

Problems for the course
Statistical Physics
(FYS3130)

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Contents

1	General Comments	5
2	Introduction to Thermodynamics	7
2.1	Additional Problems: Fluctuations	28
2.2	Mini-tests	30
2.2.1	A	30
2.2.2	B	31
3	The Thermodynamics of Phase Transitions	33
3.1	Mini-tests	44
3.1.1	A	44
3.1.2	B	46
4	Elementary Probability Theory ...	49
5	Stochastic dynamics ...	59
6	The Foundations of Statistical Mechanics	77
7	Equilibrium Statistical Mechanics	79
8	Tests and training	103
A	Additional information	107
A.1	Thermodynamics	107
A.1.1	Thermodynamic potentials	107
A.1.2	Variable transformation	107
A.1.3	Derivatives from the equation of state	107
A.2	Main distributions	109
A.3	The Dirac delta-function	110
A.4	Fourier Series and Transforms	111
B	Maple Printouts	115

Chapter 1

General Comments

This year the course will be delivered along the lines of the book [1]. The problems will also be selected from this book. It is *crucially important* for students to solve problems independently.

The problems will be placed on the course homepage. The same page will contain solutions of the problems. So if a student is not able to solve the problem without assistance, then she/he should come through the solution. In any case, student have to able to present solutions, obtained independently, or with help of the course homepage.

FYS 3130 (former FYS 203) is a complicated course, which requires basic knowledge of classical and quantum mechanics, electrodynamics, as well as basics of mathematics.

Using a simple test below please check if your knowledge is sufficient. Answers can be found either in the Maple file.

A simple test in mathematics

Elementary functions

Problem 1.1: Function is given by the definition

$$f(x) = x^4 + ax^3 + bx^2.$$

(a) Show that by a proper rescaling it can be expressed as

$$f(x) = a^4 \mathcal{F}_\eta(\xi) \quad \text{where} \quad \mathcal{F}_\eta(\xi) = \xi^4 + \xi^3 + \eta\xi^2,$$

$\xi \equiv x/a$, $\eta \equiv b/a^2$. Function $\mathcal{F}_\eta(\xi)$ is very important in theory of phase transitions.

(b) Investigate $\mathcal{F}_\eta(\xi)$.

- How many extrema it has?
- When it has only 1 minimum? When it has 2 minima? At what value of η it has an inflection point?

- Plot $\mathcal{F}_\eta(\xi)$ for this value of η .

Problem 1.2: Logarithmic functions are very important in statistical physics. Check your memory by the following exercises:

- Plot function

$$f_1(x) = \ln \frac{1-x}{1+x} \quad \text{for } |x| \leq 1.$$

Discuss properties of this function at $|x| > 1$.

- Plot function

$$f_2(x) = \ln(\tan \pi x).$$

- Simplify the expression

$$e^{4 \ln x} - (x^2 + 1)^2 + 2x^2 + 1.$$

Problem 1.3: Do you remember trigonometry? Test it!

- Simplify

$$\sin^{-2} x - \tan^{-2} x - 1.$$

- Calculate infinite sums

$$C(\alpha, \beta) = \sum_{n=0}^{\infty} e^{-\alpha n} \cos \beta n, \quad \alpha > 0.$$

$$S(\alpha, \beta) = \sum_{n=0}^{\infty} e^{-\alpha n} \sin \beta n, \quad \alpha > 0.$$

Hint: take into account that $\cos x = \operatorname{Re}(e^{ix})$, $\sin x = \operatorname{Im}(e^{ix})$.

Basic integrals

Problem 1.4: Calculate integrals:

-

$$I_n(\gamma) = \int_0^{\infty} x^n e^{-\gamma x} dx, \quad \gamma > 0.$$

-

$$\int \frac{dx}{x^2 \pm a^2}, \quad \int \frac{dx}{x(1-x)}.$$

-

$$G(\gamma) = \int_0^{\infty} e^{-\gamma x^2/2} dx, \quad \gamma > 0.$$

Chapter 2

Introduction to Thermodynamics

Quick access: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22

Problem 2.1: Test the following differentials for exactness. For those cases in which the differential is exact, find the function $u(x, y)$.

(a) $du_a = \frac{-y dx}{x^2 + y^2} + \frac{x dy}{x^2 + y^2}$.

(b) $du_b = (y - x^2) dx + (x + y^2) dy$.

(c) $du_c = (2y^2 - 3x) dx - 4xy dy$.

Solution 2.1:

(a) The differential is exact, $u_a(x, y) = -\arctan(x/y)$.

Here one point worth discussion. The function $u_a(x, y) = -\arctan(x/y)$ has a singularity at $x = 0, y = 0$. As a result, any close path embedding this point contributes 2π to the variation of the quantity $u(x, y)$. Consequently, this function cannot serve as a thermodynamic potential if both positive and negative values of x and y have physical meaning.

(b) The differential is exact, $u_b(x, y) = yx + (y^3 - x^3)/3$.

(c) The differential is not exact.

The function $u(x, y)$ is reconstructed in the following way. For an exact differential, $du = u_x dx + u_y dy$,

$$u_x = \frac{\partial u(x, y)}{\partial x}, \quad u_y = \frac{\partial u(x, y)}{\partial y}.$$

If we introduce

$$u_1(x, y) = \int_0^x u_x(\xi, y) d\xi,$$

then the difference $f \equiv u(x, y) - u_1(x, y)$ is a function only of y . Consequently,

$$\frac{df}{dy} = \frac{\partial u(x, y)}{\partial y} - \frac{\partial u_1(x, y)}{\partial y} = u_y(x, y) - \int_0^x \frac{\partial u_x(x, y)}{\partial y} dx.$$

As a result,

$$f(y) = \int_0^y d\eta u_y(x, \eta) - \int_0^y \int_0^x d\xi d\eta \frac{\partial u_x(\xi, \eta)}{\partial \eta}.$$

Finally,

$$u(x, y) = \int_0^x d\xi u_x(\xi, y) + \int_0^y d\eta u_y(x, \eta) - \int_0^y \int_0^x d\xi d\eta \frac{\partial u_x(\xi, \eta)}{\partial \eta}.$$

For calculation see the Maple file it1.mws.

Problem 2.2: Consider the two differentials

1. $du_1 = (2xy + x^2) dx + x^2 dy$, and
2. $du_2 = y(x - 2y) dx - x^2 dy$.

For both differentials, find the change $u(x, y)$ between two points, (a, b) and (x, y) . Compute the change in two different ways:

- (a) Integrate along the path $(a, b) \rightarrow (x, b) \rightarrow (x, y)$,
- (b) Integrate along the path $(a, b) \rightarrow (a, y) \rightarrow (x, y)$.

Discuss the meaning of your results.

Solution 2.2: The calculations are shown in the Maple file. In the case (b) the results are different because the differential is not exact.

Problem 2.3: Electromagnetic radiation in an evacuated vessel of volume V at equilibrium with the walls at temperature T (black body radiation) behaves like a gas of photons having internal energy $U = aVT^4$ and pressure $P = (1/3)aT^4$, where a is Stefan's constant.

- (a) Plot the closed curve in the $P - V$ plane for a Carnot cycle using black body radiation.
- (b) Derive *explicitly* the efficiency of Carnot engine which uses black body radiation as its working substance.

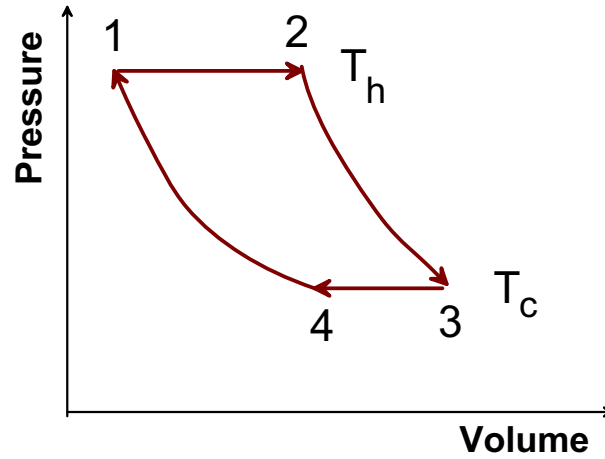


Figure 2.1: On the Carnot cycle with black-body radiation.

Solution 2.3: We will follow example shown in Exercise 2.2. Let us start with *isotherms*. At the isotherms the pressure is V -independent, thus isotherms are *horizontal*, see Fig. 2.1 Along the first isothermal path,

$$\Delta Q_{1 \rightarrow 2} = \Delta U + P\Delta V = (4/3)aT_h^4(V_2 - V_1) = \frac{4}{3}aT_h^4V_1 \left[\frac{V_2}{V_1} - 1 \right]. \quad (2.1)$$

In a similar way,

$$\Delta Q_{3 \rightarrow 4} = \frac{4}{3}aT_c^4V_4 \left[1 - \frac{V_3}{V_4} \right]. \quad (2.2)$$

Now let us consider an adiabatic path. Along an adiabatic path,

$$dQ = 0 = dU + PdV = 4aVT^3 dT + aT^4 dV + (1/3)aT^4 dV = 4aVT^3 dT + (4/3)aT^4 dV.$$

Consequently,

$$\frac{dT}{T} = -\frac{1}{3} \frac{dV}{V} \quad \rightarrow \quad VT^3 = \text{const}, \quad PV^{4/3} = \text{const}.$$

Let us start from the point 2 characterized by the values P_1, V_2 and adiabatically expand the gas to the point 3 characterized by the volume V_3 . We have $V_2T_h^3 = V_3T_c^3$. In a similar way, $V_4T_c^3 = V_1T_h^3$. Combining these equalities, we get:

$$V_2T_h^3 = V_3T_c^3, \quad V_4T_c^3 = V_1T_h^3 \quad \rightarrow \quad \frac{V_2}{V_3} = \frac{V_1}{V_4} = \left(\frac{T_c}{T_h} \right)^3 \quad (2.3)$$

Combining Eqs. (2.1), (2.2) and (2.3), we find

$$\Delta W = \Delta Q_{1 \rightarrow 2} + \Delta Q_{3 \rightarrow 4} = \frac{4}{3}aT_h^4V_1 \left(\frac{V_3}{V_4} - 1 \right) \left(1 - \frac{T_c}{T_h} \right).$$

Remember: along a closed path $\Delta U = 0$ and the total heat consumption is equal to mechanical work.

On the

$$\Delta Q_{1 \rightarrow 2} = \frac{4}{3} a T_h^4 V_1 \left(\frac{V_2}{V_1} - 1 \right).$$

As a result,

$$\eta = \frac{\Delta W}{\Delta Q_{1 \rightarrow 2}} = \frac{T_h - T_c}{T_h}$$

as it should be.

Problem 2.4: A Carnot engine uses a paramagnetic substance as its working substance. The equation of state is

$$M = \frac{nDH}{T}$$

where M is magnetization, H is the magnetic field, n is the number of moles, D is a constant determined by the type of substance, and T is the temperature.

- show that the internal energy U , and therefore the heat capacity C_M , can only depend on the temperature and not the magnetization.
- Let us assume that $C_M = C = \text{constant}$. Sketch a typical Carnot cycle in the $M - H$ plane.
- Compute the total heat absorbed and the total work done by the Carnot engine.
- Compute the efficiency of the Carnot engine.

Solution 2.4:

- By definition [see Eq. [1](2.23)],

$$dU = T dS + \mathbf{H} d\mathbf{M}.$$

Thus at $M = \text{const}$ the internal energy is independent of the magnetization.

- Since $C = \text{const}$, $U_0 = N c_M T$, where c_M is the specific heat per one particle while N is the number of particles. Introducing molar quantities we get $U_0 = n c T$.

A Carnot cycle is shown in Fig. 2.2. We have:

- For an isothermal process at $T = T_c$,

$$Q_{1 \rightarrow 2} = - \int_{H_1}^{H_2} H(M) dM = \frac{T_c}{2nD} (M_1^2 - M_2^2).$$

In a similar way,

$$Q_{3 \rightarrow 4} = \frac{T_h}{2nD} (M_3^2 - M_4^2).$$

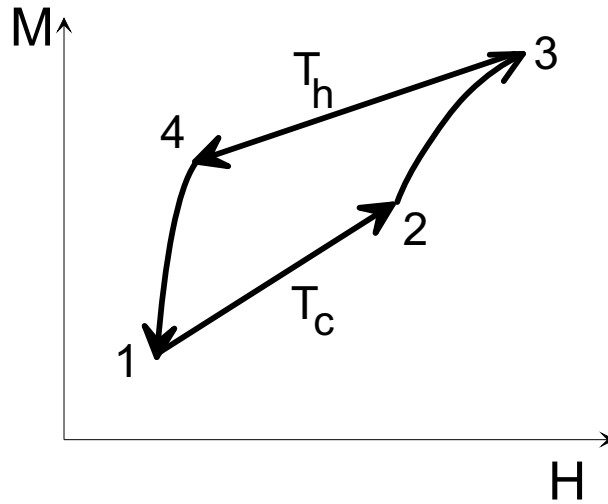


Figure 2.2: Sketch of the Carnot cycle.

The total work is then $W = Q_{1 \rightarrow 2} + Q_{3 \rightarrow 4}$, and the efficiency is

$$\eta = \frac{W}{Q_{3 \rightarrow 4}} = 1 + \frac{T_c M_1^2 - M_2^2}{T_h M_3^2 - M_4^2}.$$

Now let us discuss adiabatic paths. We have at each path,

$$0 = dQ = dU - H dM = nc dT - \frac{MT}{nD} dM.$$

Immediately we get

$$\frac{dT}{T} = \frac{1}{n^2 c D} M dM.$$

Integrating this equality from point 2 to point 3 we obtain,

$$2n^2 c D \ln \frac{T_h}{T_c} = M_3^2 - M_2^2.$$

In a similar way, integrating from 4 to 1 we obtain

$$2n^2 c D \ln \frac{T_c}{T_h} = M_1^2 - M_4^2.$$

As a result,

$$M_3^2 - M_2^2 = M_4^2 - M_1^2 \quad \rightarrow \quad M_3^2 - M_4^2 = -(M_1^2 - M_2^2).$$

(d) Using this expression we obtain the efficiency

$$\eta = \frac{Q_{1 \rightarrow 2} + Q_{3 \rightarrow 4}}{Q_{3 \rightarrow 4}} = \frac{T_h - T_c}{T_h}.$$

Coming back to the item (c) we find

$$W = Q_{3 \rightarrow 4} \eta = \frac{M_3^2 - M_4^2}{2nD} \frac{T_h - T_c}{T_h^2}.$$

Problem 2.5: Find the efficiency of the engine shown in Fig. 2.3 ([1] -Fig.2.18). Assume that

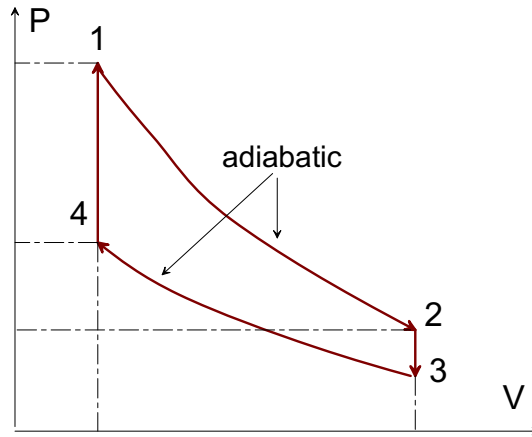


Figure 2.3: Sketch of the cycle.

the operating substance is an ideal monoatomic gas. Express your answer in terms of V_1 and V_2 . (The processes $1 \rightarrow 2$ and $3 \rightarrow 4$ are adiabatic. The processes $4 \rightarrow 1$ and $2 \rightarrow 3$ occur at constant volume).

v

Solution 2.5: Let us start with the processes at constant volume. The mechanical work during these processes does not take place. Consequently,

$$\begin{aligned} Q_{2 \rightarrow 3} &= (3/2)nR(T_3 - T_2), \\ Q_{4 \rightarrow 1} &= (3/2)nR(T_1 - T_4), \\ W &= (3/2)nR(T_1 + T_3 - T_2 - T_4). \end{aligned}$$

The efficiency is given by the expression

$$\eta = \frac{T_1 + T_3 - T_2 - T_4}{T_1 - T_4} = 1 - \frac{T_2 - T_3}{T_1 - T_4}. \quad (2.4)$$

Now let us consider the adiabatic processes where $TV^{2/3} = \text{const}$ (monoatomic ideal gas!). Thus,

$$\frac{T_1}{T_2} = \frac{T_4}{T_3} = \left(\frac{V_2}{V_1} \right)^{2/3} \equiv \alpha.$$

Substituting this expression into Eq. (2.4) we obtain:

$$\eta = 1 - \frac{1}{\alpha} = 1 - \left(\frac{V_1}{V_2}\right)^{2/3}.$$

Problem 2.6: One kilogram of water is compressed isothermally at 20° C from 1 atm to 20 atm.

- (a) How much work is required?
- (b) How much heat is rejected?

Assume that the average isothermal compressibility of water during this process is $\kappa_T = 0.5 \times 10^{-4} \text{ (atm)}^{-1}$ and the average thermal expansivity of water during this process is $\alpha_P = 2 \times 10^{-4} \text{ (}^\circ\text{C)}^{-1}$.

Solution 2.6: Since for an isothermal process $dQ = T dS$ we have

$$Q = T \int_{P_1}^{P_2} \left(\frac{\partial S}{\partial P}\right)_T dP.$$

Using the Maxwell relation for the Gibbs free [see Eq. [1]-(2.112)] energy we obtain

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha_P.$$

Thus

$$Q = -T \int_{P_1}^{P_2} V(P)\alpha_T(P) dP$$

Now let us assume that α_T is P -independent, and

$$V(P) = V_0[1 - \kappa_T(P - P_0)] = (M/\rho)[1 - \kappa_T(P - P_0)].$$

As a result,

$$Q = -(M/\rho)T\alpha_T(P_2 - P_1)[1 - \kappa_T(P - P_0)/2].$$

We see that since the compressibility of water is very low one can neglect the correction due to change in the volume and assume $V \approx M/\rho$. The mechanical work is

$$W = -\int_{P_1}^{P_2} P dV = -\int_{P_1}^{P_2} P \left(\frac{\partial V}{\partial P}\right)_T dP = (M/2\rho)\kappa_T(P_2^2 - P_1^2).$$

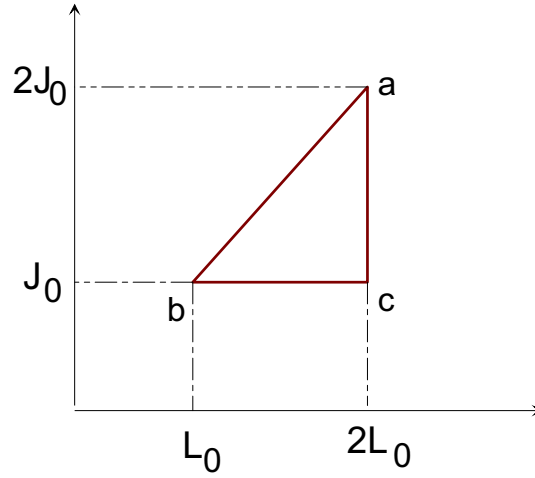


Figure 2.4:

Problem 2.7: Compute the efficiency of the heat engine shown in Fig. 2.4 (Fig. [1]-2.19). The engine uses a rubber band whose equation of state is

$$J = \alpha LT, \quad (2.5)$$

where α is a constant, J is the tension, L is the length per unit mass, and T is the temperature in Kelvins. The specific heat (heat capacity per unit mass) is a constant, $c_L = c$.

Solution 2.7: From Fig. 2.4 we see that the path $a \rightarrow b$ is *isothermal*. Indeed, since $J \propto L$, it follows from Eq. (2.5) that $T = \text{const}$. Then, from the same equation we get,

$$T_a = T_b = J_0/\alpha L_0, \quad T_c = J_0/2\alpha L_0 = T_a/2.$$

As a result,

$$Q_{b \rightarrow a} = M\alpha T_a \int_{L_0}^{2L_0} L dL = (3/2)M\alpha L_0^2 T_a = (3/2)MJ_0 L_0,$$

$$Q_{a \rightarrow c} = Mc(T_c - T_a) = -(1/2)McT_a,$$

$$Q_{c \rightarrow b} = Mc(T_b - T_c) - MJ_0 L_0 = (1/2)McT_a - MJ_0 L_0.$$

Hence, the total work is

$$W = Q_{b \rightarrow a} + Q_{a \rightarrow c} + Q_{c \rightarrow b} = (1/2)MJ_0 L_0$$

and

$$\eta = \frac{W}{Q_{b \rightarrow a}} = \frac{1}{3}.$$

This result is also clear from geometrical point of view.

Problem 2.8: Experimentally one finds that for a rubber band

$$\left(\frac{\partial J}{\partial L}\right)_T = \frac{aT}{L_0} \left[1 + 2\left(\frac{L_0}{L}\right)^3\right],$$

$$\left(\frac{\partial J}{\partial T}\right)_L = \frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L}\right)^3\right],$$

where J is the tension, $a = 1.0 \times 10^3$ dyne/K, and $L_0 = 0.5$ m is the length of the band when no tension is applied. The mass of the rubber band is held fixed.

- Compute $(\partial L/\partial T)_J$ and discuss its physical meaning.
- Find the equation of state and show that dJ is an exact differential.
- Assume that heat capacity at constant length is $C_L = 1.0$ J/K. Find the work necessary to stretch the band reversibly and adiabatically to a length 1 m. Assume that when no tension is applied, the temperature of the band is $T = 290$ K. What is the change in temperature?

Solution 2.8:

- We have

$$\left(\frac{\partial L}{\partial T}\right)_J \cdot \left(\frac{\partial T}{\partial J}\right)_L \cdot \left(\frac{\partial J}{\partial L}\right)_T = -1.$$

Consequently,

$$\left(\frac{\partial L}{\partial T}\right)_J = - \left[\left(\frac{\partial T}{\partial J}\right)_L \cdot \left(\frac{\partial J}{\partial L}\right)_T \right]^{-1} = - \frac{\left(\frac{\partial J}{\partial T}\right)_L}{\left(\frac{\partial J}{\partial L}\right)_T} = - \frac{L}{T} \frac{1 - \left(\frac{L_0}{L}\right)^3}{1 + 2\left(\frac{L_0}{L}\right)^3}.$$

Physical meaning -

$$\alpha_J = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_J$$

is the thermal expansion coefficient at given tension.

- The equation of state has the form

$$J = \frac{aTL}{L_0} \left[1 - \left(\frac{L_0}{L}\right)^3\right].$$

The proof of the exactness is straightforward.

(c) Consider adiabatic expansion of the band,

$$0 = dQ = C_L dT + J(L, T) dL.$$

Consequently,

$$\frac{dT}{dL} = -\frac{J(L, T)}{C_L} = -\frac{aTL}{C_L L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right].$$

Measuring length in units of L_0 as $L = \ell \cdot L_0$ and introducing $\beta \equiv aL_0/C_L$ we obtain the following differential equation

$$dT/T = -\beta \ell (1 - \ell^{-3}) d\ell.$$

Its solution is

$$\ln \frac{T_f}{T_0} = -\frac{\beta}{2} \left(\frac{L_f}{L_0} \right)^2 \left[1 + 2 \left(\frac{L_0}{L_f} \right)^3 \right].$$

Here L_f and T_f are final values of the length and temperature, respectively. This is the equation for adiabatic process which provides the change in the temperature. The mechanical work is then

$$W = C_L(T_f - T_0).$$

Problem 2.9: Blackbody radiation in a box of volume V and at temperature T has internal energy $U = aVT^4$ and pressure $P = (1/3)aT^4$, where a is the Stefan-Boltzmann constant.

- (a) What is the fundamental equation for the blackbody radiation (the entropy)?
- (b) Compute the chemical potential.

Solution 2.9:

- (a) Let us first find the Helmholtz free energy. From the relation $P = -\left(\frac{\partial A}{\partial V}\right)_T$ we get

$$A = -PV = -\frac{1}{3}aVT^4 = -\frac{1}{3}U.$$

Consequently,

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = \frac{4}{3}aVT^3 = \frac{4}{3}\frac{U}{T}.$$

As a result,

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{\partial(S, V)}{\partial(U, V)} = \frac{\partial(S, V)/\partial(T, V)}{\partial(U, V)/\partial(T, V)} = \frac{(\partial S/\partial T)_V}{(\partial U/\partial T)_V} = \frac{1}{T}.$$

- (b) Since A is N -independent, $\mu = 0$.

Problem 2.10: Two vessels, insulated from the outside world, one of volume V_1 and the other of volume V_2 , contain equal numbers N of the same ideal gas. The gas in each vessel is originally at temperature T_i . The vessels are then connected and allowed to reach equilibrium in such a way that the combined vessel is also insulated from the outside world. The final volume is $V = V_1 + V_2$. What is the maximum work, δW_{free} , that can be obtained by connecting these insulated vessels? Express your answer in terms of T_i , V_1 , V_2 , and N .

Solution 2.10: The Gibbs free energy of an ideal gas is given by the equation

$$G = NkT \ln P + N\chi(T)$$

where $\chi(T)$ is some function of the gas excitation spectrum.¹

Consequently,

$$S = - \left(\frac{\partial G}{\partial T} \right)_P = -Nk \ln P - N\chi'(T).$$

Before the vessels are connected,

$$S_i = -Nk \ln(P_1 P_2) - 2N\chi'(T).$$

After the vessels are connected the temperature remains the same, as it follows from the conservation law, the entropy being

$$S_f = -2Nk \ln P - 2N\chi'(T).$$

Consequently, $\Delta S = -Nk \ln(P^2/P_1 P_2)$. On the other hand,

$$\frac{1}{P} = \frac{V_1 + V_2}{2NkT_i}, \quad \frac{1}{P_i} = \frac{V_i}{NkT_i} \quad \rightarrow \quad \frac{P^2}{P_1 P_2} = \frac{4V_1 V_2}{(V_1 + V_2)^2}.$$

¹ For an ideal gas, the energy of the particle can be written as a sum of the kinetic energy, $\epsilon_{\mathbf{p}} = \mathbf{p}^2/2m$, and the energy of internal excitations, ϵ_{α} (characterized by some quantum numbers α),

$$\epsilon_{\mathbf{p}\alpha} = \epsilon_{\mathbf{p}} + \epsilon_{\alpha}.$$

As we will see later, the free energy of the ideal gas can be constructed as

$$\begin{aligned} A &= -\frac{kT}{N!} \ln \left(\sum_{\mathbf{p}\alpha} e^{-\epsilon_{\mathbf{p}\alpha}/kT} \right)^N \approx -NkT \ln \left[\frac{eV}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \sum_{\alpha} e^{-\epsilon_{\alpha}/kT} \right] \\ &= -NT \ln(eV/N) + Nf(T), \\ f(T) &= -kT \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \sum_{\alpha} e^{-\epsilon_{\alpha}/kT} \right]. \end{aligned}$$

The Gibbs free energy is then

$$G = A + PV = NkT \ln P + N\chi(T), \quad \chi(T) \equiv f(T) - kT \ln kT.$$

As a result, the maximum work is

$$\Delta W_{free} = T_i \Delta S = NkT_i \ln \frac{(V_1 + V_2)^2}{4V_1V_2}.$$

Problem 2.11: For a low-density gas the virial expansion can be terminated at first order in the density and the equation of state is

$$P = \frac{NkT}{V} \left[1 + \frac{N}{V} B_2(T) \right],$$

where $B_2(T)$ is the second virial coefficient. The heat capacity will have corrections to its ideal gas value. We can write it in the form

$$C_{V,N} = \frac{3}{2}Nk - \frac{N^2k}{V} f(T).$$

- (a) Find the form that $f(T)$ must have in order for the two equations to be thermodynamically consistent.
- (b) Find $C_{P,N}$.
- (c) Find the entropy and internal energy.

Solution 2.11:

- (c) The equation of state under consideration can be obtained from the Helmholtz free energy²

$$A = A_{ideal} + kTB_2(T) \frac{N^2}{V}.$$

Then

$$S = - \left(\frac{\partial A}{\partial T} \right)_V = S_{ideal} + \delta S, \quad \delta S \equiv -k \frac{N^2}{V} [B_2(T) + TB_2'(T)].$$

Since we know both entropy and Helmholtz free energy, we find the internal energy as

$$\begin{aligned} U &= A + TS = U_{ideal} + kTB_2(T) \frac{N^2}{V} - kT \frac{N^2}{V} [B_2(T) + TB_2'(T)] \\ &= U_{ideal} + \delta U, \quad \delta U \equiv -kT^2 B_2'(T) \frac{N^2}{V}. \end{aligned}$$

²Remember that $P = - \left(\frac{\partial A}{\partial V} \right)_T$.

(a) As a result,

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = C_V^{\text{ideal}} + \delta C_V, \quad \delta C_V \equiv -kT \frac{N^2}{V} [2B_2'(T) + TB_2''(T)].$$

We find in this way,

$$f(T) = 2TB_2'(T) + T^2B_2''(T).$$

(b) Let us express the equation of state as $V(P, T)$. Since the density is assumed to be small in the correction one can use equation for the ideal gas to find the the volume. We have,

$$V = \frac{NkT}{P} + NB_2(T).$$

Consequently, the entropy can be expressed as

$$S = S_{\text{ideal}} + \delta S_1, \quad \delta S_1 \equiv -kN \frac{B_2 + TB_2'}{kT/P + B_2}.$$

Now

$$\begin{aligned} C_P &= C_P^{\text{ideal}} + T \left(\frac{\partial \delta S_1}{\partial T} \right)_P \\ &= -kN \frac{(B_2 + TB_2)'(kT/P + B_2) - (k/P + B_2')(B_2 + TB_2')}{(kT/P + B_2)^2} \\ &= C_P^{\text{ideal}} - k \frac{N^2}{V} [T(2B_2' + TB_2'') - (B_2 + TB_2')] \\ &= C_P^{\text{ideal}} + \delta C_V + k \frac{N^2}{V} (B_2 + TB_2'). \end{aligned}$$

Here in all corrections we used equation of state for an ideal gas. As a result,

$$C_P - C_V = (C_P - C_V)^{\text{ideal}} + k \frac{N^2}{V} (B_2 + TB_2').$$

Problem 2.12: Prove that

$$C_{Y,N} = \left(\frac{\partial H}{\partial T} \right)_{Y,N} \quad \text{and} \quad \left(\frac{\partial H}{\partial Y} \right)_{T,N} = T \left(\frac{\partial X}{\partial T} \right)_{Y,N} - X.$$

Solution 2.12: Let us first recall definitions for X , Eq. ([1]-2.66), $U = ST + YX + \sum_J j\mu'_j dN_j$. The enthalpy is defined as

$$H = U - XY = ST + \sum_J \mu'_j dN_j.$$

Since $dU = T dS + Y dX$ we get

$$dH = T dS - X dY.$$

Consequently,

$$C_{Y,N} = T \left(\frac{\partial S}{\partial T} \right)_{Y,N} = \left(\frac{\partial H}{\partial T} \right)_{Y,N}.$$

To prove the second relation we do the following

$$\left(\frac{\partial H}{\partial Y} \right)_{T,N} = \left(\frac{\partial H}{\partial Y} \right)_{S,N} + \left(\frac{\partial H}{\partial S} \right)_{Y,N} \left(\frac{\partial S}{\partial Y} \right)_T.$$

Now,

$$\left(\frac{\partial H}{\partial Y} \right)_{S,N} = -X, \quad \left(\frac{\partial H}{\partial S} \right)_{Y,N} = T.$$

Now we have to use the Maxwell relation, which emerges for the *Gibbs* free energy $G = H - TS$. From

$$dG = -S dT - X dY$$

we get

$$\left(\frac{\partial S}{\partial Y} \right)_T = \left(\frac{\partial X}{\partial T} \right)_{Y,N}.$$

Thus we obtain the desired result.

Problem 2.13: Compute the entropy, enthalpy, Helmholtz free energy, and Gibbs free energy for a paramagnetic substance and write them explicitly in terms of their natural variables if possible. Assume that mechanical equation of state is $m = (D/T)H$ and the the molar heat capacity at constant magnetization is $c_m = c$, where m is the molar magnetization, H is the magnetic field, D is a constant, c is a constant, and T is the temperature.

Solution 2.13: Let us start with the internal energy $u(T, m)$ per one mole. We have the magnetic contribution $u_{\text{mag}} = \int_0^m H(m) dm$. Since $H(m) = (T/D)m$ we get $u_{\text{mag}} = (T/2D)m^2$. The “thermal” contribution is cT . As a result,

$$u(T, m) = T(c + m^2/2D), \quad T(u, m) = \frac{u}{c + m^2/2D}.$$

The molar entropy s is then derived from the definition

$$\left(\frac{\partial s}{\partial u} \right)_m = \frac{1}{T} = \frac{c + m^2/2D}{u} \quad \rightarrow \quad s(u, m) = (c + m^2/2D) \ln(u/u_0).$$

Here u_0 is a constant. As a result, in “natural” variables

$$u(s, m) = u_0 \exp\left(\frac{s}{c + m^2/2D}\right).$$

To find other thermodynamic potentials we need $s(T, m)$. We can rewrite the above expression for the entropy as

$$s(T, m) = (c + m^2/2D) \ln \frac{T(c + m^2/2D)}{u_0}.$$

In particular, the Helmholtz free energy is

$$a(T, m) = u - Ts = T(c + m^2/2D) \left[1 - \ln \frac{T(c + m^2/2D)}{u_0}\right].$$

To get enthalpy we have to subtract from u the quantity $Hm = (D/T)H^2$ and to express m through H as $m = (D/T)H$. As a result, we obtain:

$$h(T, H) = u - Hm = T(c + DH^2/2T^2) - (D/T)H^2 = T(c - DH^2/2T^2).$$

Finally, Gibbs free energy is $g = a - Hm$, which has to be expressed through T and H . We get

$$\begin{aligned} g &= a - Hm = T(c + DH^2/2T^2) \left[1 - \ln \frac{T(c + DH^2/2T^2)}{u_0}\right] - (D/T)H^2 \\ &= T(c - DH^2/2T^2) - T(c + DH^2/2T^2) \ln \frac{T(c + DH^2/2T^2)}{u_0}. \end{aligned}$$

Problem 2.14: Compute the Helmholtz free energy for a van der Waals gas. The equation of state is

$$\left(P + \alpha \frac{n^2}{V^2}\right)(V - nb) = nRT,$$

where α and b are constants which depend on the type of gas and n is the number of moles. Assume that heat capacity is $C_{V,n} = (3/2)nR$.

Is this a reasonable choice for the heat capacity? Should it depend on volume?

Solution 2.14: Let us express pressure through the volume,

$$P = \frac{nRT}{V - nb} - \frac{\alpha n^2}{V^2}.$$

Since $P = -\partial A/\partial V$ we obtain

$$A = - \int P(V) dV = -nRT \ln(V - nb) - (\alpha n^2/V) + \mathcal{A}(T).$$

Here $\mathcal{A}(T)$ is the integration constant, which can be found from the given specific heat. Indeed,

$$S = \int^T \frac{C_{V,n} dT'}{T'} = (3/2)nR \ln(T/T_0).$$

Consequently,

$$\mathcal{A}(T) = - \int^T S(T') dT' = (3/2)nRT[1 - \ln(T/T_0)].$$

Here we omit temperature-independent constant.

The suggestion regarding specific heat is OK since the difference between the entropies of van der Waals gas and the ideal gas is *temperature independent*. (Check!)

Problem 2.15: Prove that

(a) $\kappa_T(C_P - C_V) = TV\alpha_P^2$

(b) $C_P/C_V = \kappa_T/\kappa_S$.

Solution 2.15: We use the method of Jacobians:

(a)

$$\begin{aligned} C_V &= T(\partial S/\partial T)_V = T\partial(S, V)/\partial(T, V) = \frac{\partial(S, V)/\partial(T, P)}{\partial(T, V)/\partial(T, P)} \\ &= T \frac{(\partial S/\partial T)_P (\partial V/\partial P)_T - (\partial S/\partial P)_T (\partial V/\partial T)_P}{(\partial V/\partial P)_T} \\ &= C_P - T \frac{(\partial S/\partial P)_T (\partial V/\partial T)_P}{(\partial V/\partial P)_T}. \end{aligned}$$

Now, from the Maxwell relations $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$. Thus,

$$C_P - C_V = -T \frac{[(\partial V/\partial T)_P]^2}{(\partial V/\partial P)_T} = TV \frac{\alpha_P^2}{\kappa_T}.$$

The first relation follows from this in a straightforward way from definitions.

(b) Let us first calculate the adiabatic compressibility $(\partial V/\partial P)_S$ as

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{\partial(V, S)}{\partial(P, S)} = \frac{\partial(V, S)/\partial(V, T)}{\partial(P, S)/\partial(P, T)} \cdot \frac{\partial(V, T)}{\partial(P, T)} = \frac{(\partial S/\partial T)_V}{(\partial S/\partial T)_P} \cdot \left(\frac{\partial V}{\partial P}\right)_T.$$

Consequently,

$$\frac{C_P}{C_V} = \frac{(\partial V/\partial P)_T}{(\partial V/\partial P)_S} = \frac{\kappa_T}{\kappa_S}.$$

Problem 2.16: Show that

$$T ds = c_x (\partial T / \partial Y)_x dY + c_Y (\partial T / \partial x)_Y dx,$$

where $x = X/n$ is the amount of extensive variable, X , per mole, c_x is the heat capacity per mole at constant x , and c_Y is the heat capacity per mole at constant Y .

Solution 2.16: Let us substitute the definitions

$$c_x = T (\partial S / \partial T)_x, \quad c_Y = T (\partial S / \partial T)_Y.$$

Now the combination $c_x (\partial T / \partial Y)_x dY + c_Y (\partial T / \partial x)_Y dx$ can be rewritten as

$$\begin{aligned} T (\partial S / \partial T)_x (\partial T / \partial Y)_x dY + T (\partial S / \partial T)_Y (\partial T / \partial x)_Y dx \\ = T (\partial S / \partial Y)_x dY + T (\partial S / \partial x)_Y dx = T ds. \end{aligned}$$

Problem 2.17: Compute the molar heat capacity c_P , the compressibilities, κ_T and κ_S , and the thermal expansivity α_P of a monoatomic van der Waals gas. Start from the fact that the mechanical equation of state is

$$P = \frac{RT}{v-b} - \frac{\alpha}{v^2}.$$

and the molar heat capacity is $c_v = 3R/2$, where $v = V/n$ is the molar volume.

Solution 2.17: Let us start with the specific heat. Using the method similar to the Problem 2.15 we can derive the relation

$$c_P - c_v = -T \frac{[(\partial P / \partial T)_v]^2}{(\partial P / \partial v)_T} = \frac{R}{1 - 2\alpha(v-b)^2 / RTv^3}.$$

Now let us compute the compressibility

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = -\frac{1}{v} \left(\frac{\partial P}{\partial v} \right)_T^{-1} = \frac{(v-b)^2}{vRT} \frac{1}{1 - 2\alpha(v-b)^2 / RTv^3}.$$

Given c_v , other quantities can be calculated using results of the Problem 2.15.

Problem 2.18: Compute the heat capacity at constant magnetic field $C_{H,n}$, the susceptibilities $\chi_{T,n}$ and $\chi_{S,n}$, and the thermal expansivity $\alpha_{H,n}$ for a magnetic system, given that the mechanical equation of state is $M = nDH/T$ and the heat capacity $C_{M,n} = nc$, where M is the magnetization, H is the magnetic field, n is the number of moles, c is the molar heat capacity, and T is the temperature.

Solution 2.18: Let us start with susceptibilities. By definition,

$$\chi_{T,n} = \left(\frac{\partial M}{\partial H} \right)_{T,n} = \frac{nD}{T}.$$

Now,

$$\left(\frac{\partial M}{\partial H} \right)_S = \frac{\partial(M,S)}{\partial(H,S)} = \frac{\partial(M,S)/\partial(M,T)}{\partial(H,S)/\partial(H,T)} \cdot \frac{\partial(M,T)}{\partial(H,T)} = \chi_{T,n} \frac{C_{M,n}}{C_{H,n}}.$$

Thus we have found one relation between susceptibilities and heat capacities,

$$\frac{\chi_{S,n}}{\chi_{T,n}} = \frac{C_{M,n}}{C_{H,n}}.$$

Now let us find $C_{H,n}$. At constant H , M becomes dependent only on temperature. Then,

$$dM = \frac{dM}{dT} dT = -\frac{nDH}{T^2} dT.$$

Consequently, the contribution to the internal energy is

$$dU = -H dM = \frac{nDH^2}{T^2} dT.$$

As a result,

$$C_{H,n} - C_{M,n} = \frac{nDH^2}{T^2}.$$

Given $C_{H,n} = nc$ we easily compute $C_{M,n}$ and $\chi_{S,n}$.

According to Eq. (R2.149), α_H is defined as

$$\alpha_H = \left(\frac{\partial M}{\partial T} \right)_H = -\frac{nDH}{T^2}.$$

Problem 2.19: A material is found to have a thermal expansivity $\alpha_P = v^{-1}(R/P + a/RT^2)$ and an isothermal compressibility $\kappa_T = v^{-1}[Tf(P) + b/P]$. Here $v = V/n$ is the molar volume.

- Find $f(P)$.
- Find the equation of state.
- Under what condition this materials is stable?

Solution 2.19:

(a) By definition, we have

$$\begin{aligned}\frac{\partial v}{\partial T} &= \frac{R}{P} + \frac{a}{RT^2} \\ \frac{\partial v}{\partial P} &= -Tf(P) - \frac{b}{P}.\end{aligned}$$

To make dv an exact differential we need:

$$-\frac{R}{P^2} = -f(p).$$

Thus

$$f(p) = R/P^2.$$

(b) We can reconstruct the equation of state as:

$$\begin{aligned}v &= \int^P \frac{\partial v}{\partial P} dP = \int^P dP \left[-\frac{RT}{P^2} - \frac{b}{P} \right] \\ &= \frac{RT}{P} - b \ln P + g(T).\end{aligned}$$

Here $g(T)$ is some function of the temperature. Now,

$$\frac{\partial v}{\partial T} = \frac{R}{P} + g'(T) \equiv \frac{R}{P} + \frac{a}{RT^2}.$$

Thus $g(T) = -a/RT + \text{const}$. As a result, we can express the equation of state as

$$v - v_0 = \frac{RT}{P} + b \ln \frac{P_0}{P} - \frac{a}{RT}.$$

(c) Since the compressibility must be positive, we have the stability condition

$$Tf(P) + \frac{b}{P} > 0 \quad \rightarrow \quad \frac{TR}{P^2} + \frac{b}{P} > 0.$$

Consequently, the stability condition is

$$P/T < R/b.$$

Problem 2.20: Compute the efficiency of the reversible two heat engines in Fig. 2.5 (R2.20). Which engine is the most effective? (Note that these are not Carnot cycles. The efficiency of a heat engine is $\eta = \Delta W_{total} / \Delta Q_{absorbed}$.)

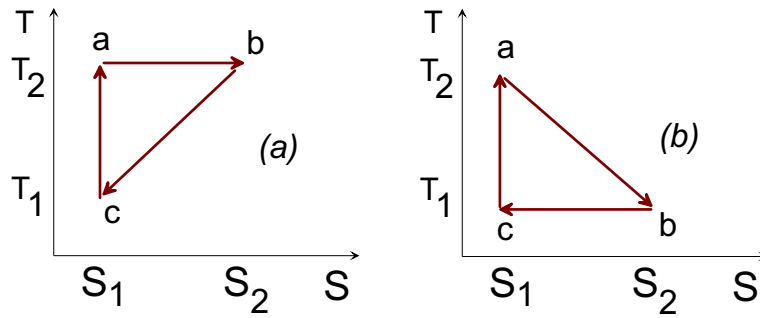


Figure 2.5:

Solution 2.20: Since $dQ = T dS$, we immediately get for any closed path in the $T - S$ plane:

$$\Delta W_{total} = \oint T dS.$$

This is just the area of the triangle,

$$\Delta W_{total} = (1/2)(T_2 - T_1)(S_2 - S_1).$$

The heat absorbed in the case (a) is

$$\Delta Q_{absorbed} = T_2(S_2 - S_1).$$

Thus,

$$\eta_a = \frac{T_2 - T_1}{2T_2}.$$

In the case (b), it easy to show that

$$\Delta Q_{absorbed} = (1/2)(T_2 + T_1)(S_2 - S_1).$$

Thus

$$\eta_b = \frac{T_2 - T_1}{T_2 + T_1} > \eta_a.$$

Problem 2.21: It is found for a gas that $\kappa_T = Tvf(P)$ and $\alpha_P = Rv/P + Av/T^2$, where T is the temperature, v is the molar volume, P is the pressure, A is a constant, and $f(P)$ is unknown function.

- (a) What is $f(P)$?
- (b) Find $v = v(P, T)$.

Solution 2.21: The solution is similar to the problem 2.19. We have:

$$\begin{aligned}\frac{\partial v}{\partial T} &= v^2 \left(\frac{R}{P} + \frac{A}{T^2} \right), \\ \frac{\partial v}{\partial P} &= -v^2 T f(P).\end{aligned}$$

Let us introduce $\gamma(P, T) \equiv [v(P, T)]^{-1}$. We get,

$$\begin{aligned}\frac{\partial \gamma}{\partial T} &= -\frac{R}{P} - \frac{A}{T^2}, \\ \frac{\partial \gamma}{\partial P} &= T f(P).\end{aligned}$$

Again, from the Maxwell relation we get $\frac{R}{P^2} = f(P)$. Then we can express γ as

$$\gamma = \int^P \frac{\partial \gamma}{\partial P} dP = TR \int^P \frac{dP}{P^2} = -\frac{RT}{P} + g(T).$$

Then, $g'(T) = -A/T^2$, or $g(T) = A/T + \text{const}$. As a result,

$$\gamma = \gamma_0 + \frac{A}{T} - \frac{RT}{P}.$$

Consequently,

$$v(P, T) = \frac{1}{\gamma_0 + A/T - RT/P}.$$

Problem 2.22: A monomolecular liquid at volume V_L and pressure P_L is separated from a gas of the same substance by a rigid wall which is permeable to the molecules, but does not allow liquid to pass. The volume of the gas is held fixed at V_G , but the volume of the liquid can be varied by moving a piston. If the pressure of the liquid is increased by pushing in on the piston, by how much does the pressure of the gas change? [Assume the liquid is incompressible (its *molar volume* is independent of the pressure) and describe the gas by the ideal gas equation of state. The entire process occurs at fixed temperature T].

Solution 2.22: Let us consider the part of the system, which contains both liquid and gas particles. In this part the chemical potentials must be equal, $\mu_L = \mu_G$. On the other hand, the chemical potentials and pressures of gas in both parts must be equal. Thus we arrive at the equation,

$$\mu_L(P_L, T) = \mu_G(P_G, T).$$

If one changes the pressure of liquid by δP_L , then

$$\left(\frac{\partial \mu_L}{\partial P_L} \right)_T \delta P_L = \left(\frac{\partial \mu_G}{\partial P_G} \right)_T \delta P_G.$$

For an ideal gas, $(\partial\mu/\partial P)_T = kT/P_G = V_G/N_G \equiv \tilde{v}_L$. the quantity \tilde{v}_L has a physical meaning of the *volume per particle*. For a liquid, the relation is the same,

$$\left(\frac{\partial\mu}{\partial P}\right)_T = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial N}\right)_{P,T} = \frac{\partial}{\partial N} \left(\frac{\partial G}{\partial P}\right)_{N,T} = \left(\frac{\partial V}{\partial N}\right)_T = \tilde{v}_L.$$

The last relation is a consequence of *incompressible* character of the liquid. As a result,

$$\frac{\delta P_G}{\delta P_L} = \frac{\tilde{v}_L}{\tilde{v}_G}.$$

2.1 Additional Problems: Fluctuations

Quick access: 23 24 25 26 27

Problem 2.23: Find the mean square fluctuation of the internal energy (using V and T as independent variables). What is the mean square fluctuation of the internal energy for a monoatomic ideal gas?

Solution 2.23: We have

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_T \Delta V + \left(\frac{\partial U}{\partial T}\right)_V \Delta T = \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] \Delta V + C_V \Delta T.$$

Here we use Maxwell relation which can be obtained from Helmholtz free energy. Squaring and averaging we obtain (note that $\langle \Delta V \Delta T \rangle = 0$)

$$\langle (\Delta U)^2 \rangle = \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right]^2 \langle (\Delta V)^2 \rangle + C_V^2 \langle (\Delta T)^2 \rangle.$$

Now,

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

Thus

$$\langle (\Delta U)^2 \rangle = -kT \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right]^2 \left(\frac{\partial V}{\partial P}\right)_T + C_V kT^2.$$

For the ideal gas,

$$P = NkT/V, \quad C_V = (3/2)Nk.$$

Thus,

$$\langle (\Delta U)^2 \rangle = (3/2)N(kT)^2.$$

Problem 2.24: Find $\langle \Delta T \Delta P \rangle$ (with variables V and T) in general case and for a monoatomic ideal gas.

Solution 2.24: We have

$$\Delta P = \left(\frac{\partial P}{\partial V} \right)_T \Delta V + \left(\frac{\partial P}{\partial T} \right)_V \Delta T.$$

Squaring and averaging we obtain (note that $\langle \Delta V \Delta T \rangle = 0$)

$$\langle \Delta T \Delta P \rangle = \left(\frac{\partial P}{\partial T} \right)_V \langle (\Delta T)^2 \rangle = \left(\frac{kT^2}{C_V} \right) \left(\frac{\partial P}{\partial T} \right)_V.$$

For an ideal gas,

$$\langle \Delta T \Delta P \rangle = \frac{2}{3} \frac{kT^2}{V}.$$

Problem 2.25: Find $\langle \Delta V \Delta P \rangle$ with variable (V and T).

Solution 2.25: Using results of the previous problem we get

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

Problem 2.26: Using the same method show that

$$\langle \Delta S \Delta V \rangle = kT \left(\frac{\partial V}{\partial T} \right)_P, \quad \langle \Delta S \Delta T \rangle = kT.$$

Solution 2.26: Straightforward.

Problem 2.27: Find a mean square fluctuation deviation of a simple pendulum with the length ℓ suspended vertically.

Solution 2.27: Let m be the pendulum mass, and ϕ is the angle of deviation from the vertical. The minimal work is just the mechanical work done against the gravity force. For small ϕ ,

$$W_{\min} = mg \cdot \ell (1 - \cos \phi) \approx mg\ell\phi^2/2.$$

Thus,

$$\langle \phi^2 \rangle = kT/mg\ell.$$

2.2 Mini-tests

2.2.1 A

The Helmholtz free energy of the gas is given by the expression

$$A = N\epsilon_0 - NkT \ln(eV/N) - NcT \ln T - N\zeta T.$$

Here $e = 2.718\dots$ is the base of natural logarithms, N is the number of particles, V is the volume, T is the temperature in the energy units, while ϵ_0 , c and ζ are constants.

- Find the entropy as function of V and T .
- Find internal energy U as a function of the temperature T and number of particles N .
- Show that c is the heat capacity per particle at given volume, c_v .
- Find equation of state.
- Find Gibbs free energy, enthalpy. Find the entropy as a function of P and T .
- Using these expression find the heat capacity at constant pressure, c_p .
- Show that for an adiabatic process

$$T^\gamma P^{1-\gamma} = \text{constant}, \text{ where } \gamma = c_p/c_v.$$

Solution

By definition,

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V,N} = N \ln \frac{eV}{N} + Nc(1 + \ln T) + N\zeta T.$$

Now,

$$\begin{aligned} U &= A + TS = N\epsilon_0 + NcT, \\ P &= - \left(\frac{\partial A}{\partial V} \right)_{T,N} = \frac{NT}{V}, \\ G &= A + PV = A + NT = N\epsilon_0 - NT \ln \frac{V}{N} - NcT \ln T + N\zeta T \\ &= N\epsilon_0 + NT \ln P - NT(1+c) \ln T - N\zeta T, \\ W &= U + PV = U + NT = N\epsilon_0 + N(c+1)T, \\ S &= -N \ln P + N(1+c) \ln T + N(\zeta + 1 + c), \\ c_p &= T \left(\frac{\partial S}{\partial T} \right)_{P,N} = 1 + c. \end{aligned}$$

Immediately, to keep entropy constant we get

$$-N \ln P + N c_P \ln T = \text{const} \quad \rightarrow \quad T^{c_P} / P = \text{const}.$$

Since $c_P - c_V = c_P - c = 1$, we obtain

$$T^{c_P} P^{c_P - c_V} = \text{const}, \quad \rightarrow \quad T^\gamma P^{1-\gamma} = \text{const}.$$

2.2.2 B

Problem 1

Discuss entropy variation for

- (a) adiabatic process,
- (b) isothermic process,
- (c) isochoric process,
- (d) isobaric process.

Problem 2

- (a) Discuss the difference between Gibbs and Helmholtz free energy.
- (b) Prove the relation

$$U = -T^2 \left(\frac{\partial A}{\partial T} \frac{1}{T} \right).$$

- (c) A body with constant specific heat C_V is heated under constant volume from T_1 to T_2 . How much entropy it gains?
- (d) Discuss the heating if the same body is in contact with a thermostat at T_2 . In the last case the heating is irreversible. Show that the total entropy change is positive.
- (e) Two similar bodies with temperatures T_1 and T_2 brought into contact. Find the final temperature and the change in entropy.

Solution

Problem 1

- (a) Constant
- (b)

$$S = Q/T.$$

- (c)

$$S = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT = C_V \ln \frac{T_2}{T_1}.$$

(d)

$$S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT = C_P \ln \frac{T_2}{T_1}.$$

Problem 2

Mechanical work under *isothermic process* is given by

$$dW = dU - dQ = dU - T dS = d(U - TS).$$

The function of state

$$A = U - TS$$

is called *Helmholtz free energy*. We have

$$dA = dU - T dS - S dT = (T dS - P dV) - T dS - S dT = -S dT - P dV.$$

Thus,

$$S = - \left(\frac{\partial A}{\partial T} \right)_V, \quad P = - \left(\frac{\partial A}{\partial V} \right)_T.$$

Thus, A is the *thermodynamic potential* with respect to V and T .

The thermodynamic potential with respect to P and T is called *Gibbs free energy*. We have

$$G = U - TS - PV \rightarrow dG = -S dT + V dP.$$

(b) Substituting

$$S = - \left(\frac{\partial A}{\partial T} \right)_V$$

into definition of A we get the result.

(c) We have

$$S = \int_{T_1}^{T_2} \frac{C_V}{T} dT = C_V \ln \left(\frac{T_2}{T_1} \right).$$

(d) Use 2nd law of thermodynamics

(e) Energy conservation law yields

$$C_V(T_2 - T_B) = C_V(T_B - T_1) \rightarrow T_B = (T_1 + T_2)/2.$$

for the entropy change we have

$$\delta S = C_V \ln \frac{T_B}{T_1} + C_V \ln \frac{T_B}{T_2} = 2C_V \ln \left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right) \geq 0.$$

Chapter 3

The Thermodynamics of Phase Transitions

Quick access: 1 2 3 4 5 6 7 8 9 10 11 12 13

Problem 3.1: A condensible vapor has a molar entropy

$$s = s_0 + R \ln \left[C(v-b) \left(u + \frac{a}{v} \right)^{5/2} \right],$$

where c and s_0 are constants.

- Compute equation of state.
- Compute the molar heat capacities, c_c and c_p .
- Compute the latent heat between liquid and vapor phases temperature T in terms of the temperature T , the gas constant R and gas molar volumes v_l and v_g . How can you find explicit values of v_l and v_g if you need to?

Solution 3.1:

- Let us first find the temperature as function of u and s . We have

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u} \right)_v = \frac{5R}{2} \left(u + \frac{a}{v} \right)^{-1}.$$

Thus,

$$\begin{aligned} s &= s_0 + R \ln \left[C(5RT/2)^{5/2}(v-b) \right], \\ u &= \frac{5}{2}RT - \frac{a}{v}, \\ a &= u - Ts = \frac{5}{2}RT - \frac{a}{v} - T \left\{ s_0 + R \ln \left[C(v-b)(5RT/2)^{5/2} \right] \right\}. \end{aligned}$$

As a result,

$$P = - \left(\frac{\partial a}{\partial v} \right)_T = \frac{RT}{v-b} - \frac{a}{v^2}.$$

This is the van der Waals equation.

(b) We have,

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v = \frac{5}{2} RT.$$

The result for c_p can be obtained in the same way as in the problem 2.17.

(c) The latent heat q is just

$$q = T(s_g - s_l) = RT \ln \frac{v_g - b}{v_l - b}.$$

Since the pressure should be constant along the equilibrium line, $P_l = P_g$, we have

$$\frac{RT}{v_g - b} - \frac{a}{v_g^2} = \frac{RT}{v_l - b} - \frac{a}{v_l^2}.$$

Another equation is the equality of chemical potentials, $\mu_l = \mu_g$. We know that $\mu = (\partial a / \partial n)_{T,v}$, so everything could be done. Another way is to plot the isotherm and find the volumes using the Maxwell rule.

Problem 3.2: Find the coefficient of thermal expansion, $\alpha_{coex} = v^{-1} (\partial v / \partial T)_{coex}$, for a gas maintained in equilibrium with its liquid phase. Find an approximate explicit expression for α_{coex} , using the ideal gas equation of state. Discuss its behavior.

Solution 3.2: It is implicitly assumed that the total volume of the system is kept constant. We have,

$$\frac{\partial v}{\partial T} = \left(\frac{\partial v}{\partial T} \right)_P + \left(\frac{\partial v}{\partial P} \right)_T \frac{dP}{dT}.$$

For an ideal gas, $v = RT/P$. Thus

$$\left(\frac{\partial v}{\partial T} \right)_P = R/P, \quad \left(\frac{\partial v}{\partial P} \right)_T = -RT/P^2.$$

Consequently,

$$\alpha_{coex} = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_{coex} = \frac{1}{T} \left[1 - \frac{T}{P} \left(\frac{\partial P}{\partial T} \right)_{coex} \right].$$

According to the Clapeyron-Clausius formula,

$$\left(\frac{\partial P}{\partial T} \right)_{coex} = \frac{q}{T(v_g - v_l)} \approx \frac{q}{Tv_g},$$

where $q = (\Delta h)_{lg}$, we can rewrite this expression as

$$\alpha_{coex} \approx \frac{1}{T} \left(1 - \frac{q}{RT} \right).$$

The coefficient of thermal expansion is less because with the increase of the temperature under given pressure the heat is extracted from the system.

Problem 3.3: Prove that the slope of the sublimation curve of a pure substance at the triple point must be greater than that of the vaporization curve at the triple point.

Solution 3.3: The triple point is defined by the following equations for the 2 phases:

$$P_1 = P_2 = P_3, \quad T_1 = T_2 = T_3, \quad \mu_1 = \mu_2 = \mu_3.$$

The definitions of the sublimation and vaporization curves are given in Fig. 3.4 of the textbook [1]. Consequently, the slopes of the vaporization and sublimation curves are given by the relations

$$\left(\frac{\partial P}{\partial T} \right)_{lg} = \frac{s_g - s_l}{v_g - v_l} \approx \frac{s_g - s_l}{v_g}, \quad \left(\frac{\partial P}{\partial T} \right)_{sg} = \frac{s_g - s_s}{v_g - v_s} \approx \frac{s_g - s_s}{v_g}.$$

Since solid state is more ordered, $s_s < s_l$, and

$$\left(\frac{\partial P}{\partial T} \right)_{lg} - \left(\frac{\partial P}{\partial T} \right)_{sg} = \frac{s_s - s_l}{v_g} < 0.$$

Problem 3.4: Consider a monoatomic fluid along its fluid-gas coexistence curve. Compute the rate of change of chemical potential along the coexistence curve, $(\partial\mu/\partial T)_{coex}$, where μ is the chemical potential and T is the temperature. Express your answer in terms of s_l, v_l and s_g, v_g which are the molar entropy and molar volume of the liquid and gas, respectively.

Solution 3.4: We have $\mu(P, T) = \mu_l(P, T) = \mu_g(P, T)$. Thus,

$$\frac{d\mu}{dT} = \left(\frac{\partial\mu_g}{\partial T} \right)_P + \left(\frac{\partial\mu_g}{\partial P} \right)_T \frac{dP}{dT}.$$

Consequently,

$$\left(\frac{d\mu}{dT} \right)_{coex} = -s_g + v_g \frac{s_g - s_l}{v_g - v_l} = \frac{s_g v_l - v_g s_l}{v_g - v_l}.$$

Problem 3.5: A system in its solid phase has a Helmholtz free energy per mole, $a_s = B/Tv^3$, and in its liquid phase it has a Helmholtz free energy per mole, $a_l = A/Tv^2$, where A and B are constants, v is the volume per mole, and T is the temperature.

- Compute the Gibbs free energy density of the liquid and solid phases.
- How are the molar volumes, v , of the liquid and solid related at the liquid-solid phase transition?
- What is the slope of the coexistence curve in the $P - T$ plane?

Solution 3.5:

- By definition, $g = a + Pv$, and $P = -(\partial a/\partial v)_T$. Thus,

$$g = a - v(\partial a/\partial v)_T, \quad g_s = 4B/Tv_s^3, \quad g_l = 3A/Tv_l^2.$$

- Since $P = -(\partial a/\partial v)_T$ we have,

$$P_s = 3B/Tv_s^4, \quad P_l = 2A/Tv_l^3.$$

Since at the phase transition $P_s = P_l = P$, we obtain

$$\frac{v_l^3}{v_s^4} = \frac{2A}{3B}.$$

- Now we can express the Gibbs free energies per mole in terms of P ,

$$g_s = \frac{4}{3}(3B)^{1/4}P^{3/4}T^{-1/4}, \quad g_l = \frac{3}{2}(2A)^{1/3}P^{2/3}T^{-1/3}.$$

Since at the transition point $g_l = g_s$, we have

$$\frac{P}{T} = \left(\frac{3^{7/4} A^{1/3}}{2^{8/3} B^{1/4}} \right)^{12} = \frac{3^{21} A^4}{2^{24} B^3}.$$

Problem 3.6: Deduce the Maxwell construction using stability properties of the Helmholtz free energy rather than the Gibbs free energy.

Solution 3.6: Since the system in the equilibrium, the maximum work extracted during the process of the phase transition is $\Delta A - P_0 \Delta V$. Let us look at Fig. 3.1.

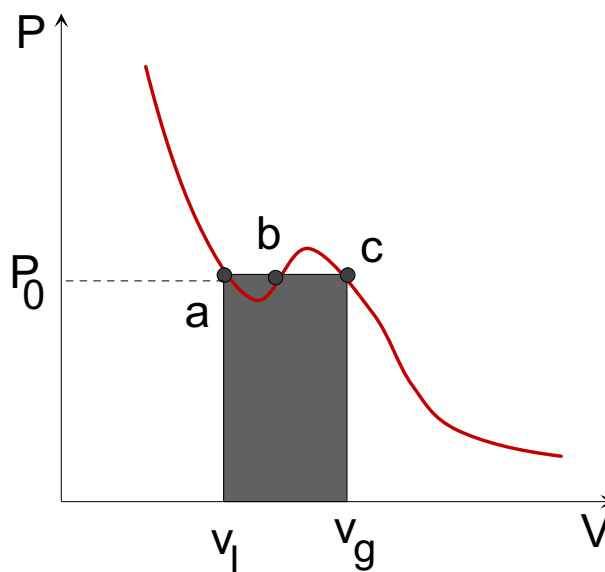


Figure 3.1:

We see that $P_0 \Delta V = P_0(V_g - V_l)$ is just the area of the dashed rectangle. To find ΔA let us follow isotherm. Since $T = \text{const}$,

$$\Delta A = \int_a^c P dV,$$

which is just the area *below* the isotherm $a-b-c$. Subtracting areas we reconstruct the Maxwell rule.

Problem 3.7: For a van der Waals gas, plot the isotherms in the $\bar{P} - \bar{V}$ plane (\bar{P} and \bar{V} are the reduced pressure and volume) for reduced temperatures $\bar{T} = 0.5$, $\bar{T} = 1.0$, and $\bar{T} = 1.5$. For $\bar{T} = 0.5$, is $\bar{P} = 0.1$ the equilibrium pressure of the liquid gas coexistence region?

Solution 3.7: We use Maple to plot the curves. The graphs have the form We see that for $\bar{T} = 0.5$ there is no stable region at all. To illustrate the situation we plot the curves in the vicinity of $\bar{T} = 1$.

Problem 3.8: Consider a binary mixture composed of two types of particles, A and B . For this system the fundamental equation for the Gibbs energy is

$$G = n_A \mu_A + n_B \mu_B, \quad (3.1)$$

the combined first and second laws are

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B \quad (3.2)$$

(S is the total entropy and V is the total volume of the system), and the chemical potentials μ_A and μ_B are intensive so that

$$\mu_A = \mu_A(P, T, x_A) \quad \text{and} \quad \mu_B(P, T, x_B).$$

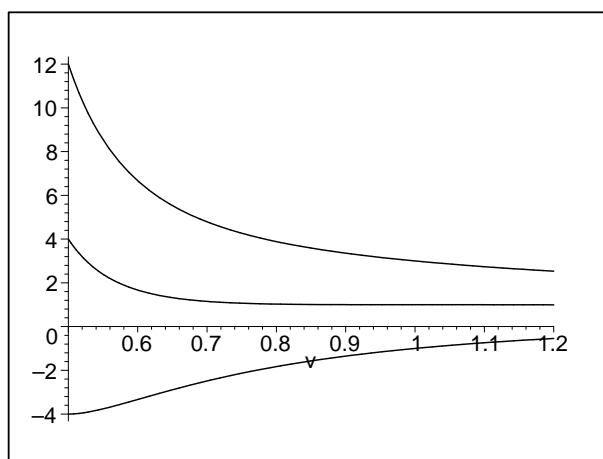


Figure 3.2: The upper curve corresponds $\bar{T} = 1.5$, the lower one - to $\bar{T} = 0.5$.

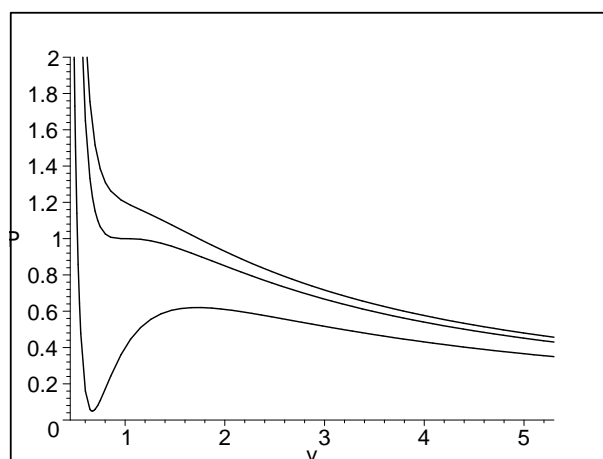


Figure 3.3: The upper curve corresponds $\bar{T} = 1.05$, the lower one - to $\bar{T} = 0.85$.

Use these facts to derive the relations

$$s dT - v dP + \sum_{\alpha=A,B} x_{\alpha} d\mu_{\alpha} = 0 \quad (3.3)$$

and

$$\sum_{\alpha=A,B} x_{\alpha} (d\mu_{\alpha} + s_{\alpha} dT - v_{\alpha} dP) = 0, \quad (3.4)$$

where $s = S/n$, $n = n_A + n_B$, $s_{\alpha} = (\partial S / \partial n_{\alpha})_{P,T,n_{\beta \neq \alpha}}$, and $v_{\alpha} = (\partial V / \partial n_{\alpha})_{P,T,n_{\beta \neq \alpha}}$ with $\alpha = A, B$ and $\beta = A, B$.

Solution 3.8: Let us express n_{α} as $n_{\alpha} = n x_{\alpha}$ and divide Eq. (3.1) by n . We get

$$dg = d \left(\sum_{\alpha} x_{\alpha} \mu_{\alpha} \right) = \sum_{\alpha} (x_{\alpha} d\mu_{\alpha} + \mu_{\alpha} dx_{\alpha}) \quad (3.5)$$

Let us divide Eq. (3.2) by n to obtain

$$dg = -s dT + v dP + \sum_{\alpha} \mu_{\alpha} dx_{\alpha}. \quad (3.6)$$

Equating the right hand sides of these equations we prove Eq. (3.3). Further, the entropy is an extensive variable. Consequently, it should be a *homogeneous* function of n_{α} .

$$S = \sum_{\alpha} (\partial S / \partial n_{\alpha})_{P,T,n_{\beta \neq \alpha}} n_{\alpha} = n \sum_{\alpha} s_{\alpha} x_{\alpha}.$$

Substituting these expressions into Eq. (3.3) we prove Eq. (3.4).

Problem 3.9: Consider liquid mixture (l) of particles A and B coexisting in equilibrium with vapor mixture (g) of particles A and B . Show that the generalization of the Clausius-Clapeyron equation for the coexistence curve between the liquid and vapor phases when the mole fraction of A in the liquid phase is fixed is given by

$$\left(\frac{\partial P}{\partial T} \right)_{x_A^l} = \frac{x_A^g (s_A^g - s_A^l) + x_B^g (s_B^g - s_B^l)}{x_A^g (v_A^g - v_A^l) + x_B^g (v_B^g - v_B^l)}, \quad (3.7)$$

where $s_{\alpha} = (\partial S / \partial n_{\alpha})_{P,T,n_{\beta \neq \alpha}}$, and $v_{\alpha} = (\partial V / \partial n_{\alpha})_{P,T,n_{\beta \neq \alpha}}$ with $\alpha = A, B$ and $\beta = A, B$. [Hint: Equation (b) of the Problem (3.8) is useful.]

Solution 3.9: Let us apply Eq. (3.4) to the *gas* phase. We get

$$\sum_{\alpha} x_{\alpha}^g (d\mu_{\alpha}^g + s_{\alpha}^g dT - v_{\alpha}^g dP_g) = 0.$$

Dividing this equation by dT we obtain

$$\sum_{\alpha} x_{\alpha}^g \left(\frac{d\mu_{\alpha}^g}{dT} + s_{\alpha}^g - v_{\alpha}^g \frac{dP_g}{dT} \right) = 0.$$

Now, let us take into account that at the coexistence curve $\mu_{\alpha}^g = \mu_{\alpha}^l$. Thus

$$\frac{d\mu_{\alpha}^g}{dT} = \frac{d\mu_{\alpha}^l}{dT} = -s_{\alpha}^l + v_{\alpha}^l \frac{dP_l}{dT}.$$

Since at the equilibrium $P_g = P_l$, we prove Eq. (3.7).

Problem 3.10: A PVT system has a line of continuous phase transitions (a lambda line) separating two phases, I and II, of the system. The molar heat capacity c_P and the thermal expansivity α_P are different in the two phases. Compute the slope $(dP/dT)_{coex}$ of the λ line in terms of the temperature T , the molar volume v , $\Delta c_P = c_P^I - c_P^{II}$, and $\Delta \alpha_P = \alpha_P^I - \alpha_P^{II}$.

Solution 3.10: At a continuous phase transition the entropy is continuous, $\Delta s = 0$. At the same time, $s = s(P, T)$ and along the coexistence curve P is a function of the temperature. For each phase, we get

$$\frac{ds}{dT} = \frac{\partial s}{\partial T} + \frac{\partial s}{\partial P} \frac{dP}{dT}.$$

We know that $(\partial S/\partial T)_P = c_P/T$ and from the Maxwell relation

$$(\partial s/\partial P)_T = -(\partial v/\partial T)_P.$$

Since $\Delta s = 0$,

$$(\Delta c_P)/T = (dP/dT) \Delta(\partial v/\partial T)_P = (dP/dT) v(\Delta \alpha_P).$$

The answer is

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta c_P}{T \Delta \alpha_P}.$$

Problem 3.11: Water has a latent heat of vaporization, $\Delta h = 540$ cal/gr. One mole of steam is kept at its condensation point under pressure at $T_1 = 373$ K. The temperature is then lowered to $T_2 = 336$ K. What fraction of the steam condenses into water? (Treat the steam as an ideal gas and neglect the volume of the water.)

Solution 3.11: Let us use the Clausius-Clapeyron equation for the case of liquid-vapor mixture. Since $v^g \ll v^l$ we get

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{q}{T v^g}.$$

Here q is the latent heat *per mole*. Considering vapor as an ideal gas we get

$$\frac{dP}{dT} = \frac{qP}{RT^2} \quad \rightarrow \quad P = P_0 e^{-q/RT}.$$

As a consequence,

$$\frac{P_1}{P_2} = \exp \left[\frac{q(T_1 - T_2)}{RT_1 T_2} \right].$$

Since the volume is kept constant,

$$\frac{n_1^g}{n_2^g} = \frac{P_1}{P_2} = \exp \left[\frac{q(T_1 - T_2)}{RT_1 T_2} \right] = \exp \left[\frac{18 \Delta h (T_1 - T_2)}{RT_1 T_2} \right].$$

Here we have taken into account that the molecular weight of H_2O is 18. The relative number of condensed gas is then

$$\frac{n_1 - n_2}{n_1} = 1 - \exp \left[-\frac{18 \Delta h (T_1 - T_2)}{RT_1 T_2} \right].$$

Problem 3.12: A liquid crystal is composed of molecules which are elongated (and often have flat segments). It behaves like a liquid because the locations of the center of mass of the molecules have no long-range order. It behaves like crystal because the orientation of the molecules does have long range order. The order parameter of the liquid crystal is given by the diatic

$$\mathbf{S} = \eta [\mathbf{nn} - (1/3)\mathbf{I}],$$

where \mathbf{n} is a unit vector (called the director), which gives the average direction of alignment of the molecules. The free energy of the liquid crystal can be written as

$$\Phi = \Phi_0 + \frac{1}{2}A S_{ij}S_{ij} - \frac{1}{3}B S_{ij}S_{jk}S_{ki} + \frac{1}{4}C S_{ij}S_{jk}S_{kl}S_{kl}, \quad (3.8)$$

where $A = A_0(T - T^*)$, A_0 , B and C are constants, \mathbf{I} is the unit tensor so

$$\hat{\mathbf{x}}_i \cdot \mathbf{I} \cdot \hat{\mathbf{x}}_j = \delta_{ij}, \quad S_{ij} = \hat{\mathbf{x}}_i \cdot \mathbf{S} \cdot \hat{\mathbf{x}}_j,$$

and the summation is over repeated indices. The quantities $\hat{\mathbf{x}}_i$ are the unit vectors

$$\hat{\mathbf{x}}_1 = \mathbf{x}, \quad \hat{\mathbf{x}}_2 = \mathbf{y}, \quad \hat{\mathbf{x}}_3 = \mathbf{z}.$$

- Perform the summations in the expression for Φ and write Φ in terms of η , A , B , C .
- Compute the critical temperature T_c , at which the transition from isotropic liquid to liquid crystal takes place.
- Compute the difference between the entropies between the isotropic liquid ($\eta = 0$) and the liquid crystal at the critical temperature.

Solution 3.12:

- First, for brevity, let us express the matrix \mathbf{S} as $\eta(\hat{s} - \mathbf{I}/3)$, where

$$\hat{s} = \mathbf{nn} = \begin{pmatrix} n_1^2 & n_1n_2 & n_1n_3 \\ n_2n_1 & n_2^2 & n_2n_3 \\ n_3n_1 & n_3n_2 & n_3^2 \end{pmatrix}.$$

The Eq. (3.8) can be expressed as

$$\begin{aligned} \Phi &= \Phi_0 + \frac{1}{2}Aa_2\eta^2 - \frac{1}{3}Ba_3\eta^3 + \frac{1}{4}Ca_4\eta^4, \\ a_2 &= \text{Tr} \left(\hat{s} - \frac{1}{3}\mathbf{I} \right)^2, \quad a_3 = \text{Tr} \left(\hat{s} - \frac{1}{3}\mathbf{I} \right)^3, \quad a_4 = \left[\text{Tr} \left(\hat{s} - \frac{1}{3}\mathbf{I} \right)^2 \right]^2. \end{aligned} \quad (3.9)$$

It is easy to calculate $b_m = \text{Tr} \left(\hat{s} - \frac{1}{3}\mathbf{I} \right)^m$. Indeed,

$$\text{Tr} \left(\hat{s} - \frac{1}{3}\mathbf{I} \right)^m = \sum_{k=0}^m \frac{m!}{k!(m-k)!} \frac{(-1)^k}{3^k} \text{Tr} \left(\hat{s}^k \mathbf{I}^{m-k} \right).$$

It is straightforward that for $m > 1$ and $k \neq 0$ we get

$$\text{Tr}(\hat{s}^k \mathbf{I}^{m-k}) = \text{Tr}(\hat{s}^k \mathbf{I}) = \text{Tr}(\hat{s}^k) = 1, \quad \text{Tr} \mathbf{I}^m = \text{Tr} \mathbf{I} = 3.$$

Here we have used the properties of trace and of \hat{s} operators. Since trace is independent of the presentation, let us direct the axis I along the vector \mathbf{n} . Then

$$\hat{s} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \rightarrow \text{Tr}(\hat{s}^k) = \text{Tr} \hat{s} = 1.$$

Consequently,

$$b_m = \left(1 - \frac{1}{3}\right)^m + 2 \left(\frac{-1}{3}\right)^m, \quad a_2 = b_2 = \frac{2}{3}, \quad a_3 = b_3 = \frac{2}{9}, \quad a_4 = b_2^2 = \frac{4}{9}.$$

Finally, we get

$$\Phi = \Phi_0 + \frac{1}{3}A\eta^2 - \frac{2}{27}B\eta^3 + \frac{1}{9}C\eta^4. \quad (3.10)$$

- (b) At the transition point the dependence $\Phi(\eta)$ has two equal minima. To find this point, let us shift the origin of η by some η_0 in order to kill *odd* in $\eta - \eta_0$ items. If we put $\eta = \eta_0 + \xi$ we have

$$\Phi - \Phi_0 = \frac{1}{3}A(\xi + \eta_0)^2 - \frac{2}{27}B(\xi + \eta_0)^3 + \frac{1}{9}C(\xi + \eta_0)^4. \quad (3.11)$$

In order to kill the term proportional to ξ^3 one has to put (see the Maple file) $\eta_0 = B/6C$. Substituting this value into the expression for the coefficient ξ ,

$$(2/3)A\eta_0 - (2/9)B\eta_0^2 + (4/9)C\eta_0^3,$$

and equating the result to 0 we get $A = B^2/27C$. Since $A = A_0(T - T^*)$ we have

$$T_c = T^* + \frac{B^2}{27A_0C}.$$

- (c) Since $S = -\partial\Phi/\partial T = -(1/3)A_0\eta^2$ we get

$$\Delta S = -(1/3)A_0(\eta_+ - \eta_-)(\eta_+ + \eta_-) = -(2/3)A_0\eta_0(\xi_+ - \xi_-),$$

where η_{\pm} are the roots of the equation $\partial\Phi/\partial\eta = 0$ while ξ_{\pm} are the roots of the equation $\partial\Phi/\partial\xi = 0$. Note that the potential $\Phi(\xi)$ is *symmetric*, thus $\xi_+ + \xi_- = 0$. The important part $\Phi(\xi)$ at the critical point can be obtained substituting η_0 and A into Eq. (3.11). It has the form,

$$\delta\Phi(\xi) = \frac{C}{9} \left(\xi^4 - \frac{B^2}{18C^2} \xi^2 \right).$$

Thus,

$$\xi_{\pm} = \pm \frac{B}{6C}, \quad \xi_+ - \xi_- = \frac{B}{3C}.$$

As a result,

$$\Delta S = -\frac{1}{27} \frac{A_0 B^2}{C^2}.$$

Problem 3.13: The equation of state of a gas is given by the Berthelot equation

$$\left(P + \frac{a}{Tv^2}\right)(v - b) = RT.$$

- (a) Find values of the critical temperature T_c , the critical molar volume v_c , and the critical pressure, P_c in terms of a , b , and R .
- (b) Does the Berthelot equation satisfy the law of corresponding states.?
- Find the critical exponents β , δ , and γ from the Berthelot equation.

Solution 3.13:

- (a) Let us express the pressure as a function of volume,

$$P = \frac{RT}{v - b} - \frac{a}{Tv^2}.$$

For the critical temperature we have

$$\begin{aligned} \left(\frac{\partial P}{\partial V}\right)_T &= -\frac{RT_c}{(v_c - b)^2} + \frac{2a}{T_c v_c^3} = 0, \\ \left(\frac{\partial^2 P}{\partial V^2}\right)_T &= \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{T_c v_c^4} = 0. \end{aligned}$$

From this we obtain:

$$v_c = 3b, \quad T_c = \sqrt{\frac{8a}{27Rb}}, \quad P_c = \frac{RT_c}{8b}.$$

- (b) We put

$$P = P_c \cdot \bar{P}, \quad T = T_c \cdot \bar{T}, \quad v = v_c \cdot \bar{v}$$

to get:

$$\left(\bar{P} + \frac{3}{\bar{T}\bar{v}^2}\right)(3\bar{v} - 1) = 8\bar{T}.$$

(c) First let us simplify the equation of state near the critical point. Putting

$$\bar{P} = 1 + p, \quad \bar{v} = 1 + v, \quad \bar{T} = 1 + \tau$$

and expanding in p , v , and τ up to lowest non-trivial order (see Maple file), we get

$$p = -\frac{3}{2}v^3 - 12v\tau + 7\tau. \quad (3.12)$$

The derivative $(\partial p / \partial v)_\tau$ is

$$\left(\frac{\partial p}{\partial v}\right)_\tau = -\frac{9}{2}v^2 - 12\tau. \quad (3.13)$$

Since this function is *even* in v the Maxwell construction

$$\int_{v_l}^{v_g} v dp = \int_{v_l}^{v_g} v \left(\frac{\partial p}{\partial v}\right)_\tau dv = 0$$

requires $-v_l = v_g$. Since along the coexistence curve $p(v_g, \tau) = p(-v_g, \tau)$ we get

$$v_g = \sqrt{-8\tau} \quad \rightarrow \quad \beta = 1/2.$$

Substituting this value of v_g into Eq. (3.13) we observe that

$$\left(\frac{\partial p}{\partial v}\right)_\tau = 24\tau \quad \rightarrow \quad \gamma = 1.$$

To obtain the critical exponent δ let us introduce $\rho = 1/\bar{v}$, the equation of state being

$$\bar{P}(\rho, \bar{T}) = \frac{8\bar{T}\rho}{3-\rho} - \frac{3\rho^2}{\bar{T}}.$$

Expanding near the critical point $\bar{P} = \bar{T} = \rho = 1$ we get

$$\bar{P} = 1 + (3/2)(\rho - 1)^3 \quad \rightarrow \quad \delta = 3.$$

3.1 Mini-tests

3.1.1 A

Properties of Van der Waals (VdW) liquid

- (i) Find the critical temperature T_c at which the Van der Waals isotherm has an inflection point. Determine the pressure P_c and volume, V_c , for a system of N particles at $T = T_c$.

(ii) Express the VdW equation in units of T_c , P_c , and V_c . Show that it has the form

$$\left(P' + \frac{3}{V'^2}\right)(3V' - 1) = 8T' \quad (3.14)$$

where $P' \equiv P/P_c$, $V' \equiv V/V_c$, and $T' \equiv T/T_c$

(iii) Analyze the equation of state (3.14) near the critical point. Assume that

$$P' = 1 + p, \quad T' = 1 + \tau, \quad V' = 1 - n$$

and show that for small p , τ and n the equation of state has the approximate form

$$p = 4\tau + 6\tau n + (3/2)n^3. \quad (3.15)$$

(iv) Plot $p(n, \tau)$ versus n for $\tau = \pm 0.05$ and discuss the plots.

(v) Using the above equation find the stability region. Show this region in the plot.

(vi) Show that the Maxwell relation can be expressed as

$$\int_{n_l}^{n_r} n (\partial p / \partial n)_\tau dn = 0 \quad (3.16)$$

along the equilibrium liquid-gas line. Using this relation and the equation of state find n_l and n_r .

(vii) Discuss why the stability condition and Maxwell relation lead to different stability criteria? Illustrate discussion using the plot.

Solution

(i) Writing the VdW equation as

$$P = \frac{NkT}{V - Nb} - \frac{N^2a}{V^2}$$

and requiring

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

we obtain

$$T_c = \frac{8}{27} \frac{a}{bk}, \quad V_c = 3Nb, \quad P_c = \frac{1}{27} \frac{a}{b^2}.$$

(ii) The result is straightforward in one substitutes $P = P_c P'$, $V = V_c V'$ and $T = T_c T'$.

(iii) Straightforward.

(iv) Straightforward.

(v) The stability region is determined by the equation $(\partial p/\partial n)_\tau = 0$. We have

$$(\partial p/\partial n)_\tau = 6\tau + (9/2)n^2.$$

Consequently

$$n_{st} = \pm 2\sqrt{-\tau/3}.$$

(vi) Since in the main approximation $(\partial p/\partial n)_\tau$ is an odd function of n , $n_l = -n_r$. Using Eq. (3.15) we get (see the Maple file)

$$n_r = \sqrt{-4\tau}.$$

3.1.2 B

Curie-Weiss theory of a magnet

The simplest equation for a non-ideal magnet has the form

$$m = \tanh[\beta(Jm + h)] \quad (3.17)$$

where $\beta = 1/kT$, J is the effective interaction constant, while h is the magnetic field measured in proper units.

- (i) Consider the case $h = 0$ and analyze graphically possible solutions of this equation.
Hint: rewrite equation in terms of an auxiliary dimensional variable $\tilde{m} \equiv \beta Jm$. Show that a spontaneous magnetization appears at $T < T_c = J/k$.
- (ii) Simplify Eq. (3.17) at $h = 0$ near the critical temperature and analyze the spontaneous magnetization as a function of temperature.
Hint: Put $T = T_c(1 + \tau)$ and consider solutions for small \tilde{m} and τ .
- (iii) Analyze the magnetization curve $m(h)$ near T_c . Hint: express Eq. (3.17) in terms of the variables \tilde{m} and $\tilde{h} \equiv \beta h \approx h/J$ and plot \tilde{h} as a function of \tilde{m} .
- (iv) Plot and analyze the magnetization curves for $T/T_c = 0.6$ and $T/T_c = 1.6$.

Solution

(i) At $h = 0$ the equation (3.17) has the form:

$$(\beta J)^{-1}\tilde{m} = \tanh \tilde{m}.$$

From the graph of the function $F(\tilde{m}) \equiv (\beta J)^{-1}\tilde{m} - \tanh \tilde{m}$ (see the Maple file) one observes that only trivial solution $\tilde{m} = 0$ exists at $\beta J < 1$, or at $T \geq T_c = J/k$. At $T < T_c$ there exists 2 non-trivial solutions corresponding spontaneous magnetization. Thus $(\beta J)^{-1} = T/T_c$

- (ii) The dimensionless function $F(\tilde{m}) \equiv (T/T_c)\tilde{m} - \tanh \tilde{m}$, near T_c acquires the form $F(\tilde{m}) = \tau\tilde{m} + \tilde{m}^3/3$. Thus the solutions have the form

$$\tilde{m} = 0, \pm\sqrt{-3\tau}.$$

Since near T_c the ratio T_c/T can be substituted by 1, the same result is true for m .

- (iii) In general, Eq. (3.17) can be rewritten as

$$(T/T_c)\tilde{m} = \tanh(\tilde{m} + \tilde{h}) \quad \rightarrow \quad \tilde{m} + \tilde{h} = \operatorname{artanh} [(1 + \tau)\tilde{m}].$$

Consequently,

$$\tilde{h} = \operatorname{artanh} [(1 + \tau)\tilde{m}] - \tilde{m}$$

To plot the magnetization curve one has to come back to the initial variables.

Chapter 4

Elementary Probability Theory and Limit Theorems

Quick access: [1](#) [2](#) [3](#) [4](#) [5](#) [6](#) [7](#) [8](#) [9](#) [10](#) [11](#) [12](#) [13](#) [14](#) [15](#)

Problem 4.1: A bus has 9 seats facing forward and 8 seats facing backward. In how many ways can 7 passengers be seated if 2 refuse to ride facing forward and 3 refuse to ride facing backward?

Solution 4.1: Three people refuse ride facing backward, and they should be definitely placed to 9 seats facing forward. The number of ways to do that is $9 \cdot 8 \cdot 7$. In a similar way, 2 people can occupy 8 seats facing backward in $8 \cdot 7$ ways. Now $17 - 5 = 12$ seats left. They can be occupied by $7 - 3 - 2 = 2$ nice people in $12 \cdot 11$ ways. As a result, we get

$$9 \cdot 8 \cdot 7 \times 8 \cdot 7 \times 12 \cdot 11 = 3725568$$

ways.

Problem 4.2: Find the number of ways in which 8 persons can be assigned to 2 rooms (A and B) if each room must have at least 3 persons in it.

Solution 4.2: The number of persons in the room is between 3 and 5. Let us start with the situation where room A has 3 persons. The number of ways to do that is $8 \cdot 7 \cdot 6$. The total number of ways is then

$$8 \cdot 7 \cdot 6 + 8 \cdot 7 \cdot 6 \cdot 5 + 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 = 8736.$$

Problem 4.3: Find the number of permutations of the letters in the word MONOTONOUS. In how many ways are 4 O's together? In how many ways are (only) 3 O's together?

Solution 4.3: The total number of the letters is 10, we have 4 O's, 2 N's, and other letters do not repeat. Thus the total number of permutations is $10!/(4!2!) = 75600$. To get the number of ways to have 4 O's together we have to use model word MONTNUS which has 7 letters with 2 repeated N's. Thus the number of ways is $7!/2! = 2520$. To have three O's together we have 6 places to insert a separate O to the word MONTNUS, thus the number of ways is $6 \times 2520 = 15120$.

Problem 4.4: In how many ways can 5 red balls, 4 blue balls, and 4 white balls be placed in a row so that the balls at the ends of the row are of the same color?

Solution 4.4: Let us start with 5 red balls and choose 2 of them to be at the ends. The rest $5 + 4 + 4 - 2 = 11$ balls are in the middle. They have to be permuted, but permutation of the balls of the color must be excluded. Among them they have 3 rest red balls, 4 blue balls and 4 white balls. Thus we have $11!/(3!4!4!) = 11550$ ways. Now let us do the same with white balls. Now we have 2 rest white balls, but 5 blue balls to permute. We get $11!/(2!5!4!) = 6930$ ways. The same is true for blue balls. The total number of ways is $138600 + 2 \times 83160 = 25410$ ways.

Problem 4.5: Three coins are tossed.

- (a) Find the probability of getting *no* heads.
- (b) Find the probability of getting *at least one head*.
- (c) Show that the event "heads on the first coin" and the events "tails on the last coin" are independent.
- (d) Show that the event "only two coins heads" and the event "three coin heads" are dependent and mutually exclusive.

Solution 4.5:

- (a) The answer is $(1/2)^3 = 1/8$.
 - (b) The sum of the probabilities is 1. Since the probability to get no heads is $1/8$, the answer is $1 - 1/8 = 7/8$.
 - (c) We assume that result of coin tossing is fully random.
 - (d) The event "3 heads" contradicts the requirement "only 2".
-

Problem 4.6: Various 6 digit numbers can be formed by permuting the digits 666655. All arrangements are equivalently likely. Given that the number is even, what is the probability that two fives are together?

Hint: You must find a conditional probability.

Solution 4.6: Since the number must be even, the last number is 6, and there are 4 ways to choose this number. There are 5 digits left, and the total number of their permutations give $5!$. We have to divide it by $3!$ of permutations of 6 and $2!$ permutations between 5. We end at the number of different numbers is $4 \cdot 5! / 3! 2! = 40$. If we want to have two fives together, it is the same as permute 4 units, the number of permutations $4 \cdot 4! / 3! = 16$. Thus the probability is

$$P = 16/40 = 2/5.$$

Problem 4.7: Fifteen boys go hiking. 5 get lost, 8 get sunburned, and 6 return home without problems.

- (a) What is the probability that a sunburned boy got lost?
- (b) What is the probability that a lost boy got sunburned?

Solution 4.7: See. pp. 176-177 of the book [1].

Let us define the event to get sunburned as A , and the event to get lost - B . The probability to get sunburned is $P(A) = 8/15$, while the probability to get lost is $P(B) = 5/15 = 1/3$. Thus

We know that $15 - 6 = 9$ boys had problems. Thus, the joint probability to be either sunburned or lost is, $P(A \cup B) = 9/15$. Thus the probability to be both sunburned and lost is

$$P(A \cap B) = P(A) + P(B) - P(A \cup B) = (8 + 5 - 9)/15 = 4/15.$$

Consequently, conditional probabilities are

$$P(A|B) = P(A \cap B)/P(B) = 1/2 \text{ (a), } P(B|A) = P(A \cap B)/P(A) = 4/5 \text{ (b),}$$

respectively.

Problem 4.8: A stochastic variable X can have values $x = 1$ and $x = 3$. A stochastic variable Y can have values $y = 2$ and $y = 4$. Denote the joint probability density

$$P_{X,Y}(x,y) = \sum_{i=1,3} \sum_{j=2,4} p_{i,j} \delta(x-i) \delta(y-j).$$

Compute the covariance of X and Y for the following 2 cases:

- (a) $p_{1,2} = p_{1,4} = p_{3,2} = p_{3,4} = 1/4$;
- (b) $p_{1,2} = p_{3,4} = 0$ and $p_{1,4} = p_{3,2} = 1/2$.

For each case decide if X and Y are independent.

Solution 4.8:

(a) First let us calculate

$$\langle XY \rangle = (1 \cdot 2 + 1 \cdot 4 + 3 \cdot 2 + 3 \cdot 4) / 4 = 6.$$

At the same time $\langle X \rangle = 2$ and $\langle Y \rangle = 3$. Since $\langle XY \rangle = \langle X \rangle \cdot \langle Y \rangle$ the variables are independent.

(b) We have,

$$\langle XY \rangle = (1 \cdot 4 + 3 \cdot 2) / 2 = 5.$$

It is not equal to $\langle X \rangle \cdot \langle Y \rangle$, so the variables are dependent.

Problem 4.9: The stochastic variables X and Y are independent and Gaussian distributed with first moment $\langle x \rangle = \langle y \rangle = 0$ and standard deviation $\sigma_X = \sigma_Y = 1$. Find the characteristic function for the random variable $Z = X^2 + Y^2$, and compute the moments $\langle z \rangle$, $\langle z^2 \rangle$ and $\langle z^3 \rangle$. Find the first 3 cumulants.

Solution 4.9: First let us find the distribution function for Z . Let us do the problem in two ways.

Simple way:

Let us transform the problem to the cylindrical coordinates, $x, y \rightarrow \rho, \phi$. We have

$$P(x)P(y) = \frac{1}{2\pi} e^{-(x^2+y^2)} = \frac{1}{2\pi} e^{-\rho^2}, \quad dx dy = \rho d\rho d\phi, .$$

Thus,

$$P_Z(z) = \frac{1}{2\pi} \int \rho d\rho d\phi e^{-\rho^2/2} \delta(z - \rho^2) = \frac{1}{2} e^{-z/2}.$$

General way:

$$\begin{aligned} P_Z(z) &= \int dx P_X(x) \int dy P_Y(y) \delta(x^2 + y^2 - z) \\ &= \int_{-\sqrt{z}}^{\sqrt{z}} \frac{dx}{2\sqrt{z-x^2}} P_X(x) \sum_{\pm} P_Y(\pm\sqrt{z-x^2}) \\ &= \frac{1}{\pi} \int_0^{\sqrt{z}} \frac{dx}{\sqrt{z-x^2}} \exp\left(-\frac{x^2}{2} - \frac{z-x^2}{2}\right) = \frac{1}{2} e^{-z/2}. \end{aligned}$$

Now, the characteristic function is

$$f_Z(k) = \langle e^{ikz} \rangle = \frac{1}{2} \int_0^{\infty} dz e^{(ik-1/2)z} = \frac{1}{1-2ik}.$$

Then,

$$\langle z^n \rangle = (-i)^n \left. \frac{d^n f_Z(k)}{dk^n} \right|_{k \rightarrow 0}.$$

Performing calculations (see the Maple file), we obtain:

$$\langle z \rangle = 2, \quad \langle z^2 \rangle = 8, \quad \langle z^3 \rangle = 48.$$

Thus,

$$\begin{aligned} C_1(Z) &= \langle z \rangle = 2, \quad C_2(Z) = \langle z^2 \rangle - \langle z \rangle^2 = 4, \\ C_3(Z) &= \langle z^3 \rangle - 3\langle z \rangle \langle z^2 \rangle + 2\langle z \rangle^3 = 48 - 3 \cdot 2 \cdot 8 + 3 \cdot 2^3 = 24. \end{aligned}$$

Problem 4.10: A die is loaded so that even numbers occur 3 times as often as odd numbers.

- (a) If the die is thrown $N = 12$ times, what is the probability that odd numbers occur 3 times? If it is thrown $N = 120$ times, what is the probability that odd numbers occur 30 times? Use the binomial distribution.

- (b) Compute the same quantities as in part (a), but use the Gaussian distribution

Note: For parts (a) and (b) compute your answers to four places.

- (c) Compare answers (a) and (b). Plot the binomial and Gaussian distributions for the case $N = 12$.

Solution 4.10:

- (a) For the random process, the partial probability for an odd number $p = 1/4$ and for an even number is $q = 1 - p = 3/4$. The probability to have k odd numbers, according to binomial distribution is

$$P_N^b(k) = \frac{N!}{k!(N-k)!} p^k q^{N-k}.$$

Consequently (see Maple file),

$$P_{12}^b(3) = \frac{12!}{3!9!} \frac{3^9}{4^{12}} = 0.2881.$$

In a similar way, $P_{120}^b(30) = 0.08385$.

- (b) The number of odd numbers is $\langle k \rangle = N/4$ and the dispersion is $\sigma = Np \cdot q = 3N/16$. Thus

$$P_N^G(k) = \frac{1}{\sqrt{3N\pi/8}} \exp\left(-\frac{(k - N/4)^2}{3N/8}\right).$$

As a result,

$$P_{12}^G(3) = 0.2660, \quad P_{120}^G(30) = 0.0841.$$

- (c) Plots are shown in the Maple file.

Problem 4.11: A book with 700 misprints contains 1400 pages.

- (a) What is the probability that one page contains no mistakes?
 (b) What is the probability that one pages contains 2 mistakes?

Solution 4.11: n mistakes can be distributed between g pages by

$$w_g(n) = \frac{(g+n-1)!}{(g-1)!n!}.$$

If one has a page without mistakes, it means that n mistakes are distributed between $g-1$ pages. The probability of that event is

$$P(0) = \frac{(g+n-2)!}{(g-2)!n!} \frac{n!(g-1)!}{(g+n-1)!} = \frac{g-1}{g+n-1}.$$

In our case $g = 1400$ and $n = 700$, thus $P(0) = 1399/2099 \approx 0.67$. In a similar way, if we have two misprints at a page, then $n-2$ misprints are distributed between $g-1$ pages. Thus, the number of ways to do that is $w_{g-1}(n-2)$. Consequently,

$$P(2) = \frac{w_{g-1}(n-2)}{w_g(n)} = \frac{(g+n-4)!}{(g-2)!(n-2)!} \frac{n!(g-1)!}{(g+n-1)!} = \frac{(g-1)n(n-1)}{(g+n-1)(g+n-2)(g+n-3)}.$$

We get $P(2) \approx 0.07$.

Problem 4.12: There old batteries and a resistor, R , are used to construct a circuit. Each battery has a probability p to generate voltage $V = v_0$ and has a probability $1-p$ to generate voltage $V = 0$ Neglect internal resistance in the batteries.

Find the average power, $\langle V^2 \rangle / R$, dissipated in the resistor if

- (a) the batteries are connected in the series and
 (b) the batteries are connected in parallel.

In cases (a) and (b), what would be the average power dissipated in all batteries were certain to generate voltage v_0 .

- (c) How you realize the conditions and results in this problem in the laboratory?

Solution 4.12: Let us start with series connection and find the probability to find a given value of the voltage. We have 4 possible values of the voltage. In units v_0 they are 0, 1, 2, and 3. We have,

$$P(0) = (1-p)^3, \quad P(1) = 3p(1-p)^2, \quad P(2) = 3p^2(1-p), \quad P(3) = p^3.$$

Consequently,

$$\langle W \rangle = \langle V^2 \rangle / R = *(v_0^2/R) [3p(1-p)^2 + 12p^2(1-p) + 9p^3] = (3v_0^2/R) p(1+2p).$$

Now let us turn to parallel connection. Let us for a while introduce conductance $G_i = 1/R_i$ of the batteries, as well as conductance $G = 1/R$ of the resistor. The voltage at the resistor is given by the expression

$$V = \frac{\sum_{i=1,2,3} E_i G_i}{G + \sum_{i=1,2,3} G_i}.$$

Here E_i are *electro-motive forces* of the batteries. Now the crucial point is to assume something about the resistances of the batteries. Let us for simplicity assume that they are equal, and $G_i \gg G$. Actually, it is a very bad assumption for old batteries. Under this assumption, $V = (E_1 + E_2 + E_3)/3$. The result is just 9 times less than that for series connection.

To check this kind of phenomena in the lab one has to find many old batteries at a junk-yard, first check distribution of their voltages and then make circuits.

The problem is badly formulated.

Problem 4.13: Consider a random walk in one dimension. In a single step the probability of displacement between x and $x + dx$ is given by

$$P(x) dx = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-a)^2}{2\sigma^2}\right) dx. \quad (4.1)$$

After N steps the displacement of the walker is $S = X_1 + X_2 + \dots + X_N$ where X_i is the displacement after i th step. After N steps,

- what is the probability density for the displacement, S , of the walker, and
- what is his standard deviation?

Solution 4.13:

- By definition,

$$P_S(s) = \int dx_1 P(x_1) \int dx_2 P(x_2) \dots \int dx_N P(x_N) \delta(s - x_1 - x_2 - \dots - x_N).$$

To calculate this integral we expand δ -function into Fourier integral

$$\delta(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ikx}.$$

In this way we get

$$\begin{aligned} P_S(s) &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{iks} \int dx_1 e^{-ikx_1} P(x_1) \int dx_2 e^{-ikx_2} P(x_2) \dots \int dx_N e^{-ikx_N} P(x_N) \\ &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{iks} \left(\int_{-\infty}^{\infty} dx e^{-ikx} P(x) \right)^N = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{iks} [\mathcal{P}(k)]^N. \end{aligned} \quad (4.2)$$

Here

$$\mathcal{P}(k) = \int_{-\infty}^{\infty} dx e^{-ikx} P(x)$$

is the Fourier component of the single-step probability. From Eq. (4.1) we obtain

$$\mathcal{P}(k) = \exp(-ika - k^2\sigma^2/2) \rightarrow [\mathcal{P}(k)]^N = \exp(-iNka - k^2N\sigma^2/2).$$

Now,

$$P_S(s) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp[ik(s - Na) - k^2N\sigma^2/2] = \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left(-\frac{(s - Na)^2}{2N\sigma^2}\right).$$

(b) We have (see Maple file),

$$\langle S \rangle = \int ds s P_S(s) = Na, \quad \langle S^2 \rangle - \langle S \rangle^2 = N\sigma^2.$$

Problem 4.14: Consider a random walk in one dimension for which the walker at each step is equally likely to take a step with displacement anywhere in the interval $d - a \leq x \leq d + a$, where $a < d$. Each step is independent of others. After N steps the displacement of the walker is $S = X_1 + X_2 + \dots + X_N$ where X_i is the displacement after i th step. After N steps,

- (a) what is the average displacement, $\langle S \rangle$, of the walker, and
- (b) what is his standard deviation?

Solution 4.14: Starting from the definition, we have

$$\begin{aligned} \langle S \rangle &= \int s P_S(s) ds = \int s ds \int dx_1 P(x_1) \dots \int dx_N P(x_N) \delta(s - x_1 - \dots - x_N) \\ &= \int dx_1 P(x_1) \dots \int dx_N P(x_N) (x_1 + x_2 + \dots + x_N) = N \langle X \rangle = Nd. \end{aligned}$$

In a similar way,

$$\langle S^2 \rangle = \int dx_1 P(x_1) \dots \int dx_N P(x_N) (x_1 + x_2 + \dots + x_N)^2.$$

We know that

$$\left(\sum_i x_i \right)^2 = \sum_i x_i^2 + \sum_{i \neq j} x_i x_j.$$

The number of pairs with non-equal i and j is $N(N-1)$. After averaging the obtain

$$\langle S^2 \rangle = N \langle X^2 \rangle + N(N-1) \langle X \rangle^2.$$

To calculate $\langle X^2 \rangle$ let us specify the normalized probability as

$$P(x) = \frac{1}{2a} \begin{cases} 1, & d-a \leq x \leq d+a \\ 0, & \text{otherwise} \end{cases}.$$

Then,

$$\langle X^2 \rangle = \frac{1}{2a} \int_{d-a}^{d+a} x^2 dx = d^2 + a^2/3.$$

Summarizing we get (see Maple file)

$$\langle S^2 \rangle - \langle S \rangle^2 = N(d^2 + a^2/3) + N(N-1)d^2 - (Nd)^2 = Na^2/3.$$

Problem 4.15: Consider a random walk in one dimension. In a single step the probability of displacement between x and $x+dx$ is given by

$$P(x) dx = \frac{1}{\pi} \frac{a}{x^2 + a^2} dx. \quad (4.3)$$

Find the probability density for the displacement of the walker after N steps. Does it satisfy the *Central Limit Theorem*? Should it?

Solution 4.15: Using the method of the Problem 4.13 we get

$$\mathcal{P}(k) = e^{-a|k|} \rightarrow P_S(s) = 2 \int_0^\infty \frac{dk}{2\pi} e^{-Nka} \cos ks = \frac{1}{\pi} \frac{Na^2}{Na^2 + s^2}.$$

It does not satisfy the Central Limit Theorem. It should not because $\langle X^2 \rangle$ is divergent.

Chapter 5

Stochastic Dynamics and Brownian Motion

Quick access: 1 2 3 4 5 6 7 8 9 10 11 Test 1

Problem 5.1: Urn A has initially 1 red and 1 white marble, and urn B initially has 1 white and 3 red marbles. The marbles are repeatedly interchanged. In each step of the process one marble is selected from each urn at random and the two marbles selected are interchanged. Let the stochastic variable Y denote “configuration of the units”. There configurations are possible. They are shown in Fig. 5.1

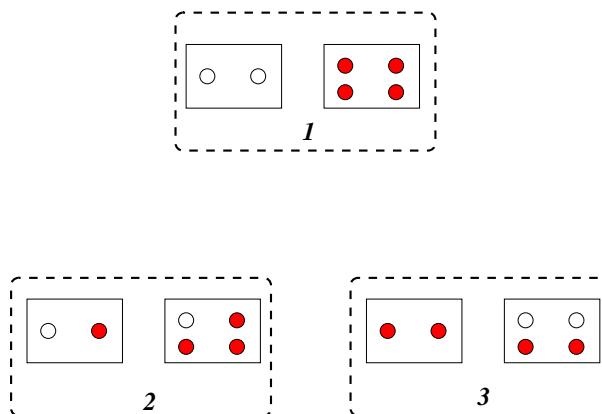


Figure 5.1: To the problem 5.1

We denote these 3 realizations as $y(n)$ where $n = 1, 2$ and 3 .

- Compute the transition matrix \mathbf{Q} and the conditional probability matrix $\mathbf{P}(s_0|s)$.
- Compute the probability vector, $\langle \mathbf{P}(s) \rangle$, at time s , given the initial condition stated above. What is the probability that there are 2 red marbles in urn A after 2 steps? After many steps?
- Assume that the realization, $y(n)$, equals to n^2 . Compute the moment, $\langle y(s) \rangle$, and the autocorrelation function, $\langle y(0)y(s) \rangle$, for the same initial conditions as in part (b).

Solution 5.1: The configurations are shown in Fig. 5.1. By inspection of the figure we get,

$$\begin{aligned} Q_{11} &= 0, & Q_{12} &= 1, & Q_{13} &= 0, \\ Q_{21} &= \frac{1}{2} \cdot \frac{1}{4} = \frac{1}{8}, & Q_{22} &= \frac{1}{2} \cdot \frac{1}{4} + \frac{1}{2} \cdot \frac{3}{4} = \frac{1}{2}, & Q_{23} &= \frac{1}{2} \cdot \frac{3}{4} = \frac{3}{8}, \\ Q_{31} &= 0, & Q_{32} &= \frac{1}{2}, & Q_{33} &= \frac{1}{2}. \end{aligned}$$

Thus the transition matrix \mathbf{Q} is given by the expression

$$\mathbf{Q} = \begin{pmatrix} 0 & 1 & 0 \\ 1/8 & 1/2 & 3/8 \\ 0 & 1/2 & 1/2 \end{pmatrix},$$

while the initial condition corresponds to the probability vector

$$\langle \mathbf{p}(0) | = (0, 1, 0).$$

Below we proceed as in exercise 5.1 of the book [1].

The following procedure is clear from the Maple printout. First we find eigenvalues of \mathbf{Q} which are equal to $1, \mp 1/4$. The corresponding “right” eigenvectors are:

$$[1, 1, \{[1, 1, 1]\}], \left[\frac{-1}{4}, 1, \left\{\left[6, \frac{-3}{2}, 1\right]\right\}\right], \left[\frac{1}{4}, 1, \{[4, 1, -2]\}\right]$$

Thus we denote $\lambda_1 = 1, \lambda_2 = -1/4, \lambda_3 = 1/4$, and

$$|1\rangle = (1, 1, 1), \quad |2\rangle = (6, -3/2, 1), \quad |3\rangle = (1, 2, -3).$$

The “left” eigenvectors are just the right eigenvalues of the transposed matrix, \mathbf{Q}^T . We have for them the Maple result

$$\left[\frac{1}{4}, 1, \{[1, 2, -3]\}\right], \left[\frac{-1}{4}, 1, \{[1, -2, 1]\}\right], [1, 1, \{[1, 8, 6]\}]$$

Thus,

$$\langle 1| = (1, 8, 6), \quad \langle 2| = (1, -2, 1), \quad \langle 3| = (1, -2, 1).$$

It is easy to prove that

$$\langle i|k\rangle = n_i \delta_{ik}, \quad \text{where } n_1 = 15, n_2 = 10, n_3 = 12.$$

Now we construct matrices $P_i = |i\rangle\langle i|$ to get

$$P_1 = \begin{pmatrix} 1 & 8 & 6 \\ 1 & 8 & 6 \\ 1 & 8 & 6 \end{pmatrix}, \quad P_2 = \begin{pmatrix} 6 & -12 & 6 \\ -3/2 & 3 & -3/2 \\ 1 & -2 & 1 \end{pmatrix}, \quad P_3 = \begin{pmatrix} 4 & 8 & -12 \\ 1 & 2 & -3 \\ -2 & -4 & 6 \end{pmatrix}.$$

Now, $\mathbf{P}(s_0|s) = \mathbf{P}(s - s_0)$ with

$$\begin{aligned} \mathbf{P}(s) &= \sum_i \frac{\lambda_i^s}{n_i} P_i \\ &= \begin{bmatrix} \frac{1}{15} + \frac{3}{5} \left(\frac{-1}{4}\right)^s + \frac{1}{3} \left(\frac{1}{4}\right)^s & \frac{8}{15} - \frac{6}{5} \left(\frac{-1}{4}\right)^s + \frac{2}{3} \left(\frac{1}{4}\right)^s & \frac{2}{5} + \frac{3}{5} \left(\frac{-1}{4}\right)^s - \left(\frac{1}{4}\right)^s \\ \frac{1}{15} - \frac{3}{20} \left(\frac{-1}{4}\right)^s + \frac{1}{12} \left(\frac{1}{4}\right)^s & \frac{8}{15} + \frac{3}{10} \left(\frac{-1}{4}\right)^s + \frac{1}{6} \left(\frac{1}{4}\right)^s & \frac{2}{5} - \frac{3}{20} \left(\frac{-1}{4}\right)^s - \frac{1}{4} \left(\frac{1}{4}\right)^s \\ \frac{1}{15} + \frac{1}{10} \left(\frac{-1}{4}\right)^s - \frac{1}{6} \left(\frac{1}{4}\right)^s & \frac{8}{15} - \frac{1}{5} \left(\frac{-1}{4}\right)^s - \frac{1}{3} \left(\frac{1}{4}\right)^s & \frac{2}{5} + \frac{1}{10} \left(\frac{-1}{4}\right)^s + \frac{1}{2} \left(\frac{1}{4}\right)^s \end{bmatrix} \end{aligned}$$

As it should be, $\mathbf{P}(0) = \mathbf{I}$. In this way we solve the part (a).

Now we come to the point (b). Straightforward calculation gives

$$\begin{aligned} \langle \mathbf{P}(s) | &= \langle \mathbf{p}(0) | \mathbf{P}(s) \\ &= \left[\frac{1}{15} - \frac{3}{20} \left(\frac{-1}{4}\right)^s + \frac{1}{12} \left(\frac{1}{4}\right)^s, \frac{8}{15} + \frac{3}{10} \left(\frac{-1}{4}\right)^s + \frac{1}{6} \left(\frac{1}{4}\right)^s, \frac{2}{5} - \frac{3}{20} \left(\frac{-1}{4}\right)^s - \frac{1}{4} \left(\frac{1}{4}\right)^s \right]. \end{aligned}$$

We are asked to find the probability of the configuration 3. After 2 steps it is 3/8, and at $s \rightarrow \infty$ we get 2/5.

The part (c) is calculated in a straightforward way. We obtain

$$\begin{aligned} \langle y(s) \rangle &= \frac{29}{5} - \frac{3}{10} \left(\frac{-1}{4}\right)^s - \frac{3}{2} \left(\frac{1}{4}\right)^s, \\ \langle y(0)y(s) \rangle &= \frac{79}{50} (-1)^{(1+s)} 4^{(-s)} - \frac{33}{4} 16^{(-s)} + \frac{81}{100} (-1)^{(1+2s)} 16^{(-s)} \\ &\quad + \frac{11}{2} (-1)^{(1+s)} 16^{(-s)} - \frac{3}{2} 4^{(-s)} + \frac{841}{25} \end{aligned}$$

Problem 5.2: Three boys, A, B, and C, stand in a circle and play catch (B stands to the right of A). Before throwing the ball, each boy flips a coin to decide whether to throw to the boy on his right or left. If “heads” comes up, the boy throws to his right. If “tails” come up, the boy throws to his right.

The coin of boy A is “fair” (50% heads and 50% tails), the coin of boy B has head of both sides, and the coin of boy C is weighted (75% heads and 25% tails).

- Compute the transition matrix, its eigenvalues, and its left and right eigenvalues.
- If the ball is thrown in regular intervals, approximately what fraction of time each boy have the ball (assuming they throw the ball many times)?
- If boy A has the ball to begin with, what is the chance it has it after 2 throws? What is the chance he will have in after s throws.

Solution 5.2: The problem is similar to the previous one. Let us map the notations

$$A \rightarrow 1, \quad B \rightarrow 2, \quad C \rightarrow 3,$$

and note that “right” means counterclockwise. Then

$$Q_{12} = Q_{13} = 1/2, \quad Q_{23} = 1, \quad Q_{21} = 0, \quad Q_{31} = 3/4, \quad Q_{32} = 1/4.$$

At the same time $Q_{11} = Q_{22} = Q_{33} = 0$. As a result, the transition matrix has the form

$$\mathbf{Q} = \begin{pmatrix} 0 & 1/2 & 1/2 \\ 0 & 0 & 1 \\ 3/4 & 1/4 & 0 \end{pmatrix}.$$

The following solution is similar to the previous problem (see the Maple printout). Note that the eigenvalues and eigenvectors are complex, but conjugated. It means that the probability is real, but oscillates in time).

The answers are: after many throws the chance for the boy A to hold the ball is $6/19$; starting from the given initial conditions his chance to hold the ball after 2 throws is $3/8$.

Problem 5.3: A trained mouse lives in the house shown in Fig. 5.2.

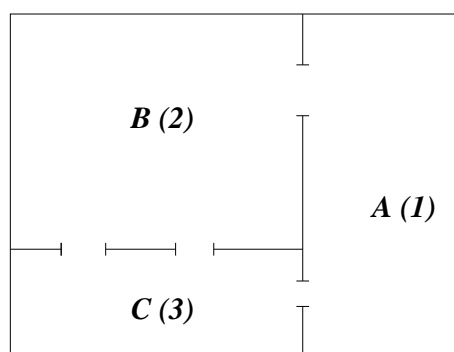


Figure 5.2:

A bell rings at regular intervals (short compared with the mouse's lifetime). Each time it rings, the mouse changes rooms. When he changes rooms, he is equally likely to pass through any of the doors of the room he is in.

Let the stochastic variable Y denote “mouse in a particular room”. There are 3 realizations of Y :

1. “Mouse in room A”
2. “Mouse in room B”
3. “Mouse in room C”

which we denote as $y(1)$, $y(2)$, and $y(3)$, respectively.

- compute the transition matrix, \mathbf{Q} , and the conditional probability matrix, $\mathbf{P}(s_0|s)$.
- . Compute the probability vector, $\langle \mathbf{P}(s) |$, at time s , given that the mouse starts in room C. Approximately, what fraction of his life does he spend in each room?
- Assume that the realization, $y(n)$ equals to n . Compute the moment, $\langle y(s) \rangle$, and the auto-correlation function, $\langle y(0)y(s) \rangle$, for the same initial condition as in part (b).

Solution 5.3: The problem is very much similar to the previous ones. We have

$$Q_{12} = Q_{13} = 1/2, \quad Q_{21} = 1/3, \quad Q_{23} = Q_{32} = 2/3, \quad Q_{31} = 1/3, \quad Q_{ii} = 0.$$

Thus

$$\mathbf{Q} = \begin{pmatrix} 0 & 1/2 & 1/2 \\ 1/3 & 0 & 2/3 \\ 1/3 & 2/3 & 0 \end{pmatrix}.$$

Now we do the same as in previous problems (see Maple printout). The answers are obvious from the printout.

Problem 5.4: The doors in the mouse's house shown in Fig. 5.2 so they get periodically larger and smaller. This causes the mouse's transition between the rooms to become time periodic. Let the stochastic variable Y have the same meaning as in Problem 5.3. The transition matrix is now given by

$$\begin{aligned} Q_{11}(s) = Q_{22}(s) = Q_{33}(s) &= 0, & Q_{12}(s) &= \cos^2(\pi s/2), & Q_{13}(s) &= \sin^2(\pi s/2), \\ Q_{21}(s) &= 1/4 + (1/2) \sin^2(\pi s/2), & Q_{23}(s) &= 1/4 + (1/2) \cos^2(\pi s/2) \\ Q_{31}(s) &= (1/2) \cos^2(\pi s/2), & Q_{32}(s) &= (1/2) + (1/2) \sin^2(\pi s/2), \end{aligned}$$

- If initially the mouse is in room A, what is the probability to find it in room A after $2s$ room changes?
- If initially the mouse is in room B, what is the probability to find it in room A after $2s$ room changes? In room B?

Solution 5.4: The solution is rather tedious, but obvious from the Maple file.

Problem 5.5: Consider a discrete random walk on a one-dimensional *periodic* lattice with $2N + 1$ sites (label the sites from $-N$ to N). Assume that the walker is equally likely to move on the lattice site to the left or right at each step. Treat this problem as a Markov chain.

- Compute the transition matrix, \mathbf{Q} , and the conditional probability, $\mathbf{P}(s_0|s)$.
- Compute the probability $P_1(n, s)$ at time s , given the walker starts at site $n = 0$.
- If the lattice has 5 sites ($N = 2$), compute the probability to find the walker on each site after $s = 2$ steps and after $s = \infty$ steps. Assume that the walker starts at site $n = 0$.

Hint: Let us understand the word *periodic* as periodically extended, i. e. possessing the property

$$P[n + (2N + 1), t] = P(n, t).$$

Solution 5.5: The transition probabilities are given by the expressions

$$w_{n-1, n} = w_{n, n-1} = w_{n+1, n} = w_{n, n+1} = 1/2.$$

The Master equation has the form

$$\begin{aligned} dP_n/ds &= w_{n-1, n}P_{n-1} + w_{n+1, n}P_{n+1} - P_n(w_{n, n-1} + w_{n, n+1}) \\ &= (1/2)(P_{n-1} + P_{n+1} - 2P_n). \end{aligned}$$

Let us look for the solution in the form

$$P_n(s) \propto e^{\lambda s + i\kappa n}.$$

Then we get

$$\lambda = -[1 - \cos(\kappa)] = -2 \sin^2(\kappa/2).$$

Now we have to find κ . If we apply cyclic boundary conditions (assuming that the word *periodic* in the problem formulation means that) we have to require: $P(n + 2N + 1) = P(n)$ at any s . Thus

$$e^{i\kappa(2N+1)} = 1 \quad \rightarrow \quad \kappa(2N + 1) = 2\pi k,$$

where k is the integer number ranging from $-N$ to N . Thus, the general solution is

$$P(n, s) = \sum_{k=-N}^N P_k \exp \left[-in \frac{2\pi k}{2N+1} - 2s \sin^2 \frac{\pi k}{2N+1} \right].$$

The quantities P_k should be found from the initial conditions. At $s = 0$ we can rewrite the l. h. s. of the requirement $P(n, 0) = \delta_{n,0}$ in the form

$$P(n, 0) = \sum_{k=-N}^N P_k e^{-in2\pi k/(2N+1)}.$$

On the other hand,

$$\delta_{n,0} = \frac{1}{2N+1} \sum_{k=-N}^N e^{-in2\pi k/(2N+1)}.$$

From that we immediately get $P_k = \text{const}(k)$. The proper constant $1/\mathcal{N}(s)$ is the normalization coefficient found from the condition

$$\sum_{n=-N}^N P(n,s) = 1.$$

Finally

$$P(n,s) = \frac{1}{\mathcal{N}(s)} \sum_{k=-N}^N \exp \left[-in \frac{2\pi k}{2N+1} - 2s \sin^2 \frac{\pi k}{2N+1} \right].$$

Here

$$\mathcal{N}(s) = \sum_{n=-N}^N \exp \left[-in \frac{2\pi k}{2N+1} - 2s \sin^2 \frac{\pi k}{2N+1} \right] = 2N+1.$$

Now let us find the conditional probability $P(n,s|m,0)$. Now we have to apply the initial condition $P(n,0) = \delta_{n,0}$, or

$$P(n,0) = \sum_{k=-N}^N P_k e^{-in2\pi k/N} = \delta_{n,m} = \sum_{k=-N}^N P_k e^{-i(n-m)2\pi k/(2N+1)}.$$

Thus,

$$P_k = \infty e^{im2\pi k/(2N+1)}.$$

Consequently,

$$\mathbf{P}(s-s_0|0)_{mn} = P(n,s|m,0) = \frac{1}{2N+1} \sum_{k=-N}^N \exp \left[-i(n-m) \frac{2\pi k}{2N+1} - 2s \sin^2 \frac{\pi k}{2N+1} \right].$$

As $s \rightarrow \infty$ the probability tends to $1/(2N+1)$. The calculation for $N=2$ is straightforward, see Maple file. Finally, the matrix $\mathbf{Q}_{mn} = \mathbf{P}(1|0)_{mn}$.

Problem 5.6: At time t , a radioactive sample contains n identical undecayed nuclei, each with the probability for the unit time, λ , of decaying. The probability of decay during the time $t \rightarrow t + \Delta t$ is $\lambda \Delta t$. Assume that at time $t = 0$ there are n_0 undecayed nuclei present.

- Write down and solve the master equation of the process [find $P_1(n,t)$].
- Compute the the mean number of undecayed nuclei and the variance as a function of time.
- What is the half-life of this decay process?

Solution 5.6: The master equation has the form

$$\frac{dP}{dt} = -\lambda n P(n, t) + \lambda(n+1) P(n+1, t).$$

This is a linear master equation, and we solve it by the method of generating functional, p. 262 of the book [1]. We introduce

$$F(z, t) = \sum_{n=-\infty}^{\infty} z^n P_1(n, t).$$

Then we multiply the master equation by z^n and sum over n . We get

$$\frac{\partial F}{\partial t} = -\lambda(z-1) \frac{\partial F}{\partial z}. \quad (5.1)$$

Indeed,

$$\sum_n z^n (n+1) P(n+1, t) = \frac{d}{dz} \sum_n z^{n+1} P(n+1, t) = \frac{\partial F}{\partial z}.$$

In a similar way

$$\sum_n z^n n P(n, t) = z \sum_n z^{n-1} n P(n, t) = z \frac{\partial F}{\partial z}$$

Introducing $\tau = \lambda t$ we rewrite Eq. 5.1 in the form

$$\frac{\partial F}{\partial \tau} + (z-1) \frac{\partial F}{\partial z} = 0. \quad (5.2)$$

The characteristics of this equation meet the equation

$$d\tau = \frac{dz}{z-1} \quad \rightarrow \quad \ln(z-1) - \tau = \text{const}.$$

Consequently,

$$F(z, t) = \Phi \left(e^{-\tau + \ln(z-1)} \right) = \Phi \left[(z-1) e^{-\tau} \right].$$

Since $P(n, 0) = \delta_{n, n_0}$ we get

$$\Phi(z-1) = z^{n_0} \quad \rightarrow \quad \Phi(u) = (u+1)^{n_0}.$$

As result,

$$F(z, t) = [(z-1)e^{-\tau} + 1]^{n_0}.$$

Now,

$$\langle n(t) \rangle = \left(\frac{\partial F}{\partial z} \right)_{z=1} = n_0 e^{-\tau}.$$

In a similar way,

$$\langle n^2(t) \rangle - \langle n(t) \rangle^2 = n_0 e^{-\tau} (1 - e^{-\tau}).$$

To find the probabilities let us express the quantity

$$[(z-1)e^{-\tau} + 1]^{n_0} = e^{-n_0\tau} [z + (e^\tau - 1)]^{n_0} = e^{-n_0\tau} \sum_{n=0}^{n_0} \frac{n_0!}{n!(n_0-n)!} z^n (e^\tau - 1)^{n_0-n}.$$

Thus,

$$P_1(n, \tau) = \frac{n_0!}{n!(n_0-n)!} e^{-n_0\tau} (1 - e^{-\tau})^{n_0-n}.$$

Problem 5.7: Consider a random walk on the lattice shown in Fig. 5.3. The transition rates are

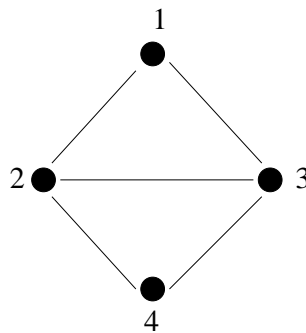


Figure 5.3: A sketch to the problem 5.7.

$$w_{12} = w_{13} = 1/2, \quad w_{21} = w_{23} = w_{24} = 1/3, \quad w_{31} = w_{32} = w_{34} = 1/3, \\ w_{42} = w_{43} = 1/2, \quad w_{14} = w_{41} = 0.$$

- Write the transition matrix, \mathbf{W} , and show that that this system obey detailed balance.
- Compute the symmetric matrix, \mathbf{V} , and find its eigenvalues and eigenvectors.
- Write $P_1(n, t)$ for the case $P(n, 0) = \delta_{n,1}$. What is $P(4, t)$?

Solution 5.7: The solution is similar to the Exercise 5.2 in p. 245 of the book [1]. The answers are obvious from the Maple file.

Problem 5.8: Consider a random walk on the lattice shown in Fig. 5.4. The site P absorbs the walker. The transition rates are

$$w_{12} = w_{13} = 1/2 \quad w_{21} = w_{23} = w_{2P} = 1/3, \\ w_{31} = w_{32} = w_{3P} = 1/3, \quad w_{P1} = w_{P2} = 1/2.$$

- Write the transition matrix, \mathbf{M} , and compute its eigenvalues and eigenvectors.
- In the walker starts at site $n = 1$ at time $t = 0$, compute the mean first passage time.

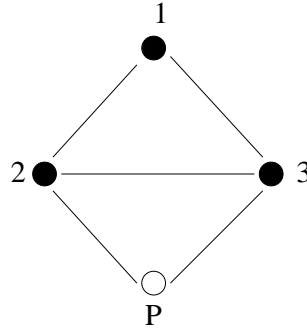


Figure 5.4: A sketch to the problem 5.8.

Solution 5.8: The solution is similar to the Exercise 5.4 of the book [1]. The answers are clear from the Maple file.

Problem 5.9: Let us consider on RL electric circuit with resistance, R , and inductance, L , connected in series. Even there is no average electromotive force (EMF) exists across the resistor, because of the discrete character of electrons in the circuit and their random motion, a fluctuating EMF, $\xi(t)$, exists whose strength is determined by the temperature, T . This, in turn, induces the fluctuating current, $I(t)$, in the circuit. The Langevin equation for the current is

$$L \frac{dI(t)}{dt} + RI(t) = \xi(t). \quad (5.3)$$

If the EMF is delta-correlated,

$$\langle \xi(t_2)\xi(t_1) \rangle = g \delta(t_2 - t_1)$$

and $\langle \xi(t) \rangle_\xi = 0$, compute g and the current correlation function $\langle \langle I(t_2)I(t_1) \rangle_\xi \rangle_T$. Assume that the average magnetic energy $L \langle I_0^2 \rangle_T / 2 = kT/2$ and $\langle I_0 \rangle_T = 0$ where $I(0) = I_0$.

Solution 5.9: Let us divide Eq. (5.3) by R , denote $L/R \equiv \tau$ and measure time in units of τ and the current in units $I_1 \equiv R^{-1} \sqrt{g}$. Namely, define $\theta = t/\tau$, and $j(t) = I(t)/I_1$. Then the equation for the current has the form

$$dj/d\theta + j = \eta(\theta), \quad \langle \eta(\theta_2)\eta(\theta_1) \rangle = \delta(\theta - \theta_1).$$

Its solution has the form

$$j(\theta) = j_0 e^{-\theta} + \int_0^\theta ds e^{s-\theta} \eta(s).$$

Multiplying solutions for $j(\theta_2)$ and for $j(\theta_1)$ and averaging over realizations of η we get

$$\begin{aligned} \langle j(\theta_2)j(\theta_1) \rangle_\eta &= j_0^2 e^{-(\theta_2+\theta_1)} \\ &+ \int_0^{\theta_2} ds_2 \int_0^{\theta_1} ds_1 \delta(s_2 - s_1) e^{s_1+s_2-\theta_1-\theta_2} \\ &= \left(j_0^2 - \frac{1}{2} \right) e^{-\theta_1-\theta_2} + \frac{1}{2} e^{-|\theta_2-\theta_1|}. \end{aligned}$$

The first item must vanish since in the equilibrium the process must be *stationary*, i. e. it must depend only on the difference $\theta_2 - \theta_1$. Thus,

$$\langle j_0^2 \rangle_T = \frac{1}{2} \quad \rightarrow \quad \langle I_0^2 \rangle_T = \frac{g}{2R^2}.$$

On the other hand,

$$L \langle I_0^2 \rangle = kT \quad \rightarrow \quad g = 2R^2 kT / L.$$

Consequently,

$$\langle \langle j(\theta_2) j(\theta_1) \rangle_\eta \rangle_T = \frac{1}{2} e^{-|\theta_2 - \theta_1|},$$

In dimensional variables,

$$\langle \langle I(t_2) I(t_1) \rangle_\xi \rangle_T = I_1^2 \langle \langle j(\theta_2) j(\theta_1) \rangle_\eta \rangle_T = \frac{kT}{L} e^{-|t_2 - t_1|/\tau}.$$

Problem 5.10: Due to the random motion and discrete nature of electrons, an LRC series circuit experience a random electromotive force (EMF), $\xi(t)$. This, in turn, induces a random varying charge, $Q(t)$, on the capacitor plates and a random current, $I(t) = dQ(t)/dt$, through the resistor and inductor. The random charge, $Q(t)$, satisfies the Langevin equation

$$L \frac{d^2 Q}{dt^2} + R \frac{dQ}{dt} + \frac{Q}{C} = \xi(t).$$

Assume that EMF is delta-correlated,

$$\langle \xi(t_2) \xi(t_1) \rangle = g \delta(t_2 - t_1)$$

and $\langle \xi(t) \rangle_\xi = 0$. Assume that the circuit is at the temperature T and the average magnetic energy in the inductor and average electric energy in the capacitor satisfy the equipartition theorem,

$$\frac{1}{2} L \langle I_0^2 \rangle_T = \frac{1}{2C} \langle Q_0^2 \rangle_T,$$

where $Q(0) = Q_0$, $I(0) = I_0$. Assume that $\langle I_0 \rangle_T = 0$, $\langle Q_0 \rangle_T = 0$, $\langle Q_0 I_0 \rangle_T = 0$.

(a) Compute the current correlation function $\langle \langle I(t_2) I(t_1) \rangle_\xi \rangle_T$.

(b) Compute the variance of the charge distribution, $\langle \langle (Q(t) - Q_0)^2 \rangle_\xi \rangle_T$.

Solution 5.10: The problem is exactly the same as in the Exercise 5.5 of the book [1]. After mapping

$$Q \rightarrow x, \quad I \rightarrow v, \quad L \rightarrow m, \quad LC \rightarrow \omega_0^2, \quad R \rightarrow \gamma$$

we obtain the same equation. Thus,

$$\langle\langle I(t+\tau)I(t) \rangle\rangle_{\xi T} = \frac{kT}{L} e^{-\Gamma|\tau|} C(|\tau|),$$

where

$$C(\tau) = \cosh \delta\tau - (\Gamma/\delta) \sinh \delta\tau, \quad \Gamma = R/L, \quad \delta = \sqrt{\Gamma^2 - \omega_0^2}.$$

The variance of charge distribution can be calculated by integrating the formal solution

$$I(t) = I_0 e^{-\Gamma t} - Q_0 \frac{\omega_0^2}{\delta} e^{-\Gamma t} \sinh \delta t + \frac{1}{L} \int_0^t dt' \xi(t') e^{-\Gamma(t-t')} C(t-t')$$

over time:

$$\begin{aligned} Q(t) = & Q_0 + I_0 \frac{1 - e^{-\Gamma t}}{\Gamma} - Q_0 \frac{\omega_0^2}{2\delta} \left(\frac{1 - e^{-(\Gamma-\delta)t}}{\Gamma-\delta} - \frac{1 - e^{-(\Gamma+\delta)t}}{\Gamma+\delta} \right) \\ & + \frac{1}{L} \int_0^t dt'' \int_0^{t''} dt' \xi(t') e^{-\Gamma(t''-t')} C(t''-t') \end{aligned}$$

Now we do averages over ξ and T to obtain (linear terms vanish!)

$$\begin{aligned} \langle\langle Q^2(t) \rangle\rangle_{\xi T} = & \langle Q_0^2 \rangle_T \left[1 - \frac{\omega_0^2}{2\delta} \left(\frac{1 - e^{-(\Gamma-\delta)t}}{\Gamma-\delta} - \frac{1 - e^{-(\Gamma+\delta)t}}{\Gamma+\delta} \right) \right]^2 + \langle I_0^2 \rangle_T \left(\frac{1 - e^{-\Gamma t}}{\Gamma} \right)^2 \\ & + \frac{g}{L^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 e^{-\Gamma(t_1-t_2+t_3-t_4)} C(t_1-t_2) C(t_3-t_4) \delta(t_2-t_4) \end{aligned}$$

Now we substitute $\langle Q_0^2 \rangle_T = CkT$, $\langle I_0^2 \rangle_T = kT/L$, and $g = 4RkT$, and then apply δ function. The last term becomes

$$\frac{4RkT}{L^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 e^{-\Gamma(t_1-2t_2+t_3)} C(t_1-t_2) C(t_3-t_2).$$

The rest integrations must be done explicitly which results in lengthy expressions.

Problem 5.11: Consider a Brownian particle of mass m in one dimension in the presence of a constant force f_0 in a fluid with force constant γ and in the presence of a delta-correlated random force $\xi(t)$ such that $\langle \xi(t_1)\xi(t_2) \rangle_{\xi} = g\delta(t_1-t_2)$ and $\langle \xi(t) \rangle_{\xi} = 0$. Assume that the velocity and displacement of the Brownian particle at $t=0$ are v_0 and x_0 , respectively.

- Compute the velocity correlation function $\langle v(t_1)v(t_2) \rangle_{\xi}$.
- Compute the displacement variance $\langle (x(t) - x_0)^2 \rangle$.

Solution 5.11: The differential equation for the particle is

$$\frac{dv(t)}{dt} + \frac{\gamma}{m}v(t) - \frac{f_0}{m} = \frac{1}{m}\xi(t), \quad \frac{dx}{dt} = v(t).$$

Its solution is

$$v(t) = v_0 e^{-(\gamma/m)t} + \frac{f_0}{\gamma} \left(1 - e^{-(\gamma/m)t}\right) + \frac{1}{m} \int_0^t dt' e^{(\gamma/m)(t'-t)} \xi(t').$$

The quantity

$$v_d(t) = \frac{f_0}{\gamma} \left(1 - e^{-(\gamma/m)t}\right)$$

is just the drift velocity in the force f_0 . Using results of the Sec. 5.E.1 of the book [1] we obtain

$$\langle\langle [v(t+\tau) - v_d(t+\tau)][v(t) - v_d(t)] \rangle\rangle_{\xi} = \frac{kT}{m} e^{-(\gamma/m)|\tau|}.$$

Since $\langle v(t) \rangle_T = v_d(t)$ we obtain

$$\langle\langle v(t+\tau)v(t) \rangle\rangle_{\xi} = v_d(t+\tau)v_d(t) + \frac{kT}{m} e^{-(\gamma/m)|\tau|}.$$

In a similar way, we can introduce drift displacement

$$x_d(t) = \int_0^t dt' \frac{f_0}{\gamma} \left(1 - e^{-(\gamma/m)t'}\right) = \frac{f_0}{\gamma} \left[t - \frac{m}{\gamma} \left(1 - e^{-(\gamma/m)t}\right) \right].$$

Finally we obtain

$$\langle\langle [x(t) - x_0 - x_d(t)]^2 \rangle\rangle_{\xi} = \frac{2kT}{\gamma} \left[t - \frac{m}{\gamma} \left(1 - e^{-(\gamma/m)t}\right) \right].$$

Tests for training

Problem 5.12: Stochastic processes

Consider an electron (spin $S = 1/2$) bounded to an impurity center and assume that the temperature T is much less than the energy difference between the levels of orbital motion. Consequently, only spin degrees of freedom are excited.

Let the system be placed in external magnetic field B , the additional energy in magnetic field is $\pm\beta B$ where \pm corresponds to the values $\pm 1/2$ of the spin component along the field. Here $\beta = |e|\hbar/2mc$ is the Bohr magneton, c is the velocity of light since the Gaussian system is used. The magnetic moment of the states with $S_z = \pm 1/2$ is $\mp\beta$.

(a) Find the stationary probabilities for the states with $S_z = \pm 1/2$, P_{\pm} .

- Find average magnetic moment of the system as function of temperature T and magnetic field B .

(b) Find mean square fluctuation of magnetic moment, $\langle(\Delta M)^2\rangle$ and the ratio $\langle(\Delta M)^2\rangle/\langle M\rangle^2$.

- Show that

$$\langle(\Delta M)^2\rangle = \frac{\beta^2}{\cosh^2(\beta B/T)}. \quad (5.4)$$

- Discuss limiting cases of large and low temperatures. Explain these results qualitatively.

(c) Write down the Master Equation for the probability $P_i(t)$ to find the system in the state $i = \pm$ at time t .

- Using the result for the stationary case find the relation between the transition probabilities W_{+-} and W_{-+} for the transition from the state “+” to the state “-” and for the reverse transition, respectively. Express the probabilities W_{+-} and W_{-+} through the quantity $W = W_{+-} + W_{-+}$.

- Derive the Master Equation for the population difference, $\mathcal{P}(t) \equiv w_+(t) - w_-(t)$.

(d) Write down the Master Equation for the *conditional probability*, $P(f, t|i, t_0)$, to find the system in the state f at time t under the conditions that at time t_0 it was in the state i .

- Specify initial conditions to this equation.

- Show that solution of this equation with proper initial condition is

$$P(f, t|i, t_0) = w_f + (\delta_{if} - w_f)e^{-W|t-t_0|} \quad (5.5)$$

where w_f is the stationary probability to find the system in the state f .

Hint: It is convenient to express the set of Master Equations for the quantities $P(f, t|i, t_0)$ at different i and f as an equation for the 2×2 matrix \hat{P} with matrix elements $P_{fi}(t|t_0) \equiv P(f, t|i, t_0)$. The solution of the matrix Master Equation $\partial\hat{P}/\partial T = \hat{W}\hat{P}$ at $t \geq t_0$ can then be searched in the matrix as $\hat{P} \propto \sum_k \hat{C}^{(k)} e^{-\lambda_k(t-t_0)}$. Here λ_k are eigenvalues of the matrix W , while $\hat{C}^{(k)}$ are time-independent matrices. They are determined from the initial conditions and from the fact that at $t - t_0 \rightarrow \infty$ the conditional probabilities tend to the stationary ones.

(e) Using Eq. (5.5) show that the correlation function $\langle\Delta M(t)\Delta M(0)\rangle$ has the form

$$\langle\Delta M(t)\Delta M(0)\rangle = \langle(\Delta M)^2\rangle e^{-W|t|} \quad (5.6)$$

where $\langle(\Delta M)^2\rangle$ is given by Eq. (5.4) while $W = W_{+-} + W_{-+}$.

- Find the fluctuation spectrum.

Solution 5.12: (a) Denote w_{\pm} the probabilities of the states $S_z = \pm 1/2$. We have

$$M = -\beta(w_+ - w_-). \quad (5.7)$$

According to the Gibbs distribution,

$$w_+/w_- = e^{-2\beta B/T}. \quad (5.8)$$

Since only 2 spin levels are involved,

$$w_+ + w_- = 1. \quad (5.9)$$

Combining Eqs. (5.8) and (5.9) we obtain,

$$w_+ = \frac{1}{e^{2\beta B/T} + 1}, \quad w_- = \frac{e^{2\beta B/T}}{e^{2\beta B/T} + 1}, \quad w_- - w_+ = \tanh\left(\frac{\beta B}{T}\right) \quad (5.10)$$

As a result,

$$M = \beta \tanh\left(\frac{\beta B}{T}\right) \quad (5.11)$$

(b) We get:

$$\begin{aligned} \langle M^2 \rangle &= \beta^2 (w_+ + w_-) = \beta^2 \\ \langle M \rangle^2 &= \beta^2 \tanh^2(\beta B/T). \end{aligned} \quad (5.12)$$

As a result,

$$\langle (\Delta M)^2 \rangle = \frac{\beta^2}{\cosh^2(\beta B/T)}, \quad \frac{\langle (\Delta M)^2 \rangle}{\langle M \rangle^2} = \frac{1}{\sinh^2(\beta B/T)} \quad (5.13)$$

At low temperatures, $T \ll \beta B$, fluctuations are exponentially suppressed because spin is aligned to magnetic field.

(c) The equation reads,

$$\frac{\partial w_i(t)}{\partial t} = - \sum_{s=\pm} [W_{i \rightarrow s} w_i(t) - W_{s \rightarrow i} w_s(t)] \quad (5.14)$$

- In the stationary situation, using the detailed equilibrium principle,

$$W_{i \rightarrow s} w_i(t) = W_{s \rightarrow i} w_s(t)$$

we obtain

$$\frac{W_{+-}}{W_{-+}} = \frac{w_-}{w_+} = e^{2\beta B/T}, \quad W_{-+} = \frac{W}{1 + e^{2\beta B/T}}, \quad W_{+-} = \frac{W}{1 + e^{-2\beta B/T}} \quad (5.15)$$

- Coming back to Eq. (5.14) we get

$$\begin{aligned} \frac{\partial w_+(t)}{\partial t} &= -W_{+-} w_+(t) + W_{-+} w_-(t), \\ \frac{\partial w_-(t)}{\partial t} &= -W_{-+} w_-(t) + W_{+-} w_+(t). \end{aligned} \quad (5.16)$$

Subtracting equations we arrive at the result,

$$\frac{\partial \mathcal{P}(t)}{\partial t} = -W \mathcal{P}(t) \quad (5.17)$$

(d) We consider a *stationary* random process, and $P(f, t|i, t_0)$ is a function of $t - t_0$. Let us assume $t_0 = 0$, $t \geq 0$ and denote Let us for brevity denote $P(f, t|i, 0) \equiv P_{fi}(t)$. The Master Equation for $P_{fi}(t)$ has the form

$$\frac{\partial P_{fi}(t)}{\partial t} = - \sum_s [W_{f \rightarrow s} P_{fi}(t) - W_{s \rightarrow f} P_{si}(t)]. \quad (5.18)$$

The initial condition to this equation is

$$P_{fi}(t) = \delta_{if} \quad \text{at} \quad t \rightarrow 0. \quad (5.19)$$

Let us introduce the matrix $\hat{P}(t)$ with matrix elements $P_{if}(t) = P(f, t|i, 0)$. Then Eq. (5.18) can be rewritten as

$$\frac{\partial \hat{P}(t)}{\partial t} = \hat{W} \hat{P}(t), \quad \text{with} \quad \hat{W} = \begin{pmatrix} -W_{f \rightarrow s} & W_{s \rightarrow f} \\ W_{f \rightarrow s} & -W_{s \rightarrow f} \end{pmatrix}. \quad (5.20)$$

It is natural to search the solution of Eq. (5.18) in the form $\hat{P}(t) \sum_k \hat{C}^{(k)} e^{-\lambda_k t}$. Then λ_k are the eigenvalues of the matrix \hat{W} while \hat{C}_k are the numerical matrices to be determined from initial conditions at $t = 0$ and from the fact that $P_{fi}(t) \rightarrow w_f$ at $t \rightarrow \infty$. Here w_f is the stationary probability of the state f .

Equating the determinant of $\hat{W} - \lambda \hat{I}$ we get

$$\lambda_1 = 0, \quad \lambda_2 = -W_{f \rightarrow s} + W_{s \rightarrow f} \equiv -W.$$

Here \hat{I} is the unit matrix Then, in general,

$$P_{fi}(t) = C_{fi}^{(1)} + C_{fi}^{(2)} e^{-Wt}$$

where $\hat{C}^{(k)}$ are time-independent matrices. From the initial conditions (5.19),

$$C_{fi}^{(1)} + C_{fi}^{(2)} = \delta_{fi}.$$

On the other hand, at $t \rightarrow \infty$ the conditions probability tends to the stationary one, w_f . Consequently,

$$C_{fi}^{(1)} = w_f.$$

Finally, because of the time reversibility, $P_{fi}(t)$ depends only on $|t|$. As result,

$$P_{fi}(t) = w_f + (\delta_{fi} - w_f) e^{-W|t|}$$

This expression coincides with Eq. (5.5).

(e) By definition,

$$\langle \Delta M(t) \Delta M(0) \rangle = \langle M(t) M(0) \rangle - \langle M \rangle^2 = \sum_{if} M_i M_f [P(f, t|i, 0) - w_f] w_i.$$

Using Eq. (5.5), one can rewrite the above equation as

$$\langle \Delta M(t) \Delta M(0) \rangle = e^{-W|t|} \sum_{if} M_i M_f (\delta_{if} - w_f) w_i = \langle (\Delta M)^2 \rangle e^{-W|t|}$$

This expression coincides with Eq. (5.6).

The fluctuation spectrum is

$$(\Delta M)_\omega = \int_{-\infty}^{\infty} dt e^{-\omega t} \langle \Delta M(t) \Delta M(0) \rangle = \langle (\Delta M)^2 \rangle \int_{-\infty}^{\infty} dt e^{-\omega t - W|t|}.$$

The result reads as,

$$(\Delta M)_\omega = 2 \langle (\Delta M)^2 \rangle \cdot \frac{W}{\omega^2 + W^2}$$

Chapter 6

The Foundations of Statistical Mechanics

This chapter will be skipped this year

Chapter 7

Equilibrium Statistical Mechanics

Quick access: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

Problem 7.1: Compute the structure function for N noninteracting harmonic oscillators, each with frequency ω and mass m . Assume the system has total energy E . Using this structure function and the microcanonical ensemble, compute the entropy and the heat capacity of the system.

Solution 7.1: One can use either classical, or quantum Hamiltonian. Let us do the problem classically. For brevity let us assume the the oscillators are one-dimensional. Then the Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{m\omega^2 x_i^2}{2} \right) = E.$$

The total number of states is

$$\Omega(E) = \int_V dx_1 \int_V dx_2 \dots \int_V dx_N \int dp_1 \int dp_2 \dots \int dp_N \Theta \left[E - \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{m\omega^2 x_i^2}{2} \right) \right].$$

Here

$$\Theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases}$$

is the Heaviside unit step function. We have

$$d\Theta(x)/dx = \delta(x),$$

thus the structure function $\Sigma(E) = \partial\Omega(E)/\partial E$ is given by the equation

$$\Sigma(E) = \int_V dx_1 \int_V dx_2 \dots \int_V dx_N \int dp_1 \int dp_2 \dots \int dp_N \delta \left[E - \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{m\omega^2 x_i^2}{2} \right) \right].$$

Let us use the following trick. Denote $q_i = x_i \sqrt{m\omega^2/2}$, $i = 1..N$, $q_{i+N} = p_i \sqrt{1/2m}$ and $R^2 = E$. Then

$$\Omega = \left(\frac{2}{\omega}\right)^N \int dq_1 \dots \int dq_{2N} \Theta \left(R^2 - \sum_{j=1}^{2N} q_j^2 \right) \equiv \left(\frac{2}{\omega}\right)^N \tilde{\Omega}(R).$$

From the dimensionality considerations,

$$\tilde{\Omega}(R) = A_{2N} R^{2N}.$$

To find the coefficient A_{2N} let us consider the integral

$$\int_{-\infty}^{\infty} dq_1 \dots \int_{-\infty}^{\infty} dq_{2N} \exp \left(- \sum_{j=1}^{2N} q_j^2 \right) = \left(\int_{-\infty}^{\infty} dq e^{-q^2} \right)^{2N} = \pi^N.$$

On the other hand, the same integral is

$$\int_0^{\infty} dR \frac{\partial \tilde{\Omega}}{\partial R} e^{-R^2} = 2NA_{2N} \int_0^{\infty} dR R^{2N-1} e^{-R^2} = NA_{2N} \Gamma(N)$$

Thus

$$A_{2N} = \frac{\pi^N}{N\Gamma(N)}.$$

Finally,

$$\Omega(E) = \frac{1}{N\Gamma(N)} \left(2\pi \frac{E}{\omega} \right)^N, \quad \Sigma(E) = \frac{1}{E\Gamma(N)} \left(2\pi \frac{E}{\omega} \right)^N.$$

Now, the entropy is

$$S/k = \ln \frac{\Omega(E)}{N!h^N} = \ln \left(\frac{E}{\hbar\omega} \right)^N \frac{1}{(N!)^2} = N \ln(E/\hbar\omega) - 2N \ln N + 2N.$$

Here we used the Stirling's formula. Now,

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{Nk}{E} \quad \rightarrow \quad E = NkT, \quad C = kN.$$

This is the classical answer. The quantum calculation is demonstrated in the Exercise 7.1 of the book [1].

Problem 7.2: A system consists of N noninteracting, distinguishable two-level atoms. Each atom can exist in one of two states, $E_0 = 0$, and $E_1 = \varepsilon$. The number of atoms in energy level E_1 is n_1 . The internal energy of the system is $U = n_0 E_0 + n_1 E_1$.

- Compute the entropy of the system as a function of internal energy.
- Compute the heat capacity of a fixed number of atoms, N .

Solution 7.2: Since $E_0 = 0$ the energy U can be realized in $U/\varepsilon \equiv n_1$ particles are in the state 1, and $(N - U/\varepsilon) = N - n_1$ particles are in the state 0. The number of ways to do that is

$$W = \frac{N!}{n_1!(N - n_1)!}$$

Consequently,

$$\frac{S}{k} = \ln \frac{N!}{(N - n_1)!} \approx N \ln N - N - n_1 \ln n_1 + n_1 - (N - n_1) \ln(N - n_1) + (N - n_1).$$

Finally

$$\frac{S}{k} \approx N \ln N - \frac{U}{\varepsilon} \ln \frac{U}{\varepsilon} - \left(N - \frac{U}{\varepsilon}\right) \ln \left(N - \frac{U}{\varepsilon}\right).$$

To find temperature we do usual procedure:

$$\frac{1}{T} = \frac{\partial S}{\partial U} \approx \frac{k}{\varepsilon} \ln \frac{N\varepsilon - U}{U}.$$

As result,

$$U = \frac{N\varepsilon}{e^{\varepsilon/kT} + 1}, \quad C = Nk \left(\frac{\varepsilon}{kT}\right)^2 \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} + 1)^2}.$$

Problem 7.3: A lattice contains N normal lattice sites and N interstitial lattice sites. N identical atoms sit on the lattice, M on the interstitial sites and $N - M$ on the normal sites ($N \gg M \gg 1$). If an atom occupies a normal sites, its energy $E = 0$. If an atom occupies an interstitial site, its energy is $E = \varepsilon$. Compute the internal energy and heat capacity as a function of temperature for this lattice.

Solution 7.3: The internal energy is $U = M\varepsilon$, so we have to express M as a function of temperature. The number of ways in which one can place M atoms at N interstitial sites is

$$W_i = \frac{N!}{M!(N - M)!}.$$

The rest $N - M$ atoms can be placed at N normal states in the same number of ways. Thus

$$W = \left(\frac{N!}{M!(N - M)!}\right)^2 \rightarrow \frac{S}{k} = 2 \ln \frac{N!}{M!(N - M)!}.$$

Using the Stiling's formula we get

$$\begin{aligned} S/k &\approx 2[N \ln N - N - M \ln M + M - (N - M) \ln(N - M) + (N - M)] \\ &\approx 2[N \ln N - M \ln M - (N - M) \ln(N - M)], \\ T^{-1} &= (2k/\varepsilon) \ln(N - M)/M, \quad M = U/\varepsilon. \end{aligned}$$

Thus,

$$U = \frac{N\varepsilon}{e^{\varepsilon/2kT} + 1} \approx N\varepsilon e^{-\varepsilon/2kT}, \quad C \approx 2kN(\varepsilon/2kT)^2 e^{-\varepsilon/2kT}.$$

Problem 7.4: Consider a lattice with N spin-1 atoms with magnetic moment μ . Each atom can be in one of 3 spin states: $S_z = -1, 0, +1$. Let n_{-1} , n_0 and n_1 denote the respective number of atoms in each of those spin states. Find the total entropy and the configuration which maximizes the total entropy. What is the maximum entropy? (Assume that no magnetic field is present, so all atoms have the same energy. Also assume that atoms on different lattice sites cannot be exchanged, so they are distinguishable).

Solution 7.4: We have

$$W = \frac{N!}{n_{-1}!n_0!(N-n_{-1}-n_0)!},$$

$$\ln W \approx N \ln N - n_{-1} \ln n_{-1} - n_0 \ln n_0 - (N - n_{-1} - n_0) \ln(N - n_{-1} - n_0).$$

Differentiating this function by n_{-1} and n_0 and equating the derivatives to 0 we get:

$$n_0 = (N - n_{-1} - n_0) = n_{-1} \quad \rightarrow \quad n_0 = n_1 = n_{-1} = N/3$$

The maximum entropy is

$$S_{\max} = kN \ln 3.$$

Problem 7.5: A system has 3 distinguishable molecules at rest, each with a quantized magnetic moment which can have z -components $+\mu/2$ or $-\mu/2$. Find an expression for the distribution function, f_i (i denotes the configuration), which maximizes entropy subject to the conditions

$$\sum_i f_i = 1, \quad \sum_i M_{i,z} f_i = \gamma \mu,$$

where $M_{i,z}$ is the magnetic moment of the system in the i -th configuration. For the case $\gamma = 1/2$ compute the entropy and compute f_i .

Solution 7.5: Let us measure magnetic moment in units μ . We have 4 configurations with magnetic moments in parentheses

$$\uparrow\uparrow\uparrow (3/2), \quad \uparrow\uparrow\downarrow (1/2), \quad \uparrow\downarrow\downarrow (-1/2), \quad \downarrow\downarrow\downarrow (-3/2).$$

The configurations with magnetic moments $\pm 1/2$ are triply degenerated. Denoting the configurations as 1, 2, 3 and 4, we construct the functional

$$\frac{\tilde{S}}{k} = \sum_i g_i f_i (\alpha + \beta M_{i,z} - \ln f_i).$$

From this expression we get

$$\alpha + \beta M_{i,z} - \ln f_i - 1 = 0 \quad \rightarrow \quad f_i = \exp(1 - \alpha - \beta M_{i,z}).$$

Here g_i is the degeneracy factor: $g_{1,4} = 1$, $g_{2,3} = 3$. We have 2 equations for α and β :

$$\begin{aligned}\sum_i g_i \exp(1 - \alpha - \beta M_{i,z}) &= 1, \\ \sum_i g_i M_{i,z} \exp(1 - \alpha - \beta M_{i,z}) &= \gamma.\end{aligned}$$

or

$$\begin{aligned}2e^{1-\alpha} \left(\cosh \frac{3\beta}{2} + 3 \cosh \frac{\beta}{2} \right) &= 1 \\ 2e^{1-\alpha} \left(\frac{3}{2} \sinh \frac{3\beta}{2} + \frac{3}{2} \sinh \frac{\beta}{2} \right) &= \gamma.\end{aligned}$$

For $\gamma = 1/2$ that yields:

$$\cosh \frac{3\beta}{2} + 3 \cosh \frac{\beta}{2} = 3 \sinh \frac{3\beta}{2} + 3 \sinh \frac{\beta}{2}$$

Denoting $x = e^{\beta/2}$ we can rewrite this equation as

$$x^6 - 3x^2 - 4 = 0,$$

the meaningful solution being

$$x = \sqrt{2}, \quad \text{or} \quad \beta = \ln 2.$$

Consequently,

$$\alpha = 1 + \ln \frac{27\sqrt{2}}{4}.$$

As a result, we have

$$f_i = \mathcal{N} e^{M_{i,z} \ln 2}, \quad \mathcal{N} = \frac{2^{3/2}}{27}.$$

The entropy is

$$\frac{S}{k} = - \sum_i g_i f_i \ln f_i = - \sum_i g_i f_i (\ln \mathcal{N} + M_{i,z} \ln 2) = - \ln \mathcal{N} - \frac{1}{2} \ln 2 = \ln \frac{27}{4}.$$

Problem 7.6: A fluid in equilibrium is contained in the insulated box of volume V . The fluid is divided (conceptually) into m cells. Compute the variance of the enthalpy fluctuations, $\langle (\Delta H_i)^2 \rangle$ in the i -th cell. (For simplicity assume the fluctuations occur at fixed particle number, N_i).

Hint: Use P and S as independent variables.

Solution 7.6: We have

$$\Delta H = T \Delta S + V \Delta P.$$

Thus

$$\langle (\Delta H)^2 \rangle = T^2 \langle (\Delta S)^2 \rangle + V^2 \langle (\Delta P)^2 \rangle.$$

From the general theory the fluctuation probability is proportional to

$$w \propto e^{W_{\min}/kT}, \quad W_{\min} = \Delta U - T \Delta S + P \Delta V \quad (7.1)$$

is the minimum work needed to carry out reversibly the given change in the thermodynamic quantities of small part considered (relative to which the remainder of the body acts as a medium). Expanding ΔU in the series, we obtain

$$\begin{aligned} W_{\min} &= \frac{1}{2} \left[\frac{\partial^2 U}{\partial S^2} (\Delta S)^2 + 2 \frac{\partial U}{\partial S \partial V} \Delta S \Delta V + \frac{\partial^2 U}{\partial V^2} (\Delta V)^2 \right] \\ &= \frac{1}{2} \left[\Delta S \Delta \left(\frac{\partial U}{\partial S} \right)_V + \Delta V \Delta \left(\frac{\partial U}{\partial V} \right)_S \right] \\ &= \frac{1}{2} (\Delta S \Delta T - \Delta P \Delta V). \end{aligned}$$

Thus

$$w \propto \exp \left(\frac{\Delta P \Delta V - \Delta S \Delta T}{2kT} \right). \quad (7.2)$$

One can use this general formula and choose different couples as independent variables. In our case the proper pair is SP . We get

$$\begin{aligned} \Delta V &= \left(\frac{\partial V}{\partial P} \right)_S \Delta P + \left(\frac{\partial V}{\partial S} \right)_P \Delta S, \\ \Delta T &= \left(\frac{\partial T}{\partial P} \right)_S \Delta P + \left(\frac{\partial T}{\partial S} \right)_P \Delta S \\ &= \left(\frac{\partial T}{\partial P} \right)_S \Delta P + \frac{T}{C_P} \Delta S. \end{aligned}$$

The Maxwell relation following from $dH = T dS + V dP$ is

$$\left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial T}{\partial P} \right)_S.$$

Thus

$$\Delta V = \left(\frac{\partial V}{\partial P} \right)_S \Delta P + \left(\frac{\partial T}{\partial P} \right)_S \Delta S.$$

Substituting the above relations into Eq. (7.2) we obtain

$$w \propto \exp \left[\frac{1}{2kT} \left(\frac{\partial V}{\partial P} \right)_S (\Delta P)^2 - \frac{1}{2C_P} (\Delta S)^2 \right].$$

As a result,

$$\langle \Delta S \Delta P \rangle = 0, \quad \langle (\Delta S)^2 \rangle = k C_P, \quad \langle (\Delta P)^2 \rangle = -kT \left(\frac{\partial P}{\partial V} \right)_S.$$

Using these relations we get

$$\langle (\Delta H)^2 \rangle = kT^2 C_P - V^2 kT \left(\frac{\partial P}{\partial V} \right)_S.$$

Problem 7.7: A fluid in equilibrium is contained in the insulated box of volume V . The fluid is divided (conceptually) into m cells. Compute the variance of the internal energy fluctuations, $\langle (\Delta U_i)^2 \rangle$ in the i -th cell. (For simplicity assume the fluctuations occur at fixed particle number, N_i). What happens to the internal energy fluctuations near the critical point?

Solution 7.7: We have,

$$\Delta U = \left(\frac{\partial U}{\partial V} \right)_T \Delta V + \left(\frac{\partial U}{\partial T} \right)_V \Delta T = \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] \Delta V + C_V \Delta T.$$

Now we can use Eq. (7.2) and choose V, T as independent variables. We have:

$$\begin{aligned} \Delta S &= \left(\frac{\partial S}{\partial T} \right)_V \Delta T + \left(\frac{\partial S}{\partial V} \right)_T \Delta V = \frac{C_V}{T} \Delta T + \left(\frac{\partial P}{\partial T} \right)_V \Delta T, \\ \Delta P &= \left(\frac{\partial P}{\partial T} \right)_V \Delta T + \left(\frac{\partial P}{\partial V} \right)_T \Delta V. \end{aligned}$$

The we get

$$\begin{aligned} w &\propto \exp \left[-\frac{C_V}{2kT} (\Delta T)^2 + \frac{1}{2kT} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2 \right], \\ \langle \Delta T \Delta V \rangle &= 0 \quad \langle (\Delta T)^2 \rangle = kT^2 / C_V, \quad \langle (\Delta V)^2 \rangle = -kT \left(\frac{\partial V}{\partial P} \right)_T. \end{aligned}$$

Finally,

$$\langle (\Delta U)^2 \rangle = -kT \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right]^2 \left(\frac{\partial V}{\partial P} \right)_T + kT^2 C_V.$$

Near the critical point $\langle (\Delta U)^2 \rangle \rightarrow \infty$.

Problem 7.8: What is the partition function for a van der Waals gas with N particles? Note that the result is phenomenological and might involve some guessing. It is useful to compare it to the partition function for an ideal gas. Remember that the particles are indistinguishable, so when using a partition function one must insert a counting factor. Use this partition function to compute the internal energy, $U(N, T, V)$, the pressure, $P(N, T, V)$, and the entropy, $S(N, T, V)$.

Solution 7.8: The partition function is ($\beta \equiv (kT)^{-1}$),

$$Z_N = \frac{1}{N!h^{3N}} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \int d\mathbf{p}_1 \dots d\mathbf{p}_N e^{-\beta \mathcal{H}(\{\mathbf{r}, \mathbf{p}\})}.$$

First we can integrate out the momenta,

$$Z_N^{(k)} = \frac{1}{N!h^{3N}} \int d\mathbf{p}_1 \dots d\mathbf{p}_N e^{-\beta \sum_i \mathbf{p}_i^2 / 2m} = \frac{1}{N! \lambda_T^{3N}},$$

where $\lambda_T = h/\sqrt{2\pi mkT}$. Since the partition function for the ideal gas is $Z_N^{(0)} = V^N Z_N^{(k)}$ Then we are left with

$$\frac{Z_N}{Z_N^{(0)}} = \frac{1}{V^N} \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta V(\{\mathbf{r}_i\})} = 1 + \frac{1}{V^N} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \left[e^{-\beta V(\{\mathbf{r}_i\})} - 1 \right] \equiv 1 + z_N.$$

Let us try to consider rarefied gas where only pair interaction is important. Then we can choose $N(N-1)/2$ pair to get

$$z_n \approx \frac{N^2}{2V^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \left[e^{-\beta V(\mathbf{r}_1 - \mathbf{r}_2)} - 1 \right].$$

Introducing the virial coefficient

$$B(T) = \frac{1}{2} \int d\mathbf{r} \left(1 - e^{-\beta V(\mathbf{r})} \right),$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, we obtain

$$z_N = -N^2 B(T)/V.$$

We get

$$A = A_0 - kT \ln(1 + z_n) \approx A_0 - kT z_N = A_0 + kT N^2 B(T)/V, \quad A_0 \equiv -kT \ln Z_N^{(0)}.$$

In the spirit of the van der Waals model let us assume that the interaction is large at $r \leq 2r_0$, and at $r > 2r_0$ the interaction is small. Then

$$\begin{aligned} B(T) &= 2\pi \int_0^{2r_0} r^2 dr \left(1 - e^{-\beta V(\mathbf{r})} \right) + 2\pi \int_{2r_0}^{\infty} r^2 dr \left(1 - e^{-\beta V(\mathbf{r})} \right) \\ &\approx 16\pi r_0^3 / 3 + 2\pi\beta \int_{2r_0}^{\infty} r^2 dr V(\mathbf{r}) \equiv b - a/kT, \end{aligned}$$

where $b = 16\pi r_0^3 / 3$ and $a = \pi \int_{2r_0}^{\infty} r^2 dr V(\mathbf{r})$. Finally,

$$z_n = -\frac{N^2}{V} \left(b - \frac{a}{kT} \right).$$

For an ideal gas,

$$A_0 = -NkT \ln \frac{eV}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} = Nf(T) - NkT \ln(eV/N).$$

Thus,

$$A = Nf(T) - NkT \ln(e/N) - NkT(\ln V - Nb/V) - N^2a/V.$$

Since $\ln(V - Nb) \approx -Nb/V + \ln V$ we get

$$A \approx A_0 - NkT \ln(1 - Nb/V) - N^2a/V.$$

From this we get

$$P = -\frac{\partial A}{\partial V} = \frac{NkT}{V-b} - \frac{N^2a}{V}, \quad S = -\frac{\partial A}{\partial T} = S_0 + kN \ln\left(1 - \frac{Nb}{V}\right),$$

$$U = U_0 - \frac{N^2a}{V} = \frac{3}{2}kT - \frac{N^2a}{V}.$$

Problem 7.9: Consider a solid surface to be a two-dimensional lattice with N_s sites. Assume that N_a atoms ($N_a \ll N_s$) are adsorbed on the surface, so that each site has either 0 or 1 adsorbed atom. At adsorbed atom has energy $E = -\varepsilon$, where $\varepsilon > 0$. Assume that atoms on the surface do not interact with each other.

- If the surface is at temperature T , compute chemical potential of the adsorbed atoms as a function of T , ε , and N_a/N_s (use the canonical ensemble).
- If the surface is in equilibrium with an ideal gas of similar atoms at temperature T , compute the ratio N_a/N_s as a function of pressure, P of the gas. Assume the gas has number density n . (Hint: equate chemical potentials of the adsorbed atoms and the gas).

Solution 7.9:

- The canonical partition function is

$$Z = \frac{1}{N_a!} \sum_{i=1}^{N_s} e^{-\beta E_i} = \frac{N_s!}{N_a!(N_s - N_a)!} e^{\beta N_a \varepsilon}.$$

Here $\beta = 1/kT$. Since $N_a \ll N_s$,

$$Z \approx \frac{N_s^{N_a}}{N_a!} e^{\beta N_a \varepsilon}.$$

Equating this expression to $e^{-N_a \beta \mu}$ we get

$$\mu = -\varepsilon - kT \ln(N_s/N_a).$$

(b) For an ideal gas,

$$\mu = kT \ln \left(\frac{P\lambda_T^3}{kT} \right).$$

Equating chemical potentials, we obtain

$$-\frac{\varepsilon}{kT} - \ln \frac{N_s}{N_a} = \ln \left(\frac{P\lambda_T^3}{kT} \right) \rightarrow \frac{N_a}{N_s} = \frac{P\lambda_T^3}{kT} e^{\varepsilon/kT}.$$

This expression is valid at high temperatures when

$$n\lambda_T^3 \ll e^{-\varepsilon/kT}.$$

Problem 7.10: Consider a two-dimensional lattice lattice lattice in the $x-y$ plane with sides of length L_x and L_y which contain N atoms (N is very large) coupled by nearest neighbor harmonic forces.

- (a) Compute the Debye frequency for this lattice.
 (b) In the limit $T \rightarrow 0$, what is the heat capacity?

Solution 7.10: We follow the section 7.E of the book [1]. Since $N \gg 1$ the boundary conditions are not important, and we can apply zero boundary conditions. As in this exercise, we use continual approximation and replace

$$\sum_{\mathbf{k}} \dots \rightarrow \frac{L_x L_y}{(2\pi)^2} \int dk_x dk_y \dots$$

The the density of states is

$$g(\omega) = \sum_{\mathbf{k}, \alpha} \delta(\omega - \omega_{\mathbf{k}, \alpha}) = \frac{L_x L_y}{(2\pi)^2} \sum_{\alpha} \int d\mathbf{k} \delta(\omega - \omega_{\mathbf{k}, \alpha}).$$

Here α denotes the vibrational mode. In two-dimensional lattice we have two modes, longitudinal, l , and transverse, t . In the Debye approximation it is assumed that the dispersion law $\omega_{\mathbf{k}, \alpha}$ is linear and isotropic:

$$\omega_{\mathbf{k}, \alpha} = c_{\alpha} k, \quad k_i = \frac{\pi}{L_i} s_i, \quad s_i = 1, 2, \dots$$

where c_{α} is the sound velocity for each mode. Since in two-dimensional case

$$\int d\mathbf{k} \dots = \int k dk d\phi \dots = 2\pi \int k dk \dots$$

we obtain

$$g(\omega) = \frac{L_x L_y}{2\pi \hbar^2} \left(\frac{1}{c_l^2} + \frac{1}{c_t^2} \right) \omega.$$

Since the total number of vibrations should be normalized to $2N$, where 2 is the number of modes and N is number of atoms, we should get

$$\int_0^{\omega_D} g(\omega) d\omega = 2N.$$

Consequently

$$2N = \frac{L_x L_y}{4\pi\hbar^2} \left(\frac{1}{c_l^2} + \frac{1}{c_t^2} \right) \omega_D^2$$

and

$$\frac{1}{\omega_D} = \sqrt{\frac{L_x L_y}{8N\pi\hbar^2} \left(\frac{1}{c_l^2} + \frac{1}{c_t^2} \right)}.$$

The density of states can be expressed as

$$g(\omega) = \frac{4N}{\omega_D^2} \omega.$$

As result,

$$C = \frac{4kN}{(\hbar\beta\omega_D)^2} \int_0^{T_D/T} dx \frac{x^3 e^x}{(e^x - 1)^2} = \begin{cases} 2kN, & T \rightarrow \infty \\ 24\zeta(3)kN(T/T_D)^2, & T \rightarrow 0. \end{cases}$$

Here $\zeta(x)$ is the Riemann ζ -function, $\zeta(3) \approx 1.20$, $T_D = \hbar\omega_D/k$.

Problem 7.11: A cubic box (with infinitely hard walls) of volume $V = L^3$ contains an ideal gas of N rigid HCl molecules (assume the effective distance between the H atom and the Cl atom $d = 1.3 \text{ \AA}$).

- If $L = 1.0 \text{ cm}$, what is the spacing between the translation energy levels?
- Write the partition function for this system (include the translational and rotational contributions). At what temperature do rotational degrees of freedom become important.
- Write expressions for the Helmholtz free energy, the entropy, and the heat capacity of the system for temperatures where the rotational degrees of freedom make a significant contributions.

Solution 7.11: Let us put the origin of the reference frame in the cube's corner. Since at the walls the wave function should vanish, for each component α of the momentum \mathbf{p} we get:

$$\sin(p^\alpha L/\hbar) = 0 \quad \rightarrow \quad k_\alpha = n_\alpha \pi/L, \quad k_\alpha \equiv p_\alpha/\hbar.$$

Here n_α is an integer number. Thus the energy levels of translational motion are given by the expression

$$\epsilon_{\mathbf{n}} = \epsilon_0(n_x^2 + n_y^2 + n_z^2), \quad \epsilon_t = \frac{\hbar^2 \pi^2}{2mL^2}.$$

Thus the spacing between the levels is

$$\varepsilon_{n_i+1} - \varepsilon_{n_i} = (2n_i + 1)\varepsilon_t.$$

The rotational degrees of freedom are determined by the moment of inertia,

$$I = \frac{m_1 m_2}{m_1 + m_2} d^2,$$

the energy of rotation being

$$\varepsilon_K = \varepsilon_r K(K+1), \quad K = 0, 1, \dots, \quad \varepsilon_r = \frac{\hbar^2}{2I}.$$

Thus the spacing between the levels is

$$\varepsilon_{K+1} - \varepsilon_K = 2(K+1)\varepsilon_r.$$

It is important that each rotational level is degenerate by the factor $(2K+1)$.

Thus $Z = Z_{\text{tr}} \cdot Z_{\text{rot}}$ where

$$Z_{\text{tr}} = \left(\sum_{n_x=1}^{\infty} e^{-\beta \varepsilon_x n_x^2} \right)^3 = \begin{cases} V/\lambda_T^3, & \beta \varepsilon_t \ll 1, \\ \exp(-\beta \varepsilon_t), & \beta \varepsilon_t \gg 1, \end{cases}$$

$$Z_{\text{rot}} = \sum_{K=0}^{\infty} (2K+1) e^{-\beta \varepsilon_r K(K+1)} = \begin{cases} kT/\varepsilon_r, & \beta \varepsilon_r \ll 1, \\ 1 + 3e^{-2\beta \varepsilon_r}, & \beta \varepsilon_r \gg 1. \end{cases}$$

The following is straightforward.

$$A = -kT \ln Z_{\text{tr}} - kT \ln Z_{\text{rot}};$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_V, \quad C = T \left(\frac{\partial S}{\partial T} \right)_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_V.$$

The calculations are obvious.

Problem 7.12: An ideal gas is composed of N “red” atoms of mass m , N “blue” atoms of mass m , and N “green” atoms of mass m . Atoms of the same color are indistinguishable. Atoms of different color are distinguishable.

- Use the canonical ensemble to compute the entropy of this gas.
- Compute the entropy of ideal gas of $3N$ “red” atoms of mass m . Does it differ from that of the mixture. If so, by how much.

Solution 7.12: Since the atoms of different color distinguishable the partition function is just the product of partition function. For each component

$$Z_N = \left(\sum_{\mathbf{k}} e^{-\beta p^2/2m} \right)^N = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N.$$

From this expression,

$$A_N = -NkT \ln \frac{eV}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} = Nf(T) - NkT \ln(eV/N).$$

Here

$$f(T) = \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2}.$$

Thus, $Z = Z_N^3$, and

$$A = 3Nf(T) - 3NkT \ln(eV/N), \quad S = 3NK \ln(eV/N) - 3Nf'(T).$$

In the case of single-color gas of $3N$ particles we have

$$S_1 = 3Nk \ln(eV/3N) - 3Nf'(T) \quad \rightarrow \quad S - S_1 = 3N \ln 3.$$

Problem 7.13: An ideal gas consists of a mixture of “green” and “red” spin-1/2 particles. All particles have mass m . A magnetic field, B , is applied to the system. The “green” particles have magnetic moment γ_G , and the “red” particles have magnetic moment γ_R , where $\gamma_R < \gamma_G$. Assume that temperature is high enough that Fermi statistics can be neglected. The system will be in equilibrium if chemical potentials the the “red” and the “green” gases are equal. Compute the ratio N_R/N_G , where N_R is the number of “red” atoms and N_G is the number of “red” particles. Use the canonical ensemble (no other ensembles will be accepted).

Solution 7.13: Let us consider one of the gases since they are noninteracting. We have $Z = Z_{tr} \cdot Z_s$ where Z_{tr} is the usual transport partition function while

$$Z_s = \left(e^{-\beta\gamma B} + e^{\beta\gamma B} \right)^N = 2^N \cosh^N(\beta\gamma B).$$

Since

$$\mu = -\frac{kT}{N} \ln \frac{1}{N!} \left(\frac{V \cosh(\beta\gamma B)}{\lambda_T} \right)^N = -kT \ln \left(\frac{eV \cosh(\beta\gamma B)}{N\lambda_T} \right).$$

Equating chemical potentials for “red” and “green” gases we get

$$\frac{\cosh(\beta\gamma_R B)}{N_R} = \frac{\cosh(\beta\gamma_G B)}{N_G} \quad \rightarrow \quad \frac{N_R}{N_G} = \frac{\cosh(\beta\gamma_R B)}{\cosh(\beta\gamma_G B)}.$$

Problem 7.14: Consider a one-dimensional lattice with N lattice sites and assume that i -th lattice site has spin $s_i = \pm 1$. The Hamiltonian describing this lattice is

$$\mathcal{H} = -\varepsilon \sum_{i=1}^N s_i s_{i+1}.$$

Assume periodic boundary condition, so $s_{N+1} = s_1$. Compute the correlation function, $\langle s_1 s_2 \rangle$. How does it behave at very high temperature and at very low temperature?

Solution 7.14: We have,

$$Z_N(T) = \sum_{s_1=\pm 1} \dots \sum_{s_N=\pm 1} \exp \left(\beta \varepsilon \sum_i s_i s_{i+1} \right).$$

As it is recommended in the book [1], we introduce the matrix

$$\bar{\mathbf{P}} = \begin{pmatrix} e^{\beta \varepsilon} & e^{-\beta \varepsilon} \\ e^{-\beta \varepsilon} & e^{\beta \varepsilon} \end{pmatrix} = e^{\beta \varepsilon} \mathbf{I} + e^{-\beta \varepsilon} \boldsymbol{\sigma}_1.$$

We have

$$\langle s_i | \bar{\mathbf{P}} | s_{i+1} \rangle = e^{\beta \varepsilon s_i s_{i+1}}.$$

Then

$$Z_N(T) = \sum_{s_1=\pm 1} \dots \sum_{s_N=\pm 1} \langle s_1 | \bar{\mathbf{P}} | s_2 \rangle \langle s_2 | \bar{\mathbf{P}} | s_3 \rangle \dots \langle s_N | \bar{\mathbf{P}} | s_1 \rangle = \text{Tr} \bar{\mathbf{P}}^N.$$

The matrix $\bar{\mathbf{P}}$ has eigenvalues

$$\lambda_1 = 2 \cosh \beta \varepsilon, \quad \lambda_2 = 2 \sinh \beta \varepsilon.$$

Thus

$$Z_N(\beta) = 2^N (\cosh^N \beta \varepsilon + \sinh^N \beta \varepsilon).$$

We have

$$\langle s_i s_{i+1} \rangle = \frac{1}{N \varepsilon} \frac{\partial \ln Z_N}{\partial \beta} = \frac{\cosh^{N-1}(\beta \varepsilon) \sinh(\beta \varepsilon) + \sinh^{N-1}(\beta \varepsilon) \cosh(\beta \varepsilon)}{\cosh^N(\beta \varepsilon) + \sinh^N(\beta \varepsilon)}.$$

At low temperature, $\beta \varepsilon \gg 1$, $\cosh(\beta \varepsilon) \approx \sinh(\beta \varepsilon)$ and $\langle s_i s_{i+1} \rangle = 1$. Thus we have ferromagnet ordering.

At high temperature,

$$\cosh(\beta \varepsilon) \rightarrow 1, \quad \sinh(\beta \varepsilon) \rightarrow 0 \quad \rightarrow \quad \langle s_i s_{i+1} \rangle = \beta \varepsilon \ll 1.$$

Problem 7.15: In the mean field approximation to the Ising lattice, the order parameter, $\langle s \rangle$, satisfied the equation

$$\langle s \rangle = \tanh \left(\langle s \rangle \frac{T_c}{T} \right),$$

where $T_c = v\varepsilon/2k$ where ε is the strength of the coupling between lattice sites and v is the number of nearest neighbors.

(a) Show that $\langle s \rangle$ is the following temperature dependence

$$\langle s \rangle \approx \begin{cases} 1 - e^{-2T_c/T}, & T \rightarrow 0, \\ \sqrt{3(1 - T/T_c)}, & T \rightarrow T_c. \end{cases}$$

(b) Compute the jump in the heat capacity at $T = T_c$.

(c) Compute the magnetic susceptibility, $\chi(T, N)_{B=0}$, in the neighborhood of T_c both for $T > T_c$ and $T < T_c$. What is the critical exponent for both cases?

Solution 7.15:

(a) Since $\tanh \xi \approx 1 - 2e^{-2\xi}$ at large ξ , we get

$$\langle s \rangle \approx 1 - 2e^{-2\langle s \rangle T_c/T} \quad \rightarrow \quad \langle s \rangle \approx 1 - 2e^{-2T_c/T}.$$

At small ξ , $\tanh \xi \approx \xi - \xi^3/3$, we obtain

$$\langle s \rangle \approx \langle s \rangle \frac{T_c}{T} + \frac{\langle s \rangle^3}{3} \left(\frac{T_c}{T} \right)^3.$$

Thus,

$$\langle s \rangle \approx \sqrt{3(1 - T/T_c)}.$$

(b) We will use notations of Sec. 7.F.2 of the book [1]. The the Hamiltonian is

$$\mathcal{H} = - \sum_{i=1}^N E(\varepsilon, B) s_i, \quad E(\varepsilon, B) = \frac{v\varepsilon}{2} \langle s \rangle + \mu B. \quad (7.3)$$

Thus $U = -NE\langle s \rangle = -NE\langle s \rangle$, and

$$C = -N \left(\frac{\partial E(\varepsilon, B) \langle s \rangle}{\partial T} \right)_{N, B} = -N \left[E + \langle s \rangle \frac{\partial E}{\partial \langle s \rangle} \right] \left(\frac{\partial \langle s \rangle}{\partial T} \right)_{N, B}.$$

At $T \rightarrow T_c - 0$ and $B = 0$ we get

$$\langle s \rangle = \sqrt{3(1 - T/T_c)} \quad \rightarrow \quad C|_{T_c-0} = \frac{3}{2} \frac{Nv\varepsilon}{T_c}.$$

At $T > T_c$ the average spin is zero, thus the jump in specific heat is given by $C|_{T_c-0}$.

- (c) To get magnetic susceptibility we have to differentiate the magnetic moment $N = N\mu\langle s \rangle$ with respect to B :

$$\chi = N\mu \left(\frac{\partial \langle s \rangle}{\partial B} \right)_{N, B \rightarrow 0}.$$

Defining $\eta = (\partial \langle s \rangle / \partial B)_{N, B \rightarrow 0}$ we get the following equation at $B \rightarrow 0$:

$$\eta = \frac{1}{\cosh^2(\langle s \rangle T_c / T)} \left[\frac{\beta v \epsilon}{2} \eta + \beta \mu \right].$$

Its solution is

$$\eta = \frac{2\beta\mu}{2 \cosh^2(\langle s \rangle T_c / T) - T_c / T}.$$

Finally,

$$\chi = \frac{N\mu^2}{v\epsilon} \frac{T_c / T}{\cosh^2(\langle s \rangle T_c / T) - T_c / T}.$$

Above T_c we have $\langle s \rangle = 0$, and

$$\chi = \frac{N\mu^2}{v\epsilon} \frac{T_c}{T - T_c}.$$

Below T_c we get

$$\cosh^2(\langle s \rangle T_c / T) \approx \left[1 + \frac{\langle s \rangle^2}{2} \left(\frac{T_c}{T} \right)^2 \right]^2 \approx 1 + 3 \left(1 - \frac{T}{T_c} \right).$$

As a result, below T_c

$$\chi = \frac{N\mu^2}{v\epsilon} \frac{T_c}{2(T_c - T)}.$$

Thus there is a divergence at $T \rightarrow T_c$, $\chi \propto |T - T_c|^{-1}$, with critical exponent equal to -1.

Problem 7.16: The density of states of an ideal Bose-Einstein gas is

$$g(E) = \begin{cases} \alpha E^2, & E > 0, \\ 0, & E < 0, \end{cases}$$

where α is a constant. Compute the temperature for Bose-Einstein condensation.

Solution 7.16: We have the equation for $\beta_c = 1/kT_c$:

$$N = \int_{E_{\min}}^{\infty} \frac{g(E) dE}{e^{\beta_c E} - 1} = \frac{\alpha}{\beta_c^3} \int_0^{\infty} \frac{x^2 dx}{e^x - 1} = \frac{2\alpha\zeta(3)}{\beta_c^3}.$$

Here $\zeta(x)$ is the Riemann zeta-function. Finally,

$$kT_c = \left(\frac{N}{2\alpha\zeta(3)} \right)^{1/3}.$$

Problem 7.17: An ideal Bose-Einstein gas consists of noninteracting bosons with mass m which have an internal degree of freedom which can be described by assuming, that the bosons are two-level atoms. Bosons in the ground state have the energy $E_0 = p^2/2m$, while bosons in the excited state have the energy $E_1 = p^2/2m + \Delta$, where p is the momentum and Δ is the excitation energy. Assume that $\Delta \gg kT$. Compute the Bose-Einstein condensation temperature, T_c , for this gas of two-level bosons. Does the existence of internal degree of freedom raise or lower the condensation temperature?

Solution 7.17: We start with calculation of density of states.

$$g_0(E) = \int d\mathbf{p} \delta\left(E - \frac{p^2}{2m}\right) = \frac{4\pi}{h^3} \int p^2 dp \delta\left(E - \frac{p^2}{2m}\right) = a\sqrt{E}, \quad a \equiv \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3}}.$$

In a similar way,

$$g_1(E) = a\sqrt{E - \Delta}.$$

The equation for $\beta_c = 1/kT_c$ is:

$$\frac{N\beta_c^{3/2}}{a} = \int_0^\infty \frac{\sqrt{x} dx}{e^x - 1} + \int_{\beta_c\Delta}^\infty \frac{\sqrt{x - \beta_c\Delta} dx}{e^x - 1} \approx \frac{\zeta(3/2)\sqrt{\pi}}{2} + \frac{\sqrt{\pi}}{2} e^{-\beta_c\Delta}.$$

We can solve this equation by iterations since Δ is large. Denoting

$$\beta_0 = \left(\frac{a\zeta(3/2)\sqrt{\pi}}{2N}\right)^{2/3}$$

we get

$$\beta_c = \beta_0 \left(1 + \frac{\sqrt{\pi}a}{2N\beta_0^{3/2}} e^{-\beta_0\Delta}\right)^{2/3} \approx \beta_0 + \frac{2\sqrt{\pi}a}{6N\sqrt{\beta_0}} e^{-\beta_0\Delta}.$$

Thus the internal degree of freedom *decreases* the condensation temperature.

Problem 7.18: Compute the Clausius-Clapeyron equation for an ideal Bose-Einstein gas and sketch the coexistence curve. Show that the line of transition points in the $P - v$ plane obeys the equation

$$pv^{5/3} = \frac{2\pi\hbar^2}{m} \frac{g_{5/2}(1)}{[g_{5/2}(1)]^{5/3}}.$$

Solution 7.18: Let us first recall the notations. The quantity $z = e^{\beta\mu}$ is called the *fugacity*, the distribution function is written as

$$\langle n_l \rangle = \frac{1}{e^{\beta(\epsilon_l - \mu)} - 1} = \frac{z}{e^{\beta\epsilon_l} - z}.$$

The functions $g_i(z)$ are introduced as

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^\infty x^2 dx \ln(1 - z^{-x^2}) = \sum_{\alpha=1}^{\infty} \frac{z^\alpha}{\alpha^{5/2}}, \quad (7.4)$$

$$g_{3/2}(z) = z \frac{d}{dz} g_{5/2}(z) = \sum_{\alpha=1}^{\infty} \frac{z^\alpha}{\alpha^{3/2}}. \quad (7.5)$$

Now, the grand canonical potential is

$$\Omega = \frac{V(kT)^{5/2} m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty dy \sqrt{y} \ln(1 - z e^{-y}) = -V \frac{kT}{\lambda_T^3} g_{5/2}(z).$$

Thus the equation of state is

$$P = \frac{kT}{\lambda_T^3} g_{5/2}(z).$$

In equilibrium with the condensate at $T = T_c$,

$$P_c = \frac{kT_c}{\lambda_T^3} g_{5/2}(1).$$

The critical particle density in the condensation point is

$$\langle n_c \rangle = \frac{g_{3/2}(1)}{\lambda_T^3}.$$

Denoting $\lambda_T = a/T^{1/2}$ where $a = \sqrt{2\pi\hbar^2/mk}$ we get at the critical point:

$$\frac{N}{V} = \frac{g_{3/2}(1) T_c^{3/2}}{a^3} \quad \rightarrow \quad T_c = \left(\frac{Na^3}{V g_{3/2}(1)} \right)^{2/3}.$$

Thus,

$$P_c = \frac{kT_c g_{5/2}(1)}{\lambda_T^3} = ka^2 \frac{g_{5/2}(1)}{[V g_{3/2}(1)]^{5/3}} = \frac{2\pi\hbar^2}{m} \frac{g_{5/2}(1)}{[V g_{3/2}(1)]^{5/3}}.$$

Problem 7.19: Show that the pressure, P , of an ideal Bose-Einstein gas can be written in the form $P = \alpha u$, where “ u ” is the internal energy per unit volume and a is a constant.

(a) what is u ?

(b) What is α ?

Solution 7.19: Let us do integration by parts in Eq. 7.5 to get

$$\begin{aligned} g_{5/2}(z) &= -\frac{2}{\sqrt{\pi}} \int_0^\infty dy \sqrt{y} \ln(1 - ze^{-y}) \\ &= \frac{2}{\sqrt{\pi}} \cdot \frac{2}{3} \int_0^\infty dy y^{3/2} \frac{z}{e^y - z} \end{aligned}$$

Calculation the average energy

$$U = \int_0^\infty g(\epsilon) \epsilon d\epsilon \frac{z}{e^{\beta\epsilon} - z}$$

and recalling that $g(\epsilon) \propto \sqrt{\epsilon}$ we immediately see that

$$PV = \frac{2}{3}U \quad \rightarrow \quad P = \frac{2}{3}u.$$

Thus, $\alpha = 2/3$.

Problem 7.20: Electrons in a piece of Cu metal can be assumed to behave as an ideal Fermi gas. Cu metal in the solid state has mass density $\rho = 9 \text{ gr/cm}^3$. Assume that each Cu atom donates an electron to the Fermi gas. Assume the system is at $T = 0 \text{ K}$.

- Compute the Fermi energy, ϵ_F , of the electron gas.
- Compute the Fermi temperature, $T_F = \epsilon_F/k$.

Solution 7.20: Let us start with the calculation of the density of states:

$$\begin{aligned} g(\epsilon) &= \frac{2V \cdot 4\pi}{h^3} \int p^2 dp \delta\left(\epsilon - \frac{p^2}{2m}\right) \\ &= \frac{\sqrt{2}Vm^{3/2}}{\pi^2\hbar^3} \sqrt{\epsilon} \equiv Vg_0 \sqrt{\epsilon}. \end{aligned}$$

Here $g_0 = \sqrt{2}m^{3/2}/\pi^2\hbar^3$, we have taken into account that spin degeneracy for electrons 2. Integration expression for density of states from 0 to ϵ_F and equating to the number of electrons we obtain

$$(2/3)g_0\epsilon_F^{3/2} = n_e \quad \rightarrow \quad \epsilon_F = (3n_e/2g_0)^{2/3},$$

Here $n_e = N_e/V = \rho/m_{\text{Cu}}$ is the electron density.

Problem 7.21: The density of states of an ideal Fermi-Dirac gas is

$$f(E) = \begin{cases} D, & \text{if } E > 0, \\ 0, & \text{if } E < 0, \end{cases}$$

where D is a constant.

- (a) Compute the Fermi energy.
- (b) Compute the specific heat at low temperature.

Solution 7.21: We have,

$$N = D \int_0^{\infty} \frac{dE}{e^{\beta(E-\mu)} + 1} = \frac{D}{\beta} \int_{-\beta\mu}^{\infty} \frac{dx}{e^x + 1} = \frac{D}{\beta} \ln(1 + e^{\beta\mu}).$$

Thus

$$e^{\beta\mu} = e^{\beta N/D} - 1 \quad \rightarrow \quad \mu = \frac{1}{\beta} \ln(e^{\beta N/D} - 1) \approx \frac{N}{D} - kT e^{-N/DkT}.$$

The energy is then

$$U = D \int_0^{\infty} \frac{E dE}{e^{\beta(E-\mu)} + 1}.$$

Let us use the trick called the Sommerfeld expansion. Consider an auxiliary integral,

$$\begin{aligned} I &= \int_0^{\infty} \frac{f(E) dE}{e^{(E-\mu)/kT} + 1} = \int_{-\mu/kT}^{\infty} \frac{f(\mu + kTz) dE}{e^z + 1} \\ &= kT \int_0^{\mu/kT} \frac{f(\mu - kTz) dE}{e^{-z} + 1} + kT \int_0^{\infty} \frac{f(\mu + kTz) dE}{e^z + 1} \\ &= \int_0^{\mu} f(E) dE + kT \int_0^{\infty} dE \frac{f(\mu + kTz) - f(\mu - kTz)}{e^z + 1} \end{aligned}$$

Here we have used the fact that $(e^{-z} + 1)^{-1} = 1 - (e^z + 1)^{-1}$ and that $e^{\mu/kT} \gg 1$. Expanding the integrand, we obtain

$$I \approx \int_0^{\mu} f(E) dE + 2(kT)^2 f'(\mu) \int_0^{\infty} \frac{z dz}{e^z + 1} + \dots = \int_0^{\mu} f(E) dE + \frac{\pi^2}{6} (kT)^2 f'(\mu) + \dots$$

In our case, $f(E) = DE$, $f'(\mu) = D$, and we get

$$\frac{U}{D} \approx \frac{\mu^2}{2} + \frac{\pi^2}{6} (kT)^2.$$

The specific heat is then

$$\frac{C}{D} = \mu \frac{\partial \mu}{\partial T} + \frac{\pi^2}{3} k^2 T.$$

The first item is exponentially small at low temperatures, and

$$C \approx \frac{\pi^2}{3} D k^2 T \approx k \frac{\pi^2 kT}{3 \mu}.$$

Problem 7.22: Compute the magnetization of an ideal gas of spin-1/2 fermions in the presence of magnetic field. Assume that fermions each have magnetic moment μ_e . Find the expression for magnetization in the limit of weak magnetic field and $T \rightarrow 0$ K.

Solution 7.22: We will calculate here only spin (Pauli) susceptibility. Since the spin degree of freedom leads to additional energy $\pm\mu_e B$ we get

$$\Omega(\mu) = \frac{1}{2}\Omega_0(\mu - \mu_e B) + \frac{1}{2}\Omega_0(\mu + \mu_e B)$$

where Ω_0 is the grand potential in the absence of magnetic field,

$$\Omega_0(\mu) = -\frac{2}{3}U = -\frac{2A}{3} \int_0^\infty \frac{E^{3/2} dE}{e^{(E-\mu)/kT} + 1}, \quad A = \frac{\sqrt{2}Vm^{3/2}}{\pi^2\hbar^3}.$$

As a result,

$$-\frac{\Omega(\mu)}{A} = \frac{1}{3} \int_0^\infty \frac{E^{3/2} dE}{e^{(E-\mu-\mu_e B)/kT} + 1} + \frac{1}{3} \int_0^\infty \frac{E^{3/2} dE}{e^{(E-\mu+\mu_e B)/kT} + 1}.$$

In small magnetic fields or at large temperature,

$$\Omega(\mu) \approx \Omega_0(\mu) + \frac{(\mu_e B)^2}{2} \frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2}.$$

Consequently,

$$M = -\left(\frac{\partial \Omega}{\partial B}\right)_{T,V,\mu} = \mu_e^2 B \frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2}.$$

Since $\frac{\partial \Omega}{\partial \mu} = -N$ we get

$$M = \mu_e^2 B \left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

This formula works in the wide region

$$\mu_e B \ll \mu.$$

In very strong magnetic fields the analysis is more complicated. First the chemical potential is given by the expression

$$\frac{N}{A} = \frac{1}{3} \left[(\mu + \mu_e B)^{3/2} + (\mu - \mu_e B)^{3/2} \right].$$

In a similar way,

$$-\frac{\Omega(\mu)}{A} = \frac{2}{15} \left[(\mu + \mu_e B)^{5/2} + (\mu - \mu_e B)^{5/2} \right].$$

These equations are written assuming that $\mu_e B \leq \mu$, otherwise only one item is present. Physically it means that only spins-up-states are occupied. Let us consider the case of very strong magnetic field, $\mu_e B \gg \mu$. Then

$$\Omega(\mu) = -\frac{2A}{15} (\mu + \mu_e B)^{5/2} \quad \rightarrow \quad M = \frac{A\mu_e}{3} (\mu + \mu_e B)^{3/2} = N\mu_e.$$

Problem 7.23: Show that the entropy for an ideal Fermi-Dirac gas (neglecting spin) can be written in the form

$$S = -k \sum_l [\langle n_l \rangle \ln \langle n_l \rangle + (1 - \langle n_l \rangle) \ln(1 - \langle n_l \rangle)],$$

where $\langle n_l \rangle = \left(e^{\beta(\epsilon_l - \mu)} + 1 \right)^{-1}$.

Solution 7.23: The number of ways to distribute N_l identical particles among G_l states with not more than 1 particle per state is just

$$W_l = \frac{G_l!}{N_l!(G_l - N_l)!}.$$

Using the Stirling's formula we obtain

$$S = k \sum_l \ln [G_l \ln G_l - N_l \ln N_l - (G_l - N_l) \ln(G_l - N_l)].$$

Using the mean occupation number $\langle n_l \rangle = N_l/G_l$ we can rewrite this formula as

$$S = -k \sum_l G_l [\langle n_l \rangle \ln \langle n_l \rangle + (1 - \langle n_l \rangle) \ln(1 - \langle n_l \rangle)].$$

If we ignore spin, then $G_l = 1$.

Problem 7.24: To the lowest order in the density, find the difference in the pressure and the isothermal compressibility between an ideal boson and ideal fermion gas. Assume that the fermions and bosons have the same mass and both are spin-less. (Note: You are now considering fairly high temperature).

Solution 7.24: Assuming that the density of states is given by the expression

$$g(\epsilon) = g_0 V \epsilon^{1/2}$$

we obtain

$$\Omega = -\frac{2}{3} g_0 V \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon - \mu)} \pm 1} \approx -\frac{2}{3} g_0 V \int_0^\infty \epsilon^{3/2} d\epsilon e^{\beta(\mu - \epsilon)} \left(1 \mp e^{\beta(\mu - \epsilon)} \right).$$

Introducing the fugacity $z = e^{\beta\mu}$ we get

$$P = \frac{2}{3} g_0 (kT)^{5/2} z \int_0^\infty \xi^{3/2} d\xi e^{-\xi} \left(1 \mp z e^{-\xi} \right) = \frac{\sqrt{\pi}}{2} g_0 (kT)^{5/2} z \left(1 \mp z \frac{\sqrt{2}}{8} \right).$$

The normalization condition in this case gives

$$N = g_0 V (kT)^{3/2} z \int_0^\infty \xi^{1/2} d\xi e^{-\xi} (1 \mp z e^{-\xi}) = \frac{\sqrt{\pi}}{2} z g_0 V \left(1 \mp z \frac{\sqrt{2}}{4} \right).$$

As result,

$$z_0 = \frac{2}{\sqrt{\pi} g_0 (kT)^{3/2}} \frac{N}{V}.$$

We obtain

$$P \approx \frac{NkT}{V} \frac{\left(1 \mp z_0 \frac{\sqrt{2}}{8} \right)}{\left(1 \mp z_0 \frac{\sqrt{2}}{4} \right)} \approx \frac{NkT}{V} \left(1 \pm z_0 \frac{\sqrt{2}}{8} \right) \approx \frac{NkT}{V} \left(1 \pm \frac{\sqrt{2}}{4\sqrt{\pi} g_0 (kT)^{3/2}} \frac{N}{V} \right).$$

The sign “+” hold for the Fermi statistics, the sign “-” holds for the Bose statistics. The compressibility is calculated in a straightforward way since

$$V \approx \frac{NkT}{P} \left(1 \pm \frac{\sqrt{2}}{4\sqrt{\pi} g_0 (kT)^{5/2} P} \right).$$

Chapter 8

Tests and training

Here we put some exercises for self-testing.

Problem 8.1:

- (a) Discuss the difference between Gibbs and Helmholtz free energy.
 (b) Prove the relation

$$U = -T^2 \left(\frac{\partial A}{\partial T} \right)_V,$$

where U is the internal energy.

- (c) A body with constant specific heat C_V is heated under constant volume from T_1 to T_2 . How much entropy it gains?
 (d) Discuss the heating if the same body is in contact with a thermostat at T_2 . In the last case the heating is irreversible. Show that the total entropy change is positive.
 (e) Two similar bodies with temperatures T_1 and T_2 brought into contact. Find the final temperature and the change in entropy.

Solution 8.1:

- (a) Mechanical work under *isothermic process* is given by

$$dW = dU - dQ = dU - T dS = d(U - TS).$$

The function of state

$$F = U - TS$$

is called *Helmholtz free energy*. We have

$$dF = dU - T dS - S dT = (T dS - P dV) - T dS - S dT = -S dT - P dV.$$

Thus,

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad P = - \left(\frac{\partial F}{\partial V} \right)_T.$$

Thus, F is the *thermodynamic potential* with respect to V and T .

The thermodynamic potential with respect to P and T is called *Gibbs free energy*. We have

$$G = U - TS - PV \rightarrow dG = -S dT + V dP.$$

- (b) Substituting

$$S = - \left(\frac{\partial F}{\partial T} \right)_V$$

into definition of F we get the result.

(c) We have

$$S = \int_{T_1}^{T_2} \frac{C_V}{T} dT = C_V \ln \left(\frac{T_2}{T_1} \right).$$

(d) Use 2nd law of thermodynamics

(e) Energy conservation law yields

$$C_V(T_2 - T_B) = C_V(T_B - T_1) \rightarrow T_B = (T_1 + T_2)/2.$$

for the entropy change we have

$$\delta S = C_V \ln \frac{T_B}{T_1} + C_V \ln \frac{T_B}{T_2} = 2C_V \ln \left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right) \geq 0.$$

Problem 8.2: Find fluctuation of the energy per particle for the Boltzmann gas of spinless particles at a given temperature. Assume that $\epsilon_p = p^2/2m$.

Solution 8.2:

$$\langle (\delta \epsilon)^2 \rangle = \langle (\epsilon_i - \langle \epsilon \rangle)^2 \rangle = \langle \epsilon^2 \rangle - \langle \epsilon \rangle^2.$$

Now

$$\begin{aligned} \langle \epsilon \rangle &= \frac{1}{Z_1} \sum_i \epsilon_i e^{-\beta \epsilon_i} = -\frac{1}{Z_1} \frac{\partial Z_1(\beta)}{\partial \beta} \\ \langle \epsilon^2 \rangle &= \frac{1}{Z_1} \sum_i \epsilon_i^2 e^{-\beta \epsilon_i} = \frac{1}{Z_1} \frac{\partial^2 Z_1(\beta)}{\partial \beta^2}. \end{aligned}$$

Thus

$$\langle (\delta \epsilon)^2 \rangle = \frac{1}{Z_1} \frac{\partial^2 Z_1(\beta)}{\partial \beta^2} - \left(\frac{1}{Z_1} \frac{\partial Z_1(\beta)}{\partial \beta} \right)^2 = \frac{\partial^2 \log Z_1}{\partial \beta^2}.$$

Now we have to specify Z_1 for $\epsilon_i = p^2/2m$.

$$Z_1 = \sum_{\mathbf{p}} \exp(-\beta \epsilon_p) = \frac{1}{(2\pi\hbar)^3} \int_0^\infty 4\pi p^2 dp \exp(-\beta \epsilon_p).$$

It is convenient to introduce the *density of states* as number of states per energy interval.

$$g(\epsilon) = \sum_{\mathbf{p}} \delta(\epsilon - \epsilon_i) = \frac{4\pi}{(2\pi\hbar)^3} \int_0^\infty p^2 dp \sum_i \delta(\epsilon - \epsilon_i) = \frac{m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \sqrt{\epsilon}.$$

In this way,

$$Z_1 = \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty d\varepsilon \varepsilon^{1/2} \exp(-\beta\varepsilon) = \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3\beta^{3/2}}} \int_0^\infty dx x^{1/2} \exp(-x).$$

As

$$\int_0^\infty dx x^{1/2} \exp(-x) = \Gamma(3/2) = (1/2)\sqrt{\pi}$$

we get

$$Z_1 = \frac{a}{\beta^{3/2}}, \quad a = \sqrt{\frac{\pi}{8}} \frac{m^{3/2}}{\pi^2 \hbar^3} \quad \rightarrow \quad \log Z_1 = \log a - \frac{3}{2} \log \beta.$$

Thus

$$\langle (\delta\varepsilon)^2 \rangle = \frac{3}{2\beta^2}.$$

Problem 8.3: Two-level systems with random energy spacings ε are distributed with a constant probability

$$p(\varepsilon) = P_0.$$

Find specific heat of the system.

Solution 8.3: As we know from the lecture,

$$\frac{n_+}{n_-} = e^{-\beta\varepsilon}, \quad n_+ + n_- = 1.$$

Thus

$$n_{\pm} = \frac{1}{\exp(\pm\beta\varepsilon) + 1}.$$

The average energy is (we start from the middle of the distance between the levels)

$$\langle \varepsilon \rangle_\varepsilon = \frac{\varepsilon}{2}(n_+ - n_-) = \frac{\varepsilon}{2} \tanh \frac{\beta\varepsilon}{2}.$$

The contribution to specific heat is

$$c(\varepsilon) = \frac{\partial \langle \varepsilon \rangle_\varepsilon}{\partial T} = -\beta^2 \frac{\partial \langle \varepsilon \rangle_\varepsilon}{\partial \beta} = \frac{1}{4} \frac{1}{\cosh^2(\beta\varepsilon/2)}.$$

The total specific heat is

$$C = \int_0^\infty p(\varepsilon) d\varepsilon c(\varepsilon) = P_0 \int_0^\infty d\varepsilon \frac{1}{4} \frac{1}{\cosh^2(\beta\varepsilon/2)} = \frac{P_0}{2\beta} \int_0^\infty \frac{dx}{\cosh^2 x} = \frac{P_0}{2\beta}.$$

Note that it is proportional to T .

Appendix A

Additional information

A.1 Thermodynamics

A.1.1 Thermodynamic potentials

Thermodynamic potential	Notation	Independent variables	Differential
Internal energy	U	S, V, N	$T dS - P dV + \mu dN$
Heat function (enthalpy)	H	S, P, N	$T dS + V dP + \mu dN$
Helmholtz free energy	F	T, V, N	$-S dT - P dV + \mu dN$
Gibbs free energy	G	T, P, N	$-S dT + V dP + \mu dN$
Landau free energy	Ω	T, V, μ	$-S dT - P dV - N d\mu$

Table A.1: Thermodynamic potentials (summary)

A.1.2 Variable transformation

Jacobian $\partial(u, v)/\partial(x, y)$ is defined as the determinant

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \partial u/\partial x & \partial u/\partial y \\ \partial v/\partial x & \partial v/\partial y \end{vmatrix} \quad (\text{A.1})$$

The following relations can be useful:

$$\frac{\partial(v, u)}{\partial(x, y)} = -\frac{\partial(u, v)}{\partial(x, y)}, \quad \frac{\partial(u, y)}{\partial(x, y)} = \left(\frac{\partial u}{\partial x} \right)_y, \quad \frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(t, s)} \cdot \frac{\partial(t, s)}{\partial(x, y)}. \quad (\text{A.2})$$

A.1.3 Derivatives from the equation of state

Important relations arise from the properties of partial differentiations. Consider 3 quantities, X, Y, Z , related by the equation of state $\mathcal{K}(X, Y, Z) = \text{const}$. Now let us consider X, Y as indepen-

dent variables, while $Z = Z(X, Y)$. We have

$$\left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY - dZ = 0. \quad (\text{A.3})$$

If Y, Z are taken as independent variables, then

$$-dX + \left(\frac{\partial X}{\partial Y}\right)_Z dY + \left(\frac{\partial X}{\partial Z}\right)_Y dZ = 0 \quad (\text{A.4})$$

Now we multiply Eq. A.3 by $\left(\frac{\partial X}{\partial Y}\right)_Z$ and Eq. A.4 by $\left(\frac{\partial Z}{\partial Y}\right)_X$ and subtract the results. We obtain

$$\left[\left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_Z + \left(\frac{\partial Z}{\partial Y}\right)_X\right] dX + \left[-\left(\frac{\partial X}{\partial Y}\right)_Z - \left(\frac{\partial X}{\partial Z}\right)_Y \left(\frac{\partial Z}{\partial Y}\right)_X\right] dZ = 0.$$

Since dX and dY are *independent*, this equation is compatible if

$$\begin{aligned} \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_Z + \left(\frac{\partial Z}{\partial Y}\right)_X &= 0 \\ \left(\frac{\partial X}{\partial Y}\right)_Z + \left(\frac{\partial X}{\partial Z}\right)_Y \left(\frac{\partial Z}{\partial Y}\right)_X &= 0, \end{aligned}$$

or

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1, \quad (\text{A.5})$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial Y}{\partial X}\right)_Z^{-1}. \quad (\text{A.6})$$

General scheme for transformation: Consider any quantity $\mathcal{F}(X, Y)$, the differential of which can be expressed as

$$d\mathcal{F} = \left(\frac{\partial \mathcal{F}}{\partial X}\right)_Y dX + \left(\frac{\partial \mathcal{F}}{\partial Y}\right)_X dY.$$

Then we divide it by dZ and assume $Y = \text{const}$, ($dY = 0$). We get

$$\left(\frac{\partial \mathcal{F}}{\partial Z}\right)_Y = \left(\frac{\partial \mathcal{F}}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Z}\right)_Y. \quad (\text{A.7})$$

Another important relation arises if one divides the expression for $d\mathcal{F}$ by dX ,

$$\left(\frac{\partial \mathcal{F}}{\partial X}\right)_Z = \left(\frac{\partial \mathcal{F}}{\partial X}\right)_Y + \left(\frac{\partial \mathcal{F}}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z. \quad (\text{A.8})$$

Equations (A.7), (A.8) together with Eqs. (A.5), (A.6) and the Maxwell relations are usually used for transformations and computation of derivatives from the equation of state.

A.2 Main distributions

Binomial distribution

$$W_N(m) = \frac{N!}{m!(N-m)!} p^m (1-p)^{N-m}. \quad (\text{A.9})$$

Poisson distribution

$$P(m) = \frac{\bar{m}^m}{m!} e^{-\bar{m}}. \quad (\text{A.10})$$

Gaussian distribution

$$G(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{-(x-\bar{x})/2\sigma}. \quad (\text{A.11})$$

Distribution of displacement for 1D random walk with the step l

$$G(x) = \frac{1}{2l\sqrt{2\pi Np(1-p)}} e^{-[x-(p-q)l]^2/8Nl^2p(1-p)}. \quad (\text{A.12})$$

Gaussian integrals

$$I_1(a) = \int_{-\infty}^{\infty} dz e^{-az^2/2} = \sqrt{2\pi/a}. \quad (\text{A.13})$$

$$\int_{-\infty}^{\infty} z^2 dz e^{-z^2/2} = 2 \left[\frac{dI_1(a)}{da} \right]_{a=1} = I_1(a) \sqrt{2\pi}. \quad (\text{A.14})$$

Gaussian distribution for more than one variables Define entropy as $S(x_1, \dots, x_n)$. Then

$$S - S_0 = -\frac{1}{2} \sum_{i,k} \beta_{ik} x_i x_k, \quad \beta_{ik} = \beta_{ki}.$$

For convenience, let us assume summation over repeated subscripts and rewrite the above equation

$$S - S_0 = -\frac{1}{2} \beta_{ik} x_i x_k. \quad (\text{A.15})$$

Consequently,

$$w = A e^{-\frac{1}{2} \beta_{ik} x_i x_k}.$$

Let us first calculate the normalization factor A from

$$\int dw dx_1 \cdots dx_n = 1.$$

To calculate the integral let us introduce the linear transform

$$x_i = a_{ik} y_k$$

to make the quadratic form (refmgs01 *diagonal*. In order that

$$\beta_{ik}x_i x_k = y_i y_i = y_i y_k \delta_{ik}$$

the relation

$$\beta_{ik} a_{il} a_{km} = \delta_{km} \quad (\text{A.16})$$

should be valid. Denoting determinants of the matrices $\hat{\beta}$ and \hat{a} as β and a , respectively, we get the relation $\beta a^2 = 1$. The Jacobian of the transformation $x_i \rightarrow y_i$ is just a ,

$$J = \left| \frac{\partial(x_1, \dots, x_n)}{\partial(y_1, \dots, y_n)} \right| = |\hat{a}| = a.$$

Consequently,

$$Aa \left[\int dy e^{-y^2/2} \right]^n = \frac{A(2\pi)^{n/2}}{\sqrt{\beta}} = 1.$$

Thus

$$w = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \exp\left(-\frac{1}{2}\beta_{ik}x_i x_k\right). \quad (\text{A.17})$$

Let define generalized forces as

$$X_i = -\partial S / \partial x_i = \beta_{ik}x_k, \quad (\text{A.18})$$

and first calculate

$$\langle x_i X_k \rangle = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \int x_i \beta_{ik} x_k e^{-\beta_{ik}x_i x_k/2} dx_1 \dots dx_n. \quad (\text{A.19})$$

The easiest way to calculate this integral is to calculate to assume for a while that $\bar{x}_i \neq 0$. Then

$$\bar{x} = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \int x_i e^{-\beta_{ik}(x_i - x_{i0})(x_k - x_{k0})/2} dx_1 \dots dx_n = x_{i0}.$$

Then we can differentiate both sides with respect to x_{k0} and then put $x_{i0} = x_{k0} = 0$. The l.h.s. is just $\langle x_i X_k \rangle$ while the r.h.s. is δ_{ik} . Thus

$$\langle x_i X_k \rangle = \delta_{ik}, \quad \text{or} \quad \beta_{ik} \langle x_i x_k \rangle = \delta_{ik}, \quad \langle x_i x_k \rangle = \left(\hat{\beta}^{-1}\right)_{ik}. \quad (\text{A.20})$$

A.3 The Dirac delta-function

The main property is to single-out one particular value $x - x_0$ of a variable x . It is defined by the characteristic properties

$$\delta(x - x_0) = \begin{cases} 0 & \text{for } x \neq x_0 \\ \infty & \text{for } x = x_0 \end{cases} \quad (\text{A.21})$$

but in such way that for any $\varepsilon > 0$

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon} \delta(x-x_0) dx = 1. \quad (\text{A.22})$$

Since delta-function has a very (infinitely) sharp peak at $x = x_0$ and a unit area

$$\int_A^B f(x) \delta(x-x_0) dx = \begin{cases} f(x_0) & \text{if } A < x_0 < B \\ 0 & \text{otherwise} \end{cases}. \quad (\text{A.23})$$

Representations for the Dirac δ -function

Let introduce a positive parameter γ and at final stage tend it to zero. Physically it means that γ is less than all other involved scales. The main representations are the following: rectangular,

$$\delta(x) = \begin{cases} \gamma^{-1} & \text{for } -\gamma/2 < x < \gamma/2 \\ 0 & \text{otherwise} \end{cases}, \quad (\text{A.24})$$

Lorentzian,

$$\delta(x) = \frac{1}{\pi} \frac{\gamma}{x^2 + \gamma^2}, \quad (\text{A.25})$$

Gaussian,

$$\delta(x) = \frac{1}{\gamma\sqrt{2\pi}} e^{-x^2/2\gamma^2}, \quad (\text{A.26})$$

and integral,

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk \quad (\text{A.27})$$

We will also need a representation for the Kronecker's symbol

$$\delta_{n,0} = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{-n\phi} d\phi. \quad (\text{A.28})$$

A.4 Fourier Series and Transforms

Fourier series

Generally the Fourier series is defined as an expansion of a real function in series as

$$f(x) = \frac{a_0}{2} + \sum_{k=1}^{\infty} (a_k \sin kx + b_k \cos kx). \quad (\text{A.29})$$

The sum of the series is periodic with the period 2π .

Another form is complex Fourier series

$$f(x) = \sum_{k=-\infty}^{\infty} c_k e^{ikx}, \quad c_{\pm k} = (a_k \mp b_k)/2, \quad c_0 = a_0/2. \quad (\text{A.30})$$

Since

$$\begin{aligned}\int_0^{2\pi} \sin mx \sin nx dx &= \begin{cases} \pi \delta_{mn}, & m \neq 0, \\ 0, & m = 0, \end{cases} \\ \int_0^{2\pi} \cos mx \cos nx dx &= \begin{cases} \pi \delta_{mn}, & m \neq 0, \\ 2\pi, & m = n = 0, \end{cases} \\ \int_0^{2\pi} \sin mx \cos nx dx &= \begin{cases} 0, & \text{for integer } m, n \end{cases}\end{aligned}$$

we have

$$\begin{pmatrix} a_k \\ b_k \\ c_k \end{pmatrix} = \frac{1}{\pi} \int_0^{2\pi} dt f(t) \begin{pmatrix} \cos kt \\ \sin kt \\ \frac{1}{2} e^{-ikt} \end{pmatrix}, \quad k \neq 0. \quad (\text{A.31})$$

At $k = 0$,

$$a_0 = c_0 = \frac{1}{2\pi} \int_0^{2\pi} dt f(t).$$

If the function has a discontinuity at $x = x_0$ then the series gives

$$f(x_0) = \frac{1}{2} [f(x_0 + 0) + f(x_0 - 0)].$$

If one is willing to change the interval $2\pi \rightarrow 2L$ than k has to be replaced by $\pi k/L$ and the normalization factor is $1/L$ rather than $1/\pi$.

Advantages of the Fourier series: it can represent discontinuous functions. Let us take an example of periodic function with the period 2π defined as

$$F(x) = \begin{cases} 1, & -\pi/2 < x < \pi/2 \\ 0, & -\pi < x < -\pi/2, \pi/2 < x < \pi, \end{cases}$$

This function is even, thus

$$b_k = 0, \quad a_k = (2/\pi k) \sin \pi k/2.$$

Below we plot the sum of 5 and 50 Fourier harmonics. It is useful to know the Parseval's identity

$$\frac{1}{\pi} \int_{-\pi}^{\pi} [f(x)]^2 dx = \frac{a_0^2}{2} + \sum_{k=1}^{\infty} (a_k^2 + b_k^2).$$

Fourier transform

We assume $L \rightarrow \infty$ and replace

$$\sum_{k=-\infty}^{\infty} (\dots) \rightarrow L \int_{-\infty}^{\infty} dk (\dots).$$

$$g(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(t) e^{-ikt} dt. \quad (\text{A.32})$$

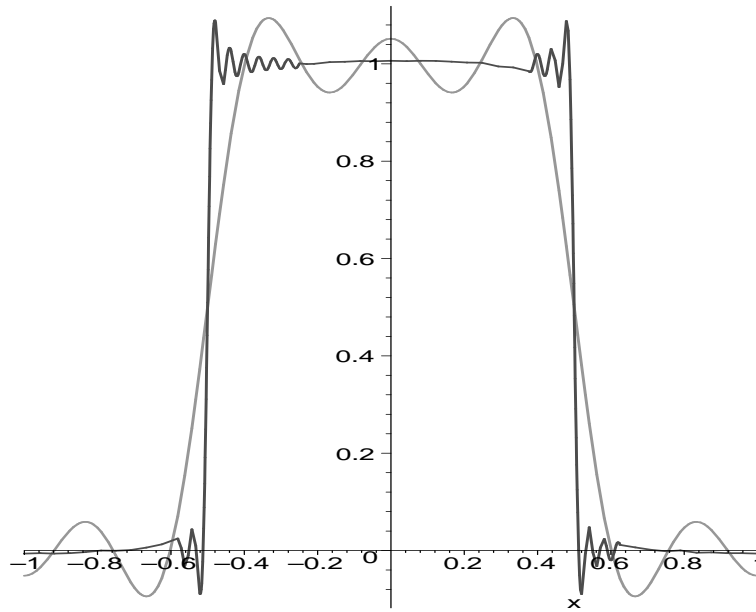


Figure A.1:

The completeness condition

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ikt} \int_{-\infty}^{\infty} dx f(x) e^{-ikx}. \quad (\text{A.33})$$

The Dirac delta-function is represented as

$$\delta(x-t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ik(t-x)}. \quad (\text{A.34})$$

We have several useful rules for the Fourier transform. If $g(k)$ is the Fourier transform of $f(x)$ then

$$\begin{aligned} f'(x) &\equiv df/dx \rightarrow ik g(k); \\ f^{(n)}(x) &\equiv d^n f/dx^n \rightarrow (ik)^n g(k); \\ \int_{-\infty}^{\infty} dy f_1(y) f_2(x-y) &\rightarrow g_1(k) \cdot g_2(k) \quad (\text{convolution theorem}); \\ \int_{-\infty}^{\infty} f_1(t) f_2(t) dt &\rightarrow \int_{-\infty}^{\infty} g_1(k) f_2(-k) dk; \\ \int_{-\infty}^{\infty} f_1(t) f_2^*(t) dt &\rightarrow \int_{-\infty}^{\infty} g_1(k) f_2^*(k) dk \quad \text{the Parseval's theorem.} \end{aligned} \quad (\text{A.35})$$

These properties are very important for solving differential equations, etc.

$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) e^{-i\omega x} dx$	$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-i\omega x} dx$
$\frac{1}{a^2+x^2}, a > 0$	$\sqrt{\frac{\pi}{2}} \frac{e^{-a \omega }}{a}$
$f(x) = \begin{cases} 1, & x < a \\ 0, & x > a \end{cases}$	$\sqrt{\frac{2}{\pi}} \frac{\sin(a\omega)}{\omega}$
$e^{-a^2x^2}$	$\frac{1}{a\sqrt{2}} e^{-\omega^2/4a}$

Table A.2: Table of Fourier transform pairs

Examples

One-dimensional diffusion: The equation has the form

$$\frac{\partial n(x,t)}{\partial t} = -D \frac{\partial^2 n(x,t)}{\partial x^2}.$$

Let us assume that we add a particle at time $t = 0$ at the point $x = 0$. Then the equation together with initial condition can be written as

$$\frac{\partial n(x,t)}{\partial t} + D \frac{\partial^2 n(x,t)}{\partial x^2} = \delta(x) \delta(t).$$

The Fourier transform of this equation has the form:

$$(Dk^2 - i\omega) n(k, \omega) = 1 \quad \rightarrow \quad n(k, \omega) = \frac{1}{(2\pi)^2} \frac{1}{Dk^2 - i\omega}.$$

Now we can come back to real space-time representation:

$$\begin{aligned} n(x,t) &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{1}{Dk^2 - i\omega} \\ &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-Dk^2|t|} = \frac{1}{2\sqrt{\pi D|t|}} e^{-x^2/4D|t|}. \end{aligned}$$

Appendix B

Maple Printouts

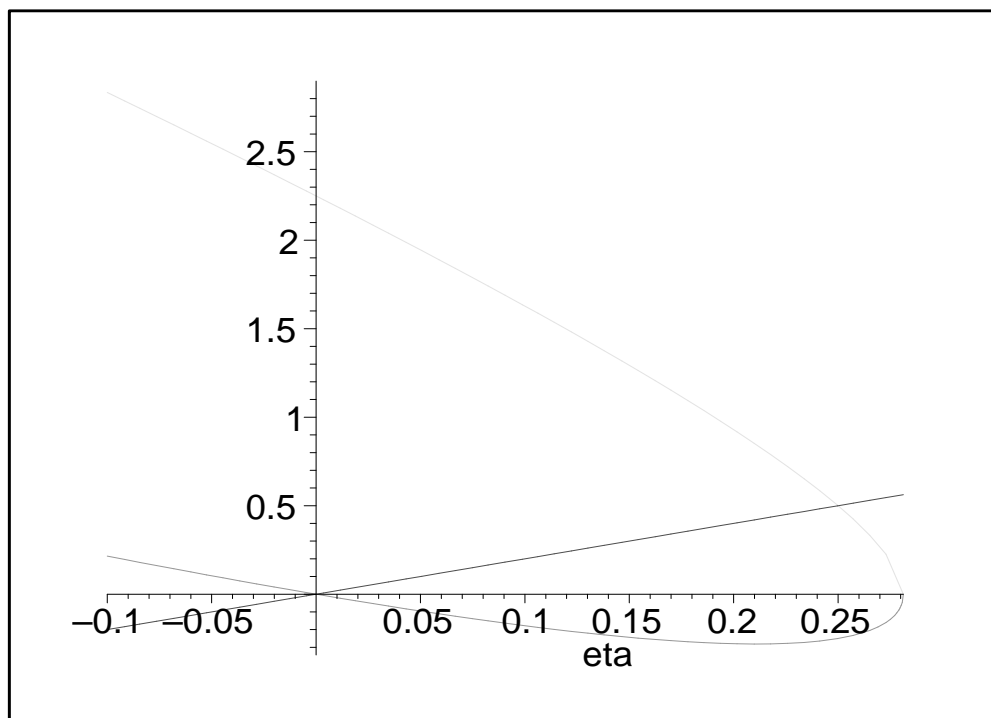
Quick access: 1, 2.1, 2.2, 2.17, 3.7, 3.12, 3.13, 4.9, 4.10, 4.13, 4.14, 5.1, 5.2, 5.3, 5.4, 5.5, 5.7, 5.8

Test in mathematics

```
> F:=(xi,eta)->xi^4+xi^3+eta*xi^2:
> F1:=(xi,eta)->subs(y=xi,diff(F(y,eta),y)): solve(F1(xi,eta)=0,xi);
0, -3/8 + 1/8*sqrt(9-32*eta), -3/8 - 1/8*sqrt(9-32*eta)
```

One extremum at $\eta > 9/32$, otherwise 3 extrema

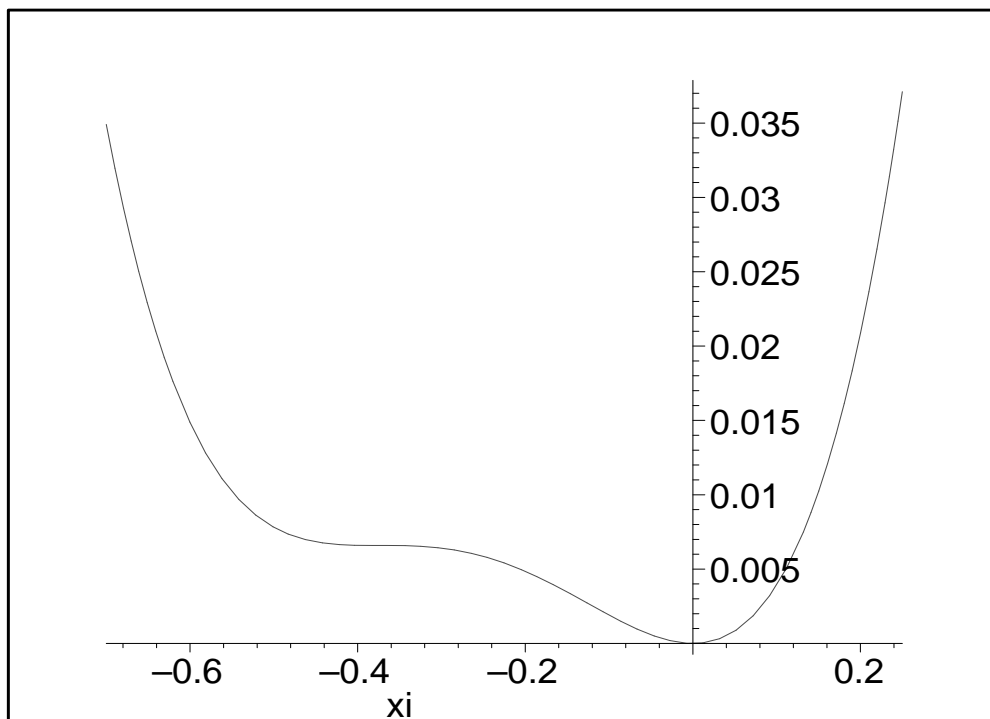
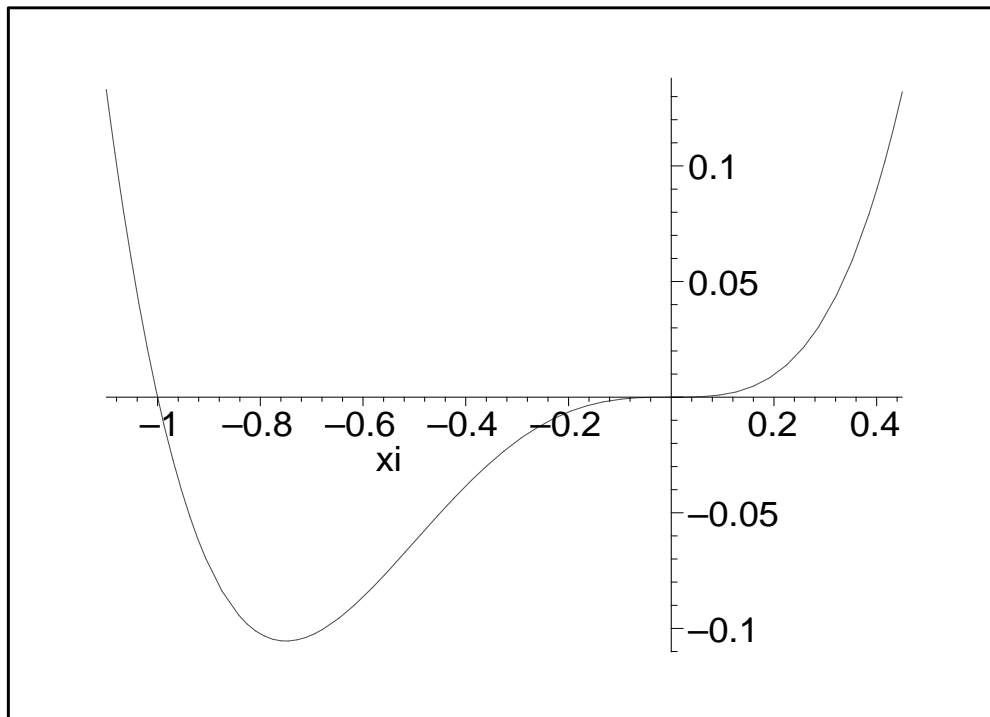
```
> x1:=-3/8+1/8*sqrt(9-32*eta): x2:=-3/8-1/8*sqrt(9-32*eta):
> F2:=(xi,eta)->subs(y=xi,diff(F1(y,eta),y)):
> g0:=eta->simplify(F2(0,eta)): g1:=eta->simplify(F2(x1,eta)):
> g2:=eta->simplify(F2(x2,eta)):
> g0(eta); g1(eta); g2(eta);
2*eta
9/8 - 3/8*sqrt(9-32*eta) - 4*eta
9/8 + 3/8*sqrt(9-32*eta) - 4*eta
> plot({g0(eta),g1(eta),g2(eta)},eta=-0.1..9/32);
```



x_0 -> maximum at $\eta < 0$, otherwise minimum; x_1 -> minimum at $\eta > 0$, maximum at $9/32 > \eta > 0$; x_2 -> minimum at $9/32 > \eta$.

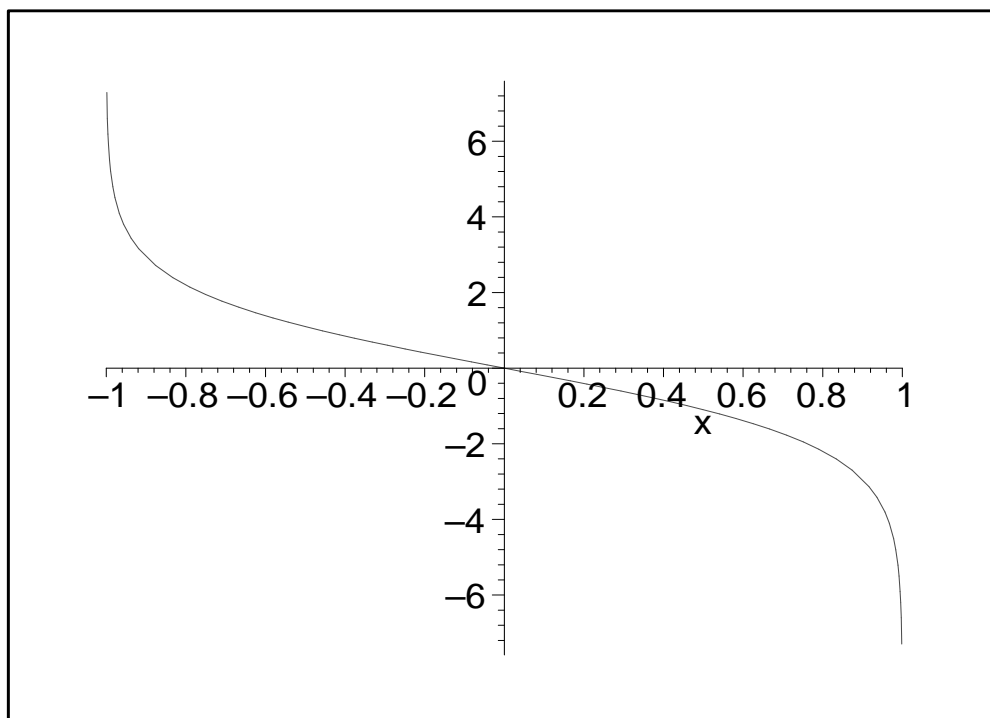
Two specific values: $\eta=0$ and $\eta=9/32$.

```
> plot(F(xi,0), xi=-1.1..0.45); plot(F(xi,9/32), xi=-0.7..0.25);
```

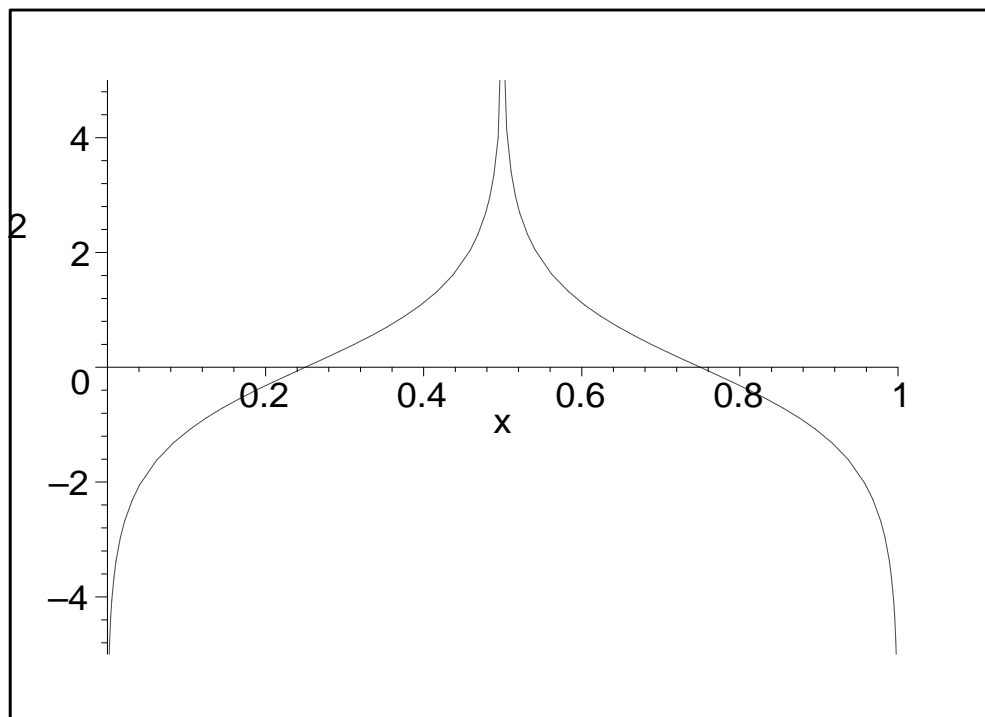


Problem 1.2

```
> f1:=x->ln((1-x)/(1+x)): plot(f1(x),x=-1..1);
```



```
> f2:=x->ln(abs(tan(Pi*x))): plot(f2(x),x=0..1,f2=-5..5);
```



```
> simplify(exp(4*ln(x))-(x^2+1)^2+2*x^2+1);
0
```

Problem 1.3

```
> simplify((sin(x))^(-2)-(tan(x))^(-2)-1,trig);
0
> assume(alpha>0): assume(beta>0):
> k:=alpha->sum(exp((I*beta-alpha)*n),n=0..infinity):

> a1:=alpha->evalc(Re(k(alpha))): a2:=alpha->evalc(Im(k(alpha))):
> a1(alpha); a2(alpha);
```

$$-\frac{e^{\alpha}(\cos(\beta) - e^{\alpha})}{(\cos(\beta) - e^{\alpha})^2 + \sin(\beta)^2}$$

$$\frac{e^{\alpha} \sin(\beta)}{(\cos(\beta) - e^{\alpha})^2 + \sin(\beta)^2}$$

Problem 1.4

```
> assume(zeta>0): assume(n,natural):
> simplify(int(x^n*exp(-zeta*x),x=0..infinity));
```

$$\zeta^{-(n+1)} \Gamma(n+1)$$

```
> int((x^2+a^2)^(-1),x); int((x^2-a^2)^(-1),x);
```

$$\frac{\arctan\left(\frac{x}{a}\right)}{a}$$

$$\frac{1}{2} \frac{\ln(x-a)}{a} - \frac{1}{2} \frac{\ln(a+x)}{a}$$

```
> int(exp(-zeta*x^2/2),x=0..infinity);
```

$$\frac{1}{2} \frac{\sqrt{2} \sqrt{\pi}}{\sqrt{\zeta}}$$

Problem 2.1

(a)

```
> uax:=(x,y)->-y/(x^2+y^2): uay:=(x,y)->x/(x^2+y^2):
> simplify(diff(uax(x,y),y)-diff(uay(x,y),x));
0
```

The differential is exact

```
> ua:=(x,y)->int(uax(xi,y),xi=0..x): ua(x,y);
-arctan(x/y)
```

(b)

```
> ubx:=(x,y)->(y-x^2):  uby:=(x,y)->(x+y^2):
> simplify(diff(ubx(x,y),y)-diff(uby(x,y),x));
0
```

The differential is exact

```
> ub:=(x,y)->int(ubx(xi,y),xi=0..x)+int(uby(x,eta),eta=0..y)-int(int(diff(ubx(xi,eta),eta),eta=0..y),xi=0..x);
```

$$ub := (x, y) \rightarrow \int_0^x ubx(\xi, y) d\xi + \int_0^y uby(x, \eta) d\eta - \int_0^x \int_0^y \frac{\partial}{\partial \eta} ubx(\xi, \eta) d\eta d\xi$$

```
> ub(x,y);
```

$$yx - \frac{1}{3}x^3 + \frac{1}{3}y^3$$

(c)

```
> ucx:=(x,y)->(2*y^2-3*x):  ucy:=(x,y)->-4*x*y:
> simplify(diff(ucx(x,y),y)-diff(ucy(x,y),x));
8y
```

The differential is not exact

Problem 2.2**General definitions**

```
> ua:=(x,y)->int(ux(xi,b),xi=a..x)+int(uy(x,eta),eta=b..y);
```

$$ua := (x, y) \rightarrow \int_a^x ux(\xi, b) d\xi + \int_b^y uy(x, \eta) d\eta$$

```
> ub:=(x,y)->int(uy(a,eta),eta=b..y)+int(ux(xi,y),xi=a..x);
```

$$ub := (x, y) \rightarrow \int_b^y uy(a, \eta) d\eta + \int_a^x ux(\xi, y) d\xi$$

```
> ux1:=(x,y)->2*x*y+x^2:  uy1:=(x,y)->x^2:
```

```
> ua1:=(x,y)->int(ux1(xi,b),xi=a..x)+int(uy1(x,eta),eta=b..y):
```

```
> ub1:=(x,y)->int(uy1(a,eta),eta=b..y)+int(ux1(xi,y),xi=a..x):
```

```
> ua1(x,y); ub1(x,y); simplify(ua1(x,y)-ub1(x,y));
```

$$b(x^2 - a^2) + \frac{1}{3}x^3 - \frac{1}{3}a^3 + x^2(y - b)$$

$$a^2(y - b) + y(x^2 - a^2) + \frac{1}{3}x^3 - \frac{1}{3}a^3$$

0

```
> ux2:=(x,y)->y*(2-2*y):  uy2:=(x,y)->-x^2:
```



```

> ua2:=(x,y)->int(ux2(xi,b),xi=a..x)+int(uy2(x,eta),eta=b..y):
> ub2:=(x,y)->int(uy2(a,eta),eta=b..y)+int(ux2(xi,y),xi=a..x):
> ua2(x,y); ub2(x,y); simplify(ua2(x,y)-ub2(x,y));
      b(2-2b)(x-a)-x^2(y-b)
     -a^2(y-b)+y(2-2y)(x-a)
2bx-2ba-2b^2x+2b^2a-x^2y+x^2b+a^2y-a^2b-2yx+2ya+2y^2x-2y^2a

```

Why?

```

> simplify(diff(ux2(x,y),y)-uy2(x,y),x);
      2-4y+x^2

```

The differential is not exact.

Problem 2.17

```

> P:=(T,v)->R*T/(v-b)-alpha/v^2:
> num:=(diff(P(T,v),T))^2: den:=diff(P(T,v),v);
      den := -\frac{RT}{(v-b)^2} + \frac{2\alpha}{v^3}
> simplify(-T*num/den);
      \frac{v^3 R^2 T}{-RT v^3 + 2\alpha v^2 - 4\alpha v b + 2\alpha b^2}
> factor(2*alpha*v^2-4*alpha*v*b+2*alpha*b^2);
      2\alpha(-v+b)^2

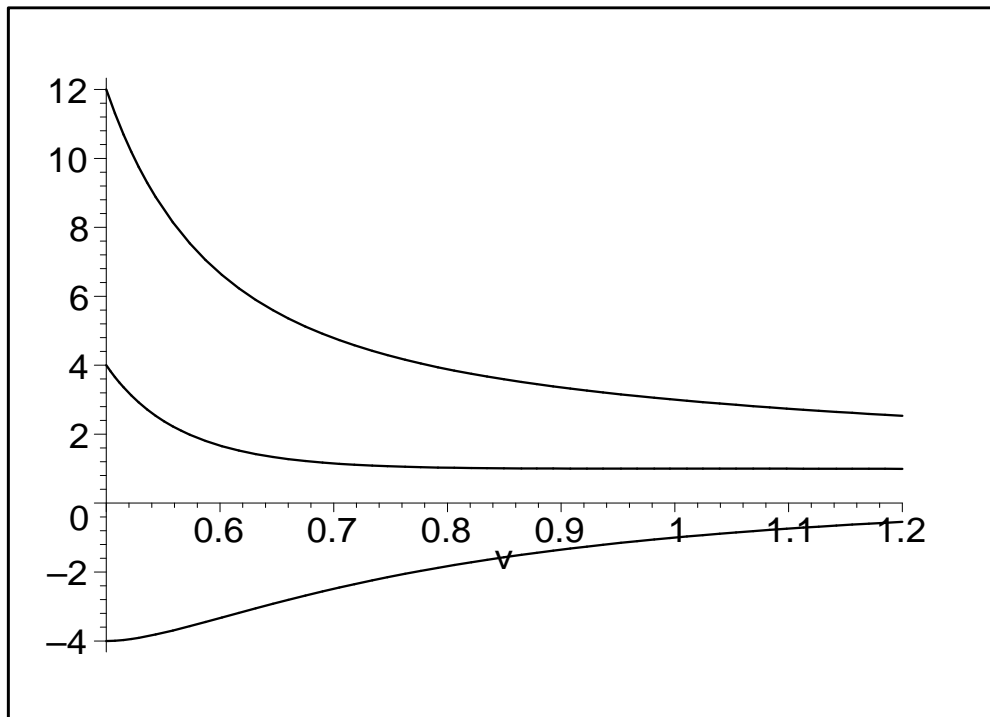
```

Problem 3.7

```

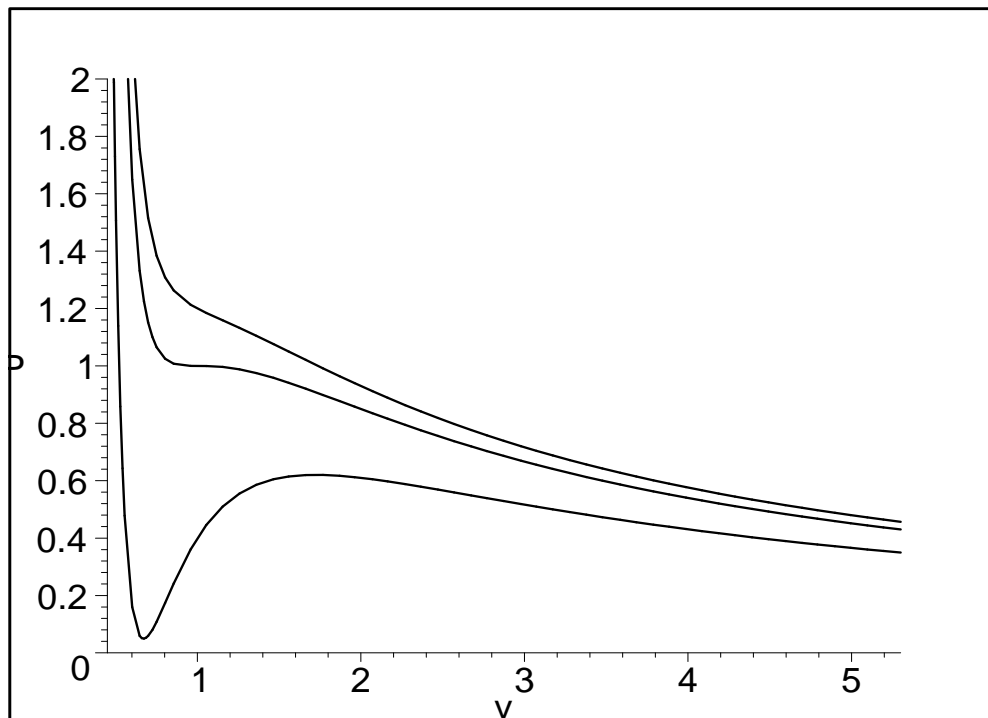
> P:=(v,T)->(8*T/(3*v-1))-3/v^2;
      P := (v, T) \to 8 \frac{T}{3v-1} - \frac{3}{v^2}
> plot({P(v,1.5),P(v,1),P(v,0.5)}
> },v=0.5..1.2,thickness=3,color=black);

```



For $T=0.5$ there is no stable region at all. The phase transition can exist only near $T=1$.

```
> plot({P(v,1.05),P(v,1),P(v,0.85)
> },v=0.45..5.3,P=0..2,thickness=3,color=black);
```



> ?plot,color

Problem 3.12

> phi:=xi->(A/3)*(xi+eta)^2-(2*B/27)*(xi+eta)^3+(C/9)*(xi+eta)^4:
 > series(phi(xi),xi=0,5);

$$\left(\frac{1}{3}A\eta^2 - \frac{2}{27}B\eta^3 + \frac{1}{9}C\eta^4\right) + \left(\frac{2}{3}A\eta - \frac{2}{9}B\eta^2 + \frac{4}{9}C\eta^3\right)\xi + \left(\frac{1}{3}A - \frac{2}{9}B\eta + \frac{2}{3}C\eta^2\right)\xi^2 + \left(-\frac{2}{27}B + \frac{4}{9}C\eta\right)\xi^3 + \frac{1}{9}C\xi^4$$

> c3:=eta->-2/27*B+4/9*C*eta: solve(c3(eta)=0,eta);

$$\frac{1}{6} \frac{B}{C}$$

> c1:=(A,eta)->2/3*A*eta-2/9*B*eta^2+4/9*C*eta^3;

$$c1 := (A, \eta) \rightarrow \frac{2}{3}A\eta - \frac{2}{9}B\eta^2 + \frac{4}{9}C\eta^3$$

> solve(c1(A,B/(6*C)),A);

$$\frac{1}{27} \frac{B^2}{C}$$

> c2:=subs({eta=B/(6*C),A=B^2/(27*C)},1/3*A-2/9*B*eta+2/3*C*eta^2);

$$c2 := -\frac{1}{162} \frac{B^2}{C}$$

> delta:=xi->(C/9)*xi^4+c2*xi^2:

> delta1:=xi->subs(y=xi,diff(delta(y),y)): delta1(xi);

$$\frac{4}{9}C\xi^3 - \frac{1}{81} \frac{B^2\xi}{C}$$

> solve(4/9*C*xi^2-1/81*B^2/C,xi);

$$-\frac{1}{6} \frac{B}{C}, \frac{1}{6} \frac{B}{C}$$

Problem 3.13

> P:=(v,T)->8*T/(3*v-1)-3/(T*v^2);

$$P := (v, T) \rightarrow 8 \frac{T}{3v-1} - \frac{3}{Tv^2}$$

> p1:=(nu,epsilon)=P(1+nu,1+epsilon)-1;

$$p1 := (v, \epsilon) = 8 \frac{1+\epsilon}{2+3v} - \frac{3}{(1+\epsilon)(1+v)^2} - 1$$

> aux:=series(8*(1+epsilon)/(2+3*nu)-3/(1+epsilon)/(1+nu)^2-1,nu=0,4):a

> ux;

$$(3 + 4\varepsilon - \frac{3}{1+\varepsilon}) + (-6 - 6\varepsilon + \frac{6}{1+\varepsilon})v + (-9\frac{1}{1+\varepsilon} + 9 + 9\varepsilon)v^2 + (12\frac{1}{1+\varepsilon} - \frac{27}{2} - \frac{27}{2}\varepsilon)v^3 + O(v^4)$$

```
> aux1:=(epsilon)->3+4*epsilon-3/(1+epsilon)+(-6-6*epsilon+6/(1+epsilon
> ))*nu+(-9*1/(1+epsilon)+9+9*epsilon)*nu^2
> +(12*1/(1+epsilon)-27/2-27/2*epsilon)*nu^3;
```

$$aux1 := \varepsilon \rightarrow 3 + 4\varepsilon - \frac{3}{1+\varepsilon} + (-6 - 6\varepsilon + \frac{6}{1+\varepsilon})v + (-9\frac{1}{1+\varepsilon} + 9 + 9\varepsilon)v^2 + (12\frac{1}{1+\varepsilon} - \frac{27}{2} - \frac{27}{2}\varepsilon)v^3$$

```
> aux2:=series(aux1(epsilon), epsilon=0,2);
```

$$aux2 := -\frac{3}{2}v^3 + (7 - \frac{51}{2}v^3 + 18v^2 - 12v)\varepsilon + O(\varepsilon^2)$$

Simplified equation of state

```
> p:=(nu, epsilon)->-3/2*nu^3+(7-12*nu)*epsilon;
```

$$p := (v, \varepsilon) \rightarrow -\frac{3}{2}v^3 + (7 - 12v)\varepsilon$$

Critical point - epsilon=0;

```
> d1:=(nu, epsilon)->subs(y=nu, diff(p(y, epsilon), y)): d1(nu, epsilon);
-\frac{9}{2}v^2 - 12\varepsilon
```

The curve is symmetric. That leads to $v_g = -v_l = v$

```
> solve(p(v, epsilon) = p(-v, epsilon), v);
0, 2\sqrt{-2\varepsilon}, -2\sqrt{-2\varepsilon}
```

Critical exponent beta=1/2

Along the coexistence curve, $v^2 = -8\varepsilon$. exponent gamma=1

Function of pressure

```
> P1:=(rho, T)->8*T*rho/(3-rho)-3*rho^2/T:
```

Near the critical point

```
> P1(1+xi, 1);
```

$$8\frac{1+\xi}{2-\xi} - 3(1+\xi)^2$$

> series(8*(1+xi)/(2-xi)-3*(1+xi)^2,xi=0);

$$1 + \frac{3}{2}\xi^3 + \frac{3}{4}\xi^4 + \frac{3}{8}\xi^5 + O(\xi^6)$$

the exponent delta=3

Problem 4.9

> assume(z>0): int(1/sqrt(z-x^2),x=0..sqrt(z));

$$\frac{1}{2}\pi$$

> f:=k->1/(1-2*I*k): d1:=k->subs(y=k,diff(f(y),y)):

> d2:=k->subs(y=k,diff(d1(y),y)): d3:=k->subs(y=k,diff(d2(y),y)):

> d1(0); d2(0); d3(0);

$$\begin{aligned} & 2I \\ & -8 \\ & -48I \end{aligned}$$

Problem 4.10

> P:=(N,k)->(N!/(k!*(N-k)!))*(1/4)^k*(3/4)^(N-k):

> evalf(P(12,3));

$$.2581036091$$

> evalf(P(120,30));

$$.08385171464$$

> G:=(N,k)->(1/sqrt(3*N*Pi/8))*exp(-(k-N/4)^2*8/(3*N));

$$G := (N, k) \rightarrow \frac{e^{(-8/3 \frac{(k-1/4N)^2}{N})}}{\sqrt{\frac{3}{8} N \pi}}$$

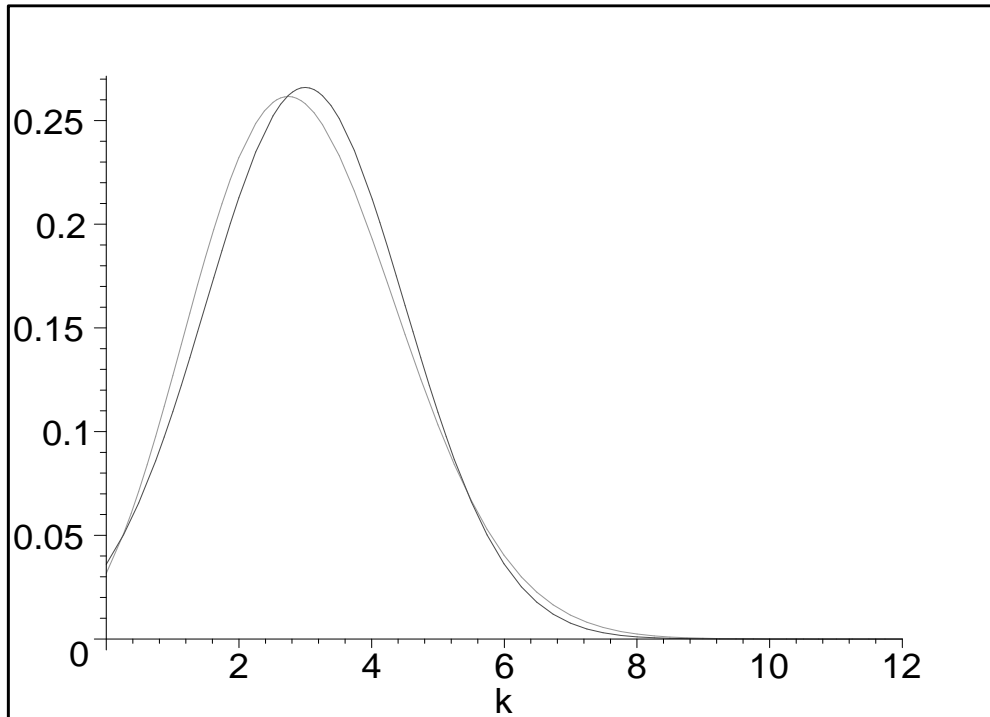
> evalf(G(12,3));

$$.2659615201$$

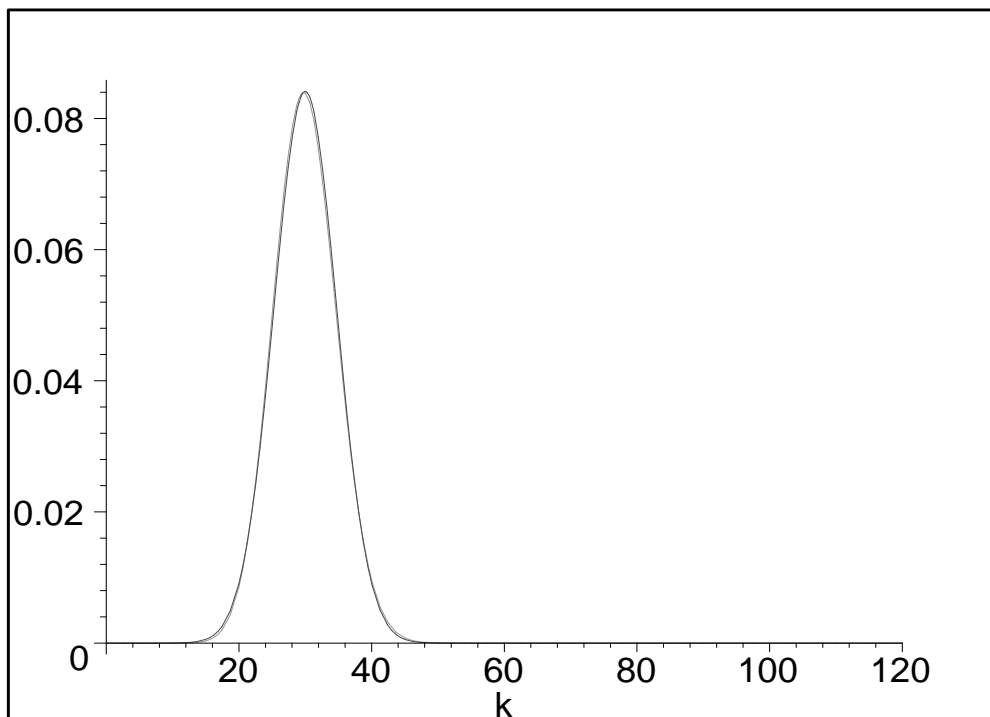
> evalf(G(120,30));

$$.08410441740$$

> plot({P(12,k),G(12,k)},k=0..12);



```
> plot({P(120,k),G(120,k)},k=0..120);
```



Problem 4.13

beta = sigma^2

```
> assume(beta>0): assume(a,real): assume(N>0):
> P:=k->(2*Pi*beta)^(-1/2)*int(exp(-(x-a)^2/(2*beta)-I*k*x),x=-infinity.
> .infinity): simplify(P(k));
```

$$e^{(1/2Ik(-2a + Ik\beta))}$$

```
> P1:=s->(2*Pi)^(-1)*int(exp(I*(s-N*a)*k-k^2*N*beta/2),k=-infinity..inf
> inity): P1(s);
```

$$\frac{1}{2} \frac{e^{(-1/2 \frac{(-s+N\tilde{a})^2}{N\tilde{\beta}})} \sqrt{2}}{\sqrt{\pi} \sqrt{N\tilde{\beta}}}$$

```
> int(s*P1(s),s=-infinity..infinity);
```

$$N\tilde{a}$$

```
> int(s^2*P1(s),s=-infinity..infinity)-N^2*a^2;
```

$$N\tilde{\beta}$$

Problem 4.14

```
> assume(a>0): assume(d>a): assume(N>0):
> simplify((2*a)^(-1)*int(x^2,x=d-a..d+a));
```

$$d^2 + \frac{1}{3}a^2$$

```
> simplify(N*(d^2+1/3*a^2)+N*(N-1)*d^2-N^2*d^2);
```

$$\frac{1}{3}N\tilde{a}^2$$

Problem 5.1

```
> with(linalg):
> Q:=array([[0,1,0],[1/8,1/2,3/8],[0,1/2,1/2]]);
```

$$Q := \begin{bmatrix} 0 & 1 & 0 \\ \frac{1}{8} & \frac{1}{2} & \frac{3}{8} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{bmatrix}$$

```
> QT:=transpose(Q):
```

```
> eigenvectors(Q);
```

$$[1, 1, \{[1, 1, 1]\}], \left[\frac{-1}{4}, 1, \left\{\left[6, \frac{-3}{2}, 1\right]\right\}\right], \left[\frac{1}{4}, 1, \{[4, 1, -2]\}\right]$$

```
> eigenvectors(QT);
```

$$\left[\frac{1}{4}, 1, \{[1, 2, -3]\}\right], \left[\frac{-1}{4}, 1, \{[1, -2, 1]\}\right], [1, 1, \{[1, 8, 6]\}]$$

> r1:=vector([1, 1, 1]); r2:=vector([6, -3/2, 1]); r3:=vector([4, 1,
> -2]);

$$r1 := [1, 1, 1]$$

$$r2 := \left[6, \frac{-3}{2}, 1\right]$$

$$r3 := [4, 1, -2]$$

> l1:=vector([1, 8, 6]); l2:=vector([1, -2, 1]); l3:=vector([1, 2,
> -3]);

$$l1 := [1, 8, 6]$$

$$l2 := [1, -2, 1]$$

$$l3 := [1, 2, -3]$$

> n1:=15: n2:=10: n3:=12:

> P1:=array([[l1[1]*r1[1], l1[2]*r1[1], l1[3]*r1[1]], [l1[1]*r1[2],
> l1[2]*r1[2], l1[3]*r1[2]], [l1[1]*r1[3], l1[2]*r1[3], l1[3]*r1[3]]);

$$P1 := \begin{bmatrix} 1 & 8 & 6 \\ 1 & 8 & 6 \\ 1 & 8 & 6 \end{bmatrix}$$

> P2:=array([[l2[1]*r2[1], l2[2]*r2[1], l2[3]*r2[1]], [l2[1]*r2[2],
> l2[2]*r2[2], l2[3]*r2[2]], [l2[1]*r2[3], l2[2]*r2[3], l2[3]*r2[3]]);

$$P2 := \begin{bmatrix} 6 & -12 & 6 \\ \frac{-3}{2} & 3 & \frac{-3}{2} \\ 1 & -2 & 1 \end{bmatrix}$$

> P3:=array([[l3[1]*r3[1], l3[2]*r3[1], l3[3]*r3[1]], [l3[1]*r3[2],
> l3[2]*r3[2], l3[3]*r3[2]], [l3[1]*r3[3], l3[2]*r3[3], l3[3]*r3[3]]);

$$P3 := \begin{bmatrix} 4 & 8 & -12 \\ 1 & 2 & -3 \\ -2 & -4 & 6 \end{bmatrix}$$

> P:=s->(1/n1)*P1+(1/n2)*(-1/4)^s*P2+(1/n3)*(1/4)^s*P3;
> Question (a)

$$P := s \rightarrow \frac{P1}{n1} + \frac{\left(\frac{-1}{4}\right)^s P2}{n2} + \frac{\left(\frac{1}{4}\right)^s P3}{n3}$$

> Pr:=s->evalm(P(s)): Pr(s); Pr(0);

$$\begin{bmatrix} \frac{1}{15} + \frac{3}{5} \left(\frac{-1}{4}\right)^s + \frac{1}{3} \left(\frac{1}{4}\right)^s & \frac{8}{15} - \frac{6}{5} \left(\frac{-1}{4}\right)^s + \frac{2}{3} \left(\frac{1}{4}\right)^s & \frac{2}{5} + \frac{3}{5} \left(\frac{-1}{4}\right)^s - \left(\frac{1}{4}\right)^s \\ \frac{1}{15} - \frac{3}{20} \left(\frac{-1}{4}\right)^s + \frac{1}{12} \left(\frac{1}{4}\right)^s & \frac{8}{15} + \frac{3}{10} \left(\frac{-1}{4}\right)^s + \frac{1}{6} \left(\frac{1}{4}\right)^s & \frac{2}{5} - \frac{3}{20} \left(\frac{-1}{4}\right)^s - \frac{1}{4} \left(\frac{1}{4}\right)^s \\ \frac{1}{15} + \frac{1}{10} \left(\frac{-1}{4}\right)^s - \frac{1}{6} \left(\frac{1}{4}\right)^s & \frac{8}{15} - \frac{1}{5} \left(\frac{-1}{4}\right)^s - \frac{1}{3} \left(\frac{1}{4}\right)^s & \frac{2}{5} + \frac{1}{10} \left(\frac{-1}{4}\right)^s + \frac{1}{2} \left(\frac{1}{4}\right)^s \end{bmatrix}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

> p0:=vector([0,1,0]);

$$p0 := [0, 1, 0]$$

> PS:=s->evalm(p0&*P(s)): PS(s);

Question (b)

$$\left[\frac{1}{15} - \frac{3}{20} \left(\frac{-1}{4}\right)^s + \frac{1}{12} \left(\frac{1}{4}\right)^s, \frac{8}{15} + \frac{3}{10} \left(\frac{-1}{4}\right)^s + \frac{1}{6} \left(\frac{1}{4}\right)^s, \frac{2}{5} - \frac{3}{20} \left(\frac{-1}{4}\right)^s - \frac{1}{4} \left(\frac{1}{4}\right)^s \right]$$

> PS(2); PS(infinity);

> Answer: after 2 steps $\frac{3}{8}$, after many steps $\frac{2}{5}$

$$\left[\frac{1}{16}, \frac{9}{16}, \frac{3}{8} \right]$$

$$\left[\frac{1}{15}, \frac{8}{15}, \frac{2}{5} \right]$$

> av:=s->1*PS(s)[1]+4*PS(s)[2]+9*PS(s)[3]: av(s);

> Moment

$$\frac{29}{5} - \frac{3}{10} \left(\frac{-1}{4}\right)^s - \frac{3}{2} \left(\frac{1}{4}\right)^s$$

> av:=sum(m^2*PS(s)[m],m=1..3);

$$\frac{29}{5} - \frac{3}{10} \left(\frac{-1}{4}\right)^s - \frac{3}{2} \left(\frac{1}{4}\right)^s$$

> corr:=s->simplify(sum(n^2*sum(m^2*PS(s)[m]*Pr(s)[m,n],

> m=1..3),n=1..3)): corr(s);

$$\frac{79}{50} (-1)^{(1+s)} 4^{(-s)} - \frac{33}{4} 16^{(-s)} + \frac{81}{100} (-1)^{(1+2s)} 16^{(-s)} + \frac{11}{2} (-1)^{(1+s)} 16^{(-s)} - \frac{3}{2} 4^{(-s)} + \frac{841}{25}$$

> corr(0);

> corr(infinity);

$$\frac{841}{25}$$

Problem 5.2

> with(linalg):

Warning, the protected names norm and trace have been redefined and unprotected

> Q:=array([[0,1/2,1/2],[0,0,1],[3/4,1/4,0]]);

$$Q := \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 1 \\ \frac{3}{4} & \frac{1}{4} & 0 \end{bmatrix}$$

> QT:=transpose(Q):

> r:=eigenvectors(Q):

> l:=eigenvectors(QT):

> r[1][1]; r[2][1]; r[3][1];

$$\begin{array}{c} 1 \\ -\frac{1}{2} + \frac{1}{4}I\sqrt{2} \\ -\frac{1}{2} - \frac{1}{4}I\sqrt{2} \end{array}$$

> l[1][1]; l[2][1]; l[3][1];

$$\begin{array}{c} 1 \\ -\frac{1}{2} + \frac{1}{4}I\sqrt{2} \\ -\frac{1}{2} - \frac{1}{4}I\sqrt{2} \end{array}$$

> r[1][3]; r[2][3]; r[3][3];

$$\begin{array}{c} \{[1, 1, 1]\} \\ \left\{ \left[-\frac{1}{6} - \frac{1}{3}I\sqrt{2}, 1, -\frac{1}{2} + \frac{1}{4}I\sqrt{2} \right] \right\} \\ \left\{ \left[-\frac{1}{6} + \frac{1}{3}I\sqrt{2}, 1, -\frac{1}{2} - \frac{1}{4}I\sqrt{2} \right] \right\} \end{array}$$

> l[1][3]; l[2][3]; l[3][3];

$$\left\{ \left[\frac{6}{5}, 1, \frac{8}{5} \right] \right\}$$

$$\left\{ \left[1, -\frac{1}{3} - \frac{1}{3}I\sqrt{2}, -\frac{2}{3} + \frac{1}{3}I\sqrt{2} \right] \right\}$$

$$\left\{ \left[1, -\frac{1}{3} + \frac{1}{3}I\sqrt{2}, -\frac{2}{3} - \frac{1}{3}I\sqrt{2} \right] \right\}$$

```

> r1:=vector([1, 1, 1]): r2:=vector([-1/6-1/3*I*sqrt(2), 1,
> -1/2+1/4*I*sqrt(2)]): r3:=vector([-1/6+1/3*I*sqrt(2), 1,
> -1/2-1/4*I*sqrt(2)]): l1:=vector([6/5, 1, 8/5]): l2:=vector([1,
> -1/3-1/3*I*sqrt(2), -2/3+1/3*I*sqrt(2)]): l3:=vector([1,
> -1/3+1/3*I*sqrt(2), -2/3-1/3*I*sqrt(2)]):
> n1:=evalm(l1&*r1): n2:=evalc(evalm(l2&*r2)):
> n3:=evalc(evalm(l3&*r3)):

```

Probability matrices.

```

> P1:=array([[l1[1]*r1[1], l1[2]*r1[1],l1[3]*r1[1]], [l1[1]*r1[2],
> l1[2]*r1[2],l1[3]*r1[2]], [l1[1]*r1[3], l1[2]*r1[3],l1[3]*r1[3]]);

```

$$P1 := \begin{bmatrix} \frac{6}{5} & 1 & \frac{8}{5} \\ \frac{6}{5} & 1 & \frac{8}{5} \\ \frac{6}{5} & 1 & \frac{8}{5} \end{bmatrix}$$

```

> P2:=array([[l2[1]*r2[1], l2[2]*r2[1],l2[3]*r2[1]], [l2[1]*r2[2],
> l2[2]*r2[2],l2[3]*r2[2]], [l2[1]*r2[3], l2[2]*r2[3],l2[3]*r2[3]]);

```

$$P2 := \begin{bmatrix} -\frac{1}{6} - \frac{1}{3}I\sqrt{2} & \left(-\frac{1}{3} - \frac{1}{3}I\sqrt{2}\right)\left(-\frac{1}{6} - \frac{1}{3}I\sqrt{2}\right) & \left(-\frac{2}{3} + \frac{1}{3}I\sqrt{2}\right)\left(-\frac{1}{6} - \frac{1}{3}I\sqrt{2}\right) \\ 1 & -\frac{1}{3} - \frac{1}{3}I\sqrt{2} & -\frac{2}{3} + \frac{1}{3}I\sqrt{2} \\ -\frac{1}{2} + \frac{1}{4}I\sqrt{2} & \left(-\frac{1}{3} - \frac{1}{3}I\sqrt{2}\right)\left(-\frac{1}{2} + \frac{1}{4}I\sqrt{2}\right) & \left(-\frac{2}{3} + \frac{1}{3}I\sqrt{2}\right)\left(-\frac{1}{2} + \frac{1}{4}I\sqrt{2}\right) \end{bmatrix}$$

```

> P3:=array([[l3[1]*r3[1], l3[2]*r3[1],l3[3]*r3[1]], [l3[1]*r3[2],
> l3[2]*r3[2],l3[3]*r3[2]], [l3[1]*r3[3], l3[2]*r3[3],l3[3]*r3[3]]);

```

$$P3 := \begin{bmatrix} -\frac{1}{6} + \frac{1}{3}I\sqrt{2} & \left(-\frac{1}{3} + \frac{1}{3}I\sqrt{2}\right)\left(-\frac{1}{6} + \frac{1}{3}I\sqrt{2}\right) & \left(-\frac{2}{3} - \frac{1}{3}I\sqrt{2}\right)\left(-\frac{1}{6} + \frac{1}{3}I\sqrt{2}\right) \\ 1 & -\frac{1}{3} + \frac{1}{3}I\sqrt{2} & -\frac{2}{3} - \frac{1}{3}I\sqrt{2} \\ -\frac{1}{2} - \frac{1}{4}I\sqrt{2} & \left(-\frac{1}{3} + \frac{1}{3}I\sqrt{2}\right)\left(-\frac{1}{2} - \frac{1}{4}I\sqrt{2}\right) & \left(-\frac{2}{3} - \frac{1}{3}I\sqrt{2}\right)\left(-\frac{1}{2} - \frac{1}{4}I\sqrt{2}\right) \end{bmatrix}$$

```

> P:=s->(1/n1)*P1+(1/n2)*(r[2][1])^s*P2+(1/n3)*(r[3][1])^s*P3;
> Question (a)

```

$$P := s \rightarrow \frac{P1}{n1} + \frac{r_{21}^s P2}{n2} + \frac{r_{31}^s P3}{n3}$$

```

> Pr:=s->evalm(P(s)):

```



```

                                -2
                                3
> r[3][3]; r[1][3]; r[2][3];
                                {1, 1, 1}
                                {-3, 1, 1}
                                {0, -1, 1}
> l[2][3]; l[1][3]; l[3][3];
                                {1, 3/2, 3/2}
                                {-2, 1, 1}
                                {0, -1, 1}
> r1:=vector([1, 1, 1]): r2:=vector([-3, 1, 1]): r3:=vector([0, -1,
> 1]): l1:=vector([1, 3/2, 3/2]): l2:=vector([-2, 1, 1]): l3:=vector([0,
> -1, 1]):
> n1:=evalm(l1&*r1): n2:=evalc(evalm(l2&*r2)):
> n3:=evalc(evalm(l3&*r3)):

```

Probability matrices.

```

> P1:=array([[l1[1]*r1[1], l1[2]*r1[1], l1[3]*r1[1]], [l1[1]*r1[2],
> l1[2]*r1[2], l1[3]*r1[2]], [l1[1]*r1[3], l1[2]*r1[3], l1[3]*r1[3]]);

```

$$P1 := \begin{bmatrix} 1 & \frac{3}{2} & \frac{3}{2} \\ 1 & \frac{3}{2} & \frac{3}{2} \\ 1 & \frac{3}{2} & \frac{3}{2} \end{bmatrix}$$

```

> P2:=array([[l2[1]*r2[1], l2[2]*r2[1], l2[3]*r2[1]], [l2[1]*r2[2],
> l2[2]*r2[2], l2[3]*r2[2]], [l2[1]*r2[3], l2[2]*r2[3], l2[3]*r2[3]]);

```

$$P2 := \begin{bmatrix} 6 & -3 & -3 \\ -2 & 1 & 1 \\ -2 & 1 & 1 \end{bmatrix}$$

```

> P3:=array([[l3[1]*r3[1], l3[2]*r3[1], l3[3]*r3[1]], [l3[1]*r3[2],
> l3[2]*r3[2], l3[3]*r3[2]], [l3[1]*r3[3], l3[2]*r3[3], l3[3]*r3[3]]);

```

$$P3 := \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{bmatrix}$$

```

> P:=s->(1/n1)*P1+(1/n2)*(r[3][1])^s*P2+(1/n3)*(r[2][1])^s*P3;
> Question (a)

```

$$P := s \rightarrow \frac{P1}{n1} + \frac{r_{31}^s P2}{n2} + \frac{r_{21}^s P3}{n3}$$

```
> Pr:=s->evalm(P(s)): Pr(s);
> Conditional probability
```

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2} + \frac{1}{2}\left(\frac{-2}{3}\right)^s & \frac{1}{2} - \frac{1}{2}\left(\frac{-2}{3}\right)^s \\ 0 & \frac{1}{2} - \frac{1}{2}\left(\frac{-2}{3}\right)^s & \frac{1}{2} + \frac{1}{2}\left(\frac{-2}{3}\right)^s \end{bmatrix}$$

```
> p0:=vector([0,0,1]):
> PS:=s->evalm(p0&*P(s)): PS(s);
```

Probability vector

$$\left[\frac{1}{4} - \frac{1}{4}\left(\frac{-2}{3}\right)^s, -\frac{1}{8} + \frac{1}{8}\left(\frac{-2}{3}\right)^s, \frac{7}{8} + \frac{1}{8}\left(\frac{-2}{3}\right)^s \right]$$

```
> PS(infinity); PS(0);
```

$$\begin{bmatrix} 0, \frac{1}{2}, \frac{1}{2} \\ 0, 0, 1 \end{bmatrix}$$

```
> moment:=1*PS(s)[1]+2*PS(s)[2]+3*PS(s)[3]: moment;
```

$$\frac{5}{2} + \frac{1}{2}\left(\frac{-2}{3}\right)^s$$

```
> corr:=s->simplify(sum(n*sum(m*PS(s)[m]*Pr(s)[m,n], m=1..3), n=1..3)):
> corr(s);
```

$$\frac{25}{4} + \frac{5}{4}3^{(-2s)}(-1)^{(2s)}2^{(2s)} + (-1)^s3^{(1-s)}2^{(-1+s)}$$

```
> corr(0); corr(infinity);
```

$$\frac{9}{25}$$

Problem 5.4

```
> with(linalg):
```

Warning, the protected names norm and trace have been redefined and unprotected

```
> Q0:=s->array([[0, (cos(Pi*s/2))^2, (sin(Pi*s/2))^2], [1/4
> +1/2*(sin(Pi*s/2))^2, 0, 1/4+1/2*(cos(Pi*s/2))^2], [1/2*(cos(Pi*s/2))^2, 1
> /2+1/2*(sin(Pi*s/2))^2, 0]]): Q0(s);
```

$$\begin{bmatrix} 0 & \cos\left(\frac{1}{2}\pi s\right)^2 & \sin\left(\frac{1}{2}\pi s\right)^2 \\ \frac{1}{4} + \frac{1}{2}\sin\left(\frac{1}{2}\pi s\right)^2 & 0 & \frac{1}{4} + \frac{1}{2}\cos\left(\frac{1}{2}\pi s\right)^2 \\ \frac{1}{2}\cos\left(\frac{1}{2}\pi s\right)^2 & \frac{1}{2} + \frac{1}{2}\sin\left(\frac{1}{2}\pi s\right)^2 & 0 \end{bmatrix}$$

> simplify(Q0(2*s));

$$\begin{bmatrix} 0 & \cos(\pi s)^2 & 1 - \cos(\pi s)^2 \\ \frac{3}{4} - \frac{1}{2}\cos(\pi s)^2 & 0 & \frac{1}{4} + \frac{1}{2}\cos(\pi s)^2 \\ \frac{1}{2}\cos(\pi s)^2 & 1 - \frac{1}{2}\cos(\pi s)^2 & 0 \end{bmatrix}$$

Since $[\cos(\pi s)]^2=1$, we get

> Q:=array([[0,1,0],[1/4,0,3/4],[1/2,1/2,0]]);

$$Q := \begin{bmatrix} 0 & 1 & 0 \\ \frac{1}{4} & 0 & \frac{3}{4} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{bmatrix}$$

> QT:=transpose(Q):
 > r:=eigenvectors(Q):
 > l:=eigenvectors(QT):
 > r[1][1]; r[2][1]; r[3][1];

$$\begin{array}{c} 1 \\ -\frac{1}{2} + \frac{1}{4}I\sqrt{2} \\ -\frac{1}{2} - \frac{1}{4}I\sqrt{2} \end{array}$$

> l[1][1]; l[2][1]; l[3][1];

$$\begin{array}{c} -\frac{1}{2} + \frac{1}{4}I\sqrt{2} \\ -\frac{1}{2} - \frac{1}{4}I\sqrt{2} \\ 1 \end{array}$$

> r[3][3]; r[1][3]; r[2][3];

$$\left\{ \left[1, -\frac{1}{2} - \frac{1}{4}I\sqrt{2}, -\frac{1}{6} + \frac{1}{3}I\sqrt{2} \right] \right\}$$

$$\{[1, 1, 1]\}$$

$$\left\{ \left[1, -\frac{1}{2} + \frac{1}{4}I\sqrt{2}, -\frac{1}{6} - \frac{1}{3}I\sqrt{2} \right] \right\}$$

> l[3][3]; l[1][3]; l[2][3];

$$\left\{ \left[1, \frac{8}{5}, \frac{6}{5} \right] \right\}$$

$$\left\{ \left[-\frac{1}{3} - \frac{1}{3}I\sqrt{2}, -\frac{2}{3} + \frac{1}{3}I\sqrt{2}, 1 \right] \right\}$$

$$\left\{ \left[-\frac{1}{3} + \frac{1}{3}I\sqrt{2}, -\frac{2}{3} - \frac{1}{3}I\sqrt{2}, 1 \right] \right\}$$

> r1:=vector([1, 1, 1]): r2:=vector([1, -1/2+1/4*I*sqrt(2),
 > -1/6-1/3*I*sqrt(2)]): r3:=vector([1, -1/2-1/4*I*sqrt(2),
 > -1/6+1/3*I*sqrt(2)]): l1:=vector([1, 8/5, 6/5]):
 > l2:=vector([-1/3-1/3*I*sqrt(2), -2/3+1/3*I*sqrt(2), 1]):
 > l3:=vector([-1/3+1/3*I*sqrt(2), -2/3-1/3*I*sqrt(2), 1]):

> n1:=evalm(l1&*r1): n2:=evalc(evalm(l2&*r2)):
 > n3:=evalc(evalm(l3&*r3)):

Probability matrices.

> P1:=array([[l1[1]*r1[1], l1[2]*r1[1], l1[3]*r1[1]], [l1[1]*r1[2],
 > l1[2]*r1[2], l1[3]*r1[2]], [l1[1]*r1[3], l1[2]*r1[3], l1[3]*r1[3]]);

$$P1 := \begin{bmatrix} 1 & \frac{8}{5} & \frac{6}{5} \\ 1 & \frac{8}{5} & \frac{6}{5} \\ 1 & \frac{8}{5} & \frac{6}{5} \end{bmatrix}$$

> P2:=array([[l2[1]*r2[1], l2[2]*r2[1], l2[3]*r2[1]], [l2[1]*r2[2],
 > l2[2]*r2[2], l2[3]*r2[2]], [l2[1]*r2[3], l2[2]*r2[3], l2[3]*r2[3]]);

$$P2 := \begin{bmatrix} -\frac{1}{3} - \frac{1}{3}I\sqrt{2} & -\frac{2}{3} + \frac{1}{3}I\sqrt{2} & 1 \\ (-\frac{1}{3} - \frac{1}{3}I\sqrt{2})(-\frac{1}{2} + \frac{1}{4}I\sqrt{2}) & (-\frac{2}{3} + \frac{1}{3}I\sqrt{2})(-\frac{1}{2} + \frac{1}{4}I\sqrt{2}) & -\frac{1}{2} + \frac{1}{4}I\sqrt{2} \\ (-\frac{1}{3} - \frac{1}{3}I\sqrt{2})(-\frac{1}{6} - \frac{1}{3}I\sqrt{2}) & (-\frac{2}{3} + \frac{1}{3}I\sqrt{2})(-\frac{1}{6} - \frac{1}{3}I\sqrt{2}) & -\frac{1}{6} - \frac{1}{3}I\sqrt{2} \end{bmatrix}$$

> P3:=array([[l3[1]*r3[1], l3[2]*r3[1], l3[3]*r3[1]], [l3[1]*r3[2],
 > l3[2]*r3[2], l3[3]*r3[2]], [l3[1]*r3[3], l3[2]*r3[3], l3[3]*r3[3]]);

$$P3 := \begin{bmatrix} -\frac{1}{3} + \frac{1}{3}I\sqrt{2} & -\frac{2}{3} - \frac{1}{3}I\sqrt{2} & 1 \\ (-\frac{1}{3} + \frac{1}{3}I\sqrt{2})(-\frac{1}{2} - \frac{1}{4}I\sqrt{2}) & (-\frac{2}{3} - \frac{1}{3}I\sqrt{2})(-\frac{1}{2} - \frac{1}{4}I\sqrt{2}) & -\frac{1}{2} - \frac{1}{4}I\sqrt{2} \\ (-\frac{1}{3} + \frac{1}{3}I\sqrt{2})(-\frac{1}{6} + \frac{1}{3}I\sqrt{2}) & (-\frac{2}{3} - \frac{1}{3}I\sqrt{2})(-\frac{1}{6} + \frac{1}{3}I\sqrt{2}) & -\frac{1}{6} + \frac{1}{3}I\sqrt{2} \end{bmatrix}$$

> P:=s->(1/n1)*P1+(1/n2)*(r[1][1])^(2*s)*P2+(1/n3)*(r[2][1])^(2*s)*P3;
> Question (a)

$$P := s \rightarrow \frac{P1}{n1} + \frac{r_{11}^{(2s)} P2}{n2} + \frac{r_{21}^{(2s)} P3}{n3}$$

> Pr:=s->evalm(P(s)):
> Conditional probability

> p01:=vector([1,0,0]): p02:=vector([0,1,0]):

> PS1:=s->evalm(p01&*P(s)): PS2:=s->evalm(p02&*P(s)):

> PS1(s)[1];

$$\frac{5}{19} + \frac{-\frac{1}{3} - \frac{1}{3}I\sqrt{2}}{-\frac{1}{3} - I\sqrt{2}} + \frac{(-\frac{1}{2} + \frac{1}{4}I\sqrt{2})^{(2s)} (-\frac{1}{3} + \frac{1}{3}I\sqrt{2})}{-\frac{1}{3} + I\sqrt{2}}$$

> PS1(s)[2];

$$\frac{8}{19} + \frac{-\frac{2}{3} + \frac{1}{3}I\sqrt{2}}{-\frac{1}{3} - I\sqrt{2}} + \frac{(-\frac{1}{2} + \frac{1}{4}I\sqrt{2})^{(2s)} (-\frac{2}{3} - \frac{1}{3}I\sqrt{2})}{-\frac{1}{3} + I\sqrt{2}}$$

> PS2(s)[1];

$$\frac{5}{19} + \frac{(-\frac{1}{3} - \frac{1}{3}I\sqrt{2})(-\frac{1}{2} + \frac{1}{4}I\sqrt{2})}{-\frac{1}{3} - I\sqrt{2}} + \frac{(-\frac{1}{2} + \frac{1}{4}I\sqrt{2})^{(2s)} (-\frac{1}{3} + \frac{1}{3}I\sqrt{2})(-\frac{1}{2} - \frac{1}{4}I\sqrt{2})}{-\frac{1}{3} + I\sqrt{2}}$$

> PS2(s)[2];

$$\frac{8}{19} + \frac{(-\frac{2}{3} + \frac{1}{3}I\sqrt{2})(-\frac{1}{2} + \frac{1}{4}I\sqrt{2})}{-\frac{1}{3} - I\sqrt{2}} + \frac{(-\frac{1}{2} + \frac{1}{4}I\sqrt{2})^{(2s)} (-\frac{2}{3} - \frac{1}{3}I\sqrt{2})(-\frac{1}{2} - \frac{1}{4}I\sqrt{2})}{-\frac{1}{3} + I\sqrt{2}}$$

The results can be transformed to polar form by the command polar.

Problem 5.5

> assume(N,natural): assume(k,real): assume(s>0); assume(n,integer):
> P:=(n,s,N)->(1/(2*N+1))*(1+2*sum(cos(2*Pi*k*n/(2*N+1))*exp(-2*s*(sin(Pi*k/(2*N+1)))^2),k=1..N)):

> P(n,s,N);

$$\frac{1 + 2 \left(\sum_{k=1}^{N^{\sim}} \cos\left(2 \frac{\pi k^{\sim} n^{\sim}}{2N^{\sim} + 1}\right) e^{(-2s^{\sim} \sin(\frac{\pi k^{\sim}}{2N^{\sim} + 1})^2)} \right)}{2N^{\sim} + 1}$$

> Pm:=[seq(P(i,2,2),i=-2..2)]: evalf(Pm);

[.1220644066, .2223516301, .3111679263, .2223516301, .1220644066]

Problem 5.8

> with(linalg):

Warning, the protected names norm and trace have been redefined and unprotected

> w:=matrix(3,3,[0,1/2,1/2,1/3,0,1/3,1/3,1/3,0]);

$$w := \begin{bmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{3} & 0 & \frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & 0 \end{bmatrix}$$

> M:=matrix(3,3,[-1,1/2,1/2,1/3,-1,1/3,1/3,1/3,-1]);

$$M := \begin{bmatrix} -1 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{3} & -1 & \frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & -1 \end{bmatrix}$$

> MT:=transpose(M):

> eigenvectors(M);

$$\left[-\frac{5}{6} + \frac{1}{6}\sqrt{13}, 1, \left\{ \left[-\frac{1}{2} + \frac{1}{2}\sqrt{13}, 1, 1 \right] \right\} \right], \left[-\frac{5}{6} - \frac{1}{6}\sqrt{13}, 1, \left\{ \left[-\frac{1}{2} - \frac{1}{2}\sqrt{13}, 1, 1 \right] \right\} \right],$$

$$\left[\frac{-4}{3}, 1, \{[0, -1, 1]\} \right]$$

> eigenvectors(MT);

$$\left[\frac{-4}{3}, 1, \{[0, -1, 1]\} \right], \left[-\frac{5}{6} + \frac{1}{6}\sqrt{13}, 1, \left\{ \left[-\frac{1}{3} + \frac{1}{3}\sqrt{13}, 1, 1 \right] \right\} \right],$$

$$\left[-\frac{5}{6} - \frac{1}{6}\sqrt{13}, 1, \left\{ \left[-\frac{1}{3} - \frac{1}{3}\sqrt{13}, 1, 1 \right] \right\} \right]$$

> lambda:=vector([-5/6+1/6*sqrt(13), -5/6-1/6*sqrt(13), -4/3]):

```
> r1:=vector([-1/2+1/2*sqrt(13), 1, 1]); r2:=vector([-1/2-1/2*sqrt(13),
> 1, 1]); r3:=vector([0, -1, 1]);
```

$$r1 := \left[-\frac{1}{2} + \frac{1}{2}\sqrt{13}, 1, 1 \right]$$

$$r2 := \left[-\frac{1}{2} - \frac{1}{2}\sqrt{13}, 1, 1 \right]$$

$$r3 := [0, -1, 1]$$

```
> l1:=vector([-1/3+1/3*sqrt(13), 1, 1]); l2:=vector([-1/3-1/3*sqrt(13),
> 1, 1]); l3:=vector([0, -1, 1]);
```

$$l1 := \left[-\frac{1}{3} + \frac{1}{3}\sqrt{13}, 1, 1 \right]$$

$$l2 := \left[-\frac{1}{3} - \frac{1}{3}\sqrt{13}, 1, 1 \right]$$

$$l3 := [0, -1, 1]$$

1

```
> n1:=evalm(l1&*r1): n2:=evalm(l2&*r2): n3:=evalm(l3&*r3):
```

```
> Q1:=-sum((1/n1)*r1[1]*l1[k]/lambda[1],k=1..3):
```

```
> Q2:=-sum((1/n2)*r1[1]*l1[k]/lambda[2],k=1..3):
```

```
> Q3:=-sum((1/n3)*r1[1]*l1[k]/lambda[1],k=1..3):
```

```
> evalf(Q1+Q2+Q3);
```

```
> First passage time
```

13.64536110

```
> :
```


Bibliography

- [1] L. E. Reichl *A modern course in statistical physics*, 1998.