

Problem 1.

- a) Using the definitions of c_p and c_v and the first law of thermodynamics and the, derive the general relation:

$$c_p - c_v = \left[P + \left(\frac{\partial E}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p,$$

where c_p and c_v are the specific heat capacities at constant pressure and volume, respectively, and E and V are the internal energy and volume of 1 mol.

Solution:

The first law relates $dE = dQ - PdV$

At constant volume: $c_v = \left(\frac{\partial Q}{\partial T} \right)_v \rightarrow c_v = \left(\frac{\partial E}{\partial T} \right)_v,$

At constant pressure: $dQ = dE + PdV = dE + d(PV) - VdP = d(E + PV) = dH \rightarrow$

$$c_p = \left(\frac{\partial Q}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial E}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p$$

For $E=E(T,V)$ $dE = \left(\frac{\partial E}{\partial T} \right)_v dT + \left(\frac{\partial E}{\partial V} \right)_T dV$, dividing throughout by dT at a constant pressure:

$$\left(\frac{\partial E}{\partial T} \right)_p = \left(\frac{\partial E}{\partial T} \right)_v + \left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p, \text{ thus}$$

$$c_p - c_v = \left(\frac{\partial E}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_v = \left(\frac{\partial E}{\partial T} \right)_v + \left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_v$$

$$c_p - c_v = \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_p$$

- b) From the fundamental differential relation for dE and the differential relation for Helmholtz free energy $dF = -SdT - PdV$ show that for a constant number of particles:

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

Solution:

The fundamental differential relation $dE = TdS - PdV$

Taking partial derivative with respect to volume with $T=\text{const}$: $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

Rearranging $\left(\frac{\partial E}{\partial V}\right)_T + P = T\left(\frac{\partial S}{\partial V}\right)_T$

From $dF = -SdT - PdV$ $-S = \left(\frac{\partial F}{\partial T}\right)_V$ and $-P = \left(\frac{\partial F}{\partial V}\right)_T$

Differentiating with respect to the other variables:

$$-\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 F}{\partial V \partial T} \quad \text{and} \quad -\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial^2 F}{\partial T \partial V}$$

One arrives at Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, with which

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

c) Use the above results to find $c_p - c_v$ for Ideal Gas

Solution:

Combining results from a) and b) one gets

$$c_p - c_v = \left[\left(\frac{\partial E}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial T}\right)_P = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Pressure equation of state for one mol of ideal gas is $PV = RT$, thus

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}, \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}, \quad c_p - c_v = T \frac{R}{V} \frac{R}{P} = \frac{TR^2}{RT} = R$$

d) Use the above results to find $c_p - c_v$ a Van der Waals gas $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

Solution:

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2}, \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V-b)}$$

$$T = \frac{\left(P + \frac{a}{V^2}\right)(V-b)}{R}, \quad \left(\frac{\partial T}{\partial V}\right)_P = \frac{P - \frac{a}{V^2} + \frac{2ab}{V^3}}{R} = \frac{\frac{RT}{(V-b)} - \frac{2a(V-b)}{V^3}}{R}$$

$$\text{Then, } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\frac{RT}{(V-b)} - \frac{2a(V-b)}{V^3}}$$

$$c_p - c_v = T \frac{R}{(V-b)} \frac{R}{\frac{RT}{(V-b)} - \frac{2a(V-b)}{V^3}} = \frac{TR^2}{RT - 2a(V-b)^2/V^3} = \frac{R}{1 - 2a(V-b)^2/V^3RT}$$

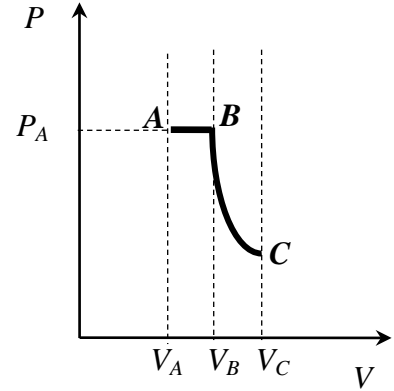
e) Show that at a constant pressure in the limit $V \rightarrow \infty$ the result for $c_p - c_v$ of a Van der Waals gas is the same as for $c_p - c_v$ of an ideal gas.

Solution:

$$c_p - c_v \xrightarrow{V \rightarrow \infty} \frac{R}{1 - 2a(V-b)^2/V^3RT} \xrightarrow{V \rightarrow \infty} \frac{R}{1 + O(2)} \approx R$$

Problem 2.

The initial state of monoatomic ideal gas is described by T_A , P_A and V_A (the temperature, pressure, and volume, respectively). The gas is taken over the path $A \rightarrow B \rightarrow C$ quasistatically as shown in the sketch. The volumes are related as $V_B = 1.5V_A, V_C = 2V_A$. Find:



- a) How much work does the gas do on the path $A \rightarrow B$ and what is the change in its internal energy?

Solution:

$$\text{External work: } W = P_A (V_B - V_A) = \frac{1}{2} P_A V_A$$

The change in external energy:

$$\Delta E = \frac{3}{2} nR \Delta T = \frac{3}{2} nR \left(\frac{P_B V_B}{nR} - \frac{P_A V_A}{nR} \right) = \frac{3}{2} P_A (V_B - V_A) = \frac{3}{4} P_A V_A$$

- b) How much heat is absorbed in going from $A \rightarrow B$?

Solution:

$$\text{From the first law: } dE = dQ - PdV, \quad Q = \Delta E + W = \frac{3}{4} P_A V_A + \frac{1}{2} P_A V_A = \frac{5}{4} P_A V_A$$

- c) Derive the expression for the entropy change for an arbitrary process $B \rightarrow C$.

Solution:

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV, \quad \text{with } \left(\frac{\partial S}{\partial T} \right)_V = \frac{nc_v}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}$$

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

$$\Delta S = \int_{T_B}^{T_C} \frac{nc_v}{T} dT + \int_{V_B}^{V_C} \frac{nR}{V} dV = nc_v \ln \frac{T_C}{T_B} + nR \ln \frac{V_C}{V_B} = nc_v \ln \frac{T_C}{T_B} + n[c_p - c_v] \ln \frac{V_C}{V_B} = nc_v \ln \frac{T_C V_C^{\gamma-1}}{T_B V_B^{\gamma-1}} = 0,$$

since $TV^{\gamma-1} = \text{const}$ for adiabatic reversible process.

- d) If $B \rightarrow C$ is an adiabatic process, find the final gas pressure and the entropy change (from the general expression obtained in part c).

Solution: For adiabatic expansion of ideal gas $PV^\gamma = \text{const}$, with $\gamma = \frac{C_p}{C_v} = 5/3$

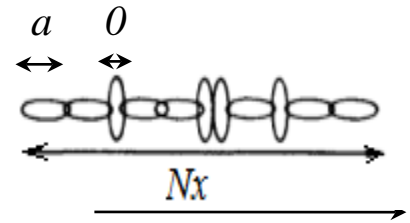
$$\text{Then } P_B V_B^\gamma = P_C V_C^\gamma, P_C = P_A \left(\frac{V_B}{V_C} \right)^\gamma = P_A \left(\frac{1.5}{2.0} \right)^{\frac{5}{3}} \approx 0.62 P_A$$

If the process is reversible, one expects $\Delta S = 0$.

$$\Delta S = n c_v \ln \frac{T_C}{T_B} + n [c_p - c_v] \ln \frac{V_C}{V_B} = n c_v \ln \frac{T_C V_C^{\gamma-1}}{T_B V_B^{\gamma-1}} = 0$$

Problem 3.

Consider a one-dimensional chain consisting on $N \gg 1$ segments as illustrated in the sketch. Let the length of each segment be a when the long dimension is parallel to the chain and zero when the segment is vertical (i.e. long dimension is perpendicular to the chain direction). Each segment has just two states, horizontal and vertical, and each of these states is not degenerate. The distance between the chain ends is fixed.



- a) For a given length $L=Nl$ ($0 < l < a$) of chain what is the total number of microstates accessible by the system and what is the entropy of the system as a function of l ?

Solution:

For the chain length to be Nl , there will be $m=Nl/a$ horizontal segments, so that total number of possible microstates is:

$$\Omega = C_m^N \frac{N!}{m!(N-m)!}, \text{ then } S = k \ln \Omega = k \ln \left[\frac{N!}{\left(\frac{Nl}{a}\right)! \left(N - \frac{Nl}{a}\right)!} \right]$$

- b) Write down the appropriate thermodynamic identity for the system (equivalent to the first law) and describe (qualitatively) how one could obtain an expression for tension force F , necessary to maintain the length Nl (assuming the joints turn freely), from the result obtained in part a)

Solution:

The appropriate thermodynamic identity is $dE = TdS + Fdl$

It follows, that $F = \left(\frac{\partial E}{\partial l}\right)_S$ and $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_l$

Using the reciprocity relation $\left(\frac{\partial S}{\partial E}\right)_l \left(\frac{\partial E}{\partial l}\right)_S \left(\frac{\partial l}{\partial S}\right)_E = -1$, one gets $F = -T \left(\frac{\partial S}{\partial l}\right)_E$ which could be calculated from the result for S in part a).

- c) Obtain the relationship between that tension force F maintaining the distance Nl and the temperature T using the canonical ensemble description.

Solution:

Energy contribution for a horizontal link is $e = Fa$, thus average link length is

$$l = \frac{0e^{0/kT} + ae^{Fa/kT}}{1 + e^{Fa/kT}}, \text{ for } N \text{ links: } Nl = \frac{Na e^{Fa/kT}}{1 + e^{Fa/kT}} = \frac{Na}{e^{-Fa/kT} + 1},$$

$$l = \frac{a}{e^{-Fa/kT} + 1}, \quad e^{-Fa/kT} = \left(\frac{a}{l} - 1 \right), \quad F = \frac{kT}{a} \ln \left(\frac{l}{a-l} \right)$$

d) Under which conditions does your answer lead to Hooke's law and what is corresponding expression for the spring constant?

At high T or low F $\frac{Fa}{kT} \rightarrow 0, \quad e^{\frac{Fa}{kT}} \approx 1 + \frac{Fa}{kT}$

$$l = \frac{ae^{Fa/kT}}{1 + e^{Fa/kT}} \approx \frac{a(1 + Fa/kT)}{2 + Fa/kT} = \frac{a(1 + Fa/kT)(2 - Fa/kT)}{(2 + Fa/kT)(2 - Fa/kT)} \approx \frac{a}{2} + \frac{a^2 F}{2kT},$$

$$F = \left(l - \frac{a}{2} \right) \cdot C, \text{ with spring constant } C = \frac{2kT}{a^2}$$

Problem 4.

A system of two energy levels E_0 and E_1 is populated by N particles at temperature T . Assume that $E_1 > E_0$, so that $\Delta E = E_1 - E_0$ is positive.

a) Derive an expression for the average energy per particle as function of temperature.

$$e = \frac{E}{N} = \frac{E_0 e^{-\beta E_0} + E_1 e^{-\beta E_1}}{e^{-\beta E_0} + e^{-\beta E_1}} = \frac{E_0 + E_1 e^{-\beta \Delta E}}{1 + e^{-\beta \Delta E}}$$

b) Determine the limiting behavior and value for average energy per particle in the limits of $T \rightarrow 0$ and $T \rightarrow \infty$.

For $T \rightarrow 0, \beta \rightarrow \infty$, so

$$e = \frac{E_0 + E_1 e^{-\beta \Delta E}}{1 + e^{-\beta \Delta E}} = (E_0 + E_1 e^{-\beta \Delta E}) \frac{(1 - e^{-\beta \Delta E})}{(1 + e^{-\beta \Delta E})(1 - e^{-\beta \Delta E})} \approx (E_0 + E_1 e^{-\beta \Delta E})(1 - e^{-\beta \Delta E}) \approx E_0 + \Delta E e^{-\beta \Delta E}$$

With a limiting value $\lim_{T \rightarrow 0} e = E_0$

For $T \rightarrow \infty$, $\beta \rightarrow 0$, so

$$e = \frac{E_0 + E_1 e^{-\beta \Delta E}}{1 + e^{-\beta \Delta E}} \approx \frac{E_0 + E_1 (1 - \beta \Delta E)}{(2 - \beta \Delta E)} = \frac{1}{2} \frac{(E_0 + E_1 (1 - \beta \Delta E)) \left(1 + \frac{\beta \Delta E}{2}\right)}{\left(1 - \frac{\beta \Delta E}{2}\right) \left(1 + \frac{\beta \Delta E}{2}\right)} \approx \frac{1}{2} (E_0 + E_1) - \frac{1}{4} \beta \Delta E^2$$

With a limiting value $\lim_{T \rightarrow \infty} e = \frac{(E_0 + E_1)}{2}$

c) Derive an expression for specific heat of the system.

$$\text{For 1 mole: } C = N_A \frac{\partial e}{\partial T} = N_A \frac{\partial e}{\partial \beta} \frac{\partial \beta}{\partial T} = R \left(\frac{\Delta E}{kT} \right)^2 \frac{e^{-\beta \Delta E}}{(1 + e^{-\beta \Delta E})^2}$$

d) Compute specific heat in the limits of $T \rightarrow 0$ and $T \rightarrow \infty$.

$$\text{For } T \rightarrow 0: C \approx R \left(\frac{\Delta E}{kT} \right)^2 e^{-\beta \Delta E},$$

$$\text{For } T \rightarrow \infty: C \approx \frac{R}{4} \left(\frac{\Delta E}{kT} \right)^2$$

Problem 5.

Consider an ideal gas of N spin- $1/2$ fermions is confined to an area A in 2 dimensions. Consider the ground state ($T=0$) for such system.

a) Derive the expression for the number of single particle microstates in the momentum interval $p, p+dp$ for the given system.

$$\text{Solution: In 2D, } \Gamma(n) = \frac{1}{4} \pi n^2, \bar{k} = (n_1, n_2) \frac{\pi}{L}, \Gamma(k) = \frac{1}{4} \frac{\pi k^2}{\left(\pi/L\right)^2}$$

$$g(k)dk = \frac{d\Gamma(k)}{dk} dk = L^2 \frac{kdk}{2\pi} = A \frac{kdk}{2\pi}$$

$$p = \hbar k, \quad dp = \hbar dk, \quad g(p)dp = A \frac{2\pi}{h^2} p dp$$

For Fermions, there are two possible spin states for a given energy, thus the density of states doubles:

$$g(p)dp = A \frac{4\pi}{h^2} p dp$$

b) Find the Fermi momentum and chemical potential of the system.

Solution:

The chemical potential at $T=0$ is called Fermi energy, and it is related to Fermi momentum as follows

$$\mu = \varepsilon_F = \frac{p_F^2}{2m}. \text{ The total number of electrons is } N = \int_0^\infty n(p)g(p)dp$$

$$\text{In the ground state } N = \int_0^{p_F} 1 \cdot g(p)dp = \frac{4\pi A}{h^2} \int_0^{p_F} p dp = \frac{2\pi A}{h^2} p_F^2 = \frac{4\pi mA}{h^2} \mu$$

$$\mu = \frac{h^2}{4m\pi A} N$$

$$p_F = \sqrt{2m\mu}$$

c) Find the average energy per particle for the system.

Solution:

$$\frac{\bar{E}}{N} = \frac{\int_0^{p_F} \varepsilon(p)g(p)dp}{\int_0^{p_F} g(p)dp} = \frac{\frac{1}{2m} \int_0^{p_F} p^3 dp}{\int_0^{p_F} p dp} = \frac{\frac{1}{2m} \frac{p_F^4}{4}}{\frac{p_F^2}{2}} = \frac{p_F^2}{4m} = \frac{1}{2} \mu$$

d) Now assume the gas system is placed in the uniform magnetic field H which makes an additional single particle energy contribution $\pm\mu_B H$ (depending on the spin orientation). Find the Fermi momenta for spin-up and spin-down fermions.

Solution:

The single particle energy in the magnetic field would be

$$e = \frac{p^2}{2m} \pm \mu_B H$$

Fermi momentum is maximum accessible momentum, so for the spin-up fermions:

$$e_F - \mu_B H = \frac{p_{F+}^2}{2m}, \text{ thus } p_{F+} = \sqrt{2m(e_F - \mu_B H)}$$

Spin-down:

$$e_F + \mu_B H = \frac{p_{F-}^2}{2m}, \text{ thus } p_{F-} = \sqrt{2m(e_F + \mu_B H)}$$

e) Calculate the average magnetization m per area for the system.

Solution:

The average number of spin-down particles:

$$N_- = \frac{2\pi A}{h^2} \int_0^{p_{F-}} p dp = \frac{\pi A}{h^2} p_{F-}^2 = \frac{\pi A}{h^2} 2m\mu(1 + \mu_B H / \mu) \xrightarrow{\text{plugin } \mu} \frac{N}{2} (1 + \mu_B H / \mu)$$

Similarly,

$$N_+ = \frac{2\pi A}{h^2} \int_0^{p_{F+}} p dp = \frac{N}{2} (1 - \mu_B H / \mu)$$

Average magnetization per area

$$m = \mu_B \frac{N_- - N_+}{A} = \frac{N\mu_B^2 H}{A\mu}$$