Theoretische Physik IV: Statistische Physik und Thermodynamik
Übungsblatt 12½

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***Info**: Bitte schreiben Sie Name und Ihre Übungsgruppe auf das Übungsblatt und tackern Sie dieses. Sie dürfen in Gruppen von bis zu drei Personen abgeben.*

Aufgabe 1: Phase diagrams of the van der Waals model (*17 Punkte*)

This problem comprises the revised last parts of Aufgabe 1 from the Blatt 11½.
Recall the reduced van der Waals equation of state

$$(p' + 3/V'^2)(3V' - 1) = 8T' \tag{1}$$

in terms of $T' = T/T_c$, $V' = V/V_c$, and $p' = p/p_c$. Here T_c, V_c, and p_c are the state variables in the critical point.
First, we are interested in the position of points l and g. Recall what are those points: Let us start in the liquid phase and gradually increase V while keeping $T = \text{const}$. l is the point where the vaporization just starts and the majority of the fluid is still liquid. g is the point where almost all liquid has already vaporized. In between two phases exist simultaneously.
In the Blatt 11½ you have obtained

$$\ln\frac{x_+}{x_-} = \frac{(x_+ - x_-)(x_+ + x_- + 2)}{x_+ + x_- + 2x_+x_-}, \tag{2}$$

$$x_+ = 1/(3V_l' - 1), \quad x_- = 1/(3V_g' - 1), \tag{3}$$

where V_g' and V_l' are the reduced volumes in the points g and l, respectively. From the Eq. (2) one can find the function $x_-(x_+)$. However the function can only be expressed in a parametric form. That is, we find $x_-(\Delta s)$ and $x_+(\Delta s)$ in terms of a parameter Δs. (This is an analogue of 2D trajectory given by $x(t)$ and $y(t)$ as functions of time t.)

f) i) Show that

$$x_+ = e^{+\Delta s/2} f(\Delta s/2), \quad x_- = e^{-\Delta s/2} f(\Delta s/2), \tag{4}$$

where

$$f(x) = \frac{x\cosh x - \sinh x}{\sinh x \cosh x - x}$$

is the parametrical solution of Eq. (2). For this you need to equate both sides of Eq. (2) to Δs. With the equation that involves the left-hand side you can then express x_+ in terms of x_-. Substituting this into the remaining equation, you can express x_- in terms of Δs. (*2 Punkte*)

ii) Show that

$$\begin{gathered} V_l' = e^{-\Delta s/2}/3f + 1/3, \quad V_g' = e^{\Delta s/2}/3f + 1/3, \\ T' = \frac{27f}{4}\frac{\cosh(\Delta s/2) + f}{g^2}, \quad p' = 27f^2(1 - f^2)/g^2, \\ f = f(\Delta s/2), \quad g = 1 + 2f\cosh(\Delta s/2) + f^2. \end{gathered} \tag{5}$$

Additionally to the solutions (4) of Eq. (2), use the van der Waals equations on V_l' and V_g'. In obtaining the expression for $T(\Delta s)$ it is also convenient to use the equations

$$p'(V_g' - V_l') = \frac{8}{3}T' \ln \frac{3V_g' - 1}{3V_l' - 1} + 3\left(\frac{1}{V_g'} - \frac{1}{V_l'}\right),$$
$$\ln \frac{3V_g' - 1}{3V_l' - 1} = \frac{V_g' - V_l'}{V_g' + V_l'}\left(\frac{V_g'}{V_g' - 1/3} + \frac{V_l'}{V_l' - 1/3}\right)$$

you have obtained in the Blatt 11.5. *(3 Punkte)*

Now we plot points l and g for each T' in the diagrams for different variables. These points mark the boundary between different phases. *Plots where the regions of all possible phases of matter are marked are called phase diagrams.*
In this problem, it is preferable to do the plots with computer.

g) Plot the p'-T' phase diagram. Mark the liquid and the gaseous regions. Mark the critical point. *(3 Punkte)*

g') On the dividing curve in the p-T diagram both the liquid and the gaseous phases coexist. The curve ends in the critical point. Where does the coexistence curve starts from? Determine this by carrying out the limit of the expressions for p' and T' (5). *(1 Punkt)*

h) Plot the p'-V' phase diagram. Mark the liquid and the gaseous regions. Mark the critical point. *(3 Punkte)*

i) Can one convert a liquid state into a gaseous without a phase transition? If no, explain why; if yes, mark a possible path on the phase diagrams in g)–h). *(2 Punkte)*

Now we are interested in other, yet related, region.

j) i) Find the boundary of the region where the existence of a homogeneous phase is thermodynamically impossible. Use the condition $(dp/dV)_T > 0$ for an impossible state and the van der Waals equation (1). *(2 Punkte)*

ii) In the p-V phase diagram you have plot in h), mark the region where a homogeneous phase cannot exist. *(1 Punkt)*

Aufgabe 2: A phase diagram of the 2D Ising model (*8+4* Punkte*)

This problem is a revised version of the Aufgabe 2 of Blatt 11.5. It is a continuation of the first problem of Blatt 11.

Let us recall possible types of magnetization. Paramagnetic phase is a phase where there is no spontaneous magnetization. That is, $\langle\sigma\rangle = 0$ for $h = 0$ in it. Ferromagnetic phase is the opposite of this: $\langle\sigma\rangle \neq 0$ for $h = 0$ there.

In what follows it is convenient to use the result of Aufgabe 1i) from Blatt 11. There, you have shown that, up to a term constant in $\langle\sigma\rangle$,

$$F/N \approx -h\langle\sigma\rangle + a(T - T_\mathrm{c})\langle\sigma\rangle^2 + b\langle\sigma\rangle^4, \quad a, b > 0. \tag{6}$$

(Sign of the first term was corrected here.) In part a) you are expected to reason in the spirit of the solution to Aufgabe 1j) in the Blatt 11.

a) i. Consider the temperature higher or equal than critical, $T \geq T_\mathrm{c}$. Let us continuously vary h from a negative to a positive value. Argue that the magnetization changes its sign continuously. (*1 Punkt*)

   ii. Consider the magnitude of h needed to get rid of a higher local minimum in F. Explain why it decreases with T. How the wells around minima in F change with increase of T? (*1 Punkt*)

   iii. Sketch the h-T phase diagram. Mark the ferro- and the paramagnetic phases; mark the critical point. Mark by $\uparrow$ and $\downarrow$ the regions where there is only one stable solution for $\langle\sigma\rangle$. In sketching the boundary of these regions, it might be useful to recall the result of part g) of the Blatt 11 for $\langle\sigma\rangle$ at $T \to 0$. (*3 Punkte*)

b) On the previous diagram, mark the regions where a metastable state can exist. Metastable state occupies a local minimum of F which is higher than the global one. (*1 Punkt*)

c) For a point in such a region, show a path on the graph to prepare a stable state. Show the same for a metastable state. (*2 Punkte*)

d) (BONUS) In the h-T diagram, precisely plot the boundary for the metastable state existence. To do this, consider the self-consistency equation on $\langle\sigma\rangle$. We are interested in the point where it transitions from having one solution to having three solutions. (*4* Punkte*)