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Modul 2
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Chapter 2

Introduction to Thermodynamics

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Problem 2.1: Test the following differentials for exactness. For those cases in which the differential is exact, find the function $u(x, y)$.

(a) $du_a = \frac{-y dx}{x^2 + y^2} + \frac{x dy}{x^2 + y^2}$.

(b) $du_b = (y - x^2) dx + (x + y^2) dy$.

(c) $du_c = (2y^2 - 3x) dx - 4xy dy$.

Solution 2.1:

(a) The differential is exact, $u_a(x, y) = -\arctan(x/y)$.

Here one point worth discussion. The function $u_a(x, y) = -\arctan(x/y)$ has a singularity at $x = 0, y = 0$. As a result, any close path embedding this point contributes 2π to the variation of the quantity $u(x, y)$. Consequently, this function cannot serve as a thermodynamic potential if both positive and negative values of x and y have physical meaning.

(b) The differential is exact, $u_b(x, y) = yx + (y^3 - x^3)/3$.

(c) The differential is not exact.

The function $u(x, y)$ is reconstructed in the following way. For an exact differential, $du = u_x dx + u_y dy$,

$$u_x = \frac{\partial u(x, y)}{\partial x}, \quad u_y = \frac{\partial u(x, y)}{\partial y}.$$

If we introduce

$$u_1(x, y) = \int_0^x u_x(\xi, y) d\xi,$$

then the difference $f \equiv u(x, y) - u_1(x, y)$ is a function only of y . Consequently,

$$\frac{df}{dy} = \frac{\partial u(x, y)}{\partial y} - \frac{\partial u_1(x, y)}{\partial y} = u_y(x, y) - \int_0^x \frac{\partial u_x(x, y)}{\partial y} dx.$$

As a result,

$$f(y) = \int_0^y d\eta u_y(x, \eta) - \int_0^y \int_0^x d\xi d\eta \frac{\partial u_x(\xi, \eta)}{\partial \eta}.$$

Finally,

$$u(x, y) = \int_0^x d\xi u_x(\xi, y) + \int_0^y d\eta u_y(x, \eta) - \int_0^y \int_0^x d\xi d\eta \frac{\partial u_x(\xi, \eta)}{\partial \eta}.$$

For calculation see the Maple file it1.mws.

Problem 2.2: Consider the two differentials

1. $du_1 = (2xy + x^2)dx + x^2dy$, and
2. $du_2 = y(x - 2y)dx - x^2dy$.

For both differentials, find the change $u(x, y)$ between two points, (a, b) and (x, y) . Compute the change in two different ways:

- (a) Integrate along the path $(a, b) \rightarrow (x, b) \rightarrow (x, y)$,
- (b) Integrate along the path $(a, b) \rightarrow (a, y) \rightarrow (x, y)$.

Discuss the meaning of your results.

Solution 2.2: The calculations are shown in the Maple file. In the case (b) the results are different because the differential is not exact.

Problem 2.3: Electromagnetic radiation in an evacuated vessel of volume V at equilibrium with the walls at temperature T (black body radiation) behaves like a gas of photons having internal energy $U = aVT^4$ and pressure $P = (1/3)aT^4$, where a is Stefan's constant.

- (a) Plot the closed curve in the $P - V$ plane for a Carnot cycle using black body radiation.
- (b) Derive *explicitly* the efficiency of Carnot engine which uses black body radiation as its working substance.

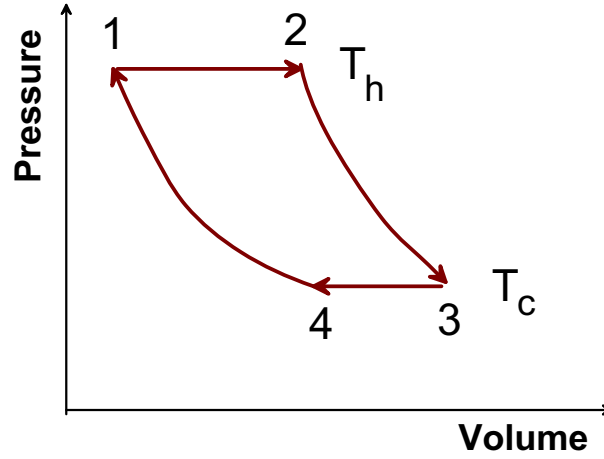


Figure 2.1: On the Carnot cycle with black-body radiation.

Solution 2.3: We will follow example shown in Exercise 2.2. Let us start with *isotherms*. At the isotherms the pressure is V -independent, thus isotherms are *horizontal*, see Fig. 2.1 Along the first isothermal path,

$$\Delta Q_{1 \rightarrow 2} = \Delta U + P\Delta V = (4/3)aT_h^4(V_2 - V_1) = \frac{4}{3}aT_h^4V_1 \left[\frac{V_2}{V_1} - 1 \right]. \quad (2.1)$$

In a similar way,

$$\Delta Q_{3 \rightarrow 4} = \frac{4}{3}aT_c^4V_4 \left[1 - \frac{V_3}{V_4} \right]. \quad (2.2)$$

Now let us consider an adiabatic path. Along an adiabatic path,

$$dQ = 0 = dU + PdV = 4aVT^3 dT + aT^4 dV + (1/3)aT^4 dV = 4aVT^3 dT + (4/3)aT^4 dV.$$

Consequently,

$$\frac{dT}{T} = -\frac{1}{3} \frac{dV}{V} \rightarrow VT^3 = \text{const}, \quad PV^{4/3} = \text{const}.$$

Let us start from the point 2 characterized by the values P_1, V_2 and adiabatically expand the gas to the point 3 characterized by the volume V_3 . We have $V_2T_h^3 = V_3T_c^3$. In a similar way, $V_4T_c^3 = V_1T_h^3$. Combining these equalities, we get:

$$V_2T_h^3 = V_3T_c^3, \quad V_4T_c^3 = V_1T_h^3 \rightarrow \frac{V_2}{V_3} = \frac{V_1}{V_4} = \left(\frac{T_c}{T_h} \right)^3 \quad (2.3)$$

Combining Eqs. (2.1), (2.2) and (2.3), we find

$$\Delta W = \Delta Q_{1 \rightarrow 2} + \Delta Q_{3 \rightarrow 4} = \frac{4}{3}aT_h^4V_1 \left(\frac{V_3}{V_4} - 1 \right) \left(1 - \frac{T_c}{T_h} \right).$$

Remember: along a closed path $\Delta U = 0$ and the total heat consumption is equal to mechanical work.

On the

$$\Delta Q_{1 \rightarrow 2} = \frac{4}{3} a T_h^4 V_1 \left(\frac{V_2}{V_1} - 1 \right).$$

As a result,

$$\eta = \frac{\Delta W}{\Delta Q_{1 \rightarrow 2}} = \frac{T_h - T_c}{T_h}$$

as it should be.

Problem 2.4: A Carnot engine uses a paramagnetic substance as its working substance. The equation of state is

$$M = \frac{nDH}{T}$$

where M is magnetization, H is the magnetic field, n is the number of moles, D is a constant determined by the type of substance, and T is the temperature.

- (a) show that the internal energy U , and therefore the heat capacity C_M , can only depend on the temperature and not the magnetization.
- (b) Let us assume that $C_M = C = \text{constant}$. Sketch a typical Carnot cycle in the $M - H$ plane.
- (c) Compute the total heat absorbed and the total work done by the Carnot engine.
- (d) Compute the efficiency of the Carnot engine.

Solution 2.4:

- (a) By definition [see Eq. [1](2.23)],

$$dU = T dS + \mathbf{H} d\mathbf{M}.$$

Thus at $M = \text{const}$ the internal energy is independent of the magnetization.

- (b) Since $C = \text{const}$, $U_0 = N c_M T$, where c_M is the specific heat per one particle while N is the number of particles. Introducing molar quantities we get $U_0 = n c T$.

A Carnot cycle is shown in Fig. 2.2. We have:

- (c) For an isothermal process at $T = T_c$,

$$Q_{1 \rightarrow 2} = - \int_{H_1}^{H_2} H(M) dM = \frac{T_c}{2nD} (M_1^2 - M_2^2).$$

In a similar way,

$$Q_{3 \rightarrow 4} = \frac{T_h}{2nD} (M_3^2 - M_4^2).$$

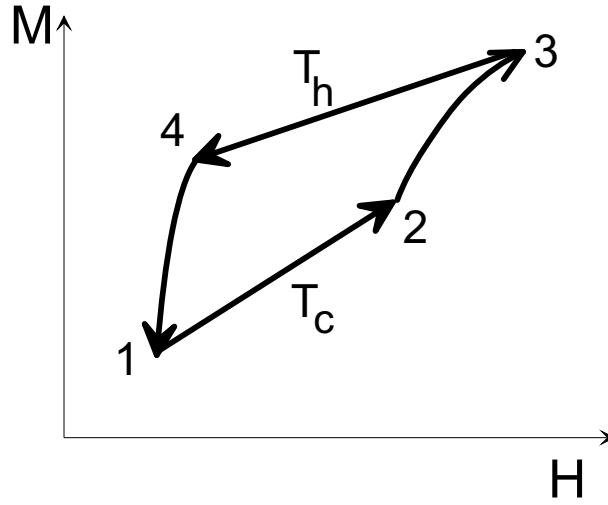


Figure 2.2: Sketch of the Carnot cycle.

The total work is then $W = Q_{1 \rightarrow 2} + Q_{3 \rightarrow 4}$, and the efficiency is

$$\eta = \frac{W}{Q_{3 \rightarrow 4}} = 1 + \frac{T_c M_1^2 - M_2^2}{T_h M_3^2 - M_4^2}.$$

Now let us discuss adiabatic paths. We have at each path,

$$0 = dQ = dU - H dM = nc dT - \frac{MT}{nD} dM.$$

Immediately we get

$$\frac{dT}{T} = \frac{1}{n^2 c D} M dM.$$

Integrating this equality from point 2 to point 3 we obtain,

$$2n^2 c D \ln \frac{T_h}{T_c} = M_3^2 - M_2^2.$$

In a similar way, integrating from 4 to 1 we obtain

$$2n^2 c D \ln \frac{T_c}{T_h} = M_1^2 - M_4^2.$$

As a result,

$$M_3^2 - M_2^2 = M_4^2 - M_1^2 \quad \rightarrow \quad M_3^2 - M_4^2 = -(M_1^2 - M_2^2).$$

(d) Using this expression we obtain the efficiency

$$\eta = \frac{Q_{1 \rightarrow 2} + Q_{3 \rightarrow 4}}{Q_{3 \rightarrow 4}} = \frac{T_h - T_c}{T_h}.$$

Coming back to the item (c) we find

$$W = Q_{3 \rightarrow 4} \eta = \frac{M_3^2 - M_4^2}{2nD} \frac{T_h - T_c}{T_h^2}.$$

Problem 2.5: Find the efficiency of the engine shown in Fig. 2.3 ([1] -Fig.2.18). Assume that

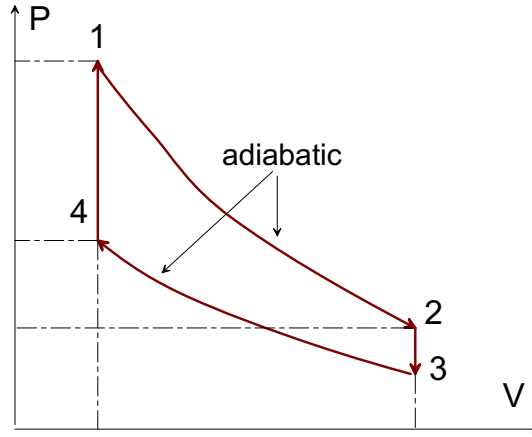


Figure 2.3: Sketch of the cycle.

the operating substance is an ideal monoatomic gas. Express your answer in terms of V_1 and V_2 . (The processes $1 \rightarrow 2$ and $3 \rightarrow 4$ are adiabatic. The processes $4 \rightarrow 1$ and $2 \rightarrow 3$ occur at constant volume).

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Solution 2.5: Let us start with the processes at constant volume. The mechanical work during these processes does not take place. Consequently,

$$\begin{aligned} Q_{2 \rightarrow 3} &= (3/2)nR(T_3 - T_2), \\ Q_{4 \rightarrow 1} &= (3/2)nR(T_1 - T_4), \\ W &= (3/2)nR(T_1 + T_3 - T_2 - T_4). \end{aligned}$$

The efficiency is given by the expression

$$\eta = \frac{T_1 + T_3 - T_2 - T_4}{T_1 - T_4} = 1 - \frac{T_2 - T_3}{T_1 - T_4}. \quad (2.4)$$

Now let us consider the adiabatic processes where $TV^{2/3} = \text{const}$ (monoatomic ideal gas!). Thus,

$$\frac{T_1}{T_2} = \frac{T_4}{T_3} = \left(\frac{V_2}{V_1} \right)^{2/3} \equiv \alpha.$$

Substituting this expression into Eq. (2.4) we obtain:

$$\eta = 1 - \frac{1}{\alpha} = 1 - \left(\frac{V_1}{V_2} \right)^{2/3}.$$

Problem 2.6: One kilogram of water is compressed isothermally at 20° C from 1 atm to 20 atm.

- (a) How much work is required?
- (b) How much heat is rejected?

Assume that the average isothermal compressibility of water during this process is $\kappa_T = 0.5 \times 10^{-4} \text{ (atm)}^{-1}$ and the average thermal expansivity of water during this process is $\alpha_P = 2 \times 10^{-4} \text{ (}^\circ\text{C)}^{-1}$.

Solution 2.6: Since for an isothermal process $dQ = T dS$ we have

$$Q = T \int_{P_1}^{P_2} \left(\frac{\partial S}{\partial P} \right)_T dP.$$

Using the Maxwell relation for the Gibbs free [see Eq. [1]-(2.112)] energy we obtain

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = -V\alpha_P.$$

Thus

$$Q = -T \int_{P_1}^{P_2} V(P)\alpha_T(P) dP$$

Now let us assume that α_T is P -independent, and

$$V(P) = V_0 [1 - \kappa_T(P - P_0)] = (M/\rho) [1 - \kappa_T(P - P_0)].$$

As a result,

$$Q = -(M/\rho)T\alpha_T(P_2 - P_1) [1 - \kappa_T(P - P_0)/2].$$

We see that since the compressibility of water is very low one can neglect the correction due to change in the volume and assume $V \approx M/\rho$. The mechanical work is

$$W = - \int_{P_1}^{P_2} P dV = - \int_{P_1}^{P_2} P \left(\frac{\partial V}{\partial P} \right)_T dP = (M/2\rho)\kappa_T(P_2^2 - P_1^2).$$

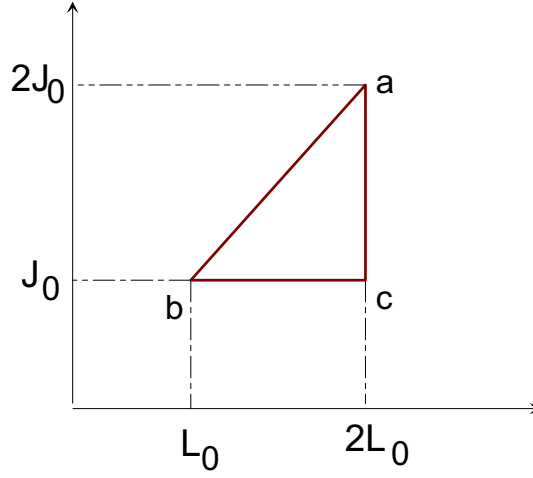


Figure 2.4:

Problem 2.7: Compute the efficiency of the heat engine shown in Fig. 2.4 (Fig. [1]-2.19). The engine uses a rubber band whose equation of state is

$$J = \alpha LT, \quad (2.5)$$

where α is a constant, J is the tension, L is the length per unit mass, and T is the temperature in Kelvins. The specific heat (heat capacity per unit mass) is a constant, $c_L = c$.

Solution 2.7: From Fig. 2.4 we see that the path $a \rightarrow b$ is *isothermal*. Indeed, since $J \propto L$, it follow from Eq. (2.5) that $T = \text{const}$. Then, from the same equation we get,

$$T_a = T_b = J_0/\alpha L_0, \quad T_c = J_0/2\alpha L_0 = T_a/2.$$

As a result,

$$Q_{b \rightarrow a} = M\alpha T_a \int_{L_0}^{2L_0} L dL = (3/2)M\alpha L_0^2 T_a = (3/2)MJ_0 L_0,$$

$$Q_{a \rightarrow c} = Mc(T_c - T_a) = -(1/2)McT_a,$$

$$Q_{c \rightarrow b} = Mc(T_b - T_c) - MJ_0 L_0 = (1/2)McT_a - MJ_0 L_0.$$

Hence, the total work is

$$W = Q_{b \rightarrow a} + Q_{a \rightarrow c} + Q_{c \rightarrow b} = (1/2)MJ_0 L_0$$

and

$$\eta = \frac{W}{Q_{b \rightarrow a}} = \frac{1}{3}.$$

This result is also clear from geometrical point of view.

Problem 2.8: Experimentally one finds that for a rubber band

$$\begin{aligned}\left(\frac{\partial J}{\partial L}\right)_T &= \frac{aT}{L_0} \left[1 + 2\left(\frac{L_0}{L}\right)^3\right], \\ \left(\frac{\partial J}{\partial T}\right)_L &= \frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L}\right)^3\right],\end{aligned}$$

where J is the tension, $a = 1.0 \times 10^3$ dyne/K, and $L_0 = 0.5$ m is the length of the band when no tension is applied. The mass of the rubber band is held fixed.

- (a) Compute $(\partial L/\partial T)_J$ and discuss its physical meaning.
- (b) Find the equation of state and show that dJ is an exact differential.
- (c) Assume that heat capacity at constant length is $C_L = 1.0$ J/K. Find the work necessary to stretch the band reversibly and adiabatically to a length 1 m. Assume that when no tension is applied, the temperature of the band is $T = 290$ K. What is the change in temperature?

Solution 2.8:

- (a) We have

$$\left(\frac{\partial L}{\partial T}\right)_J \cdot \left(\frac{\partial T}{\partial J}\right)_L \cdot \left(\frac{\partial J}{\partial L}\right)_T = -1.$$

Consequently,

$$\left(\frac{\partial L}{\partial T}\right)_J = - \left[\left(\frac{\partial T}{\partial J}\right)_L \cdot \left(\frac{\partial J}{\partial L}\right)_T \right]^{-1} = - \frac{\left(\frac{\partial J}{\partial T}\right)_L}{\left(\frac{\partial J}{\partial L}\right)_T} = - \frac{L}{T} \frac{1 - \left(\frac{L_0}{L}\right)^3}{1 + 2\left(\frac{L_0}{L}\right)^3}.$$

Physical meaning -

$$\alpha_J = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_J$$

is the thermal expansion coefficient at given tension.

- (b) The equation of state has the form

$$J = \frac{aTL}{L_0} \left[1 - \left(\frac{L_0}{L}\right)^3\right].$$

The proof of the exactness is straightforward.

(c) Consider adiabatic expansion of the band,

$$0 = dQ = C_L dT + J(L, T) dL.$$

Consequently,

$$\frac{dT}{dL} = -\frac{J(L, T)}{C_L} = -\frac{aTL}{C_L L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right].$$

Measuring length in units of L_0 as $L = \ell \cdot L_0$ and introducing $\beta \equiv aL_0/C_L$ we obtain the following differential equation

$$dT/T = -\beta \ell (1 - \ell^{-3}) d\ell.$$

Its solution is

$$\ln \frac{T_f}{T_0} = -\frac{\beta}{2} \left(\frac{L_f}{L_0} \right)^2 \left[1 + 2 \left(\frac{L_0}{L_f} \right)^3 \right].$$

Here L_f and T_f are final values of the length and temperature, respectively. This is the equation for adiabatic process which provides the change in the temperature. The mechanical work is then

$$W = C_L(T_f - T_0).$$

Problem 2.9: Blackbody radiation in a box of volume V and at temperature T has internal energy $U = aVT^4$ and pressure $P = (1/3)aT^4$, where a is the Stefan-Boltzmann constant.

- (a) What is the fundamental equation for the blackbody radiation (the entropy)?
- (b) Compute the chemical potential.

Solution 2.9:

- (a) Let us first find the Helmholtz free energy. From the relation $P = -\left(\frac{\partial A}{\partial V}\right)_T$ we get

$$A = -PV = -\frac{1}{3}aVT^4 = -\frac{1}{3}U.$$

Consequently,

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = \frac{4}{3}aVT^3 = \frac{4}{3} \frac{U}{T}.$$

As a result,

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{\partial(S, V)}{\partial(U, V)} = \frac{\partial(S, V)/\partial(T, V)}{\partial(U, V)/\partial(T, V)} = \frac{(\partial S/\partial T)_V}{(\partial U/\partial T)_V} = \frac{1}{T}.$$

- (b) Since A is N -independent, $\mu = 0$.

Problem 2.10: Two vessels, insulated from the outside world, one of volume V_1 and the other of volume V_2 , contain equal numbers N of the same ideal gas. The gas in each vessel is originally at temperature T_i . The vessels are then connected and allowed to reach equilibrium in such a way that the combined vessel is also insulated from the outside world. The final volume is $V = V_1 + V_2$. What is the maximum work, δW_{free} , that can be obtained by connecting these insulated vessels? Express your answer in terms of T_i , V_1 , V_2 , and N .

Solution 2.10: The Gibbs free energy of an ideal gas is given by the equation

$$G = NkT \ln P + N\chi(T)$$

where $\chi(T)$ is some function of the gas excitation spectrum.¹

Consequently,

$$S = - \left(\frac{\partial G}{\partial T} \right)_P = -Nk \ln P - N\chi'(T).$$

Before the vessels are connected,

$$S_i = -Nk \ln(P_1 P_2) - 2N\chi'(T).$$

After the vessels are connected the temperature remains the same, as it follows from the conservation law, the entropy being

$$S_f = -2Nk \ln P - 2N\chi'(T).$$

Consequently, $\Delta S = -Nk \ln(P^2/P_1 P_2)$. On the other hand,

$$\frac{1}{P} = \frac{V_1 + V_2}{2NkT_i}, \quad \frac{1}{P_i} = \frac{V_i}{NkT_i} \quad \rightarrow \quad \frac{P^2}{P_1 P_2} = \frac{4V_1 V_2}{(V_1 + V_2)^2}.$$

¹ For an ideal gas, the energy of the particle can be written as a sum of the kinetic energy, $\epsilon_{\mathbf{p}} = \mathbf{p}^2/2m$, and the energy of internal excitations, ϵ_{α} (characterized by some quantum numbers α),

$$\epsilon_{\mathbf{p}\alpha} = \epsilon_{\mathbf{p}} + \epsilon_{\alpha}.$$

As we will see later, the free energy of the ideal gas can be constructed as

$$\begin{aligned} A &= -\frac{kT}{N!} \ln \left(\sum_{\mathbf{p}\alpha} e^{-\epsilon_{\mathbf{p}\alpha}/kT} \right)^N \approx -NkT \ln \left[\frac{eV}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \sum_{\alpha} e^{-\epsilon_{\alpha}/kT} \right] \\ &= -NT \ln(eV/N) + Nf(T), \\ f(T) &= -kT \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \sum_{\alpha} e^{-\epsilon_{\alpha}/kT} \right]. \end{aligned}$$

The Gibbs free energy is then

$$G = A + PV = NkT \ln P + N\chi(T), \quad \chi(T) \equiv f(T) - kT \ln kT.$$

As a result, the maximum work is

$$\Delta W_{free} = T_i \Delta S = NkT_i \ln \frac{(V_1 + V_2)^2}{4V_1 V_2}.$$

Problem 2.11: For a low-density gas the virial expansion can be terminated at first order in the density and the equation of state is

$$P = \frac{NkT}{V} \left[1 + \frac{N}{V} B_2(T) \right],$$

where $B_2(T)$ is the second virial coefficient. The heat capacity will have corrections to its ideal gas value. We can write it in the form

$$C_{V,N} = \frac{3}{2}Nk - \frac{N^2 k}{V} f(T).$$

- (a) Find the form that $f(T)$ must have in order for the two equations to be thermodynamically consistent.
- (b) Find $C_{P,N}$.
- (c) Find the entropy and internal energy.

Solution 2.11:

- (c) The equation of state under consideration can be obtained from the Helmholtz free energy²

$$A = A_{ideal} + kTB_2(T) \frac{N^2}{V}.$$

Then

$$S = - \left(\frac{\partial A}{\partial T} \right)_V = S_{ideal} + \delta S, \quad \delta S \equiv -k \frac{N^2}{V} [B_2(T) + TB'_2(T)].$$

Since we know both entropy and Helmholtz free energy, we find the internal energy as

$$\begin{aligned} U &= A + TS = U_{ideal} + kTB_2(T) \frac{N^2}{V} - kT \frac{N^2}{V} [B_2(T) + TB'_2(T)] \\ &= U_{ideal} + \delta U, \quad \delta U \equiv -kT^2 B'_2(T) \frac{N^2}{V}. \end{aligned}$$

²Remember that $P = - \left(\frac{\partial A}{\partial V} \right)_T$.

(a) As a result,

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = C_V^{\text{ideal}} + \delta C_V, \quad \delta C_V \equiv -kT \frac{N^2}{V} [2B'_2(T) + TB''_2(T)].$$

We find in this way,

$$f(T) = 2TB'_2(T) + T^2B''_2(T).$$

(b) Let us express the equation of state as $V(P, T)$. Since the density is assumed to be small in the correction one can use equation for the ideal gas to find the the volume. We have,

$$V = \frac{NkT}{P} + NB_2(T).$$

Consequently, the entropy can be expressed as

$$S = S_{\text{ideal}} + \delta S_1, \quad \delta S_1 \equiv -kN \frac{B_2 + TB'_2}{kT/P + B_2}.$$

Now

$$\begin{aligned} C_P &= C_P^{\text{ideal}} + T \left(\frac{\partial \delta S_1}{\partial T} \right)_P \\ &= -kN \frac{(B_2 + TB'_2)'(kT/P + B_2) - (k/P + B'_2)(B_2 + TB'_2)}{(kT/P + B_2)^2} \\ &= C_P^{\text{ideal}} - k \frac{N^2}{V} [T(2B'_2 + TB''_2) - (B_2 + TB'_2)] \\ &= C_P^{\text{ideal}} + \delta C_V + k \frac{N^2}{V} (B_2 + TB'_2). \end{aligned}$$

Here in all corrections we used equation of state for an ideal gas. As a result,

$$C_P - C_V = (C_P - C_V)^{\text{ideal}} + k \frac{N^2}{V} (B_2 + TB'_2).$$

Problem 2.12: Prove that

$$C_{Y,N} = \left(\frac{\partial H}{\partial T} \right)_{Y,N} \quad \text{and} \quad \left(\frac{\partial H}{\partial Y} \right)_{T,N} = T \left(\frac{\partial X}{\partial T} \right)_{Y,N} - X.$$

Solution 2.12: Let us first recall definitions for X , Eq. ([1]-2.66), $U = ST + YX + \sum_j j\mu'_j dN_j$. The enthalpy is defined as

$$H = U - XY = ST + \sum_j \mu'_j dN_j.$$

Since $dU = T dS + Y dX$ we get

$$dH = T dS - X dY.$$

Consequently,

$$C_{Y,N} = T \left(\frac{\partial S}{\partial T} \right)_{Y,N} = \left(\frac{\partial H}{\partial T} \right)_{Y,N}.$$

To prove the second relation we do the following

$$\left(\frac{\partial H}{\partial Y} \right)_{T,N} = \left(\frac{\partial H}{\partial Y} \right)_{S,N} + \left(\frac{\partial H}{\partial S} \right)_{Y,N} \left(\frac{\partial S}{\partial Y} \right)_T.$$

Now,

$$\left(\frac{\partial H}{\partial Y} \right)_{S,N} = -X, \quad \left(\frac{\partial H}{\partial S} \right)_{Y,N} = T.$$

Now we have to use the Maxwell relation, which emerges for the *Gibbs* free energy $G = H - TS$. From

$$dG = -S dT - X dY$$

we get

$$\left(\frac{\partial S}{\partial Y} \right)_T = \left(\frac{\partial X}{\partial T} \right)_{Y,N}.$$

Thus we obtain the desired result.

Problem 2.13: Compute the entropy, enthalpy, Helmholtz free energy, and Gibbs free energy for a paramagnetic substance and write them explicitly in terms of their natural variables if possible. Assume that mechanical equation of state is $m = (D/T)H$ and the the molar heat capacity at constant magnetization is $c_m = c$, where m is the molar magnetization, H is the magnetic field, D is a constant, c is a constant, and T is the temperature.

Solution 2.13: Let us start with the internal energy $u(T, m)$ per one mole. We have the magnetic contribution $u_{\text{mag}} = \int_0^m H(m) dm$. Since $H(m) = (T/D)m$ we get $u_{\text{mag}} = (T/2D)m^2$. The “thermal” contribution is cT . As a result,

$$u(T, m) = T(c + m^2/2D), \quad T(u, m) = \frac{u}{c + m^2/2D}.$$

The molar entropy s is then derived from the definition

$$\left(\frac{\partial s}{\partial u} \right)_m = \frac{1}{T} = \frac{c + m^2/2D}{u} \rightarrow s(u, m) = (c + m^2/2D) \ln(u/u_0).$$

Here u_0 is a constant. As a result, in “natural” variables

$$u(s, m) = u_0 \exp \left(\frac{s}{c + m^2/2D} \right).$$

To find other thermodynamic potentials we need $s(T, m)$. We can rewrite the above expression for the entropy as

$$s(T, m) = (c + m^2/2D) \ln \frac{T(c + m^2/2D)}{u_0}.$$

In particular, the Helmholtz free energy is

$$a(T, m) = u - Ts = T(c + m^2/2D) \left[1 - \ln \frac{T(c + m^2/2D)}{u_0} \right].$$

To get enthalpy we have to subtract from u the quantity $Hm = (D/T)H^2$ and to express m through H as $m = (D/T)H$. As a result, we obtain:

$$h(T, H) = u - Hm = T(c + DH^2/2T^2) - (D/T)H^2 = T(c - DH^2/2T^2).$$

Finally, Gibbs free energy is $g = a - Hm$, which has to be expressed through T and H . We get

$$\begin{aligned} g &= a - Hm = T(c + DH^2/2T^2) \left[1 - \ln \frac{T(c + DH^2/2T^2)}{u_0} \right] - (D/T)H^2 \\ &= T(c - DH^2/2T^2) - T(c + DH^2/2T^2) \ln \frac{T(c + DH^2/2T^2)}{u_0}. \end{aligned}$$

Problem 2.14: Compute the Helmholtz free energy for a van der Waals gas. The equation of state is

$$\left(P + \alpha \frac{n^2}{V^2} \right) (V - nb) = nRT,$$

where α and b are constants which depend on the type of gas and n is the number of moles. Assume that heat capacity is $C_{V,n} = (3/2)nR$.

Is this a reasonable choice for the heat capacity? Should it depend on volume?

Solution 2.14: Let us express pressure through the volume,

$$P = \frac{nRT}{V - nb} - \frac{\alpha n^2}{V^2}.$$

Since $P = -\partial A / \partial V$ we obtain

$$A = - \int P(V) dV = -nRT \ln(V - nb) - (\alpha n^2/V) + \mathcal{A}(T).$$

Here $\mathcal{A}(T)$ is the integration constant, which can be found from the given specific heat. Indeed,

$$S = \int^T \frac{C_{V,n} dT'}{T'} = (3/2)nR \ln(T/T_0).$$

Consequently,

$$\mathcal{A}(T) = - \int^T S(T') dT' = (3/2)nRT[1 - \ln(T/T_0)].$$

Here we omit temperature-independent constant.

The suggestion regarding specific heat is OK since the difference between the entropies of van der Waals gas and the ideal gas is *temperature independent*. (Check!)

Problem 2.15: Prove that

(a) $\kappa_T(C_P - C_V) = TV\alpha_P^2$

(b) $C_P/C_V = \kappa_T/\kappa_S$.

Solution 2.15: We use the method of Jacobians:

(a)

$$\begin{aligned} C_V &= T(\partial S/\partial T)_V = T\partial(S,V)/\partial(T,V) = \frac{\partial(S,V)/\partial(T,P)}{\partial(T,V)/\partial(T,P)} \\ &= T \frac{(\partial S/\partial T)_P(\partial V/\partial P)_T - (\partial S/\partial P)_T(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \\ &= C_P - T \frac{(\partial S/\partial P)_T(\partial V/\partial T)_P}{(\partial V/\partial P)_T}. \end{aligned}$$

Now, from the Maxwell relations $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$. Thus,

$$C_P - C_V = -T \frac{[(\partial V/\partial T)_P]^2}{(\partial V/\partial P)_T} = TV \frac{\alpha_P^2}{\kappa_T}.$$

The first relation follows from this in a straightforward way from definitions.

(b) Let us first calculate the adiabatic compressibility $(\partial V/\partial P)_S$ as

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{\partial(V,S)}{\partial(P,S)} = \frac{\partial(V,S)/\partial(V,T)}{\partial(P,S)/\partial(P,T)} \cdot \frac{\partial(V,T)}{\partial(P,T)} = \frac{(\partial S/\partial T)_V}{(\partial S/\partial T)_P} \cdot \left(\frac{\partial V}{\partial P}\right)_T.$$

Consequently,

$$\frac{C_P}{C_V} = \frac{(\partial V/\partial P)_T}{(\partial V/\partial P)_S} = \frac{\kappa_T}{\kappa_S}.$$

Problem 2.16: Show that

$$T ds = c_x (\partial T / \partial Y)_x dY + c_Y (\partial T / \partial x)_Y dx,$$

where $x = X/n$ is the amount of extensive variable, X , per mole, c_x is the heat capacity per mole at constant x , and c_Y is the heat capacity per mole at constant Y .

Solution 2.16: Let us substitute the definitions

$$c_x = T (\partial S / \partial T)_x, \quad c_Y = T (\partial S / \partial T)_Y.$$

Now the combination $c_x (\partial T / \partial Y)_x dY + c_Y (\partial T / \partial x)_Y dx$ can be rewritten as

$$\begin{aligned} T (\partial S / \partial T)_x (\partial T / \partial Y)_x dY + T (\partial S / \partial T)_Y (\partial T / \partial x)_Y dx \\ = T (\partial S / \partial Y)_x dY + T (\partial S / \partial x)_Y dx = T ds. \end{aligned}$$

Problem 2.17: Compute the molar heat capacity c_P , the compressibilities, κ_T and κ_S , and the thermal expansivity α_P of a monoatomic van der Waals gas. Start from the fact that the mechanical equation of state is

$$P = \frac{RT}{v-b} - \frac{\alpha}{v^2}.$$

and the molar heat capacity is $c_v = 3R/2$, where $v = V/n$ is the molar volume.

Solution 2.17: Let us start with the specific heat. Using the method similar to the Problem 2.15 we can derive the relation

$$c_P - c_v = -T \frac{[(\partial P / \partial T)_v]^2}{(\partial P / \partial v)_T} = \frac{R}{1 - 2\alpha(v-b)^2 / RTv^3}.$$

Now let us compute the compressibility

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = -\frac{1}{v} \left(\frac{\partial P}{\partial v} \right)_T^{-1} = \frac{(v-b)^2}{vRT} \frac{1}{1 - 2\alpha(v-b)^2 / RTv^3}.$$

Given c_v , other quantities can be calculated using results of the Problem 2.15.

Problem 2.18: Compute the heat capacity at constant magnetic field $C_{H,n}$, the susceptibilities $\chi_{T,n}$ and $\chi_{S,n}$, and the thermal expansivity $\alpha_{H,n}$ for a magnetic system, given that the mechanical equation of state is $M = nDH/T$ and the heat capacity $C_{M,n} = nc$, where M is the magnetization, H is the magnetic field, n is the number of moles, c is the molar heat capacity, and T is the temperature.

Solution 2.18: Let us start with susceptibilities. By definition,

$$\chi_{T,n} = \left(\frac{\partial M}{\partial H} \right)_{T,n} = \frac{nD}{T}.$$

Now,

$$\left(\frac{\partial M}{\partial H} \right)_S = \frac{\partial(M,S)}{\partial(H,S)} = \frac{\partial(M,S)/\partial(M,T)}{\partial(H,S)/\partial(H,T)} \cdot \frac{\partial(M,T)}{\partial(H,T)} = \chi_{T,n} \frac{C_{M,n}}{C_{H,n}}.$$

Thus we have found one relation between susceptibilities and heat capacities,

$$\frac{\chi_{S,n}}{\chi_{T,n}} = \frac{C_{M,n}}{C_{H,n}}.$$

Now let us find $C_{H,n}$. At constant H , M becomes dependent only on temperature. Then,

$$dM = \frac{dM}{dT} dT = -\frac{nDH}{T^2} dT.$$

Consequently, the contribution to the internal energy is

$$dU = -H dM = \frac{nDH^2}{T^2} dT.$$

As a result,

$$C_{H,n} - C_{M,n} = \frac{nDH^2}{T^2}.$$

Given $C_{H,n} = nc$ we easily compute $C_{H,n}$ and $\chi_{S,n}$.

According to Eq. (R2.149), α_H is defined as

$$\alpha_H = \left(\frac{\partial M}{\partial T} \right)_H = -\frac{nDH}{T^2}.$$

Problem 2.19: A material is found to have a thermal expansivity $\alpha_P = v^{-1}(R/P + a/RT^2)$ and an isothermal compressibility $\kappa_T = v^{-1}[Tf(P) + b/P]$. Here $v = V/n$ is the molar volume.

- (a) Find $f(P)$.
- (b) Find the equation of state.
- (c) Under what condition this materials is stable?

Solution 2.19:

(a) By definition, we have

$$\begin{aligned}\frac{\partial v}{\partial T} &= \frac{R}{P} + \frac{a}{RT^2} \cdot \\ \frac{\partial v}{\partial P} &= -Tf(P) - \frac{b}{P}.\end{aligned}$$

To make dv an exact differential we need:

$$-\frac{R}{P^2} = -f(p).$$

Thus

$$f(p) = R/P^2.$$

(b) We can reconstruct the equation of state as:

$$\begin{aligned}v &= \int^P \frac{\partial v}{\partial P} dP = \int^P dP \left[-\frac{RT}{P^2} - \frac{b}{P} \right] \\ &= \frac{RT}{P} - b \ln P + g(T).\end{aligned}$$

Here $g(T)$ is some function of the temperature. Now,

$$\frac{\partial v}{\partial T} = \frac{R}{P} + g'(T) \equiv \frac{R}{P} + \frac{a}{RT^2}.$$

Thus $g(T) = -a/RT + \text{const.}$ As a result, we can express the equation of state as

$$v - v_0 = \frac{RT}{P} + b \ln \frac{P_0}{P} - \frac{a}{RT}.$$

(c) Since the compressibility must be positive, we have the stability condition

$$Tf(P) + \frac{b}{P} > 0 \quad \rightarrow \quad \frac{TR}{P^2} + \frac{b}{P} > 0.$$

Consequently, the stability condition is

$$P/T < R/b.$$

Problem 2.20: Compute the efficiency of the reversible two heat engines in Fig. 2.5 (R2.20). Which engine is the most effective? (Note that these are not Carnot cycles. The efficiency of a heat engine is $\eta = \Delta W_{\text{total}} / \Delta Q_{\text{absorbed}}$.)

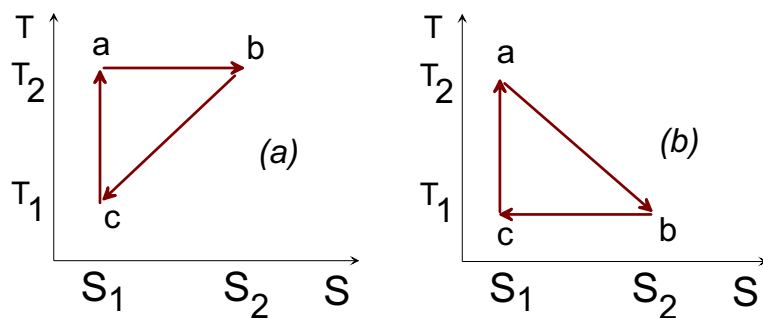


Figure 2.5:

Solution 2.20: Since $dQ = T dS$, we immediately get for any closed path in the $T - S$ plane:

$$\Delta W_{total} = \oint T dS.$$

This is just the area of the triangle,

$$\Delta W_{total} = (1/2)(T_2 - T_1)(S_2 - S_1).$$

The heat absorbed in the case (a) is

$$\Delta Q_{absorbed} = T_2(S_2 - S_1).$$

Thus,

$$\eta_a = \frac{T_2 - T_1}{2T_2}.$$

In the case (b), it easy to show that

$$\Delta Q_{absorbed} = (1/2)(T_2 + T_1)(S_2 - S_1).$$

Thus

$$\eta_b = \frac{T_2 - T_1}{T_2 + T_1} > \eta_a.$$

Problem 2.21: It is found for a gas that $\kappa_T = Tvf(P)$ and $\alpha_P = Rv/P + Av/T^2$, where T is the temperature, v is the molar volume, P is the pressure, A is a constant, and $f(P)$ is unknown function.

(a) What is $f(P)$?

(b) Find $v = v(P, T)$.

Solution 2.21: The solution is similar to the problem 2.19. We have:

$$\begin{aligned}\frac{\partial v}{\partial T} &= v^2 \left(\frac{R}{P} + \frac{A}{T^2} \right), \\ \frac{\partial v}{\partial P} &= -v^2 T f(P).\end{aligned}$$

Let us introduce $\gamma(P, T) \equiv [v(P, T)]^{-1}$. We get,

$$\begin{aligned}\frac{\partial \gamma}{\partial T} &= -\frac{R}{P} - \frac{A}{T^2}, \\ \frac{\partial \gamma}{\partial P} &= T f(P).\end{aligned}$$

Again, from the Maxwell relation we get $\frac{R}{P^2} = f(P)$. Then we can express γ as

$$\gamma = \int^P \frac{\partial \gamma}{\partial P} dP = TR \int^P \frac{dP}{P^2} = -\frac{RT}{P} + g(T).$$

Then, $g'(T) = -A/T^2$, or $g(T) = A/T + \text{const}$. As a result,

$$\gamma = \gamma_0 + \frac{A}{T} - \frac{RT}{P}.$$

Consequently,

$$v(P, T) = \frac{1}{\gamma_0 + A/T - RT/P}.$$

Problem 2.22: A monomolecular liquid at volume V_L and pressure P_L is separated from a gas of the same substance by a rigid wall which is permeable to the molecules, but does not allow liquid to pass. The volume of the gas is held fixed at V_G , but the volume of the liquid can be varied by moving a piston. If the pressure of the liquid is increased by pushing in on the piston, by how much does the pressure of the gas change? [Assume the liquid is incompressible (its *molar volume* is independent of the pressure) and describe the gas by the ideal gas equation of state. The entire process occurs at fixed temperature T].

Solution 2.22: Let us consider the part of the system, which contains both liquid and gas particles. In this part the chemical potentials must be equal, $\mu_L = \mu_G$. On the other hand, the chemical potentials and pressures of gas in both parts must be equal. Thus we arrive at the equation,

$$\mu_L(P_L, T) = \mu_G(P_G, T).$$

If one changes the pressure of liquid by δP_L , then

$$\left(\frac{\partial \mu_L}{\partial P_L} \right)_T \delta P_L = \left(\frac{\partial \mu_G}{\partial P_G} \right)_T \delta P_G.$$

For an ideal gas, $(\partial\mu/\partial P)_T = kT/P_G = V_G/N_G \equiv \tilde{v}_L$. the quantity \tilde{v}_L has a physical meaning of the *volume per particle*. For a liquid, the relation is the same,

$$\left(\frac{\partial\mu}{\partial P}\right)_T = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial N}\right)_{P,T} = \frac{\partial}{\partial N} \left(\frac{\partial G}{\partial P}\right)_{N,T} = \left(\frac{\partial V}{\partial N}\right)_T = \tilde{v}_L.$$

The last relation is a consequence of *incompressible* character of the liquid. As a result,

$$\frac{\delta P_G}{\delta P_L} = \frac{\tilde{v}_L}{\tilde{v}_G}.$$

2.1 Additional Problems: Fluctuations

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Problem 2.23: Find the mean square fluctuation of the internal energy (using V and T as independent variables). What is the mean square fluctuation of the internal energy for a monoatomic ideal gas?

Solution 2.23: We have

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_T \Delta V + \left(\frac{\partial U}{\partial T}\right)_V \Delta T = \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] \Delta V + C_V \Delta T.$$

Here we use Maxwell relation which can be obtained from Helmholtz free energy. Squaring and averaging we obtain (note that $\langle \Delta V \Delta T \rangle = 0$)

$$\langle (\Delta U)^2 \rangle = \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right]^2 \langle (\Delta V)^2 \rangle + C_V^2 \langle (\Delta T)^2 \rangle.$$

Now,

$$\langle (\Delta T)^2 \rangle = kT^2/C_V, \quad \langle (\Delta V)^2 \rangle = -kT \left(\frac{\partial V}{\partial P}\right)_T.$$

Thus

$$\langle (\Delta U)^2 \rangle = -kT \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right]^2 \left(\frac{\partial V}{\partial P}\right)_T + C_V kT^2.$$

For the ideal gas,

$$P = NkT/V, \quad C_V = (3/2)Nk.$$

Thus,

$$\langle (\Delta U)^2 \rangle = (3/2)N(kT)^2.$$
