

Theoretische Physik IV: Statistische Mechanik, Exercise 7

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1. Phase diagrams (Oral)

The aim of this exercise is a better understanding of phase diagrams and their construction by means of empiric facts. In the following the phase diagram is identified with the two-dimensional manifold of equilibrium states given by $p = p(V, T)$.

- (a) **Ordinary liquids:** Employ the following facts to derive the qualitative phase diagram $p = p(V, T)$ of an *ordinary liquid* (that is, a liquid without an anomaly as it characterizes e.g. water):

- There are three phases: solid, liquid and gaseous. At very low and very high temperatures the solid and gaseous phases coexist. For intermediate temperatures there is an additional liquid phase separating the solid and gaseous phases.
- Thermodynamic stability demands

$$\left. \frac{\partial p}{\partial V} \right|_T < 0 \quad \text{and} \quad \left. \frac{\partial p}{\partial T} \right|_V > 0 \quad (1)$$

at all points in thermodynamic equilibrium.

- The solid phase is denser than the liquid phase.
- The slope of the lines of phase coexistence in the T - p -diagram is positive. All three lines of coexistence emanate from the triple point. The line of coexistence that separates gaseous and liquid phase terminates at a critical point; the line that separates solid and gaseous phase terminates at the origin $p = 0 = T$. The line of coexistence that separates the solid and liquid phase emanates from the triple point and does not terminate.

Sketch $p = p(V, T)$ in a V - T - p -diagram. Deduce the two-dimensional projections of the phase diagram on the T - p -, V - T -, and V - p -planes. Highlight the lines of phase coexistence in all diagrams and, in addition, the isotherms in the V - p -diagram.

- (b) **Water:** Employ the previous facts to derive the qualitative phase diagram $p = p(V, T)$ of an *anomalous liquid*, that is, water. The anomaly results in the following modifications of the last two statements above:

- The solid phase is *less* dense than the liquid phase.
- The slope of the line separating solid and liquid phases is *negative* in the T - p -diagram.

Sketch the same diagrams as in (a).

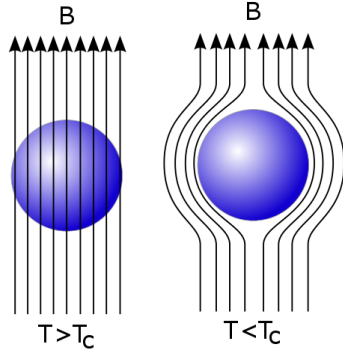


Figure 1: Meissner effect: The B -field cannot penetrate the superconductor for $T < T_c$ and $H < H_c(T)$.

2. Meissner effect (Oral)

The magnetic field B cannot penetrate the bulk of a Type-I superconductor (actually, the magnetic field is exponentially suppressed on length scales given by the *London penetration depth* λ — we can safely ignore this subtlety in the following). This is known as the *Meissner effect*. In this field-free state it holds

$$B = H + 4\pi m = 0 \quad (2)$$

where B denotes the magnetic flux density, H the magnetic field strength, and $m = M/V$ the magnetization (dipole moment per volume; M is the *extensive* magnetization, that is, total dipole moment). If the temperature is too high, $T > T_c$, or the magnetic field too strong, $H > H_c$, a phase transition from superconductivity to a normal conducting phase occurs. The critical magnetic field strength $H_c = H_c(T)$ depends on the temperature and is approximately given by

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c} \right)^2 \right] \quad \text{for } T \leq T_c. \quad (3)$$

- Sketch the phase diagram in the T - H -plane.
- Use the *Clausius-Clapeyron relation* to derive the latent heat for this phase transition. To this end neglect the magnetization M_n of the normal conducting phase and consider only the magnetization M_s of the superconducting phase. What is the order of the considered phase transition?
Hint: Recall that $dU = TdS + HdM$ and make the substitutions $-p \rightarrow H$ and $V \rightarrow M$ in the Clausius-Clapeyron relation as derived in the script.
- Why is it reasonable to describe the superconductor by its Gibbs free energy $G(T, H)$? Calculate the change $\Delta G(T) := G_s(T, H = 0) - G_n(T, H = 0)$ of this quantity when the system traverses the phase boundary from a superconducting (s) to a normal conducting (n) phase. What is the physical meaning of $\Delta G(T)$?
Hint: Use the continuity condition $G_s(T, H_c(T)) = G_n(T, H_c(T))$.
- Derive the change of entropy $\Delta S(T) := S_s(T, H = 0) - S_n(T, H = 0)$ for $T \leq T_c$ via the results in (c). Give a physical interpretation of both the sign of $\Delta S(T)$ and the value of $\Delta S(T = T_c)$. Calculate the change $\Delta C(T_c) := C_s(T_c) - C_n(T_c)$ of the specific heat at the critical temperature T_c .
Hint: The specific heat is defined as $C := T \left. \frac{\partial S}{\partial T} \right|_H$.

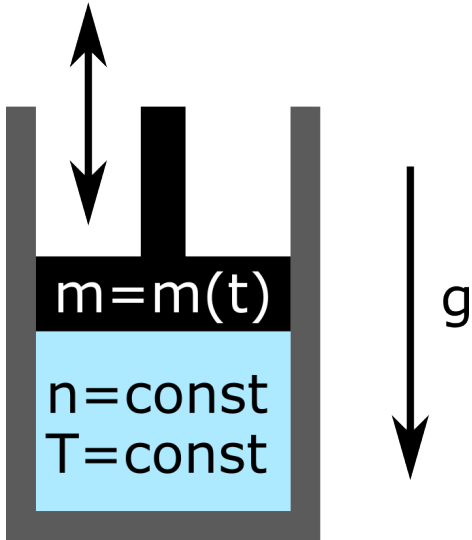


Figure 2: Van der Waals gas: A piston of mass m stabilized by a van der Waals gas.

3. Van der Waals gas (Written)

Here we revisit the phase transition of the van der Waals gas and consider its thermodynamic stability. In the lecture the equation of state for the van der Waals gas was introduced as

$$(v - b) \left(p + \frac{a}{v^2} \right) = RT \quad (4)$$

with molar volume $v = V/n$ and the (molar) parameters a and b .

- (a) Calculate the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_T \quad (5)$$

for the critical molar volume $v_c = 3b$ as a function of T . Describe the behaviour of κ_T for $T \rightarrow T_c + 0$ with the critical temperature $T_c = 8a/(27bR)$.

- (b) Using these results, discuss the thermodynamic stability of the van der Waals gas for $T < T_c$ and $T \geq T_c$.
- (c) Consider the setup shown in Fig. 2: A vertical cylinder is filled with a van der Waals gas which stabilizes a piston of mass m . Assume the temperature is fixed at $T < T_c$. What happens if the mass $m = m(t)$ is slowly increased as a function of time? (Let $m(t = 0)$ be very small.)
- (d) Calculate the (molar) free energy $f(T, v)$ for fixed temperature T as a function of v and discuss the qualitative differences for $T > T_c$ and $T < T_c$, respectively. Sketch the (molar) Gibbs free energy $g(T, p)$ for fixed T as a function of p for $T > T_c$ and $T < T_c$.

Hint: The Gibbs free energy is defined as Legendre transform of $f(T, v)$, i.e.

$$g(T, p) := \inf_v [f(T, v) + pv] = \inf_v [f(T, v) - (-pv)] = -\sup_v [-pv - f(T, v)].$$

Sketch this function by hand or use a CAS to derive a qualitative result.