

Solution 1

a) At $T = T_C$ there's only one extremum that is a saddle point, so we can conclude that $\frac{\partial p}{\partial v}|_{v_c, T_c} = 0$ and $\frac{\partial^2 p}{\partial v^2}|_{v_c, T_c} = 0$ and we obtain

$$\begin{cases} -\frac{k_B T_C}{(v_C - b)^2} + 2\frac{a}{v_C^3} = 0 \\ 2\frac{k_B T_C}{(v_C - b)^3} - 6\frac{a}{v_C^4} = 0 \end{cases} \Leftrightarrow \begin{cases} -k_B T_C v_C^3 + 2a(v_C - b)^2 = 0 \\ 2k_B T_C v_C^4 - 6a(v_C - b)^3 = 0 \end{cases}$$

and we obtain $v_C = 3b$ and $k_B T_C = \frac{8a}{27b}$.

b) Consider a piston in equilibrium with the external environment ($p_{int} = p_{ext}$). An infinitesimal increase of the volume Δv brings an increase in p_{int} , so that the piston moves until another equilibrium point with a bigger volume. On the other hand, a negative variation $-\Delta v$ of the volume decreases the internal pressure and the piston moves to an equilibrium position where the volume is smaller. This is a consequence of the "negative compressibility" arising from this model.

c) We are interested in the cycle ABCDEF CGA. We made the hypothesis that this cycle exists at constant temperature and we also assume that this cycle is reversible. Along a cycle the variation of internal energy is zero and, from the 1st law of thermodynamics, the work is equal to the exchanged heat. Moreover if the cycle is reversible we have

$$\oint ds = 0 \Leftrightarrow \oint \frac{dQ}{T} = 0.$$

Since we are discussing isothermal transformations we can pull out the temperature and we observe that the total exchange of heat along the cycle has to vanish. The same holds for the total work:

$$\oint p(v)dv = 0 \Leftrightarrow \int_{ABCDE} p_{exp}(v)dv = \int_{AGCFE} p_w(v)dv,$$

where p_{exp} is the experimental curve, while p_w is the Van der Waals one. The previous condition means that the areas ABCGA and CDEFC have to be the same. This gives the following conditions:

$$\begin{cases} p(v_A) = p(v_E) \\ \int_{v_A}^{v_E} p_w(v)dv = (v_A - v_E)p(v_E) \end{cases}$$

(N.B. the same construction cannot be applied to the cycle ABCGA or EFCDE separately because they are non-reversible).

Let's focus on the shape of the experimental isotherm. During the transition, as it's known from experience, we have the coexistence of two phases: the liquid one appears when the gaseous state cannot compress further (the molecules are so close each others that it's energetically advantageous to switch to the liquid state instead of increasing the pressure). The decrease of volume is only due to the fact that the liquid phase occupies less space than the gaseous one, so we can conclude that the pressure of the gas during the phase transition do not increase (otherwise it would be sufficient to convert a further portion of gas to the liquid phase, moreover the capacity of the gas to condense doesn't depend on the fraction of gas already condensed). Since the two states must have the same

pressure (and obviously temperature) to coexist, we can conclude that the system pressure do not change during the transition and that explains the shape of the experimental diagram.

d) Define $F(v) = -\int p_w(v)dv$ and $G(v) = -\int p_{exp}(v)dv$, then in the interval $[v_A, v_E]$

$$F(v) = -k_B T \ln(v-b) - a/v \quad (1)$$

$$G(v) = -p_0 v \quad (2)$$

where we choose the integration constant in such a way that $F(v_A) = G(v_A) = 0$.

Moreover, $F(v) = G(v)$ for $v \leq v_A$ by construction and, from the result obtained in c) ($\text{area(ABCG)} = \text{area(CFED)}$):

$$\int_{v_A}^v p_w(v')dv' = \int_{v_A}^v p_{exp}(v')dv' \Rightarrow F(v) = G(v) \quad \forall v \geq v_E,$$

Also, remembering that A and E are the same state in both the cases:

$$p_w(v_A) = p_{exp}(v_A) = p_0 \Leftrightarrow F'(v_A) = p_0 = G'(v_A) \quad (3)$$

$$p_w(v_E) = p_{exp}(v_E) = p_0 \Leftrightarrow F'(v_E) = p_0 = G'(v_E),$$

so we conclude that $G(v)$ is a straight line tangent to $F(v)$ in v_E and v_A (Fig.1).

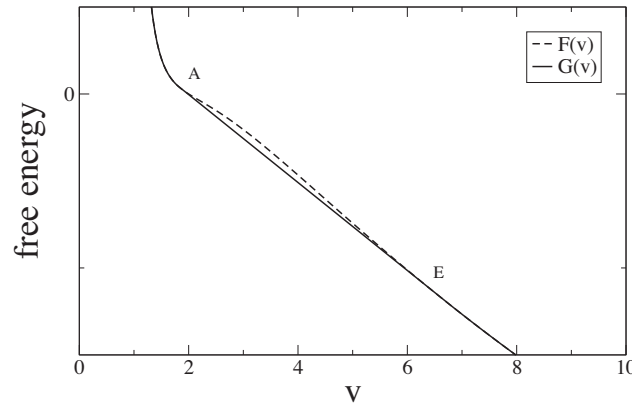


FIG. 1 – Energie libre, $a=1$, $b=1$, $k_B T = 0.27$

We started from the experimental remark that the pressure approximately follows the Van der Waals equation apart from the interval between v_A and v_E where it is constant. This means that the system initially follows the Van der Waals free energy until a point where it is convenient to keep the same pressure, so the system minimizes his free energy keeping a constant pressure and then recovers the Van der Waals trend once that the transition is finished.

This last analysis gives a good qualitative explanation of why the system prefers a transition where the two phases coexist.

This exercise is partially extracted from Enrico's Fermi, *Thermodynamics*, 1937.