



UNIVERSITY OF STRASBOURG

Problem Set 4

The liquid-gas phase transition

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Reminder

1 Lattice gas model

In this problem, we are attempting to describe the properties of a classical fluid composed of N molecules at the temperature T . Toward this goal, we will use an extremely simplified model, the lattice gas model. The volume V in which the molecules are enclosed is divided into small cubic boxes of volume v_0 (indexed with the label i). Each box can be either empty (occupation number $n_i = 0$) or occupied by one molecule ($n_i = 1$). Let $N_0 (> N)$ be the number of boxes occupying the whole volume V . The fact that the occupation number of a box is $n_i = 1$ at most models the repulsive part of the interaction between two molecules. In order to describe the attractive short-range interactions between the molecules, we attribute the energy $-\epsilon$ whenever two neighboring sites are both occupied. The Hamiltonian of the lattice gas model then reads

$$\mathcal{H} = -\epsilon \sum_{\langle i,j \rangle} n_i n_j, \quad n_i, n_j = 0 \text{ or } 1 \quad (1)$$

where $\langle i, j \rangle$ corresponds to a pair of nearest-neighbor sites.

1.1 Study of the ideal gas with an excluded volume

In the first part of this Problem, we consider the case of an ideal gas with an excluded volume (*i.e.*, we neglect the attractive interactions among the molecules, $\epsilon = 0$). We describe the system in the canonical ensemble, where the number N of particles is fixed.

- (a) Show that the canonical partition function Z of the system corresponds to the total number of configurations that the system can take, *i.e.*,

$$Z = \frac{N_0!}{N!(N_0 - N)!}$$

$$\begin{aligned} Z &= \sum_l e^{-\beta E_l} \\ &= \sum_l 1 \end{aligned}$$

The N particles are indistinguishable,

$$Z = \frac{N_0!}{N!(N_0 - N)!}$$

- (b) At the thermodynamical limit ($N_0 > N \gg 1$), deduce from the question above expressions for the free energy, the average energy, the entropy, and the pressure of the gas. Comment on your results.

Reminder : Stirling approximation for $x \gg 1$,

$$\ln x! = x \ln x - x$$

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -k_B T [N_0 \ln(N_0) - N_0 - N \ln(N) + N - (N_0 - N) \ln(N_0 - N) + (N_0 - N)] \\ &= -k_B T N_0 \left[\ln(N_0) - \frac{N}{N_0} \ln(N) - \left(1 - \frac{N}{N_0}\right) \ln(N_0 - N) \right] \end{aligned}$$

We can define the filling ratio, $\theta = N/N_0$, indeed $\theta \in [0, 1]$,

$$\begin{aligned} F &= N_0 k_B T \left[\ln\left(\frac{N_0 - N}{N_0}\right) - \frac{N}{N_0} \ln\left(\frac{N_0}{N} - 1\right) \right] \\ &= N_0 k_B T \left[\ln(1 - \theta) - \theta \ln\left(\frac{1 - \theta}{\theta}\right) \right] \\ &= N_0 k_B T [\ln(1 - \theta) - \theta \ln(1 - \theta) + \theta \ln(\theta)] \\ &= N_0 k_B T [\theta \ln(\theta) + (1 - \theta) \ln(1 - \theta)] \end{aligned}$$

We recognize the entropy of a two levels system.

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial(\beta F)}{\partial \beta} = 0$$

$$F = \langle E \rangle - T \langle S \rangle \longrightarrow \langle S \rangle = -\frac{F}{T} = -N_0 k_B [\theta \ln(\theta) + (1 - \theta) \ln(1 - \theta)]$$

$$\begin{aligned} P &= -\frac{\partial F}{\partial V} \\ &= -\frac{\partial F}{\partial N_0} \frac{1}{v} \\ &= -\frac{1}{v} \frac{\partial F}{\partial \theta} \frac{\partial \theta}{\partial N_0} \\ &= -\frac{N k_B T \ln(1 - \theta)}{V \theta} \end{aligned}$$

1.2 Interacting gas

We now consider the full Hamiltonian (1) of the system and look for an approximate expression of the grand-canonical partition function Ξ . We call μ the chemical potential.

1.2.1 Approximate calculation of the partition function

Let us suppose that we know the average occupation number $\langle n_i \rangle = n$ of a site i , which is assumed to be the same for all sites of the lattice.

- (a) Give an expression for the average number of molecules $\langle N \rangle$ as a function of n .

$$\langle N \rangle = \left\langle \sum_{i=1}^{N_0} n_i \right\rangle = \sum_{i=1}^{N_0} \langle n_i \rangle = \sum_{i=1}^{N_0} n = N_0 n$$

- (b) Let us define the correlation function $\mathcal{C}_{ij} = \langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle$. By decomposing n_i into its average n and the fluctuations δn_i around it, perform a mean field approximation and show that $\mathcal{C}_{ij} \simeq 0$. Deduce from this result that within the mean field approximation, one can replace the product $n_i n_j$ ($i \neq j$) by $n(n_i + n_j) - n^2$.

$$C_{ij} = \langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle$$

We can denote $n_i = n + \delta n_i$ where the δ is accounting for the fluctuations,

$$C_{ij} = \langle \delta n_i \delta n_j \rangle \approx 0$$

This approximation is what the *Mean Field Approximation* (MFA) does.

$$\begin{aligned} n_i n_j &= n^2 + n(\delta n_i + \delta n_j) + \mathcal{O}(\delta_n^2) \\ &= n^2 + n(n_i - n + n_j - n) \\ &= n(n_i + n_j) - n^2 \end{aligned}$$

We now see that there is no more product of n_i and n_j but just a sum.

- (c) Show that, within the mean field approximation, the Hamiltonian (1) takes the simplified form

$$\mathcal{H} \simeq -6\epsilon n \sum_{i=1}^{N_0} n_i + 3\epsilon N_0 n^2$$

Deduce from the expression above the grand-canonical partition function Ξ and the grand potential Ω as a function of n .

$$\begin{aligned} \mathcal{H} &\approx -\epsilon \sum_{\langle i,j \rangle} (n(n_i + n_j) - n^2) & \sum_{\langle i,j \rangle} &= \frac{1}{2} \sum_{i=1}^{N_0} \sum_{j \in \text{nn}(i)} \\ &= \frac{1}{2} \epsilon N_0 6 n^2 - 2\epsilon n \frac{1}{2} 6 \sum_i n_i \end{aligned}$$

The 6 comes from the fact that the coordination number of a cubic lattice is 6. Meaning,

$$\begin{aligned}
\mathcal{H} &\simeq -6\epsilon n \sum_{i=1}^{N_0} n_i + 3\epsilon N_0 n^2 \\
\Xi &= \sum_l e^{-\beta(E_l - \mu N_l)} \\
&= \sum_{n_1=0}^1 \cdots \sum_{n_{N_0}=0}^1 e^{-\beta[-6\epsilon n \sum_{i=1}^{N_0} n_i + 3\epsilon N_0 n^2 - \mu \sum_{i=1}^{N_0} n_i]} \\
&= e^{-3\beta\epsilon N_0 n^2} \underbrace{\sum_{n_1=0}^1 \cdots \sum_{n_{N_0}=0}^1}_{\text{they are the same}} \prod_{i=1}^{N_0} e^{\beta[6\epsilon n + \mu]n_i} \\
&= e^{-3\beta\epsilon N_0 n^2} (1 + e^{\beta[6\epsilon n + \mu]})^{N_0}
\end{aligned}$$

Meaning,

$$\Xi = \xi^{N_0}, \quad \xi = e^{-3\beta\epsilon n^2} (1 + e^{\beta[6\epsilon n + \mu]})$$

So, we can deduce the grand potential,

$$\begin{aligned}
\Omega &= -k_B T \ln \Xi \\
&= -N_0 k_B T \ln \xi \\
&= 3\epsilon N_0 n^2 - N_0 k_B T \ln(1 + e^{\beta[6\epsilon n + \mu]})
\end{aligned}$$

We assumed we know n , but of course we do not know it. In order to fix it, we need to find a self-consistent equation.

- (d) Using your results for Ω and question 1.2.1(a), calculate the average number of molecules as a function of n . Deduce from the above calculation a self-consistent equation for n .

$$\begin{aligned}
\langle N \rangle &= N_0 n \\
&= -\frac{\partial \Omega}{\partial \mu} &= k_B T \frac{\partial \ln \Xi}{\partial \mu} \\
&= N_0 k_B T \beta \frac{e^{\beta[6\epsilon n + \mu]}}{1 + e^{\beta[6\epsilon n + \mu]}} \\
&= N_0 \frac{1}{e^{-\beta[6\epsilon n + \mu]} + 1}
\end{aligned}$$

Meaning,

$$n = \frac{1}{e^{-\beta[6\epsilon n + \mu]} + 1}$$

This equation is our *self-consistent equation*.

It does look like the Fermi-Dirac distribution. Effectively, we have a system of fermions-like behavior.

(e) Show that the equation of state of the system reads

$$P = -\frac{k_B T}{v_0} \ln \left(1 - \frac{N}{V} v_0 \right) - 3\epsilon \left(\frac{N}{V} \right)^2 v_0$$

$$\begin{aligned} P &= -\frac{\partial \Omega}{\partial V} \Big|_{T, \mu} \\ &= -\frac{\partial \Omega}{\partial N_0} \frac{\partial N_0}{\partial V} \\ &= -\frac{1}{v_0} \frac{\partial \Omega}{\partial N_0} \end{aligned}$$

$$\langle N \rangle = N = N_0 n \longrightarrow n = \frac{N}{N_0}, \quad N_0 = \frac{N}{n}$$

$$\begin{aligned} P &= -\frac{1}{v_0} \frac{\partial \Omega}{\partial n} \left(-\frac{N}{N_0^2} \right) \\ &= \frac{n}{V} \frac{\partial \Omega}{\partial n} \\ &= \frac{n}{V} \frac{\partial}{\partial n} \left\{ 3N\epsilon n - \frac{N}{n} k_B T \ln[1 + e^{\beta(6\epsilon n + \mu)}] \right\} \\ &= \frac{n}{V} \left\{ 3N\epsilon + \frac{N}{n^2} k_B T \ln[1 + e^{\beta(6\epsilon n + \mu)}] - \frac{N}{n} \frac{e^{\beta(6\epsilon n + \mu)}}{1 + e^{\beta(6\epsilon n + \mu)}} 6\epsilon \right\} \\ &= \frac{n}{V} \left\{ 3N\epsilon + \frac{N}{n^2} k_B T \ln[1 + e^{\beta(6\epsilon n + \mu)}] - 6N\epsilon \right\} \\ &= \frac{n}{V} \left\{ -3N\epsilon + \frac{N}{n^2} k_B T \ln[1 + e^{\beta(6\epsilon n + \mu)}] \right\} \\ &= -\frac{k_B T}{v_0} \ln \left(1 - \frac{N}{V} v_0 \right) - 3\epsilon \left(\frac{N}{V} \right)^2 v_0 \end{aligned}$$

Remark : We used,

$$n \frac{e^{\beta(6\epsilon n + \mu)}}{1 + e^{\beta(6\epsilon n + \mu)}} = n \frac{1}{e^{-\beta(6\epsilon n + \mu)} + 1} = 1$$

$$n = \frac{1}{e^{-\beta(6\epsilon n + \mu)} + 1} \longrightarrow 1 + e^{\beta(6\epsilon n + \mu)} = \frac{1}{1 - n}$$

$$n = \frac{N}{N_0} = \frac{N}{V} v_0$$

Remark : Indeed, if we set $\epsilon = 0$, we recover what we found earlier.

- (f) Sketch the isothermal curves and comment on the phase diagram. Show that if the temperature is lower than a critical temperature T_c , the system becomes unstable for a certain range of volume. Show that the critical point is located at

$$k_B T_c = \frac{3}{2} \epsilon \qquad V_c = 2Nv_0 \qquad P_c = \frac{3}{2} \left(\ln 2 - \frac{1}{2} \right) \frac{\epsilon}{v_0}$$

Give the values n_c and μ_c of, respectively, n and μ at the critical point.

Let's introduce reduced units,

$$\left. \begin{array}{ll} \text{reduced volume} & v = \frac{V}{Nv_0} \\ \text{reduced energy} & \tau = \frac{k_B T}{\epsilon} \\ \text{reduced pressure} & p = \frac{Pv_0}{\epsilon} \\ \text{reduced chemical potential} & \alpha = \frac{\mu}{\epsilon} \end{array} \right\}$$

Remark :

$$\tau \geq 0 \qquad v \in [1, +\infty[$$

In those units,

$$p = -\tau \ln \left(1 - \frac{1}{v} \right) - \frac{3}{v^2}$$

Remark : as v goes to 1, p goes to $+\infty$: $\lim_{v \rightarrow 1} p = +\infty$ and as v goes to $+\infty$, p goes to 0 : $\lim_{v \rightarrow +\infty} p = 0$. Those two obvious limiting cases indeed yield the correct results.

In order to understand the behavior of p , one has to study it's derivative,

$$\begin{aligned}\frac{\partial p}{\partial v} &= -\tau \frac{1}{v^2} \frac{1}{1 - \frac{1}{v}} + \frac{6}{v^3} \\ &= \frac{-\tau}{v(v-1)} + \frac{6}{v^3} \\ &= \frac{-\tau v^2 + 6(v-1)}{v^3(v-1)}\end{aligned}$$

We're interested in finding the values of v for which this derivative is equal to 0 :

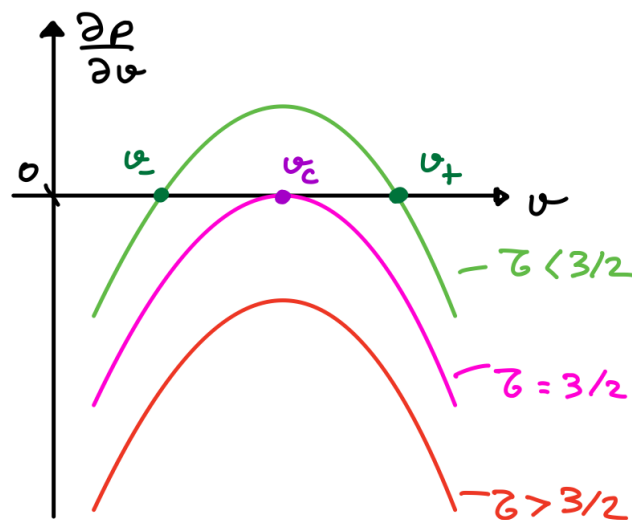
$$-\tau v^2 + 6v - 6 = 0$$

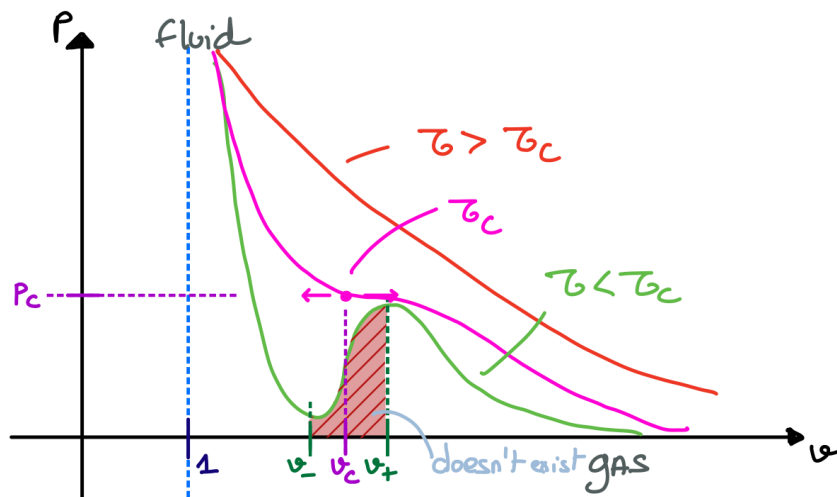
We know the solutions of a second order polynomial,

$$\begin{aligned}v_{\pm} &= -\frac{1}{2\tau} \left(-6 \pm \sqrt{6^2 - 4(-\tau)(-6)} \right) \\ &= -\frac{6}{2\tau} \left(-1 \pm \sqrt{1 - \frac{2}{3}\tau} \right) \\ &= \frac{3}{\tau} \left(1 \mp \sqrt{1 - \frac{2}{3}\tau} \right)\end{aligned}$$

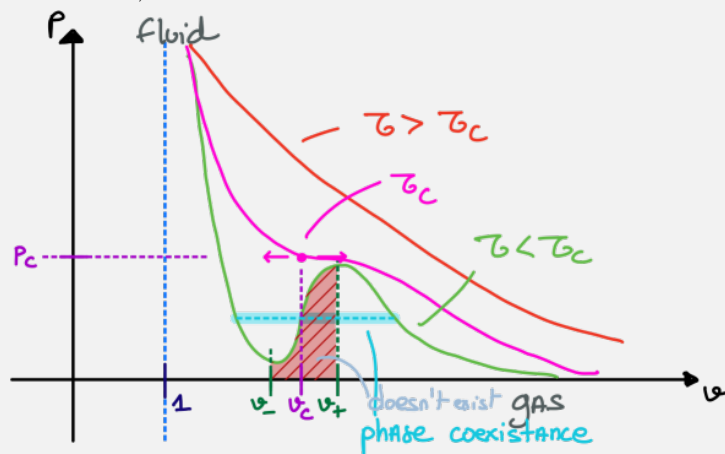
There is three cases,

- $\tau > 3/2$, meaning the solutions $v_{\pm}$ are in fact, complex valued, $v_{\pm} \in \mathbb{C}$. Meaning, there is no real roots.
- $\tau < 3/2$, meaning the solutions $v_{\pm}$ are real values, $v_{\pm} \in \mathbb{R}$.
- $\tau = 3/2$, there is one solution, $v_c = 2$.





Remark : the red-crossed area doesn't exist in real life, and we'll see latter on that, there is in fact, a phase coexistence, a *phase transition*, a plateau here, so the real scheme should look like,



Remark : for $\tau > \tau_c$, the fluid is called a *supercritical fluid*.

So, we find,

$$p_c = \frac{3}{2} \left(\ln(2) - \frac{1}{2} \right) \approx 0.29$$

$$n_c = \frac{N_c}{N_0} = \frac{N_c v_0}{V} = \frac{1}{v_c} = \frac{1}{2}$$

For μ_c , we have to use the self-consistent equation,

$$n_c = \frac{1}{e_c^{-\beta}(6\epsilon n_c + \mu_c) + 1} \rightarrow \alpha_c = -3$$

1.2.2 Study of the critical point

We now consider that the system is close to the critical point. We hence assume that $\mu = \mu_c$ and that n is close to n_c . We therefore set $n = n_c(1 + m)$, with $m \ll 1$.

(a) Show that the self-consistent equation for n now reads

$$m = \tanh\left(\frac{T_c}{T}m\right) \quad (2)$$

We assume $\mu = \mu_c = -3\epsilon$ and $n = n_c(1 + m) = \frac{1}{2}(1 + m)$ where m can be understood as a slight variation from n_c , $m \ll 1$.

Remark : this m here represent the *order parameter*, so it's exactly analogous to the m of the magnetization in the Ising model.

We start from the self-consistent equation of n ,

$$n = \frac{1}{e^{-\beta(6\epsilon n + \mu)} + 1}$$

we also know that $\tau = k_B T / \epsilon = 1 / \beta \epsilon$,

$$\begin{aligned} \frac{1}{2}(1 + m) &= \frac{1}{e^{-\beta(3\epsilon(1+m) - 3\epsilon)} + 1} \\ &= \frac{1}{e^{-\frac{2\tau_c}{\tau}m} + 1} \\ &= \frac{1}{e^{-\frac{2T_c}{T}m} + 1} \end{aligned}$$

Meaning,

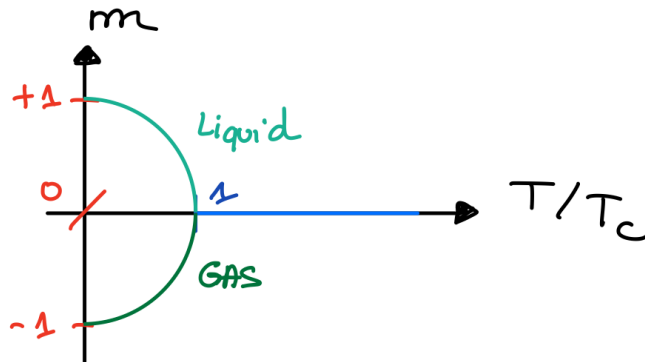
$$\begin{aligned} m &= \frac{1}{e^{-\frac{2T_c}{T}m} + 1} - 1 \\ &= \frac{1 - e^{-\frac{2T_c}{T}m}}{1 + e^{-\frac{2T_c}{T}m}} \\ &= \left(\frac{e^{\frac{T_c}{T}m}}{e^{\frac{T_c}{T}m}} \right) \left(\frac{1 - e^{-\frac{2T_c}{T}m}}{1 + e^{-\frac{2T_c}{T}m}} \right) \\ &= \tanh\left(\frac{T_c}{T}m\right) \end{aligned}$$

So, indeed we found (2),

$$m = \tanh\left(\frac{T_c}{T}m\right)$$

Remark : we already know the solutions from the Ising model.

- (b) Solve for Eq. (2) graphically and show that for $T \geq T_c$, there exists one solution $m = 0$, while for $T < T_c$, $m = 0, \pm m_0(T)$.



- (c) Taylor-expand the grand-potential found at question 1.2.1(c) to fourth order in m and show that for T close to T_c , one has

$$\Omega = N_0 k_B T_c \left(\frac{1}{2} - \ln 2 + \frac{1}{2} \frac{T - T_c}{T_c} m^2 + \frac{1}{12} m^4 \right)$$

Discuss then the stability of the solutions found at the preceding question. What is the physical meaning of your results?

$$\Omega = 3\epsilon N_0 n^2 - N_0 k_B T \ln[1 + e^{\beta(6\epsilon n + \mu)}]$$

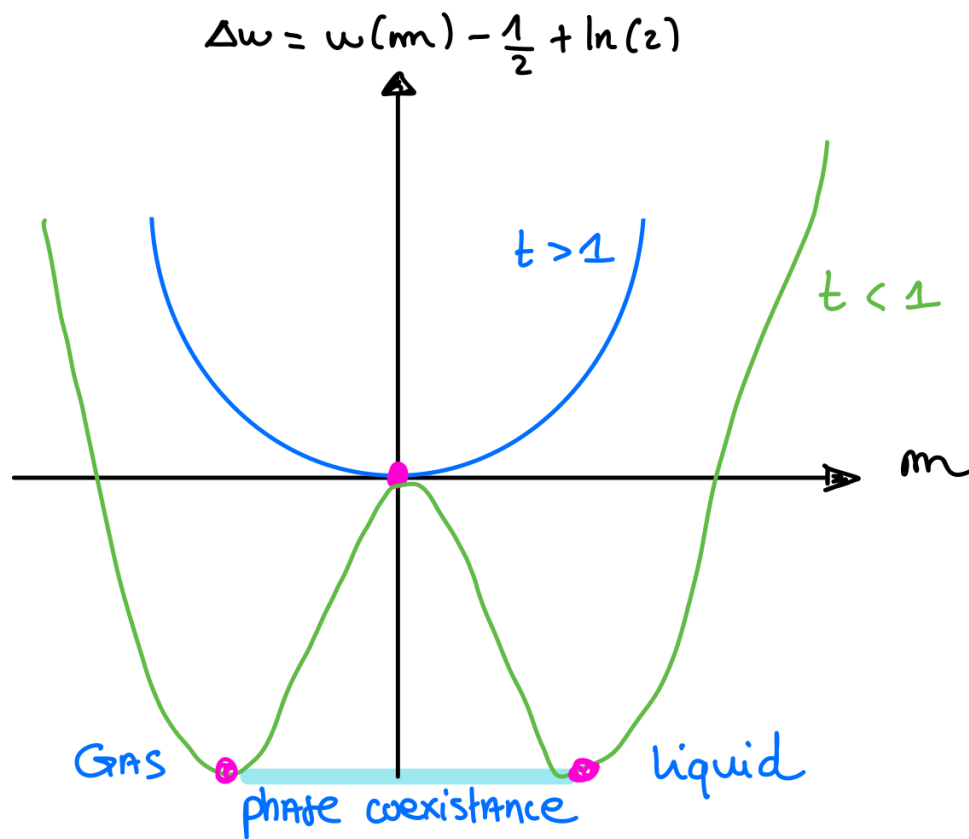
We want to express the order parameter m , we're gonna use reduced unit again,

$$\omega = \frac{\Omega}{N_0 k_B T_c}, \quad t = \frac{T}{T_c} = \frac{\tau}{\tau_c}$$

Meaning,

$$\omega = \frac{3}{\tau_c} \left[\frac{1}{2} (1 + m) \right]^2 - t \ln[1 + e^{2m/t}]$$

$$\omega \approx \frac{1}{2} - \ln(2) + \frac{1}{2} (1 - t) m^2 + \frac{m^4}{12}$$

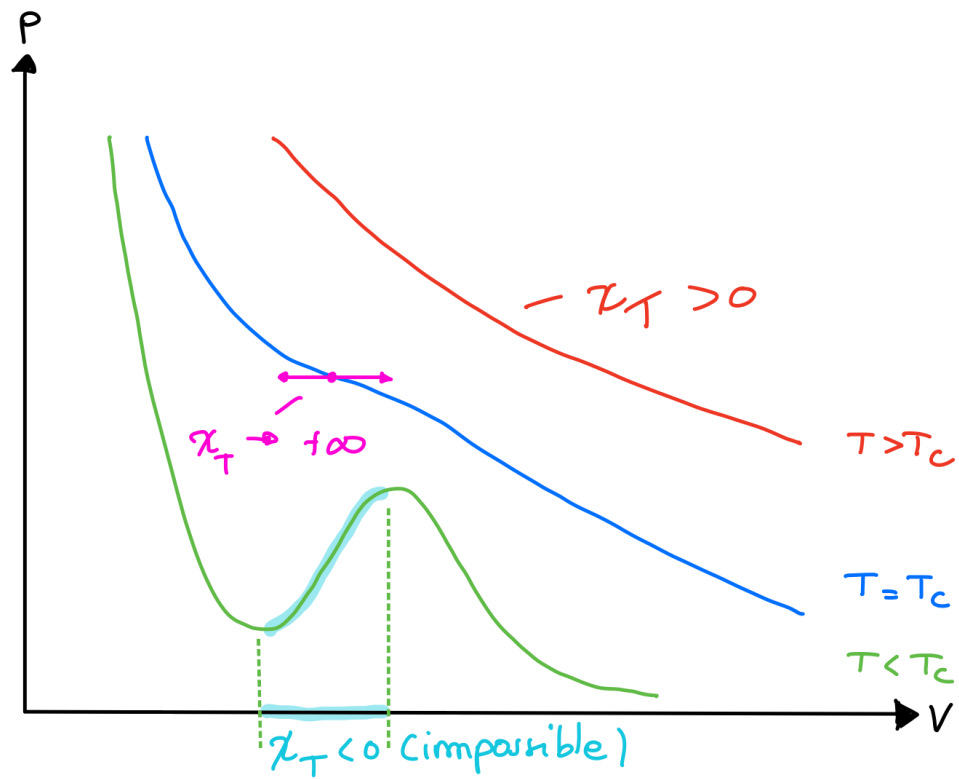


(d) Calculate the isothermal compressibility

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

of the system in the vicinity of the critical point. How does it behave in the limit $T \rightarrow T_c$?

$$\chi_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$$



We can show that,

$$\chi_T \sim \frac{1}{(T - T_c)^1}$$

1.2.3 Universality classes

- (a) Compare the mean-field critical exponents of the lattice gas and Ising models (cf. Problem Set 3).

We found,

$$m \sim (T_c - T)^{1/2}$$

meaning that the β exponent is $1/2$, and,

$$\chi \sim (T_c - T)^{-1}$$

meaning that the γ exponent is -1 .

- (b) By introducing $n_i = (1 + s_i)/2$ with $s_i = \pm 1$, show that close to the critical point, $\mathcal{H} - \mu N$ can be mapped into an Ising Hamiltonian with $J = \epsilon/4$ and zero magnetic field.

$$\mathcal{H} - \mu N = -\epsilon \sum_{\langle i,j \rangle} n_i n_j - \mu \sum_{i=1}^{N_0} n_i$$

$n_i \in \{0, 1\}$ but we want to express it using $s_i \in \{-1, +1\}$,

$$n_i = \frac{1}{2}(s_i + 1)$$

Meaning,

$$\begin{aligned} \mathcal{H} - \mu N &= \frac{\epsilon}{4} \sum_{\langle i,j \rangle} (s_i s_j + s_i + s_j + 1) - \frac{\mu}{2} \sum_{i=1}^{N_0} (s_i + 1) \\ &= -\frac{\epsilon}{4} \sum_{\langle i,j \rangle} s_i s_j - \frac{1}{2}(\mu + 3\epsilon) \sum_{i=1}^{N_0} s_i - \underbrace{\frac{N_0}{2} \left(\mu + \frac{3\epsilon}{2} \right)}_{\text{constant we can drop}} \end{aligned}$$

$$J = \frac{\epsilon}{4}, \quad h = \frac{1}{2}(\mu + 3\epsilon) = 0 \text{ because } \mu_c = 3\epsilon$$

Meaning,

$$\mathcal{H} - \mu N = -J \sum_{\langle i,j \rangle} s_i s_j$$

We find

$$k_B T_c = 6J = \frac{3}{2}\epsilon$$

which is exactly what we found.

2 Van der Waals equation of state

Let us consider a fluid of N monatomic molecules with mass m occupying a volume V at the temperature T . Here we shall describe the liquid-gas phase transition with a slightly more realistic model as that in Problem 1. We recall that the canonical partition function of the system is given by

$$Z = \frac{1}{N! \Lambda_T^{3N}} \int d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)}$$

where $\Lambda_T = (2\pi\hbar^2/mk_B T)^{1/2}$ is the thermal de Broglie wavelength, $\beta = 1/k_B T$, and $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the potential energy of the fluid.

2.1 The ideal gas case

Let us first consider the case of an ideal gas, where we assume that $U(\mathbf{r}_1, \dots, \mathbf{r}_N) = 0$.

- (a) Calculate the free energy, and deduce from your result the equation of state of the system.

$$Z = \frac{V^N}{N! \Lambda_T^{3N}}$$

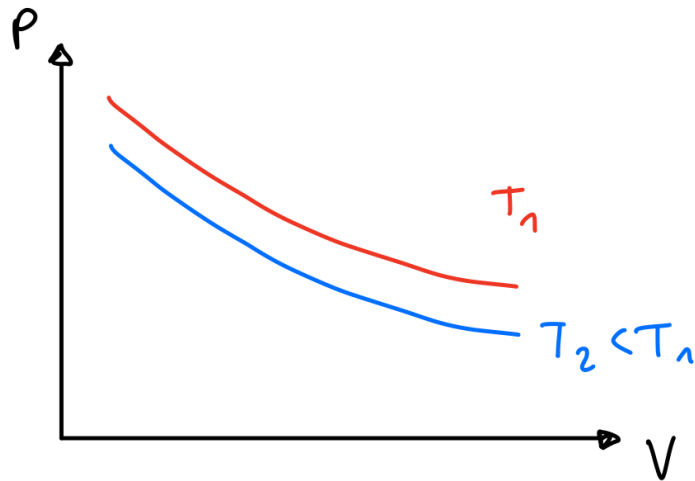
$$F = -Nk_B T \left(\ln \left(\frac{V}{N \Lambda_T^3} \right) + 1 \right)$$

$$P = -\frac{\partial F}{\partial V} = \frac{Nk_B T}{V}$$

Meaning,

$$PV = Nk_B T$$

- (b) In a P - V diagram, sketch the isothermal curves. Does the ideal gas model enable one to describe the liquid-gas phase transition?



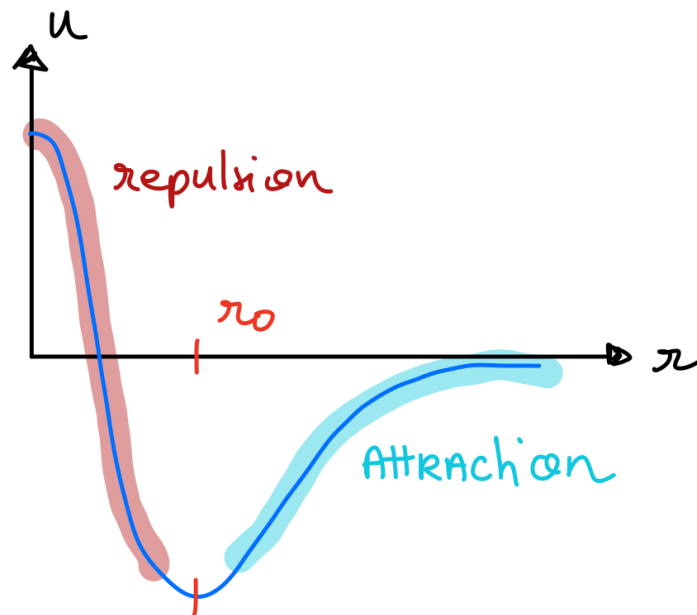
There is no phase transition, indeed, we need to have interactions in order to exhibit a phase transition.

2.2 Role of the molecular interactions

- (a) Let us now consider the interactions between pairs of molecules only. Show that the interaction energy reads

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{2} \sum_{i,j=1}^N u(r_{ij})$$

where $u(r_{ij})$ is the potential energy between two pairs of molecules separated by the distance r_{ij} . Sketch $u(r)$.



- (b) Consider first the attractive part of $u(r)$ and neglect the correlations between particles.
- What is the average number of particles in an infinitesimal volume $d^3\mathbf{r}$?
 - Show that the system behaves as an independent-particle one, subject to the potential $U/N \simeq -aN/V$, with $a = -(1/2) \int d^3\mathbf{r} u(r)$ a constant which only depends on the chosen form for $u(r)$. (Determine, e.g., a for $u(r) = -u_0(r_0/r)^s$. What happens if $s \leq 3$?).
 - Determine the partition function of the system, as well as its free energy. What kind of approximation have you performed?
- (c) Close to a given molecule, the approximation above is not valid any longer. Why? In the following, we will assume that one can take care of excluded-volume effects by replacing V by $V - Nb$ in the contribution of the ideal gas to the free energy. Justify such an approximation and give the free energy of the system. Deduce from the above results the van der Waals equation of state

$$\left(P + a \frac{N^2}{V^2}\right) (V - Nb) = Nk_B T \quad (3)$$

$$U(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{2} \sum_{i=1}^N \underbrace{\left[\sum_{j=1}^N u(r_{ij}) \right]}_{i \text{ is fixed}}$$

We can fix $\vec{r}_i$, so we can take $\vec{r}_i = \vec{0}$,

$$\sum_{j=1}^N u(r_{ij}) = \sum_{j=1}^N u(r_j)$$

But, there is a lot's of particles, so we can replace the summation by an integral,

$$\sum_{j=1}^N u(r_j) \approx \int d^3\vec{r} n(\vec{r}) u(r)$$

where $n(\vec{r})$ is the density of particles, we can say that this density is homogeneous,

$$n(\vec{r}) = \frac{N}{V}$$

So,

$$\sum_{j=1}^N u(r_{ij}) \approx \frac{N}{V} \int d^3\vec{r} u(r)$$

This integral doesn't depend on i , we can call it $-2a$, so,

$$U(\vec{r}_1, \dots, \vec{r}_N) \approx \frac{1}{2} \left(-\frac{2aN}{V} \right) N$$

where the right N comes from the summation over i . Meaning, that, in the end,

$$U(\vec{r}_1, \dots, \vec{r}_N) \approx -\frac{aN^2}{V}$$

$$Z = \frac{1}{N! \Lambda_T^{3N}} \int d^3\vec{r}_1 \dots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)}$$

Each particles is seen as a finite ball of radius R , meaning an excluded volume of $\frac{4}{3}\pi(2R)^3$, it is the b parameter in the Van-der-Waals model. So, each ball has a volume,

$$V_{\text{tot}} - (N-1)b \approx V_{\text{tot}} - Nb$$

Meaning,

$$\begin{aligned} Z &= \frac{1}{N! \Lambda_T^{3N}} \int d^3\vec{r}_1 \dots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} \\ &\approx \frac{1}{N! \Lambda_T^{3N}} \int_{V-Nb} d^3\vec{r}_1 \dots d^3\vec{r}_N e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} \\ &= \frac{1}{N! \Lambda_T^{3N}} (V - Nb)^N e^{\beta \frac{aN^2}{V}} \end{aligned}$$

if we set $a = b = 0$ we recover what we did earlier.

If we set $b = 0$,

$$Z = Z_{\text{ideal gas}} e^{\beta \frac{aN^2}{V}}$$

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -Nk_B T \ln \left(\frac{V - Nb}{\Lambda_T^3} \right) - \frac{aN^2}{V} + \underbrace{(-N \ln N + N)}_{\text{Stirling}} (-k_B T) \end{aligned}$$

$$P = -\frac{\partial F}{\partial V} = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

We indeed recover Van-der-Waals state equation,

$$\left(P + a \frac{N^2}{V^2} \right) (V - Nb) = Nk_B T$$

$$\begin{aligned}
 a &= -\frac{1}{2} \int d^3\vec{r} u(r) \\
 &= -\frac{1}{2} \int_{r_0}^{+\infty} dr r^2 u(r)
 \end{aligned}$$

We can approximate,

$$u(r) \propto \frac{1}{r^\alpha}$$

$\alpha = 6$ for Lennard-Jones, 3 for dipole-dipole interaction, 1 for Coulomb.

$$\int_{r_0}^{+\infty} dr r^2 u(r) \approx \int_{r_0}^{+\infty} \frac{1}{r^{\alpha-2}}$$

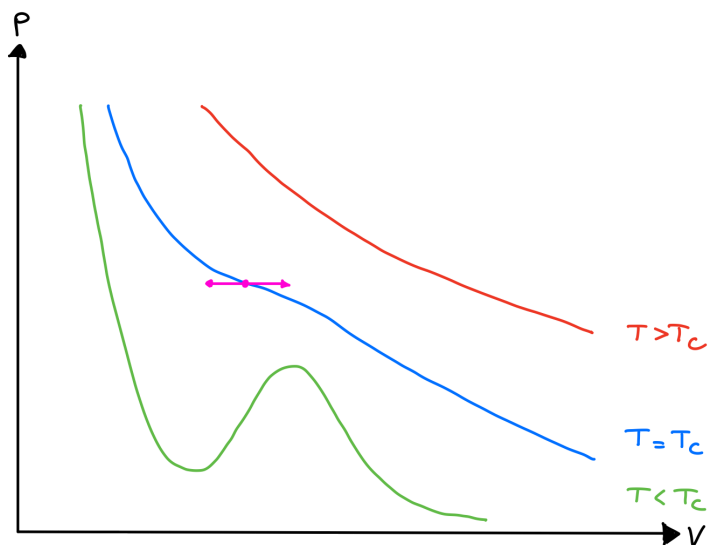
if $\alpha - 2 = 1$ we have a divergence at $+\infty$, it only converges if $\alpha - 2 > 1$, meaning that $\alpha > 3$.

2.3 The liquid-gas phase transition

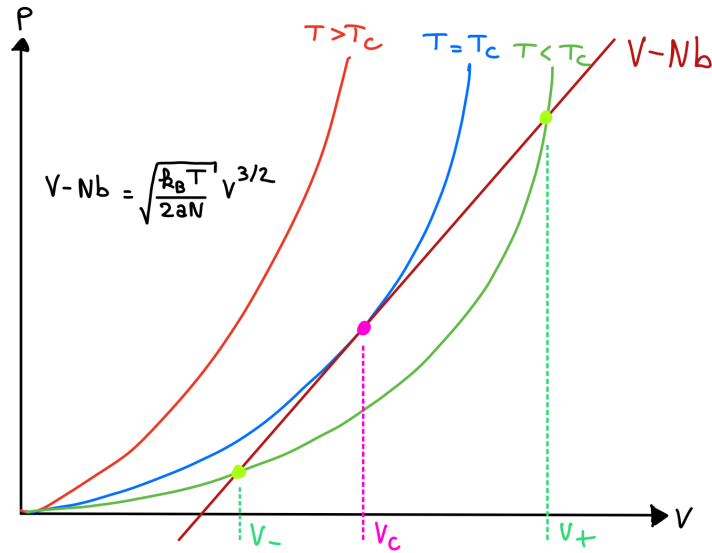
We now aim at describing the liquid-gas phase transition, using the van der Waals equation of state (3).

2.3.1 Isothermal curves

- (a) Sketch the isothermal curves in a P - V diagram. In particular, show that there exists a critical temperature T_c below which the isothermal curves are no longer monotonic functions. (Denote V_- and V_+ the positions of the two extrema.)



- (b) For the critical isothermal curve, there exists an inflection point (P_c, V_c) called the critical point. Give the expressions of P_c , V_c , and T_c as a function of a and b . For water, one has $a = 9.62 \text{ eV}\cdot\text{\AA}$ and $b = 51.1 \text{ \AA}$. Give an estimate of T_c and P_c .



At V_c , the slopes are equal, meaning,

$$\begin{cases} \frac{\partial}{\partial V}(V - Nb) = \frac{\partial}{\partial V} \left(\sqrt{\frac{k_B T}{2aN}} V^{3/2} \right) \\ V - Nb = \sqrt{\frac{k_B T}{2aN}} V^{3/2} \end{cases}$$

From the first equation we get,

$$1 = \sqrt{\frac{k_B T_c}{2aN}} V_c^{1/2}$$

Meaning,

$$k_B T_c = \frac{8aN}{9V_c}$$

From the second equation,

$$\begin{aligned} V - Nb &= \sqrt{\frac{k_B T}{2aN}} V^{3/2} \\ &= \frac{2}{3} V_c \end{aligned}$$

Meaning,

$$V_c = 3Nb$$

So now,

$$k_B T_c = \frac{8 a N}{9 V_c} = \frac{8 a N}{9 3 N b} = \frac{8 a}{27 b}$$

Then, the pressure,

$$\begin{aligned} P_c &= \frac{N k_B T_c}{V_c - N b} - a \frac{N^2}{V_c^2} \\ &= \frac{N \frac{8 a}{27 b}}{2 N b} - \frac{a N^2}{9 N^2 b^2} \end{aligned}$$

Meaning,

$$P_c = \frac{1}{27} \frac{a}{b^2}$$

Example : for water,

$$a = 9.62 \text{ eV} \cdot \text{\AA}^3,$$

$$b = 51.1 \text{ \AA}^3$$

So,

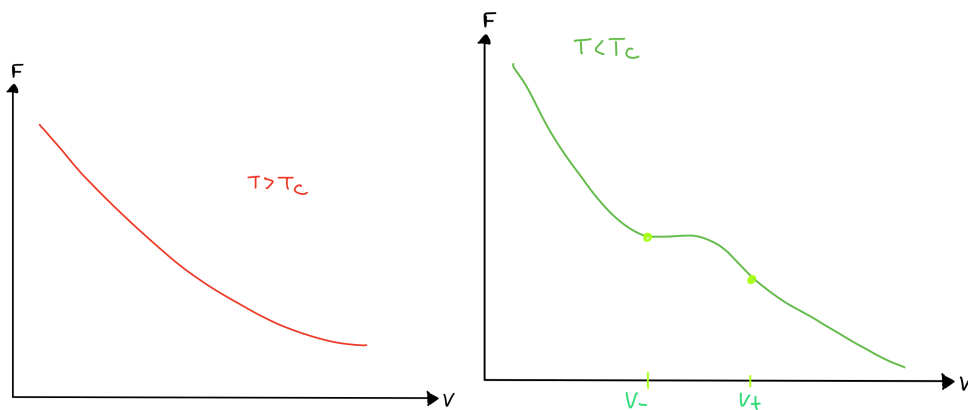
$$k_B T_c = \frac{8 a}{9 b} = 55.8 \text{ meV},$$

$$T_c = 647 \text{ K}$$

$$P_c = 216 \text{ atm}$$

$$V_c = 3 N b = 20 \text{ cl for } N = \mathcal{N}_A$$

- (c) Plot the free energy as function of V for $T > T_c$ and $T < T_c$.

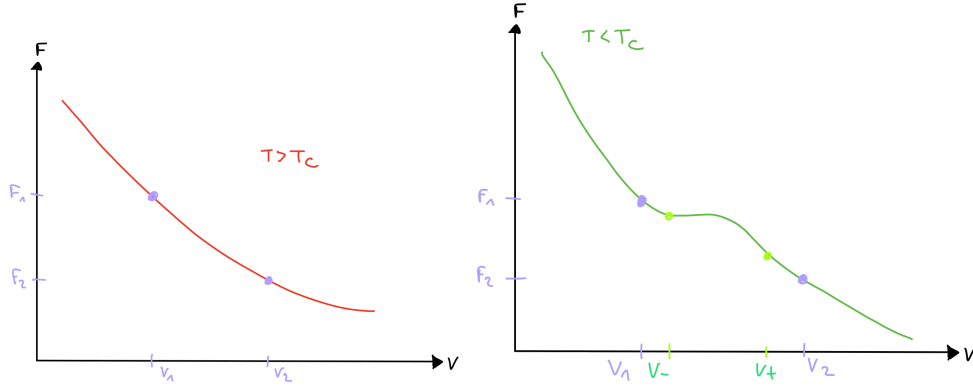


- (d) One can show that a thermodynamical system for which $(\partial P / \partial V)_T > 0$ is unstable. What are the regions in the P - V and F - V diagrams which correspond to thermodynamically un-stable states?

2.3.2 Critical instability

We are now aiming at describing the system in the unstable regions of the P - V or F - V diagrams. Let us denote $F(T, V, N)$ the free energy calculated above. We assume that the unstable system (P, V, N) separates into two homogeneous phases and aim at calculating the free energy F_b of the biphasic system. If F_b corresponds to a minimum, the system will choose such a biphasic equilibrium state. Let $F_1 = F(T, V_1, N)$ be the free energy of the homogeneous system of N molecules described by the van der Waals equation of state (3) at the temperature T when its volume is V_1 , and $F_2 = F(T, V_2, N)$ its free energy when its volume is V_2 . (Note that $V \neq V_1 + V_2$!) In what follows, we denote by N_1 and N_2 the number of molecules in the phase 1 and 2, respectively, with $N = N_1 + N_2$.

- (a) Recall what are the equilibrium conditions between the two phases. What is the proportion of molecules in phase 1? In phase 2? Deduce from your results above an expression for the volume V as a function of N_1 , N_2 , V_1 , and V_2 .



At equilibrium,

$$\begin{cases} \mu_1 = \mu_2 \\ T_1 = T_2 \\ P_1 = P_2 \end{cases}$$

We also have $N = N_1 + N_2$, meaning that the proportions are N_1/N and N_2/N of each populations. The total volume is,

$$V = \frac{N_1}{N}V_1 + \frac{N_2}{N}V_2$$

- (b) Give an expression of the free energy F_b of the biphasic system as a function of V , V_1 , V_2 , F_1 , and F_2 . Plot F_b in the F - V diagram. Discuss the stability of the system in the different regions of the diagram. What happens for $V \in [V_1, V_-] \cup [V_+, V_2]$?

$$\begin{aligned}
 F_b &= \frac{N_1}{N} F_1 + \frac{N_2}{N} F_2 \\
 &= \left(1 - \frac{N_2}{N}\right) F_1 + \frac{N_2}{N} F_2 \\
 &= F_1 + \frac{N_2}{N} (F_2 - F_1)
 \end{aligned}$$

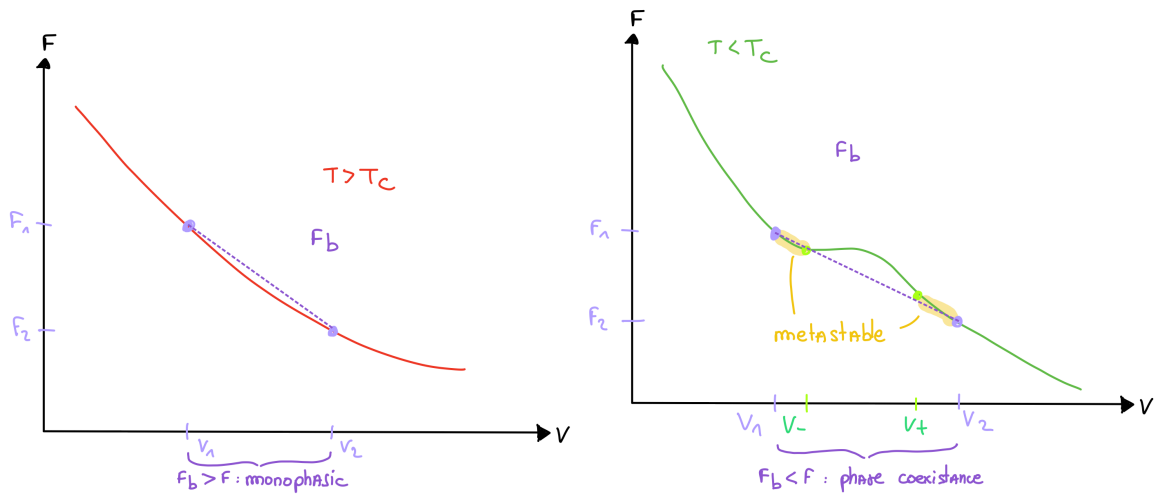
$$\begin{aligned}
 V &= \frac{N_1}{N} V_1 + \frac{N_2}{N} V_2 \\
 &= \left(1 - \frac{N_2}{N}\right) V_1 + \frac{N_2}{N} V_2 \\
 &= V_1 + \frac{N_2}{N} (V_2 - V_1)
 \end{aligned}$$

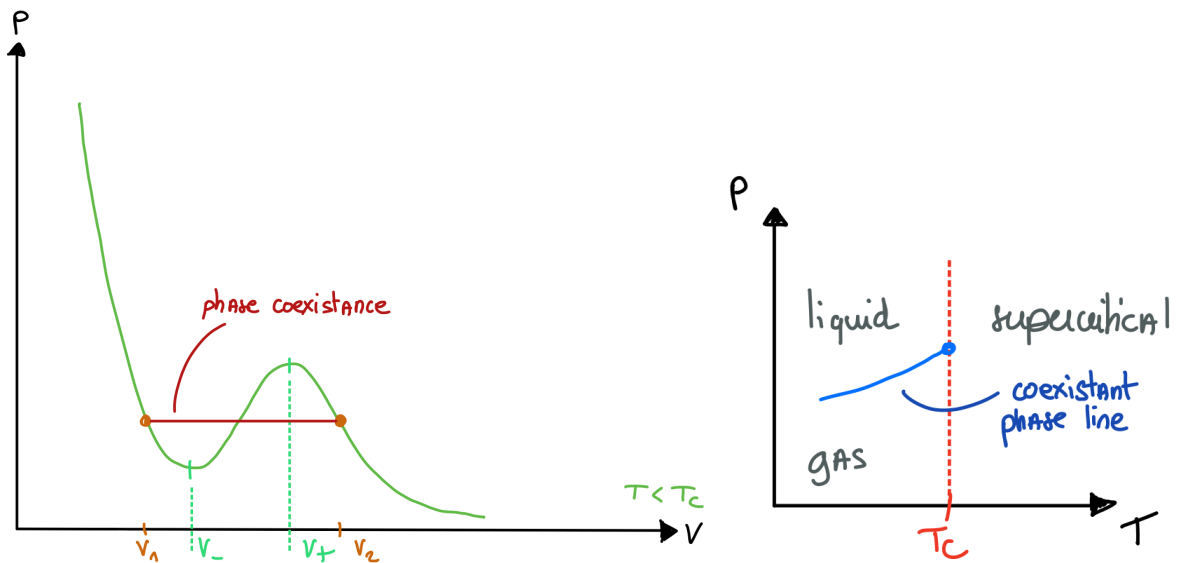
$$\frac{N_2}{N} = \frac{V - V_1}{V_2 - V_1}$$

So,

$$F_b = F_1 + \underbrace{\frac{F_2 - F_1}{V_2 - V_1}}_{<0} (V - V_1)$$

This is a straight line.



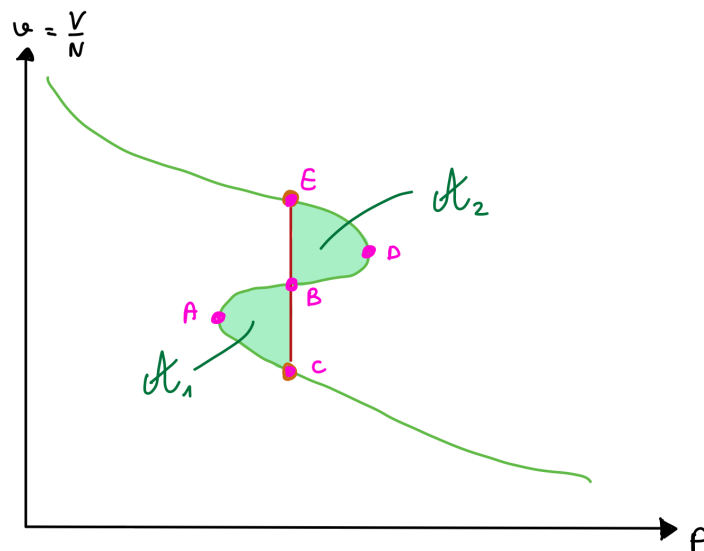


- (c) How should the van der Waals isothermal curves be transformed? Show that the equilibrium conditions of the two phases translate into a simple geometrical property (i.e., the Maxwell construction).

Hint : Plot $v = V/N$ as a function of P for $T < T_c$ and use the Gibbs–Duhem equation : $d\mu = -sdT + vdP$, where $s = S/N$.

From Gibbs-Duhem equation we know that,

$$v = \left. \frac{d\mu}{dP} \right|_T$$



$$\begin{aligned}
\mathcal{A}_1 &= \int_A^B v dP - \int_A^C v dP \\
&= \mu(B) - \mu(A) - (\mu(C) - \mu(A)) \\
&= \mu(B) - \mu(C)
\end{aligned}$$

$$\begin{aligned}
\mathcal{A}_2 &= \int_E^D v dP - \int_B^D v dP \\
&= \mu(D) - \mu(E) - (\mu(D) - \mu(B)) \\
&= \mu(B) - \mu(E)
\end{aligned}$$

At equilibrium the condition is that,

$$\mu(C) = \mu(E)$$

Meaning that,

$$\mathcal{A}_1 = \mathcal{A}_2$$

This is called the *Maxwell's construction*.

Intermezzo : how do we get the Gibbs-Duhem equation,

$$dE = TdS - PdV + \mu dN$$

$$G = F + PV = E - TS + PV \longrightarrow dG = -SdT + VdP + \mu dN$$

And we know Euler's relation for G ,

$$G = \mu N$$

Meaning,

$$Nd\mu = -SdT + VdP \longrightarrow d\mu = -sdT + vdP$$

- (d) Recall how the P - T diagram looks like for an elementary body. What is the region which we have described in this Problem?

2.3.3 Critical fluctuations

We now describe the fluctuations of the density $\rho = N/V$ close to the phase transition. One can show that such fluctuations are related to the isothermal compressibility by the following

expression :

$$\frac{\langle(\rho - \langle\rho\rangle)^2\rangle}{\langle\rho\rangle^2} = \frac{k_B T}{V} \chi_T$$

where

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T$$

What can you say about the fluctuations at the critical point ? Show that for $\rho = \rho_c$, one has

$$\sqrt{\frac{\langle(\rho - \langle\rho\rangle)^2\rangle}{\langle\rho\rangle^2}} = \frac{2}{3\sqrt{N}} \frac{1}{\sqrt{T/T_c - 1}}$$