Homework 04, Statistical Mechanics: Concepts and applications
2017/18 ICFP Master (first year)

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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), $P_1 = P2$ (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 qualitative 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.

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.
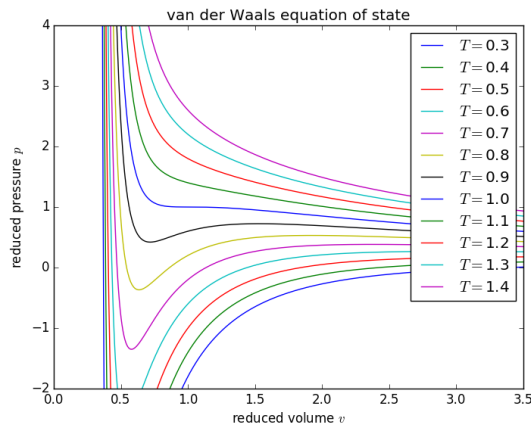

FIG. 1: Van der Waals equation of state, as it comes out of the provided program. Not all of this plot shows physical points.

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 $p(v)$.

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 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). Interpret 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.

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.

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)!

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.
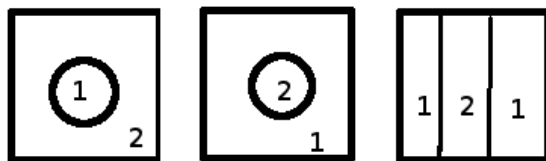

FIG. 2: The three possible scenarios for the mixture of phases 1 and 2 in a finite box with periodic boundary conditions: Bubble of 1 inside 2 (*left*), bubble of 2 inside 1 (*center*), stripes of 1 and 2. Note that periodic boundary conditions are assumed both in x and in y direction.

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. 2: 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.

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. 2), but not a configuration with many bubbles (of the same total volume), as in vinaigrette.

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. 2, where γ is the surface tension (surface free energy per unit length) between the two phases:

$$f_{2 \text{ in } 1} = f_1(1 - x) + f_2 x + \frac{2\gamma}{\sqrt{N}} \sqrt{\pi v_2 x} \tag{4}$$

$$f_{1 \text{ in } 2} = f_1(1 - x) + f_2 x + \frac{2\gamma}{\sqrt{N}} \sqrt{\pi v_1 (1 - x)} \tag{5}$$

$$f_{\parallel} = f_1(1 - x) + f_2 x + \frac{2\gamma}{\sqrt{N}} \sqrt{\frac{V}{N}} \tag{6}$$

Two of these three graphs are plotted in Fig. 3, 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 $\frac{2\gamma}{\sqrt{N}} = 0.04$.

D.   Interpretation of a free-energy curve

Interpret each of the three curves in Fig. 3, 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).
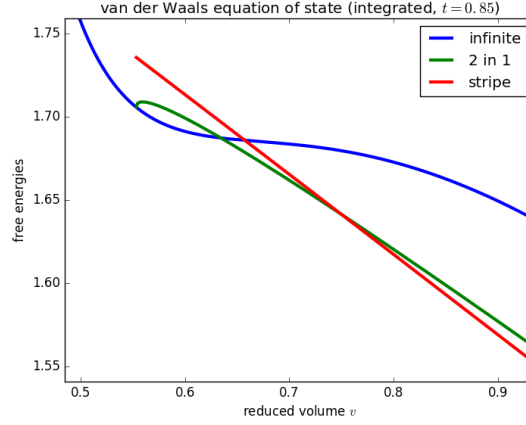
FIG. 3: Van der Waals free energy for the infinite system at $t = 0.85$, compared to the free energies of the bubble 2 in 1 and the stripe free energy. Note that $v_1 = 0.55336$

E. Minimization of the free energy

Without doing any calculation (only by inspection of Fig. 3), 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.

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. 3. Then explain (in simple terms) what happens if we go to larger systems ($N \to \infty$ with $N/V =$ const and constant surface tension γ).