

Solutions

1. Van der Waals Fluid

(a) Show that the specific heat at constant volume (C_V) is a function of T only.

Remember the

$$C_V = T \cdot \left(\frac{\partial S}{\partial T} \right)_V.$$

To show that C_V is a function of T only, we need to show that

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

So:

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left(\frac{\partial}{\partial V} \left(T \cdot \left(\frac{\partial S}{\partial T} \right)_V \right) \right)_T = T \cdot \left(\frac{\partial^2 S}{\partial V \partial T} \right) = T \cdot \left(\frac{\partial}{\partial T} \right)_V \left(\frac{\partial S}{\partial V} \right)_T$$

Using

$$F(T, V) = -S dT - p dV = \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right)_T dV \text{ and } \frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \\ \Leftrightarrow \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

Plugging this into the equation above, we can find:

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \cdot \left(\frac{\partial^2 p}{(\partial T)^2} \right)_V$$

Using

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \\ \Leftrightarrow \left(\frac{\partial C_V}{\partial V} \right)_T = 0$$

(b) Are the results still true if the fluid obeys the Dieterici equation of state?

No, for the Dieterici equation of state, we find that:

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_V = \frac{1}{R^2 V^2 T^3 (V-b)} e^{-\frac{1}{RTV}} \neq 0.$$

(c) Find the entropy $S(T, V)$ for the van der Waals fluid.

Remember that we can write:

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV = \left(\frac{1}{T} C_V \right) dT + \left(\frac{\partial p}{\partial T} \right)_V dV$$

Using:

$$\frac{\partial p}{\partial T} = \frac{R}{V-b}$$

we can find for the entropy S :

$$dS = \left(\frac{1}{T} C_V \right) dT + \left(\frac{R}{V-b} \right) dV$$
$$\Leftrightarrow S = \int C_V \frac{1}{T} dT + R \ln(V-b)$$

If C_V is independent of T , this can be simplified to:

$$S = C_V \ln T + R \ln(V-b) + \text{constants}$$

2. Simple paramagnet

(a) Show that the thermodynamic potential

Using the partition function Z for the spin- $\frac{1}{2}$ system:

$$Z = e^{\beta\mu H_{ext}} + e^{-\beta\mu H_{ext}} = 2 \cosh(\beta\mu H_{ext}), \text{ for one particle.}$$

For N particles:

$$Z_N = [2 \cosh(\beta\mu H_{ext})]^N$$

Using $G = -k_B T \ln Z_N$:

$$G = -N k_B T \ln [2 \cosh(\beta\mu H_{ext})] = -N k_B T \ln [2 \cosh(\beta\mu H_{ext})]$$

This means that $a = N k_B$ and $b = \frac{\mu}{k_B}$.

(b) Find the expression of the magnetization M and the magnetic enthalpy $H = G + TS$ in terms of H_{ext} and T . Verify that $H = -M H_{ext}$.

The magnetization M is given by

$$M = \bar{\mu}_z \cdot N.$$

To find $\bar{\mu}_z$, we use:

$$\begin{aligned} \bar{\mu}_z &= \sum_s \mu_z(s) \cdot P(s) = \mu P_{\uparrow} - \mu P_{\downarrow}, \text{ where } P_{\uparrow} = \frac{e^{\frac{\mu H_{ext}}{k_B T}}}{Z} = \frac{e^{\frac{\mu H_{ext}}{k_B T}}}{2 \cosh \frac{\mu H_{ext}}{k_B T}} \text{ and} \\ P_{\downarrow} &= \frac{e^{-\frac{\mu H_{ext}}{k_B T}}}{Z} = \frac{e^{-\frac{\mu H_{ext}}{k_B T}}}{2 \cosh \frac{\mu H_{ext}}{k_B T}}. \\ \Rightarrow \bar{\mu}_z &= \frac{\mu}{2 \cosh \frac{\mu H_{ext}}{k_B T}} \left[e^{\frac{\mu H_{ext}}{k_B T}} - e^{-\frac{\mu H_{ext}}{k_B T}} \right] = \mu \tanh \frac{\mu H_{ext}}{k_B T}. \end{aligned}$$

So,

$$M = N \mu \tanh \frac{\mu H_{ext}}{k_B T}.$$

The entropy S is given by:

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

Using the results from part (a), we find that:

$$S = - \left(\frac{\partial G}{\partial T} \right)_V = Nk \ln \left(2 \cosh \frac{\mu H_{ext}}{k_B T} \right) - \frac{N\mu H_{ext}}{T} \tanh \frac{\mu H_{ext}}{k_B T}$$

Using $H = G + TS$:

$$H = -NK_B T \ln \left(2 \cosh \frac{\mu H_{ext}}{k_B T} \right) + NK_B T \ln \left(2 \cosh \frac{\mu H_{ext}}{k_B T} \right) - T \frac{N\mu H_{ext}}{T} \tanh \frac{\mu H_{ext}}{k_B T}$$

$$\Leftrightarrow H = -M \cdot H_{ext}$$

(c) Show that the expression of the entropy S obeys the Planck formulation of the third principle.

We have shown in part (b) that the entropy S is given by:

$$S = - \left(\frac{\partial G}{\partial T} \right)_V = Nk \ln \left(2 \cosh \frac{\mu H_{ext}}{k_B T} \right) - \frac{N\mu H_{ext}}{T} \tanh \frac{\mu H_{ext}}{k_B T}$$

The third principle states that the specific heat will go to 0 for T approaching $0K$.

we can use:

$$C_V = T \frac{\partial S}{\partial T}$$

$$\Leftrightarrow T \frac{\partial S}{\partial T} = \frac{N\mu^2 H_{ext}^2}{k_B T} \frac{1}{\cosh^2 \left(\frac{\mu H_{ext}}{k_B T} \right)}$$

Since $\cosh x \rightarrow \infty$ for large x , and C_V is proportional to $\frac{1}{\cosh x}$, the third principle is fulfilled.

(d) Is the expression of the isothermal susceptibility χ_T in terms of H_{ext} and T consistent with the postulates of thermodynamics?

The isothermal susceptibility is give by:

$$\chi_T = \left(\frac{\partial M}{\partial H_{ext}} \right)_T = \frac{N\mu^2}{k_B T} \frac{1}{\cosh^2 \left(\frac{\mu H_{ext}}{k_B T} \right)}$$

For $\frac{\mu H_{ext}}{k_B T} \ll 1$, $\cosh \left(\frac{\mu H_{ext}}{k_B T} \right) \rightarrow 1$, which means that in the limit of high temperatures:

$$\boxed{\chi_T = \frac{N\mu^2}{k_B T}} \quad \text{Curie's Law.}$$

In the limit of low temperature, $\frac{\mu H_{ext}}{k_B T} \rightarrow \infty$, $\cosh \left(\frac{\mu H_{ext}}{k_B T} \right) \rightarrow \infty$, so that:

$$\boxed{\lim_{T \rightarrow 0} \chi_T = 0}$$

3. Degenerate Fermi Gas

(a) For the low temperature limit (i.e. $T = 0K$), find the Fermi energy E_F and the total energy U_0 of all electrons in the conduction band (per unit volume). Express your answer in eV.

The number of electrons per unit volume N is given by:

$$N = \int_0^{\infty} g(\varepsilon)f(\varepsilon) d\varepsilon.$$

At $T = 0$, all the states are completely filled up to the Fermi-energy (ε_f):

$$\begin{aligned} N &= \int_0^{\varepsilon_f} g(\varepsilon)f(\varepsilon) d\varepsilon = \int_0^{\varepsilon_f} g(\varepsilon) d\varepsilon = \int_0^{\varepsilon_f} \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2} d\varepsilon = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{3} \varepsilon_f^{3/2} \\ &\Leftrightarrow \varepsilon_f = \frac{\hbar^2}{2m} (3\pi^2 N)^{2/3} \end{aligned}$$

Assuming $\hbar = 1.05 \times 10^{-34} Js$, $m_e = 9.1 \times 10^{-31} kg$, and $N = 8.46 \times 10^{28} m^{-3}$:

$$\boxed{\varepsilon_f = 1.1 \times 10^{-18} J \approx 7 eV}$$

The total energy U_0 is given by:

$$\begin{aligned} U_0 &= \int_0^{\varepsilon_f} g(\varepsilon)\varepsilon d\varepsilon = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\varepsilon_f} \varepsilon^{3/2} d\varepsilon = \frac{2}{5} \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon_f^{5/2} \\ &\boxed{U_0 = \frac{2}{5} N \varepsilon_f} \end{aligned}$$

(b) Calculate the energy interval that is occupied by the electrons that participate in the current flow at room temperature (i.e. $T = 300K$). The occupancy at non-zero temperature is given by:

$$\bar{n}(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \varepsilon_f}{k_B T}} + 1}$$

So, the lower limit is given by:

$$0.9 = \frac{1}{e^{\frac{\varepsilon_1 - \varepsilon_f}{k_B T}} + 1}$$

$$\varepsilon_1 = \varepsilon_f - k_B T \ln 9$$

and the upper limit:

$$0.1 = \frac{1}{e^{\frac{\varepsilon_2 - \varepsilon_f}{k_B T} + 1}}$$

$$\varepsilon_2 = \varepsilon_f + k_B T \ln 9$$

This will result in a total energy interval at room temperature:

$$\boxed{\Delta\varepsilon = 0.11 \text{ eV}}$$

(c) Using your answers to part (b), find the fraction of “current carrying” electrons N_1 over the total number of electrons in the conduction band N_{total} (i.e. $\frac{N_1}{N_{total}}$).

First, find the number of “current carrying” electrons N_1 in the energy window $\varepsilon_f \pm \frac{\Delta\varepsilon}{2}$, using $\Delta\varepsilon = 0.11 \text{ eV}$ and $\varepsilon_f = 7 \text{ eV}$:

$$N_1 = \int_{\varepsilon_f - \frac{\Delta\varepsilon}{2}}^{\varepsilon_f + \frac{\Delta\varepsilon}{2}} \bar{n}(\varepsilon)g(\varepsilon) d\varepsilon$$

For a small energy window, we can assume that $g(\varepsilon)$ is independent of energy ε (i.e. $g(\varepsilon_f \pm \frac{\Delta\varepsilon}{2}) = \frac{3}{2} \frac{N}{\varepsilon_f}$, and \bar{n} varies linearly with energy, i.e. $\bar{n}(\varepsilon_f \pm \frac{\Delta\varepsilon}{2}) = \frac{1}{2} - \frac{\varepsilon}{4k_B T}$ (using only the linear term in the series expansion of the Fermi-Dirac distribution).

Using these approximations, we can find for N_1 :

$$N_1 = \int_{\varepsilon_f - \frac{\Delta\varepsilon}{2}}^{\varepsilon_f + \frac{\Delta\varepsilon}{2}} \bar{n}(\varepsilon)g(\varepsilon) d\varepsilon \approx \frac{3N}{2\varepsilon_f} \int_{-\frac{\Delta\varepsilon}{2}}^{\frac{\Delta\varepsilon}{2}} \left(\frac{1}{2} - \frac{\varepsilon}{4k_B T} \right) d\varepsilon = \frac{3N}{2\varepsilon_f} \frac{1}{2} \Delta\varepsilon$$

So, the fraction of charges contributing to the current $\frac{N_1}{N}$ is now given by:

$$\frac{N_1}{N} = \frac{3N}{3N\varepsilon_f} \Delta\varepsilon = \frac{3\Delta\varepsilon}{4\varepsilon_f}$$

$$\boxed{\frac{N_1}{N} = 0.012}$$

This means that only 1.2% of all the electrons in the conduction band contribute to the current in Cu at 300K.

4. The Ideal Gas

(a) Determine the kind of compression that took place here. Explain!

This is an adiabatic compression with $\Delta Q = 0$.

(b) Find the temperature T_2 and the volume V_2 in terms of V_1 , p_2 and T_1 after the thermodynamic equilibrium has been reached.

For adiabatic processes

$$\Delta U = \Delta Q - pdV$$

Combining these two equations, we will get:

$$C_V (T_2 - T_1) = -p_2 (V_2 - V_1)$$

We also know that $C_V = \frac{\partial U}{\partial T}$ or $\Delta U = C_V \Delta T$. The equation of state for an ideal gas is given by $pV = Nk_B T$ and $C_P - C_V = Nk_B$.

This will lead to:

$$(T_2 - T_1) = -\frac{p_2}{C_V} (V_2 - V_1) \Leftrightarrow T_2 = -\frac{p_2}{C_V} (V_2 - V_1) + T_1$$

Now use $p_2 V_2 = Nk_B T_2 \Leftrightarrow V_2 = \frac{Nk_B T_2}{p_2}$:

$$T_2 = -\frac{p_2}{C_V} \left(\frac{Nk_B T_2}{p_2} - V_1 \right) + T_1$$

This can now be rearranged to:

$$\boxed{T_2 = -\frac{p_2 V_1 + C_V T_1}{C_p}}$$

(c) Find the final values of the temperature T_f and volume V_f in terms of p_1 , V_2 , and T_2 after the thermodynamic equilibrium is reached again.

Rearranging the solution to part (a) will lead to:

$$\boxed{T_f = -\frac{C_V T_2 + p_1 V_2}{C_P}} \quad \text{and} \quad \boxed{V_f = \frac{N k_B T_f}{p_1}}$$

Using $C_V \Delta T + p \Delta V = 0$ for the two parts of the experiments, we will find:

$$\begin{aligned} C_V (T_2 - T_1) + p_2 (V_2 - V_1) &= 0 \\ C_V (T_f - T_2) + p_1 (V_1 - V_2) &= 0 \\ \Leftrightarrow C_V (T_f - T_1) + p_2 (V_2 - V_1) + p_1 (V_f - V_2) &= 0 \end{aligned}$$

using $pV = Nk_B T$

$$\Delta(pV) = p\Delta V + V\Delta p = Nk_B \Delta T$$

Using $C_V \Delta T + p \Delta V = 0$:

$$p\Delta V + V\Delta p = Nk_B \left(\frac{p\Delta V}{C_V} \right)$$

Using $C_V + Nk_B T = C_P$, we can find:

$$C_P p \Delta V + C_V V \Delta p = 0$$

Using this expression for the two experiments:

$$\begin{aligned} C_P p_2 (V_2 - V_1) + C_V V_2 (p_2 - p_1) &= 0 \\ C_P p_1 (V_f - V_2) + C_V V_f (p_f - p_2) &= 0 \\ \Leftrightarrow p_2 (V_2 - V_1) + p_1 (V_f - V_2) &= \frac{C_V}{C_P} [V_2 (p_1 - p_2) + V_f (p_2 - p_f)] \end{aligned}$$

Using $p_f = p_1$ and $V_f = V_1$, we can plug this into the equation above and find:

$$\begin{aligned} C_V (T_f - T_1) &= \frac{C_V}{C_P} [V_2 (p_1 - p_2) - V_1 (p_1 - p_2)] \\ T_f - T_1 &= \frac{1}{C_P} (V_2 - V_1) (p_1 - p_2) \end{aligned}$$

Eliminating $(V_2 - V_1)$, we can finally find:

$$\boxed{T_f - T_1 = \frac{C_V}{(C_P)^2} (p_1 - p_2)^2 \frac{V_2}{P_2}}$$

This result shows that the temperature difference $T_f - T_1$ will always be positive, as required by the thermodynamic principles. Also, it appears that the temperature difference is only a 2^{nd} -order correction term, which will become very small for $\Delta P \rightarrow 0$.

5. Einstein Solid

(a) For the most probable macrostate, determine the number of units of heat energy in each of the two systems. Explain your approach.

The most probable state will have the highest multiplicity Ω :

$$\Omega = \binom{q + N - 1}{q} = \frac{(q+N-1)!}{q!(N-1)!}$$

and

$$\Omega_{total} = \Omega_A \cdot \Omega_B$$

For $N_A = 4$ and $N_B = 6$, we can assemble the following table:

q_A	Ω_A	q_B	Ω_B	Ω_{total}
8	165	12	6188	1.021×10^6
7	120	13	8568	1.028×10^6
6	84	14	11628	0.98×10^6

So, $q_A = 7$ and $q_B = 13$ will be the most probable state.

(b) Determine the probability of finding the system in the most probable macrostate.

To determine the probability of a macrostate, we need to calculate:

$$P = \frac{\Omega_A \Omega_B}{\Omega_{total}}$$

using

$$\Omega_{total} = \binom{q + N_{total} - 1}{q} = \binom{20 + 10 - 1}{20} = 10.02 \times 10^7$$

$$\Leftrightarrow P = \frac{\Omega_A \Omega_B}{\Omega_{total}} = 0.1$$