

Problems in thermodynamics and statistical physics

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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) $\frac{\partial^2 F}{\partial y^2}$.

Solution:

$$\begin{aligned} \text{(a)} \quad \frac{\partial(x \cdot e^{x^2+y^2})}{\partial x} &= \exp(x^2 + y^2) + 2x^2 \exp(x^2 + y^2) = \exp(x^2 + y^2)(1 + 2x^2), \\ \text{(b)} \quad \frac{\partial(x \cdot e^{x^2+y^2})}{\partial y} &= 2xy \exp(x^2 + y^2), \\ \text{(c)} \quad \frac{\partial^2(x \cdot e^{x^2+y^2})}{\partial x^2} &= 4x \exp(x^2 + y^2) + (1 + 2x^2) 2x \exp(x^2 + y^2) = \exp(x^2 + y^2)(4x + 2x + 4x^3) = \\ &= \exp(x^2 + y^2)(6x + 4x^3) = 2x(3 + 2x^2) \exp(x^2 + y^2) \\ \text{(d)} \quad \frac{\partial^2(x \cdot e^{x^2+y^2})}{\partial x \partial y} &= 2y(1 + 2x^2) \exp(x^2 + y^2), \\ \text{(e)} \quad \frac{\partial^2(x \cdot e^{x^2+y^2})}{\partial y \partial x} &= 2y \exp(x^2 + y^2) + 4x^2y \exp(x^2 + y^2) = 2y \exp(x^2 + y^2)(1 + 2x^2), \\ \text{(f)} \quad \frac{\partial^2(x \cdot e^{x^2+y^2})}{\partial y^2} &= 2x \exp(x^2 + y^2) + 4xy^2 \exp(x^2 + y^2) = 2x \exp(x^2 + y^2)(1 + y^2). \end{aligned}$$

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.

Solution:

(a) Assuming satisfied

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy = A(x, y)dx + B(x, y)dy$$

since the interchangeability of the second derivatives holds:

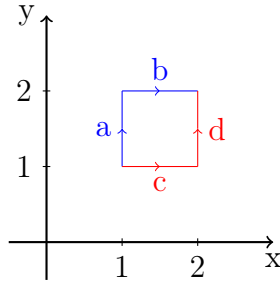
$$\frac{\partial}{\partial x} \frac{\partial f}{\partial y} = \frac{\partial}{\partial y} \frac{\partial f}{\partial x} = \frac{\partial B(x, y)}{\partial x} = \frac{\partial A(x, y)}{\partial y}$$

because apparently it fullfills

$$A(x, y) = \frac{\partial f}{\partial x}, B(x, y) = \frac{\partial f}{\partial y}$$

(b) For the calculation, we use Stokes' theorem, which is of the form

$$\int_V d\omega = \int_{\partial V} \omega$$



Obrázek 1: Representation of the circular process for task 3.

We calculate the left side

$$\oint_{\mathcal{C}} df = \oint_{\mathcal{C}} \left(dx \frac{\partial f}{\partial x} + dy \frac{\partial f}{\partial y} \right) = \int_{\mathcal{S}(\partial \mathcal{S} = \mathcal{C})} d \left(dx \frac{\partial f}{\partial x} + dy \frac{\partial f}{\partial y} \right) = \int_{\mathcal{S}(\partial \mathcal{S} = \mathcal{C})} d(df) = 0,$$

because the outer derivative of the outer derivative of any form is always zero.

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 $(1, 1) \rightarrow (2, 1) \rightarrow (2, 2)$.

Solution:

Since the derivative of the term udx with respect to y is equal to -1 and the derivative of the second term with respect to x is equal to 1 , the term is not an exact differential. Dividing by x^2 both derivatives become equal $-\frac{1}{x^2}$, so the term is an exact differential. We calculate the curve integral as follows: we can divide the integral into two parts

$$\int_{\mathcal{C}} d\omega_1 = \int_{\mathcal{C}_1} d\omega_1 + \int_{\mathcal{C}_2} d\omega_1$$

Subsequently, we parameterize the integration path, which is shown in Figure 1. For path a and b, the parameters are as follows:

$$(a): x = 1, y = t, t \in [1, 2],$$

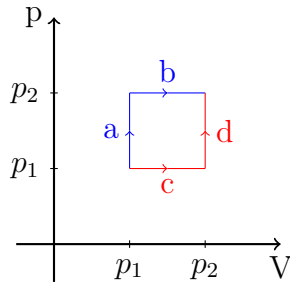
$$(b): x = t, y = 2, t \in [1, 2].$$

So we can calculate the relevant integrals:

$$\int_{\mathcal{C}_1} d\omega_1 = \int_1^2 dt = 1$$

since $dx = 0$. Second part:

$$\int_{\mathcal{C}_2} d\omega_1 = \int_1^2 dt (t^2 - 2) = \left[\frac{t^3}{3} - 2t \right]_1^2 = -\frac{2}{3}$$



Obrázek 2: Representation of the circular process for task 4.

So the result is equal

$$\int_{\mathcal{C}} d\omega_1 = \frac{1}{3}$$

In the case of integration along the blue integration path, we get the result of $\frac{10}{3}$. Integrating $d\omega_1/x^2$, we get same result 1 for both cases.

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 $(V_1, p_1) \rightarrow (V_2, p_1) \rightarrow (V_2, p_2)$.

Solution:

It follows from the integrability conditions that it is an exact differential. The function ω is easy to find. We know that

$$\frac{\partial F}{\partial V} = p$$

after that

$$F = pv + g(p)$$

the derivative of this function with respect to pressure is equal to V , from here

$$\frac{\partial F}{\partial p} = V = V + \frac{dg(p)}{dp}$$

for the derivative of the function $g(p)$ we get that it is zero, and therefore the function $g(p)$ must be some constant. So the function F is equal to

$$F(p, V) = pV + \text{konst}$$

We calculate the curve integral analogously to the previous case. Fig. 2 shows the integration paths. the curve integral along the blue path comes out as $-V_1p_1 + V_2p_2$ and of course exactly the same along the red path.

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.

Solution:

Since the derivative of the first term with respect to volume is zero and the derivative of the second term with respect to temperature is equal to $\frac{R}{V}$, it is not a complete differential. The integration takes place along similar integration paths as shown in 2, the integral along the blue integration path is equal to $RT_2 \ln \frac{V_2}{V_1} + c(T_2 - T_1)$ and along the red integration path: $RT_1 \ln \frac{V_2}{V_1} + c(T_2 - T_1)$.

Next comes the slightly more complicated part. We need to find a function $f(T, V)$, such that the condition is satisfied

$$\frac{\partial(f(T, V)c)}{\partial V} = \frac{\partial(f(T, V)R\frac{T}{V})}{\partial T}$$

We calculate the derivative on both sides:

$$c \frac{\partial f}{\partial V} = R \frac{T}{V} \frac{\partial f}{\partial T} + fR$$

after multiplying by V we get an equation with separated variables

$$cV \frac{\partial f}{\partial V} = RT \frac{\partial f}{\partial T} + fR$$

we can then assume the function f in the form

$$f(T, V) = g(T) \cdot h(V)$$

Substitute and divide by $V \cdot g(T) \cdot h(V)$

$$cV \frac{1}{h(V)} \frac{\partial h(V)}{\partial V} = RT \frac{1}{g(T)} \frac{\partial g(T)}{\partial T} + R$$

The left side now depends only on volume, the right side only on temperature. In order to satisfy the equality for any V and T , both sides must be constant. Thus, two differential equations for volume and temperature fall out of this equation:

$$cV \frac{1}{h(V)} \frac{\partial h(V)}{\partial V} = \text{konst.}$$

the solution is, after dividing the equation by the volume

$$c \ln(h(V)) = \text{konst} \cdot \ln(V)$$

then the function $h(V)$ is equal to

$$h(V) = V^{\frac{\text{konst.}}{c}}.$$

Let's focus on the right side:

$$RT \frac{1}{g(T)} \frac{\partial g(T)}{\partial T} + R = \text{konst}$$

we also solve by separating variables:

$$\frac{1}{g(T)} \frac{\partial g(T)}{\partial T} = \frac{k}{R} - 1$$

and the result is

$$\ln(g(T)) = \left(\frac{\text{konst.}}{R} - 1 \right) \ln(T)$$

after that

$$g(T) = T^{\frac{\text{konst.}}{R} - 1}$$

Let us now recall the function $f(T, V) = g(T) \cdot h(V)$, into which we will substitute the result of our calculations

$$f(T, V) = V^{\frac{\text{konst.}}{c}} \cdot T^{\frac{\text{konst.}}{R} - 1}$$

where Const. is arbitrary. Therefore, we choose the simplest solution konst.= 0:

$$f(V, T) = \frac{1}{T}$$

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

$$\left(\frac{\partial x}{\partial y} \right)_z = \left(\frac{\partial y}{\partial x} \right)_z^{-1} \quad (1)$$

$$\left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \quad (2)$$

and

$$\left(\frac{\partial x}{\partial y} \right)_z = \left(\frac{\partial x}{\partial y} \right)_w + \left(\frac{\partial x}{\partial w} \right)_y \left(\frac{\partial w}{\partial y} \right)_z \quad (3)$$

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

Solution:

We calculate the partial derivatives with respect to x and y assuming that z is constant:

$$\begin{aligned} \frac{df}{dx} &= \left(\frac{\partial f}{\partial x} \right)_{y,z} + \left(\frac{\partial y}{\partial x} \right)_z \left(\frac{\partial f}{\partial y} \right)_{x,z} = 0 \\ \frac{df}{dy} &= \left(\frac{\partial f}{\partial y} \right)_{x,z} + \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial f}{\partial x} \right)_{y,z} = 0 \end{aligned}$$

from each equation we express the term not containing f :

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{\left(\frac{\partial f}{\partial x}\right)_{y,z}}{\left(\frac{\partial f}{\partial y}\right)_{x,z}}, \quad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial f}{\partial y}\right)_{x,z}}{\left(\frac{\partial f}{\partial x}\right)_{y,z}}$$

after multiplying both the two expressions we have:

$$\left(\frac{\partial y}{\partial x}\right)_z \cdot \left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial f}{\partial x}\right)_{y,z}}{\left(\frac{\partial f}{\partial y}\right)_{x,z}} \cdot \frac{\left(\frac{\partial f}{\partial y}\right)_{x,z}}{\left(\frac{\partial f}{\partial x}\right)_{y,z}} = 1$$

which proves (1). Let's now write the right side of the expression

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{\left(\frac{\partial f}{\partial x}\right)_{y,z}}{\left(\frac{\partial f}{\partial y}\right)_{x,z}}$$

we transform the derivatives on the right-hand side into z z-coordinates

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial f}{\partial z}\right)_{y,z}}{\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial f}{\partial z}\right)_{x,z}} = -\frac{\left(\frac{\partial z}{\partial x}\right)_y}{\left(\frac{\partial z}{\partial y}\right)_x} = -\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x$$

this proves expression (2). Recall the coordinate transformation formula $(x, y, z) \rightarrow (u, v, w)$ for the derivative:

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial y}{\partial u}\right)_{v,w} \left(\frac{\partial u}{\partial x}\right)_{y,z} + \left(\frac{\partial y}{\partial v}\right)_{u,w} \left(\frac{\partial v}{\partial x}\right)_{y,z} + \left(\frac{\partial y}{\partial w}\right)_{u,v} \left(\frac{\partial w}{\partial x}\right)_{y,z}$$

we will make use of this relationship assuming that we are only transforming a single coordinate from $z \rightarrow w$

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

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

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

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

Solution:

So let's look at the individual equations one by one:

$$\begin{aligned} \left(\frac{\partial p}{\partial V}\right)_T &= -\frac{NkT}{V^2} = -\frac{p}{V}, \quad \left(\frac{\partial V}{\partial p}\right)_T^{-1} = \left(-\frac{NkT}{p^2}\right)^{-1} = \left(-\frac{V}{p}\right)^{-1} = -\frac{p}{V} \\ \left(\frac{\partial p}{\partial T}\right)_V &= \frac{Nk}{V} = \frac{p}{T}, \quad \left(\frac{\partial T}{\partial p}\right)_V^{-1} = \left(\frac{V}{Nk}\right)^{-1} = \left(\frac{T}{p}\right)^{-1} = \frac{p}{T} \\ \left(\frac{\partial p}{\partial V}\right)_T &= -\frac{NkT}{V^2} = -\frac{p}{V}, \quad -\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p = -\frac{p}{T} \frac{p}{Nk} = -\frac{p}{T} \cdot \frac{T}{V} = -\frac{p}{V} \\ \left(\frac{\partial T}{\partial V}\right)_p &= \frac{T}{V}, \quad -\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_T = \frac{T}{p} \left(-\frac{p}{V}\right) = -\frac{T}{V} \end{aligned}$$

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 ($N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$).

Solution:

We determine the dimensions of the individual constants from the respective state equations

$$\begin{aligned} [k] &= \frac{[p][V]}{[N][T]} = \frac{\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} \cdot \text{m}^3}{\text{K}} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \\ [R] &= \frac{[p][V]}{[n_1][T]} = \frac{\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} \cdot \text{m}^3}{\text{mol} \cdot \text{K}} = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{mol}^{-1} \end{aligned}$$

n has unit of m^{-3} . It is the concentration of particles. Now to derive the equivalence between the individual forms of the equation: We derive the second equation from the first very easily: we expand the right-hand side of the equation by Avogadro's constant

$$pV = N \frac{N_A}{N_A} kT$$

since $N_A k = R$ - molar gas constant and $N/N_A = n$, we get the second equation

$$pV = nRT$$

To derive the third equation, we start again from the first equation. Assume that we know the average molecular weight μ , with which we expand the right-hand side of the equation of state

$$pV = N \frac{\mu}{\mu} kT$$

here again $N\mu$ is the mean mass of N particles. We divide the equation by the volume

$$p = \frac{m}{V} \frac{1}{\mu} kT$$

and we see that we got the desired density in the expression

$$p = \frac{\rho}{\mu} kT$$

The derivation of the last equation of state is simple. It is enough to divide the first equation by the volume and realize that $\rho N/V = n$, i.e. the number density of particles

$$p = nkT$$

That's all.

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?

Solution:

The work is generally equal to

$$W = \int_{V_1}^{V_2} dV p(T) = \int_{V_1(p_1)}^{V_2(p_2)} dV \frac{nRT}{V} = nR \ln(V) \Big|_{V_1(p_1)}^{V_2(p_2)} = nRT \ln \frac{V_2(p_2)}{V_1(p_1)} = nRT \ln \frac{\frac{nRT}{p_2}}{\frac{nRT}{p_1}} = nRT \ln \frac{p_1}{p_2} \approx 8.31 \cdot 293.15 \cdot \ln(10) \text{ J} \approx 5.6 \text{ kJ} \quad (4)$$

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.

Solution:

It is true for the adiabatic process

$$pV^\kappa = \text{konst.}$$

after that

$$p_0 V_0^K = p_1 V_1^K$$

i.e. the new volume is equal to

$$V_1 = \sqrt[\kappa]{\frac{p_0}{p_1}} V_0 = {}^{1.63}\sqrt{40} \cdot 61 \approx 571$$

To calculate the temperature, we must first find out the mass of the gas. We can do this easily from the equation of state of an ideal gas, where we use the quantities from the initial state of the gas

$$p_0 V_0 = nRT_0 \rightarrow n = \frac{p_0 V_0}{RT_0}$$

the temperature itself is also calculated from the equation of state, but for the final state

$$p_1 V_1 = nRT_1 \rightarrow T_1 = \frac{p_1 V_1}{nR} = \frac{p_1 V_1}{p_0 V_0} T_0 = \frac{p_1 V_1}{p_0 V_0} T_0 = \frac{p_1}{p_0} \sqrt[\kappa]{\frac{p_0}{p_1}} T_0 = \left(\frac{p_0}{p_1}\right)^{\frac{1}{\kappa}-1} T_0 \approx 40^{\frac{1}{1.63}} - 1 \cdot 350 \text{ K} = 84.11 \text{ K}$$

Now let's focus on the comparison with isothermal expansion. The temperature is the same, we don't have to deal with it. From the equation $p_0 V_0 = p_1 V_1$ we can easily find that the volume will be

$$V_1 = \frac{p_0}{p_1} V_0 = 40 \cdot 61 = 2401$$

thus, the final volume is approximately four times larger than in the case of adiabatic expansion.

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.

Solution:

For an adiabatic process, $pV^\kappa = \text{konst.} = p_1 V_1^\kappa = p_2 V_2^\kappa$. The work can then be easily

$$\begin{aligned} W &= \int_{V_1}^{V_2} dV p = \int_{V_1}^{V_2} dV \frac{p_1 V_1^\kappa}{V^\kappa} = p_1 V_1^\kappa \frac{V^{1-\kappa}}{1-\kappa} \Bigg|_{V_1}^{V_2} = \frac{p_1 V_1^\kappa}{1-\kappa} (V_2^{1-\kappa} - V_1^{1-\kappa}) \\ &= \frac{p_1 V_1}{1-\kappa} \left[\left(\frac{V_2}{V_1}\right)^{1-\kappa} - 1 \right] \end{aligned}$$

We can easily calculate the second part of the example by reasoning. The work done is equal to the area between the curve and the V . axis. If we look at the pV diagram of individual processes 2, it is clear that no work is done during isochoric events, so isobaric events will have the main contribution. The calculation of the work is therefore limited to the calculation of the content of the rectangle. If the process is first isochoric and then isobaric, the work done is equal

$$W_1 = p_2 (V_2 - V_1)$$

for the second case

$$W_1 = p_1 (V_2 - V_1).$$

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.)

Solution:

First, let's review the basic equations we'll be using: this is an ideal gas, so its equation of state will do

$$pV = nRT$$

and also from the information that the process can be considered adiabatic

$$pV^\kappa = \text{konst.}$$

However, we want to express this equation using temperature instead of volume, so we use the equation of state and get

$$p \left(\frac{RT}{p} \right)^\kappa = p^{1-\kappa} R^\kappa T^\kappa = p^{1-\kappa} T^\kappa = \text{konst.}$$

we differentiate the expression

$$(1 - \kappa)p^{-\kappa} R^\kappa T^\kappa dp = p^{1-\kappa} R^\kappa \kappa T^{\kappa-1} dT = 0$$

something is shortened here and the equation is then simplified to

$$(1 - \kappa)dp + \frac{p\kappa}{T} dT = 0 \tag{5}$$

We will now be interested in where to take the height dependence. Therefore, we will recall Euler's fluid flow equation (which will also be useful in some other examples)

$$\frac{d\mathbf{v}}{dt} + (\mathbf{v} \cdot \nabla)\mathbf{v} = -\frac{\nabla p}{\rho} - g \tag{6}$$

Assume stationary flow and also neglect the nonlinear term. Then we get the hydrostatic equilibrium equation in the form

$$\nabla p = -\rho g$$

which we can rewrite to

$$dp = -\rho g dh$$

and substitute in

$$-\rho g \frac{\kappa - 1}{\kappa} \frac{dh}{p} = \frac{dT}{T} = \frac{1}{T} \frac{dT}{dh} dh$$

in the equation we are still hindered by the pressure, which we get rid of using the equation of state of an ideal gas in the form

$$p = \frac{\rho}{\mu} kT$$

after that

$$\frac{dT}{dh} = -\frac{\mu g}{k} \frac{\kappa - 1}{\kappa}$$

For $g = 9.81 \text{ m} \cdot \text{s}^{-2}$, $\mu = 29m_{\text{H}}$ a $\kappa = 1.4$ will work out

$$\frac{dT}{dh} \approx 10 \text{ K} \cdot \text{km}^{-1}$$

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_v 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 $M_m(\text{CO}_2) = 44.0 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$, $M_m(\text{N}_2) = 28.0 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$.

Solution:

(a) We determine the density of the atmosphere using an equation of state of the form

$$p = \frac{\rho k_{\text{B}} T}{\mu}$$

where μ is the average molecular weight, which we calculate using the formula

$$\mu = \frac{k_1 M_{m_1} + k_2 M_{m_2}}{N_A} = 7.21 \times 10^{-24} \text{ kg}$$

The density of the atmosphere is then equal

$$\rho = \frac{\mu p}{k_B T} = 64.518 \text{ kg} \cdot \text{m}^{-3}$$

We calculate the magnitude of the gravitational acceleration by direct substitution in the formula

$$a_g = \frac{GM}{R^2} = 8.87 \text{ m} \cdot \text{s}^{-2}$$

(b) We will use Archimedes' law to calculate the temperature. The magnitude of the buoyant force must be greater than or equal to the magnitude of the gravity force, broken down

$$\rho_{\text{atm.}} V_{\text{bal}} g \geq mg = (m_{\text{bal}} + m_{\text{plyn}}) g = \frac{m}{V} + \frac{\mu p}{k_B T}$$

from this equation we can easily express the temperature in the form

$$T \geq \frac{T_{\text{atm}}}{1 - \frac{mk_B T_{\text{atm.}}}{V\mu p}} = 760.73 \text{ K}$$

To calculate the temperature required for the balloon to take off to a height of 1 km, we need to determine the density/pressure of the atmosphere at the appropriate height. We can derive the barometric equation from the hydrostatic equilibrium equation, which we write in the form

$$\frac{\partial p}{\partial h} = -\rho g$$

into which we substitute the equation of state of an ideal gas

$$\frac{\partial p}{\partial h} = -\frac{p\mu}{k_B T} g$$

the solution of this equation is of the form

$$p(h) = p_0 \exp\left(-\frac{\mu}{k_B T} h\right)$$

respectively density (substitution into equation of state)

$$\rho(h) = \frac{\mu p_0}{k_B T} \exp\left(-\frac{\mu}{k_B T} h\right) = 64.063 \text{ kg} \cdot \text{m}^{-3}$$

Assuming that the gas in the balloon has the same pressure as the gas in the atmosphere, then we can use the equation of state to write

$$p = \frac{\rho_{\text{ball}}}{\mu} k_B T = \frac{\rho_{\text{atm.}}}{\mu} k_B T_{\text{atm}}$$

where do we get

$$\rho_{\text{bal.}} = \rho_{\text{atm.}} \frac{T_{\text{atm.}}}{T_{\text{bal.}}}$$

The condition for temperature is then

$$T_2 \geq \frac{T}{1 - \frac{m}{V\rho_0} \exp\left(\frac{\mu}{k_B T} h\right)} = 762 \text{ K}$$

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.

Solution:

We start from the first theorem of thermodynamics $dE = \delta Q - p dV$, from which we express δQ

$$\delta Q = dE + p dV$$

we can break down the energy differential in temperature and volume variables, then

$$\delta Q = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + p\right] dV$$

We recall what condition must hold for a complete differential and apply it to the appropriate formula

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

due to the interchangeability of partial derivatives, we get

$$\left(\frac{\partial p}{\partial T}\right)_V = 0$$

however, this contradicts the assumption that pressure is a function of volume. Therefore, this condition is not fulfilled and apparently it is not a complete 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.

Solution:

A macrostate is characterized by macroscopic parameters of a system that we can directly measure. In this case, the macrostate is characterized by energy $E(L, n_x, n_y, n_z)$. For a given macrostate, there are several microstates that we cannot distinguish. Here, the microstate is characterized by the values n_x, n_y, n_z .

Let's write how the energy of the system changes when it is moved by a bit dx . Since we assume a really gradual change, we will then perform the expansion only to the first order

$$E(L + dx, L, L) = E(L, L, L) - \frac{\hbar^2 \pi^2}{mL^3} n_x^2 dx$$

After that

$$dE = -\frac{\hbar^2 \pi^2}{mL^3} n_x^2 dx$$

Since the relation $dE = -\mathbf{F} \cdot d\mathbf{r}$ is valid, we get a formula for the acting force

$$F_x = \frac{\hbar^2 \pi^2 n_x^2}{mL^3}$$

the pressure is equal to $p = F/S$, and therefore

$$p = \frac{\hbar^2 \pi^2 n_x^2}{mL^5}$$

Mean values are as follows: pressure:

$$\langle p_x \rangle = \left\langle \frac{\hbar^2 \pi^2 n_x^2}{mL^5} \right\rangle = \frac{\hbar^2 \pi^2}{mL^5} \langle n_x^2 \rangle$$

and energy

$$\langle E \rangle = \frac{\hbar^2 \pi^2}{mL^3} (\langle n_x^2 \rangle + \langle n_y^2 \rangle + \langle n_z^2 \rangle) = \frac{\langle p \rangle}{2L^3}.$$

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

Solution:

We substitute the appropriate expressions on the right side

$$p \cdot \beta \cdot \kappa = p \cdot \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V \left[-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \right] = -\frac{1}{V} \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \alpha$$

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

Solution:

(a) We express the expression $\delta Q/T$ from the first law of thermodynamics

$$\frac{\delta Q}{T} = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V dT + \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_T + p \right] dV$$

The following formula will be used a lot, so the derivation needs to be done properly! Since this is an exact differential, the derivative of the first term with respect to the volume must be equal derivation of the second term according to temperature, i.e. We will use the second law of thermodynamic for quasi-static processes, which we will insert into the first thermodynamic theorem

$$dS = \frac{dE}{T} + \frac{p}{T} dV \quad (7)$$

We know that dE is the complete differential, which we will break down into the variables of temperature and volume

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad (8)$$

we will get

$$dS = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_T dT + \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_T + p \right] dV \quad (9)$$

We know that dS is also an exact differential and therefore must hold

$$\left\{ \frac{\partial}{\partial V} \left[\frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V \right] \right\}_T = \left\{ \frac{\partial}{\partial T} \left\{ \frac{1}{T} \left[\left(\frac{\partial E}{\partial V}\right)_T + p \right] \right\} \right\}_V$$

whence

$$\frac{1}{T} \left[\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial T}\right)_T \right]_V = -\frac{1}{T^2} \left[\left(\frac{\partial E}{\partial V}\right)_T + p \right] + \frac{1}{T} \left\{ \left[\frac{\partial}{\partial T} \left(\frac{\partial E}{\partial V}\right)_V \right]_T + \left(\frac{\partial P}{\partial T}\right)_V \right\}.$$

The second derivative disappears and we finally multiply the expression by T^2 . We will get

$$\left(\frac{\partial E}{\partial V}\right)_T + p = T \left(\frac{\partial P}{\partial T}\right)_V \quad (10)$$

Now it is enough to calculate the relevant partial derivatives

$$\left(\frac{\partial E}{\partial V}\right)_T = T f(V) - f(V)T = 0$$

(b) We rewrite the derivative of energy with respect to volume as follows

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

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

Solution:

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

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

Solution:

We break down the left side using the new variable T

$$\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial V}\right)_T + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_S \quad (11)$$

Now we can prove three important formulas resulting from the first theorem of thermodynamics, from which we will express heat

$$\delta Q = dE + p dV \quad (12)$$

First, we derive another important formula describing the difference between c_p and c_v . We start again from (12), where we break down dE again

$$\delta Q = \left(\frac{\partial E}{\partial T}\right)_T dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + p\right] dV$$

Now we will break down the volume as a function of pressure and temperature

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

Since we want to express the heat capacity at constant pressure, we put $dp = 0$. Moreover, it applies

$$c_v = \left(\frac{\delta Q}{\partial T}\right)_V \quad (13)$$

We substitute in the relation for δQ

$$\delta Q = c_v dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p dT = \left[c_v + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p\right] dT$$

where we used formula (10). It already follows from this formula

$$c_p = \left(\frac{\delta Q}{\partial T} \right)_p = c_V + T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p \quad (14)$$

Before the actual calculation, it will still be necessary to express the adiabatic derivative. We start again with (12). We are interested in adiabatic processes and therefore $\delta Q = 0$

$$0 = dE + p dV$$

dE is classically broken down into volume and temperature variables. We will use the first derived formula for the derivative of energy with respect to volume. We will get

$$0 = T \left(\frac{\partial p}{\partial T} \right)_V dV + c_V dT$$

where we now write dT as a function of volume and entropy. We are interested in processes where the entropy is constant, so we can take the sdS term to be zero

$$0 = T \left(\frac{\partial p}{\partial T} \right)_V dV + c_V \left(\frac{\partial T}{\partial V} \right)_S dV$$

That's where we get it from

$$\left(\frac{\partial T}{\partial V} \right)_S = -\frac{T}{c_V} \left(\frac{\partial p}{\partial T} \right)_V \quad (15)$$

We have derived all the important identities, which now just need to be combined correctly. We substitute formula (14) into (15) for the derivation of pressure by temperature

$$\left(\frac{\partial T}{\partial V} \right)_S = -\frac{c_p - c_V}{c_V} \left(\frac{\partial T}{\partial V} \right)_p$$

We can substitute this formula in (11), we get

$$\left(\frac{\partial P}{\partial V} \right)_S = \left(\frac{\partial P}{\partial V} \right)_T - \frac{c_p - c_V}{c_V} \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_p$$

We can modify the product of partial derivatives

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

After substitution

$$\left(\frac{\partial P}{\partial V} \right)_S = \left(\frac{\partial P}{\partial V} \right)_T + \frac{c_p - c_V}{c_V} \left(\frac{\partial P}{\partial V} \right)_T = \left[1 + \frac{c_p - c_V}{c_V} \right] \left(\frac{\partial P}{\partial V} \right)_T = \frac{c_p}{c_V} \left(\frac{\partial P}{\partial V} \right)_T$$

and finally we get the search term. When using Maxwell relations, the procedure is simpler.

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.

Solution:

It is sufficient to calculate this equation from the previously proven formula (14). We substitute the ideal gas equation

$$c_p - c_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p = T \frac{p}{T} \frac{V}{T} = \frac{pV}{T} = nR$$

For 1 mol of gas this is exactly R , so Mayer's relation is proved.

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.

Solution:

We proceed from the formula (9), where we substitute (10), we have

$$dS = \frac{c_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV$$

We substitute the derivation valid for an ideal gas

$$dS = \frac{c_V}{T} dT + \frac{nR}{V} dV$$

Obviously, this is a full differential. From the first equation

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

we will get

$$S(V, T) = c_V \ln(T) + C(V)$$

we now derive by volume

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial C(V)}{\partial V} \right)_T = \frac{nR}{V}$$

after that

$$C(V) = nR \ln(V) + \text{konst.}$$

The entropy sought is equal to

$$S(T, V) = c_V \ln(T) + nR \ln(V) + \text{konst.}$$

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 $c_V = \frac{3}{2}R$.

Solution:

We start from the calculated entropy of an ideal gas, which is constant

$$S(T, V) = c_V \ln(T) + nR \ln(V) + \text{konst.} = \text{konst.}$$

Const. we hide in const. and we will edit further

$$\ln(T) + \ln\left(V^{\frac{nR}{c_V}}\right) = \ln\left(TV^{\frac{nR}{c_V}}\right) = \text{konst.}$$

from this equation

$$TV^{\frac{nR}{c_V}} = \text{konst.}$$

Now let's substitute for temperature from the equation of state of an ideal gas

$$\frac{pV}{nR} V^{\frac{nR}{c_V}} = \text{konst.}$$

nR can be included in the const.

$$pV^{1+\frac{nR}{c_V}} = \text{konst.}$$

We will use Mayer relation

$$pV^{1+\frac{c_p-c_V}{c_V}} = pV^{\frac{c_p}{c_V}} = pV^\kappa = \text{konst.}$$

So we have a proven adiabat equation for an ideal gas. It is good to emphasize that this really only applies to an ideal gas and not, for example, to a van der Waals gas.

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?

Solution:

We calculate the function by substituting the state equation $p = f(T)/V$ into

$$\left(\frac{\partial E}{\partial V}\right)_T + p = T \left(\frac{\partial P}{\partial T}\right)_V \quad (16)$$

after substitution

$$\frac{f(T)}{V} = T \left(\frac{\partial \frac{f(T)}{V}}{\partial T}\right)_V = \frac{T}{V} \left(\frac{\partial f(T)}{\partial T}\right)_V$$

and integration

$$f(T) = \text{konst.} \cdot T \quad (17)$$

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.

Solution:

(a) We calculate the function u by substituting the state equation into

$$\left(\frac{\partial E}{\partial V}\right)_T + p = T \left(\frac{\partial P}{\partial T}\right)_V \quad (18)$$

since we know that $E = Vu(T)$, then

$$u(T) + \frac{1}{3}u(T) = T \frac{1}{3} \frac{\partial u(T)}{\partial T} \quad (19)$$

whose solution is

$$u(T) = \text{konst.} \cdot T^4 \quad (20)$$

(b) Entropy is equal

$$dS = \frac{c_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV$$

we will calculate the heat capacity from the input

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = 4V \text{ konst.} T^3$$

then for dS we get

$$dS = 4V \text{ konst.} T^2 dT + \frac{4}{3} \text{ konst.} T^3 dV$$

This is a complete differential, so by simple integration (or two integrations and one derivative) we get entropy equal to

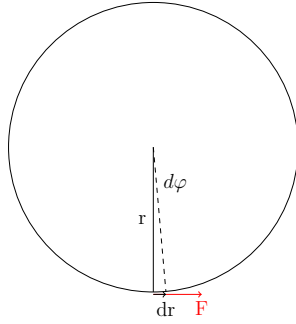
$$S(T, V) = \frac{8}{3}V \text{ konst.} T^3 + \text{konst} 2. \quad (21)$$

(c) The adiabat equation is easily determined from the last calculated expression for entropy, ta namely, it must be constant in the case of quasi-static events:

$$S(T, V) = \text{konst.}$$

from the expression, we can include all the constants by division or subtraction into the constant on the right-hand side, then

$$V \cdot T^3 = \text{konst} \quad (22)$$



Obrázek 3: Twisting the bar.

We find the equation of the isotherm from the equation of state, which says that if the temperature is constant, the pressure must also be constant. The equation does not depend on the volume.

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

$$dE = \delta Q + M d\varphi. \quad (23)$$

(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 $\left(\frac{\partial M}{\partial \varphi}\right)_{\text{izoterm}}$.

Solution:

(a) From the expression of work in the form

$$dW = \mathbf{F} \cdot d\mathbf{r} = -\mathbf{F} \cdot (\mathbf{r} \times d\varphi), \quad (24)$$

where \mathbf{F} is the acting force, $d\mathbf{r}$ is the displacement element of the point and $d\varphi$ the rotation vector by the angle $d\varphi$ in the axis of rotation. We will show that $dW = -(\mathbf{F} \times \mathbf{r}) \cdot d\varphi$, e.g. by means of expression through the antisymmetric tensor ε_{ijk} . We express the element of work dW by notation using the antisymmetric epsilon tensor

$$-\mathbf{F} \cdot (\mathbf{r} \times d\varphi) = -F_i \cdot (\varepsilon_{ijk} \cdot r_j \cdot d\varphi_k) = -\varepsilon_{kij} \cdot F_i \cdot r_j \cdot d\varphi_k = -(\mathbf{F} \times \mathbf{r}) \cdot d\varphi = \mathbf{M} \cdot d\varphi$$

where we used the definition of moment of force $\mathbf{M} = -\mathbf{F} \times \mathbf{r}$. With a suitable choice of coordinate system: the main axis of the Cartesian coordinate system merges with the axis of symmetry of the bar, then the scalar product is simplified to the product of two scalars and we can write the first thermodynamic theorem in the form

$$dE = \delta Q + M d\varphi \quad (25)$$

(b) we express c_φ analogously c_V , for $\varphi = \text{konst.}$ we have 1LT:

$$dE = \delta Q$$

from where

$$\left(\frac{\partial E}{\partial T}\right)_\varphi = \left(\frac{\delta Q}{\partial T}\right)_\varphi = c_\varphi \quad (26)$$

c_M is a bit more complicated, we express δQ from 1LT and write dE as a function of temperature and angle:

$$\delta Q = \left(\frac{\partial E}{\partial T}\right)_\varphi dT + \left(\frac{\partial E}{\partial \varphi}\right)_T d\varphi - M d\varphi = c_\varphi dT + \left[\left(\frac{\partial E}{\partial \varphi}\right)_T - M\right] d\varphi$$

The next task is to calculate the partial derivative with respect to the angle at constant temperature. This is done analogously to the previous case where we had pressure and volume variables. We know that $\delta Q/T$ is a complete differential, so after dividing both sides of the equation by the temperature we use the condition necessary for a complete differential, then

$$\left(\frac{\partial E}{\partial \varphi}\right)_T - M = -T \left(\frac{\partial M}{\partial T}\right)_\varphi \quad (27)$$

we insert into modified 1LT

$$\delta Q = c_\varphi dT - T \left(\frac{\partial M}{\partial T}\right)_\varphi d\varphi$$

we are interested in the heat capacity, which is given by the ratio of δQ and the differential of temperature at constant M , so we rewrite everything in the variables of temperature and moment of force; members with a moment of force they drop out, since M is constant

$$\left(\frac{\delta Q}{\partial T}\right)_M dT = \left[c_\varphi - T \left(\frac{\partial M}{\partial T}\right)_\varphi \left(\frac{\partial \varphi}{\partial T}\right)_M \right] dT$$

the partial derivative on the left side of the equation is the definition of c_M , since the equation holds for any dT , we can write

$$c_M = c_\varphi - T \left(\frac{\partial M}{\partial T}\right)_\varphi \left(\frac{\partial \varphi}{\partial T}\right)_M \quad (28)$$

(c) First we have to express some partial derivative for adiabatic processes, we get this from 1LT, adiabatic (quasi-static) processes are for constant Q , i.e.

$$0 = c_\varphi dT - T \left(\frac{\partial M}{\partial T}\right)_\varphi d\varphi = -T \left(\frac{\partial M}{\partial T}\right)_\varphi \left(\frac{\partial \varphi}{\partial T}\right)_{\text{ad.}} dT$$

after that

$$\left(\frac{\partial \varphi}{\partial T}\right)_{\text{ad.}} = \frac{c_\varphi}{T} \left(\frac{\partial T}{\partial M}\right)_\varphi$$

we substitute 28) for $\left(\frac{\partial T}{\partial M}\right)_\varphi$ and express $\left(\frac{\partial T}{\partial \varphi}\right)_a d$.

$$\left(\frac{\partial T}{\partial \varphi}\right)_{\text{ad.}} = \left(1 - \frac{c_M}{c_\varphi}\right) \left(\frac{\partial T}{\partial \varphi}\right)_M$$

now we will use the formula (derived at the beginning)

$$\left(\frac{\partial M}{\partial \varphi}\right)_{\text{ad.}} = \left(\frac{\partial M}{\partial \varphi}\right)_T + \left(\frac{\partial M}{\partial T}\right)_\varphi \left(\frac{\partial T}{\partial \varphi}\right)_{\text{ad}}$$

and we substitute for the last partial derivative

$$\left(\frac{\partial M}{\partial \varphi}\right)_T + \left(\frac{\partial M}{\partial T}\right)_\varphi \left(1 - \frac{c_M}{c_\varphi}\right) \left(\frac{\partial T}{\partial \varphi}\right)_M = \left(\frac{\partial M}{\partial \varphi}\right)_T + \left(\frac{\partial M}{\partial T}\right)_T \left(1 - \frac{c_M}{c_\varphi}\right) = \frac{c_M}{c_\varphi} \left(\frac{\partial M}{\partial \varphi}\right)_T$$

So the desired formula is

$$\left(\frac{\partial M}{\partial \varphi}\right)_{\text{ad.}} = \frac{c_M}{c_\varphi} \left(\frac{\partial M}{\partial \varphi}\right)_T \quad (29)$$

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?

Solution:

(a) In the calculation, we assume that the body is so large compared to the water that its temperature changes negligibly. The entropy change is then equal to

$$\begin{aligned} \Delta S_R &= \frac{\Delta Q}{T} = \frac{mc_V(T_1 - T_2)}{T_2} = mc_V \left(\frac{T_1}{T_2} - 1\right) = -1125.6 \text{ J} \cdot \text{K}^{-1} \\ \Delta S_T &= \int_{T_1}^{T_2} dT \frac{mc_V(T_2 - T_1)}{T} = mc_V(T_2 - T_1) \ln(T) \Big|_{T_1}^{T_2} \\ &= mc_V(T_2 - T_1) \ln\left(\frac{T_2}{T_1}\right) = 131022 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

the total entropy change of the system is therefore

$$\Delta S = \Delta S_R + \Delta S_T = 1298896.4 \text{ J} \cdot \text{K}^{-1}$$

(b) Substitute again into the previous formulas, but with different temperatures. The following entropy change occurs on first heating:

$$\Delta S_{R1} = -649.9 \text{ J} \cdot \text{K}^{-1}, \Delta S_{R2} = -562.8 \text{ J} \cdot \text{K}^{-1}$$

and body

$$\Delta S_{T1} = 35300 \text{ J} \cdot \text{K}^{-1}, \Delta S_{T2} = 30211 \text{ J} \cdot \text{K}^{-1}$$

(c) Consider that we have $N + 1$ reservoirs. The zero reservoir is in thermal equilibrium with the body. We will gradually add the body to the individual reservoirs gradually according to the increasing temperature, until it is heated to the temperature T_2 . The temperature of the reservoirs always increases by the same temperature, so the temperature of the i -th reservoir is the same

$$T(i) = \frac{T_2 - T_1}{N}i - T_1 \quad (30)$$

let's say that the body now has a temperature of $T(i)$ and we will heat it to a temperature of $T(i + 1)$. We calculate the change in entropy of the reservoir analogously to the previous example

$$\Delta S_R = mc_V \frac{T(i) - T(i + 1)}{T(i + 1)} \quad (31)$$

and body

$$\Delta S_T = mc_V \ln \frac{T(i + 1)}{T(i)} \quad (32)$$

after substituting specific $T(i)$ we obtain, denote the expression $a = \frac{T_2 - T_1}{N}$

$$\Delta S_R = mc_V \frac{-a}{a(i + 1) - T_2} \quad (33)$$

and body

$$\Delta S_T = mc_V a \ln \frac{a(i + 1) - T_2}{a - T_2} \quad (34)$$

the total entropy change is obtained by summing the entropy changes over all cycles

$$\Delta S_R = mc_V \sum_{i=1}^N \frac{-a}{a(i + 1) - T_2} \quad (35)$$

and body

$$\Delta S_T = mc_V a \sum_{i=1}^N \ln \frac{a(i + 1) - T_2}{a - T_2} \quad (36)$$

The sum of logarithms is simple, the middle terms are subtracted and only the extreme terms remain, i.e.

$$\Delta S_T = mc_V a \ln \frac{a(N + 1) - T_2}{a - T_2} \quad (37)$$

the final sum of the harmonic series cannot be calculated analytically, we know that the sum can be approximately replaced by an integral and then

$$\begin{aligned} \Delta S_R &= mc_V \sum_{i=1}^N \frac{-a}{a(i + 1) - T_2} \approx - \int_1^N \text{dim } c_V a \frac{1}{a(i + 1) - T_2} \\ &= -mc_V a \ln \frac{a(N + 1) - T_2}{a - T_2} \end{aligned}$$

for sufficiently high N this is exactly the case. Obviously, this is exactly the opposite value to the entropy change of the body, so the sum approaches zero as N , increases, as the summation approximation by integration made in the last step is refined.

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

$$\frac{\partial^2 \delta p}{\partial t^2} = c^2 \frac{\partial^2 \delta p}{\partial x^2}, \quad (38)$$

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 $\kappa = c_p / c_V = 7/5$.

Solution:

We start from Euler's equation for fluid motion

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{\nabla p}{\rho}$$

we simplify the case to 1 D , we assume that the waves move along a straight line and we point the x-axis in the direction of the group velocity vector of these waves, Euler's equation will then be

$$\rho \frac{\partial v}{\partial t} + \rho v \frac{\partial v}{\partial x} = -\frac{\partial p}{\partial x} \quad (39)$$

and the continuity equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v)}{\partial x} = 0 \quad (40)$$

Subsequently, we will assume that the density changes by a small value compared to its mean value, which we write as

$$\rho = \rho_0 + \delta\rho = \rho_0 + \left(\frac{\partial \rho}{\partial p} \right)_{\text{ad.}} \delta p \quad (41)$$

on the right side of the equation, we assume that the sound wave is an adiabatic process. Similarly, we break down the velocity v , for which we can appropriately choose a coordinate system such that $v_0 = 0$, then

$$v = \delta v \quad (42)$$

we substitute the relevant developments into the individual equations, then:

$$\rho_0 \frac{\partial \delta v}{\partial t} + \delta \rho \frac{\partial \delta v}{\partial t} + \rho_0 \delta v \frac{\partial \delta v}{\partial x} + \delta \rho \delta v \frac{\partial \delta v}{\partial x} =$$

$$\rho_0 \frac{\partial \delta v}{\partial t} + \left(\frac{\partial \rho}{\partial p} \right)_{\text{ad.}} \delta p \frac{\partial \delta v}{\partial t} + \rho_0 \delta v \frac{\partial \delta v}{\partial x} + \left(\frac{\partial \rho}{\partial p} \right)_{\text{ad.}} \delta v \frac{\partial \delta v}{\partial x} = -\frac{\partial(p_0 + \delta p)}{\partial x} = \frac{\partial \delta p}{\partial x},$$

in the equation, we will neglect the second, third and fourth terms on the left side,

because they are significantly smaller than the first term, on the right side only the derivative of the pressure fluctuation will remain

$$\rho_0 \frac{\partial \delta v}{\partial t} = - \frac{\partial \delta p}{\partial x} \quad (43)$$

we substitute the same in the continuity equation

$$\left(\frac{\partial \rho}{\partial p} \right)_{\text{ad.}} \frac{\partial \delta p}{\partial t} + \rho_0 \frac{\partial \delta v}{\partial x} + \left(\frac{\partial \rho}{\partial p} \right)_{\text{ad.}} \frac{\partial(\delta p \delta v)}{\partial x} = 0$$

we neglect the third term again because the fluctuation multiple is significantly lower than the first two terms, then

$$\left(\frac{\partial \rho}{\partial p} \right)_{\text{ad.}} \frac{\partial \delta p}{\partial t} = - \rho_0 \frac{\partial \delta v}{\partial x} \quad (44)$$

we derive equation (51) according to time, equation (52) again according to the x -coordinate, the right-hand sides are equal due to the interchangeability of the derivatives, then we get

$$\left(\frac{\partial \rho}{\partial p} \right)_{\text{ad.}} \rho_0 \frac{\partial^2 \delta v}{\partial t^2} = \rho_0 \frac{\partial^2 \delta v}{\partial x^2} \quad (45)$$

and finally, after a simple modification, we get the equation we are looking for

$$\frac{\partial^2 \delta p}{\partial t^2} = c^2 \frac{\partial^2 \delta p}{\partial x^2} \quad (46)$$

To rewrite the speed of sound using adiabatic compressibility, we modify the partial derivative

$$c = \sqrt{\left(\frac{\partial p}{\partial \rho} \right)_{\text{ad}}} = \sqrt{\left(\frac{\partial p}{\partial V} \right)_{\text{ad.}} \left(\frac{\partial V}{\partial \rho} \right)_{\text{ad.}}} = \sqrt{\left(\frac{\partial p}{\partial V} \right)_{\text{ad.}} \left(- \frac{m}{\rho^2} \right)}$$

we rewrite the fraction as

$$\frac{m}{\rho^2} = \frac{V}{\rho}$$

since $m = \rho V$. Eventually

$$c = \sqrt{- \frac{V}{\rho} \left(\frac{\partial p}{\partial V} \right)_{\text{ad.}}} = \sqrt{\frac{\kappa_{\text{ad}}}{\rho}}. \quad (47)$$

To calculate the speed of sound, we will use the knowledge of the ideal gas adiabat equation

$$pV^\kappa = p \frac{\mu^\kappa}{\mu^\kappa} V^\kappa = \frac{p\mu^\kappa}{\rho^\kappa} = \text{konst.} = K$$

from here we can easily determine the derivative

$$\left(\frac{\partial p}{\partial \rho} \right)_{\text{ad}} = \kappa K \frac{\rho^{\kappa-1}}{\mu^\kappa} = \kappa K \frac{\rho^\kappa}{\mu^\kappa} \rho^{-1} = \kappa \frac{p}{\rho} = \kappa \frac{k_{\text{B}} T}{\mu}$$

where we substituted the ideal gas equation of state $p = \rho k_B T / \mu$. The speed of sound is then

$$c = \sqrt{\kappa \frac{k_B T}{\mu}} = 493.67 \text{ m} \cdot \text{s}^{-1} \quad (48)$$

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.

Solution:

First, I will list the formulas that we will use in the calculation. You should find their derivation in the workbook. The first formula follows from the first law of thermodynamics

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

another important formula is the expression of entropy (or complete differential) from the first theorem of thermodynamics

$$dS = \frac{c_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV$$

Energy is a state quantity. Therefore, its change is determined only by the initial and final conditions, regardless of the intermediate states through which the gas passed. Therefore, we can write the energy change in the form

$$\Delta E = \left(\frac{\partial E}{\partial T}\right)_V \Delta T + \left(\frac{\partial E}{\partial V}\right)_T \Delta V = c_V \Delta T + \left[T \left(\frac{\partial p}{\partial T}\right)_V - p\right] \Delta V$$

Since this is an isolated system, the total energy must be constant, i.e. $\Delta E = 0$. From here we easily find that

$$\Delta T = \frac{1}{c_V} \left[p - T \left(\frac{\partial p}{\partial T}\right)_V \right] \Delta V$$

Entropy is also a state variable, so it can be written for the same reasons

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V = \frac{c_V}{T} \Delta T + \left(\frac{\partial p}{\partial T}\right)_V \Delta V$$

where we substitute for ΔT and get

$$\Delta S = \frac{p}{T} \Delta V$$

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

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (49)$$

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 $V' = V/V_c$.

Solution:

First, we calculate the first and second derivatives of pressure with respect to volume at constant temperature:

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \quad (50)$$

and

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0 \quad (51)$$

We express the expression from both equation $\frac{RT}{(V-b)^2}$, that is

$$\frac{3a}{V^4} = \frac{2a}{V^3(V-b)}$$

hence the critical volume $V_c = 3b$. By substituting into (40), we obtain the value of the critical temperature, which is equal to

$$T_c = \frac{8a}{27Rb}$$

and we substitute the critical volume and the critical temperature into the equation of state, from which we get for the critical pressure

$$p_c = \frac{a}{27b^2}$$

Just put in the equation of state $T = T' \cdot T_c$,

$$p' = \frac{8T'}{V' - 1} - \frac{3}{V'^2} \quad (52)$$

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.

Solution:

(a) We calculate the internal energy by substituting into the formula

$$dE = c_V dT + \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] dV = c_V dT + \frac{a}{V^2} dV$$

from here we easily find that

$$E = c_V T - \frac{a}{V} + \text{konst.}$$

We determine the entropy from the formula

$$dS = \frac{c_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV = \frac{c_V}{T} dT + \frac{R}{V-b} dV$$

After that

$$S = c_V \ln(T) + R \ln(V-b) + \text{konst.}$$

(b) We determine the work by substituting the equation of state into

$$\begin{aligned} W &= \int_{V_1}^{V_2} dV p(T, V) = \int_{V_1}^{V_2} dV \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) = \\ &RT \ln(V-b) + \frac{a}{V} \Big|_{V_1}^{V_2} = RT \ln \frac{V_2-b}{V_1-b} + a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \end{aligned}$$

(c) We work out the entropy equation, the entropy change of the gas itself depends only on initial and final state, therefore we can write:

$$\Delta S = \frac{c_V}{T} \Delta T + \left(\frac{\partial p}{\partial T} \right)_V \Delta V \quad (53)$$

since we are calculating an adiabatic process, $\Delta S = 0$ and after substituting from the equation of state::

$$0 = \frac{c_V}{T} \Delta T + \frac{R}{V-b} \Delta V \quad (54)$$

from here

$$\Delta T = -\frac{T}{c_V} \frac{R}{V-b} \Delta V \quad (55)$$

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.

Solution:

(a) Since $H = H(S, p)$, it is logical that by Legendre transformation we get $dH = T dS + V dp$. From this formula we also know that

$$\left(\frac{\partial H}{\partial S} \right)_p = T, \quad \left(\frac{\partial H}{\partial p} \right)_S = V \quad (56)$$

We start editing the expression for λ , into which we substitute the given α_p and

$$c_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

we will start modifying the right-hand side of the expression step by step, using the identities for the partial derivatives that we know

$$\begin{aligned} \frac{V}{C_p} (1 - T\alpha_p) &= \frac{V}{T \left(\frac{\partial S}{\partial T} \right)_p} \left[1 - \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p \right] = \frac{V}{T} \left(\frac{\partial T}{\partial S} \right)_p - \left(\frac{\partial T}{\partial S} \right)_p \left(\frac{\partial V}{\partial T} \right)_p = \\ &= \left(\frac{\partial H}{\partial p} \right)_S \left(\frac{\partial S}{\partial H} \right)_p \left(\frac{\partial T}{\partial S} \right)_p - \left(\frac{\partial T}{\partial S} \right)_p \left(\frac{\partial V}{\partial T} \right)_p = \\ &= - \left(\frac{\partial S}{\partial p} \right)_H \left(\frac{\partial T}{\partial S} \right)_p - \left(\frac{\partial V}{\partial S} \right)_p = \\ &= - \left(\frac{\partial S}{\partial p} \right)_H \left(\frac{\partial T}{\partial S} \right)_p - \left(\frac{\partial T}{\partial p} \right)_S = - \left(\frac{\partial T}{\partial p} \right)_H = \lambda \end{aligned}$$

(b) The procedure is the same as in the previous case: we break down the right-hand side of a we gradually adjust the partial derivatives:

$$\begin{aligned}
\frac{T \left(\frac{\partial p}{\partial T}\right)_V + V \left(\frac{\partial p}{\partial V}\right)_T}{C_p \cdot \left(\frac{\partial p}{\partial V}\right)_T} &= \frac{T \left(\frac{\partial p}{\partial T}\right)_V + V \left(\frac{\partial p}{\partial V}\right)_T}{T \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T} = \\
\left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V + \frac{V}{T} \left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T &= \\
- \left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial V}{\partial T}\right)_p + \frac{V}{T} \left(\frac{\partial T}{\partial S}\right)_p &= \\
- \left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial H}{\partial p}\right)_S \left(\frac{\partial S}{\partial H}\right)_p \left(\frac{\partial T}{\partial S}\right)_p &= \\
- \left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial S}{\partial p}\right)_H \left(\frac{\partial T}{\partial S}\right)_p &= \\
- \left(\frac{\partial V}{\partial S}\right)_p - \left(\frac{\partial S}{\partial p}\right)_H \left(\frac{\partial T}{\partial S}\right)_p &= - \left(\frac{\partial T}{\partial p}\right)_S - \left(\frac{\partial S}{\partial p}\right)_H \left(\frac{\partial T}{\partial S}\right)_p = - \left(\frac{\partial p}{\partial T}\right)_H = \lambda
\end{aligned}$$

(c) for an ideal gas we know the equation of state $pV = nRT$. We will therefore use the expression for λ from the previous subtask. If λ is to be zero, either the numerator will be zero or the denominator will go to infinity. Let's look at the numerator first:

$$T \left(\frac{\partial p}{\partial T}\right)_V + V \left(\frac{\partial p}{\partial V}\right)_T = T \frac{nR}{V} - V \frac{nRT}{V^2} = \frac{nRT}{V} - \frac{nRT}{V} = 0 = \lambda$$

(d) First, we adjust the denominator to the desired form:

$$\begin{aligned}
C_p \cdot \left(\frac{\partial p}{\partial V}\right)_T &= C_p \cdot \left[\frac{RT}{(V-b)^2 - \frac{2a}{V^3}} \right] = \\
-C_p \frac{1}{V-b} \left[\frac{RT}{V-b} - \frac{2a(V-b)}{V^3} \right] &= -C_p \frac{1}{V-b} \left[\frac{RT}{V-b} - \frac{2a}{V^2} + \frac{2ab}{V^3} \right] = \\
-C_p \frac{1}{V-b} \left(p - \frac{a}{V^2} + \frac{2ab}{V^3} \right) &
\end{aligned}$$

Analogously, we will adjust the nominator

$$\begin{aligned}
\frac{RT}{V-b} - \frac{V}{V-b} \left(p - \frac{a}{V^2} + \frac{2ab}{V^3} \right) &= \frac{1}{V-b} \left[RT - V \left(p - \frac{a}{V^2} + \frac{2ab}{V^3} \right) \right] = \\
\frac{1}{V-b} \left[\left(p + \frac{a}{V^2} \right) (V-b) - pV + \frac{a}{V^2} - \frac{2ab}{V^3} \right] &= \frac{1}{V-b} \left(-bp - \frac{3ab}{V^2} + \frac{2a}{V} \right) = \\
-\frac{1}{V-b} \left(bp + \frac{3ab}{V^2} - \frac{2a}{V} \right) &
\end{aligned}$$

In the fraction, the factors $-1/(V-b)$, are divided, and thus we get the formula we are looking for..

(e) From the condition that the numerator must be equal to zero, we calculate the equation

$$p = a \left(\frac{2}{bV} - \frac{3}{V^2} \right) \quad (57)$$

32. Show that the thermal coefficient of expansion

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

meets the relation

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

Solution:

The first equality is the Maxwell relation resulting from the Gibbs potential. If we expand the middle expression by the volume, the expression for α drops out and we get the right side we are looking for.

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

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

Solution:

The left and middle sides are derived earlier, see (14). Individual partial derivatives can be rewritten on the right-hand side using Maxwell's relations.

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.

Solution:

- pressure: from the free energy equation

$$dF = -S dT - p dV$$

we easily find that

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{1}{3} \cdot \text{const.} \cdot T^4$$

- entropy: analogously to the previous point:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = \frac{4}{3} \cdot \text{const.} \cdot VT^3$$

- we can easily calculate the internal energy from the free energy:

$$E = F + TS = \text{konst. } VT^4 = \left(\frac{4}{3}\right)^{\frac{4}{3}} \frac{V}{C^{\frac{1}{3}}} S^{\frac{4}{3}}$$

- for enthalpy:

$$H = E + PV = \frac{4}{3} \text{konst. } VT^4$$

if we want to express using pressure and entropy, we express V konst. T^3 from entropy and T , from pressure, then

$$H = \left(\frac{3}{4}\right)^{\frac{1}{4}} Sp^{\frac{1}{4}}$$

- We can express the Gibbs potential as

$$G = F + PV = F + \frac{1}{3} \text{konst. } VT^3 = 0$$

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.

Solution:

First, we write down the work and heat produced during the individual processes:

(a) Isothermal expansion $(p_1, V_1) \rightarrow (p_2, V_2)$:

$$W_1 = nRT_1 \ln \frac{V_2}{V_1}$$

$$Q_1 = nRT_1 \ln \frac{V_2}{V_1}$$

(b) adiabatic expansion $(p_2, V_2) \rightarrow (p_3, V_3)$:

$$W_2 = p_3 V_3^\kappa \frac{(V_3^{1-\kappa} - V_2^{1-\kappa})}{1 - \kappa} = \frac{p_3 V_3}{1 - \kappa} \left[1 - \left(\frac{V_3}{V_2}\right)^{\kappa-1} \right] = \frac{nRT_2}{1 - \kappa} \left[1 - \left(\frac{V_3}{V_2}\right)^{\kappa-1} \right]$$

$$Q_2 = 0$$

(c) Isothermic compression $(p_3, V_3) \rightarrow (p_4, V_4)$:

$$W_3 = nRT_2 \ln \frac{V_4}{V_3}$$

$$Q_3 = nRT_2 \ln \frac{V_4}{V_3}$$

(d) adiabatic compression $(p_4, V_4) \rightarrow (p_1, V_1)$:

$$W_4 = p_1 V_1^\kappa \frac{(V_1^{1-\kappa} - V_4^{1-\kappa})}{1-\kappa} = \frac{p_1 V_1}{1-\kappa} \left[1 - \left(\frac{V_1}{V_4} \right)^{\kappa-1} \right] = \frac{nRT_1}{1-\kappa} \left[1 - \left(\frac{V_1}{V_4} \right)^{\kappa-1} \right] \quad (58)$$

$$Q_4 = 0 \quad (59)$$

it will be most advantageous to express as many quantities as possible in terms of temperature, for the adiabatic process $TV^{\kappa-1}$, applies, i.e. for adiabatic expansion

$$\begin{aligned} T_1 V_2^{\kappa-1} &= T_2 V_3^{\kappa-1} \\ T_2 V_4^{\kappa-1} &= T_1 V_1^{\kappa-1} \end{aligned}$$

then we get

$$\frac{T_1}{T_2} = \left(\frac{V_3}{V_2} \right)^{\kappa-1} = \left(\frac{V_4}{V_1} \right)^{\kappa-1} \quad (60)$$

then we can rewrite the individual work in adiabatic processes as

$$W_2 = \frac{nRT_2}{1-\kappa} \left(1 - \frac{T_1}{T_2} \right) \quad (61)$$

and

$$W_4 = \frac{nRT_1}{1-\kappa} \left(1 - \frac{T_2}{T_1} \right) \quad (62)$$

work during isothermal compression

$$W_3 = nRT_1 \ln \frac{V_1}{V_2} = Q_3 \quad (63)$$

the efficiency of the machine is then equal

$$\begin{aligned} \eta = \frac{W}{Q_+} &= \frac{nRT_1 \ln \frac{V_2}{V_1} + \frac{nRT_2}{1-\kappa} \left(1 - \frac{T_1}{T_2} \right) + nRT_2 \ln \frac{V_1}{V_2} + \frac{nRT_1}{1-\kappa} \left(1 - \frac{T_2}{T_1} \right)}{nRT_1 \ln \frac{V_2}{V_1}} \\ &= 1 - \frac{T_2}{T_1} + \frac{nR}{1-\kappa} \left[T_2 \left(1 - \frac{T_1}{T_2} \right) + T_1 \left(1 - \frac{T_2}{T_1} \right) \right] \\ &= 1 - \frac{T_2}{T_1} + \frac{nR}{1-\kappa} (T_2 - T_1 + T_1 - T_2) = 1 - \frac{T_2}{T_1} \end{aligned}$$

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 $V_1 = \text{konst}$.

Solution:

Work and heat done in individual processes:

(a) isothermal expansion $(p_1, V_1) \rightarrow (p_2, V_2)$

$$W_1 = \int_{V_1}^{V_2} dV \frac{nRT_2}{V} = nRT_2 \ln \frac{V_2}{V_1} = Q_1 \quad (64)$$

(b) isochoric cooling $(p_2, V_2) \rightarrow (p_3, V_2)$

$$Q_2 = -c_V n (T_2 - T_1), W_2 = 0 \quad (65)$$

(c) isothermal compression $(p_3, V_2) \rightarrow (p_4, V_1)$

$$W_3 = -nRT_1 \ln \frac{V_2}{V_1} = Q_3 \quad (66)$$

(d) isochoric heating $(p_4, V_1) \rightarrow (p_1, V_1)$

$$Q_4 = c_V n (T_2 - T_1), W_4 = 0 \quad (67)$$

The total work is then equal

$$W = nR \ln \frac{V_2}{V_1} (T_2 - T_1) \quad (68)$$

and the supplied heat $Q = Q_1 + Q_4$, then the efficiency is equal

$$\eta = \frac{nR \ln \frac{V_2}{V_1} (T_2 - T_1)}{nRT_2 \ln \frac{V_2}{V_1} + c_V n (T_2 - T_1)} = \frac{T_2 - T_1}{T_2 + \frac{c_V}{nR \ln \frac{V_2}{V_1}} (T_2 - T_1)} < \eta_{\text{Carnot}} \quad (69)$$

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).

Solution:

Work and heat done in each process:

(a) Adiabatic compression $(p_1, V_1) \rightarrow (p_2, V_2)$

$$W_1 = \frac{nRT_1}{1 - \kappa} (V_2^{1-\kappa} - V_1^{1-\kappa}) = \frac{nRT_1}{1 - \kappa} (\varepsilon^{1-\kappa} - 1) \quad (70)$$

where we modify the expression with κ

$$W_1 = \frac{nRT_1}{1 - \frac{c_p}{c_V}} (\varepsilon^{1-\kappa} - 1) = -\frac{nc_V RT_1}{c_p - c_V} (\varepsilon^{1-\kappa} - 1) = -nc_V T_1 (\varepsilon^{1-\kappa} - 1) \quad (71)$$

Here we used the knowledge of Mayer's relation for an ideal gas.

$$Q_1 = 0 \quad (72)$$

(b) Isochoric heating $(p_2, V_2) \rightarrow (p_3, V_2)$

$$W_2 = 0, Q_2 = nc_V (T_3 - T_2) \quad (73)$$

(c) Adiabatic expansion $(p_3, V_2) \rightarrow (p_4, V_1)$

$$W_3 = \frac{nRT_1}{1 - \frac{c_p}{c_V}} (\varepsilon^{1-\kappa} - 1) = -nc_V T_4 (1 - \varepsilon^{1-\kappa}) \quad (74)$$

(d) Isochoric cooling $(p_4, V_1) \rightarrow (p_1, V_1)$

$$W_4 = 0, Q_4 = nc_V (T_1 - T_4) \quad (75)$$

We can then write the efficiency in the form

$$\eta = \frac{-nc_V T_1 (\varepsilon^{1-\kappa} - 1) - nc_V T_4 (1 - \varepsilon^{1-\kappa})}{nc_V (T_3 - T_2)} = \frac{T_4 - T_1}{T_3 - T_2} (\varepsilon^{1-\kappa} - 1) \quad (76)$$

We will now use the adiabatic equation in the form of the $TV^{\kappa-1} = \text{konst.}$, which we write for both adiabatic process

$$T_1 V_1^{\kappa-1} = T_2 V_2^{\kappa-1}, T_3 V_2^{\kappa-1} = T_4 V_1^{\kappa-1} \quad (77)$$

where do we get

$$T_1 = T_2 \left(\frac{V_2}{V_1} \right)^{\kappa-1} = T_2 \varepsilon^{\kappa-1} \quad (78)$$

and

$$T_4 = T_3 \left(\frac{V_2}{V_1} \right)^{\kappa-1} = T_3 \varepsilon^{\kappa-1} \quad (79)$$

we substitute in the equation for efficiency, we get

$$\eta = \frac{T_3 \varepsilon^{\kappa-1} - T_2 \varepsilon^{\kappa-1}}{T_3 - T_2} (\varepsilon^{1-\kappa} - 1) = 1 - \varepsilon^{\kappa-1} \quad (80)$$

For the given $\varepsilon = \frac{1}{10}$ a $\kappa = \frac{R+c_V}{c_V} = \frac{7}{5}$ it turns out $\eta = 0.6$.

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.

Solution:

Work and heat done in each process:

(a) Adiabatic compression

$$W_1 = -nc_V T_1 \left[\left(\frac{V_2}{V_1} \right)^{1-\kappa} - 1 \right] = -nc_V (T_2 - T_1), Q_1 = 0 \quad (81)$$

where we used the adiabatic equation

$$T_1 V_1^{\kappa-1} = T_2 V_2^{\kappa-1}$$

(b) Isobaric expansion

$$W_2 = p_2 (V_3 - V_2) = p_2 V_2 \left(\frac{V_3}{V_2} - 1 \right) \quad (82)$$

using the equation for the isobar $\frac{V_2}{T_2} = \frac{V_3}{T_3}$ and the equations of state for an ideal gas we can T3 rewrite work using temperature to

$$nRT_2 \left(\frac{T_3}{T_2} - 1 \right) = nR (T_3 - T_2) \quad (83)$$

and heat

$$Q_2 = nc_p (T_3 - T_2) \quad (84)$$

(c) Adiabatic expansion

$$Q_3 = 0, W_3 = -nc_V T_3 \left[\left(\frac{V_1}{V_3} \right)^{1-\kappa} - 1 \right] = -nc_V (T_4 - T_3) \quad (85)$$

(d) Isochoric cooling

$$W_4 = 0, Q_4 = nc_V (T_1 - T_4) \quad (86)$$

We then calculate the efficiency classically

$$\eta = \frac{-nc_V (T_2 - T_1) - nc_V (T_4 - T_3) + nR (T_3 - T_2)}{nc_p (T_3 - T_2)} \quad (87)$$

when using Mayer's formula, we substitute after R

$$\eta = \frac{c_V (T_1 - T_2 + T_3 - T_4 - T + T_2) + c_p (T_3 - T_2)}{c_p (T_3 - T_2)} = 1 - \frac{c_V (T_4 - T_1)}{c_p (T_3 - T_2)} \quad (88)$$

Efficiency can still be overridden using compression ratios. Let us recall from the equations of adiabats and the equation of isobars

$$T_1 = \left(\frac{V_2}{V_1} \right)^{\kappa-1} T_2, T_3 = \frac{V_3}{V_2} T_2, T_4 = \left(\frac{V_3}{V_1} \right)^{\kappa-1} T_3 = \left(\frac{V_3}{V_1} \right)^{\kappa-1} \frac{V_3}{V_2} T_2 \quad (89)$$

Substitute for temperature in the equation for efficiency

$$\eta = 1 - \frac{\left(\frac{V_3}{V_1}\right)^{\kappa-1} \frac{V_3}{V_2} T_2 - \left(\frac{V_2}{V_1}\right)^{\kappa-1} T_2}{\kappa \left(\frac{V_3}{V_2} T_2 - T_2\right)} = 1 - \frac{\frac{1}{V_2} (V_3^\kappa - V_2^\kappa) \frac{1}{V_1^{\kappa-1}}}{\frac{1}{V_2} \kappa (V_3 - V_2)} \quad (90)$$

Expressions $\frac{1}{V_2}$ will be shortened. From the numerator, we will write V_2^K and from the denominator in parentheses V_2 , then

$$\eta = 1 - \frac{\left(\frac{V_3}{V_2}\right)^\kappa - 1}{\left(\frac{V_1}{V_2}\right)^{\kappa-1} \kappa \left(\frac{V_3}{V_2} - 1\right)} \quad (91)$$

Let us now denote $\rho = \frac{V_3}{V_2}$ a $\varepsilon = \frac{V_1}{V_2}$, then

$$\eta = 1 - \frac{1}{\kappa} \frac{1}{\varepsilon^{\kappa-1}} \frac{\rho^\kappa - 1}{\rho - 1} \quad (92)$$

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? ($c_p = 4184 \text{ J/Kkg}$)

Solution:

First, it will be necessary to calculate the resulting temperature, let's denote it by T . The first body must give up the heat Q , which the second body receives, i.e.

$$m_1 c_p (T_1 - T) = m_2 c_p (T - T_2)$$

from here

$$T = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2}$$

The entropy change of one body is equal to

$$\Delta S_1 = \int dQ \frac{1}{T} = m_1 c_p \int_{T_1}^T dT \frac{1}{T} = m_1 c_p \ln \frac{m_1 + m_2 \frac{T_2}{T_1}}{m_1 + m_2}$$

analogously, we calculate the change in entropy of the second body

$$\Delta S_2 = m_2 c_p \ln \frac{m_1 + m_2}{m_1 \frac{T_1}{T_2} + m_2} = m_2 c_p \ln \frac{m_1 + m_2}{m_1 + m_2 \frac{T_2}{T_1}} + m_2 c_p \ln \frac{T_2}{T_1}$$

The sum is then equal

$$\Delta S = \Delta S_1 + \Delta S_2 = (m_1 - m_2) c_p \ln \frac{m_1 + m_2 \frac{T_2}{T_1}}{m_1 + m_2} + m_2 c_p \ln \frac{T_2}{T_1} \quad (93)$$

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 ($27,3^\circ\text{C}$). What is the minimum power the refrigerator must have?

Solution:

Assume that this is a Carnot cycle, the efficiency of which is equal to

$$\eta = 1 - \frac{T_1}{T_2} \quad (94)$$

where T_1 is the temperature in the refrigerator and T_2 is the ambient temperature. Let us denote Q_1 the heat that must be removed from the refrigerator, W the work that the working machine will do and Q_2 the heat that will pass into the external environment, apparently this heat is equal to

$$Q_2 = W + Q_1 \quad (95)$$

At the same time, we know that the basic definition of the efficiency of a heat engine is

$$\eta = \frac{W}{Q_2} = \frac{W}{W + Q_1} \quad (96)$$

from where we can easily calculate the job sought

$$W = \frac{\eta Q_1}{1 - \eta} = \frac{Q_1}{\frac{1}{1 - \frac{T_1}{T_2}} - 1} \quad (97)$$

Q_1 is equal to the quantity Q from the specification, after calculation we get

$$W = 93 \text{ W} \cdot \text{h} \quad (98)$$

from which it is clear that the power consumption must be equal to $P_0 = 93 \text{ W}$.

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

Solution:

We can write the pressure of the system as

$$p = \text{konst.} \frac{T}{V} \quad (99)$$

where T and V are the independent variables. Free energy is also expressed in these variables

$$dF = -S dT - p dV \quad (100)$$

According to the third law of thermodynamics $\lim_{T \rightarrow 0^+} = 0$ regardless of pressure, volume, density, etc. Therefore, it must also be true that

$$\left(\frac{\partial S}{\partial V} \right)_T \rightarrow 0 \quad (101)$$

From the free energy we find that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{\text{konst.}}{V} \neq 0 \quad (102)$$

which contradicts the third law of thermodynamics.

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?

Solution:

Subsystems can be described by changing individual physical quantities. Since the sub-systems form a system isolated from the surroundings, so the total energy does not change, i.e.

$$dE = dE_1 + dE_2 \quad (103)$$

whence apparently $dE_1 = -dE_2$.

(a) the same is also true for entropy

$$dS_1 = -dS_2 \quad (104)$$

and for volume change

$$dV_1 = -dV_2 \quad (105)$$

for the total entropy change we can write

$$dS = 0 = \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 + \frac{1}{T_2} dE_2 + \frac{p_2}{T_2} dV_2 \quad (106)$$

where we substitute the equations written for the change in volume and energy

$$0 = \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 - \frac{1}{T_2} dE_1 - \frac{p_2}{T_2} dV_1 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 \quad (107)$$

for the expression to be equal to zero, the individual parentheses must be equal. The first parenthesis implies equality of temperatures, the second parenthesis equality of pressures.

(b) the same conditions apply here as in the previous point, in addition also the condition for the number of particles $dN_1 = -dN_2$, by analogous calculation we arrive at the equation

$$0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 + \left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1}\right) dN_1 \quad (108)$$

which also results in the equality of chemical potentials.

(c) In this case, $dS_1 = dS_2 = 0$, also for heat and number of particles, only for volume change we can still write $dV_1 = -dV_2$. We describe the change in internal energy

$$dE(S, V) = p_1 dV_1 + p_2 dV_2 = (p_1 - p_2) dV_1 \quad (109)$$

from which it follows that only the pressures must be equal.

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.

Solution:

The entropy of an ideal gas is given by the relation

$$S = nc_V \ln T + nR \ln V - Rn \ln n \quad (110)$$

The entropy of the separated gases is given by

$$S_1 = n(c_V \ln T + R \ln V_1) - Rn \ln n, S_2 = n(c_V \ln T + R \ln V_2) - Rn \ln n \quad (111)$$

the entropy after mixing the gases is equal

$$S_{12} = 2n[c_V \ln T + R \ln (V_1 + V_2)] - 2Rn \ln(2n) \quad (112)$$

the difference of these entropies is then equal

$$\begin{aligned} \Delta S &= S_{12} - S_1 - S_2 = nR [2 \ln (V_1 + V_2) - \ln (V_1 \cdot V_2)] - 2nR \ln 2 \\ &= nR \left[2 \ln \left(\frac{nRT}{p_1} + \frac{nRT}{p_2} \right) - \ln \left(\frac{n^2 R^2 T^2}{p_1 p_2} \right) \right] - 2nR \ln 2 \\ &= nR \ln \left(\frac{(p_1 + p_2)^2}{p_1 \cdot p_2} \right) - Rn \ln 4 = nR \ln \left(\frac{(p_1 + p_2)^2}{4p_1 p_2} \right) \end{aligned}$$

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).

Solution:

The entropy of the gas before mixing is equal

$$S_1 = n(c_V \ln T_0 + R \ln V_1) - Rn \ln n, S_2 = n(c_V \ln T_0 + R \ln V_2) - Rn \ln n \quad (113)$$

after mixing the gases is entropy

$$S_{12} = 2n[c_V \ln T + R \ln (V_1 + V_2)] - 2Rn \ln(2n) \quad (114)$$

We first determine the sum of entropies before mixing

$$S_1 + S_2 = 2nc_V \ln T_0 + nR \ln (V_1 \cdot V_2) - 2nR \ln n \quad (115)$$

Again we calculate the entropy difference, so that the work is maximal, the entropy change must be zero, from here I get the econdition

$$2c_V \ln \frac{T}{T_0} = R \ln \frac{V_1 \cdot V_2}{(V_1 + V_2)^2} + 2R \ln 2 \quad (116)$$

by combining the logarithms on the right-hand side and taking the logarithm, we obtain

$$\left(\frac{T}{T_0}\right)^{Rc_V} = \left[\frac{4V_1V_2}{(V_1 + V_2)^2}\right]^R \quad (117)$$

from where we calculate the resulting temperature

$$T = T_0 \left[\frac{4V_1 \cdot V_2}{(V_1 + V_2)^2}\right]^{\frac{R}{2c_V}} = T_0 \left[\frac{4V_1V_2}{(V_1 + V_2)^2}\right]^{\frac{\kappa-1}{2}} \quad (118)$$

The maximum work is then equal

$$\Delta W = 2nc_V (T_0 - T) \quad (119)$$

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.

Solution:

We will use the Clausius-Capperian equation

$$\frac{dT}{dp} = \frac{T \Delta v}{q} \quad (120)$$

it is enough to substitute the entered values in the right side. Difference in molar volumes

$$\Delta v = v^{(2)} - v^{(1)} = 0.091 \cdot 18 \cdot 10^{-6} = 1.64 \cdot 10^{-6} \text{ m}^{-3} \cdot \text{mol}^{-1} \quad (121)$$

latent heat is equal

$$q = ml = 3300000 \text{ J} \cdot \text{mol}^{-1} \cdot 0.018 \text{ mol} = 5900 \text{ J} \cdot \text{mol}^{-1} \quad (122)$$

After substituting into the CC equation

$$\frac{dT}{dp} = 7.5 \cdot 10^{-8} \text{ K} \cdot \text{Pa}^{-1} \quad (123)$$

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 $V = \text{konst.} = 1$.) Determine the difference in heat capacities $c_H - c_M$ at a constant field H and at a constant magnetization.

Solution:

The first law of thermodynamics is of the form

$$dE = \delta Q + \mathbf{H} \cdot d\mathbf{M} \quad (124)$$

according to the condition of constant field \mathbf{H} and \mathbf{M} we can choose a coordinate system by rewriting the scalar product as $H \cdot dM$. We can now proceed analogously as in the case with volume and pressure: for c_M for $M = \text{konst.}$:

$$dE = \delta Q$$

from where

$$\left(\frac{\partial E}{\partial T}\right)_M = \left(\frac{\delta Q}{\partial T}\right)_M = c_M \quad (125)$$

to calculate c_H we express δQ term from 1LT and rewrite $dE = dE(T, M)$

$$\delta Q = \left(\frac{\partial E}{\partial T}\right)_M dT + \left[\left(\frac{\partial E}{\partial M}\right)_T - H\right] dM = c_M dT - T \left(\frac{\partial H}{\partial T}\right)_M dM$$

we convert to the variables of temperature and magnetic field intensity

$$\left(\frac{\delta Q}{\partial T}\right)_H dT = c_M dT - T \left(\frac{\partial H}{\partial T}\right)_M \left(\frac{\partial M}{\partial T}\right)_H dT$$

whence apparently it is true that

$$\left(\frac{\delta Q}{\partial T}\right)_H = c_H = c_M - T \left(\frac{\partial H}{\partial T}\right)_M \left(\frac{\partial M}{\partial T}\right)_H \quad (126)$$

then the desired result is of the form

$$c_H - c_M = -T \left(\frac{\partial H}{\partial T}\right)_M \left(\frac{\partial M}{\partial T}\right)_H \quad (127)$$

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

Solution:

from the previous example we can easily determine δQ from dS

$$dS = \frac{c_M}{T} dT - \left(\frac{\partial H}{\partial T}\right)_M dM$$

or the derivative at dM we substitute the result $c_H - c_M$, and $dT = dT(M, H)$, then

$$dS = \frac{c_M}{T} \left[\left(\frac{\partial T}{\partial M} \right)_H dM + \left(\frac{\partial T}{\partial H} \right)_M dH \right] - \frac{c_H - c_M}{-T} \left(\frac{\partial T}{\partial M} \right)_H dM = 0$$

after editing

$$c_H \left(\frac{\partial T}{\partial M} \right)_H dM + c_M \left(\frac{\partial T}{\partial H} \right)_M dH = 0$$

in the end we multiply

$$\frac{1}{c_M} \left(\frac{\partial H}{\partial T} \right)_M$$

and we get (using the formula for the relationship between partial derivatives)

$$\frac{c_H}{c_M} dM - \left(\frac{\partial M}{\partial H} \right)_T dH = 0 \quad (128)$$

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

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

Solution:

In the expression derived in the previous example

$$\frac{c_H}{c_M} dM - \left(\frac{\partial M}{\partial H} \right)_T dH = 0$$

we rewrite $dH = dH(M, S)$, then

$$\frac{c_H}{c_M} dM - \left(\frac{\partial M}{\partial H} \right)_T \left(\frac{\partial H}{\partial M} \right)_S dM = \frac{c_H}{c_M} dM - \frac{\chi_T}{\chi_S} dM = 0$$

apparently it applies from there

$$\frac{c_H}{c_M} = \frac{\chi_T}{\chi_S} \quad (129)$$

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

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

Solution:

We will prove 1, first, as we will use this formula in the following points as well. So let's write the relation for $\Gamma(n+1)$ from the definition and adjust this expression using per partes

$$\Gamma(n+1) = \int_0^{\infty} dt \exp(-t)t^n = \underbrace{-t^n \exp(-t)|_0^{\infty}}_0 + n \int_0^{\infty} dt t^{n-1} \exp(-t) = n\Gamma(n).$$

In part 2 we first determine $\Gamma(1)$:

$$\Gamma(1) = \int_0^{\infty} dt \exp(-t) = -\exp(-t)|_0^{\infty} = 1.$$

We will now use the formula from 1 to calculate the values of gamma functions for other natural numbers

$$\Gamma(2) = \Gamma(1+1) = 1 \cdot \Gamma(1) = 1,$$

$$\Gamma(3) = 2 \cdot \Gamma(2) = 1 \cdot 2,$$

$$\Gamma(4) = 3 \cdot \Gamma(3) = 1 \cdot 2 \cdot 3 = 6,$$

$$\Gamma(5) = 4 \cdot \Gamma(4) = 1 \cdot 2 \cdot 3 \cdot 4 = 24,$$

we can therefore determine a formula for general n :

$$\Gamma(n+1) = n \cdot (n-1) \cdot \dots \cdot 3 \cdot 2 \cdot 1 = n!.$$

Analogously, we calculate 3: first $\Gamma(1/2)$:

$$\Gamma\left(\frac{1}{2}\right) = \int_0^{\infty} dt \exp(-t)t^{-\frac{1}{2}} = 2 \int_0^{\infty} ds \exp(-s^2) = \sqrt{\pi},$$

where in the last integral we substituted $t = s^2$. Now we will calculate the values of the gamma function for the next n :

$$\Gamma\left(\frac{3}{2}\right) = \Gamma\left(\frac{1}{2} + 1\right) = \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{1}{2}\sqrt{\pi},$$

$$\begin{aligned}\Gamma\left(\frac{5}{2}\right) &= \frac{3}{2}\Gamma\left(\frac{3}{2}\right) = \frac{1}{2} \cdot \frac{3}{2}\sqrt{\pi} = \frac{3}{4}\sqrt{\pi}, \\ \Gamma\left(\frac{7}{2}\right) &= \frac{5}{2}\Gamma\left(\frac{5}{2}\right) = \frac{1}{2} \cdot \frac{3}{2} \cdot \frac{5}{2}\sqrt{\pi} = \frac{15}{8}\sqrt{\pi}, \\ \Gamma\left(\frac{9}{2}\right) &= \frac{7}{2}\Gamma\left(\frac{7}{2}\right) = \frac{1}{2} \cdot \frac{3}{2} \cdot \frac{5}{2} \cdot \frac{7}{2}\sqrt{\pi} = \frac{105}{16}\sqrt{\pi},\end{aligned}$$

generally for n

$$\Gamma\left(n + \frac{1}{2}\right) = \frac{n-1}{2} \cdot \frac{n-3}{2} \cdots \frac{7}{2} \cdot \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2}\sqrt{\pi} = \frac{(n-1)!!}{2^n}\sqrt{\pi}.$$

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

Solution:

From the previous example, we know that $\Gamma(n+1) = n!$. We will use this fact in the calculation. So let's write the Gamma function and adjust the argument accordingly

$$\Gamma(n+1) = \int_0^{\infty} dt \exp(-t)t^n = \int_0^{\infty} dt \exp(-t) \cdot \exp[n \ln(t)] = \int_0^{\infty} dt \exp[n \ln(t) - t].$$

We make the substitution $t = n + x$

$$\begin{aligned}\int_0^{\infty} dt \exp[n \ln(t) - t] &= \int_{-n}^{\infty} dx \exp[n \ln(n+x) - n - x] \\ &\approx \int_{-n}^{\infty} dt \exp\left[n \ln(n) - n - \frac{x^2}{2n}\right] = \exp[n \ln(n) - n] \int_{-n}^{\infty} dt \exp\left(-\frac{x^2}{2n}\right).\end{aligned}$$

Since the Gaussian function is non-zero only on a certain interval, the width of which, however, is much smaller than n , we can send the lower limit of the integral to $-\infty$. Then we have a Gaussian function that we can integrate

$$\exp[n \ln(n) - n] \int_{-n}^{\infty} dt \exp\left(-\frac{x^2}{2n}\right) = \int_{-\infty}^{+\infty} dt \exp\left(-\frac{x^2}{2n}\right) = \sqrt{2\pi n} \exp[n \ln(n) - n].$$

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 .

Solution:

First, it is necessary to determine the number of possible states for each quantum state described by l . For $n = 3$ the possible quantum numbers are $l = \{0, 1, 2\}$. Each state with the orbital quantum number l is further divided according to magnetic quantum numbers, namely $m = \{-l, -l + 1, \dots, l - 1, l\}$. Each such state is further divided according to the spin quantum number $s = \pm 1/2$. Now we count the number of all possible states for each state with a given l :

- $l = 0$: $m = \{0\}$, $s = \{\pm 1/2\}$, and thus two states are possible,
- $l = 1$: $m = \{-1, 0, +1\}$, $s = \{\pm 1/2\}$, six possible states,
- $l = 2$: $m = \{-2, -1, 0, +1, +2\}$, $s = \{\pm 1/2\}$, ten possible states.

We can easily calculate the probability using a formula

$$w_i = \frac{\# \text{ states with quantum number } l = i}{\# \text{ all possible states}},$$

from here we easily find that

$$w_0 = \frac{1}{9}, w_1 = \frac{1}{3}, w_2 = \frac{5}{9}.$$

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.

Solution:

The system is divided into (body) and A' The energy of the isolated system is the sum of the energies of these two systems, whose energy is equal to $E_0 = E + E' = \text{konst.}$ Let us now calculate the entropy in individual cases. In an isolated system A each state n is associated with $\Gamma(E_0 - E_n)$ states of the system A' . We can modify this expression, let's take the logarithm of the number of states, which we expand according to the Taylor formula to the first order according to E_n

$$k_B \ln[\Gamma(E_0 - E_n)] \approx k_B \ln \Gamma(E_0) - \frac{\partial}{\partial E} k_B \ln \Gamma(E) E_n = k_B \ln \Gamma(E_0) - \frac{\partial S}{\partial E} E_n = k_B \ln \Gamma(E_0) - \frac{E_n}{T}, \quad (130)$$

after subtracting the logarithm and dividing k_B in this relation, we get

$$\Gamma(E_0 - E_n) \approx \Gamma(E_0) \exp\left(-\frac{E_n}{k_B T}\right). \quad (131)$$

The total entropy of the isolated system is then equal to

$$S_0 = k_B \ln \left[\sum_n \Gamma(E_0) \exp\left(-\frac{E_n}{k_B T}\right) \right] = k_B \ln \Gamma(E_0) + k_B \ln \sum_n \exp\left(-\frac{E_n}{k_B T}\right) = k_B \ln \Gamma(E_0) + k_B \ln Z. \quad (132)$$

In the case of a closed system, it is necessary to add the entropy in both subsystems

$$\begin{aligned}
S_0 = S + S' &= -k_B \sum_n w_n \ln w_n + k_B \ln \Gamma(E_0 - E) = \\
&= -k_B \sum_n \frac{1}{Z} \exp\left(-\frac{E_n}{k_B T}\right) \left(-\ln Z - \frac{E_n}{k_B T}\right) + k_B \ln \Gamma(E_0) - \frac{\partial k_B \ln \Gamma(E_0)}{\partial E_0} E = \\
k_B \ln Z + \frac{1}{T} \sum_n \frac{1}{Z} \exp\left(-\frac{E_n}{k_B T}\right) E_n + k_B \ln \Gamma(E_0) - \frac{E}{T} &= k_B \ln Z \frac{E}{T} + k_B \ln \Gamma(E_0) - \frac{E}{T} = \\
&= k_B \ln \Gamma(E_0) + k_B \ln Z. \quad (133)
\end{aligned}$$

In both cases, the entropy is given by the same expression.

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

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

Solution:

The mean energy of the system is equal to

$$E = \sum_n w_n E_n,$$

for $V = \text{konst.}$ E_n does not change, then we can write for the heat capacity

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = \sum_n E_n \left(\frac{\partial w_n}{\partial T} \right)_V.$$

The probability of occupying a given state is equal

$$w_n = \exp\left(\frac{F - E_n}{k_B T}\right),$$

from which we easily obtain the derivative with respect to temperature

$$\left(\frac{\partial w_n}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{F - E_n}{k_B T} \right)_V \exp\left(\frac{F - E_n}{k_B T}\right) = \frac{T \left(\frac{\partial F}{\partial T} \right)_V - F + E_n}{k_B T^2} \exp\left(\frac{F - E_n}{k_B T}\right).$$

Now we will use the knowledge from thermodynamics, from which we know the definition of free energy

$$F = E - TS, \quad dF = -pdV - SdT,$$

after that

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

and

$$E = F + TS,$$

which we substitute in the relation for the derivative w_n with respect to temperature

$$\left(\frac{\partial w_n}{\partial T}\right)_V = \frac{E_n - E}{k_B T^2} \exp\left(\frac{F - E_n}{k_B T}\right) = \frac{E_n - E}{k_B T^2} w_n.$$

The heat capacity is then in the form

$$c_V = \sum_n E_n w_n \frac{E_n - E}{k_B T^2} = \frac{1}{k_B T^2} \left(\sum_n E_n^2 w_n - E \sum_n E_n w_n \right) = \frac{1}{k_B T^2} (\langle E^2 \rangle - E^2),$$

from there we get the relationship we are looking for

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

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

Solution:

The energy of the system of harmonic oscillators is equal

$$E = \sum_{n=1}^N \left(\frac{p_n^2}{2m} + \frac{1}{2} m \omega^2 q_n^2 \right). \quad (134)$$

We first calculate the statistical sum

$$\begin{aligned} Z &= \frac{1}{h^N} \int_{\mathbb{R}^{2N}} d^N q \cdot d^N p \cdot \exp \left[- \sum_{n=1}^N \left(\frac{p_n^2}{2mk_B T} + \frac{m\omega^2 q_n^2}{2k_B T} \right) \right] = \\ &= \frac{1}{h^N} \int_{\mathbb{R}^{2N}} d^N p \cdot d^N q \cdot \prod_{n=1}^N \exp \left(\frac{p_n^2}{2mk_B T} + \frac{m\omega^2 q_n^2}{2k_B T} \right) = \\ &= \frac{1}{h^N} \prod_{n=1}^N \int_{\mathbb{R}} dp_n \cdot dq_n \cdot \exp \left(\frac{p_n^2}{2mk_B T} + \frac{m\omega^2 q_n^2}{2k_B T} \right) = \\ &= \frac{1}{h^N} \left[\int_0^\infty dp \cdot \exp \left(\frac{p^2}{2mk_B T} \right) \right]^N \left[\int_0^\infty dq \exp \left(\frac{m\omega^2 q^2}{2k_B T} \right) \right]^N = \\ &= \frac{1}{h^N} \left(\sqrt{2mk_B T \pi} \cdot \frac{2\pi k_B T}{m\omega^2} \right)^N = \left(\frac{2\pi k_B T}{h\omega} \right)^N = \left(\frac{k_B T}{\hbar\omega} \right)^N. \quad (135) \end{aligned}$$

We can easily calculate the free energy from the relation

$$F = -k_B T \ln(Z) = -k_B T \ln \left(\frac{k_B T}{\hbar\omega} \right)^N = -N k_B T \ln \left(\frac{k_B T}{\hbar\omega} \right). \quad (136)$$

We will use Maxwell's relations to calculate pressure and entropy

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = 0, \quad (137)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = Nk_B \left[\ln \left(\frac{k_B T}{\hbar \omega} \right) + 1 \right] \quad (138)$$

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

$$E_n = \hbar \omega \left(n + \frac{1}{2} \right). \quad (139)$$

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.

Solution:

We calculate the statistical sum (partition function)

$$Z = \sum_{n=0}^{\infty} \exp \left(- \frac{E_n}{k_B T} \right) = \sum_{n=0}^{\infty} \exp \left[- \frac{\hbar \omega \left(n + \frac{1}{2} \right)}{k_B T} \right] = \exp \left(- \frac{\hbar \omega}{2k_B T} \right) \sum_{n=0}^{\infty} \exp \left(- \frac{\hbar \omega}{k_B T} n \right). \quad (140)$$

An infinite series is a geometric series for which we can find the sum. Then we can write the statistical sum in the form

$$Z = \frac{\exp \left(- \frac{\hbar \omega}{2k_B T} \right)}{1 - \exp \left(- \frac{\hbar \omega}{k_B T} \right)} = \frac{2}{2 \left[\exp \left(\frac{\hbar \omega}{2k_B T} \right) - \exp \left(- \frac{\hbar \omega}{2k_B T} \right) \right]} = \frac{1}{2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right)}. \quad (141)$$

The free energy can be easily found using the statistical sum

$$F = -k_B T \ln(Z) = k_B T \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right].$$

From a computational point of view, the most advantageous procedure seems to be to first calculate the internal energy using a formula

$$E = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V.$$

After substitution and derivating it comes out

$$E = k_B T \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right] - k_B T \ln \left[2 \sinh \left(\frac{\hbar \omega}{2k_B T} \right) \right] + \frac{\hbar \omega}{2} \operatorname{coth} \left(\frac{\hbar \omega}{2k_B T} \right) = \frac{\hbar \omega}{2} \operatorname{coth} \left(\frac{\hbar \omega}{2k_B T} \right).$$

We can easily calculate the required heat capacity from the energy

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = \left(\frac{\hbar\omega}{T} \right)^2 \frac{1}{k_B \cosh^2 \left(\frac{\hbar\omega}{k_B T} \right)}. \quad (142)$$

Finally, we will determine the heat capacity for high and for low temperatures:

- approximation of low temperatures: in the equation for heat capacity, we break down the cosh function using exponentials

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = 4 \left(\frac{\hbar\omega}{T} \right)^2 \frac{1}{k_B \left[\exp \left(\frac{\hbar\omega}{k_B T} \right) - \exp \left(-\frac{\hbar\omega}{k_B T} \right) \right]^2}.$$

The first exponential acquires significantly larger values than the second exponential, so we can write the heat capacity in the form

$$c_V \approx \frac{4}{k_B} \left(\frac{\hbar\omega}{T} \right)^2 \exp \left(-\frac{2\hbar\omega}{k_B T} \right). \quad (143)$$

- approximation of high temperatures: in this case, sinh acquires very small values, therefore we develop according to the Taylor formula to the first order, then

$$c_V \approx 4 \left(\frac{\hbar\omega}{T} \right)^2 \frac{1}{k_B \left(\frac{2\hbar\omega}{k_B T} \right)^2} = k_B. \quad (144)$$

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.

Solution:

Let us denote the desired function $f(\mathbf{p}) = f(p_x, p_y, p_z)$. Equations follow from the conditions of the assignment: independence of direction

$$f(p_x, p_y, p_z) = f_x(p_x) \cdot f_y(p_y) \cdot f_z(p_z) \quad (145)$$

isotropy of the space

$$f(p_x, p_y, p_z) = f(\|p\|) \quad (146)$$

from here we get the equation

$$f_x(p_x) \cdot f_y(p_y) \cdot f_z(p_z) = f(\|p\|) \quad (147)$$

which we logarithmize (denote $f_x(p_x) = f_x$ a $f(\|p\|) = f$)

$$\ln f_x + \ln f_y + \ln f_z = \ln f \quad (148)$$

we calculate the derivative with respect to v_x , only the first term remains from the left side, the right side is derived using the knowledge of the norm $\|p\| = \sqrt{p_x^2 + p_y^2 + p_z^2}$

$$\frac{f'_x}{f_x} = \frac{\partial f}{\partial p_x} \frac{1}{f} = \frac{p_x}{\|p\|} \frac{f'}{f} \quad (149)$$

In this equation, the equations can be separated

$$\frac{f'_x}{p_x \cdot f_x} = \frac{f'}{f\|p\|} \quad (150)$$

Both sides must be equal to a constant. Let's take the right side, which we multiply by the speed norm

$$\frac{f'}{f} = \text{konst.} \cdot \|p\| \quad (151)$$

we can find the solution easily

$$f = C \exp\left(\frac{k\|p\|^2}{2}\right) \quad (152)$$

for a physically acceptable result, k must be negative.

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

Solution:

Normovací konstantu nalezneme zintegrováním funkce přes celý hybnostní prostor, takový integrál musí být roven jedné

$$1 = \int_{-\infty}^{+\infty} \iint_{-\infty} C \exp\left(-\frac{p^2}{2mkT}\right) \quad (153)$$

Převědeme na sférický integrál

$$\int_{-\infty}^{+\infty} \iint_{-\infty} C \exp\left(-\frac{p^2}{2mkT}\right) = C \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin(\theta) \int_0^\infty dp p^2 \exp\left(-\frac{p^2}{2mkT}\right) \quad (154)$$

Úhlová část je rovna 4π . U radiální části provedeme substituci $t = \frac{p^2}{2mk_B T}$

$$\int_0^\infty dp p^2 \exp\left(-\frac{p^2}{2mkT}\right) = \int_0^\infty dt \sqrt{\frac{mk_B T}{2t}} 2mk_B T t \exp(-t) = \sqrt{2} (mk_B T)^{\frac{3}{2}} \int_0^\infty dt \sqrt{t} \exp(-t) \quad (155)$$

integrál je roven gamma funkci $\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{\sqrt{\pi}}{2}$ Následně

$$1 = C\sqrt{2} (mk_B T)^{\frac{3}{2}} \frac{\sqrt{\pi}}{2} = (2\pi mk_B T)^{\frac{3}{2}} \quad (156)$$

normovací konstanta je tedy rovna

$$C = \frac{1}{(2\pi mk_{\text{B}}T)^{\frac{3}{2}}} \quad (157)$$

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 $p_z > 0$.

Solution:

At the beginning, we calculate the general integral

$$\iiint_{-\infty}^{+\infty} \mathbf{p} \mathbf{p}^n \cdot \exp(-a\mathbf{p}^2)$$

Again we convert to spherical coordinates. We will perform the integration over the angular part in exactly the same way as in the previous example. The radial part throws out the Jacobian p^2 , then

$$\int_{-\infty}^{+\infty} \iint_{-\infty}^{\infty} d\mathbf{p} \mathbf{p}^n \cdot \exp(-a\mathbf{p}^2) = 4\pi \int_0^{\infty} dp p^{n+2} \exp(-ap^2) \quad (158)$$

by substituting $t = ap^2$ we arrive at the integral

$$\frac{\pi}{2a^{n+\frac{1}{2}}} \int_0^{\infty} dt t^{\frac{n}{2}+\frac{1}{2}} \exp(-t) \quad (159)$$

from where we get the desired value of the integral

$$\iiint_{-\infty}^{+\infty} d\mathbf{p} \mathbf{p}^n \cdot \exp(-a\mathbf{p}^2) = \frac{2\pi}{a^{\frac{n}{2}+\frac{3}{2}}} \Gamma\left(\frac{n}{2} + \frac{3}{2}\right) \quad (160)$$

(a) We don't even need to calculate this integral. If we write the triple integral, it is easy we convert to three integrals. The only integral over the x coordinate is of the form

$$\int_{-\infty}^{+\infty} dp_x p_x \exp\left(-\frac{p_x^2}{2mk_{\text{B}}T}\right) \quad (161)$$

at first sight it is obvious that we are integrating an odd function over a symmetric interval. The integral is apparently equal to zero.

(b) Using the formula for the integral for $n = 1$, then

$$\langle p \rangle = \frac{2\pi C}{a^2} \Gamma(2) = \frac{2\pi (2mk_{\text{B}}T)^{\frac{3}{2}}}{(2\pi mk_{\text{B}}T)^{\frac{3}{2}}} = 2\sqrt{\frac{2mk_{\text{B}}T}{\pi}} \quad (162)$$

where C is the normalization constant, which we also need for the calculation.

(c) We apply exactly the same formula as in the previous case, only for $n = 2$.

$$\langle p^2 \rangle = 3mk_{\text{B}}T \quad (163)$$

(d) Assuming the classical relationship between momentum and velocity $p = mv$ we can write

$$\langle v^2 \rangle = \left\langle \frac{p^2}{m^2} \right\rangle = \frac{1}{m^2} \langle p^2 \rangle = \frac{3k_B T}{m} \quad (164)$$

(e) First we need to modify the fluctuation equation

$$\Delta E = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 - 2E\langle E \rangle + \langle E \rangle^2 \rangle = \langle E^2 \rangle - 2\langle E \rangle + \langle E \rangle^2 = \langle E^2 \rangle - \langle E \rangle^2 \quad (165)$$

we assume the classical dispersion relation $E = \frac{p^2}{2m}$, which we substitute in the fluctuation equation

$$\Delta E = \left\langle \frac{p^4}{4m^2} \right\rangle - \left\langle \frac{p^2}{2m} \right\rangle^2 = \frac{1}{4m^2} (\langle p^4 \rangle - \langle p^2 \rangle^2) \quad (166)$$

the calculation was thus reduced to the calculation of mean values. In addition, we have already calculated the mean squared value, so all that remains is to calculate the fourth power, then

$$\Delta E = \frac{1}{4m^2} (15 (mk_B T)^2 - 9 (mk_B T)^2) = \frac{6 (mk_B T)^2}{4m^2} = \frac{6}{4} (k_B T)^2 \quad (167)$$

after square root we get

$$\Delta E = \sqrt{\frac{3}{2}} k_B T \quad (168)$$

(f) We must determine the most probable magnitude of momentum from the definition of probability density

$$dW = f(p_x, p_y, p_z) dp_x \cdot dp_y \cdot dp_z = 4\pi p^2 f(p) dp = 4\pi^2 p^2 \exp\left(-\frac{p^2}{2mk_B T}\right) dp \quad (169)$$

so the expression in front of dp is enough to differentiate to find the extremum of the function

$$2p \exp\left(-\frac{p^2}{2mk_B T}\right) - p^2 \frac{2p}{2mk_B T} \exp\left(-\frac{p^2}{2mk_B T}\right) = 0 \quad (170)$$

after a simple modification, we obtain $p^2 = 2mk_B T$. Then $p = \sqrt{2mk_B T}$.

(g) this case, we solve the triple integral with the only difference that the integration over z takes place only in the interval $(0, \infty)$. Considering that we are integrating over a symmetric interval an even function, the contribution of both the positive and negative parts must be equal. Then the probability is equal to one half.

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 .

Solution:

Again, we start by calculating the statistical sum. We write this for a system of indistinguishable particles in the form

$$Z = \frac{1}{N!(2\pi\hbar)^3} \int_{\mathbb{R}^{3N} \times \Omega} d^{3N}p \cdot d^{3N}q \cdot \exp \left[- \sum_n \left(\frac{\mathbf{p}_n^2}{2mk_B T} + \frac{m\mathbf{g}\mathbf{q}}{k_B T} \right) \right],$$

where $\Omega = \{[x, y, z]; x \in [-L, L], y \in [-L, L], z \in [0, \infty), L \in \mathbb{R}^+\}$. We calculate the statistical sum for one particle

$$Z = \frac{1}{(2\pi\hbar)^3} \left[\int_{\mathbb{R}} dp \cdot \exp \left(- \frac{\mathbf{p}^2}{2mk_B T} \right) \int_{\Omega} dq \cdot \exp \left(- \frac{m\mathbf{g}\mathbf{q}}{k_B T} \right) \right],$$

the first integral is from a rescaled Gaussian, therefore it is equal

$$\int_{\mathbb{R}} dp \cdot \exp \left(- \frac{\mathbf{p}^2}{2mk_B T} \right) = \sqrt{(2\pi mk_B T)^3}.$$

Second integral

$$\int_{\Omega} dq \cdot \exp \left(- \frac{m\mathbf{g}\mathbf{q}}{k_B T} \right) = \underbrace{\int_{-L}^L dx \int_{-L}^L dy}_A \underbrace{\int_0^{\infty} dz \exp \left(- \frac{mgz}{k_B T} \right)}_{\frac{k_B T}{mg}} = A \frac{k_B T}{mg}.$$

After that

$$Z = \frac{1}{(2\pi\hbar)^3} (2\pi mk_B T)^{\frac{3}{2}} A \frac{k_B T}{mg}. \quad (171)$$

The probability density that the particle occurs in the phase volume $d^3p \cdot d^3q$ is given

$$dw_n = \frac{1}{Z} \frac{d^3p \cdot d^3q}{(2\pi\hbar)^3} \exp \left(- \frac{\mathbf{p}^2}{2mk_B T} \right) \exp \left(- \frac{m\mathbf{g}\mathbf{q}}{k_B T} \right) = \frac{mg}{(2\pi mk_B T)^{\frac{3}{2}} A k_B T} \exp \left(- \frac{\mathbf{p}^2}{2mk_B T} \right) \exp \left(- \frac{m\mathbf{g}\mathbf{q}}{k_B T} \right) d^3p \cdot d^3q.$$

We will only be interested in the probability of finding a particle in a given position \mathbf{q} , therefore we will integrate w_n over the momentum space \mathbf{p} , where w_n denotes the probability density of the given particle in the element

$$\int_{\mathbf{p}} dw_n = \underbrace{\frac{mg}{A k_B T} \exp \left(- \frac{mgq_3}{k_B T} \right)}_{\mathcal{P}} \cdot d^3q,$$

where \mathcal{P} denotes the probability density of the given particle in the element d^3q . Then we get the number density

$$n = \frac{Nmg}{A k_B T} \exp \left(- \frac{mgq_3}{k_B T} \right). \quad (172)$$

The density is equal

$$\varrho(z) = \varrho(0) \cdot \exp\left(-\frac{mgq_3}{k_B T}\right). \quad (173)$$

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

Solution:

ověříme jednotky z definičních vztahů:

$$[p] = \frac{[F]}{[S]} = \frac{\text{kg} \cdot \text{m} \cdot \text{s}^{-2}}{\text{m}^2} = \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2},$$

$$[e] = \frac{[E]}{[V]} = \frac{\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}}{\text{m}^3} = \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}.$$

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

Solution:

The relation holds for the density of states

$$\rho(E) = \frac{gV}{\pi^d} \frac{1}{2^d} \text{Vol}(S^{d-1}) \frac{[k(E)]^{d-1}}{\left|\frac{dE}{dk}\right|}, \quad (174)$$

where g is the degeneracy of energy levels, d the dimension of space, and $\text{Vol}(S^{d-1})$ surface of $d-1$ dimensional sphere. In our case, we have $d = 3$. The dispersion relationship $E(k)$ is given by the relation

$$E = \sqrt{m^2 c^4 + \hbar^2 k^2 c^2},$$

from here

$$k = \frac{\sqrt{E^2 - m^2 c^4}}{\hbar c}.$$

Substituting the appropriate quantities into (174) we get

$$\rho(E) = \frac{4\pi gV}{(2\pi\hbar)^3} \frac{1}{c^3} E \sqrt{E^2 - m^2 c^4}. \quad (175)$$

- Classical limit – Energy in this case is equal to:

$$E_{\text{kl.}} \approx E - mc^2 = \sqrt{m^2 c^4 + \hbar^2 k^2 c^2} - mc^2 = mc^2 \sqrt{1 + \frac{\hbar^2 k^2}{m^2 c^2}} - mc^2 \approx$$

$$mc^2 \left(1 + \frac{1}{2} \frac{\hbar^2 k^2}{m^2 c^2}\right) - mc^2 = \frac{\hbar^2 k^2}{2m}. \quad (176)$$

- Ultrarelativistic limit – in this case $E \gg mc^2$, applies, then we can neglect the second term in the square root

$$\rho(E) = \frac{4\pi gV}{(2\pi\hbar)^3} \frac{1}{c^3} E^2.$$

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.

Solution:

It holds for the number of boson states in the energy interval $(E, E + dE)$

$$dN = \frac{\rho(E)dE}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1}.$$

Since in the classic case it is

$$\exp\left(-\frac{E-\mu}{k_B T}\right) \ll 1,$$

we can neglect the one in the denominator. Then, after substituting for $\rho(E)$ we get

$$dN = \frac{4\pi gV}{(2\pi\hbar)^3} \sqrt{2m^3 E} \exp\left(\frac{E-\mu}{k_B T}\right) dE.$$

We transform the expression from energy coordinates to velocity coordinates

$$dE = \frac{\partial E}{\partial v} dv = mv,$$

because we consider the classical formula for kinetic energy $E = 0.5 \cdot mv^2$

$$dw = \frac{4\pi gV}{(2\pi\hbar)^3} \sqrt{2m^3} \sqrt{\frac{m}{2}} \exp\left(\frac{0.5mv^2 - \mu}{k_B T}\right) m dv = \frac{4\pi gV}{(2\pi\hbar)^3} m^3 v^2 \exp\left(-\frac{v^2}{2mk_B T}\right) \exp\left(-\frac{\mu}{k_B T}\right) dv.$$

To calculate μ we start from the relation for one particle

$$1 = N = \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} F_{\frac{3}{2}}\left(\frac{\mu}{k_B T}\right) = \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} \frac{1}{\Gamma\left(\frac{3}{2}\right)} \int_0^\infty dx \frac{x^{\frac{1}{2}}}{\exp\left(x - \frac{\mu}{k_B T}\right) + 1}.$$

In the integral, the exponential acquires significantly larger values than one, so we neglect the number one, we get

$$\int_0^\infty dx x^{\frac{1}{2}} \exp\left(-x + \frac{\mu}{k_B T}\right) \approx \exp\left(\frac{\mu}{k_B T}\right) \int_0^\infty dx x^{\frac{1}{2}} \exp(-x) = \exp\left(\frac{\mu}{k_B T}\right) \Gamma\left(\frac{3}{2}\right).$$

We substitute in the previous formula

$$\frac{gV}{(2\pi\hbar)^3} \exp\left(\frac{\mu}{k_B T}\right) = (2\pi m k_B T)^{-\frac{3}{2}}.$$

Where do we receive

$$dw = 4\pi \left(\frac{m}{2\pi k_B T}\right) v^2 \exp\left(\frac{v^2}{2k_B T}\right) dv. \quad (177)$$

63. Let's define functions

$$B_n(y) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{\exp(x-y) - 1}, \quad (178)$$

and

$$F_n(y) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{\exp(x-y) + 1}. \quad (179)$$

For these functions prove

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

and

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

Solution:

Let's do the math first

$$\frac{dB_{n+1}(y)}{dy} = \frac{d}{dy} \left[\frac{1}{\Gamma(n+1)} \int_0^\infty dx \frac{x^n}{\exp(x-y) - 1} \right] = \frac{1}{\Gamma(n+1)} \int_0^\infty dx x^n \frac{d}{dy} \frac{1}{\exp(x-y) - 1}.$$

In this phase, we will use the knowledge of the derivative of the function in the argument of the integral. As

$$\frac{d}{dy} \frac{1}{\exp(x-y) - 1} = -\frac{d}{dx} \frac{1}{\exp(x-y) - 1},$$

we can substitute the expression on the right-hand side into the integral, in which we get integrating by parts

$$-\frac{1}{\Gamma(n+1)} \int_0^\infty dx x^n \frac{d}{dx} \frac{1}{\exp(x-y) - 1} = \frac{1}{\Gamma(n+1)} \left\{ \underbrace{\left[-\frac{x^n}{\exp(x-y) - 1} \right]_0^\infty}_0 + \int_0^\infty dx \frac{n \cdot x^{n-1}}{\exp(x-y) - 1} \right\}.$$

Furthermore, we know that $\Gamma(n+1) = n\Gamma(n)$. Then we get

$$\frac{dB_{n+1}(y)}{dy} \frac{d}{dy} = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{\exp(x-y) - 1} = B_n(y). \quad (180)$$

The relation for fermions can be proved analogously.

64. From a relationship

$$\Omega = -k_B T \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} B_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right), \quad (181)$$

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.

Solution:

The number of particles is given by the relation

$$N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V},$$

where we substitute relation (181), then we get

$$N = -k_B T \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} \frac{\partial}{\partial \mu} B_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right).$$

From the previous example we know that

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

from where

$$\frac{dB_{n+1} \left(\frac{\mu}{k_B T} \right)}{d\mu} = \frac{1}{k_B T} B_n \left(\frac{\mu}{k_B T} \right).$$

The number of particles will then work out for us

$$N = \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} B_{\frac{3}{2}} \left(\frac{\mu}{k_B T} \right). \quad (182)$$

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

Solution:

In the calculation, we will use the knowledge of the internal energy of the fermion gas in the classical case

$$E = \frac{3}{2} \frac{gV}{\lambda_T^3} k_B T F_{\frac{3}{2}} \left(\frac{\mu}{k_B T} \right), \quad (183)$$

and the relation for the number of particles

$$N = \frac{gV}{\lambda_T^3} F_{\frac{3}{2}} \left(\frac{\mu}{k_B T} \right), \quad (184)$$

where

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}. \quad (185)$$

We expand the energy using the expression indicating the number of particle $N/N(T, \mu)$, we get

$$E = \frac{3}{2} N k_B T \frac{F_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right)}{F_{\frac{3}{2}} \left(\frac{\mu}{k_B T} \right)},$$

We will introduce

$$F_n \left(\frac{\mu}{k_B T} \right) = F_n.$$

We calculate the heat capacity according to the well-known formula

$$c_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} N k_B \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} + \frac{3}{2} N k_B T \frac{\frac{\partial F_{\frac{5}{2}}}{\partial T} F_{\frac{3}{2}} - F_{\frac{5}{2}} \frac{\partial F_{\frac{3}{2}}}{\partial T}}{\left(F_{\frac{3}{2}} \right)^2},$$

the derivative of the function F_n with respect to T looks as follows

$$\left(\frac{\partial F_n}{\partial T} \right)_{V,T} = \frac{\partial}{\partial T} \left(\frac{\mu}{k_B T} \right) F_n' = \left[\left(\frac{\partial \mu}{\partial T} \right)_{V,N} \frac{1}{k_B T} - \frac{\mu}{k_B T^2} \right] F_{n-1}.$$

We put in the relationship for c_V and receive

$$c_V = \frac{3}{2} N k_B \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} + \frac{3}{2} N \left[\left(\frac{\partial \mu}{\partial T} \right)_{V,N} - \frac{\mu}{T} \right] \left[1 - \frac{F_{\frac{5}{2}} F_{\frac{1}{2}}}{\left(F_{\frac{3}{2}} \right)^2} \right].$$

For the next calculation, we will use the fact that the total number of particles does not depend on the temperature, i.e

$$\left(\frac{\partial N}{\partial T} \right)_{V,N} = \frac{3}{2} F_{\frac{3}{2}} + \left[\frac{1}{k_B} \left(\frac{\partial \mu}{\partial T} \right)_{V,N} - \frac{\mu}{k_B T} \right] F_{\frac{1}{2}} = 0.$$

From there we express the partial derivative of the chemical potential with respect to temperature

$$\left(\frac{\partial \mu}{\partial T} \right)_{V,N} = \frac{\mu}{T} - \frac{3}{2} k_B \frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}}. \quad (186)$$

After replacing it in c_V we get

$$c_V = \frac{3}{2}N \left[1 - \frac{F_{\frac{5}{2}}F_{\frac{1}{2}}}{\left(F_{\frac{3}{2}}\right)^2} \right] \left(-\frac{3}{2}k_B \frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}} \right) + \frac{3}{2}Nk_B \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} = \frac{3}{2}Nk_B \left\{ \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} - \frac{3}{2}N \frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}} \left[1 - \frac{F_{\frac{5}{2}}F_{\frac{1}{2}}}{\left(F_{\frac{3}{2}}\right)^2} \right] \right\}.$$

In the classic case, we can approximate the function F_n by

$$F_n \approx \exp\left(\frac{\mu}{k_B T}\right), \quad (187)$$

then all the ratios of the function F are equal to one and we get the well-known relation for the heat capacity

$$c_V \approx \frac{3}{2}Nk_B. \quad (188)$$

Another way of solving: First, using thermodynamics, we calculate what $c_{V,N}$ is equal to. We know that

$$c_{V,\mu} = T \left(\frac{\partial S}{\partial T} \right)_{V,\mu},$$

we introduce entropy as $S = S(N(\mu, V, T), V, T)$, then

$$T \left(\frac{\partial S}{\partial T} \right)_{V,\mu} = T \left(\frac{\partial S(N(\mu, V, T), V, T)}{\partial T} \right)_{V,\mu} = T \left(\frac{\partial S}{\partial N} \right)_{V,\mu} \left(\frac{\partial N}{\partial T} \right)_{V,\mu} + T \left(\frac{\partial S}{\partial T} \right)_{V,N}.$$

We will use Maxwell's relations arising from the free energy relation

$$dF = -SdT - pdV + \mu dN,$$

from where

$$\left(\frac{\partial S}{\partial N} \right)_{V,T} = - \left(\frac{\partial \mu}{\partial T} \right)_{N,V}.$$

Assuming that at constant volume the number of particles does not change, i.e.

$$dN = \left(\frac{\partial N}{\partial \mu} \right)_{T,V} + \left(\frac{\partial N}{\partial T} \right)_{\mu,V} = 0,$$

we get a relationship

$$\left(\frac{\partial \mu}{\partial T} \right)_{N,V} = - \left(\frac{\partial \mu}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial T} \right)_{\mu,V}.$$

We substitute the calculated partial derivatives into the expression for $c_{V,\mu}$

$$c_{V,\mu} = T \left(\frac{\partial N}{\partial \mu} \right)_{T,V}^{-1} \left(\frac{\partial N}{\partial T} \right)_{\mu,V}^2 + T \underbrace{\left(\frac{\partial S}{\partial T} \right)_{V,N}}_{c_{V,N}}.$$

For the heat capacity we then get the relation

$$c_{V,N} = c_{V,\mu} - T \frac{\left(\frac{\partial N}{\partial T}\right)_{\mu,V}^2}{\left(\frac{\partial N}{\partial \mu}\right)_{T,V}}. \quad (189)$$

In this step, we will finish with thermodynamics and use the results of statistical physics. It is enough to just substitute the relevant quantities for the classical fermion gas. The thermodynamic potential of such a system of particles is equal to

$$\Omega = -\frac{gV}{\lambda_T^3} k_B T F_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right). \quad (190)$$

From (190) we find the entropy of the gas

$$S = - \left(\frac{\partial \Omega}{\partial T} \right)_{V,\mu} = \frac{-gV k_B}{\lambda_T^3} \left(\frac{5}{2} F_{\frac{5}{2}} - \frac{\mu}{k_B T} F_{\frac{3}{2}} \right).$$

From the entropy, we can easily find the heat capacity $c_{V,\mu}$

$$c_{V,\mu} = T \left(\frac{\partial S}{\partial T} \right)_{V,\mu} = -\frac{gV k_B}{\lambda_T^3} \left(\frac{15}{4} F_{\frac{5}{2}} - 3 \frac{\mu}{k_B T} F_{\frac{3}{2}} + \frac{\mu^2}{k_B^2 T^2} F_{\frac{1}{2}} \right).$$

Z (184) We calculate the partial derivative from

$$\left(\frac{\partial N}{\partial T} \right)_{V,\mu} = \frac{gV}{\lambda_T^3} \left(\frac{3}{2T} F_{\frac{3}{2}} - \frac{\mu}{k_B T^2} F_{\frac{1}{2}} \right).$$

And finally

$$\left(\frac{\partial N}{\partial \mu} \right)_{V,T} = \frac{gV}{\lambda_T^3} \frac{1}{k_B T} F_{\frac{1}{2}}.$$

Substituting everything back into (189), we obtain

$$c_{V,N} = \frac{gV k_B}{\lambda_T^3} \left[\left(\frac{15}{4} F_{\frac{5}{2}} - 3 \frac{\mu}{k_B T} F_{\frac{3}{2}} + \frac{\mu^2}{k_B^2 T^2} F_{\frac{1}{2}} \right) - T^2 \left(\frac{9}{4T^2} \frac{F_{\frac{3}{2}}^2}{F_{\frac{1}{2}}} - \frac{3\mu}{k_B T^3} F_{\frac{3}{2}} + \frac{\mu^2}{k_B^2 T^4} F_{\frac{1}{2}} \right) \right],$$

We divide the whole expression by $k_B N$, we substitute (184) on the right-hand side

$$\frac{c_{V,N}}{k_B N} = \frac{15}{4} \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} - 3 \frac{\mu}{k_B T} + \frac{\mu^2}{k_B^2 T^2} \frac{F_{\frac{1}{2}}}{F_{\frac{3}{2}}} - \frac{9}{4} \frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}} + \frac{3\mu}{k_B T} - \frac{\mu^2}{k_B^2 T^2} \frac{F_{\frac{1}{2}}}{F_{\frac{3}{2}}}.$$

In the classical case, we can again approximate the function F_n by expression (187), then

$$\frac{c_{V,N}}{k_B N} = \frac{15}{4} - 3 \frac{\mu}{k_B T} + \frac{\mu^2}{k_B^2 T^2} - \frac{9}{4} + 3 \frac{\mu}{k_B T} - \frac{\mu^2}{k_B^2 T^2}.$$

We get to the best part of the calculation, the only non-zero term will be 3/2, the others disappear, then we have the result

$$\frac{c_{V,N}}{k_B N} = \frac{3}{2}, \quad (191)$$

which is the same result as in the previous case.