Retake for Advanced Statistical Physics: NS-370B

Date: January 7th, 2020

Time for Regular Students: 09:00h - 12:00h

Upload to BlackBoard before 12:30h

Extra-Time Students Only: 09:00h - 12:30h, upload before 13:00h

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

You may use the lecture notes, the lecture slides, and your own exercise solutions.

You may **not** use the internet or analytic solution software (write down the intermediate steps!).

You may only use your electronic device to complete and upload the exam, and to consult the lectures and 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!**

Please complete the "verklaring student" before starting the exam and upload it as well.

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:
  $B_2 = -\dfrac{1}{2V}\displaystyle\int_V \mathrm{d}\boldsymbol{r}_1 \int_V \mathrm{d}\boldsymbol{r}_2 \, \left(\exp(-\beta\phi(r)) - 1\right).$
- $k_{\mathrm{B}} = 1.13 \times 10^{-23}\mathrm{J/K}$, $e = 1.6 \times 10^{-19}\mathrm{C}$, and $R = 8.31\mathrm{J/K/mol}$.
- 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
  $\log(1-x) = -\displaystyle\sum_{n=1}^{\infty} \frac{x^n}{n}.$
- For two angles α and γ the following identities hold:
  $\sin(\alpha \pm \gamma) = \sin\alpha\sin\gamma \pm \cos\alpha\cos\gamma$
  $\cos(\alpha \pm \gamma) = \cos\alpha\cos\gamma \mp \sin\alpha\sin\gamma$

1. Properties of Dipolar Hard Spheres: (32 points)

The interaction potential U between two hard spheres with diameter σ, located at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ ($\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$; $r = |\boldsymbol{r}|$), and with dipole moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, respectively, is given by

$$U(\boldsymbol{r}_1, \boldsymbol{\mu}_1; \boldsymbol{r}_2, \boldsymbol{\mu}_2) = \begin{cases} \infty & r \leq \sigma \\ \dfrac{\mu_0 \mu^2}{4\pi r^3} \left(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2 - 3(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{r}})(\hat{\boldsymbol{\mu}}_2 \cdot \hat{\boldsymbol{r}}) \right) & r > \sigma \end{cases}, \tag{1}$$

where μ_0 is the vacuum permeability, $\mu \equiv |\boldsymbol{\mu}_1| = |\boldsymbol{\mu}_2|$, and hats indicate unit vectors.

(a) Explain in a few words why the behavior of this system might be captured using a van der Waals equation of state, explicitly making reference to its two phenomenological parameters a and b.

(b) Provide the definition for the angular-dependent second virial coefficient that has the volume V in the denominator (hint: use the above cheat sheet). Using this expression, show (be precise and give the steps) that the orientationally averaged 2nd virial coefficient may be written as

$$B_2 = -\frac{1}{8\pi} \int_0^\infty \mathrm{d}r \int \mathrm{d}\Omega_1 \int \mathrm{d}\Omega_2 \, \left[\exp\left(-\beta U(r, \Omega_1, \Omega_2) \right) - 1 \right], \tag{2}$$

with the $\mathrm{d}\Omega_i = \sin\theta_i \mathrm{d}\theta_i \mathrm{d}\phi_i$ the solid angle corresponding to the orientation dipole i. Indicate clearly where you make an approximation to arrive at the result of Eq. (2). Skip if you get stuck!

It can be shown (not here) that

$$\frac{B_2}{B^{\mathrm{HS}}} = 1 - \frac{1}{3}\lambda^2 - \frac{1}{75}\lambda^4 - \frac{29}{55125}\lambda^6, \tag{3}$$

with B^{HS} the hard-sphere 2nd virial coefficient and $\lambda = (\mu_0 \mu^2)/(4\pi k_{\mathrm{B}} T \sigma^3)$ — k_{B} is Boltzmann's constant and T the temperature.

(c) The equation of state (EoS) for the fluid obtained from the virial expansion has limited applicability. Explain how you can compute a more precise EoS using a known value of the free energy for hard spheres. Use the expression involving the radial distribution function $g(r)$.

(d) Compute the 2nd virial coefficient for hard spheres B^{HS} **and** provide the leading-order perturbation in λ to the hard-sphere equation of state at low density.

(e) Derive the expression

$$k_{\mathrm{B}} T \left(\frac{\partial \rho}{\partial p} \right)_T = 1 + \rho \int \mathrm{d}\boldsymbol{r} \, \left(g(r) - 1 \right). \tag{4}$$

(f) Assume $p = k_{\mathrm{B}} T \left(\rho + B_2 \rho^2 \right)$; do not evaluate B_2. Use Eq. (4) to obtain a relation between B_2 and $g(r)$. Explain (in a few words) why this result is reasonable, referencing the potential of mean force and the assumption that underlies the validity of the truncated virial expansion.

(g) A crystalline nucleus might form in the sample at sufficient density. Provide the general expression for the Gibbs free energy difference and explain the parameters that you need to specify to obtain a nucleation barrier. Derive an expression for the size of the critical nucleus and nucleation barrier, under the assumption that the nucleus is a cylinder with radius $r/2$ and height r.

A researcher (falsely) assumes that for certain choices of the interaction parameters the following Landau free energy for the system holds

$$f(m, T) = p(T) m^4 + q m^6 \tag{5}$$

with p and q prefactors, of which only the first depends on the temperature.

(h) Explain in a few words supported with sketches why this theory describes a continuous phase transition. Do not forget to label your axes.

(i) Compute the critical exponent β, assuming that $p(T)$ may be written as $p'(T - T_c)$ with p' a constant and T_c the critical temperature.

The exam continues on the next page ⇒

2. Rupture of a Stretchable Network: (33 points)

A given spring is found to break when stretched to a certain length. Before the spring breaks, *i.e.*, for small extensions, the free energy A is given by

$$\frac{A}{M} = \frac{1}{2}kx^2, \tag{6}$$

with $x = L/M$ the length per unit mass; L is the length and M the mass. The free energy $A = U - TS$, with U the internal energy, T the temperature, and S the entropy, obeys $dA = -S\mathrm{d}T + f\mathrm{d}L + \mu\mathrm{d}M$, with f the tension sand μ the chemical potential. After breaking, the free energy is given by

$$\frac{A}{M} = \frac{1}{2}h(x - x_0)^2 + c. \tag{7}$$

The constants k, h, x_0, and c are all independent of x but do depend on T. Furthermore, we assume $k > h$, $c > 0$, and $x_0 > 0$ for all T.

(a) Determine the equation of state $f = f(T, x)$ for the spring at small and large extensions.

(b) Similarly, determine the chemical potentials μ.

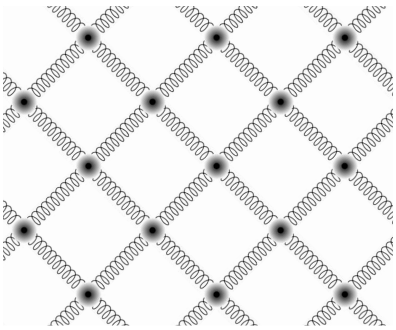
(c) Show that $\mu = A/M - fx$.

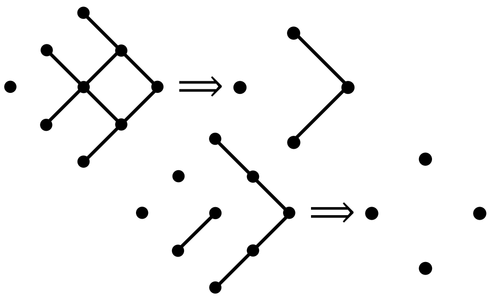
(d) Find the force that, at given T, will break the spring. Do **not** eliminate x_0 from your f.

(e) Determine the discontinuous change in x when the spring breaks. Hint: which parameter is this?

(f) Discuss in a few words how this is like a first- **or** like a second-order phase transition.

We now consider a network of springs, which represents a deformable material (think a plastic bag), we are interested in when the material ruptures into two pieces. For simplicity we take a network to be a simple square lattice of nodes, with the edges at an angle of 45° with respect to the x-axis. These nodes are connected by springs to their nearest neighbors only.





The probability of there being a whole spring (a connection) is p, while the probability of the spring being broken is $1 - p$. We consider rupture along the y-axis.

(g) Sketch three small pieces of a network that is ruptured, connected, and just connected, **and** use these configurations to explain in a few words how rupture can be seen as a percolation problem.

(h) Provide the real-space renormalization expression for the non-trivial fixed point p^* assuming that a 3-by-3 set of nodes (for which there are 12 possible springs) becomes a superblock of 2-by-2 nodes. Whenever there are at least 8 connections in the 3-by-3 set of nodes, the superblock has the right edges connected by springs, otherwise the superblock has no connections. See the picture for two examples. Springs of the super blocks are additive, hence there are only springs on the superblock's right-hand side, to avoid overlaps. **Do not try to evaluate the expression!**

Consider now instead the situation where the network is initially mostly connected. Periodically small (constant) forces are applied in the y direction and the stretching of the network is observed in response to the applied force. The researcher slowly heats the system (on a time scale much longer than the period of the applied forces) and finds that at a temperature T_r the system ruptures.

(i) Sketch the amplitude of the network extension ΔL as a function of T, label your axes, **and** explain in a few words why this should be the response to such forcing.

The exam continues on the next page ⇒

3. Rotating-Spin System: (35 points)

We consider a system that consists of unit-length spin vectors $\boldsymbol{s}_i$, which are free to rotate in the xy-plane. That is, unlike the Ising model for which the spins can point up or down along the y-axis, the spins in this model can be described by an angle $\theta \in [-\pi, \pi]$ with respect to the x-axis. This angle is defined by $\cos\theta_i = \boldsymbol{s}_i \cdot \hat{\boldsymbol{x}}$ with $\hat{\boldsymbol{x}}$ the unit vector pointing along the x-axis and '$\cdot$' the inner product. The Hamiltonian for this system can be written as

$$\mathcal{H} = -\frac{J}{2}\sum_i {\sum_j}' \boldsymbol{s}_i \cdot \boldsymbol{s}_j - \sum_i \boldsymbol{h} \cdot \boldsymbol{s}_i = -\frac{J}{2}\sum_i {\sum_j}' \cos(\theta_i - \theta_j) - h \sum_i \cos\theta_i, \tag{8}$$

where ${\sum_j}'$ indicates a sum over nearest neighbors, and $\boldsymbol{h} \equiv h\hat{\boldsymbol{x}}$ is an external field pointing along the x-axis. For the first few subproblems, we will assume $h = 0$ and that the sites are located on a **one-dimensional (1D) chain**.

(a) Assume a chain of N sites, which is **not** periodic. Sketch a few microstates.

(b) Demonstrate that the expression for the canonical partition sum $Z(N,T)$ for this **open-ended 1D chain** — N is the total number of sites and T the temperature — can be written as

$$Z(N,T) = 2\pi \left(\int_{-\pi}^{\pi} \mathrm{d}\theta \, \exp\left(\beta J \cos\theta\right) \right)^{N-1} \equiv (2\pi)^N I_0(\beta J)^{N-1}, \tag{9}$$

with $\beta = 1/(k_\mathrm{B}T)$, where k_B is Boltzmann's constant, θ is an auxiliary integration variable, and I_0 is used for notational convenience (it is the modified Bessel function of the first kind).

(c) Compute the free energy per site $f = \beta F/N$ in the thermodynamic limit. Compute the high-temperature limit of f **and** explain in a few words why your results make sense.

(d) Now assume a **closed 1D chain**, *i.e.*, periodic boundary conditions. Write down the transfer matrix belonging to angles θ and θ' for this problem. How is f (definition in part c) related to the eigenvalues of this matrix? Do **not** compute these eigenvalues!

We now consider the same rotating-spin model on a **two-dimension (2D) square lattice** of N spins. Assume $h \neq 0$ from here on. Define $z_i = \exp(\imath\theta_i)$ with i the index and $\imath$ the imaginary unit. Let $z_i = w + \delta z_i$ with $w \equiv \langle z_i \rangle$ the statistical average.

(e) Write down the complex conjugate relations for z_i using the standard $*$ notation. Show that $\cos(\theta_i - \theta_j) = \mathrm{Re}(z_i^* z_j)$, with Re indicating the real part.

(f) Use the result from (e) to expand the Hamiltonian in Eq. (8) up to $\mathcal{O}(\delta z^2)$, *i.e.*, neglecting terms such as $\delta z_i \delta z_j$. Show that the mean-field Hamiltonian is given by:

$$\mathcal{H}^{\mathrm{MF}} = 2JN|w|^2 - 2J\sum_i \mathrm{Re}\left(w^* z_i + w z_i^*\right) - \frac{h}{2}\sum_i \left(z_i^* + z_i\right). \tag{10}$$

(g) Explain in a few words why the above free energy should be minimized when w points in the same direction as the external field, *i.e.*, $w \in \mathbb{R}$ and, assuming $h > 0$, $w > 0$. Show that this leads to

$$\mathcal{H}^{\mathrm{MF}}_{\mathrm{min}} = 2JNw^2 - (h + 4Jw)\sum_i \cos\theta_i, \tag{11}$$

The corresponding mean-field free energy per site is given by

$$f^{\mathrm{MF}}_{\mathrm{min}} = 2\beta J w^2 - \log\left(2\pi I_0\left(\beta(h + 4Jw)\right)\right). \tag{12}$$

Minimizing Eq. (12) leads to $w = I_1\left(\beta(h + 4Jw)\right)/I_0\left(\beta(h + 4Jw)\right)$, with I_1 the derivative with respect to the argument of I_0.

(h) What kind of equation is this for w **and** what role does w serve in describing the phase transition? Explain in a few words.

(i) Based on the above analysis, do you think the 2D rotating-spin model has a phase transition? Explain why using only a few words.

The exam ends here!