

Problems in thermodynamics and statistical physics

1. Let $F(x, y) = x \cdot e^{x^2+y^2}$. Calculate (a) $\frac{\partial F}{\partial x}$, (b) $\frac{\partial F}{\partial y}$, (c) $\frac{\partial^2 F}{\partial x^2}$, (d) $\frac{\partial^2 F}{\partial x \partial y}$, (e) $\frac{\partial^2 F}{\partial y \partial x}$, (f) $\frac{\partial^2 F}{\partial y^2}$.

2. Let $d\omega = A(x, y)dx + B(x, y)dy$ be any differential form (Pfaffian). Show that if $d\omega$ is an exact differential (there exists a function $F(x, y)$ such that $d\omega = dF$), then it must hold

$$\text{a) } \quad \frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}, \quad \text{b) } \quad \oint d\omega = 0,$$

(b) for each closed integration path.

3. Let $d\omega_1 = (x^2 - y)dx + x dy$. Is it an exact differential, $d\omega_2 = d\omega_1/x^2$ an exact differential? Calculate the integral $\int d\omega$ between the points (1, 1) and (2, 2) along the lines (1, 1) \rightarrow (1, 2) \rightarrow (2, 2) and (1, 1) \rightarrow (2, 1) \rightarrow (2, 2).

4. Is $d\omega = p dV + V dp$ an exact differential? If so, determine the function F whose exact differential is $d\omega$. Compute the integral $\int d\omega$ between the points (V_1, p_1) and (V_2, p_2) along the lines $(V_1, p_1) \rightarrow (V_1, p_2) \rightarrow (V_2, p_2)$ a $(V_1, p_1) \rightarrow (V_2, p_1) \rightarrow (V_2, p_2)$.

5. Is the fom $dQ = c dT + R\frac{T}{V} dV$ an exact differential? Calculate the integral $\int d\omega$ between the points (V_1, T_1) and (V_2, T_2) long the lines $(V_1, T_1) \rightarrow (V_1, T_2) \rightarrow (V_2, T_2)$ a $(V_1, T_1) \rightarrow (V_2, T_1) \rightarrow (V_2, T_2)$. What function $f(V, T)$ must we multiply dQ by to make the product $f dQ$ an exact differential? Determine the function S for which $dS = f dQ$. c and R are constants.

6. Let x, y a z be 3 state variables, connected by the state equation $f(x, y, z) = 0$. Show the validity of the relations

$$\begin{aligned} \left(\frac{\partial x}{\partial y}\right)_z &= \left(\frac{\partial y}{\partial x}\right)_z^{-1}, \\ \left(\frac{\partial x}{\partial y}\right)_z &= -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \end{aligned}$$

and

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z$$

where the subscript indicates a constant variable and w is another state variable, $w = w(x, y, z)$.

7. The equation of state $pV = NkT$ connects the variables p, V and T , where N and k are constants. Verify by direct calculation that

$$\begin{aligned} \left(\frac{\partial p}{\partial V}\right)_T &= \left(\frac{\partial V}{\partial p}\right)_T^{-1} \\ \left(\frac{\partial p}{\partial T}\right)_V &= \left(\frac{\partial T}{\partial p}\right)_V^{-1} \end{aligned}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p$$

$$\left(\frac{\partial T}{\partial V}\right)_p = -\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_T$$

8. The equation of state of an ideal gas can be written as

- $pV = NkT$,
- $pV = n_1RT$,
- $p = \frac{\rho kT}{\mu}$,
- $p = nkT$,

where p, V, T are pressure, volume and temperature, N is the number of particles, n is their concentration, k is Boltzmann constant ($k = 1,38 \cdot 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$), R is the gas constant ($R = 8,31 \text{ J mol}^{-1} \text{ K}^{-1}$), n_1 is the amount of substance, ρ is the gas density and μ is the molecular weight. Verify the units of k and R . What are the units of n ? Show that the individual equations are equivalent rovnice jsou ekvivalentní ($N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$).

9. At a constant temperature of 20°C an ideal gas expands quasi-statically from a state with a pressure of 20 atm to a state with a pressure of 1 atm. What work is done by 1 mole of gas?

10. During the quasi-static adiabatic expansion of 6 liters of helium at a temperature of 350 K, the pressure drops from 40 atm to 1 atm. Calculate the resulting volume and temperature (assume the ideal gas equation of state). Compare the obtained results with the values that would be obtained for isothermal expansion ($\kappa = 1,63$). Assume it is an ideal gas.

11. Calculate the work done by an ideal gas during a quasi-static adiabatic expansion from a state characterized by p_1, V_1 to a state p_2, V_2 . Determine the work done by the gas if it passes from the initial state to the final state first by an isochoric process and then by an isobaric process, or first by an isobaric process and then by an isochoric process.

12. During the exchange of air between the lower and upper layers of the troposphere, expansion occurs, or air compression: rising air expands in an area of lower pressure. Due to the low thermal conductivity of air, the expansion and compression processes can be considered adiabatic. Calculate the change in temperature with height due to these processes. (Consider air as an ideal gas.)

13. Assume that the atmosphere of the planet Venus contains $k_1 = 96.5\%$ molecules CO_2 and $k_2 = 3.5\%$ molecules N_2 . We can neglect the other components. The temperature of the atmosphere is $t = 464^\circ\text{C}$ and the atmospheric pressure on the surface of Venus contains $p_0 = 9.1\text{MPa}$. The mass of the planet is $M = 4.87 \cdot 10^{24} \text{ kg}$ and the radius $R = 6052 \text{ km}$.

(a) Determine the density ρ_0 of the atmosphere and the gravitational acceleration g_0 at the surface of Venus.

(b) To research the planet's atmosphere, we will use an open "hot air balloon" (filled, of course, with the planet's atmosphere) with a volume of $V = 50 \text{ m}^3$. The weight of the structure is $m = 100 \text{ kg}$. To what temperature t_1 must we heat the gas in the balloon to start rising above the surface of the planet? At what temperature t_2 inside the balloon will we reach a height of 1 km?

Neglect the rotation of Venus and the drop in gravitational acceleration as the balloon exits. Consider the temperature of the atmosphere up to a height of 1 km as constant. The molar masses of the two main components of the Venus atmosphere are $M_m(\text{CO}_2) = 44.0 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$, $M_m(\text{N}_2) = 28.0 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$.

14. A gas is described by the equation of state $p = p(V, T)$. Show by direct calculation that δQ is not an exact differential.

15. The energy of a particle enclosed in an infinitely high potential well with dimensions $L_x \times L_y \times L_z$ is given by the relation

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

Assume that $L_x = L_y = L_z = L$. Assume that the system as a whole is characterized by the energy of the system. How is the microstate determined, how is the macrostate determined? Calculate the force that the particle exerts on the walls of the container. Determine the relationship between the energy of the system and the pressure.

16. Derive from the existence of the equation of state $f(p, V, T) = 0$ the relation

$$\alpha = p \cdot \beta \cdot \kappa$$

between the thermal coefficient of expansion $\alpha := \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$, isochoric expansion coefficient $\beta := \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V$ and the coefficient of isothermal compressibility $\kappa := -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$.

17. The state equation has the form $p = f(V) \cdot T$. Prove::

(a) $\left(\frac{\partial E}{\partial V} \right)_T = 0$

(b) if a holds, then $\left(\frac{\partial E}{\partial p} \right)_T = 0$.

18. For an ideal gas, calculate $\left(\frac{\partial p}{\partial V} \right)_{\text{ad}}$, $\left(\frac{\partial p}{\partial V} \right)_T$.

19. Show that for a gas described by the equation of state $f(p, V, T) = 0$ holds

$$\left(\frac{\partial p}{\partial V} \right)_{\text{ad}} = \left(\frac{\partial p}{\partial V} \right)_T \frac{c_p}{c_V}$$

20. Show the validity of the relation $c_p - c_V = R$ between the isobaric and isochoric specific heats of one mole of an ideal gas. The internal energy of an ideal gas does not depend on its volume.

21. Calculate the entropy of an ideal gas when $c_p = \text{konst.}$, $c_V = \text{konst.}$ Show that δQ is not an exact differential.

22. Prove the validity of the relation $pV^\kappa = \text{konst.}$ ($\kappa = c_p/c_V$ is the adiabatic exponent) for quasi-static adiabatic process of an ideal gas. Calculate κ assuming that $c_V = \frac{3}{2}R$.

23. For a gas, it has been found experimentally that the product of pressure and volume is a function of temperature only, teploty, $pV = f(T)$ and that the internal energy also depends only on temperature. What shape does $f(T)$ have?

24. For a photon gas, the energy density is only a function of temperature and the pressure is given by $p = \frac{1}{3}u(T)$, where $u(T) = E/V$. Calculate

(a) Function $u(T)$,

(b) entropy,

(c) isotherm and adiabat equation.

25. A rod is twisted by a moment of force M through an angle φ . (a) Prove that the first theorem of thermodynamics in this case is of the form

$$dE = \delta Q + M d\varphi.$$

(b) Derive from the definition of heat capacity (and the first theorem of thermodynamics) expressions for c_M a c_φ .

(c) Find the relationship between $\left(\frac{\partial M}{\partial \varphi}\right)_{\text{adiab}}$ a $\left(\frac{\partial M}{\partial \varphi}\right)_{\text{izoterm}}$.

26. (a) 1 kg of water at 0°C is brought into thermal contact with a large reservoir at 100°C . Calculate the entropy change of the water, the reservoir, and the entire system after equilibrium is established.

(b) Calculate the change in entropy of the entire system if the water was first in contact with a reservoir at a temperature of 50° and then with a reservoir at a temperature 100°C .

(c) How to ensure that the entropy of the system does not change when the water is heated?

27. Show that for small deviations $\delta\rho$, δp from the equilibrium values of density ρ_0 and pressure p_0 the propagation of sound waves can be described by a wave equation

$$\frac{\partial^2 \delta p}{\partial t^2} = c^2 \frac{\partial^2 \delta p}{\partial x^2},$$

where the speed of sound is given by the relation $c = \sqrt{(\partial p / \partial \rho)_{\text{ad}}}$ if we assume that events are on- ad fast that there is no heat exchange between the individual elements of the air. Show that the speed of sound can also be calculated as $c = \sqrt{\kappa_{\text{ad}} / \rho_0}$, where the adiabatic compressibility $\kappa_{\text{ad}} := -V \left(\frac{\partial p}{\partial V}\right)_{\text{ad}}$. Calculate the speed of sound in air assuming that air is made up of only N_2 molecules and that $\kappa = c_p/c_V = 7/5$.

28. An ideal gas expands adiabatically from volume V_1 into vacuum. Calculate the increase in entropy if the gas in the final state has volume V_2 and prove that the expansion process is irreversible.

29. The van der Waals equation of state for 1 mole of gas has the form

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

where a, b are constants. For a given T the curve can have two extremes given by equation

$$\left(\frac{\partial p}{\partial V}\right)_T = 0$$

In addition, at the critical point determined by the parameters T_c, p_c a V_c

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

Calculate the values of T_c, p_c a V_c . Write the state equation using the variables $T' = T/T_c, p' = p/p_c$ a $V' = V/V_c$.

30. Determine::

- (a) the internal energy and entropy of a van der Waals gas,
- (b) the work of a van der Waals gas during reversible isothermal expansion,
- (c) the temperature change of a van der Waals gas during adiabatic expansion into a vacuum.

31. The Joule-Thomson coefficient is defined using a parameter

$$\lambda = - \left(\frac{\partial T}{\partial p}\right)_H$$

(a) Show that

$$dH = T dS + V dp$$

and

$$\lambda = \frac{V}{C_p} (1 - T\alpha_p)$$

$\alpha_p := \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$ is the coefficient of isobaric expansion.

(b) Show that

$$\lambda = \frac{T \left(\frac{\partial p}{\partial T}\right)_V + V \left(\frac{\partial p}{\partial V}\right)_T}{C_p \cdot \left(\frac{\partial p}{\partial V}\right)_T}$$

(c) Verify that $\lambda = 0$ for a classical ideal gas.

(d) Show that it holds for a van der Waals gas

$$\lambda = \frac{bp + \frac{3ab}{V^2} - \frac{2a}{V}}{\left(p - \frac{a}{V^2} + \frac{2ab}{V^3}\right) \cdot C_p}$$

(e) Express the equation of the inverse curve that represents the interface between the region $\lambda > 0$ and $\lambda < 0$ in the $p - V$ diagram for the case of a van der Waals gas.

32. Show that the thermal coefficient of expansion

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

meets the relation

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p = -V\alpha$$

33. Show that the specific heat at constant pressure, c_p , and at constant volume, c_V , satisfy the relation

$$c_p - c_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p = -T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial S}{\partial p} \right)_T.$$

34. Free energy of the system $F(V, T) = -\frac{1}{3} \cdot \text{const} \cdot VT^4$. Determine its pressure, internal energy, 3 enthalpy and Gibbs potential.

35. Calculate the efficiency of the Carnot cycle (1. isothermal expansion, $T_2 = \text{konst}$, 2. adiabatic expansion, $S = \text{konst}$, 3. isothermal compression, $T_1 = \text{konst}$, 4. adiabatic compression, $S = \text{konst}$) for an ideal gas using its equations of state.

36. Calculate the efficiency of the following ideal gas cycle. Can this process be carried out reversibly?

1. isothermal expansion $T_2 = \text{konst}$
2. isochoric cooling $V_2 = \text{konst}$
3. isothermal compression $T_1 = \text{konst}$
4. isochoric heating $V_1 = \text{konst}$.

37. Determine the efficiency coefficient of an (idealized) Otto engine that works with an ideal gas 5 of specific heat $c_V = \frac{5}{2}R/\text{mol}$ at a compression ratio of 10:1.

1. adiabatic compression,,
2. isochoric heating (=burning of fuel),
3. adiabatic expansion (doing work),
4. cooling (=hot gas exhaust, new, cold gas is drawn in).

38. The Diesel cycle consists of the following parts:

1. adiabatic compression of atmospheric air,
2. combustion of the injected mixture and isobaric expansion,
3. adiabatic expansion
4. and isochoric cooling.

Determine the cycle efficiency as a function of compression ratio for an ideal gas.

39. What is the total entropy change if we mix 2 kg of water at a temperature of 363 K adiabatically and at constant pressure with 3 kg of water at a temperature of 283 K? ($c_p = 4184 \text{ J/Kkg}$)

40. A refrigerator can turn 10 liters of water at 0°C into ice at the same temperature in one hour. For this, the thermal energy $Q = 800\text{kcal}(= 800 \times 1,163\text{Wh})$ must be

transferred to the air (27, 3°C). What is the minimum power the refrigerator must have?

41. Prove that for $T \rightarrow 0$ there is no system described by $pV = \text{const} \cdot T$.

42. A closed system consists of two simple subsystems that are separated by a movable wall that allows

- (a) only heat exchange,
- (b) both heat and mass exchange,
- (c) neither heat nor mass exchange.

What are the corresponding equilibrium conditions?

43. Two equal quantities of ideal gas with the same temperature T and different pressures p_1, p_2 are separated from each other by a partition. Determine the change in entropy resulting from the mixing of the two gases.

44. Determine the maximum work that can be obtained by combining equal quantities of the same ideal gas with the same temperature T_0 (and different volumes or pressures).

45. Molar volume of water $v^{(2)} = 18 \text{ cm}^3/\text{mol}$, the molar volume of ice is 9.1% larger (at a pressure of 10^5 Pa), The molar mass of water is 18 g/mol . The latent heat of melting of ice is 330 kJ/kg . Calculate the change in melting point as the pressure changes.

46. When the magnetization M changes by dM the system performs work $dW = -H dM$, where H is the intensity of the magnetic field. (This is work done per unit volume; volume $V = \text{const.} = 1$.) Determine the difference in heat capacities $c_H - c_M$ at a constant field H and at a constant magnetization.

47. Determine the equation of the adiabat of an isotropic magnetic.

48. Show that it holds

$$\frac{c_H}{c_M} = \frac{\chi_T}{\chi_S},$$

where

$$\chi_T = \left(\frac{\partial M}{\partial H} \right)_T$$

and

$$\chi_S = \left(\frac{\partial M}{\partial H} \right)_S$$

49. The gamma function is defined by an integral

$$\Gamma(n) := \int_0^{\infty} dt \exp(-t)t^{n-1}.$$

1. Prove the relationship

$$\Gamma(n+1) = n\Gamma(n),$$

2. calculate $\Gamma(n)$, $n \in \mathbb{N}$,

3. calculate

$$\Gamma\left(n + \frac{1}{2}\right), n \in \mathbb{N}.$$

50. Using the Gamma function, calculate the approximate expression $\ln(n!)$ for large values of n (Stirling's formula).

51. A hydrogen atom is in the level $n = 3$. Assuming that the occupation of the energy levels is given by the microcanonical distribution, calculate the probability that the atom is in states with the same secondary quantum number l .

52. Entropy for an isolated system is given by the relation $S = k_B \ln \Gamma$, where Γ is the number of microstates. For a closed system $S = -k_B \sum_n w_n \ln w_n$. Show that both relations are not contradictory.

53. Show that the heat capacity c_V is given by the energy fluctuation, i.e.

$$c_V = \frac{1}{k_B T^2} \langle \Delta E^2 \rangle.$$

54. Calculate the thermodynamic properties of the system of N distinguishable classical harmonic oscillators with frequency ω .

55. Consider a gas with diatomic molecules. Calculate the molar heat capacity of the given gas. Consider only the vibrational motion of molecules, when the energy is given by the relation

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right). \quad (1)$$

First, calculate the statistical sum from which you will determine the free energy and from the free energy you can already determine the required heat capacity. You can write the resulting heat capacity in the approximation of low and high temperatures.

56. Derive the form of the Maxwell-Boltzmann distribution of the speeds of gas molecules. Proceed only from the assumption that the space is isotropic and that the movement of gas molecules in individual directions is independent.

57. Derive the Maxwell-Boltzmann distribution of atomic momentum using the canonical distribution.

58. Assuming the validity of the Maxwell-Boltzmann distribution of the speeds of gas molecules, calculate (a) $\langle p_x \rangle$, (e) $\sqrt{\Delta E^2}$, (b) $\langle p \rangle$, (c) $\langle p^2 \rangle$, (f) the most probable magnitude of momentum, (d) $\langle v^2 \rangle$, (g) probability that $p_z > 0$.

59. Calculate the density distribution in a column of gas with base A under the influence of a homogeneous gravitational field (in the atmosphere). Assume that the gas is made up of indistinguishable particles, each of mass m .

60. Show that pressure and energy density have the same unit.

61. Calculate the density of states for relativistic particles and find the limit relations for classical and ultra relativistic particles.

62. Show that in the classical case it is possible to derive the Maxwell-Boltzmann velocity distribution law from the grand canonical distribution of a single particle.

63. Let's define functions

$$B_n(y) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{\exp(x-y) - 1}, \quad (2)$$

and

$$F_n(y) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{\exp(x-y) + 1}. \quad (3)$$

For these functions prove

$$\frac{dB_{n+1}(y)}{dy} = B_n(y),$$

and

$$\frac{dF_{n+1}(y)}{dy} = F_n(y).$$

64. From a relationship

$$\Omega = -k_B T \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} B_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right), \quad (4)$$

valid for a non-relativistic ideal boson gas, count the number of particles N and derive the relation for the chemical potential within the classical limit.

65. Calculate c_V of a non-relativistic fermion gas and verify the validity of the classical limit for c_V/N .