

Statistical Physics¹

Prof. Graf, HS 2019
February 10, 2020, 17:00-17:30, Janik Schüttler

Summary The exam was held in a seminar room (HIT F32). Prof. Graf and one assistant sat in the second row, the student was expected to use the blackboard for notes. This exam was among the most unpleasant exams I have so far experienced. It was also the exam in which my final grade and my expectation differed the most. This is why I tried to write this protocol in great detail, I hope this might help others.

Description of the content: First law of thermodynamics, van der Waals gas, classical description of real interacting gases, Bose-Einstein condensation, Bose gas.

Transcript *Prof. Graf asked me in. He had the cold and recommended not to shake hands. He seemed to be in a good mood, told me that the exam will be on the blackboard, sat down in the second row and then asked the first question right away.*

Prof: Can you tell me something about the first law of thermodynamics? What is the statement, what consequences does it have?

Me: Sure. The first law states that for each two thermodynamic states there exists a work process that connects these states in at least one direction and that the associated work depends only on the states, not on the details of the process. In a sense these are the minimal requirements to build a physically useful theory.

Prof: Very nice, this is indeed the precise statement of the first law. What can you use the first law for?

Me: *I didn't know what he was referring to (and yes I admit it should have been obvious).* Mmmm, do you mean the definition of work?

Prof: Mmm. The first law allows for the definition of a specific quantity central to thermodynamics.

Me: Mm, maybe I just continue the story from the first law on and we see if I encounter what you are looking for?

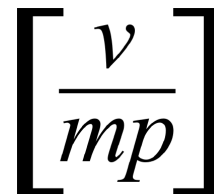
Prof: Go ahead!

Me: First we define the work for reversible quasistatic work processes...

Prof: Can you please write something down on the board?

Me: Sure, we define work as $dW =: -p dV$ for reversible quasistatic work processes.

¹MSc Physics, Core Subjects



Prof: Please be careful with the differentials...

Me: Oh sorry, it is δW .

Prof: What is the difference?

Me: A δ denotes an inexact differential, while a d denotes an exact differential.

Prof: Good. Please continue!

Me: Okay. For general quasistatic processes we then define the work as $\delta W := -pdV$ by analogy. Next we can then define the heat... Oh I see, were you referring to energy before? We first have to define the energy to proceed...

Prof: *Seems satisfied.* Yes, that is what I wanted to hear.

Me: Okay. The first law allows to define the notion of an internal energy as

$$U(z) - U(z_0) := W(z_0 \rightarrow z)$$

with an arbitrary reference state z_0 .

Prof: If you look at this definition, why is it well-defined? Imagine there could in principle be many processes from z_0 to z , what ensures that this definition is still well-defined?

Me: This is precisely the statement of the first law. Since the work depends only on z and z_0 , this ensures also the internal energy to be well-defined.

Prof: Good. Next topic is the van der Waals gas. What can you tell me about it, which equations are associated with it, and so on?

Me: The van der Waals equation is a generalization of the ideal gas law

$$pV = nRT$$

that takes interactions between molecules into account. The argumentation goes like that: since molecules have finite size, the actual volume a molecule can occupy is effectively decreased, hence we replace the volume by $V - b$, where b is a parameter. Pressure, in turn, is increased since a molecule near the wall of the container is not free to move in all directions, which results in an effective pressure that draws the molecule inwards. This effect is proportional to the density of the molecules near the walls, hence we replace the pressure by $p + \frac{a}{V^2}$, where a is again a parameter and V^2 accounts for the density effect. This results in the generalized equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = nRT. \quad (1)$$

Prof: *Did not seem satisfied.* Mm, why would the effect be proportional to the density?

Me: Ehm, well as I just explained the increase of pressure depends on the number of molecules near the wall and a molecule's number of neighbors, this in total results in the $1/V^2$ dependence...?

$$\left[\frac{v}{mp} \right]$$

Prof: Aha, so it is dependent on the square of the density?

Me: Yes.

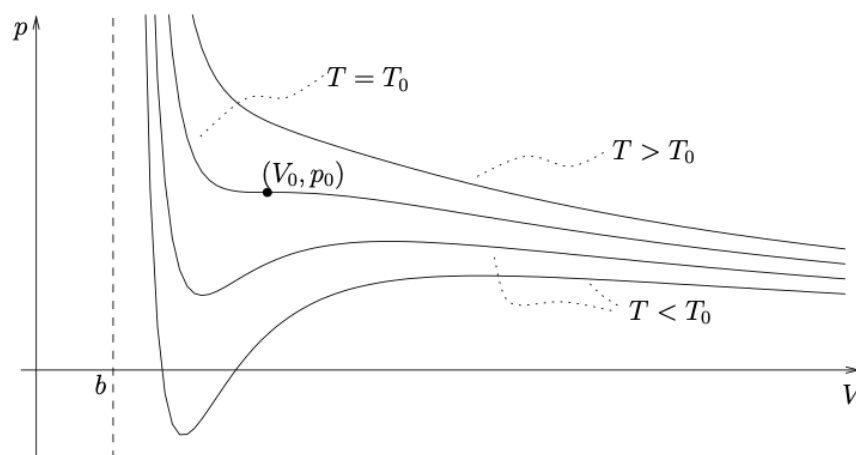
Prof: Ahaa, good. Also, in your current form of the equation what is the density?

Me: Mm yes I guess I will probably have to integrate the particle number n into V such that this becomes the density, i.e.

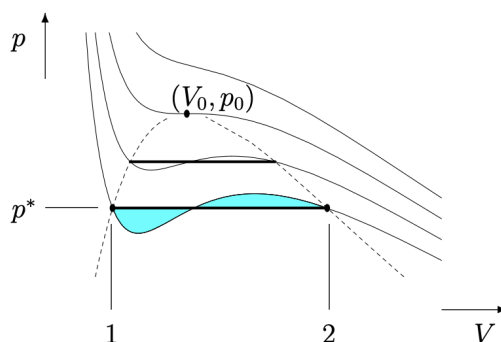
$$\left(p + \frac{a}{V^2} \right) (V - b) = RT. \quad (2)$$

Prof: Yes, I guess so too. Go on!

Me: Okay. This equation has a physical problem. If we look at the isotherms of the above equation we find something like this:



For large temperatures everything is fine, however, for low temperatures there exists regions in which p increases as V increases. In between these two regimes there exists a temperature at which the transition occurs which we call a critical temperature. An increase in pressure for an increase in volume is unphysical as it violates the stability conditions, which are one of the most fundamental properties of thermodynamics. A remedy was proposed by Maxwell, the so called Maxwell construction. It states that in this region one should replace the free energy by its convex hull. This corresponds to a straight line in the pV -diagram. *I draw in the line similar to the plot in the script*



The requirement is that the two areas in blue are of the same size, i.e. cancel out.

Prof: Good. How do you know that this line is where you drew it? Why can't it be higher or lower?

Me: This is fixed from the free energy, $p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$. Since we replaced the free energy by its convex hull, i.e. it is linear in the region of interest, p is constant within this region and called the vapor pressure $p = p^*$.

Prof: *Not satisfied.* Yes, but why is the line where it is? Or can you tell me why these blue areas should be equal? I mean, if you can, otherwise we continue.

Me: *I had no clue what he wanted to hear. Over the past questions I had lost my confidence since I had the feeling I never knew what he wanted from me when he dug deeper and now I was just fully stressed and confused.* Ehm yea well, so have $p = F(V_1 - V_2) = \int F dV \dots$

Prof: Wait, so this cannot be correct...

Me: I agree, ehm... *I added a minus to the equation.*

Prof: Yes, but this has to match your derivative $p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ you mentioned earlier.

Me: *I knew it was still wrong, but I was so stressed that I could not correct myself.*

Prof: From where to where is the integration?

Me: *I marked V_1 and V_2 as in the figure above.*

Prof: Good, and can you correct it now? *He came to the board and wrote down*

$$\int_1^2 f(x)dx = \dots$$

Can you tell me what this equals to?

Me: *I became quite insecure.* It is $f(x_1) - f(x_2)$. But please, can we go on? I am sorry, I am too confused right now to think clearly.

Prof: Sure. *He sat down again.* So what can you tell me about real interacting gases?

Me: *It took me some seconds to calm down.* Often in classical statistical mechanics we treat Hamiltonians of non-interacting particles, like

$$H = \sum_i \frac{p_i^2}{2m}.$$

This Hamiltonian's statmech is easy since the partition function splits and the resulting thermodynamics corresponds to a one-particle thermodynamics multiplied by the particle number. This particular Hamiltonian gives rise to the ideal gas law I mentioned earlier. We there saw that the ideal gas law could be generalized to the van der Waals equation that takes interactions into account. The general Hamiltonian for such a system includes an interaction term

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{i < j} V(|x_i - x_j|),$$

where V is the potential of interaction. The partition function here can be separated into a spacial and a momentum term

$$Z_N = \int_{\Lambda^N} \frac{dx}{N!} \underbrace{e^{-\beta \sum_{i < j} V(|x_i - x_j|)}}_{W(x)} \int_{\mathbb{R}^{3N}} dp e^{-\beta \sum_i \frac{p_i^2}{2m}}.$$

The momentum term splits as before and will result in the usual λ^{-3N} term, while the spacial part does not.

Prof: You do not have to compute the potential term.

Me: Okay. If we assume our potential to vanish for large enough distances,

$$V(r) = 0 \quad \text{if } r > a,$$

then also the first integral splits into clusters. This allows us to expand this part in a cluster expansion

$$W(x) = \sum_{(C_1, \dots, C_k)} U(x_{C_1}) \dots U(x_{C_k}),$$

where (C_1, \dots, C_k) denotes a set of clusters and U are the Ursell functions.

Prof: How are the U s defined and what is their advantage over the W ?

Me: They are recursively defined as

$$U(x) = W(x) - \sum_{\substack{(C_1, \dots, C_k) \\ k > 1}} U(x_{C_1}) \dots U(x_{C_k}).$$

The cool thing is that the $U(x_C)$ of a cluster C is 0 if the cluster has a refinement into sub-clusters.

Prof: *As usual not satisfied with what I said.* Mmm, we had a specific property about the Ursell functions that helped us, don't you recall it?

$$\left[\frac{v}{mp} \right]$$

Me: As usual confused and didn't know what he wanted to hear, so I additionally named the second property. Mmm well so if the cluster C is large enough, something on the order of the number of particles inside the cluster times a , then $U(x_C) = 0$.

Prof: *Still not satisfied.* Mm yes, the idea is that if a cluster can be separated into two clusters that are spaced more than a apart then the Ursell functions vanish.

Me: *I didn't believe he essentially just rephrased what I had said earlier, at least this is what I thought.*

Prof: Good, so can you tell me how this expansion helps us to derive the thermodynamics of a real interacting gas?

Me: How detailed would you like me to be?

Prof: Focus on the important bits in the argumentation.

Me: For the canonical partition function we obtain with the cluster expansion

$$\hat{Z}_N = \frac{1}{N!} \sum_{C_1, \dots, C_n} \prod_{i=1}^n l_i! V b_{l_i}$$

where l_i is the number of particles in the i -th cluster. However, we would like to represent this in a "basis" of clusters of equal size (n_1, n_2, \dots) , for which we obtain the final canonical partition function

$$\hat{Z}_N = \sum_{(n_1, n_2, \dots)} \prod_{l=1}^{\infty} \frac{(V b_l)^{n_l}}{n_l!}.$$

I first thought I had forgotten something and it took me some seconds to be sure that this is the correct expression. However, Prof. Graf also did not remember the exact details.

Prof: This is not a final expression, isn't it?

Me: Yes. The first sum is restricted to obey $\sum_{l=1}^{\infty} l n_l = N$ which prevents us from computing the canonical partition function. For this we change to the grand canonical partition ensemble since there the total particle number is variable. This results in

$$\Xi = \sum_{(n_1, n_2, \dots)} \prod_{l=1}^{\infty} \frac{(V b_l z^l)^{n_l}}{n_l!}.$$

In the grand canonical ensemble particles are independent and this partition function splits hence we can interchange the summation and the product, which gives the final expression

$$\Xi = \prod_{l=1}^{\infty} \sum_{n=0}^{\infty} \frac{(V b_l z^l)^n}{n!} = \prod_{l=1}^{\infty} \exp(V b_l z^l).$$

From the grand canonical potential we can derive the thermodynamics from the log of the partition

$$\left[\frac{v}{mp} \right]$$

function as

$$\beta pV = \log \Xi,$$

$$\frac{1}{v} = \frac{z}{\beta} \frac{\partial \log \Xi}{\partial z},$$

which gives

$$\beta pV = \sum_{l=1}^{\infty} b_l V z^l$$

$$\frac{1}{v} = \sum_{l=1}^{\infty} l b_l V z^l$$

Prof: *He came to the blackboard.* I think you are missing a V here. *He corrected my expression to $\frac{1}{v} = \frac{z}{V\beta} \frac{\partial \log \Xi}{\partial z}$ and also noted that the V s in the thermal equation of state may be cancelled.*

Me: *I nodded.*

Prof: So how is this related to the van der Waals gas we discussed earlier?

Me: The van der Waals gas is a special case of a Virial expansion that is defined as

$$\beta p = \sum_{l=1}^{\infty} \frac{a_l}{v^l}$$

with Virial coefficients a_l . We can plug the above expression for $\frac{1}{v}$ into this to obtain equations for the Virial coefficients in terms of the cluster integrals b_l

Prof: Good, that's enough. *He asked about the time, the assistant said 2 minutes left.* Where else in the course did we see such an interacting behavior between particles?

Me: *I took some seconds to think about what to present in the remaining 2 minutes.* In quantum statistical mechanics, even non-interacting quantum particles show such an interacting behavior. For quantum particles we find a similar partition function and resulting equations of state

$$\begin{cases} \beta p &= \frac{q}{\lambda^3} f_{5/2}^{\mp}(z), \\ \frac{1}{v} &= \frac{q}{\lambda^3} f_{3/2}^{\mp}(z), \\ u &= \frac{3}{2} p v, \end{cases}$$

with $f_{5/2}^{\mp}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}}$ and $f_{3/2}^{\mp}(z) = z \frac{d}{dz} f_{5/2}^{\mp}(z)$. I prefer to have Bosons on top, which is why I write \mp instead of \pm like in the script.

Prof: You are missing some signs there.

Me: Right, it should be $f_{5/2}^{\mp}(z) = \pm \sum_{l=1}^{\infty} \frac{(\pm z)^l}{l^{5/2}}$.

$$\left[\frac{v}{mp} \right]$$

Prof: Good. What physical consequences does the radius of convergence of your $f_{5/2}^{\mp}(z)$ functions have?

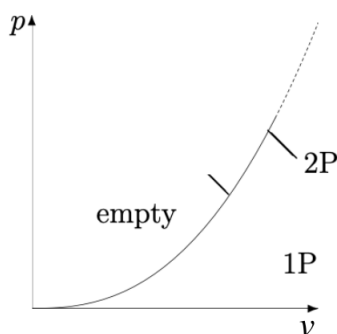
Me: For the sum to converge we need $|z| < 1$. For Bosons this is a fundamental requirement for the grand canonical ensemble to exist. However, this also means that for Bosons there exists a maximal density

$$\rho^* = \frac{q}{\lambda^3} f_{3/2}^{\mp}(1).$$

This means that above this critical density additional particles cannot occupy an excited state and hence must fall back directly into the ground state. This results in a macroscopic occupation of the ground state which is called Bose-Einstein condensation.

Prof: *The time was long over, but when I finished he just looked at me in expectation of more and so I decided to continue. When I talked about Bose-Einstein condensation he mumbled "Ah, you know all that...", really an awful sentence to hear in the context of an exam. It made me feel quite insecure again.*

Me: This Bose-Einstein condensate is a new form of phase that exists only in the quantum context. The thermodynamics of a Bose gas hence is quite interesting. For example, the phase diagram



On the left there is a region that cannot be accessed, the condensate exists exactly on the critical line. *I fucked up the axis, it should have been T instead of v, the rest was correct. However, in what follows Graf again successfully managed to confuse me so much that I did not see my mistake.*

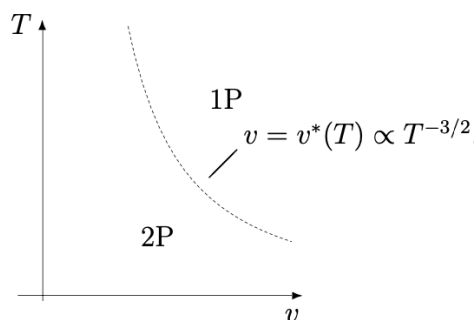
Prof: Wait, are you sure you mean v ?

Me: *I was staring at the diagram and couldn't think clearly...* Mm well so if we increase pressure for constant v , we should at some point reach the coexistence line... It should be a $5/2$ power law dependence...

Prof: *Not satisfied.* I did not ask you to do that, but since you started it please correct it.

Me: *I then started drawing a Tv -diagram next to it. The blackboard was full and it became quite a mess.*

$$\left[\frac{v}{mp} \right]$$



So this is the Tv -diagram, this should be correct.

Prof: *Not satisfied. He came to the board and started discussing the proportionalities between p, V, T with me, we both couldn't remember them properly. It became more like a discussion. How is λ proportional to T ?*

Me: $\lambda \propto T^{-1/2}$

Prof: Yes, so we see that from $\beta p^* = \frac{q}{\lambda^3} f_{5/2}^{\mp}(1) \propto T^{3/2}$.

Me: Well, the beta also contains a T , this gives us the $5/2$ dependence, i.e. $p \propto T^{5/2}$.

Prof: Good point, thank you. So how can we derive the proportionality between v and p ?

Me: We can similarly use $\rho^* = \frac{1}{v^*} = \frac{q}{\lambda^3} f_{3/2}^{\mp}(1) \propto T^{3/2}$ to obtain $v \propto T^{-3/2}$. Together this should give $p \propto (v^{3/2})^{5/2} = v^{15/4}$. Mm, this cannot be, there must be a mistake somewhere

Prof: Mmm you are right, I also don't see it right now. Anyway, time is up. *He must have noticed that I looked super depressed about this exam which I thought had fucked up completely, so he added "Isch guet gsi" (it was good).*

Final Remarks Graf is known to be a nice examiner, however, as I said, this exam was among the most unpleasant exams I have so far had. Even though I tried to add my thoughts to this protocol, it is hard to convey this feeling. Usually, I gain confidence during exams, this time I rather lost confidence with each additional question. For me it felt like Graf and me talked different languages, he did not get my points and I did not get his questions. This confused me so much that multiple times I couldn't correct the simplest mistakes. Still, he must have somehow noticed that I had studied a lot for this exam and I am glad my grade came out this well, I was expecting to be graded below 5.

Expected mark: <5

Received mark: 6