Final Exam for Advanced Statistical Physics: NS-370B

Date: November 3rd, 2020

Time for Regular Students: 13:30 - 16:30

Upload to BlackBoard before 17:00h

Extra-Time Students Only: 13:30 - 17:00, upload before 17:30h

This exam consists of **3** questions. The total number of possible points is: 100.

This is an open-book exam, *i.e.*, the use of notes is allowed.

You may only use your electronic device to upload the exam and consult the notes.

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 and using pen!**

Equation Cheat Sheet

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:

  $Z(N,V,T) = \dfrac{1}{N!h^{3N}} \displaystyle\int d\Gamma \exp[-\beta H(\Gamma)]$, where $\beta^{-1} = k_\mathrm{B}T$.

- 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:

  $f_g(\Gamma,N) = \dfrac{\exp[\beta\mu N - \beta H(\Gamma)]]}{[N!h^{3N}\Xi(\mu,V,T)]}$, with μ the chemical potential.

- The second virial coefficient B_2 for an isotropic pair potential $\phi(r)$ is given by:

  $B_2 = -\dfrac{1}{2}\displaystyle\int_V \mathrm{d}\boldsymbol{r}\ \left(\exp(-\beta\phi(r)) - 1\right).$

- $k_\mathrm{B} = 1.13 \times 10^{-23}$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:

  $\dbinom{m}{n} = \dfrac{m!}{(m-n)!n!}.$

- Stirling's approximation to order $O(N)$ is given by: $\log(N!) = N\log N - N$.

- Gaussian Integral:

  $\displaystyle\int_{-\infty}^{\infty} dx\ e^{-x^2} = \sqrt{\pi}.$

- The Taylor series of $f(x)$ around $x = a$ is given by:

  $f(x) = f(a) + \dfrac{f'(a)}{1!}(x-a) + \dfrac{f''(a)}{2!}(x-a)^2 + \dfrac{f^{(3)}(a)}{3!}(x-a)^3 + \cdots.$

- From the Taylor series we obtain:

  $e^x = \displaystyle\sum_{n=0}^{\infty} \frac{x^n}{n!}$

  and

  $\log(1-x) = -\displaystyle\sum_{n=1}^{\infty} \frac{x^n}{n}.$

1. Mixing on a Square Lattice: (32 points)

Consider a square lattice. On a square lattice, each lattice site has four nearest neighbors. Assume that each lattice site can be in one of three different states, which we will label A, B, and C. Assume that the interaction between lattice sites is such that the contribution to the energy is zero when nearest neighbor lattices are in different states, while it is $-J$ when they are in the same state. The Hamiltonian for this system can be written

$$H = -\frac{J}{2} \sum_i {\sum_j}' \delta_{\sigma_i,\sigma_j}, \tag{1}$$

where ${\sum_j}'$ indicates a sum over nearest neighbors, σ_i represents the state of the lattice site, *i.e.*, it can be either A, B, or C, and $\delta_{\sigma_i,\sigma_j}$ is the Kronecker delta function defined by

$$\delta_{\sigma_i,\sigma_j} = \begin{cases} 0 & \text{if} \quad \sigma_i \neq \sigma_j \\ 1 & \text{if} \quad \sigma_i = \sigma_j \end{cases} . \tag{2}$$

(a) Sketch a few microstates.

(b) Write down the expression for the canonical partition sum $Z(N,T)$ for this system, with N the total number of sites and T the temperature. Do not evaluate the sum. Explain in a few words by which exact method the average energy and the transition temperature can be found, support this with the relevant equations.

It is quite complicated to evaluate $Z(N,T)$. However, the random mixing approximation (a form of mean-field theory) will allow us to study the phase behavior of this system. Note that if there is a phase transition in this system, it will be between a phase where the system consists of an equal number of lattice sites in states A, B, and C, while in the ordered phase, one of the three will be more likely. For simplicity, in this problem we will assume that the ordered state consists of more A lattice sites than either B or C. Within the random mixing approximation, the states of all lattice sites are uncorrelated. Define p_A to be the probability that a particular lattice site is in state A, p_B the probability that it is in state B, and p_C the probability that it is in state C. Note that in the disordered state, $p_A = p_B = p_C$.

(c) Argue in a few words why, in both the ordered and disordered phases, $p_B = p_C = (1 - p_A)/2$.

(d) What is the expected potential energy in the system for a given value of p_A?

(e) What is the entropy for given value of p_A?

(f) Show that, within the random mixing approximation, the free energy of the system can be written

$$\frac{\beta F}{N} = -Q\left(p_A^2 + \frac{1}{2}(1-p_A)^2\right) + p_A \log(p_A) + (1-p_A)\log\left(\frac{1-p_A}{2}\right), \tag{3}$$

where $Q = 2\beta J$, and N is the number of lattice sites.

(g) In the disordered phase, $p_A = 1/3$. Define an order parameter m such that $m = \frac{3}{2}\left(p_A - 1/3\right)$. Note that is it 0 in the disordered phase and non-zero in the ordered phase. Rewrite the free energy in terms of m. Show that the Landau expansion for the free energy can then be written

$$\frac{\beta F}{N} = -\log(3) - \frac{Q}{3} + \left(1 - \frac{2}{3}Q\right)m^2 - \frac{m^3}{3} + \frac{m^4}{2} + \mathcal{O}\left(m^5\right). \tag{4}$$

Hint: it is wise to try other calculations first, if you get stuck on the maths.

(h) Using the Landau free energy, determine the temperature for which the $m \neq 0$ minimum becomes stable. What happens when $\left(1 - \frac{2}{3}Q\right) < 0$?

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2. Dieterici's Equation: (36 points)

Assume that a gas obeys Dieterici's equation of state

$$\beta p \left(\frac{1}{\rho} - b \right) = e^{-\beta a \rho}, \tag{5}$$

where p is the pressure, $\rho = N/V$ with N the number of particles and V the volume, and a and b are coefficients that set the properties of the gas.

(a) Show that in the low-density limit Dieterici's equation of state reduces to that of the Van der Waals gas and provide the expression for the third virial coefficient.

(b) Interpret the 'improvement' made to the Van der Waals gas by the exponential term on the right-hand side of Dieterici's equation of state equation using a few words.

(c) Sketch three isotherms of p as a function of $v = V/N$ for the Dieterici's equation of state above, at, and below the critical temperature T_c, respectively, indicating which is which. Label your axes and indicate the spinodal points.

(d) Show that $k_{\mathrm{B}} T_c = a/(4b)$, the critical pressure is given by $p_c = a/(4be^2)$, and critical volume per particle is $v_c = 2b$. Here k_{B} denotes the Boltzmann constant.

The isothermal compressibility can also be defined in terms of v and reads

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_{T,N} . \tag{6}$$

(e) Describe in a few words what happens with κ_T when you cross a spinodal curve for $T < T_c$.

(f) Introduce $t = k_{\mathrm{B}}(T - T_c)$ and expand the compressibility around $t = 0$ and $v = v_c$. What is the value of the critical exponent γ, *i.e.*, $\kappa_T \propto |t|^{-\gamma}$? Describe in a few words what feature of the system leads to this behavior.

A researcher has applied Dieterici's equation of state to model a gas-liquid phase separation, but is dissatisfied with the descriptiveness at high density. They measure the interaction potential between the particles and find that it is captured by

$$\phi_{\mathrm{SW}}(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases} , \tag{7}$$

with $\lambda > 1$ a measure for the range of the attraction (strength ϵ) and r the center-of-mass separation between the particles. The high-density equation of state can be determined using

$$\beta p_{\mathrm{SW}} = \rho - \frac{\beta \rho^2}{6} \int_V \mathrm{d}\boldsymbol{r}\, r \phi'_{\mathrm{SW}}(r) g_{\mathrm{SW}}(r). \tag{8}$$

with ρ the particle number density, $g_{\mathrm{SW}}(r)$ the pair-correlation function and $\phi'_{\mathrm{SW}}(r)$ the derivative with respect to r of the pair potential.

(g) Sketch the pair distribution function in the case of a dense liquid. Label your axes and provide the relevant length scales and limiting values. Graphically indicate how this relates to the concept of a correlation length in the system.

(h) Demonstrate that you can write

$$\beta p_{\mathrm{SW}} = \rho + \frac{2\pi\sigma^3}{3} \rho^2 \left[g_{\mathrm{SW}}(\sigma^+) + \lambda^3 \left(g_{\mathrm{SW}}(\lambda\sigma^+) - g_{\mathrm{SW}}(\lambda\sigma^-) \right) \right] . \tag{9}$$

with the "+" and "-" superscript indicating the direction in which the limit is taken, *i.e.*, from above and below, respectively. Explicitly, $\lim_{p \downarrow q} r(p) = r(q^+)$ for some function r, limit value q, and variable p. Hint: introduce the auxiliary functions $x(r) = \exp\left[-\beta\phi_{\mathrm{SW}}(r)\right]$ and $y(r) = g_{\mathrm{SW}}(r)/x(r)$, and properties of the Heaviside function $\Theta(x)$ $[\Theta(x < 0) = 0$ and $\Theta(x > 0) = 1]$ to arrive at this result. Hint: keep this problem for last it is not worth a huge number of points.

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3. Isotropic-Nematic Transition for Colloidal Boards: (32 points)

In a simple model of a system of plate-like particles (platelet) one views the particles as rectangular blocks with a square base of length L and thickness D, *i.e.* of the form $L \times L \times D$. A further simplification is to restrict the number of possible orientations of each platelet to three, such that the main axes of the platelets can only point in the direction of a laboratory frame $\hat{\boldsymbol{x}}_\alpha$, $\alpha = 1, 2, 3$. A particle with orientation α has its short axis along $\hat{\boldsymbol{x}}_\alpha$. The interaction between the particles is *hard*, *i.e.*, overlap is not allowed. The Helmholtz free energy $F(N, V, T)$ of N of such platelets in a volume V $(\rho = N/V)$ at temperature T is given, within the second virial approximation, by

$$\frac{F}{Vk_\mathrm{B}T} = \sum_{\alpha=1}^{3} \rho_\alpha \left(\log \rho_\alpha \mathcal{V} - 1\right) + \sum_{\alpha=1}^{3} \sum_{\alpha'=1}^{3} B_{\alpha\alpha'} \rho_\alpha \rho_{\alpha'}, \tag{10}$$

with ρ_α the density of particles with orientation α, and $\mathcal{V}$ the (irrelevant) thermal volume.

(a) Argue in a few words that $B_{\alpha\alpha'}$ is a symmetric 3×3 matrix. Calculate the second virial coefficients $B_{11} = B_{22} = B_{33} \equiv B_\parallel$ and $B_{12} = B_{13} = B_{23} \equiv B_\perp$ for pairs of parallel and perpendicular platelets, respectively.

(b) Consider from now on the "sheet" limit $D/L \to 0$. First calculate $B_\parallel/L^3$ and $B_\perp/L^3$ in this limit, and then show that the dimensionless free energy $\psi = FL^3/Vk_\mathrm{B}T$ takes the form

$$\psi = \sum_\alpha c_\alpha (\log c_\alpha - 1 + \log \frac{\mathcal{V}}{L^3}) + 2(c_1c_2 + c_1c_3 + c_2c_3), \tag{11}$$

with dimensionless densities $c_\alpha = L^3 \rho_\alpha$.

(c) Define the *nematic order parameter* S by $c_3 = c(1 + 2S)/3$ and $c_1 = c_2 = c(1 - S)/3$, with $c = c_1 + c_2 + c_3 = \rho L^3$ the total dimensionless density. Give the range of the parameter S, keeping in mind that densities are non-negative. Sketch the way the order parameter varies with c when the system undergoes a phase transition, label your axes and indicate the coexistence region!

Assume now that the system has a temperature $T < T_c$ and that it is prepared in a state that is in the region of the phase diagram between the binodal and spinodal curves. Let the surface tension be given by γ, and a supersaturation given by Δg. Further assume that the nucleus that forms for the platelets is a cube with edge length $\mathcal{L}$.

(d) Write down the appropriate Gibbs free-energy difference ΔG as a function of $\mathcal{L}$ and calculate the free-energy barrier for nucleation. What is the critical $\mathcal{L}$ and the maximum barrier height?

A scientist now adds polymers to a dilute platelet suspension.

(e) Explain in a few words (possibly supported by sketches) why it is favorable for the platelets to self-assemble into columns when sufficient polymers have been added.

(f) Assume that a column has s platelets in it, let p be the probability of there being a bond and $(1 - p)$ the probability of there not being a bond between two platelets. Argue in words (possibly supported by a sketch) that the chain-length distribution follows $c(s) \propto (1 - p)^2 p^{s-1}$.

(g) Assume that the total concentration of bonds is $p\rho$ and the total concentration of free ends is $2(1 - p)\rho$ and that all platelets are part of some stack (possibly of 1). Use a chemical equilibrium between bonds and free ends with equilibrium constant K to show that $p \approx 1 - 1/\sqrt{4K\rho}$ when p is almost 1. Hint: Do not overthink it.

(h) Suppose that for a 1D stack of hard platelets the free energy is known and given by F_0 and that spacing is also known. Explain in a few words — supported by equation(s) — what the technique you can use to compute the free energy of the stack, once polymers have been added.

The platelet columns can give rise to percolation between the bottom and the top of the sample cell. A simple model for this is a square 2D lattice with sites occupied with probability P and unoccupied with probability $1 - P$. We consider 2×2 superblocks. These are occupied if there is there is a connection from top to bottom.

(i) Compute the non-trivial fixed point for the up-down percolation transition.

The exam ends here!