\partial^2 U}{\partial y \partial x} = 3y \quad (60)$$

Therefore  $dU$  IS NOT an exact differential.

b) We have

$$\frac{\partial U}{\partial x} = \frac{-1}{y}; \quad \text{and} \quad \frac{\partial U}{\partial y} = \frac{x}{y^2} \quad (61)$$

so that

$$\frac{\partial^2 U}{\partial x \partial y} = \frac{1}{y^2} = \frac{\partial^2 U}{\partial y \partial x} = \frac{1}{y^2} \quad (62)$$

Therefore  $dU$  IS an exact differential.

c) We have

$$\frac{\partial U}{\partial x} = -y; \quad \text{and} \quad \frac{\partial U}{\partial y} = x \quad (63)$$

so that

$$\frac{\partial^2 U}{\partial x \partial y} = -1 \neq \frac{\partial^2 U}{\partial y \partial x} = 1 \quad (64)$$

Therefore  $dU$  IS NOT an exact differential.

Now we solve the three cases and if possible find  $U$ .

a) We find,

$$\frac{dy}{dx} = \frac{-2}{3y}, \quad \text{with solution} \quad y = \frac{4}{3}(c-x)^{1/2}; \quad \text{or} \quad y = -\frac{4}{3}(c+x)^{1/2} \quad (65)$$

b) In this case,

$$\frac{dy}{dx} = \frac{y}{x}, \quad \text{with solution} \quad y = cx \quad (66)$$

This is an exact differential, where  $U(x, y) = -x/y$ .

c) The solution for  $dU = 0$  is the same as b), but for finite  $U$ , it is not an exact differential so we cannot find  $U(x, y)$  to satisfy the equation.

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**Problem 11.** By using the fact that  $S$  is extensive show that

$$N \left( \frac{\partial S}{\partial N} \right)_{V,U} + V \left( \frac{\partial S}{\partial V} \right)_{N,U} + U \left( \frac{\partial S}{\partial U} \right)_{N,V} = S \quad (67)$$

and hence that  $N\mu = U + PV - TS$ .

**Solution.** Taking a derivative with respect to lambda of the homogeneous equation,

$$\lambda S(U, V, N) = S(\lambda U, \lambda V, \lambda N) \quad (68)$$

and then setting  $\lambda = 1$  yields Eq. (68). From the fundamental thermodynamic relation we have,

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN = \left( \frac{\partial S}{\partial U} \right)_{N,V} dU + \left( \frac{\partial S}{\partial V} \right)_{N,U} dV + \left( \frac{\partial S}{\partial N} \right)_{V,U} dN \quad (69)$$

Using the relations inferred from this equation in Eq. (68) yields  $N\mu = U + PV - TS$ .

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**Problem 12.** Using the fundamental thermodynamic relation and  $N\mu = U + PV - TS$  prove the Gibbs-Duhem relation.

**Solution.** From the fundamental thermodynamic relation we have,

$$dU = TdS - PdV + \mu dN = d(TS - PV + \mu N) \quad (70)$$

From the equality of the last two expressions we deduce

$$SdT - VdP + Nd\mu = 0 \quad (71)$$

---

**Problem 13.** From the fundamental thermodynamic relation show that,

$$\left(\frac{\partial\mu}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial N}\right)_{S,P}. \quad (72)$$

**Solution:** Since the independent variables are  $S, P, N$ , we choose the enthalpy and write,

$$dH = TdS + VdP + \mu dN = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN \quad (73)$$

hence,

$$\left(\frac{\partial H}{\partial P}\right)_{S,N} = V; \quad \left(\frac{\partial H}{\partial N}\right)_{S,P} = \mu. \quad (74)$$

By doing a derivative with respect to  $N$  of the first equation in (75) we find,

$$\left(\frac{\partial}{\partial N} \left(\frac{\partial H}{\partial P}\right)_{S,N}\right)_{S,P} = \left(\frac{\partial V}{\partial N}\right)_{S,P}. \quad (75)$$

while a derivative with respect to  $P$  of the second equation in (75) yields

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial N}\right)_{S,P}\right)_{S,N} = \left(\frac{\partial\mu}{\partial P}\right)_{S,N}. \quad (76)$$

Because  $dH$  is an exact differential, the order of the derivatives of  $H$  in Eq. (76) and (77) does not matter so these expressions are equivalent hence proving the Maxwell relation (73).

---

**Problem 14.** From the fundamental thermodynamic relation show that,

$$\left(\frac{\partial C_P}{\partial P}\right)_{T,N} = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N}. \quad (77)$$

**Solution:** Since the independent variables in the expression are  $T, P$ , we consider the Gibb's free energy  $G(T, P, N)$ , so that,

$$dG = -SdT + VdP + \mu dN = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN \quad (78)$$

hence,

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S; \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V. \quad (79)$$

This leads to the Maxwell relation,

$$-\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N} \quad (80)$$

Now take a temperature derivative at constant pressure of this equation, to find,

$$-\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P}\right)_{T,N}\right)_{P,N} = \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N} \quad (81)$$

We can change the order of the derivatives of the expression on the left hand side, and use the fact that  $C_P = T(\partial S/\partial T)_P$  to write,

$$-\left(\frac{\partial(C_P/T)}{\partial P}\right)_{T,N} = \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N}; \quad \text{or} \quad \left(\frac{\partial C_P}{\partial P}\right)_{T,N} = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N} \quad (82)$$

which solves the problem.

**Problem 15.** The equipartition theorem states that for a classical particle system of volume  $V$  with  $N$  particles, described by Hamiltonian  $H$ , the following relations hold,

$$\left\langle s_i \frac{\partial H}{\partial s_j} \right\rangle = kT \delta_{ij} \quad (83)$$

where  $s_i$  can be either the spatial or momentum co-ordinate. Using the canonical partition function, carry out the integrals explicitly to verify this theorem for a system described by the quadratic Hamiltonian,

$$H = \sum_i \frac{p_i^2}{2m} + \sum_i \frac{1}{2} k q_i^2. \quad (84)$$

Find the internal energy of this system as a function of temperature. Is this consistent with the equipartition theorem?

**Solution** We need to evaluate the following quantities explicitly,

$$\left\langle q_i \frac{\partial H}{\partial q_j} \right\rangle = k \left\langle q_i q_j \right\rangle; \quad \left\langle p_i \frac{\partial H}{\partial p_j} \right\rangle = \frac{1}{m} \left\langle p_i p_j \right\rangle \quad (85)$$

It is convenient to define,

$$I_i^{(l)} = \int (q_i)^l e^{-\beta k q_i^2/2} dq_i; \quad J_i^{(l)} = \int (p_i)^l e^{-\beta p_i^2/(2m)} dp_i \quad (86)$$

It is then evident that,

$$\left\langle q_i q_j \right\rangle = \frac{\int dq_i dq_j q_i q_j e^{-\beta H}}{\int d\omega e^{-\beta H}} \quad (87)$$

Reduces to,

$$\left\langle q_i q_j \right\rangle = \frac{I_i^{(1)} I_j^{(1)}}{I_i^{(0)} I_j^{(0)}}, \quad \text{for } i \neq j; \quad \left\langle q_i q_j \right\rangle = \frac{I_i^{(2)}}{I_i^{(0)}}, \quad \text{for } i = j; \quad (88)$$

Now note that  $I_i^{(l)}$  and  $J_i^{(l)}$  are zero for  $l$  odd, and also that they are independent on the index  $i$ , we thus find,

$$\left\langle q_i q_j \right\rangle = \delta_{ij} \frac{\int_{-\infty}^{\infty} q^2 e^{-\beta k q^2/2} dq}{\int_{-\infty}^{\infty} e^{-\beta k q^2/2} dq} \quad (89)$$

Now we use the standard integrals,

$$\int_{-\infty}^{\infty} q^{2n} e^{-\alpha q^2} dq = \frac{(2n-1)!!}{(2\alpha)^n} \left(\frac{\pi}{\alpha}\right)^{1/2} \quad (90)$$

where  $(2n-1)!! = (2n-1)(2n-3)\dots$  and is one for  $n = 0$  or  $n = 1$ . Using this result verifies the equipartition formula. The calculation for the momentum is essentially the same.

The internal energy is  $\langle H \rangle$  and since we have found that  $k \langle q_i^2 \rangle = \langle p_i^2 \rangle / m = k_B T$ , the internal energy of this problem is  $3Nk_B T$ . This is consistent with the equipartition formula that assigns  $k_B T/2$  for every quadratic degree of freedom. Here there are six degrees of freedom of that type.

**Problem 16.** You discover a new state of matter that has equation of state and internal energy given by,

$$P = AT^3/V, \quad U = BT^n \ln(V/V_0) + f(T) \quad (91)$$

where  $B, n, V_0$  are constants while  $f(T)$  only depends on the temperature. Find a numerical value for  $n$ , and find a relation between the constants  $B$  and  $A$ .

**Solution** It is convenient to define an entropy that is a Legendre transform of the conventional entropy so that,

$$S_L = S - \frac{U}{T} \quad (92)$$

We then have,

$$dS_L = \frac{P}{T}dV + \frac{U}{T^2}dT \quad (93)$$

where we used  $dS = dU/T + PdV/T$ . The Maxwell relation derived from  $dS_L$  in combination with the functions given in the problem definition yield,

$$\frac{\partial}{\partial T} \left( \frac{AT^2}{V} \right) = \frac{\partial}{\partial V} (BT^{n-2} \ln(V/V_0) + \frac{f(T)}{T^2}) \quad (94)$$

This equation is satisfied provided  $n = 3$  and  $B = 2A$ .

**Problem 17.** From the fundamental thermodynamic relation show that (here we use  $\beta = 1/T$ )

$$T \left( \frac{\partial N}{\partial T} \right)_{V, \beta\mu} = \left( \frac{\partial E}{\partial \mu} \right)_{T, V} \quad (95)$$

**Solution:** Since the independent variables are  $\beta, V, \beta\mu$ , we start with the entropy form of the fundamental relation,

$$dS = \beta dU + \beta P dV - \beta \mu dN \quad (96)$$

where  $\beta = 1/T$ . Since the independent variables in the desired expression are  $\beta, V, \beta\mu$ , we define,  $Y = S - \beta U + (\beta\mu)N$ , so that,

$$dY(\beta, V, \beta\mu) = -U d\beta + \beta P dV + N d(\beta\mu) = \left( \frac{\partial Y}{\partial \beta} \right)_{V, \beta\mu} d\beta + \left( \frac{\partial Y}{\partial V} \right)_{\beta, \beta\mu} dV + \left( \frac{\partial Y}{\partial \beta\mu} \right)_{\beta, V} d(\beta\mu) \quad (97)$$

hence,

$$\left( \frac{\partial Y}{\partial \beta} \right)_{V, \beta\mu} = -U; \quad \left( \frac{\partial Y}{\partial \beta\mu} \right)_{\beta, V} = N, \quad (98)$$

that leads to the Maxwell relation,

$$-\left( \frac{\partial U}{\partial \beta\mu} \right)_{\beta, V} = \left( \frac{\partial N}{\partial \beta} \right)_{V, \beta\mu} \quad (99)$$

Since  $\beta$  is constant for the left hand side derivative, we can take it outside. For the right hand derivative, we use the chain rule to find

$$\frac{-1}{\beta} \left( \frac{\partial U}{\partial \mu} \right)_{\beta, V} = \left( \frac{\partial N}{\partial T} \right)_{\beta\mu, V} \left( \frac{\partial T}{\partial \beta} \right)_{\beta\mu, V} \quad (100)$$

which reduces to the equation posed in the problem.

**Problem 18.** From the fundamental thermodynamic relation show that

$$\frac{1}{T^2} \left( \frac{\partial T}{\partial \beta \mu} \right)_{E,V} = - \left( \frac{\partial N}{\partial E} \right)_{\beta \mu, V} \quad \text{and} \quad -\rho^2 \left( \frac{\partial(S/N)}{\partial \rho} \right)_{T,N} = \left( \frac{\partial P}{\partial T} \right)_{\rho, N} \quad (101)$$

where  $\rho = N/V$  is the number density.

**Solution:** For the first equation, the variables held constant are  $\beta\mu$  and  $E$ , so we use the entropy form of the fundamental relation,  $dS = \beta dU + \beta P dV - \beta \mu dN$ . We also define  $Y = S + (\beta\mu)N$  to find a relation that has  $\beta\mu$  as an independent variable. We then have,

$$dY(U, V, \beta\mu) = \beta dU + \beta P dV + N d(\beta\mu) = \left( \frac{\partial Y}{\partial U} \right)_{V, \beta\mu} dU + \left( \frac{\partial Y}{\partial V} \right)_{U, \beta\mu} dV + \left( \frac{\partial Y}{\partial \beta\mu} \right)_{U, V} d(\beta\mu) \quad (102)$$

which leads to the Maxwell relation,

$$\left( \frac{\partial \beta}{\partial (\beta\mu)} \right)_{U, V} = \left( \frac{\partial N}{\partial U} \right)_{V, \beta\mu} \quad (103)$$

Using the chain rule on the left hand side yields,

$$\left( \frac{\partial \beta}{\partial (\beta\mu)} \right)_{U, V} = \left( \frac{\partial \beta}{\partial T} \right)_{U, V} \left( \frac{\partial T}{\partial (\beta\mu)} \right)_{U, V} = -\frac{1}{T^2} \left( \frac{\partial T}{\partial (\beta\mu)} \right)_{U, V} \quad (104)$$

which is the first relation of Eq. (101). The second relation of equation (101) has  $T, V, N$  as independent variables, so we use the Helmholtz free energy,

$$dF = -SdT - PdV + \mu dN = \left( \frac{\partial F}{\partial T} \right)_{V, N} dT + \left( \frac{\partial F}{\partial V} \right)_{T, N} dV + \left( \frac{\partial F}{\partial N} \right)_{T, V} dN \quad (105)$$

leading to the Maxwell relation,

$$\left( \frac{\partial S}{\partial V} \right)_{T, N} = \left( \frac{\partial P}{\partial T} \right)_{V, N} \quad (106)$$

The expression on the left hand side may be rewritten using the chain rule,

$$\left( \frac{\partial S}{\partial \rho} \right)_{T, N} = \left( \frac{\partial S}{\partial V} \right)_{T, N} \left( \frac{\partial V}{\partial \rho} \right)_{T, N} = -\frac{V^2}{N} \left( \frac{\partial S}{\partial V} \right)_{T, N} \quad (107)$$

Equation (106) is then,

$$-\frac{N^2}{V^2} \left( \frac{\partial(S/N)}{\partial V} \right)_{T, N} = -\rho^2 \left( \frac{\partial(S/N)}{\partial V} \right)_{T, N} = \left( \frac{\partial P}{\partial T} \right)_{V, N} = \left( \frac{\partial P}{\partial T} \right)_{\rho, N} \quad (108)$$

which is the second relation in Eq. (101)

**Problem 19.** From the second result of problem 18 show that

$$\left( \frac{\partial P}{\partial \rho} \right)_{S/N, N} = \left( \frac{\partial P}{\partial \rho} \right)_{T, N} + \left[ \left( \frac{\partial P}{\partial T} \right)_{\rho, N} \right]^2 \frac{NT}{\rho^2 C_V} \quad (109)$$

**Solution:** We use the relation for a non-natural derivative,

$$\left( \frac{\partial P}{\partial \rho} \right)_{S/N, N} = \left( \frac{\partial P}{\partial \rho} \right)_{T, N} + \left( \frac{\partial P}{\partial T} \right)_{\rho, N} \left( \frac{\partial T}{\partial \rho} \right)_{S/N, N} \quad (110)$$

Using the triple product rule, we have,

$$\left(\frac{\partial \rho}{\partial T}\right)_{S/N,N} \left(\frac{\partial(S/N)}{\partial T}\right)_{\rho,N} \left(\frac{\partial \rho}{\partial(S/N)}\right)_{T,N} = -1 \quad (111)$$

This yields,

$$\left(\frac{\partial \rho}{\partial T}\right)_{S/N,N} = - \left(\frac{\partial T}{\partial(S/N)}\right)_{\rho,N} \left(\frac{\partial(S/N)}{\partial \rho}\right)_{T,N} = \frac{NT}{C_V} \frac{1}{\rho^2} \left(\frac{\partial P}{\partial T}\right)_{\rho,N} \quad (112)$$

Using the second expression in (101) and (112) in (110) yields the desired result.

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**Problem 20.** Consider a system with an order parameter,  $x$ . If the volume( $V$ ), energy( $E$ ) and particle number( $N$ ) are fixed, then the system will choose the value of  $x$  with the maximum entropy. Now consider that the same system is connected to a reservoir that has temperature  $T$  and chemical potential  $\mu$ , so it can exchange energy and particles with the reservoir. Show that the total entropy, that is the sum of the entropy of the reservoir and the system, is maximized when

$$\left(\frac{\partial P}{\partial x}\right)_{T,\mu,V} = 0 \quad (113)$$

Hint: You can assume the system and reservoir are at the same temperature and chemical potential as required by equilibrium. Moreover you may use  $PV = TS - E + \mu N$ .

**Solution:** Since the variables that are kept fixed are  $T, \mu, V$ , we use the grand potential  $\Phi_G = U - TS - \mu N$ , so that,

$$d\Phi_G(T, V, \mu) = -SdT + PdV - Nd\mu = -d(PV) \quad (114)$$

Now we take a derivative of this expression with respect to  $x$  at fixed  $T, V, \mu$ . Since the entropy is maximized, the Grand potential is minimized, so that

$$\left(\frac{\partial \Phi_G}{\partial x}\right)_{T,V,\mu} = 0 = -V \left(\frac{\partial P}{\partial x}\right)_{T,V,\mu} \quad (115)$$

---

**Problem 21.** Consider a system where the thermodynamics are a function of temperature and another variable  $x$  which can be varied by an experimentalist. Assuming that

$$\left(\frac{\partial E}{\partial S}\right)_x = T; \quad \text{and using } F = E - TS \quad (116)$$

show that,

$$\left(\frac{\partial E}{\partial x}\right)_S = \left(\frac{\partial F}{\partial x}\right)_T \quad (117)$$

**Solution:** We take a derivative of the equation  $F = E - TS$  with respect to  $x$  at constant  $T$ , to find,

$$\left(\frac{\partial F}{\partial x}\right)_T = \left(\frac{\partial E}{\partial x}\right)_T - T \left(\frac{\partial S}{\partial x}\right)_T \quad (118)$$

Using the formula for a non-natural derivative, we have,

$$\left(\frac{\partial E}{\partial x}\right)_T = \left(\frac{\partial E}{\partial S}\right)_x \left(\frac{\partial S}{\partial x}\right)_T + \left(\frac{\partial E}{\partial x}\right)_S \quad (119)$$

Using this result, along with the first of Eq. (116), in Eq. (118) proves Eq. (117).

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**Problem 22.** Show that

$$C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{N,V} \quad (120)$$

**Solution:** The specific heat at constant volume is given by,

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_{V,N} \quad (121)$$

The Helmholtz free energy is given by,

$$F = U - TS; \quad \text{so} \quad dF = -SdT - PdV + \mu dN = \left( \frac{\partial F}{\partial T} \right)_{V,N} dT + \left( \frac{\partial F}{\partial V} \right)_{T,N} dV + \left( \frac{\partial F}{\partial N} \right)_{T,V} dN \quad (122)$$

so that,

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N}; \quad \text{and} \quad \left( \frac{\partial S}{\partial T} \right)_{V,N} = - \left( \frac{\partial^2 F}{\partial T^2} \right)_{V,N} \quad (123)$$

Multiplying by  $T$  and using Eq. (121) proves the relation (120).

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**Problem 23.** Show that

$$U = \left( \frac{\partial(F/T)}{\partial(1/T)} \right)_{N,V} \quad (124)$$

**Solution:** Defining  $\beta = 1/T$ , we have,

$$\left( \frac{\partial(\beta F)}{\partial \beta} \right)_{N,V} = F + \beta \left( \frac{\partial F}{\partial \beta} \right)_{N,V} = F - T \left( \frac{\partial F}{\partial T} \right)_{N,V} \quad (125)$$

where the last expression on the right hand side is found using the chain rule. We also have,

$$dF = -SdT - PdV + \mu dN = \left( \frac{\partial F}{\partial T} \right)_{V,N} dT + \left( \frac{\partial F}{\partial V} \right)_{T,N} dV + \left( \frac{\partial F}{\partial N} \right)_{T,V} dN \quad (126)$$

so that

$$\left( \frac{\partial F}{\partial T} \right)_{V,N} = -S. \quad (127)$$

Therefore,

$$\left( \frac{\partial(\beta F)}{\partial \beta} \right)_{N,V} = F + TS = U \quad (128)$$

as posed in Eq. (124).

---

**Problem 24.** Show that

$$V \left( \frac{\partial P}{\partial T} \right)_{\mu,N} = S; \quad \text{and} \quad V \left( \frac{\partial P}{\partial \mu} \right)_{T,N} = N \quad (129)$$



Now express the pressure of the ideal classical gas in terms of the variables  $\mu$  and  $T$  and using this expression verify the equations above.

**Solution:** We use the fact that the Gibbs free energy is  $\mu N$  to write

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = N \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \quad (130)$$

We also have,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN = -SdT + VdP + \mu dN \quad (131)$$

so that

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V. \quad (132)$$

Using this relation in Eq. (130) proves the second identity in (129). To prove the first relation in (129), we use the triple product identity,

$$\left(\frac{\partial P}{\partial T}\right)_{\mu,N} \left(\frac{\partial \mu}{\partial P}\right)_{T,N} \left(\frac{\partial T}{\partial \mu}\right)_{P,N} = -1. \quad (133)$$

From Eq. (134) and  $G = \mu N$ , we have,

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N} = N \left(\frac{\partial \mu}{\partial T}\right)_{P,N} \quad (134)$$

Using the second relation in Eq. (129) for the second term in the product (133) and using (134) leads to the first relation in (129).

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**Problem 25.** From the fundamental thermodynamic relation show that

$$\left(\frac{\partial S}{\partial P}\right)_{T,\mu} = -\left(\frac{\partial V}{\partial T}\right)_{P,\mu} \quad (135)$$

**Solution:** The fundamental thermodynamic relation is  $dU = TdS - PdV + \mu dN$ , so the independent variables are  $S, V, N$ . To find the desired expression using a Maxwell relation approach, we need independent variables  $T, P, \mu$ , so we define  $Y = U - TS + PV - \mu N$ , so that,

$$dY = -SdT + VdP - Nd\mu = \left(\frac{\partial Y}{\partial T}\right)_{P,\mu} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,\mu} dP + \left(\frac{\partial Y}{\partial \mu}\right)_{T,P} d\mu \quad (136)$$

so that,

$$\left(\frac{\partial Y}{\partial T}\right)_{P,\mu} = -S; \quad \left(\frac{\partial Y}{\partial P}\right)_{T,\mu} = V; \quad \left(\frac{\partial Y}{\partial \mu}\right)_{T,P} = -N \quad (137)$$

and hence,

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial Y}{\partial T}\right)_{P,\mu}\right)_{T,\mu} = -\left(\frac{\partial S}{\partial P}\right)_{T,\mu} \quad \left(\frac{\partial}{\partial T} \left(\frac{\partial Y}{\partial P}\right)_{T,\mu}\right)_{P,\mu} = \left(\frac{\partial V}{\partial T}\right)_{P,\mu} \quad (138)$$

Since the order of differentiation does not matter, as  $dY$  is an exact derivative, the relation (135) is proven.

---

**Problem 26.** Consider a single harmonic oscillator with energies  $\epsilon_n = \hbar\omega(n + 1/2)$ . Find the average energy of the system as a function of temperature. Find the average occupancy of each energy level as a function of temperature. Is there are regime where your result for the average energy is in agreement with the equipartition theorem?

**Solution** The energy levels of the Harmonic oscillator are given by  $\epsilon_n = \hbar\omega(n + 1/2)$ , so the canonical partition function is given by,

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \quad (139)$$

so the average energy is,

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \quad (140)$$

This can be written as,

$$\langle E \rangle = \hbar\omega(\langle n \rangle + 1/2); \quad \text{where} \quad \langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1} \quad (141)$$

In the high temperature limit, this reduces to  $\langle E \rangle = \frac{1}{2}\hbar\omega + k_B T$  which has the equipartition term (2 degrees of freedom) plus a quantum correction that is negligible at high temperature.

---

**Problem 27.** For a pure state show that

$$\hat{\rho}^2 = \hat{\rho} \quad (142)$$

Also show that for a mixed state this identity fails.

**Solution** For a pure state,

$$(\hat{\rho})_{nm} = a_{nk}a_{mk}^* \quad (143)$$

and

$$(\hat{\rho}^2)_{nm} = \sum_l a_{nl}a_l^*a_{mk}^* = a_{nk}a_{mk}^* \quad (144)$$

where we used  $\sum_l a_l^*a_l = 1$  for an orthonormal wavefunction. For a mixed state the elements of the density matrix are given by,

$$(\hat{\rho})_{nm} = \sum_k p_k a_{nk}a_{mk}^* \quad (145)$$

so the elements of the square of the density matrix are,

$$(\hat{\rho}^2)_{nm} = \sum_{kk'} \sum_l p_k p_{k'} a_{nk}a_{lk}^*a_{lk'}a_{mk'}^* \quad (146)$$

which is clearly not the same. The purity of the mixed state is,

$$P_u = \text{tr}(\hat{\rho}^2) = \sum_{kk'} \sum_l p_k p_{k'} a_{nk}a_{lk}^*a_{lk'}a_{nk'}^* \quad (147)$$


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**Problem 28.** Consider two single particle pure states with wavefunctions

$$|\psi\rangle_{\pm} = \frac{1}{\sqrt{2}}(|0\rangle \pm |1\rangle) \quad (148)$$

Write down the density matrix for each of these pure states and verify that they have purity equal to one. Now consider the density matrix of a mixed state consisting of  $\hat{\rho} = p_+ \hat{\rho}_+ + p_- \hat{\rho}_-$ , where  $p_+ + p_- = 1$ . Find the purity of this state, and the value of the mixing probability  $p_+$  at which the purity is smallest.

$$\hat{\rho}^+ = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad \hat{\rho}^- = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad (149)$$

$$(\hat{\rho}^+)^2 = \frac{1}{4} \begin{pmatrix} 2 & 2 \\ 2 & 2 \end{pmatrix} \quad (\hat{\rho}^-)^2 = \frac{1}{4} \begin{pmatrix} 2 & -2 \\ -2 & 2 \end{pmatrix} \quad (150)$$

which confirms the identity. The purity is clearly  $P_u = 1$ . For the mixed case we have,

$$\hat{\rho} = \frac{p_+}{2} \hat{\rho}^+ + \frac{p_-}{2} \hat{\rho}^- \quad (151)$$

From which we find,

$$(\hat{\rho})^2 = \left(\frac{p_+}{2} \hat{\rho}^+ + \frac{p_-}{2} \hat{\rho}^-\right)^2 = (p_+)^2 \hat{\rho}_+ + (p_-)^2 \hat{\rho}_- = (p_+)^2 + (1 - p_+)^2 = 1 - 2p_+ + 2p_+^2 \leq 1 \quad (152)$$

the minimum occurs at  $p_+ = 1/2$  and the maximum at  $p_+ = 1$ .

**Problem 29.** Show that Eqs. (179) of the lecture notes reduce to Eqs. (178) in the eigenvalue basis.

**Solution** We use the relation

$$\hat{U} \hat{H} \hat{U}^\dagger = \hat{\lambda}_E \quad (153)$$

where  $U$  is a unitary matrix and  $\lambda_E$  is the diagonal matrix with the eigenvalues of the hamiltonian  $H$  on the diagonal. We then have,

$$Z = \sum_i e^{-\beta E_i} = \text{tr}(e^{-\beta \hat{\lambda}_E}) = \text{tr}(\hat{U}^\dagger e^{-\beta \hat{\lambda}_E} \hat{U}) = \text{tr}(e^{-\beta \hat{U}^\dagger \hat{\lambda}_E \hat{U}}) = \text{tr}(e^{-\beta \hat{H}}) \quad (154)$$

where we used the trace property  $\text{tr}(ABC) = \text{Tr}(BCA)$  and the property of unitary matrices  $\hat{U}^\dagger \hat{U} = \hat{U} \hat{U}^\dagger = \hat{1}$ , where  $\hat{1}$  is the identity matrix. The other expressions are transformed in a similar way.