

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.

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. (12) of Lecture notes.

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,

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

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.

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 8.

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.

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.

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 $\sum_i p_i = 1$, $U = \sum_i p_i E_i$

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 $w_{ji} = f(x) = \min(1, x)$.

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,

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

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 Eqs. (94,95) of the notes.

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 Eqs. (134) of the notes.

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. Eq. (86) of the notes.

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 τ . Since G is bounded, as τ goes to infinity, the average of the time derivative of G goes to zero.

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.

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 $m \sim |T_c - T|^\beta$ 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 finites 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.

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 Eqs. (98-101) of the notes.

Problem 18. Show that

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

Solution. See Eq. (129-132) 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 δx and δt 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. By taking a time derivative of the definition of the density operator in terms of a set of wavefunctions drawn from an ensemble, $\hat{\rho}(t) = \sum_j |\psi_j(t)\rangle\langle\psi_j(t)|$, derive the von Neumann time evolution equation (12).

Solution. Take a time derivative of the definition to find,

$$\frac{\partial \hat{\rho}(t)}{\partial t} = \sum_j \frac{\partial |\psi_j(t)\rangle}{\partial t} \langle\psi_j(t)| + |\psi_j(t)\rangle \frac{\partial \langle\psi_j(t)|}{\partial t} \quad (36)$$

Using the Schrödinger equation $i\hbar \partial |\psi(t)\rangle / \partial t = H |\psi(t)\rangle$ and its adjoint, yields,

$$\frac{\partial \hat{\rho}(t)}{\partial t} = \frac{1}{i\hbar} \left[\sum_j \hat{H} |\psi_j(t)\rangle \langle\psi_j(t)| - |\psi_j(t)\rangle \langle\psi_j(t)| \hat{H} \right] \quad \text{or} \quad i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}] \quad (37)$$

Problem 6. 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 σ . You will need to use the integral,

$$\int_{-\infty}^{\infty} e^{-ax^2+bx} dx = \left(\frac{\pi}{a}\right)^{1/2} e^{\frac{b^2}{4a}} \quad (38)$$

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,

$$P_1(X_i) = (2\pi\sigma^2)^{-1/2} e^{-\frac{X_i^2}{2\sigma^2}} \quad (39)$$

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

$$\bar{X}_N = \frac{1}{N} \sum_{i=1}^N X_i \quad (40)$$

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

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

Using the delta function representation,

$$\delta(\alpha) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iy\alpha} dy \quad (42)$$

we find,

$$P_N(\bar{X}_N) = (2\pi\sigma^2)^{-N/2} \int_{-\infty}^{\infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \prod_i dX_i e^{-\frac{X_i^2}{2\sigma^2}} e^{iy(\sum_i X_i - N\bar{X}_N)} \quad (43)$$

which is equivalent to

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

where

$$I = \int_{-\infty}^{\infty} dX e^{-\frac{X^2}{2\sigma^2}} e^{iyX} = (2\pi\sigma^2)^{1/2} e^{-\frac{\sigma^2 y^2}{2}} \quad (45)$$

Finally,

$$P_N(\bar{X}_N) = \int_{-\infty}^{\infty} \frac{dy}{2\pi} e^{-iyN\bar{X}_N} e^{-\frac{N\sigma^2 y^2}{2}} = \frac{1}{(2\pi N)^{1/2} \sigma} e^{-\bar{X}_N^2 / 2\sigma_N^2} \quad (46)$$

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

Problem 7. 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,

$$\Omega(\{n_i\}) = \frac{N!}{n_1!n_2!\dots n_m!} \quad (47)$$

Using Stirling's approximation we find,

$$\ln(\Omega) = N \ln N - N - \left[\sum_i (n_i \ln(n_i) - n_i) \right] = N \ln N - N - \left[\sum_i (N p_i \ln(N p_i) - N p_i) \right] \quad (48)$$

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

$$S = k_B \ln(\Omega) = -k_B \sum_i p_i \ln(p_i) \quad (49)$$

which is the same as the Gibbs entropy.

Problem 8. Derive Stirling's approximation $\ln(N!) = N \ln(N) - N$.

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

$$\ln(N!) = \sum_{i=1}^N \ln(i) \approx \int_1^N \ln(x) dx = [x \ln(x) - x]_1^N = N \ln(N) - N + 1 \quad (50)$$

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

Problem 9. Which of the following is an exact differential? a) $dU(x, y) = 2x dx + 3xy dy$; b) $dU(x, y) = (-1/y) dx + (x/y^2) dy$; c) $dU(x, y) = -y dx + x dy$? 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

$$\frac{\partial U}{\partial x} = 2x; \quad \text{and} \quad \frac{\partial U}{\partial y} = 3xy \quad (51)$$

so that

$$\frac{\partial^2 U}{\partial x \partial y} = 1/y^2 \neq \frac{\partial^2 U}{\partial y \partial x} = 3y \quad (52)$$

Therefore dU IS NOT an exact differential.

b) We have

$$\frac{\partial U}{\partial x} = \frac{-1}{y}; \quad \text{and} \quad \frac{\partial U}{\partial y} = \frac{x}{y^2} \quad (53)$$

so that

$$\frac{\partial^2 U}{\partial x \partial y} = \frac{1}{y^2} = \frac{\partial^2 U}{\partial y \partial x} = \frac{1}{y^2} \quad (54)$$

Therefore dU IS an exact differential.

c) We have

$$\frac{\partial U}{\partial x} = -y; \quad \text{and} \quad \frac{\partial U}{\partial y} = x \quad (55)$$

so that

$$\frac{\partial^2 U}{\partial x \partial y} = -1 \neq \frac{\partial^2 U}{\partial y \partial x} = 1 \quad (56)$$

Therefore dU IS NOT an exact differential.

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

a) We find,

$$\frac{dy}{dx} = \frac{-2}{3y}, \quad \text{with solution} \quad y = \frac{4}{3}(c-x)^{1/2}; \quad \text{or} \quad y = -\frac{4}{3}(c+x)^{1/2} \quad (57)$$

b) In this case,

$$\frac{dy}{dx} = \frac{y}{x}, \quad \text{with solution} \quad y = cx \quad (58)$$

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.

Problem 10. By using the fact that S is extensive show that

$$N \left(\frac{\partial S}{\partial N} \right)_{V,U} + V \left(\frac{\partial S}{\partial V} \right)_{N,U} + U \left(\frac{\partial S}{\partial U} \right)_{N,V} = S \quad (59)$$

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

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

$$\lambda S(U, V, N) = S(\lambda U, \lambda V, \lambda N) \quad (60)$$

and then setting $\lambda = 1$ yields Eq. (56). From the fundamental thermodynamic relation we have,

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN = \left(\frac{\partial S}{\partial U} \right)_{N,V} dU + \left(\frac{\partial S}{\partial V} \right)_{N,U} dV + \left(\frac{\partial S}{\partial N} \right)_{V,U} dN \quad (61)$$

Using the relations inferred from this equation in Eq. (56) yields $N\mu = U + PV - TS$.

Problem 11. Using the fundamental thermodynamic relation and $N\mu = U + PV - TS$ prove the Gibbs-Duhem relation.

Solution. From the fundamental thermodynamic relation we have,

$$dU = TdS - PdV + \mu dN = d(TS - PV + \mu N) \quad (62)$$

From the equality of the last two expressions we deduce

$$SdT - VdP + Nd\mu = 0 \quad (63)$$

Problem 12. From the fundamental thermodynamic relation show that,

$$\left(\frac{\partial\mu}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial N}\right)_{S,P}. \quad (64)$$

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

$$dH = TdS + VdP + \mu dN = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN \quad (65)$$

hence,

$$\left(\frac{\partial H}{\partial P}\right)_{S,N} = V; \quad \left(\frac{\partial H}{\partial N}\right)_{S,P} = \mu. \quad (66)$$

By doing a derivative with respect to N of the first equation in (65) we find,

$$\left(\frac{\partial}{\partial N} \left(\frac{\partial H}{\partial P}\right)_{S,N}\right)_{S,P} = \left(\frac{\partial V}{\partial N}\right)_{S,P}. \quad (67)$$

while a derivative with respect to P of the second equation in (65) yields

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial N}\right)_{S,P}\right)_{S,N} = \left(\frac{\partial\mu}{\partial P}\right)_{S,N}. \quad (68)$$

Because dH is an exact differential, the order of the derivatives of H in Eq. (66) and (67) does not matter so these expressions are equivalent hence proving the Maxwell relation (65).

Problem 13. From the fundamental thermodynamic relation show that,

$$\left(\frac{\partial C_P}{\partial P}\right)_{T,N} = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N}. \quad (69)$$

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

$$dG = -SdT + VdP + \mu dN = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN \quad (70)$$

hence,

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S; \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V. \quad (71)$$

This leads to the Maxwell relation,

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

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

$$-\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P}\right)_{T,N}\right)_{P,N} = \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N} \quad (73)$$

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,

$$-\left(\frac{\partial(C_P/T)}{\partial P}\right)_{T,N} = \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N}; \quad \text{or} \quad \left(\frac{\partial C_P}{\partial P}\right)_{T,N} = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_{P,N} \quad (74)$$

which solves the problem.

Problem 14. From the fundamental thermodynamic relation show that (here we use $\beta = 1/T$)

$$T \left(\frac{\partial N}{\partial T} \right)_{V, \beta\mu} = \left(\frac{\partial E}{\partial \mu} \right)_{T, V} \quad (75)$$

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

$$dS = \beta dU + \beta P dV - \beta \mu dN \quad (76)$$

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,

$$dY(\beta, V, \beta\mu) = -U d\beta + \beta P dV + N d(\beta\mu) = \left(\frac{\partial Y}{\partial \beta} \right)_{V, \beta\mu} d\beta + \left(\frac{\partial Y}{\partial V} \right)_{\beta, \beta\mu} dV + \left(\frac{\partial Y}{\partial (\beta\mu)} \right)_{\beta, V} d(\beta\mu) \quad (77)$$

hence,

$$\left(\frac{\partial Y}{\partial \beta} \right)_{V, \beta\mu} = -U; \quad \left(\frac{\partial Y}{\partial (\beta\mu)} \right)_{\beta, V} = N, \quad (78)$$

that leads to the Maxwell relation,

$$-\left(\frac{\partial U}{\partial (\beta\mu)} \right)_{\beta, V} = \left(\frac{\partial N}{\partial \beta} \right)_{V, \beta\mu} \quad (79)$$

Since β 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

$$\frac{-1}{\beta} \left(\frac{\partial U}{\partial \mu} \right)_{\beta, V} = \left(\frac{\partial N}{\partial T} \right)_{\beta\mu, V} \left(\frac{\partial T}{\partial \beta} \right)_{\beta\mu, V} \quad (80)$$

which reduces to the equation posed in the problem.

Problem 15. From the fundamental thermodynamic relation show that

$$\frac{1}{T^2} \left(\frac{\partial T}{\partial \beta\mu} \right)_{E, V} = - \left(\frac{\partial N}{\partial E} \right)_{\beta\mu, V} \quad \text{and} \quad -\rho^2 \left(\frac{\partial (S/N)}{\partial \rho} \right)_{T, N} = \left(\frac{\partial P}{\partial T} \right)_{\rho, N} \quad (81)$$

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,

$$dY(U, V, \beta\mu) = \beta dU + \beta P dV + N d(\beta\mu) = \left(\frac{\partial Y}{\partial U} \right)_{V, \beta\mu} dU + \left(\frac{\partial Y}{\partial V} \right)_{U, \beta\mu} dV + \left(\frac{\partial Y}{\partial (\beta\mu)} \right)_{U, V} d(\beta\mu) \quad (82)$$

which leads to the Maxwell relation,

$$\left(\frac{\partial \beta}{\partial (\beta\mu)} \right)_{U, V} = \left(\frac{\partial N}{\partial U} \right)_{V, \beta\mu} \quad (83)$$

Using the chain rule on the left hand side yields,

$$\left(\frac{\partial \beta}{\partial (\beta\mu)} \right)_{U, V} = \left(\frac{\partial \beta}{\partial T} \right)_{U, V} \left(\frac{\partial T}{\partial (\beta\mu)} \right)_{U, V} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial (\beta\mu)} \right)_{U, V} \quad (84)$$

which is the first relation of Eq. (81). The second relation of equation (81) has T, V, N as independent variables, so we use the Helmholtz free energy,

$$dF = -SdT - PdV + \mu dN = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN \quad (85)$$

leading to the Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \quad (86)$$

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

$$\left(\frac{\partial S}{\partial \rho}\right)_{T,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N} \left(\frac{\partial V}{\partial \rho}\right)_{T,N} = -\frac{V^2}{N} \left(\frac{\partial S}{\partial V}\right)_{T,N} \quad (87)$$

Equation (86) is then,

$$-\frac{N^2}{V^2} \left(\frac{\partial(S/N)}{\partial V}\right)_{T,N} = -\rho^2 \left(\frac{\partial(S/N)}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} = \left(\frac{\partial P}{\partial T}\right)_{\rho,N} \quad (88)$$

which is the second relation in Eq. (81)

Problem 16. From the second result of problem 15 show that

$$\left(\frac{\partial P}{\partial \rho}\right)_{S/N,N} = \left(\frac{\partial P}{\partial \rho}\right)_{T,N} + \left[\left(\frac{\partial P}{\partial T}\right)_{\rho,N}\right]^2 \frac{NT}{\rho^2 C_V} \quad (89)$$

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

$$\left(\frac{\partial P}{\partial \rho}\right)_{S/N,N} = \left(\frac{\partial P}{\partial \rho}\right)_{T,N} + \left(\frac{\partial P}{\partial T}\right)_{\rho,N} \left(\frac{\partial T}{\partial \rho}\right)_{S/N,N} \quad (90)$$

Using the triple product rule, we have,

$$\left(\frac{\partial \rho}{\partial T}\right)_{S/N,N} \left(\frac{\partial(S/N)}{\partial T}\right)_{\rho,N} \left(\frac{\partial \rho}{\partial(S/N)}\right)_{T,N} = -1 \quad (91)$$

This yields,

$$\left(\frac{\partial \rho}{\partial T}\right)_{S/N,N} = -\left(\frac{\partial T}{\partial(S/N)}\right)_{\rho,N} \left(\frac{\partial(S/N)}{\partial \rho}\right)_{T,N} = \frac{NT}{C_V} \frac{1}{\rho^2} \left(\frac{\partial P}{\partial T}\right)_{\rho,N} \quad (92)$$

Using the second expression in (81) and (92) in (90) yields the desired result.

Problem 17. 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 μ , 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

$$\left(\frac{\partial P}{\partial x}\right)_{T,\mu,V} = 0 \quad (93)$$

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, μ, V , we use the grand potential $\Phi_G = U - TS - \mu N$, so that,

$$d\Phi_G(T, V, \mu) = -SdT + PdV - Nd\mu = -d(PV) \quad (94)$$

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

$$\left(\frac{\partial\Phi_G}{\partial x}\right)_{T,V,\mu} = 0 = -V\left(\frac{\partial P}{\partial x}\right)_{T,V,\mu} \quad (95)$$

Problem 18. Consider a system where the thermodynamics are a function of temperature and another variable x which can be varied by an experimentalist. Assuming that

$$\left(\frac{\partial E}{\partial S}\right)_x = T; \quad \text{and using } F = E - TS \quad (96)$$

show that,

$$\left(\frac{\partial E}{\partial x}\right)_S = \left(\frac{\partial F}{\partial x}\right)_T \quad (97)$$

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

$$\left(\frac{\partial F}{\partial x}\right)_T = \left(\frac{\partial E}{\partial x}\right)_T - T\left(\frac{\partial S}{\partial x}\right)_T \quad (98)$$

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

$$\left(\frac{\partial E}{\partial x}\right)_T = \left(\frac{\partial E}{\partial S}\right)_x \left(\frac{\partial S}{\partial x}\right)_T + \left(\frac{\partial E}{\partial x}\right)_S \quad (99)$$

Using this result, along with the first of Eq. (96), in Eq. (98) proves Eq. (97).

Problem 19. Show that

$$C_V = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_{N,V} \quad (100)$$

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

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_{V,N} \quad (101)$$

The Helmholtz free energy is given by,

$$F = U - TS; \quad \text{so } dF = -SdT - PdV + \mu dN = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN \quad (102)$$

so that,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}; \quad \text{and } \left(\frac{\partial S}{\partial T}\right)_{V,N} = -\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} \quad (103)$$

Multiplying by T and using Eq. (101) proves the relation (100).

Problem 20. Show that

$$U = \left(\frac{\partial(F/T)}{\partial(1/T)} \right)_{N,V} \quad (104)$$

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

$$\left(\frac{\partial(\beta F)}{\partial\beta} \right)_{N,V} = F + \beta \left(\frac{\partial F}{\partial\beta} \right)_{N,V} = F - T \left(\frac{\partial F}{\partial T} \right)_{N,V} \quad (105)$$

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

$$dF = -SdT - PdV + \mu dN = \left(\frac{\partial F}{\partial T} \right)_{V,N} dT + \left(\frac{\partial F}{\partial V} \right)_{T,N} dV + \left(\frac{\partial F}{\partial N} \right)_{T,V} dN \quad (106)$$

so that

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

Therefore,

$$\left(\frac{\partial(\beta F)}{\partial\beta} \right)_{N,V} = F + TS = U \quad (108)$$

as posed in Eq. (104).

Problem 21. Show that

$$V \left(\frac{\partial P}{\partial T} \right)_{\mu,N} = S; \quad \text{and} \quad V \left(\frac{\partial P}{\partial\mu} \right)_{T,N} = N \quad (109)$$

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

Solution: We use the fact that the Gibbs free energy is μN to write

$$\left(\frac{\partial G}{\partial P} \right)_{T,N} = N \left(\frac{\partial\mu}{\partial P} \right)_{T,N} \quad (110)$$

We also have,

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,N} dT + \left(\frac{\partial G}{\partial P} \right)_{T,N} dP + \left(\frac{\partial G}{\partial N} \right)_{T,P} dN = -SdT + VdP + \mu dN \quad (111)$$

so that

$$\left(\frac{\partial G}{\partial P} \right)_{T,N} = V. \quad (112)$$

Using this relation in Eq. (110) proves the second identity in (109). To prove the first relation in (109), we use the triple product identity,

$$\left(\frac{\partial P}{\partial T} \right)_{\mu,N} \left(\frac{\partial\mu}{\partial P} \right)_{T,N} \left(\frac{\partial T}{\partial\mu} \right)_{P,N} = -1. \quad (113)$$

From Eq. (114) and $G = \mu N$, we have,

$$-S = \left(\frac{\partial G}{\partial T} \right)_{P,N} = N \left(\frac{\partial\mu}{\partial T} \right)_{P,N} \quad (114)$$

Using the second relation in Eq. (109) for the second term in the product (113) and using (114) leads to the first relation in (109).

Problem 22. From the fundamental thermodynamic relation show that

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

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, μ , so we define $Y = U - TS + PV - \mu N$, so that,

$$dY = -SdT + VdP - Nd\mu = \left(\frac{\partial Y}{\partial T}\right)_{P,\mu} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,\mu} dP + \left(\frac{\partial Y}{\partial \mu}\right)_{T,P} d\mu \quad (116)$$

so that,

$$\left(\frac{\partial Y}{\partial T}\right)_{P,\mu} = -S; \quad \left(\frac{\partial Y}{\partial P}\right)_{T,\mu} = V; \quad \left(\frac{\partial Y}{\partial \mu}\right)_{T,P} = -N \quad (117)$$

and hence,

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial Y}{\partial T}\right)_{P,\mu}\right)_{T,\mu} = -\left(\frac{\partial S}{\partial P}\right)_{T,\mu} \quad \left(\frac{\partial}{\partial T} \left(\frac{\partial Y}{\partial P}\right)_{T,\mu}\right)_{P,\mu} = \left(\frac{\partial V}{\partial T}\right)_{P,\mu} \quad (118)$$

Since the order of differentiation does not matter, as dY is an exact derivative, the relation (115) is proven.
