Solution 6

Exercice 1

We fix the temperature (the isotherm) and the pressure $p = p(v_C, T)$. Let's see how the Gibbs free energy varies for small variations of the volume:

$$\begin{aligned} f(v_C+\Delta v, T) + p(v_C,T)(v_C+\Delta v) &= f(v_C,T) + p(v_C,T)v_C + \left.\frac{\partial f(v,T)}{\partial v}\right|_{v_C} \Delta v + p(v_C,T)\Delta v \\ &+ \frac{1}{2}\left.\frac{\partial^2 f(v,T)}{\partial v^2}\right|_{v_C} \Delta v^2 + \frac{1}{3!}\left.\frac{\partial^3 f(v,T)}{\partial v^3}\right|_{v_C} \Delta v^3 + \frac{1}{4!}\left.\frac{\partial^4 f(v,T)}{\partial v^4}\right|_{v_C} \Delta v^4 \end{aligned} \tag{1}$$

The derivatives of f are:

$$\begin{aligned} \left.\frac{\partial f(v,T)}{\partial v}\right|_{v_C} &= -p(v_C,T) \quad \text{by definition} \\ \left.\frac{\partial^2 f(v,T)}{\partial v^2}\right|_{v_C} &= \frac{kT}{(v_C-b)^2} - 2\frac{a}{v_C^3} = \frac{k_B}{4b^2}(T-T_C) \\ \left.\frac{\partial^3 f(v,T)}{\partial v^3}\right|_{v_C} &= -\frac{2kT}{(v_C-b)^3} + 6\frac{a}{v_C^4} = \frac{k_B}{4b^3}(T_C-T) \\ \left.\frac{\partial^4 f(v,T)}{\partial v^4}\right|_{v_C} &= \frac{6kT}{(v_C-b)^4} - 24\frac{a}{v_C^5} = \frac{k_B}{b^4}\left(\frac{3}{8}T - \frac{1}{3}T_C\right) \end{aligned}$$

Introducing the expressions above in (2) we obtain:

$$\begin{aligned} f(v_C+\Delta v, T) + p(v_C,T)v &= f(v_C,T) + p(v_C,T)v_C + \frac{1}{2}\frac{k_B}{4b^2}(T-T_C)\Delta v^2 \\ &+ \frac{1}{3!}\frac{k_B}{4b^3}(T_C-T)\Delta v^3 + \frac{1}{4!}\frac{k_B}{b^4}\left(\frac{3}{8}T - \frac{1}{3}T_C\right)\Delta v^4 \end{aligned} \tag{2}$$

If $T > T_C$, g is minimum in v_C (look at the sign of the second derivative), so the system is stable. One can show that the term in Δv^3 can introduce a second minimum which is always less favorable. If $T < T_C$ the second derivative of g in v_C is positive which corresponds to a maximum. Remember that in the Series 1 we saw that the region close to v_C is instable because of the positive compressibility. The term in Δv^3 introduces an asymmetry: the minumum with $\Delta v < 0$ is favorable.

Exercise 2

a) The minima F are given from

$$\frac{dF}{dm} = m(a + bm^2 + cm^4) = 0$$

so:

$$\begin{aligned} m &= 0 \\ &\text{or} \\ m_\pm^2 &= \frac{1}{2c}\left(-b \pm \sqrt{b^2-4ac}\right) \end{aligned} \tag{3}$$

1. Let's suppose $b > 0$.

   If $a < 0$, F has 3 extrema: $(0, m_+, -m_+)$ because $m_-^2 < 0$. $m = 0$ is a maximum and $\pm m_+$ are the two minima.
   If $a > 0$, then $m_\pm^2 < 0$ and $m = 0$ is the only minima.
   The limit $\lim_{a \to -0} m_+^2 = 0$ shows that the transition is continue. It is a second order transition because $\lim_{a \to -0} \frac{\partial m}{\partial a} \neq 0$.

2. Now we consider the case $b < 0$.

   If $a < 0$, F has 3 extrema: $(0, m_+, -m_+)$ because $m_-^2 < 0$. $m = 0$ is a maximum and $\pm m_+$ are two minima.
   If $a > 0$, we distinguish 3 cases:

   (i) $b^2 < 4ac$: In this case F has only one minimum and $m = 0$.

   (ii) $b^2 > 4ac$: in this case F has 5 extremas. The extremaum $m = 0$ is a minimum. Moreover s $F(0) = 0$. The condition for F to have other advantageous minima is equivalent to F to have 4 distinct zeroes (Fig. 1).

   $$F(m) = \frac{1}{2} m^2 \left(a + \frac{b}{2} m^2 + \frac{c}{3} m^4 \right)$$

   These zeroes exist if:

   $$\frac{b^2}{4} - 4a\frac{c}{3} > 0 \Leftrightarrow b^2 > 16\frac{ac}{3} \Leftrightarrow b < -4\sqrt{\frac{ac}{3}}$$

   because $b < 0$. Close to the transition we have:

   $$\lim_{b+4\sqrt{\frac{ac}{3}} \to +0} m = 0$$

   $$\lim_{b+4\sqrt{\frac{ac}{3}} \to -0} m_+ = \left(\frac{3a}{c} \right)^{\frac{1}{4}}$$

To obtain this last result, we need to insert the value $b = -4\sqrt{\frac{ac}{3}}$ into (3).
We see that the transition is discontinuous (first order)

b) We have the followinf phase diagram:

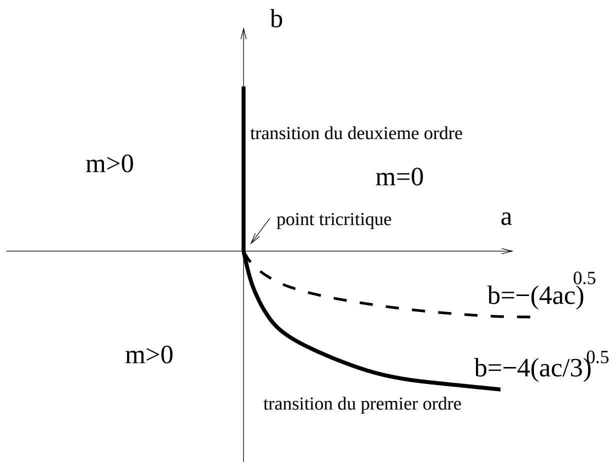

Figure 1: Diagramme de phase

he tri-critical point is given by: $a = b = 0$.

c) To calculate the critical exponents we place on the line $b = 0$. Adding to F the term $-hm$, we have to satisfy the equation for m

$$\frac{dF}{dm} = 0 \Leftrightarrow h = Atm + cm^5$$

For $h = 0$, we can conclude that

1. $m \sim t^0$ si $t > 0$
2. $m \sim (-t)^{\frac{1}{4}}$ si $t < 0$

So $\beta = \frac{1}{4}$.

The magnetic susceptibility is given by

$$\chi = \left.\frac{\partial m}{\partial h}\right|_{h=0} \Leftrightarrow \chi^{-1} = \left.\frac{\partial h}{\partial m}\right|_{h=0} = At + 5cm^4$$

1. For $t > 0$, $m = 0$, and $\chi \sim t^{-1}$.
2. For $t < 0$, $m \sim t^{\frac{1}{4}}$ and $\chi \sim t^{-1}$.

So $\gamma = 1$.