Homework 04, Statistical Mechanics: Concepts and applications
2019/20 ICFP Master (first year)

Botao Li, Valentina Ros, Victor Dagard, Werner Krauth

With solutions

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In lecture 04 (Phase equilibria and first-order phase transitions), we studied the basic van-der-Walls (mean-field) theory of the liquid-gas transition. However, time was short, and we did not explore the rigorous conditions for phase equilibria, neither the "beyond van-der-Waals" aspects that are of greatest importance for the analysis of finite systems. This is what we will concentrate on in this homework session.

I. VAN-DER-WAALS THEORY

A. Preliminaries

Remember the three ingredients of van der Waals (1873) theory:

a and b Two parameters modify the ideal gas law $PV = NRT$: a (related to the attractive part of the interparticle potential, and leading to a negative system energy) and b (related to the volume each atom occupies, and leading to a reduced entropy per particle).

Phase equilibrium Phase equilibrium is expressed through three conditions, namely $T_1 = T_2$ (thermal equilibrium), $P_1 = P_2$ (mechanical equilibrium), and $\mu_1 = \mu_2$ (equilibrium of particle flows).

Thermodynamic inequalities : The thermodynamic inequality $\partial P/\partial V < 0$ expresses the condition that the compressibility of any gas or liquid is finite.

Of course, since 1873, many things have happened, and all the above principles have found exceptions. One of these exceptions will be studied in Section III: We will explicitly construct an equation of state with a positive $\partial P/\partial V > 0$, for finite number of particles. This equation of state, however, is qualitatively correct, and still extremely useful today.

B. Van der Waals equation of state in reduced variables

Remember the van der Waals equation of state (treated in Lecture 04):

$$\left(p+\frac{3}{v^2}\right)\left(v-\frac{1}{3}\right)=\frac{8t}{3} \tag{1}$$

with $v = V/V_c$, $p = P/P_c$, and $t = T/T_c$, where V_c, T_c, P_c are the volume, the temperature and the pressure at the critical point. Note that eq. (1), the law of corresponding states, is an early illustration of universality in statistical physics, as it predicts identical phase behavior for any gas of atoms or molecules, under suitable rescaling of the thermodynamic variables.

Recap of how eq. (1) is derived:

The Van der Waals equation for a gas reads

$$\left(p+\frac{aN^2}{V^2}\right)(V-Nb)=NRT$$

Defining the molar volumes as $v = V/N$*, we can rewrite it as*

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

This is equivalent to

$$v^3-\left(b+\frac{RT}{p}\right)v^2+\frac{a}{p}-\frac{ab}{p}=0$$

We have thus that, for certain values of p *and* T *, there are three real solutions for* v *. We can define the critical quantities* p_c *and* T_c *as those values for the pressure and the temperature such that the molar volume* v *has three coincident solutions. We will denote this solution with* v_c *. This means that we can write*

$$v^3-\left(b+\frac{RT_c}{p_c}\right)v^2+\frac{a}{p_c}-\frac{ab}{p_c}=(v-v_c)^3$$

Developing this relation we can find

$$v_c=3b\ ,\ p_c=\frac{a}{27b^2}\ ,\ T_c=\frac{8a}{27bR}$$

It is convenient to define the reduced variables

$$v_r=\frac{v}{v_c}\ ,p_r=\frac{v}{v_c},\ T_c=\frac{T}{T_c}$$

The Van der Waals equation can now be rewritten as

$$\left(p_r+\frac{3}{v_r^2}\right)\left(v_r-\frac{1}{3}\right)=\frac{8}{3}T_r$$

This last expression is an example of universality. In fact it is invariant in form for any gas, since the parameters a and b do not appear explicitly. In other words, for any gas it is possible to make a rescaling of v, p and T such that this relation holds.

C. Van der Waals equation of state

Write a program to plot the van der Waals equation of state (p as a function of v) for several values of the reduced temperature. For your convenience, this program is made available on the website (see `van_der_Waals.py`), and the plot is shown in Fig. 1. Notice that not all of this plot shows physical points.

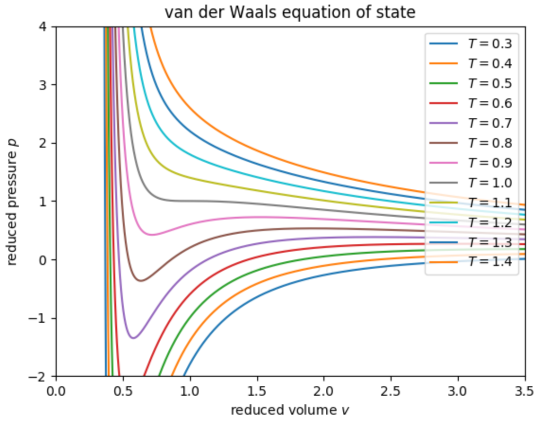

FIG. 1: Van der Waals equation of state, as it comes out of the provided program. Not all of this plot shows physical points.

In the figure (that you create yourself) identify the critical point (and state the two conditions that define it). Furthermore identify the spinodal points (and also state their defining condition) (sketch OK, but you may also modify the program). State in particular why the critical point is defined by two definitions on $p(v)$.

We can derive the explicit expression of p_r in terms of v_r and T_r . We will thus obtain

$$p_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}$$

which show that p_r is uniquely determined once fixed v_r and T_r. The same does not hold for v_r. Indeed, fixed p_r and T_r, v_r can have one or three real roots. As we have stated before, for

$T = T_c$ and $p = p_c$, v has three coincident roots. This is the case $v_r = 1$, $p_r = 1$, $T_r = 1$. The case of three roots for v_r is possible when, fixed T_r, p_r is initially a decreasing function of v_r, then become increasing and then again decreasing. Since in classical thermodynamics the pressure must decrease when the volume is growing, we will say that the portion of the isothermal where $\partial p_r/\partial v_r > 0$ is unphysical (i.e. cannot be described by the Van der Waals equation). This leads to find a line (called spinodal) locus of points such that $\partial p_r/\partial v_r = 0$. In particular, the critical point, where the three roots are coincident, is the limit when the two spinodal points on the isothermal coincide. This means that it can be defined by the two conditions

$$\begin{cases} \left(\frac{\partial p_r}{\partial v_r}\right)_{T_r} = 0 \\ \left(\frac{\partial^2 p_r}{\partial v_r^2}\right)_{T_r} = 0 \end{cases}$$

We have thus two independent conditions which have to be added to the Van der Waals equation. The fact of having three independent equations, describing three variables, means that there are no further degree of freedom. This is why we can speak of a single critical point. We can explicitly find an expression for the spinodal line from the condition $\partial p_r/\partial v_r = 0$ at fixed T_r . We will have

$$\frac{1}{v_r^3} = \frac{4T_r}{3v_r - 1}$$

and writing T_r as a function of v_r and p_r (from Van der Waals equation) we get

$$p_r = \frac{3}{v_r^3}\left(2\frac{v_r - 1/3}{v_r} - 1\right)$$

It is easy to check that the critical point ($v_r = 1$, $p_r = 1$, $T_r = 1$) lies on this line in a stationary point of p_r, as expected. The curve of spinodal points is shown in Fig. 2

D. Coexisting phases - Maxwell construction

As discussed in Lecture 04, coexisting phases are characterized through equal pressures, equal temperatures and equal chemical potentials. To illustrate this point, let us discuss the van der Walls equation of state at temperature $t = 0.75$. Performing minimal modifications of prog. `van_der_Waals.py`, you will now show that the coexisting phases are at volume $v_1 = 0.4896$ and $v_2 = 5.643$, at the coexistence pressure $p_{\text{coex}} = 0.28246$. The intermediate crossing volume with

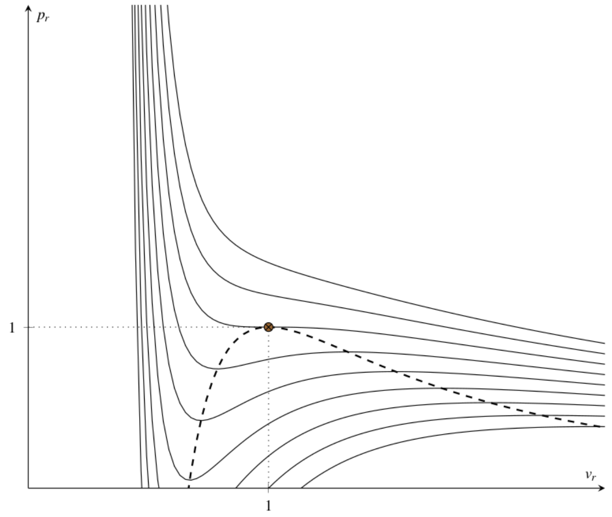

FIG. 2: This plot shows some isothermals, obtained from the Van der Waals equation, in the plan (v_r , p_r). Nine different values of T_r have been plotted, from $T_r = 0.7$ to 1.1 with a step of 0.05. The values of p_r increase as T_r grows at fixed v_r. The dashed line represents the spinodal line (obtained analytically). The critical point has been stressed.

the coexistence pressure satisfies $v_x = 1.281$ (We precomputed these values for you using a slightly more complicated program that you will not need to write yourself).

1. Volume integration

Show explicitly, through trivial numerical integration along v, from v_1 to v_x and from v_x to v_2, that

$$\int_{v_1}^{v_x} dv\,[p(v) - p_{\text{coex}}] = -\int_{v_x}^{v_2} dv\,[p(v) - p_{\text{coex}}]\,. \tag{2}$$

(sketch how you you compute these integrals). Interprete this in geometrical terms in the van der Waals equation of state that you generate for $t = 0.75$

2. Maxwell construction

Equivalently, you may integrate along the curve $p(v)$ from the pressure $p(v_1)$ (point 1) to the $p(v_x)$ (point x) and further on from $p(v_x)$ up to $p(v_2)$ (point 2).

$$\int_1^x dpv = -\int_x^2 dpv \tag{3}$$

(notice that the discretized differential dp in eq. (3) is $\Delta p = p(v+dv) - p(v)$) (sketch how you compute these integrals). Also explain why this socalled "Maxwell construction" establishes the equality of the chemical potentials at v_1 and v_2.

A trivial way of doing numerical integral is divided the region (for example, $[v_1, v_x]$) into small pieces. The length of each of them is the step size of the numerical integral Δv. Define $v_i = v_1 + i\Delta v$. The integral is approximately $\Delta v \sum_i p_r(v_i)$. There are better methods of doing numerical integral, but their implementation is more complicated. However, if possible, one should always use existing packages to do the numerical integral.

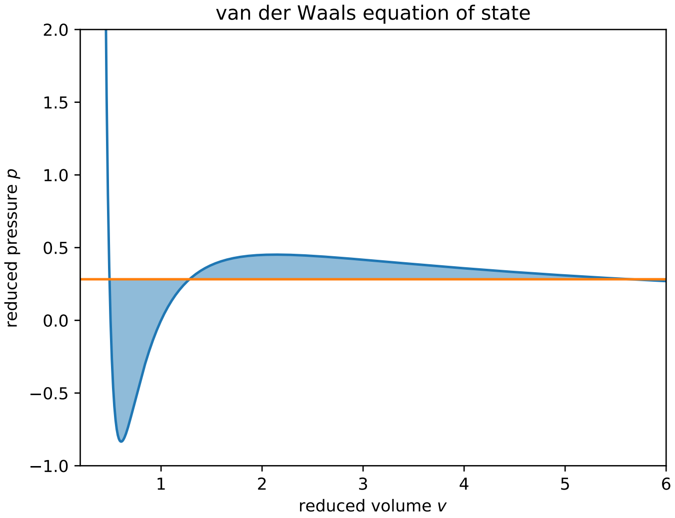

FIG. 3: The shadowed regions have identical area, which indicates $\mu_1 = \mu_2$

The equality indicated by eq. (2) means the shadowed regions in Fig. 3 have identical area. Equivalently, this relation can be expressed by another equation, which is exactly eq. (3). This equation also indicates $\mu_1 = \mu_2$. The reasoning starts from the Gibbs-Duhem relation, which writes

$$N d\mu = S dT + V dp$$

During the phase transition, T_r is identical for the whole system and is fixed in the current discussion, thus,

$$d\mu = v dp \propto v_r dp_r$$

eq. (3) can also be written as

$$\int_1^2 dpv = 0$$

which means

$$\mu_2 - \mu_1 = 0$$

In conclusion, $\mu_1 = \mu_2$ *imposed a constraint on the area shown in Fig. 3, which is related to* p_{coex}. *Thus, with the condition* $T_1 = T_2$, $p_1 = p_2$, *and* $\mu_1 = \mu_2$, *the unique value of coexisting pressure could be found.*

3. *Double tangent - Free energy*

The Maxwell construction provides only one view on the equilibrium of phases. The other one comes from the study of the free energy. Use your earlier program to plot the van-der-Waals free energy $f(v)$ (defined by $p = --df/dv$) from the curve $p(v)$. There is no need to compute the absolute value with great precision, but the relative values between some value below v_1 to some value beyond v_2 should be OK. How can you connect the points $f(v_1)$ and $f(v_2)$? Show that the interpolating line (with a variable $0 < x < 1$ expressing the concentration of phase 2) allows to mix phases 1 and 2. Express the mixture in terms of x, f_1 and f_2.

The free energy is defined as

$$F = E - TS$$

Thus,

$$dF = -SdT - PdV$$

For fixed T, $dF = -pdV$. *In the unit system used in the previous questions* ($v_c = p_c = T_c = 1$), *molar free energy has following expression*

$$f_r(v_r) = f_r(v_0) - \int_{v_0}^{v_r} p_r dv_r$$

where $f_r(v_0)$ *can be treated as a constant (which depends only on* T_r*). Using the expression of reduced Van der Waals equation*

$$f_r(v_r) = -\frac{3}{v_r} - \frac{8T_r}{3}\ln(v_r - 1/3) + c(T_r)$$

During the phase transition, the pressure between v_1 *and* v_2 *is connected by a horizontal line* $p_r = p_{coex}$*. Thus, the free energy between* v_1 *and* v_2 *is connected by a straight line, which starts at* $(v_1, f_r(v_1))$ *and ends at* $(v_2, f_r(v_2))$*. And since* $p_r(v_1) = p_r(v_2) = p_{coex}$*, the straight line in between is the double tangent line of the free energy curve. The free energy is plotted in Fig. 4 The free energy of a mixture of phase 1 and phase 2 can be also expressed as*

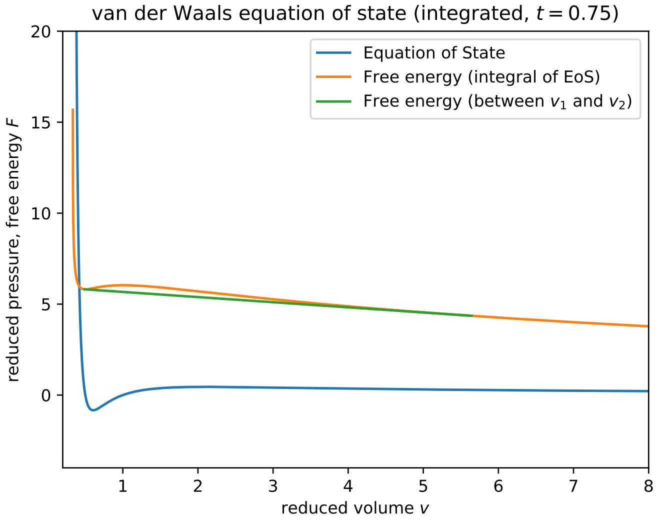

FIG. 4: Free energy of the system.

$$f(x) = xf_2 + (1-x)f_1 \tag{4}$$

where

$$x = \frac{v_r - v_1}{v_2 - v_1}$$

Let the fraction of the matter in phase 1(2) be $r_{1(2)}$*.* $r_1 + r_2 = 1$ *and* v_r *can be expressed as*

$$v_r = v_1 r_1 + v_2 r_2$$

then

$$x = \frac{v_1 r_1 + v_2 r_2 - v_1}{v_2 - v_1} = r_2$$

Thus, x *is the fraction of matter in phase 2. Thus, the expression eq. (4) is consist with the fact that the free energy is proportional to the system size.*

II. COMPARISON OF THE VAN DER WAALS THEORY WITH THE EQUATION OF STATE OF WATER

Van der Waals theory in reduced variables is called the “law of corresponding states” as it (seemingly) applies to any liquid-gas system. As mentioned, it is an early example of universality in statistical physics.

Try to apply it to water, whose critical point is at $647K$ and $22.064MPa$, while its boiling point at normal pressure is at $373.15K$ and $101.325kPa$. The Maxwell construction at $t = 0.577$ gives $v_1 = 0.426$ and $v_2 = 20.5307884385$, with $p = 0.069064$. Compare the ratios of the pressure (easy) and of the volumes (use Wikipedia)!

We will now try to apply the Van der Waals equation to the phase transition between liquid and vapor in water. The critical point of water is at $T_c \sim 647K$ *and* $p_c \sim 22.046 \times 10^6 Pa$. *Furthermore from experimental data we know that the critical molar volume is* $v_c \sim 5.6 \times 10^5 m^3/mol$. *(Datum taken from http://www.kayelaby.npl.co.uk/chemistry/3_5/3_5.html) We can immediately note that these three values are not consistent. In fact, since* $T_c = 8a/27bR$, $p_c = a/27b^2$ *and* $v_c = 3b$, *it is easy to check that it must holds*

$$p_c v_c = \frac{8}{3} R T_c$$

Taking the data we have we obtain $p_c v_c \sim 1.23 \times 10^3 J/mol$, *while* $3RT_c/8 \sim 2.02 J/mol$. *These two values are clearly incompatible. Furthermore we know that the boiling point of water at atmospherical pressure (*$p_b = p_{atm} \sim 101.325 \times 10^3 Pa$*) occurs at a temperature* $T_b = 373.15K$. *Nevertheless, the results obtained applying the Maxwell construction are inconsistent. In fact we have* $T_r = T_b/T_c \sim 0.577$, *which brings to an expected coexistence reduced pressure* $p_{coex} \sim 0.069$. *The reduced pressure obtained by* p_b/p_c *is* $p_r \sim 0.0046$, *clearly inconsistent with the previous result. A similar finding occurs when comparing the volumes obtained from Maxwell construction with the experimental data. From Maxwell construction we have that for the boiling point at* $T_r = 0.577$ *the reduced volume varies during the transition between* $v_1 \sim 0.426$ *and* $v_2 \sim 20.53$. *From the p-v diagram experimentally obtained we can deduce that the molar volume in the transition is limited by* $v_1^{(m)} \sim 1.8 \times 10^5 m^3/mol$ *and* $v_2^{(m)} \sim 5.48 \times 10^4 m^3/mol$*). (https://www.ohio.edu/mechanical/thermo/Intro/Chapt.1_6/Chapter2a.html) This leads to* $v_1 = v_1^{(m)}/v_c \sim 0.32$ *and* $v_2 = v_2^{(m)}/v_c \sim 9.79$, *which are not compatible with the values previously found. We can thus state that the transition from liquid water to vapor cannot be well described by the Van der Waals equation.*

III. BEYOND-VAN-DER-WAALS THEORY

We will now work on the van der Waals equation of state for $t = 0.85$, where the coexistence pressure is given by $p_{\text{coexist}} = 0.50449$, with $v_1 = 0.55336$ and $v_2 = 3.1276$. We now show an example where the thermodynamic inequality $\partial p/\partial v|_T < 0$ is violated. Indeed, the view of a mixture between phases 1 and 2 as a system with free energies f_1 and f_2, mixed in proportion, is too simple to describe finite systems, where the interface between the two phases provides a finite contribution to the system free energy per particle.

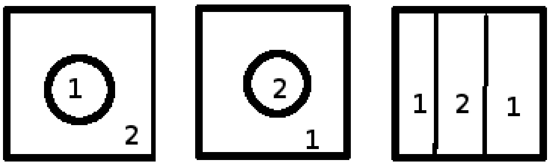

FIG. 5: The three possible scenarios for the mixture of phases 1 and 2 in a finite box with periodic boundary conditions: Bubble of 1 inside 2 (*left*), bubble of 2 inside 1 (*center*), stripes of 1 and 2. Note that periodic boundary conditions are assumed both in x and in y direction.

Let us study this effect in a two-dimensional system with periodic boundary conditions in x and in y. In fact, a mixture between phase 1 and phase 2 will look essentially like one of the three cases shown in Fig. 5: Either an approximately spherical bubble of phase 1 inside phase 2, or a bubble of phase 2 inside phase 1 or a stripe of phase 1 and a stripe of phase 2 (we suppose periodic boundary conditions in x and in y).

A. Finite system vs infinite-volume van-der-Waals theory

Explain why the interface is not considered in the infinite-volume van-der-Waals theory, but why it should be taken into account in a finite system.

The free energy of the system and the free energy of the interface have different scaling with respect to the system size. For simplicity, we assume that the following discussion takes place in a 2D system. However, the following reasoning remains qualitatively valid for arbitrary dimensional systems. Let L be the length scale of the system. Assuming the number of particles per unit *area remains constant, the free energy of the system scales with respect to the number of particles, i.e. the area of the system, which means the free energy of the system*

$$F \propto L^2$$

Assuming the free energy of the interface is constant per unit length, the interface free energy

$$F_i \propto L$$

and

$$F_i/F \propto 1/L$$

In a infinitely large system, $L \to \infty$ *and* $F_i/F \to 0$*. It also indicates that the molar free energy of the interface* $f_i \propto F_i/L^2 \to 0$*. Thus it is safe to ignore the free energy of the interface. However, in a finite system,* F_i *has to be taken into consideration.*

B. Single bubble vs vinaigrette

Suppose the existence of an interface free energy per unit length γ. Show (in simple terms) why the equilibrium configuration can be a single bubble of one phase in a sea of the other phase (as in Fig. 5), but not a configuration with many bubbles (of the same total volume), as in vinaigrette.

The configures which have less free energy are more probable. In other words, the system always chooses the configurations which have least free energy. Assuming the amount of matter in phase 2 is fixed and all the bubbles are round. Then the sum of the areas of the bubbles, i.e. $\sum_i^{N_{bubble}} r_i^2$*, is constant. The number of bubbles should minimize the total length of the surface, i.e.* $\sum_i^{N_{bubble}} r_i$*. Since all the* r_i *is positive,*

$$\left(\sum_i^{N_{bubble}} r_i\right)^2 \geq \sum_i^{N_{bubble}} r_i^2$$

and the equality is achieved only if there is one bubble. Thus, the configuration of one big bubble has less free energy than the configurations of multiple small bubbles.

C. Preliminaries of the free energy of a finite system

Consider the following simple versions of the free energy for the three scenarios in Fig. 5, where γ is the surface tension (surface free energy per unit length) between the two phases:

$$f_{2\text{ in }1} = f_1(1-x) + f_2 x + \frac{2\gamma}{\sqrt{N}}\sqrt{\pi v_2 x} \tag{5}$$

$$f_{1\text{ in }2} = f_1(1-x) + f_2 x + \frac{2\gamma}{\sqrt{N}}\sqrt{\pi v_1 (1-x)} \tag{6}$$

$$f_{||} = f_1(1-x) + f_2 x + \frac{2\gamma}{\sqrt{N}}\sqrt{\frac{V}{N}} \tag{7}$$

Two of these three graphs are plotted in Fig. 6, together with the integrated van-der-Waals equation of state, in the vicinity of $v_1 = 0.55336$, the point of the beginning two-phase region, for a value of $\frac{2\gamma}{\sqrt{N}} = 0.04$.

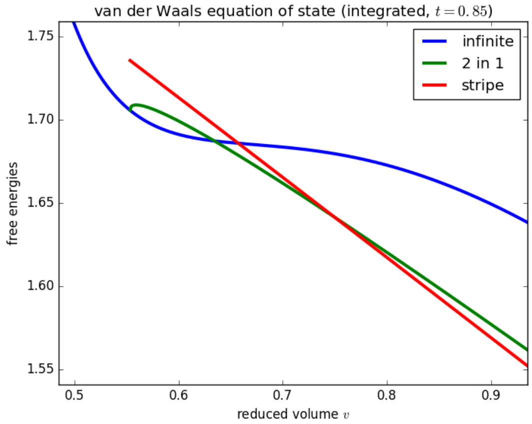

FIG. 6: Van der Waals free energy for the infinite system at $t = 0.85$, compared to the free energies of the bubble 2 in 1 and the stripe free energy. Note that $v_1 = 0.55336$

Calculation of the free energies: Assuming the system is in a square box of volumn V*. For* f_{2in1}*, the area of phase 2 is* Nxv_2*. Thus, the length of the interface is* $2\sqrt{\pi N x v_2}$*. And the contribution to molar free energy is* $\frac{2\gamma}{\sqrt{N}}\sqrt{\pi v_2 x}$*. For* f_{1in2}*, the same argument is still valid. For stripe, the length of the interface becomes* $2\sqrt{V}$*.*

D. Interpretation of a free-energy curve

Interprete each of the three curves in Fig. 6, and especially the behavior of $f_{2\text{ in }1}$ near v_1: What is the prediction for the pressure for $f_{2\text{ in }1}$? (NB: This pressure is called Laplace pressure).

As in the case of an infinite system, between v_1 and v_2 , the Van der Waals equations will not hold. Anyway, in the case of a finite system the interface contribution must be taken into account. In a neighborhood of v_1 (for $v_r > v_1$) the free energy can be reasonably approximate by f_{2in1} . In fact we will have the appearance of a bubble of component 2 in a sea of phase 1. Since the interface contribution goes as $\sqrt{x}$, for $x \to 0$ it will lead to a divergence in the first derivative of f_r. This means that even if the free energy will still be continuous, the pressure will tend to $-\infty$ for $v_r = v_1$. There will thus be a neighborhood of v_1 in which the pressure will be allowed to be negative. Analogous considerations can be done for $v_r \sim v_2$. In this case we will have a bubble of phase 1 in a sea of component 2 and for $v_r = v_2$ the pressure will diverge to $+\infty$. During the transition from v_1 to v_2 we will expect an intermediate stage, in which we will have stripes of the different phases. We will thus have, for some central values of v_r in the interval (v_1 , v_2), the free energy approximated by $f_{||}$. In our constructions the transitions between f_{1in2}, f_{2in1} and $f_{||}$, thought keeping the continuity of f_r, will bring discontinuities in its first derivative, due to the jumps between bubble and stripes configurations. It is worth to notice that all three the functions f_{1in2}, f_{2in1} and $f_{||}$ are concave in (v_1, v_2), so that in all this interval we will have $\partial p/\partial v > 0$. This result is thus allowed for finite systems.

E. Minimization of the free energy

Without doing any calculation (only by inspection of Fig. 6), explain the sequence of phases as we move from v_1 to larger volumes. Sketch the free energy as a function of the reduced volume.

The free energy between v_1 and v_2 will be given by

$$f_r(vr) = \min\left(f_{1in2}(v_r), f_{2in1}(v_r), f_{||}(v_r)\right)$$

At the v_1, a bubble of phase 2 begin to form and the free energy of the system start to follow the curve f_{2in1}. At the intersection of f_{2in1} and $f_{||}$, the bubble become a stripe and the free energy of the system begin to follow curve $f_{||}$. Out of the plot shown here, the curve $f_{||}$ and f_{1in2} will intersect. The free energy will then follow the curve f_{1in2} until it reaches $(v_2, f_r(v_2))$.

F. Pressure in a finite system

Without doing any calculation, again, sketch the pressure as a function of v throughout the whole range shown in Fig. 6. Then explain (in simple terms) what happens if we go to larger systems ($N \to \infty$ with $N/V = \text{const}$ and constant surface tension γ).

The pressure can be evaluated as $p_r = \partial f_r/\partial v_r$ *along the isothermal. For a finite system,* $p_r(v_r)$ *is sketched in the Fig. 7. As previously noticed, in a finite system* p_r *can be negative. Furthermore in the interval* (v_1, v_2) *we will have* $p_r = \partial f_r/\partial v_r > 0$. *If the system becomes infinite, the contribution due to the interfaces become negligible. Hence, the pressure keeps constant during the transition and we obtain the results of Ex. 1.*

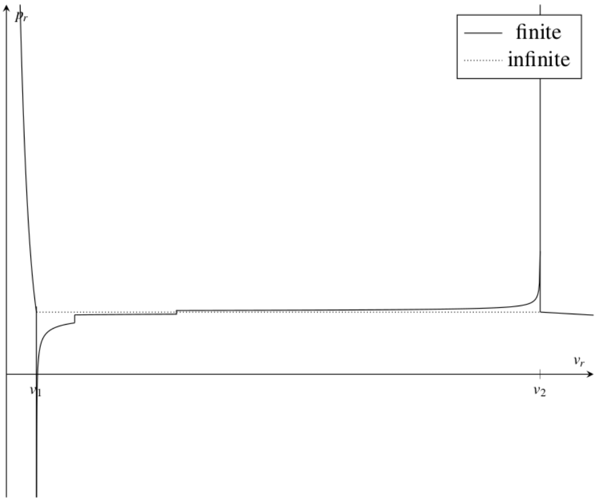

FIG. 7: Pressure of a finite system.