**Midterm Exam for Advanced Statistical Physics: NS-370B**

**Date: October 10th, 2023**

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

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***Extra-Time Students Only: 13:30 – 17:00***

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This exam consists of **4** questions of varying length.

The total number of possible points is: 100.

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!**

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**Equation Cheat Sheet**

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

  $B_2 = -\dfrac{1}{2}\displaystyle\int_V \mathrm{d}\boldsymbol{r}\ (\exp(-\beta\phi(r)) - 1)\,.$
- $k_{\mathrm{B}} = 1.13 \times 10^{-23}$ 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:

  $e^x = \displaystyle\sum_{n=0}^{\infty} \frac{x^n}{n!} \qquad \& \qquad \log(1-x) = -\sum_{n=1}^{\infty}\frac{x^n}{n}.$
- 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 $\epsilon$ is the energy (of a single-particle level) and $\mu$ 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 $\epsilon_i$ is the energy associated with the $i$-th level and $\mu$ 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:** (37 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.

(b) Provide the two standard forms of work. Ensure agreement with your choice in part (a).

(c) Combine the laws and choices of work to obtain $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$. Explain in a *few* words when it is **not** allowed to use this expression.

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

(e) Make the transition to the $\mu VT$ ensemble and provide an expression for $\mathrm{d}\Omega$. Provide the transformation and the intermediate steps.

(f) Show that $\Omega(\mu, V, T) = -p(\mu, T)V$ and explain what the implication is for the intensive variables in general using only a *few* words.

We also know that $\beta\Omega(\mu, V, T) = -\log(\Xi(\mu, V, T))$ and will for assume that the system behaves classically for the remainder of the exercise. Using the definition of $\Xi(\mu, V, T)$ it can be shown that

$$\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle} = k_\mathrm{B}T\left(\frac{\partial\rho}{\partial p}\right)_T . \tag{1}$$

(g) Explain in a *few* words: How would Eq. (1) behave when the system is unstable, does this make sense based on your understanding of variance?

Now assume we are working with an ideal gas (the net potential energy is zero) and define the fugacity to be $z(\mu, T) = e^{\beta\mu}$ with $\beta = 1/(k_\mathrm{B}T)$ and $k_\mathrm{B}$ Boltzmann's constant.

(h) Use the definition of the *canonical* partition function to derive an expression for the thermal wavelength $\Lambda$.

(i) Show that $\Xi(z, V) = \exp(zQ_1)$, where $Q_1 = V/\Lambda^3$ (for the ideal gas).

**2. Interpreting Equipartition:** (19 points)

The eigenstates of a 1D harmonic oscillator, denoted by the quantum number $n = 0, 1, 2, \cdots$, have energies $\epsilon_n = \hbar\omega(n + 1/2)$. Here, $\omega$ is the frequency and $h = 2\pi\hbar$ Planck's constant. At temperature $T$, the quantum-mechanical canonical partition function is defined by $Z_q(T) = \sum_{n=0}^{\infty} \exp[-\beta\epsilon_n]$, with $\beta = 1/(k_\mathrm{B}T)$ and $k_\mathrm{B}$ Boltzmann's constant.

(a) Show that $Z_q(T) = (2\sinh(\beta\hbar\omega/2))^{-1}$.

(b) Compute the high-temperature limit $T \gg \hbar\omega/k_\mathrm{B}$ of $Z_q(T)$.

The same oscillator is classically described by a Hamiltonian of the form $H(x, p_x) = p_x^2/(2m) + m\omega^2x^2/2$, with $m$ the mass, $p_x$ the momentum in the $x$-direction, and $x$ the amplitude of the oscillator. The classical partition function is given by

$$Z_c(T) = \frac{1}{Y}\int_{-\infty}^{\infty} \mathrm{d}p_x \int_{-\infty}^{\infty} \mathrm{d}x \, \exp[-\beta H(x, p)], \tag{2}$$

with $1/Y$ a prefactor that we will determine by imposing $Z_c(T)$ to be equal to the high-temperature limit of $Z_q(T)$, *i.e.*, where we expect the classical behavior should be recovered.

(c) Compute $Z_c(T)$ and show that matching the quantum result to the classical one leads to $Y = h$.

Next we consider a nitrogen gas.

(d) What is the internal energy $U$ according to the equipartition theorem for temperatures much smaller than those needed to ionize the molecule *and* what is it for temperatures close to ionization? Explain your results in a *few* words, referencing properties of the (quantum) harmonic oscillator.

**The exam continues on the next page ⇒**

**3. Gibbs and Boltzmann Entropy:** (23 points)

The Gibbs definition of entropy $S$ states that

$$S = -k_\mathrm{B} \sum_s p_s \log p_s, \tag{3}$$

where the sum is over all states $s$. The probability of being in that state is $p_s$ and $k_\mathrm{B}$ is Boltzmann's constant.

(a) Show that the Gibbs definition reduces to that of Boltzmann in the microcanonical ensemble.

(b) Show that in the canonical ensemble, the Gibbs definition of entropy gives rise to $F = U - TS$ where $F$ is the Helmholtz free energy, $U$ the internal energy, and $T$ the temperature.

(c) Show that the Gibbs definition leads to an extensive entropy.

(d) Use the fact that $\sum_s p_s = 1$ as a constraint to maximize Eq. (3). Show that you recover the form of the fundamental assumption underlying statistical mechanics, when there are $\Omega$ states in total.

(e) Explain in a *few* words why this is reasonable, given that you only have information on the normalization of the probability.

**4. Bosons and the Density of States:** (21 points)

Consider the density of states (DoS) for a particle with mass $m$ in a $d$-dimensional system with size $L$ that is free to move within its confining volume. The permissible energy levels for the particle are then

$$E_{\boldsymbol{n}} = \frac{\hbar^2}{2m} k^2 = \frac{\pi^2 \hbar^2}{2mL^2} (\boldsymbol{n} \cdot \boldsymbol{n}), \tag{4}$$

where $\boldsymbol{n}$ is the vector containing the quantum numbers $n_i$, with $i \in \{x, y, z, \ldots\}$ depending on the dimension and $k = |\boldsymbol{k}|$ with $k_i = \pi n_i / L$.

(a) Show that the DoS is given by

$$g(E) = \frac{1}{2} \Omega_d \left( \frac{L}{2\pi} \right)^d \left( \frac{2m}{\hbar^2} \right)^{d/2} E^{\frac{d}{2}-1} \tag{5}$$

where $\Omega_d$ represents the surface are of the $d$-dimensional unit sphere: $\Omega_1 = 2$, $\Omega_2 = 2\pi$, $\Omega_3 = 4\pi$, *etc.* Hint: Do **not** obtain a general expression for $\Omega_d$.

(b) Sketch the behavior of the three cases (one-, two-, and three-dimensional).

Using the DoS and Bose-Einstein statistics it can be shown that in three dimensions the density of the system can be written as

$$\rho = \frac{1}{\Lambda^3} \sum_{m=1}^{\infty} \frac{z^m}{m^{3/2}} + \frac{1}{V} \frac{z}{1-z}, \tag{6}$$

where $z = e^{\beta\mu}$ is the fugacity in terms of the inverse thermal energy $\beta = 1/(k_\mathrm{B} T)$ with $T$ the temperature and $k_\mathrm{B}$ Boltzmann's constant; $\Lambda$ is the thermal wavelength. We also know $\sum_{m=1}^{\infty} m^{-3/2} = \zeta(3/2) \approx 2.61$.

(c) What does $z$ tend to in the low-temperature limit? Justify your answer with a *few* words. Hint: If you do not know $\Lambda$ use that $\Lambda \propto T^{-1/2}$.

(d) Use the expression in Eq. (6) to arrive at a(n approximate) result for the critical temperature, at which bosons would undergo condensation in three dimensions. Hint: You should find $T_c \propto \rho^{2/3}$.

lose to the transition, the sum in the expression for the density may be approximated as $\sum_{m=1}^{\infty} (z^m)/(m^{3/2}) \approx \zeta(3/2) + 2\sqrt{\pi}\sqrt{1-z} + \cdots$. This allows one to write $z$ as a function of $T$ and $T_c$ as

$$z \approx 1 - \frac{\zeta(3/2)^2}{4\pi} \left[ \left( \frac{T}{T_c} \right)^{3/2} - 1 \right]^2. \tag{7}$$

(e) What do you conclude (in a *few* words) about the order of the Bose-Einstein transition, referencing the properies of phase transitions in general?

**The exam ends here ☺!**