
Final Exam for Advanced Statistical Physics: NS-370B

Date: November 4th, 2024

Time for Regular Students: 17:00 - 20:00

Extra-Time Students Only: 17:00 – 20:30

This exam consists of **7** questions of varying length.

The total number of possible points is: 100 + 10 bonus points.

This is a **closed-book** exam, no notes are allowed.

You will not require a calculator or any other electronic device and are consequently not permitted one.

Please **start every exercise on a new PAGE of paper**.

Write your name clearly on every four-page sheet of paper.

Please number your sheets (1/3, 2/3, ...) and indicate which questions are on it.

The exam can be written in English or Dutch.

Please write CLEARLY and using PEN!

Equation Cheat Sheet

A few formulas and information that may be useful for this exam:

- The canonical partition function of a classical thermodynamic system of N identical particles in a volume V a temperature T with Hamiltonian $H(\mathbf{\Gamma})$ — $\mathbf{\Gamma}$ is a point in phase space — is written:

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

- The grand partition function of identical particles is given by (pay attention to the N dependence of Z for each term in the sum):

  $\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \exp(\beta\mu N) Z(N,V,T)$,

  and the grand-canonical distribution is given by:

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

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

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

- $k_{\mathrm{B}} = 1.38 \times 10^{-23}$ J/K, $e = 1.6 \times 10^{-19}$ C, and $h = 6.63 \times 10^{-34}$ Js.

- 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:

  $e^x = \displaystyle\sum_{n=0}^{\infty}\frac{x^n}{n!} \qquad \& \qquad \log(1-x) = -\sum_{n=1}^{\infty}\frac{x^n}{n}.$

- Maxwell-Boltzmann ($s = 0$), Bose-Einstein ($s = -1$), and Fermi-Dirac ($s = 1$) statistics are:

  $f(\epsilon) = \dfrac{1}{\exp[\beta(\epsilon-\mu)] + s},$

  where ϵ is the energy (of a single-particle level) and μ the chemical potential.

- The quantum single-level 'grand'-canonical partition functions Z_i are given by:

  $Z_i = \sum_{n_i=0}^{M} \exp(\beta n_i(\mu - \epsilon_i))$,

  where ϵ_i is the energy associated with the i-th level and μ is the chemical potential. The value of M depends on the statistics; $M = 1$ for fermions and $M = \infty$ for bosons. These lead to the following grand canonical partition function

  $\Xi(\mu,V,T) = \prod_i Z_i$,

  for the system, where i runs over all available levels.

1. Thermodynamics: (12 points)

In this question, we consider several useful thermodynamic relations, identities, and transformations.

(a) Write down the mathematical expressions for the *first* and *second* law of thermodynamics. Write down what the symbols mean and explain the sign convention that you picked in a *few* words.

The laws can be combined with the standard choices of work to obtain $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$.

(b) Make the transition to the (admittedly slightly useless) $Sp\mu$ ensemble by deriving $\mathrm{d}J = T\mathrm{d}S + V\mathrm{d}p - N\mathrm{d}\mu$. Provide the transformation, name it, **and** give the intermediate steps.

(c) Derive expressions for T, V, and N in terms of $J(S, p, \mu)$ based on your result from (b).

(d) Show that $J(S, p, \mu) = T(\mu, p)S$ and explain how you arrived at this result in *few* words.

(e) Use your expression in (d) to derive the Gibbs-Duhem relation.

2. Critical Exponents: (14 points)

Consider a system with a Landau free energy given by $f(t, m) = -hm + r(t)m^2 + um^6$, with $u > 0$ a constant and $t = (T - T_c)/T_c$, where T_c is the finite critical temperature. The critical point is approached along the r-axis by setting $r(t) = r't$.

(a) Sketch the behavior of $f(t, m)$ just above and just below the critical temperature. Assume that $h > 0$, but is not the dominant term.

(b) Set $h = 0$ and determine the possible phases. Explain in a *few* words, optionally supported by a sketch, what the order of the phase transition is.

(c) On either side of the transition, determine the critical exponent β of the 'spontaneous magnetization', *i.e.*, $m \propto |t|^{\beta}$. Hint: is there a power law on either side?

(d) Establish the critical exponent γ, which is defined as $\chi \equiv \lim_{h\downarrow 0}\left(\frac{\partial m}{\partial h}\right) \propto |t|^{-\gamma}$, on either side of the transition.

3. Site Occupation: (15 points)

A scientist considers site occupation on a square (2D) lattice. Let the probability of an occupied site be p, then the probability to find an unoccupied site is $1 - p$.

(a) Use a renormalization-group argument with 2×2 superblocks that are occupied when at least half of the squares are occupied. Show (using sketches) that $R(p) = p^4 + 4p^3(1-p) + 6p^2(1-p)^2$ **and** provide the analytic (fully reduced) expression for the associated critical value of p.

The occupation model is now complemented with an interaction $\mathcal{H} = -\frac{J}{2}\sum_i {\sum_j}' \delta_{\sigma_i,\sigma_j}$, where $\sum_j'$ indicates a sum over nearest neighbors; σ_i represents the state of site i, and can be either U(noccupied) or O(ccupied); and $\delta_{\sigma_i,\sigma_j}$ is the Kronecker delta function: $\delta_{\sigma_i,\sigma_j} = 0$ if $\sigma_i \neq \sigma_j$ and $\delta_{\sigma_i,\sigma_j} = 1$ if $\sigma_i = \sigma_j$. To gain additional understanding of the system, the researcher makes the random-mixing approximation. This implies that there are no correlations between neighboring sites.

(b) Determine the average energy **and** the entropy under the random-mixing approximation. Explain your reasoning using only a *few* words! Hint: have a look at the expression in (c) if you get stuck.

(c) Show that the Helmholz free energy under this approximation may be written as

$$f \equiv \frac{\beta F}{N} = -2\beta J\left(p^2 + (1-p)^2\right) + p\log(p) + (1-p)\log(1-p), \tag{1}$$

where $\beta = 1/(k_{\mathrm{B}}T)$ with T the temperature and k_{B} the Boltzmann constant, and N is the number of lattice sites.

(d) Argue that the above reduced free energy per site f is minimized by $p = 1/2$.

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4. Fermion Ideal Gas: (26 points)

At high temperatures T, a gas of fermions in a 3D volume V behaves similar to a classical ideal gas. In this problem, the goal is to determine the leading-order corrections to the classical ideal gas law $pV = Nk_{\mathrm{B}}T$, where p is the pressure, N the particle number, and k_{B} is the Boltzmann constant. We start from the grand-canonical partition function $\Xi(\mu, V, T) = \prod_i Z_i$ with $Z_i = \sum_{n_i} \exp(\beta n_i(\mu - \epsilon_i))$, where μ is the chemical potential and ϵ_i the energy of the i-th quantum level of a single particle.

(a) Use a general relation between $\langle N \rangle$ and Ξ to show that the particle number N is given by the integral representation

$$N = \int \mathrm{d}E\, g(E) f_{\mathrm{FD}}(E), \tag{2}$$

where $g(E)$ is the density of states and $f_{\mathrm{FD}}(E)$ adheres to Fermi-Dirac statistics. Support your calculation by a *few* words of explanation.

(b) Use the definition of the wave vector $\boldsymbol{k} = \pi \boldsymbol{n}/L$, with $\boldsymbol{n}$ the vector containing the quantum numbers n_x, n_y, and n_z, and the expression for the energy $E_{\boldsymbol{n}} = (\hbar^2 k^2)/(2m)$, with m the particle mass, $k = |\boldsymbol{k}|$, and $\hbar = h/(2\pi)$ the reduced Planck constant, to arrive at the density of states

$$g(E) = \frac{L^3}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}. \tag{3}$$

We will identify $L^3 = V$ for the remainder of this exercise.

(c) Input both $g(E)$ and $f_{\mathrm{FD}}(E)$ into the expression for N and rework it using a substitution to arrive at the following scaling of the particle density $\rho = N/V$ with the thermal wavelength Λ

$$\rho = \frac{1}{\Lambda^3} \frac{2}{\sqrt{\pi}} \int \mathrm{d}x \frac{\sqrt{x}}{z^{-1} e^x + 1}, \tag{4}$$

with $z = \exp(\beta\mu)$. Hint: you can find the expression for $f_{\mathrm{FD}}(E)$ on the cheat sheet ($\hbar = h/(2\pi)$).

(d) Explain using a *few* words when quantum effects appear. Use Λ and ρ in your argument.

(e) Argue using only a *few* words and the above expression for N that at high temperatures T the chemical potential μ becomes large but negative, such that $z = e^{\beta\mu} \ll 1$. Hint: in your answer you should reference ensemble in which $\beta p = \rho$ holds and make use of $\rho \propto z/\Lambda^3$.

(f) Turning to a **classical** ideal gas, use equipartition to show that the pressure satisfies $pV = 2E/3$ with E the energy. Explain your answer in a *few* words.

5. Needle-like Objects: (15 points)

Here, we examine the phase behavior of **hard** anisotropic particles (long rods) using Onsager theory in three dimensions (3D).

(a) What are the isotropic and nematic phase for a (colloidal) liquid crystal? Illustrate using sketches and explain using a *few* words only. Hint: your sketches can be in 2D!

(b) Provide an approximate expression for the second virial coefficient $B_2(\hat{\boldsymbol{\omega}}_1, \hat{\boldsymbol{\omega}}_2)$ for thin, long rods of length L and diameter D, *i.e.*, $D \ll L$. Explain your expression using a *few* words **and** support your argument using a sketch. N.B. You need to approximate the integral! Hint: an expression for B_2 can be found on the equation cheat sheet. Your extension to hard rods should depend on the respective orientation of the rods ($\hat{\boldsymbol{\omega}}_1$ and $\hat{\boldsymbol{\omega}}_2$), which are unit vectors, and L and D only.

The nematic director is the average orientation of the rods in the liquid crystal. Let θ measure the angle between a rod-like colloid and this director. It is then appropriate to write the order parameter as a series in terms of $\cos\theta$, which takes values in the range $[-1, 1]$.

(c) Show that $S = \left\langle (1/2) \left(3\cos^2\theta - 1\right) \right\rangle$ is a suitable order parameter for identifying the disordered phase. Hint: what is the probability of finding any given orientation in the disordered phase?

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6. Chemical Reactions: (18 points)

Consider a square-lattice model with A sites and n occupied sites (or particles). If two particles are adjacent, they bond with bonding energy $-\epsilon$ (with $\epsilon > 0$). However, a particle that is already bonded cannot bond with any other particles. Thus, the system consists of monomers and dimers. Here, we develop an approximate theory that gives us the ratio. Let the average monomer density be $\rho_1 = n_1/A$ and let the dimer density be $\rho_2 = n_2/A$, with $n_{1,2}$ the number of monomers and dimers, respectively. Assume that the monomers and dimers do not interact, so both behave like an ideal gas.

(a) Show that the canonical partition sum can be written as $Q_1(n_1, A, T) = A^{n_1}/(n_1!)$ for the monomers, and as $Q_2(n_2, A, T) = \left(2e^{\beta\epsilon}A\right)^{n_2}/(n_2!)$ for the dimers; $\beta = 1/(k_B T)$ with k_B the Boltzmann constant and T the temperature. Support your result using a *few* words.

(b) Show that the reduced Helmholtz free energy is given by:

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

in the thermodynamic limit. Explain the approximation(s) you use in a *few* words.

(c) Show that in equilibrium the chemical potentials of monomers and dimers should obey: $2\mu_1 = \mu_2$. Hint: use that $n_1 + 2n_2 = n =$ constant.

(d) Use the answer from (c) to show that this requires:

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

(e) What happens in the limit where $\epsilon \to 0$ (assuming low density)? And $\epsilon \to \infty$? Provide your expectation based on physical intuition using only a *few* words. Hint: you can compute this, but it is unnecessary and rather lengthy!

7. Heat Capacity of a Metal: (10 *bonus* points)

We now consider the fermion ideal gas in 3D at very low temperatures and examine its properties.

(a) Sketch the limiting $T \downarrow 0$ behavior of $f_{FD}(E)$ as a function of E, labelling your axes and indicating the Fermi energy E_F. State in a *few* words only what this implies about the occupation of the energy levels below E_F for temperatures slightly above zero.

(b) Provide a physical argument, for which you invoke equipartition, as to why the heat capacity per volume caused by the electrons scales linear with T. Use a *few* words to support your argument.

A more careful analysis of the temperature dependence reveals that in a metal, the heat capacity scales as T^3 for slightly higher temperatures and tends to a constant at even higher temperatures.

(c) Based on your physical intuition, what is the constant that the heat capacity tends toward? Provide the scaling / an expression and explain your result using only a *few* words.

The exam ends here ☺!