

Statistical Physics and Thermodynamics (SS 2017)

Problem sheet 6

Hand in: Friday, June 2 during the lecture

<http://www.physik.fu-berlin.de/en/einrichtungen/ag/ag-netz/lehre/>

1. Entropy of a system with discrete energy levels (7 points)

Consider a system at temperature T which can be in any of n microstates, where each microstate has energy ε_i , with $0 \leq i \leq n$.

- Write down the partition function Z and the equilibrium free energy F of the system. **(1 point)**
- Calculate the derivative $\partial F/\partial T$. Express your results in terms of Z . **(1 point)**
- Identify the free energy F and the energy U in your result from (b) and use $F = U - TS$ to show that the entropy $S = -(\partial F/\partial T)$. Calculate S for the n -level system. **(2 points)**
- What is the limit of S for $T \rightarrow \infty$? Explain your result. **(1 point)**
- Express S in terms of the ground-state energy ε_0 and calculate the limits of S , F and U for $T \rightarrow 0$. Explain your results. **(2 points)**

2. The Gibbs paradox (7 points)

Consider N particles, each of mass m , in a 3-dimensional volume V at temperature T . Each particle i has momentum p_i . Assume that the particles are non-interacting (ideal gas) and distinguishable (in contrast to the lecture).

- Calculate the partition function Z for the N -particle system. Make sure to work out the integral. **(1 point)**
- Calculate the free energy F from the partition function. Is F an extensive quantity? **(1 point)**
- Calculate the entropy S from the free energy derived in part (b). **(1 point)**

Next, consider two reservoirs, each having volume V , separated by a removable plate. One reservoir contains N particles of type A , the other reservoir contains N particles of type B .

- Using your result from part (c), calculate the change in entropy ΔS of the total system (defined as the difference between the entropies of the final and the initial states) when the separating plate is removed, and the system has returned to equilibrium (the *entropy of mixing*). See Fig. 1 for an illustration. Explain your result in terms of reversibility. **(2 points)**

Finally, consider the situation in which both reservoirs contain N particles of type A .

- Again, calculate the change in entropy ΔS of the total system when the separating plate is removed, using your result of part (c). Explain whether the expressions derived in parts (a–c) are applicable to this situation. **(2 points)**

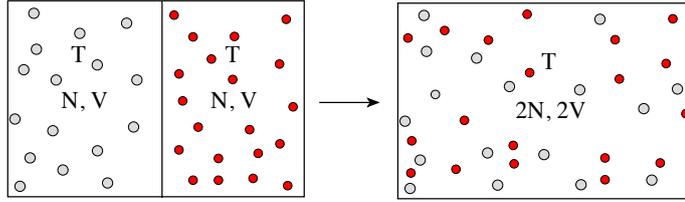


Figure 1: Mixing of gases consisting of different particle types.

3. The heat capacities of a solid and a diatomic gas (6 points)

Consider a model of a solid consisting of N independent, distinguishable, classical atoms of mass m , each constrained in a 3-dimensional harmonic potential. Each atom is described by the Hamiltonian

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \frac{m\omega^2}{2} (q_x^2 + q_y^2 + q_z^2),$$

with ω being the oscillator frequency.

a) Write down the N -particle partition function Z . (1 point)

b) Calculate the energy U of the solid from a derivative of the partition function. What is the energy per degree of freedom? (A degree of freedom is defined as a fluctuating quantity that enters the Hamiltonian quadratically.) (2 points)

Hint: Note that you do not need to calculate the Gaussian integral.

c) Calculate the heat capacity $C_V = (\partial U / \partial T)$. What is its dependence on the temperature? (1 point)

d) Now consider N independent, indistinguishable classical molecules, each consisting of two atoms of mass m connected by a harmonic spring. The center of mass of each molecule can translate with momenta (p_x, p_y, p_z) and each molecule can rotate with momenta (p_θ, p_ϕ) around the two axes perpendicular to the axis connecting the two atoms. Furthermore, the atoms can vibrate in the direction along their connecting axis with momentum p_ξ . Each molecule is then described by the Hamiltonian

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{4m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} + \frac{p_\xi^2}{2m} + \frac{m\omega^2}{2} q_\xi^2,$$

with I being the moment of inertia, ω being the oscillator frequency, and q_ξ being the distance between the two atoms. Write down the heat capacity C_V of the diatomic gas and explain your reasoning. (2 points)

Remark: In parts (a–c) of this exercise, you have derived the Dulong-Petit law for the heat capacity of a solid, which is valid for crystals at high temperature, in absence of collective lattice vibrations. The Dulong-Petit law corresponds to the high-temperature limit of the Einstein and Debye models, which include independent quantum oscillations and collective lattice vibrations, respectively. In part (d), you have derived the high-temperature limit of the heat capacity of a diatomic gas, such as hydrogen (H_2) and oxygen (O_2). Also for the diatomic gas, quantum effects reduce the heat capacity at lower temperatures.