Final Exam for Advanced Statistical Physics: NS-370B

Date: November 5th, 2019

Time: 13:30 - 16:30

This exam consists of 4 questions. The total number of possible points is: 100.

This is a closed-book exam, *i.e.*, the use of notes and electronic devices is not allowed.

Please start **every exercise on a new sheet of paper**, with your name clearly written on every page.

The exam can be written in either English or Dutch. Please write clearly!

A few formulas and information that may or may not be useful in this exam:

- The canonical partition function of a classical thermodynamic system of N identical particles in a volume V a temperature T with Hamiltonian $H(\Gamma)$ — Γ is a point in phase space — is written:
  $Z(N,V,T) = \frac{1}{N!h^{3N}} \int d\Gamma \exp[-\beta H(\Gamma)]$, where $\beta^{-1} = k_B T$.
- The grand partition function of identical particles is given by:
  $\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \exp(\beta\mu N) Z(N,V,T)$,
  and the grand-canonical distribution is given by:
  $f_g(\Gamma,N) = \frac{\exp[\beta\mu N - \beta H(\Gamma)]]}{[N!h^{3N}\Xi(\mu,V,T)]}$, with μ the chemical potential.
- The second virial coefficient B_2 for an isotropic pair potential $\phi(r)$ is given by:
  $B_2 = -\frac{1}{2}\int_V \mathrm{d}\boldsymbol{r}\ \left(\exp(-\beta\phi(r)) - 1\right).$
- $k_B = 1.13 \times 10^{-23}$J/K, $e = 1.6 \times 10^{-19}$C, and $R = 8.31$J/K/mol.
- The binomial coefficient (*i.e.*, m choose n), which is the number of ways n objects can be chosen from m objects, is given by:
  $\binom{m}{n} = \frac{m!}{(m-n)!n!}.$
- Stirling's approximation to order $O(N)$ is given by: $\log(N!) = N\log N - N$.
- Gaussian Integral:
  $\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\pi}.$
- The Taylor series of $f(x)$ around $x = a$ is given by:
  $f(x) = f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f^{(3)}(a)}{3!}(x-a)^3 + \cdots.$
- From the Taylor series we get:
  $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}.$

1. Phase Behavior and Interfacial Tension: (35 points)

Here you will consider phase coexistence and phase separation in a Van der Waals (vdW) gas.

(a) (i) State the first and second laws and combine these to obtain an expression for $\mathrm{d}U$.

(ii) Legendre transform the internal energy U into the (Helmholtz) free energy F.

(iii) Similarly transform F into the (μ,V,T) ensemble to obtain the grand potential Ω.

(b) Provide the expression for the vdW equation of state. What is the physical meaning of the two phenomenological parameters in your expression?

(c) Sketch the density-temperature (ρ-T) phase diagram of the vdW system. Indicate the critical density ρ_c and temperature T_c. Make sure to label your axes.

(d) Explain the order of the phase transition that the vdW gas undergoes upon increasing the density for temperatures below the critical point ($T < T_c$)?

(e) Sketch F/V (the free energy F per volume V) as a function of the density ρ for a temperature $T < T_c$. Draw the common tangent and indicate the coexistence densities ρ_g (gas) and ρ_l (liquid). Make sure to clearly label the axes and features on this graph.

(f) Derive what equalities follow from the common-tangent construction.

(g) Visualize in a separate graph the effect of the Legendre transform from F/V to Ω/V on the curve you drew in (e). What is the value of the minimum in Ω/V?

(h) Explain why it is (therefore) possible to write $\Omega/V \approx \mathrm{A} + \frac{C}{2}(\rho - \rho_g)^2(\rho - \rho_l)^2$, with C a constant and A consistent with your answer in (g).

(i) Explain why the answer from (h) is expected to work in the respective coexisting bulk phases, but not in the interfacial region.

2. The Spinodal Region, Percolation, and "Sticky Colloids": (15 points)

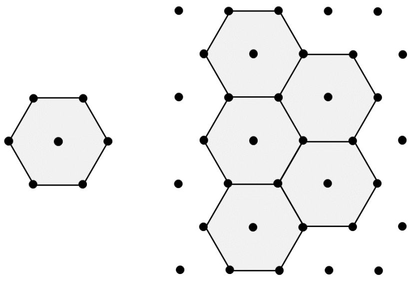
Consider a colloid-polymer mixture in the spinodal region of the phase diagram.

(a) If you bring the system rapidly into the spinodal region and allow it to evolve, what would you expect to observe?

(b) How do you determine the spinodals?

(c) Explain the concept of excluded volume for the polymers in a suspension with a single colloid.

(d) Why does this lead to an effective short-ranged attraction between more than one colloids? You should use sketches to illustrate your point.



Assume that the colloids can move on a two-dimensional (2D) triangular lattice and that they are not able to overlap. The colloids can occupy sites with probability p. Take hexagonal groupings of 7 lattice sites as the "super blocks" for a renormalization group argument, see the figure. A super block is filled whenever *at least* 4 of its 7 sites are occupied by colloids.

(e) Compute $R(p)$ and show that an unstable fixed point is given by $p^* = 1/2$ for this situation. *In fact, $p^* = 1/2$ is the only unstable fixed point, but do not show this!*

3. Equation of State for a Square-Well Fluid: (25 points)

Consider a system with a square-well (SW) pair-interaction potential given by:

$$\phi_{\mathrm{SW}}(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}, \tag{1}$$

with $\lambda > 1$ a measure for the range of the attraction (strength ϵ) and r the center-of-mass separation between the particles.

(a) Give the definition of the Mayer function and sketch this function for the SW potential.

(b) Use the definition of the second virial coefficient B_2 to show that for the SW potential this coefficient is given by:

$$B_{2,\mathrm{SW}} = \frac{2\pi}{3}\sigma^3\left[\lambda^3 + e^{\beta\epsilon}\left(1-\lambda^3\right)\right]. \tag{2}$$

(c) Provide the second-virial approximation to the equation of state (EOS) of the system.

(d) When can this EOS be trusted, in view of the approximation?

A more precise EOS can be found by thermodynamic perturbation with respect to the hard-sphere (HS) reference. For this reference system, the reduced free energy is given by

$$f_{\mathrm{HS}}(\eta) \equiv \beta\frac{\pi\sigma^3}{6}\frac{F_{\mathrm{HS}}(\eta)}{V} = \eta\log\eta - \eta + \eta\frac{4\eta - 3\eta^2}{(1-\eta)^2}, \tag{3}$$

in the Carnahan-Starling approximation, where we have ignored some constant offset and introduced the colloid volume fraction $\eta = (\pi/6)\sigma^3\rho$ with ρ the number density. The thermodynamic perturbation of the HS fluid into the SW system can be written as

$$f_*(\eta) = \frac{3\beta}{\pi\sigma^3}\eta^2\int_V \mathrm{d}\boldsymbol{r}\; g_{\mathrm{HS}}(r)\phi_*(r), \tag{4}$$

where $g_{\mathrm{HS}}(r)$ is the HS pair distribution function and $f_{\mathrm{SW}}(\eta) = f_{\mathrm{HS}}(\eta) + f_*(\eta)$.

(e) State in a few words how the Carnahan-Starling approximation is associated with the three routes to obtain thermodynamic quantities from the radial distribution function.

(f) Give an expression for $\phi_*(r)$ which defines the perturbative pair potential by which the system goes from HS to SW interactions.

(g) Sketch a temperature T, density ρ, and coupling constant λ diagram, and explain using the diagram what the purpose of thermodynamic perturbation theory can be in this regard.

4. Monomers, Dimers, Rods, and Alignment: (25 points)

Consider a square-lattice model with A sites and n occupied sites (or particles); the system is considered periodic. If two particles are adjacent, they bond with bonding energy $-\epsilon$ ($\epsilon > 0$). Once a dimer has formed it cannot bond with any other particles. The system is characterized by an average monomer density $\rho_1 = n_1/A$ and dimer density $\rho_2 = n_2/A$, with $n_{1,2}$ the number of monomers and dimers, respectively. We will assume that none of the species interact, so that they behave like an ideal gas.

(a) Show from the partition functions that the Helmholtz free energy of the system is given by:

$$\frac{\beta F(\rho_1,\rho_2,A,T)}{A} = \rho_1\left(\log\rho_1 - 1\right) + \rho_2\left(\log\rho_2 - 1 - \log 2 - \beta\epsilon\right). \tag{5}$$

(b) Derive that in equilibrium the chemical potentials of monomers and dimers should obey $2\mu_1 = \mu_2$ and that this requires:

$$\frac{\rho_2}{\rho_1^2} = 2\exp(\beta\epsilon). \tag{6}$$

Calculate ρ_1 and ρ_2 in terms of the total particle density ρ and bonding energy ϵ.

(c) What happens in the limit where $\epsilon \to 0$ (assuming low density) and when $\epsilon \to \infty$?

The system is prepared in such a manner that all the particles form dimers. Next the bonds in the dimers are made permanent, resulting in a system of rods of length two on a lattice, which can either be vertical + or horizontal −. Assume that there are N of these rods and that $\rho_+ = N_+/A$ and $\rho_- = N_-/A$ are the respective densities of the two species, with $N = N_+ + N_-$. When the rods overlap, they now incur an energy penalty ϵ'. Using a mean-field argument, a Landau-free energy can be constructed that describes the system

$$\frac{\beta F(m, \rho, A, T)}{N} = C + (2 - \beta\epsilon')m^2 + \frac{4}{3}m^4 + \frac{32}{15}m^6. \tag{7}$$

where C is a constant and m measures the deviation from $N_+/N = 1/2$.

(d) At what temperature does a phase transition occur and what kind of transition is it? Explain.

(e) Suppose the rods are much longer and $\epsilon' \gg k_\mathrm{B}T$. What are the states the system could be in at low density?

(f) Explain in a few sentences a strategy for determining the phase transition between these states.