Theoretische Physik IV: Statistische Mechanik und Thermodynamik

Problem Set No. 9

Due on: Friday, 27.6.08 in the practice groups

Exercise 9.1 *(Zipper Model – part II)* **(10 points)**

In exercise 4.2 we already dealt with the so-called zipper model. The partition sum of the model was given by

$$Z_N = \frac{1-x^N}{1-x}, \qquad x = G\exp(-\beta\epsilon)$$

Now we want to analyze whether this system has a phase transition with respect to the order parameter $\langle s \rangle$.

(a) Perform a series expansion of $\ln Z_N$ around $x = 1+\eta$ for $\eta \ll 1$. Then expand $\langle s \rangle$ for $\eta \ll 1$ and $N \gg 1$. (5 points)

(b) Show that the fraction of open linkers has a jump at $\eta = 0$ in the thermodynamic limit, i.e. show that $\frac{1}{N}\frac{d\langle s\rangle}{d\eta}$ diverges at $\eta = 0$. A jump of the order parameter indicates a *first order* phase transition. (3 points)

(c) Determine the transition temperature T_c. (2 points)

Exercise 9.2 *(Modified Van-der-Waals Gas)* **(10 points)**

Consider a modified Van-der-Waals gas which obeys the following equation of state (v is the molar volume):

$$(p + \frac{a}{Tv^2})(v-b) = RT \quad (n > 1)$$

(a) Determine the critical constants p_c, v_c and T_c (as in exercise 6.3). (3 points)

(b) Can the equation of state be written in a universal form analogous to the Van-der-Waals equation of state (i.e. a form in which the constants a and b are no longer present). If so, write down this equation. (3 points)

(c) Calculate the critical exponents γ (defined by $\kappa_T \sim |\frac{T-T_c}{T_c}|^{-\gamma}$) and δ (defined by $p - p_c \sim |v - v_c|^\delta$ at $T = T_c$) by expanding the equation of state around the critical point in analogy to the Van-der-Waals gas discussed in the lecture. (4 points)

Exercise 9.3 *(Binary Mixture)* **(10 points)**

We consider a system consisting of two types of molecules (A and B) on a cubic lattice. Each lattice site can be occupied by either a molecule of type A or a molecule of type B. Each molecule can only interact with its six nearest neighbours. The interaction energy between neighbouring molecules of equal type (A—A and B—B) is $-J$. Adjacent pairs of molecules A—B do not interact. Let the total number of lattice sites be N, the number of molecules of type A be N_A, the number of molecules of type B be N_B ($N = N_A + N_B$)

(a) Estimate the total energy of the system assuming that the atoms are distributed randomly among the N lattice sites, i.e. each lattice site is occupied by a molecule of type A with probability N_A/N and by a molecule of type B with probability N_B/N. (2 points)

(b) Calculate the entropy of this mixture using the same assumption. (2 points)

(c) In this approximation, write the free Energy $F(x)$ as a function of $x = (N_A - N_B)/N$. Expand $F(x)$ up to the fourth order and show that the free energy does not fulfill the condition of convexity below a critical temperature T_c. Calculate T_c. (4 points)

(d) Draw $F(x)$ for $T < T_c$, $T = T_c$ und $T > T_c$. (2 points)

Bonus Exercise 9.4 *(Liquid Crystals)* **(10 extra points)**

Note: This exercise is optional. You may want to solve it to improve your score.

A liquid crystal consists of anisotropic molecules. As the centers of mass of the molecules have no long-range order, it behaves like a liquid. On the other hand the direction of the molecules has long-range order, i.e. it behaves like a crystal. The order parameter of a liquid crystal is given by

$$\mathbf{S} = \eta \left[\mathbf{nn} - \frac{1}{3}\mathbf{I} \right]$$

$\mathbf{n}$ is a unit vector, pointing at the average direction of alignment of the molecules. $\mathbf{nn}$ is the dyadic product of the vectors. The free energy of a liquid crystal is given by

$$F = F_0 + \frac{1}{2} A S_{ij} S_{ij} - \frac{1}{3} B S_{ij} S_{jk} S_{ki} + \frac{1}{4} C S_{ij} S_{ij} S_{kl} S_{kl}$$

Here $A = A_0(T - T^\star)$, A_0, B and C are constants. We take the sum over repeated indices.
$\mathbf{I}$ ist the unit tensor. In the basis vectors $\mathbf{e}_i$ we have

$$\mathbf{e}_i \cdot \mathbf{I} \cdot \mathbf{e}_j = \delta_{ij}, \qquad S_{ij} = \mathbf{e}_i \cdot \mathbf{S} \cdot \mathbf{e}_j$$

(a) Calculate the free energy F, i.e. perform the summations in the expression for Φ and write F in terms of η, A, B, C. (5 points)

(b) Calculate the critical temperature T_c at which the transition from isotropic liquid to liquid crystal takes place. (5 points)