Problems for the course FYS203

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Contents

Chapter 1

Introduction to statistical methods. Simple random walks

1.1. Simple calculations with probabilities

Three people shoot the same target, partial probabilities to hit the target being p_1, p_2, and p_3, respectively.

1. Find the probability that no one will hit the target.

2. Find the probability to find at least one bullet in the target.

3. Find the distribution function P_n to find n bullets in the target and check that $\sum_n P_n = 1$.

4. Find average value of the number of bullets in the target, $\bar{n}$, and mean square deviation, $\overline{(\Delta n)^2} \equiv \overline{(n - \bar{n})^2}$.

5. Find numerical values of P_n, $\bar{n}$, and $\overline{(\Delta n)^2}$ for $p_1 = 0.8$, $p_2 = 0.9$, $p_3 = 0.7$.

1.2. One-dimensional random walk. Binomial distribution

Consider a *asymmetric* random walk with the probability p for a hop to the right and $q = 1 - p$ for a hop to the left. The probability $W_N(m)$ for for m hops to the right from total number of hops N is given by the *binomial distribution* (8.1)

$$W_N(m) = \frac{N!}{m!(N-m)!}p^m(1-p)^{N-m}.$$

1. Find the probability $P_N(M)$ for a total displacement M after N hops.

2. Find this probability for a symmetric case, $p = 1/2$.

3. Calculate average displacement $\bar{M}$ after N hops. Hint: it is easier to use the equality $\bar{M} = 2\bar{m} - N$ and calculate $\bar{m}$.

4. For the same situation calculate the dispersion $\overline{(\Delta M)^2} = \overline{(M - \bar{M})^2}$.

5. Compare $\Delta^* M \equiv \sqrt{\overline{(\Delta M)^2}}$ and $\bar{M}$. What happens for symmetric random walk?

6. Two drunks start out together at the origin, each having equal probability of making a step to the left or to the right along the x axis. Find the probability that they meet again after each one makes N steps. It is understood that they make steps simultaneously. Hint: It is practical to consider their relative motion.

1.3. Probability distribution at large N: Normal distribution

1. Plot $W_N(m)$ for $p = 0.6$. Show that it has a pronounced maximum at $m = Np = 12$.

2. Estimate the ratio $|W_N(m + 1) - W_N(m)|/W_N(m)$ and show that it is small at $N \gg 1$, $|m - Np| \ll Np(1 - p)$.

3. Consider m as a continuous variable and find maximum of $\ln W_N(m)$. Show that it corresponds to $m_0 = Np$. Then expand $\ln W_N(m)$ in powers of the difference $(m - Np)$ up to the second order. Show that the resulting distribution is the famous *Gaussian* or *normal* distribution,

$$G(m) = \frac{1}{\sqrt{2\pi\sigma}} e^{-(m-\bar{m})^2/2\sigma}, \quad \bar{m} = Np, \quad \sigma = Np(1 - p). \tag{1.1}$$

4. Plot $W_{20}(m)$ and $G(m)$ for $N = 20$ and $p = 0.6$ at the same graph and compare them.

5. Calculate $\overline{(\Delta m)^2}$ using Gaussian distribution (1.1) and show that $\overline{(\Delta m)^2} = \sigma$.

1.4. Poisson distribution

1. Consider the binomial distribution $W_N(m)$ in a situation where the probability p is *small* $(p \ll 1)$ and when one is interested in the case $m \ll N$. This case is really important because $W_N(m)$ is very small at $m \to N$.

   - Using the result that at $p \ll 1$ we have $\ln(1 - p) \approx -p$ show that $(1 - p)^{N-m} \approx e^{-Np}$.
   - Show that $N!/(N - m)! \approx N^m$.

- Hence show that the distribution (8.1) is replaced by

$$P(m) = \frac{(Np)^m}{m!} e^{-Np} . \qquad (1.2)$$

2. Consider the distribution (**??**).

   - Show that that this distribution is properly normalized, $\sum_{m=0}^{N} P(m) \approx \sum_{m=0}^{\infty} P(m) = 1$. Discuss why one can extend summation to infinity.

   - Show that the average $\bar{m} = Np$. Hence the distribution (**??**) can be rewritten in the form
   $$P(m) = \frac{\bar{m}^m}{m!} e^{-\bar{m}} , \qquad (1.3)$$
   which is called *the Poisson distribution.*

   - Calculate $\overline{(\Delta m)^2}$ for the Poisson distribution.

3. Plot on the same graph binomial, Gaussian, and Poisson distributions for $N = 200, p = 0.1$ for $m = 0 \ldots 6$ and then for $m = 0 \ldots 30$ and compare them.

1.5. Applications to physical problems

1. In the previous consideration we have assumed that all the stteps to the right and to the left are the same. In the general case one can regard the displacement as a continuous variable and define the *probability density* $w(s_i)$ such that $w(s_i) \, ds_i$ is the probability to find the step length between s_i and $s_i + ds_i$. In the following let us for simplicity assume that the probabilities for each step are *the same.*

   - Express the average $\bar{x}$ and dispersion $\overline{(\Delta x)^2}$ through the single-step probability density $w(s)$.

   - Apply these general expressions for the case of a one-dimensional random walk with the step length l. Write the Gaussian probability density for this case.

2. Express the general probability density $\mathcal{P}(x)$ through $w(s)$. Show that if one defines the *Fourier component* $\tilde{\mathcal{P}}(k)$ and $\tilde{w}(k)$ of the probability densities $\mathcal{P}(x)$ and $w(s)$, respectively, as

$$\tilde{A}(k) = \int_{-\infty}^{\infty} A(x) \, e^{-ikx} dx , \quad A(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{A}(k) \, e^{-ikx} dk ,$$

then

$$\tilde{P}(k) = \tilde{w}^N(k) . \qquad (1.4)$$

Hint: take into account the constrain $x = \sum_{i=1}^{N} s_i$ and express it using Dirac delta-function, see Ch. 8.

3. Apply Eq. (1.4) to the case of equal step length l discussed above.

4. Compare the probability distributions for the exponential and single-step models with the equivalent Gaussian distribution for $N = 10$ and $N = 1$. Plot these distributions and discuss them.

Chapter 2

Basic principles of thermostatics

2.1. Van der Waals gas

The fundamental relation for the Van der Waals gas is given by

$$s = s_0 + \mathcal{R} \ln[(v - b)/(v_0 - b)] + (3/2)\mathcal{R} \ln \sinh[c(u + a/v)] , \qquad (2.1)$$

(all notations in this section are according the the book [1].

(i) Show that the corresponding equation of state is given by

$$(P + a/v^2)(v - b) = \mathcal{R}T . \qquad (2.2)$$

(i) Expand the Van der Walls equation of state (2.2) in the form of virial expansion and determine 3 first virial coefficients.

2.2. Which of the following, offered as fundamental relations, are acceptable and which violate one or more of fundamental principles of thermostatics? (R, N_0, V_0 and S_0 are constants)

(i) $S = NR \left\{ 1 + \left[(E/E_0)^{3/2}(V/V_0)(N/N_0)^{-5/2} \right] \right\}$

(ii) $S = R(EV/E_0 V_0)^2 (N/N_0)^{-3}$

(iii) $S = \tan \left[(E/E_0)(V/V_0)^2 (N/N_0)^{-3} \right]$

(iv) $S = R(EVN/E_0 V_0 N_0)^{1/3}$

(v) $S = NR \exp \left[(E/E_0)^2 (V/V_0)^{-2} \right]$

(vi) $S = NR \coth \left[(E/E_0)^2 (V/V_0)(N/N_0) \right]$

(vii) $S = R(EN/E_0N_0)^{1/2} \exp\left[-(VN_0/V_0N)^2\right]$

(viii) $S = R(NE/N_0E_0)^2(V/V_0)^{1/5}$.

2.3. Consider an isolated composite system of constant total volume, which consists of two subsystems separated by a *movable* wall that permits flow of heat across it but is non-permeable by the flow of matter. Find out the condition of equilibrium between the two systems using

(a) the energy minimum principle

(b) the entropy maximum principle

2.4. Now assume that the wall in the problem 2.3 is permeable to the flow of molecules. Find out the condition of equilibrium between the two systems using

(a) the energy minimum principle

(b) the entropy maximum principle

2.5. Prove the following consequences of the third law of thermodynamics

(i) c_P and c_V of simple fluids must vanish at $T = 0$.

(ii) Coefficient of thermal expansion α vanishes at $T = 0$

2.6. Derive Maxwell's relations for a simple magnetic system.
Hint: Derive the conservation law for a magnetic system, then express thermodynamic potential through the proper variables.

2.7. Calculate c_P and c_V for the Van der Waals gas.
Hint: First calculate Helmholtz free energy, then entropy, and then use the definitions of the specific heat.

2.8. For blackbody radiation calculate the heat absorbed and the work done in

(a) an isothermal process (which is also isobaric in this case);

(b) an adiabatic process.

Chapter 3

Thermostatics and phase transitions

3.1. Gibbs' phase rule has been established assuming that each component occurs in all the phases. How should the phase rule be modified if each component does not occur in all phases.

3.2. The fundamental relation for a gas is known to be

$$s = s_0 + R \ln \left[\frac{v - b}{v_0 - b} \right] + R \ln \left[\frac{\cosh\{c(u + a/v)\}}{\cosh\{c(u_0 + a/v_0)\}} \right]. \tag{3.1}$$

where a, b, c, s_0, u_0 and v_0 are constants. Show that this gas is intrinsically unstable at all temperatures.

3.3. For diamagnetic substances the sero-field susceptibility $\chi_T < 0$. Since diamagnetic phase is a stable magnetic phase, does it violate the condition of intrinsic stability? Explain.

3.4. 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

$$\left(P' + \frac{3}{V'^2} \right) (3V' - 1) = 8T' \tag{3.2}$$

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

(iii) Analyze the equation of state (3.2) 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

$$p = 4\tau + 6\tau n + (3/2)n^3 . \tag{3.3}$$

(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

$$\int_{n_l}^{n_r} n \, (\partial p/\partial n)_\tau \, dn = 0 \tag{3.4}$$

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.

3.5. Curie-Weiss theory of a magnet
The simplest equation for a non-ideal magnet has the form

$$m = \tanh[\beta(Jm + h)] \tag{3.5}$$

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. (3.5) 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. (3.5) 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 $T/T_c = 1.6$.

Chapter 4

Basic principles of statistical mechanics

4.1. A long polymer under tension τ is made up of N monomers that can each be in a compact (c) or elongated (e) state. Thus, the polymer has 2^N possible states. In the compact state the length of the monomer is $\ell_c = \ell - a$, and that in the elongated state is $\ell_e = \ell + a$. The total length of the polymer is L. Calculate

  (i) the average tension $\langle \tau \rangle$ in the microcanonical ensemble at *fixed L*.

 (ii) Under certain conditions, the chain behaves effectively as a spring: find the condition and the corresponding spring constant in terms of given quantities and temperature T. Note that the spring constant is of purely entropic origin and vanishes as $T \to 0$ interpret the result physically.

4.2. Calculate the entropy of mixing two *different* ideal gases and plot it as a function of the concentration of one of the two gases.

4.3. The Hamiltonian of a collection of N non-interacting one-dimensional classic harmonic oscillators is given by

$$H = \frac{1}{2M} \sum_{i=1}^{N} p_i^2 + \frac{k}{2} \sum_{i=1}^{N} x_i^2 \,.$$

Calculate the internal energy of the system using the rules of calculation for isolated systems.
Hint: Apply the law of equipartition of the energy.

4.4. Spins in an external magnetic field

(a) Consider a system, at temperature T, consisting of N noninteracting classical n-vector spins $(n = 3)$ in external magnetic field $\boldsymbol{H}$, so that the Hamiltonian is given by

$$\mathcal{H} = -\sum_i \mu_i \cdot \boldsymbol{H} = -\mu H \cos\theta$$

where θ is the angle between $\boldsymbol{\mu}$ and $\boldsymbol{H}$. Using the canonical ensemble, show that the average magnetic moment M is equal to $\mathcal{M} = N\mu L(\beta\mu H)$ where

$$L(x) = \coth x - 1/x$$

is the *Langevin* function.

(b) An atom with angular momentum J (in the units of $\hbar$)has, in a magnetic field $\boldsymbol{H}$, an energy $g\mu_B MH$, where M is the magnetic quantum number which can take $(2J+1)$ values $-J, -J+1, \ldots, J-1, J$, and μ_B is the Bohr magneton. Show that magnetic moment of the system consisting of N such noninteracting atoms is equal to

$$\mathcal{M} = Ng\mu_B JB_J(x), \quad \text{where} \quad x = \beta g\mu_B JH.$$

The *Brillouin function* is given by

$$B_J(x) = \frac{2J+1}{2J}\coth\frac{(2J+1)x}{2J} - \frac{1}{2J}\coth\frac{x}{2J}. \tag{4.1}$$

Compare with the corresponding result for the classical Ising spin. Examine the special limits of $J = 1/2$ and $J \to \infty$.

4.5. Model for rubber elasticity.

The rubber is assumed to consist of a polymer chain of N rod-like monomers, each of length a and is sibjected to a force F in the $+X$ direction. Each monomer can point independently along any of X, Y, Z axes, in either the $+$ or $-$ direction. The energy is only X-dependent; $\epsilon = aF$ for the monomer pointimg along $-X$, $\epsilon = -aF$ for the monomer pojnting along $+X$, $\epsilon = 0$ for the monomer along $\pm Y$ and $\pm Z$.

(a) Calculate the partition function for the N-monomer chain.

(b) Show that the linear thermal expansivity is negative, as for the real rubber. Interpret the result physically.

4.6. The partition function for a system of some kind of particles is

$$Z_N = \left[(V - Nb)/\lambda^3\right]^N \exp(\beta aN^2/V),$$

where

$$\lambda = \sqrt{2\pi\hbar^2/mk_BT}$$

and a and b are constants, V is the volume and N is the number of particles; all other symbols have their usual meaning.

(a) Find the internal energy $E(N, T, V)$.

(b) Find the pressure $P(N, T, V)$.

(c) Find the entropy $S(N, T, V)$.

(d) Is this expression for S a valid fundamental relation, except perhaps at $T = O$? If not, what is wrong, and how ca Z_N be appropriately corrected?
Hint: Recall Gibbs paradox.

4.7. Calculate the partition function and the free energy for a ideal classical gas consisting of N molecules at temperature T contained in a vertical column of height H and cross-sectional area A in the presence of the of non-vanishing constant acceleration g due to gravity.

4.8. Calculate the partition function and the free energy for an ideal classical gas consisting of N molecules at temperature T contained in a vessel and subjected to a centrifugal force $-M\omega^2 z^2/2$, where z is the distance of the particle from the axis of rotation and ω is the angular velocity of rotation of the centrifuge.

4.9. Consider an ideal monoatomic gas of N molecules in the presence of an external magnetic field H, where each molecule behaves as an Ising spin. Calculate the free energy, energy, and entropy and interpret the result physically. Find the limit of S at $T \to 0$.

4.10. Following Maxwell, let us assume that in an ideal classical monoatomic gas (a) the distribution of speeds depends only on the absolute magnitude of the velocity (i. e. speed) and (b) the probability that x-component of the velocity lies within a certain range is independent of the values of y- and z-components of the velocity. From these two assumptions derive the Maxwell distribution.

4.11. J. Loschmidt claimed in 1876 that the Maxwell-Boltzmann distribution must be wrong; his claim was based on the following arguments:
in an ideal gas in equilibrium in a uniform gravitational field, every particle which moves from the top to the bottom speeds up as as its loss of potential energy should be compensated by its gain in kinetic energy. Thus the gas must be warmer at the bottom than at the top. Explain why Loschmidt was wrong.

4.12. Evaluate the contribution of a one-dimensional *anharmonic* oscillator having a potential $V(x) = cx^2 - gx^3 - fx^4$ to the heat capacity. Discuss the the dependence of

the mean value of the position x of the oscillator on the temperature T. Here c, g, f are positive constants. Usually, $g \ll c^{3/2}(k_B T)^{-1/2}$ and $f \ll c^2/k_B T$.

4.13. The energy of *anharmonic* oscillator is given by

$$H = p^2/2m + bx^{2n}$$

where n is a positive integer and $n > 1$. Consider a thermodynamic system consisting of a large number of these identical noninteracting oscillators.

(a) Derive the single oscillator partition function.

(b) Calculate an average kinetic energy of an oscillator.

(c) Calculate an average potential energy of an oscillator.

(d) Show that the heat capacity is

$$C = (Nk_B/2)(1 + 1/n).$$

4.14. A small subsystem of a very large container filled with an ideal gas of identical particles is regarded as a grand canonical ensemble. Show that the probability of finding the system with N_1 atoms is given by the Poisson distribution

$$P(N_1) = \frac{\langle N_1 \rangle^{N_1}}{N_1!} e^{-\langle N_1 \rangle}$$

where $\langle N_1 \rangle$ is the mean number of atoms present in the subsystem.

4.15. When a gas is in equilibrium with a solid wall, its molecules can become attached to that wall on special sites where they re trapped in a way which depends on the structure of the wall. Adsorption is thus an equilibrium between two phases, the gas and the system of bound molecules. similar to a chemical equilibrium. To study this consider a model: the wall has N sites on each of which a molecule can get bound with a binding energy $-u$. The molecules which are not adsorbed for a perfect gas. Calculate the grand partition function for the adsorbed molecules and, hence, using thermostatic properties of gases, calculate the average number n of adsorbed molecules as function of gas pressure and temperature.

4.16. Consider the same polymer chain described in the problem 4.1. Calculate the average length $\langle L \rangle$ as a function of τ in the canonical ensemble at fixed τ, thereby establishing the equivalence of this ensemble with that used in solving the problem 4.1.

4.17. A "pressure" ensemble is one for which the pressure and the temperature are fixed by reservoirs which which the system is in equilibrium, but the energy and volume of the system are not fixed while the number of particles is kept fixed. Derive the expression for the probability $P_r(E, V)$ that the system is in state with energy E and volume V , starting from the basic postulate of equal a priori probabilities for the composite system consisting of the system plus the reservoirs.

4.18. Solve problem 4.24 using the maximum entropy method, given that E_0 and V_0 are average values of the energy and volume.

4.19. Suppose the expression $S = -k_B \sum_r P_r \ln P_r$ is accepted as a definition of the entropy. Imagine that a system A_1 has probability $P_r^{(1)}$ of being in a state r and a system A_2 has probability $P_s^{(2)}$ of being in a state s. Then

$$S_1 = -k_B \sum_r P_r^{(1)} \ln P_r^{(1)}, \quad S_2 = -k_B \sum_s P_s^{(2)} \ln P_s^{(2)}.$$

Each state of a composite system A consisting of A_1 and A_2 can then be labeled by the pair of numbers, r, s. Let the probability of A being found in the state r, s be denoted by P_{rs}, and the corresponding entropy is $-k_B \sum_{r,s} P_{rs} \ln P_{rs}$.

(a) If A_1 and A_2 are weakly interacting so they are statistically independent, then $P_{rs} = P_r^{(1)} P_s^{(2)}$ Show that under such circumstances the entropy is simply additive, i. e. $S = S_1 + S_2$.

(b) Suppose that A_1 and A_2 are *not* weakly so that $P_{rs} \neq P_r^{(1)} P_s^{(2)}$. One has, of course, the general, relations $\sum_s P_{rs} = P_r^{(1)}$, $\sum_r P_{rs} = P_s^{(2)}$, and $\sum_{r,s} P_{rs} = 1$. Show that

$$S - (S_1 + S_2) = k_B \sum_{rs} P_{rs} \ln \frac{P_r^{(1)} P_s^{(2)}}{P_{rs}}.$$

Moreover, by using the inequality

$$- \ln x \geq 1 - x,$$

show that $S \leq S_1 + S_2$, where the equality holds only if $P_{rs} = P_r^{(1)} P_s^{(2)}$ for all r and s. This means that the existence of correlation between the systems leads to a situation less random that where the systems are completely independent of each other.

4.20. Consider a system distributed over its accessible states r in accordance with a probability distribution P_r, and let its entropy be defined by the relations

$$S = -k_B \sum_r P_r \ln P_r, \quad \sum_r P_r = 1.$$

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Compare this distribution with the canonical distribution

$$P_r^{(0)} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

corresponding to the same mean energy $\langle E \rangle$, i. e.

$$\sum_r P_r E_r = \sum_r P_r^{(0)} E_r = \langle E \rangle \,.$$

The entropy of the canonical distribution is

$$S_0 = -k_B \sum_r P_r^{(0)} \ln P_r^{(0)} \,.$$

(a) Show that

$$S - S_0 = -k_B \sum_r P_r \ln \frac{P_r^{(0)}}{P_r} \,.$$

(b) Using the inequality $\ln x \leq x - 1$ show that $S_0 \geq S$; the equality sign holds only if $P_r = P_r^{(0)}$ for all states r. This shows that, for a specific value of mean energy, the entropy S is a maximum for the canonical distribution.

4.21. A one-dimensional normal distribution of zero mean and standard deviation σ is given by

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2} \,.$$

(a) Show that it entropy is $(k_B/2)\ln(2\pi e\sigma^2)$.

(b) show that for given

$$\int_{-\infty}^{\infty} x^2 P(x)\, dx = \sigma^2$$

, the normalized probability distribution having the largest entropy in the one-dimensional normal distribution.

4.22. Consider an isolated system consisting of N identical quantum harmonic oscillators; the energy of each oscillator is given by $(n+1/2)\hbar\omega$. It is given that the total energy of the N-oscillator system is $(M + N/2)\hbar\omega$. Calculate the average energy as well as specific heat using the methods of microcanonical ensemble. Recover the classical results by taking the appropriate limit.
Hint: Calculate the number of ways in which the M quanta can be placed in N numbered boxes with no limitation on the number of quanta per box.

4.23. Using the method of canonical ensemble. calculate the partition function, average energy and specific heat of a system consisting of N noninteracting quantum harmonic oscillators and show that these expressions do reduce to the corresponding classical results in the appropriate classical limit.

4.24. Consider non-interacting particles subjected to a harmonic potential. Calculate the canonical partition function

(a) for a single particle

(b) for two distinguishable particles

(c) for two spinless fermions

(d) for two spin-zero bosons

(e) for two spin-1/2 fermions.

Compare the internal energies and entropies in these various cases. Study the limit $T \to 0$, $T \to \infty$, and $\hbar = 0$ and interpret the results physically.

4.25. Let f_n be the average occupation of the n-th single-particle level in an ideal Fermi gas. Consider the binary scattering process where two fermions in states 1 and 2 get scattered into states 3 and 4. hen , rate of forward scattering is

$$f_1 f_2 (1 - f_3)(1 - f_4) R$$

whereas the rate of reverse scattering is

$$f_3 f_4 (1 - f_1)(1 - f_2) R'$$

where $R = |M|^2$ is the square of the matrix element M of the scattering operator the states 1 and 2 and $R = |M^*|^2$. The principle of detailed balance states that. in equilibrium,

$$f_1 f_2 (1 - f_3)(1 - f_4) = f_3 f_4 (1 - f_1)(1 - f_2) \,.$$

Show that the Fermi-Dirac distribution is the non-trivial solution of this equation. (This derivation shows how Pauli exclusion principle leads to the FD distribution).

4.26. Let us denote the average occupation of the n-th single-particle level by the symbol f_n. For fermions, consider the "variational entropy"

$$S_{\text{var}} = -\sum_n [f_n \ln f_n + (1 - f_n) \ln(1 - f_n)]$$

and for bosons, consider the "variational entropy"

$$S_{\text{var}} = -\sum_n \left[f_n \ln f_n + (1 + f_n) \ln(1 + f_n) \right] .$$

Show that if S_{var} is maximized, subject to the conditions

$$\sum_n f_n = N , \quad \sum_n f_n \epsilon_n = E$$

then the resulting distribution is the FD distribution in the 1st case and BE distribution in the 2nd case. Moreover, at the maximum S_{var} is equal to the equilibrium entropy of the FD and DE systems, respectively.

Chapter 5

Fluctuations, correlations and response

5.1. Show that the most probable magnetization of a closed ideal magnet maintained at temperature T, subjected to an external magnetic field H is identical to its average magnetization in the canonical ensemble.

5.2. Consider a closed system consisting of N noninteracting classical one-dimensional harmonic oscillators at a temperature T. Using the canonical ensemble, show that the most probable energy of the system is identical to its average energy.

5.3. Solve the problem 5.2 after replacing classical oscillators by quantum oscillators.

5.4. Show that the most probable volume volume of the system in the pressure ensemble is identical to its ensemble-averaged volume.

5.5. Calculate the mean-square fluctuation in energy, and the mean-square fractional fluctuation in the energy of

(a) a quantum harmonic oscillator,

(b) a collection of N identical quantum harmonic oscillators.

Examine the results in the high-temperature limit.

5.6. Show that for an ideal classical Ising magnet

(a) the thermal fluctuation in the magnetization $\langle(\Delta M)^2\rangle$ is related to the thermal energy $k_B T$ and the corresponding response function, namely susceptibility χ through

$$\langle(\Delta M)^2\rangle = k_B T N \chi,$$

(b) and

$$\langle(\Delta M)^2\rangle^{1/2}/\langle M\rangle \propto 1/\sqrt{N}.$$

5.7. Show that is A is a generalized coordinate (i. e. an extensive variable) and X is the corresponding conjugate generalized force ((i. e. an intensive variable) for a classical system maintained at temperature T, then

$$\langle(\Delta A)^2\rangle = k_B T \left(\partial\langle A\rangle/\partial X\right)_T.$$

Hint: there is an extra term $-XA$ in the Hamiltonian.

5.8. Calculate the mean square fluctuation in

(a) the deflection angle of a galvanometer suspension at constant temperature T and constant couple M,

(b) the electric charge on a condenser of capacitance C at a constant temperature subjected to a constant potential difference V_e between the plates.

5.9. V_1 is the volume of a small subsystem of a very large container of volume V, which is filled with N atoms of an ideal classical monoatomic gas. Denote the probability of finding a particular gas particle in the subsystem volume by $p = V_1/V$. Find an expression for the Probability $P(N_1)$ that there are N_1 particles in the subsystem. From this expression , find the relative variance $\langle(N_1 - \langle N_1\rangle)^2\rangle$. Show that the relative variance vanishes in the thermodynamic limit, i. e. when $V \to \infty$, $N \to \infty$ with $N/V =$ const and simultaneously $V_1 \to \infty$ with $p =$ constant.

5.10. Define an energy-like variable $Q = E - N\langle E\rangle/\langle N\rangle$. and show that the fluctuations of N and Q in the grand canonical ensemble (GCE) are statistically independent. Give a physical explanation of this result.

5.11. Show that the energy fluctuations in the CE and GCE are related through the expression

$$\langle(\Delta E)^2\rangle_G = \langle(\Delta E)^2\rangle_C + \langle(\Delta N)^2\rangle_G \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{V,T}^2,$$

where G and C refer to GCE and CE, respectively. Interpret the results physically.

5.12. Consider a classical system. Suppose, A_1 and A_2 are two generalized coordinates and X_1 and X_2 are the corresponding generalized forces. If the system is in contact with a heat bath at a temperature T, show that

$$\langle (\Delta A_1)(\Delta A_2) \rangle = \left(\frac{\partial \langle A_1 \rangle}{\partial X_2} \right)_T = \left(\frac{\partial \langle A_2 \rangle}{\partial X_1} \right)_T .$$

5.13. Show that in the pressure ensemble

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

5.14. Show that in the grand canonical ensemble,

$$\langle \Delta N \, \Delta S \rangle = k_B T \left(\frac{\partial N}{\partial T} \right)_\mu .$$

5.15. Show that if the Hamiltonian of the system is written as

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{H}_1 ,$$

where λ is a small parameter, then

$$-\frac{1}{\beta} \frac{d \langle A \rangle}{d\lambda} = \langle \mathcal{H}_1 A \rangle - \langle \mathcal{H}_1 \rangle \langle A \rangle .$$

Hence derive the result

$$V \chi_{\mu\nu} = \beta \left[\langle S_\mu^T S_\nu^T \rangle - \langle S_\mu^T \rangle \langle S_\nu^T \rangle \right] .$$

Chapter 6

Statistical physics of ideal classical gases

6.1.

(a) Show that the probability the the α-th projection of the velocity falls in the range $v_\alpha^{(2)}$ and $v_\alpha^{(2)}$ is given by

$$W(v_\alpha^{(1)}, v_\alpha^{(2)}) = \left(\frac{M}{2\pi k_B T}\right)^{1/2} \int_{v_\alpha^{(1)}}^{v_\alpha^{(2)}} dv_\alpha \, e^{-Mv_\alpha^2/2k_B T} = \frac{1}{2}\left[\mathrm{erf}\,(\tilde{v}_\alpha^{(2)}) - \mathrm{erf}\,(\tilde{v}_\alpha^{(1)})\right],$$

where $\tilde{v}_\alpha^{(i)}) = v_\alpha^{(i)}/v_p$, $v_p = (2k_B T/M)^{1/2}$.

(b) Show that the probability that the absolute value of the velocity falls in the range between $v^{(1)}$ and $v^{(2)}$ is given by

$$
\begin{aligned}
W(v^{(1)}, v^{(2)}) &= 4\pi \left(\frac{M}{2\pi k_B T}\right)^{3/2} \int_{v^{(1)}}^{v^{(2)}} v^2 dv \, e^{-Mv^2/2k_B T} \\
&= \frac{2}{\sqrt{\pi}}\left[v_1 e^{-v_1^2} - v_2 e^{-v_2^2}\right] + \mathrm{erf}\,(v_1) - \mathrm{erf}\,(v_2),
\end{aligned}
$$

where $v_i = v^{(i)}/v_p$.

6.2. Calculate the mean speed, most probable speed, mean kinetic energy and most probable kinetic energy and, hence, check that the mean of the square of the speed is not equal to the square of the mean speed.
Hint: $v_{rms} : v_{mean} : v_{mp} = \sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$.

6.3. If, from an ideal gas at temperature T, we choose 2 particles at random, then the velocities of the particles are statistically-independent. What are the probability distributions of

(a) the velocity of the center of mass of the two-particle system, and

(b) their relative velocity?

Are these two quantities statistically correlated?

6.4. Consider an ideal classical gas obeying the Maxwell-Boltzmann distribution and having 2 energy levels ϵ_1 and ϵ_2 ($\epsilon_1 < \epsilon_2$) with degeneracies g_1 and g_2, respectively. Show that the specific heat associated with these internal degrees of freedom exhibits a maximum at a temperature T_m where its magnitude is C_m. Estimate C_m, T_m and the width of the maximum.

6.5. Consider an ideal gas mixture consisting of N_A particles of type A and N_B particles of type B, with masses m_A and m_B, respectively. Since they may interact differently with external fields, they may, in general, experience different potentials $U_A(\vec{r})$ and $U_B(\vec{r})$. Then show that the distributions for the two types of particles are

$$f_i(\vec{r}, \vec{v}) = n_i(\vec{r}) \left(\frac{m_i}{2\pi k_B T} \right)^{3/2} e^{-\beta[m_i v^2/2k_B T + U_i(\vec{r})]} \tag{6.1}$$

where $i = A$ or B. Show that the average kinetic energy per A particle is equal to the average kinetic energy per B particle.

6.6. The rotational motion of a classical diatomic molecule is specified by two angular variables θ and ϕ, so that the Lagrangian is given by

$$L = \text{kinetic energy} = 2 \times \left[(1/2)\{MR^2\dot{\theta}^2 + MR^2 \sin^2\theta \dot{\phi}^2\} \right] .$$

Hence, the corresponding canonical conjugate momenta are given by

$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = 2MR^2 \, \dot{\theta}$$

and

$$p_\phi = \frac{\partial L}{\partial \dot{\phi}} = 2MR^2 \, \sin^2\theta \, \dot{\phi} .$$

Therefore, the Hamiltonian of the molecule is given by

$$\mathcal{H} = \frac{p_\theta^2}{4MR^2} + \frac{p_\phi^2}{4MR^2 \sin^2\theta} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2\theta}$$

where $I = 2MR^2$. Derive the classical formula for the rotational partition function and hence the corresponding entropy and specific heat. Compare the expression for the specific heat with the classical limit for the corresponding quantum mechanical expression.

6.7. For a better evaluation of the sum (5.24) use the Euler-MacLaurin formula

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x)\,dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) - \frac{1}{30240}f^v(0) + \dots$$

and show that

(a)

$$(C_v)_{\text{rot}} \approx Nk_B \left[1 + (1/45)(T/T_{\text{rot}})^2 + (16/945))(T/T_{\text{rot}})^3 + \dots\right]$$

when $T \gg T_{\text{rot}}$, and

(b)

$$(C_v)_{\text{rot}} \approx 12Nk_B \left(T_{\text{rot}}/T\right)^2 e^{-2T_{\text{rot}}/T}.$$

6.8. The nuclei of D_2 molecules are bosons ($S_n = 1$). Write down the expressions

(a) $Z_{\text{nuc-rot}}$;

(b) the ratio $n_{\text{ortho}}/n_{\text{para}}$;

(c) the heat capacity c_V.

6.9. The vibrational energy levels of a diatomic molecule, because of *anharmonicity*, is given by the approximate expression

$$E_n = (n + 1/2)h\nu + x_e(n + 1/2)^2 h\nu, \quad n = 0, 1, \dots$$

where x_e is the parameter used to represent the degree of anharmonicity. Calculate the effect of anharmonicity on the vibrational specific heat up to the first order in x_2.

Chapter 7

Statistical physics of ideal quantum gases

7.1. Calculate the density of levels per unit volume, $g(\epsilon)$ in $d = 1$ and $d = 2$.

7.2. For the ideal Fermi gas at $T = 0$ and $d = 1$ and $d = 2$, derive the relations between

(a) number density and Fermi energy;

(b) total energy and the Fermi energy;

(c) pressure and the energy density;

(d) bulk modulus and pressure.

7.3. Consider an ideal Fermi gas in $d = 2$.

(a) Show that because density of states $g(\epsilon) = $ const, every term on the Sommerfeld expansion for n vanishes except that term corresponding to $T = 0$. Hence show that $\mu = \epsilon_F$ at any temperature.

(b) Using the formula
$$n = \int_0^\infty g(\epsilon) f(\epsilon) \, d\epsilon$$
and the fact that $g(\epsilon) = $ const in $d = 2$ show that
$$\mu = \epsilon_F - k_B T \ln \left[1 + e^{-\mu/k_B T} \right] \, .$$
Estimate the amount by which μ differs from ϵ_F at room temperature.

7.4. Calculate the specific heat of a ideal electron gas up to T^3.

7.5. Consider high-energy spin-1/2 particles for which the energy is given by $\epsilon = c\sqrt{p^2 + (M_0 c)^2}$ where $\vec{p}$ is momentum, M_0 is the rest mass and c is velocity of light in vacuum.

(a) Show that the average values of the total number N, the total internal energy E and the pressure P are given by the following expressions:

$$
\begin{aligned}
N &= 8\pi \frac{M_0^3 c^3}{h^3} V \int_0^\infty \frac{\sinh^2\theta \cosh\theta \, d\theta}{\exp\left(-\beta\mu + \beta M_0 c^2 \cosh\theta\right) + 1}, \\
E &= 8\pi \frac{M_0^4 c^5}{h^3} V \int_0^\infty \frac{\sinh^2\theta \cosh^2\theta \, d\theta}{\exp\left(-\beta\mu + \beta M_0 c^2 \cosh\theta\right) + 1}, \\
P &= \frac{8\pi}{3} \frac{M_0^4 c^5}{h^3} V \int_0^\infty \frac{\sinh^4\theta \, d\theta}{\exp\left(-\beta\mu + \beta M_0 c^2 \cosh\theta\right) + 1},
\end{aligned}
$$

where $p = M_0 c \sinh\theta$, $\beta = k_B T$ and μ is the chemical potential which includes the rest energy $M_0 c^2$ Estimate the value of the above quantities at $T = 0$

(b) Derive approximate relations in the (i) non-relativistic case and (ii) in the ultra-relativistic case.

(c) Find the chemical potential and the heat capacity of extreme relativistic ideal Fermi gas of spin-1/2 particles.

7.6. Show that the expression for the entropy of an ideal Bose gas reduces to the Sackur-Tetrode formula at sufficiently high temperature.

7.7. Give arguments to reproduce the trend of variation of z with v/λ_T^3 shown in Fig. 6.7.

7.8.

(a) Find the density of levels $g(\epsilon)$ of a system with energy spectrum

$$
\epsilon_{lmn} = \gamma \left[\frac{\lambda_1}{L_x} l + \frac{\lambda_2}{L_y} m + \frac{\lambda_3}{L_z} n \right]
$$

where l, m, n are non-negative integers, L_x, L_y, L_z are the dimensions of the container, γ and λ_i are constants (not necessary integers). For simplicity, consider the case when $\epsilon \gg \gamma \lambda_i / L_i$.

(b) Given an ideal Bose gas of N particles havong the energy spectrum given by part (a), find the transition T_c and its discontinuity at T_c.

7.9. Consider an ideal Bose gas consisting of particles that have internal *degrees of freedom*. Assume, for simplicity, that only one excited level, of energy ϵ_1, of these internal levels needs to be considered, besides the ground state, of energy ϵ_0. Calculate the Bose-Einstein condensation temperature of this gas as a function of ϵ_1.

7.10. Calculate the Helmholtz free energy. the entropy, the internal energy, specific heat and radiation pressure of a photon gas at an arbitrary temperature T.

Chapter 8

Useful relations

8.1 Main distributions

Binomial distribution

$$W_N(m) = \frac{N!}{m!(N-m)!} p^m (1-p)^{N-m} \,. \tag{8.1}$$

Poisson distribution

$$P(m) = \frac{\bar{m}^m}{m!} \, e^{-\bar{m}} \,. \tag{8.2}$$

Gaussian distribution

$$G(x) = \frac{1}{\sqrt{2\pi\sigma}} \, e^{-(x-\bar{x})/2\sigma} \,. \tag{8.3}$$

Distribution of displacemnet for 1D random walk with the step l

$$G(x) = \frac{1}{2l\sqrt{2\pi N p(1-p)}} \, e^{-[x-(p-q)l]^2/8Nl^2 p(1-p)} \,. \tag{8.4}$$

Gaussian integrals

$$I_1(a) = \int_{-\infty}^{\infty} dz \, e^{-az^2/2} = \sqrt{2\pi/a} \,. \tag{8.5}$$

$$\int_{-\infty}^{\infty} z^2 dz \, e^{-z^2/2} = 2 \left[\frac{dI_1(a)}{da} \right]_{a=1} = I_1(a)\sqrt{2\pi} \,. \tag{8.6}$$

Gaussian distribution for more than one variables Define entropy as $S(x_1, \ldots, x_n)$. 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

$$S - S_0 = -\frac{1}{2}\beta_{ik}x_i x_k \, . \tag{8.7}$$

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

$$\beta_{ik}a_{il}a_{km} = \delta_{km} \tag{8.8}$$

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 $x_i \to y_i$ is just a,

$$J = \left| \frac{\partial(x_1, \ldots, x_n)}{\partial(y_1, \ldots, y_n)} \right| = |\hat{a}| = a \, .$$

Consequently,

$$Aa \left[\int dy\, e^{-y^2/2} \right]^n = \frac{A(2\pi)^{n/2}}{\sqrt{\beta}} = 1 \, .$$

Thus

$$w = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \exp\left(-\frac{1}{2}\beta_{ik}x_i x_k \right) \, . \tag{8.9}$$

Let define generalized forces as

$$X_i = -\partial S/\partial x_i = \beta_{ik}x_k, \tag{8.10}$$

and first calculate

$$\langle x_i X_k \rangle = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \int x_i \beta_{ik}x_k\, e^{-\beta_{ik}x_i x_k/2}\, dx_1 \cdots dx_n \, . \tag{8.11}$$

The easiest way to calculate this integral is to calculate to assume for a while that $\bar{x}_i \neq 0$. Then

$$\bar{x} = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \int x_i\, e^{-\beta_{ik}(x_i - x_{i0})(x_k - x_{k0}/2}\, dx_1 \cdots dx_n = x_{i0} \, .$$

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

$$\langle x_i X_k \rangle = \delta_{ik} \, , \quad \text{or} \quad \beta_{ik}\langle x_i x_k \rangle = \delta_{ik} \, , \quad \langle x_i x_k \rangle = \left(\hat{\beta}^{-1} \right)_{ik} \, . \tag{8.12}$$

8.2   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

$$\delta(x - x_0) = \begin{cases} 0 & \text{for} \quad x \neq x_0 \\ \infty & \text{for} \quad x = x_0 \end{cases} \tag{8.13}$$

but in such way that for any $\epsilon > 0$

$$\int_{x_0 - \epsilon}^{x_0 + \epsilon} \delta(x - x_0)\, dx = 1\,. \tag{8.14}$$

Since delta-function has a very (infinitely) sharp peak at $x = x_0$ and a unit area

$$\int_A^B f(x)\, \delta(x - x_0)\, dx = \begin{cases} f(x_0) & \text{if} \quad A < x_0 < B \\ 0 & \text{otherwise} \end{cases}\,. \tag{8.15}$$

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,

$$\delta(x) = \begin{cases} \gamma^{-1} & \text{for} \quad -\gamma/2 < x < \gamma/e \\ 0 & \text{otherwise} \end{cases}\,, \tag{8.16}$$

Lorentzian,

$$\delta(x) = \frac{1}{\pi} \frac{\gamma}{x^2 + \gamma^2}\,, \tag{8.17}$$

Gaussian,

$$\delta(x) = \frac{1}{\gamma \sqrt{2\pi}}\, e^{-x^2/2\gamma^2}\,, \tag{8.18}$$

and integral,

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx}\, dk \tag{8.19}$$

We will also need a representation for the Kronekker's symbol

$$\delta_{n,0} = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{-n\phi} d\phi\,. \tag{8.20}$$

8.3   Thermodynamics

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	$T,\ V,\ \mu$	$-S\,dT - P\,dV - N\,d\mu$

Table 8.1: Thermodynamic potentials (summary)

Variable transformation

Jacobian $\partial(u,v)/\partial(x,y)$ is defined as the determinant

$$\frac{\partial(u,v)}{\partial(x,y)} = \left| \begin{array}{cc} \partial u/\partial x & \partial u/\partial y \\ \partial v/\partial x & \partial v/\partial y \end{array} \right| \tag{8.21}$$

The following relations can be useful:

$$\frac{\partial(v,u)}{\partial(x,y)} = -\frac{\partial(u,v)}{\partial(x,y)}, \quad \frac{\partial(u,y)}{\partial(x,y)} = \left(\frac{\partial u}{\partial x} \right)_y, \quad \frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(t,s)} \cdot \frac{\partial(t,s)}{\partial(x,y)}. \tag{8.22}$$

Bibliography

[1] D. Chaudhury, D. Stauffer, *"Principles of Equilibrium Statistical Mechanics*, Wiley-VCH, 2000.