Tutorial N2
Van-der-Waals gas and first-order phase transition

Do not hesitate to ask any questions about this tutorial or about any HomeWork assignments now, or after the classes. You can also contact me with your questions any other time by vel145@gmail.com.

1. **Basics about polynomial equations**

   (a) Plot function $y = 3x - 1$. At which point does it intersect x-axis and y-axis?

   (b) Plot function $y = 3x^2 - 3x - 6$. For which real x one has $y = 0$? Where the function $y(x)$ has its minimum?

   (c) Do the same for $y = 2x^2 + x + 3$. What is the difference? What is the condition that quadratic equation with real coefficients has real solutions?

   (d) Consider function $y = -2x^3 + 4x^2 + 2x - 4$. Find its local minimum and maximum. In this particular case it is also easy to find its zeros. Find zeros of this function. Plot the function.

   (e) Do the same for function $y = -2x^3 + 4x^2 - 2x + 4$.

   (f) Consider generic function of the form $y = x^3 + a\,x^2 + b\,x + c$ with real a, b, c. Let us call the critical line in the space of parameters $\{a, b, c\}$ such values of a, b, c for which all three zeros of $y(x)$ coincide.

   Write a parametric representation of the critical line $a = a(t), b = b(t), c = c(t)$. For this note that when three zeros coincide, one can write $y = (x - t)^3$.

   (g) Compute first and second derivatives of $y(x)$ ($\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$) for a, b, c lying on the critical line. At which values of x are these derivatives equal to zero?

   (h) Plot (schematically) the function $y(x)$ for a, b, c lying on the critical line.

   (i) Explain why a cubic equation with real coefficients has always either one or three real solutions.

2. **Van-der-Waals equation.**
   Van-der-Waals equation of state is a phenomenological equation which captures certain properties of non-ideal gases. In particular, it allows one to model liquid-gas transition. This equation reads:

   $$\left(P + \frac{N^2 a}{V^2}\right)(V - N\,b) = N\,T\,, \tag{1}$$

   where a, b are certain positive constants.

   It is more convenient to write it in terms of intensive quantities only:

   $$\left(P + \frac{a}{v^2}\right)(v - b) = T\,, \tag{2}$$

   where $v = V/N$ is specific volume.

   (a) Write this equation as a cubic equation on v. For each given P, T it has either one or three real solutions.

   (b) Critical point is a such value of P, T for which all three solutions of the Van-der-Waals equation coincide. Why do we speak about critical point but not about critical line?

   (c) Find the critical temperature, pressure (values of P, T at critical point), and critical specific volume (the latter as the solution of the Van-der-Waals equation at the critical point) as functions of the parameters a, b.

   (d) Consider two Van-der-Waals gases, with parameters a_1, b_1 and a_2, b_2 respectively. As P and v are dimensionfull quantities, we can change the measurements units (literally, replace $P \to P \times m_P$ and $v \to v \times m_v$). How this change affects a, b, T? Show that by properly adjusting measurement units (differently for each of the gases) one can achieve $a_1 = a_2$, $b_1 = b_2$. This means that in proper coordinates all Van-der-Waals gases look equivalent.

(e) Show that the choice $m_P = P_c$ and $m_V = v_c$, where P_c, v_c are P, v at the critical point, achieves the goal of the previous question. What is the value of a, b in this normalisation? If you do everything correctly, you can check that $T_c = 8/3$ in this normalisation.

(f) Consider normalised quantites with respect to the critical point (as in previous question). On the P, v - diagram (P is y-axis, v is x-axis) denote the critical point and sketch three isotherms (lines $P = P(v)$ at constant temperature) for three temperatures: critical, and above/below critical. Discuss in detail how the plot behaves in the regions $P \to \infty$ and $V \to \infty$. How equation of state is approximated in these regions? For which values of T can we approximate Van-der-Waals gas by an ideal gas?

3. **Thermodynamics of Van-der-Waals gas, phase transition**

(a) For arbitrary a and b, from $P = -\frac{\partial \mathcal{F}}{\partial V}_{|T}$ compute $\mathcal{F}$ up to an unknown function of temperature. Fix the latter by requirement that at $V \to \infty$ the Van-der-Waals gas should be approximated by the ideal gas. In this way you will derive free energy of the Van-der-Waals gas.

(b) Compute energy and C_V.

(c) On Fig.1, you can see a typical Van-der-Waals isotherm for temperature $T < T_c$. There is a region when there are three volumes v_A, v_B, v_C for a given pressure P_A. Correct physical interpretation is that v_A, v_C are two different phases and v_B is non-physical.

Consider systematic increase of pressure at a constant temperature. System does not follow curved path CBA, but when it reaches the point $\{P_A, v_C\}$, it starts to transform to the phase A which is described by point $\{P_A, v_A\}$. During transformation two phases coexist and the pressure remains constant. When the process of transformation is finished, system continues further along the isotherm starting from the point $\{P_A, v_A\}$.

Which point, A or C, corresponds to gas and which to liquid?

(d) **Maxwell construction.** Let N_A and N_C denote quantity of matter in the states A and C correspondingly, when two phases coexist. Then

$$N_{\text{tot}} = N_A + N_C, \quad V_{\text{tot}} = N_A\, v_A + N_C\, v_C\,. \tag{3}$$

Then free energy is given by

$$\mathcal{F}_{2\,\text{phases}} = N_A\, f(v_A) + N_C\, f(v_C)\,, \tag{4}$$

where $f(v) = \mathcal{F}(V, N)/N$ is the free energy, which was computed in question (a), per one particle.

$\mathcal{F}_{2\,\text{phases}}$ should be compared with the free energy of a hypothetical single phase described by the curved path CBA: $\mathcal{F}_{1\,\text{phase}} = N_{\text{tot}} f(V_{\text{tot}}/N_{\text{tot}})$. Comparison should be done at the same N_{tot} and V_{tot}. 2-phased situation should be realised each time when $\mathcal{F}_{2\,\text{phases}} < \mathcal{F}_{1\,\text{phase}}$.

Plot $\mathcal{F}/N_{\text{tot}}$ against $V_{\text{tot}}/N_{\text{tot}}$ for both $\mathcal{F}_{2\,\text{phase}}$ and $\mathcal{F}_{1\,\text{phase}}$ (for the sake of comparison, put them both on the same plot). To make plotting easier recall that f is minus surface below isotherm on Fig.1.

One of the conditions that should be satisfied by v_A and v_C is $P(v_A) = P(v_C)$ which can be also written as $\partial_v f(v_A) = \partial_v f(v_C)$. By considering your plot, find the second condition on v_A and v_C. What is the geometrical interpretation of this condition in terms of areas on Fig 1?

Fixing v_A and v_C allows to determine P_A – the pressure at a given T for which the phase transition is realised.

Do not attempt to find v_A, v_C, P_A explicitly.

(e) Show that at the critical point $v_A = v_C$. Therefore, the phase diagram should look as on Fig. 2 (ask me to draw Fig. 2).

(f) Sketch phase diagrams on PT and Tv plots.

(g) **Critical exponent.** When system approaches critical point, one can approximate $v_A - v_C \simeq$ const $\times v_{\text{critical}} \times (1 - \frac{T}{T_{\text{critical}}})^{-\beta}$. β is one of the so-called critical exponents. It does not depend on a, b and it can be measured in experiments. Compute β for the Van-der-Waals gas.

(h) **Clausius-Clapeyron equation.** From the discussion above it is clear that the phase transition occurs at a certain pressure that depends on a chosen temperature, $P_{\text{phase transition}} = P(T)$. Find expression for dP/dT (ask me for instructions).