

THERMODYNAMICS AND STATISTICAL PHYSICS

Problems

Week 1

1. One kilogram of water at 0°C is brought into contact with a large reservoir at 100°C . When the water has reached 100° , what has been the change in entropy of the water, of the heat reservoir, and of the entire system consisting of both water and heat reservoir? The heat capacity of water is $4.19 \text{ JK}^{-1}\text{g}^{-1}$.
2. The enthalpy H of a system is defined as

$$H = E + pV$$

The heat capacity at constant pressure C_p is given by

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

Find an expression for the difference $C_p - C_v$, where C_v is the heat capacity at constant volume. Show also that $c_p - c_v = R$ for one mole of an ideal gas.

3. A container is separated into two equal parts by a partition. The right hand part is empty (vacuum) whereas the left hand part contains a monoatomic ideal gas at temperature T_1 and pressure p_1 . The two halves have the same volume V_1 . The ideal gas obeys the equation of state $pV = NkT$. The container is thermally insulated from its surrounding.
 - a) The partition is slowly moved to the right so that the gas eventually fills the whole container. Calculate the temperature T_2 of the gas in this state.
 - b) A big hole is made in the partition when placed in its original position. What will be the final temperature T_3 after equilibrium is reached?
 - c) Calculate the change of entropy in the two cases.

For an adiabatic process $pV^\gamma = \text{constant}$. The heat capacity at constant volume C_V is for a monoatomic ideal gas given by $\frac{3}{2}Nk$.

4. One mole of CH_4 is heated from 300°K to 400°K at
 - a) constant pressure
 - b) constant volume

Calculate the change of entropy assuming that the gas can be considered as ideal. For the above temperature interval it has been found experimentally that $C_p(T) = (18.92 + 0.0555T)\text{JK}^{-1}\text{mole}^{-1}$.

5. In order to measure $\gamma = c_p/c_v$ for an ideal gas, the following experiment is done. A piston with mass m and area A is brought into small vertical oscillations above the gas. The time τ of an oscillation is measured. The oscillations are assumed to be so slow that the gas is in thermodynamic equilibrium at any time. Heat exchange with the surroundings during the measurement can be neglected. The volume of the gas in equilibrium is V_0 and the external pressure is p_0 . Determine γ ! [Hints. Use the equation of motion for the piston. Also, observe that $(1+x)^p \approx 1+px$ if $|x| \ll 1$].
6. A gas obeys the following equation of state: $p = T \cdot f(V)$, where p denotes the pressure, T the temperature, and $f(V)$ a (suitably chosen) function of the volume V . It puts some restrictions on the heat capacity at constant volume C_V . Which of the following expressions is (are) possible?
- $C_V = bT$
 - $C_V = bT^2$
 - $C_V = bVT^2$

In all three cases b is a constant.

Show also that $E = E(T)$ for an ideal gas.

7. The heat capacity at constant volume C_V is very difficult to measure whereas the heat capacity at constant pressure can be measured relatively simply. To determine the value of C_V one, therefore, measures the value of C_p and calculates C_V by using the relation

$$C_V = C_p - TV \frac{\alpha^2}{K}$$

where

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

and

$$K = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

is the compressibility.

Prove the above relation.

Week 2

8. A particle of mass m is free to move in one dimension. Denote its position coordinate by x and its momentum by p . Suppose that this particle is confined within a box so as to be located between $x = 0$ and $x = L$ and suppose that its energy is known to lie between E and $E + \delta E$. Draw the classical phase space of this particle, indicating the regions of this space which are accessible to the particle.
9. Consider an ensemble of classical one-dimensional harmonic oscillators.
- Let the displacement x of an oscillator as a function of time t be given by $x = A \cos(\omega t + \phi)$. Assume that the phase angle ϕ is equally likely to assume any value in

its range $0 < \phi < 2\pi$. The probability $w(\phi)d\phi$ that ϕ lies in the range between ϕ and $\phi + d\phi$ is then simply

$$w(\phi)d\phi = \frac{1}{2\pi}d\phi$$

For any fixed time t , find the probability $P(x)dx$ that x lies between x and $x + dx$ by summing $w(\phi)d\phi$ over all angles ϕ for which x lies in this range. Express $P(x)$ in terms of A and x . Compare with $P \sim 1/v$ where v is the velocity.

b) Consider the classical phase space for such an ensemble of oscillators, their energy being known to lie in the small range between E and $E + \delta E$. Calculate $P(x)dx$ by taking the ratio of that volume of phase space lying in this energy range *and* in the range between x and $x + dx$ to the total volume of phase space lying in the energy range between E and $E + \delta E$. Express $P(x)$ in terms of E and x . By relating E to the amplitude A , show that the result is the same as that obtained in part a).

10. Consider a particle confined within a box in the shape of a rectangular parallelepiped of edges $L_x = L_y = L_z$. The possible energy levels of this particle are

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

a) Show, by considering how the energy is changed when the length L_x of the box is changed quasistatically by a small amount δL_x , that the force exerted by the particle on a wall perpendicular to the x axis is given by $F = -\frac{\partial E}{\partial L_x}$

b) Calculate explicitly the force per unit area (pressure) on this wall. By averaging over all possible states, find an expression for the mean pressure on this wall. Exploit the property that the average values $\overline{n_x^2}$, $\overline{n_y^2}$ and $\overline{n_z^2}$ must all be equal by symmetry. Show that this mean pressure can be very simply expressed in terms of the mean energy \overline{E} of the particle and the volume of the box $V = L_x L_y L_z$.

11. Calculate the number of states available to the particle in problem 10 if its energy is assumed to lie in the range between E and $E + \delta E$.
12. A harmonic oscillator has energy levels given by

$$\varepsilon = \left(\frac{1}{2} + n \right) h\nu, \quad n = 0, 1, 2, 3, \dots$$

A system consists of N identical independent oscillators. Its total energy is given by

$$E_M = \left(\frac{N}{2} + M \right) h\nu \quad \text{where } M = \sum_{i=1}^N n_i$$

a) Calculate the number of available states for the system with total energy E_M . [Hints: Show that the problem is equivalent to finding the number of permutations of M white balls and $N - 1$ black balls, where the white balls correspond to filled energy levels and the black balls to the space between the lined up oscillators.]

b) What is the probability that a given oscillator has the energy $\varepsilon = \left(\frac{1}{2} + k \right) h\nu$? Consider in particular the case when $N \gg 1$ and $M \gg k$.

13. The total energy of N identical independent oscillators is given by E . The oscillator frequency is ν . Calculate the temperature T of the system and draw a graph showing $\frac{E}{N h \nu}$ as a function of $\frac{kT}{h \nu}$. [Hint: Compare with problem 12a.]
14. Assume that there are $\Omega(E) = \omega(E) \delta E$ states in the energy range between E and $E + \delta E$. Show that the parameter $\beta = \frac{1}{kT}$ does not depend on δE .
15. Using the same assumptions as in problem 14, show that the entropy's dependence on δE can, for all practical purposes, be neglected for a macroscopic system.

Week 3

16. Show that the two expressions for the entropy

$$S = k \ln \Omega(\bar{E})$$

and

$$S = k(\ln Z + \beta \bar{E})$$

are equivalent.

17. Express the entropy in terms of the canonical probabilities P_r .
18. Derive the expression for the canonical distribution

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

by using purely combinatorial arguments.

19. A simple harmonic one-dimensional oscillator has energy levels given by

$$E_n = (n + 1/2) \hbar \omega$$

where ω is the characteristic frequency of the oscillator and where the quantum number n can assume the possible integral values $n = 0, 1, 2, 3, \dots$. Suppose that such an oscillator is in thermal contact with a heat reservoir at temperature T low enough so that $kT/(\hbar \omega) \ll 1$.

- a) Find the ratio of the probability of the oscillator being in the first excited state to the probability of its being in the ground state.
 - b) Assuming that only the ground state and first excited state are appreciably occupied, find the mean energy of the oscillator as a function of the temperature T .
20. A sample of mineral oil is placed in an external magnetic field H . Each proton has spin $\frac{1}{2}$ and a magnetic moment μ . It can, therefore, have two possible energies $\epsilon = \mp \mu H$, corresponding to the two possible orientations of its spin. An applied radio-frequency field can induce transitions between these two energy levels if its frequency ν satisfies the condition $h\nu = 2\mu H$. The power absorbed from the radiation field is then proportional to the difference in the number of nuclei in the two energy levels. Assume that the protons in the mineral oil are in thermal equilibrium at a temperature T which is so high that $\mu H \ll kT$. How does the absorbed power depend on the temperature T of the sample?

21. The atomic nuclei in a certain crystalline solid have spin one. According to quantum theory, each nucleus can therefore be in any one of three quantum states labeled by the quantum number m , where $m = 1, 0$, or -1 . This quantum number measures the projection of the nuclear spin along a crystal axis of the solid. Since the electric charge distribution in the nucleus is not spherically symmetric, but ellipsoidal, the energy of a nucleus depends on its spin orientation with respect to the internal electric field existing at its location. Thus a nucleus has the same energy $E = \epsilon$ in the states $m = 1$ and $m = -1$, compared with an energy $E = 0$ in the state $m = 0$.
- Find an expression, as a function of the absolute temperature T , of the nuclear contribution to the molar internal energy of the solid.
 - Find an expression, as a function of T , of the nuclear contribution to the molar entropy of the solid.
22. An ideal monoatomic gas of N particles, each of mass m , is at thermal equilibrium at absolute temperature T . The gas is contained in a cubical box of side L , whose top and bottom sides are parallel to the earth's surface. The effect of the earth's uniform gravitational field on the particles should be considered, the acceleration due to gravity being g .
- What is the average kinetic energy of a particle?
 - What is the average potential energy of a particle?
23. A thermally insulated container is divided into two parts by a thermally insulated partition. Both parts contain ideal gases which have equal constant heat capacities c_v . One of these parts contains ν_1 moles of gas at a temperature T_1 and pressure p_1 . The other contains ν_2 moles of gas at a temperature T_2 and pressure p_2 . The partition is now removed and the system is allowed to come to equilibrium.
- Find the final pressure.
 - Find the change ΔS of total entropy if the gases are *different*.
 - Find ΔS if the gases are *identical*.
24. A rubber band at absolute temperature T is fastened at one end to a peg, and supports from its other a mass m . Assume as a simple microscopic model of the rubber band that it consists of a linked polymer chain of N segments joined end to end. Each segment has a length a and can be oriented either parallel or antiparallel to the vertical direction. Find an expression for the resultant mean length \bar{l} of the rubber band as a function of m . Neglect the kinetic energy and mass of the segments themselves or any interaction between the segments.
25. Monoatomic molecules adsorbed on a surface are free to move on this surface and can be treated as a classical ideal two-dimensional gas. At absolute temperature T , what is the heat capacity per mole of molecules adsorbed on a surface of fixed size?

Week 4

26. A very sensitive spring balance consists of a quartz spring suspended from a fixed support. The spring constant is α , i.e. the restoring force of the spring is $-\alpha x$ if the spring is stretched by an amount x . The balance is at a temperature T in a location where the acceleration due to gravity is g .
- If a very small object of mass M is suspended from the spring, what is the mean resultant elongation \bar{x} of the spring?
 - What is the magnitude $\overline{(x - \bar{x})^2}$ of the thermal fluctuations of the object about its equilibrium position?
 - It becomes impracticable to measure the mass of an object when the fluctuations are so large that $[\overline{(x - \bar{x})^2}]^{\frac{1}{2}} = \bar{x}$. What is the minimum mass M which can be measured with this balance?
27. An elastic string can be described as consisting of a large number (N) of very short elements. For each element, two states are possible. In these states, the length of the element is $a + \delta$ and $a - \delta$, respectively. The energy difference between the two states can be neglected.
- Calculate the length of the string.
 - Consider a situation when one end of the string is attached to a fixed point, from which it is hanging down freely. A small ball with mass m is attached to the lower end of the string. How much will the length of the string increase compared to case a)? The mass of the string can be neglected.
28. A rough estimate of the melting point of a metal can be made using a one-dimensional model. Each atom is assumed to move in a quadratic potential well with an energy given by
- $$\varepsilon = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2.$$
- Use classical theory to determine the melting point, assuming that the metal melts when $\overline{x^2} = \gamma d$, where d is the distance between neighboring atoms.
29. The table below shows the specific heat for a number of gases. For the monoatomic gases c_v is close to $3 \text{ cal deg}^{-1} \text{ mole}^{-1}$, whereas for several of the twoatomic gases c_v is close to $5 \text{ cal deg}^{-1} \text{ mole}^{-1}$.
- Explain this difference.
 - For monoatomic and twoatomic gases c_v can easily be calculated. Do this! The tabulated values correspond to temperatures which are too low for excitations to vibrational states.
 - Which conclusions do you draw, when you compare your calculated values of c_v with those in the table?

Gas	c_v
Argon, A	2.98
Helium, He	2.98
Mercury, Hg	2.98
Hydrogen, H ₂	4.91
Oxygen, O ₂	5.05
Nitrogen, N ₂	4.95
Chlorine, Cl ₂	6.14
Nitric oxide, NO	5.11
Carbon monoxide, CO	4.97
Hydrogen chloride, HCl	5.01

30. In certain types of elongated molecules there are metal atoms aligned in long rows. The metal atoms, which are all of the same kind, have spin $1/2$. They have a magnetic moment μ pointing in the same direction as the spin. Due to the short range of the magnetic force, spin related interactions between the metal atoms are only important between nearest neighbors. Assume that the spin can only point up or down. The spin direction of atom i is then determined by the value of the spin variable s_i which takes the value $-1/2$ for spin down and $1/2$ for spin up. The total magnetic energy for all the metal atoms can be written

$$E = -4J \sum_{i=1}^{N-1} s_i s_{i+1}$$

where J is the strength of the magnetic coupling between the metal atoms. An example of a possible configuration is shown below.

↑↑↑↑↑↓↓↓↓↑↑↓↑↑↑↑↓↓↓↑↓↓

Let n denote the number of places where two neighboring spins have opposite directions. In the illustration above there are $n = 7$ such places.

- Give an expression for the magnetic energy as a function of n .
 - Give an expression for the entropy as a function of n .
 - What is the number n that minimizes Helmholtz free energy? Draw a simple graph showing how this number depends on the temperature.
31. The vibrational energies of a twoatomic molecule can be written

$$E_{vib} = nh\nu \quad \text{where } n = 0, 1, 2, 3, \dots$$

Use this for calculation how much the vibrations contribute to the mean energy and the heat capacity for one molecule. What is the value of c_v when $T \rightarrow 0$?

32. Consider an ensemble of N one-dimensional harmonic oscillators. The Hamiltonian is given by

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

Calculate $C_v(T)$. Investigate in particular what happens in the limits $T \rightarrow 0$ and $T \rightarrow \infty$.

33. A cylinder with radius R and height H contains a monoatomic gas. The cylinder is set in rotation about its symmetry axis. Due to friction between the gas and the walls of the cylinder, the gas will start to rotate as well. The atoms of the gas will then feel a centrifugal potential

$$V = -m\omega^2 r^2 / 2$$

where r is the distance from the rotational axis, m is the mass of an atom and ω is the angular velocity. Calculate the mean energy and heat capacity of the gas when equilibrium is achieved. The cylinder contains N atoms of the gas and the thickness of its walls can be neglected. What value will the heat capacity approach, when the radius of the cylinder is made very large? How do you explain the result?

34. The allowed rotational states of a twoatomic molecule have the energies

$$E_{rot} = \frac{I(I+1)\hbar^2}{2\mathcal{J}}$$

where the angular momentum I can have the values 0, 1, 2, 3, 4, ... and \mathcal{J} is the moment of inertia. Calculate an expression for the partition function. Only the rotational motion need to be considered. You may assume that $kT \gg \hbar^2/2\mathcal{J}$. Do not forget that each rotational state is $(2I+1)$ fold degenerate!

35. A twoatomic molecule like NO has a rotational spectrum

$$\varepsilon_{rot} = \frac{\hbar^2}{2\mathcal{J}} I(I+1)$$

where \mathcal{J} is the moment of inertia and I is an integer number. Each energy level is $(2I+1)$ fold degenerate. Consider one mole of such a gas.

- What is the ratio of the number of molecules with $I=0$ compared to the number of molecules with $I=1$?
- Calculate how much the rotation contributes to the heat capacity.

Week 5

36. a) Use your knowledge of the partition function Z to derive an expression for the entropy S of an ideal Fermi-Dirac gas. Express your answer solely in terms of \bar{n}_r , the mean number of particles in state r .
- b) Derive a similar expression for the entropy of a Bose-Einstein gas.
- c) What do these expressions for S become in the classical limit when $\bar{n}_r \ll 1$?
37. Derive an expression for the entropy at low temperatures for an ideal Fermi-Dirac gas. Hint: Show first that

$$F(T) = \frac{3}{5} N \mu_0 \left[1 - \frac{5\pi^2}{12} \left(\frac{kT}{\mu_0} \right)^2 + \dots \right].$$

38. Consider a system of two single-particle levels with energy 0 and ε , respectively. Three particles are placed in these levels. The energy of the levels does not depend on the spin of the particles. The temperature is such that $kT = \varepsilon$. Calculate numerical values for the Fermi energy (use ε as energy unit) and for the average number of particles in the lowest energy level if
- The three particles have spin 1/2.
 - The three particles have spin 0.
- What causes the difference?
39. Consider an ideal Fermi gas for which the single-particle energies lie so close that the grand partition function can be calculated as an integral. Show that $pV = \frac{2}{3}E$. What is the corresponding relation for an ideal Boson gas?
40. Study the quantum mechanical corrections in first non-vanishing order to the ideal gas law ($pV = NkT$) for systems consisting of fermions and bosons, respectively. Assume that $\frac{E-\mu}{kT}$ is small and make a serial expansion of the Fermi-Dirac and Bose-Einstein distribution function. Then, calculate the internal energy and use the result of problem 39 for calculating the equation of state. (To be observed: Solving the problem requires quite a lot of work!)
41. Electromagnetic radiation at temperature T_i fills a cavity of volume V . If the volume of the thermally insulated cavity is expanded quasistatically to a volume $8V$, what is the final temperature T_f ? Neglect the heat capacity of the cavity walls.
42. Apply the thermodynamic relation $TdS = d\bar{E} + \bar{p}dV$ to a photon gas. Here one can write $\bar{E} = V\bar{u}$ where $\bar{u}(T)$, the mean energy density of the radiation field, is independent of the volume V . The radiation pressure is $\bar{p} = \bar{u}/3$.
- Considering S as a function of T and V , express dS in term of dT and dV . Find $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$.
 - Show that the mathematical identity $\partial^2 S/\partial V\partial T = \partial^2 S/\partial T\partial V$ gives immediately a differential equation for \bar{u} which can be integrated to yield the Stefan-Boltzmann law $\bar{u} \propto T^4$.
43. It has been reported that a nuclear fission explosion produces a temperature of the order of 10^6 degrees K. Assuming this to be true over a sphere 10 cm in diameter, calculate approximately
- The total rate of electromagnetic radiation from the surface of this sphere.
 - The radiation flux (power incident per unit area) at a distance of 1 km.
 - The wavelength corresponding to the maximum in the radiated power spectrum.
44. The surface temperature of the sun is T_0 ($= 5500^\circ\text{K}$). Its radius is R ($= 7 \times 10^{10}$ cm) while the radius of the earth is r ($= 6.37 \times 10^8$ cm). The mean distance between the sun and the earth is L ($= 1.5 \times 10^{13}$ cm). In first approximation one can assume that both the sun and the earth absorb all electromagnetic radiation incident upon them. The earth has reached a steady state so that its mean temperature T does not change in time despite the fact that the earth constantly absorbs and emits radiation.
- Find an approximate expression for the temperature T of the earth in terms of the parameters T_0 , R , r and L .

- b) Calculate a numerical value for T .
45. The radiation effect received by Earth from the sun is 1.35 kW/m^2 . Use this information for estimating the surface temperature on the planet Pluto. Earth's distance from the sun is one astronomical unit (1 au). Pluto's average distance from the sun is 39.5 au. You may make the following assumptions: Pluto absorbs all electromagnetic radiation hitting the planet. The temperature is the same everywhere on the planet. There is an equilibrium state, such that the temperature stays constant although radiation is absorbed and emitted all the time.

Week 6

46. Show, by expanding Gibbs free energy G , that necessary conditions for stable equilibrium are
- a) $C_V \geq 0$ (vary T while V is kept constant)
- b) $(\frac{\partial p}{\partial V})_T \leq 0$ (vary V while T is kept constant)
47. Van der Waals equation of states for one mole of a gas can be written

$$(p + \frac{a}{V^2})(V - b) = RT$$

where a and b are constants. For a given temperature T , there exist in general two points in which $(\frac{\partial p}{\partial V})_T = 0$. In the so called critical point, the two points coincide. Denote the value of the variables in the critical point by an index k .

- a) Express a and b in terms of T_k and V_k .
- b) Express p_k in terms of T_k and V_k .
- c) Introduce dimensionless variables $T' = T/T_k$, $V' = V/V_k$ and $p' = p/p_k$. Then, rewrite van der Waals equation in terms of these variables.
48. The vapor pressure p (in mm mercury) is for solid ammoniac given by

$$\ln p = 23.03 - \frac{3754}{T}$$

and for liquid ammoniac by

$$\ln p = 19.49 - \frac{3063}{T}$$

- a) What is the temperature of the triple point?
- b) Calculate the energies of vaporization and sublimation at the triple point.
- c) Calculate the energy of melting at the triple point.
49. Consider an ideal gas in thermal equilibrium in a gravitational field (assume that the acceleration due to gravitation is g in direction $-z$). Calculate the chemical potential μ as a function of p , T and z . Then, use the condition $\mu = \text{constant}$ to determine the functional relation $p = p(T, z)$.

50. In order to calculate the heat capacity C_V of a crystal with N atoms per volume unit, one may assume that each atom performs harmonic oscillations in three degrees of freedom. Thus, we have $3N$ harmonic oscillators. Oscillator number n has the frequency ν_n and therefore the energy $h\nu_n$. Such a quantum of oscillation is called a phonon. It obeys Bose-Einstein statistics. Introduce the Debye temperature

$$\theta_D = \frac{h\nu_{max}}{k} = \frac{v_0 p_{max}}{k}$$

where v_0 is the velocity of sound and p is the momentum. Calculate C_V when $T \ll \theta_D$.