Draft – Preliminary Version

Exercise 13.1: Van der Waals gas (8P)

The van-der-Waals gas is defined by the equation of state

$$p(T,V,N) = \frac{Nk_BT}{V-B} - \frac{A}{V^2}\,,$$

where A, B are parameters (which are here considered as being constant).

(a) What is the physical interpretation of the parameters A and B? (1P)

(b) Show that the change ΔF of the Helmholtz free energy $F(T,V,N)$ caused by an isothermal expansion from volume V_i to volume V_f is given by (2P)

$$\Delta F = \left(\frac{A}{V_i} - \frac{A}{V_f}\right) + Nk_B \ln\frac{V_i - B}{V_f - B}\,.$$

(c) Compute the change ΔE of the internal energy during isothermal expansion. (1P)

(d) Show that the change ΔG of the Gibbs free energy $G(T,p,N)$ during isothermal expansion can be expressed as

$$\Delta G = Vp(T,V,N)\Big|_{V_i}^{V_f} + \Delta F$$

and compute the corresponding change of the chemical potential $\Delta\mu$. (1P)

(e) Explain which quantities which coincide in the case of phase coexistence. (1P)

(f) Show that the line of phase coexistence connects two points on the isotherm obeying the condition

$$p_{eq}\Delta V + \Delta F = 0\,,$$

where p_{eq} is the coexistence pressure.[1] (1P)

(g) Demonstrate that this condition leads to the so-called Maxwell area law. (1P)

Exercise 13.2: Mean field theory of the Ising model (4P)

In the mean field approximation of the Ising model (see lecture notes) the average magnetic field per spin is given in terms of an implicit equation:

$$\langle s\rangle \;=\; \tanh(\beta\bar{H}) \;=\; \tanh\big[2dJ\beta\langle s\rangle + \beta h\big]\,.$$

The aim of this exercise is to compute the partition sum Z and the critical exponent associated with the magnetisation within mean field theory.

[1]This relation was first derived by J.C. Maxwell. The derivation is not entirely correct in so far as it treats unstable parts of the isotherm as if they were stable, but nevertheless this calculation leads to the correct result. In this exercise we shall ignore this subtle problem.

Please turn over ⇒

(a) Show that the partition sum is given by

$$Z(\beta, h) = \sum_s e^{-\beta E_s} = \Big(2\cosh(\beta\overline{H})\Big)^N \,,$$

where N is the total number of spins and $\overline{H}$ depends implicitly on β and h. (1P)

(b) Prove that the partition sum can be written in the form

$$Z(\beta, h) = \left(\frac{2}{\sqrt{1-\langle s\rangle^2}}\right)^N \,,$$

where $\langle s\rangle$ depends on β and H, and use this result in order to compute the total free energy $F = -k_B T \ln Z$. (1P)

(c) Let us assume that the external field h vanishes. Expanding the implicit equation for small magnetisation $m(\beta, h) = \langle s\rangle$ to third order, one can solve the resulting equation explicitly. In the vicinity of the critical point with the resulting expression for the magenetisation is expected to scale as

$$m(\beta, 0) \sim (\beta_c - \beta)^{\tilde{\beta}} \,,$$

where $\tilde{\beta}$ is the critical exponent associated the magnetisation (take care of the different meaning of β and $\tilde{\beta}$). Compute the critical temperature $\beta_c = 1/T_c$ and the value of the exponent $\tilde{\beta}$ within mean field theory. (2P)

(Σ = 12P)

To be handed in on Monday, January 29, 2018, at the beginning of the lecture.