Assignment 11

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PC2135
Thermodynamics and Statistical Mechanics

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Problem 1

[**13 pts**] So far, we have introduced three types of ensembles, the micro-canonical ensemble with fixed U, V and N, the canonical ensemble with T, V and N, and the grand canonical ensemble with T, V and μ. We want to see that they are equivalent when the system is in the thermodynamic limit, where N is large. Previously, we have already seen in problem 1 of assignment 9 the equivalence between the micro-canonical ensemble and canonical ensemble, by showing that the standard deviation of the energy in a canonical ensemble is small compared to the average energy, which means that there is an overwhelmingly large probability to find the energy of the system to be the average energy. In this problem, we want to similarly see the equivalence between the canonical ensemble and grand canonical ensemble. We consider a system in contact with a bath at a fixed temperature T and chemical potential μ, such that the system and the bath can exchange energy and particles. Suppose the grand partition function of the system is $Z(T, V, \mu)$.

(1) (3 points) Show that the average particle number of the system is $N = \frac{kT}{Z}\frac{\partial Z}{\partial \mu}$.

(2) (3 points) Show that the mean square particle number is $N^2 = \frac{(kT)^2}{Z}\frac{\partial^2 Z}{\partial \mu^2}$.

(3) (4 points) Show that the standard deviation of the particle number, $\sigma_N = \sqrt{N^2 - (N)^2}$, can be written as $\sigma_N = \sqrt{kT\frac{\partial N}{\partial \mu}}$.

(4) (3 points) Use the extensive or intensive nature of the various quantities to argue that $\sigma_N \ll N$ when $N \gg 1$. This shows the equivalence between the canonical and grand canonical ensembles in the thermodynamic limit.

Solution

Part (1): Average particle number

The grand potential is $\Omega = -kT \ln Z$. In the grand canonical ensemble the average particle number is

$$N = -\frac{\partial \Omega}{\partial \mu}_{T,V} = kT\frac{\partial \ln Z}{\partial \mu} = \frac{kT}{Z}\frac{\partial Z}{\partial \mu} \tag{1}$$

Here and below, N and N^2 denote grand-canonical expectation values.

Part (2): Mean square particle number

Each microstate contributes $e^{\beta\mu N_s - \beta E_s}$ to Z, where N_s is the particle number in that state. Differentiating twice with respect to μ pulls down factors of $(\beta N_s)^2$:

$$\frac{\partial^2 Z}{\partial \mu^2} = \beta^2 \sum_s N_s^2 e^{\beta\mu N_s - \beta E_s} = \beta^2 Z \langle N^2 \rangle \tag{2}$$

With $\beta = 1/(kT)$: $\langle N^2 \rangle = (kT)^2/Z \, \frac{\partial^2 Z}{\partial \mu^2}$, which is the N^2 of the problem statement.

Part (3): Fluctuation $\boldsymbol{\sigma_N}$

From part (1), $N = (kT/Z)\,\frac{\partial Z}{\partial \mu}$, so $\frac{1}{Z}\frac{\partial Z}{\partial \mu} = \frac{N}{kT}$. Differentiating N with respect to μ at fixed T, V:

$$\frac{\partial N}{\partial \mu} = kT\left[\frac{1}{Z}\frac{\partial^2 Z}{\partial \mu^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \mu}\right)^2\right] \tag{3}$$

The first bracketed term: part (2) gives $\frac{(kT)^2}{Z}\frac{\partial^2 Z}{\partial \mu^2} = \langle N^2 \rangle$, so $kT\frac{1}{Z}\frac{\partial^2 Z}{\partial \mu^2} = \frac{\langle N^2 \rangle}{kT}$. The second term: $kT\frac{1}{Z^2}\left(\frac{\partial Z}{\partial \mu}\right)^2 = kT\frac{N^2}{(kT)^2} = \frac{N^2}{kT}$. Therefore

$${\frac{\partial N}{\partial \mu}}_{T,V} = \frac{\langle N^2 \rangle - (N)^2}{kT} = \frac{\sigma_N^2}{kT} \tag{4}$$

$$\sigma_N = \sqrt{kT{\frac{\partial N}{\partial \mu}}_{T,V}} \tag{5}$$

Part (4): Thermodynamic limit

At fixed intensive (T, μ), the mean particle number scales with volume: $N \propto V$. The susceptibility $\chi = {\frac{\partial N}{\partial \mu}}_{T,V}$ is also extensive (it scales with V, hence with N), so $\chi \propto N$. Then

$$\sigma_N^2 = kT\chi \propto N \quad \Longrightarrow \quad \frac{\sigma_N}{N} \propto \frac{1}{\sqrt{N}} \tag{6}$$

As $N \to \infty$, the relative width $\sigma_N / N \to 0$. The particle number is sharply peaked around its mean, so fixing N in the canonical ensemble matches the grand canonical ensemble with the bath-adjusted μ. Same logic as for energy fluctuations in assignment 9.

Problem 2

[**12 pts**] In class, we have discussed the condition for a quantum gas to behave like a classical gas. That is, when

$$Z_1 = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \gg N \tag{7}$$

a quantum gas behaves qualitatively the same as a classical ideal gas. This condition can also be phrased as "the average distance between the particles is much larger than the thermal de Broglie wavelength" $\lambda = h/\sqrt{2\pi mkT}$. In this problem, we will examine whether this condition is met for various systems. You need to look up some data from the internet or other materials.

(1) (4 points) Let's first consider metals, such as sodium, iron and copper. What is the order of magnitude of the average distance between two atoms? Each atom is associated with a few electrons, what is the order of magnitude of the average distance between these electrons? At room temperature, what is the thermal de Broglie wavelength? Can the electron gas in these metals be viewed as a classical gas at room temperature?

(2) (4 points) In many of the cold atom labs, atoms are cooled to temperatures of the scale mili-Kelvin or even much lower, so the de Broglie wavelength is relatively large. However, the density of these ultracold atomic gases is also low. Suppose about 10^4 rubidium-87 atoms are confined into a volume of the order 10^{-15} m^3. Below roughly what temperature do quantum effects become significant?

(3) (4 points) Helium-4 atoms are bosonic and helium-3 atoms are fermionic. At high temperatures such as our room temperature, a helium gas made of either helium-4 atoms or helium-3 atoms looks like a classical ideal gas. When the temperature is lowered but the pressure is kept at the atmospherical pressure, suppose the helium remains to be a gas, at roughly which temperature do the helium gases made of these two isotopes start showing different behaviors due to their different particle statistics? Is this temperature higher or lower than the actual boiling temperature of the helium?

Solution

Part (1): Metals

The nearest-neighbour spacing in a crystal is of order the lattice constant: about 3 to 5×10^{-10} m (0.3 to 0.5 nm) for Na, Fe, and Cu (bond lengths in that range).

Conduction electrons: each atom contributes of order one conduction electron, so the electron number density n_e is comparable to the atom number density $n_{\text{ion}} \sim 10^{28}$ to 10^{29} m^{-3}. The typical spacing is $n^{-1/3} \sim 2$ to 3×10^{-10} m, again angstrom scale.

The thermal de Broglie wavelength at $T = 300$ K for the electron ($m_e = 9.11 \times 10^{-31}$ kg) is

$$\lambda = \frac{h}{\sqrt{2\pi m_e kT}} \approx \frac{6.626 \times 10^{-34}}{\sqrt{2\pi \times 9.11 \times 10^{-31} \times 1.381 \times 10^{-23} \times 300}} \approx 4.3 \times 10^{-9} \text{ m} \tag{8}$$

So $\lambda \approx 4.3$ nm, which is roughly 15–20 times **larger** than the inter-electron spacing of 2–5 Å. The classicality condition is $n\lambda^3 \ll 1$; here $n\lambda^3 \approx 5 \times 10^{28} \times \left(4.3 \times 10^{-9}\right)^3 \approx 4000 \gg 1$. The electron gas is far from classical. In physical terms, the electrons form a **degenerate Fermi gas**: the Fermi temperature $T_F = E_F/k \approx 80,000$ K for copper is far above room temperature, so virtually all states up to E_F are occupied and the Pauli exclusion principle, not classical statistics, governs the electrons. The electron gas in ordinary metals cannot be treated as a classical ideal gas at room temperature.

Part (2): Ultracold Rb-87

Number density $n = N/V \sim 10^4/10^{-15} = 10^{19}$ m^{-3}, so mean spacing $d \sim n^{-1/3} \sim 4.6 \times 10^{-7}$ m. Take $m \approx 87$ u $\approx 1.44 \times 10^{-25}$ kg. Quantum effects grow when $n\lambda^3$ is no longer $\ll 1$, i.e. when $\lambda \sim d$ or

$$\frac{h}{\sqrt{2\pi mkT}} \sim n^{-1/3} \quad \Longrightarrow \quad T \sim \frac{h^2 n^{2/3}}{2\pi mk} \tag{9}$$

Numerically $T \sim 10^{-7}$ K, about 0.1 μK. Millikelvin trap temperatures are still three orders of magnitude above this, so the gas stays classical in a typical mK experiment unless the density is raised substantially.

Part (3): He-3 vs He-4

At the same atmospheric pressure and temperature both isotopes have the same number density $n = P/(kT)$, since it is a pressure-controlled setting. Quantum statistics become relevant when $n\lambda^3 \sim 1$. At fixed P, this condition $(P/(kT))\left(h/\sqrt{2\pi mkT}\right)^3 = 1$ determines a crossover temperature:

$$T_{\text{quant}}^{5/2} = \frac{Ph^3}{k^{5/2}(2\pi m)^{3/2}} \tag{10}$$

At 1 atm: $T_{\text{quant}} \approx 1.9$ K for He-4 and $T_{\text{quant}} \approx 2.2$ K for He-3. (He-3 is lighter, so its thermal wavelength is larger at the same T, and quantum effects kick in at a slightly higher temperature.)

The actual boiling points at 1 atm are 4.2 K for He-4 and 3.2 K for He-3, both **above** the respective quantum degeneracy temperatures. So the quantum degeneracy temperature is **lower** than the boiling temperature for both isotopes. In practice, helium condenses into a liquid well before the gas phase ever reaches $n\lambda^3 \sim 1$. The quantum-statistical difference between bosons and fermions cannot be observed in the gas phase at 1 atm; it shows up only in the liquid phase (or in a gas held at much lower pressure, where condensation is suppressed).

Problem 3

[**15 pts**] In class, we have qualitatively analyzed the temperature dependence of the chemical potential of a non-interacting bosonic gas in three spatial dimensions. In this problem, we will calculate the chemical potential as a function of temperature quantitatively using a computer, in the regime where the temperature is higher than the BEC transition temperature T_c. Moreover, we will calculate the heat capacity of this bosonic gas as a function of temperature. As in class, the physical setup we consider is a non-interacting bosonic gas in a box with size $V = L \times L \times L$ and periodic boundary conditions. The energy of each boson is given by $\varepsilon = p^2/(2m)$, where p is the momentum of the boson and m is its mass. In the regime where $T > T_c$, the chemical potential μ is determined by

$$N = \int_0^\infty \mathrm{d}\varepsilon g(\varepsilon) \frac{1}{e^{(\varepsilon-\mu)/(kT)} - 1} \tag{11}$$

where N is the particle number and $g(\varepsilon)$ is the density of states.

(1) (3 points) Show that at temperature $T > T_c$, the chemical potential can be determined from

$$\int_0^\infty \mathrm{d}x \frac{\sqrt{x}}{e^{(x-c)/t} - 1} \approx 2.315 \tag{12}$$

where $x = \varepsilon/(kT_c)$, $c = \mu/(kT_c)$ and $t = T/T_c$. That is, Equation 11 can be written as Equation 12.

(2) (4 points) Now finding μ is equivalent to finding c, provided that T_c is known. For a given value of t, one can find c numerically by demanding that Equation 12 should hold. Use a computer to calculate c for a sequence of values of $t = 1, 1.1, 1.2, 1.3, ..., 3$. Plot the result of c as a function of t.

(3) (3 points) Next, we calculate the heat capacity in the regime where $T < T_c$. In this regime, the chemical potential can be taken to be $\mu = 0$, and the total energy of this bosonic gas is

$$U = \int_0^\infty \mathrm{d}\varepsilon g(\varepsilon) \varepsilon \frac{1}{e^{\varepsilon/(kT)} - 1} \tag{13}$$

It turns out that the heat capacity under a constant volume is proportional to T^α in this regime. What is the value of α?

(4) (5 points) Finally, calculate the heat capacity under a constant volume in the regime where $T > T_c$ numerically, using the chemical potential obtained in part (2). To do so, one needs to first numerically calculate the total energy and then numerically differentiate it with respect to T. After obtaining the result, plot the heat capacity (in units of Nk) as a function of T/T_c. What is the heat capacity at high temperatures? Is this result expected?

Solution

Part (1): Dimensionless form of Equation 11

For a non-relativistic gas in three dimensions, $g(\varepsilon) \propto \sqrt{\varepsilon}$. Write $g(\varepsilon) = K\sqrt{\varepsilon}$ with K fixed by V and m. At $T = T_c$ the condensate is empty and $\mu = 0$, so

$$N = K \int_0^\infty \mathrm{d}\varepsilon \frac{\sqrt{\varepsilon}}{e^{\varepsilon/(kT_c)} - 1} = K(kT_c)^{3/2} \int_0^\infty \mathrm{d}x \frac{\sqrt{x}}{e^x - 1} \tag{14}$$

Define $I_0 = \int_0^\infty \mathrm{d}x \sqrt{x}/(e^x - 1) = \Gamma(3/2)\zeta(3/2) \approx 2.315$. For $T > T_c$, set $x = \varepsilon/(kT_c)$, $t = T/T_c$, $c = \mu/(kT_c)$. Then $\varepsilon = kT_c x$, $\mathrm{d}\varepsilon = kT_c\,\mathrm{d}x$, and

$$\beta(\varepsilon - \mu) = \frac{\varepsilon - \mu}{kT} = \frac{x - c}{t} \tag{15}$$

$$N = K(kT_c)^{3/2} \int_0^\infty \mathrm{d}x \frac{\sqrt{x}}{e^{(x-c)/t} - 1} \tag{16}$$

The same prefactor $K(kT_c)^{3/2}$ appears on both sides (T_c with $t = 1$, $c = 0$, and $T > T_c$ with general t, c), so it cancels:

$$\int_0^\infty \mathrm{d}x \frac{\sqrt{x}}{e^{(x-c)/t} - 1} = \int_0^\infty \mathrm{d}x \frac{\sqrt{x}}{e^{x} - 1} = I_0 \approx 2.315 \tag{17}$$

Part (2): Numerical $c(t)$ and plot

For each $t \in \{1, 1.1, ..., 3\}$, c is the root of $F(c) = \int_0^\infty \sqrt{x}/\left(e^{(x-c)/t} - 1\right) \mathrm{d}x - I_0$, with $c < 0$ for $t > 1$ and $c = 0$ at $t = 1$. The root was found numerically at each t; the result is plotted below.

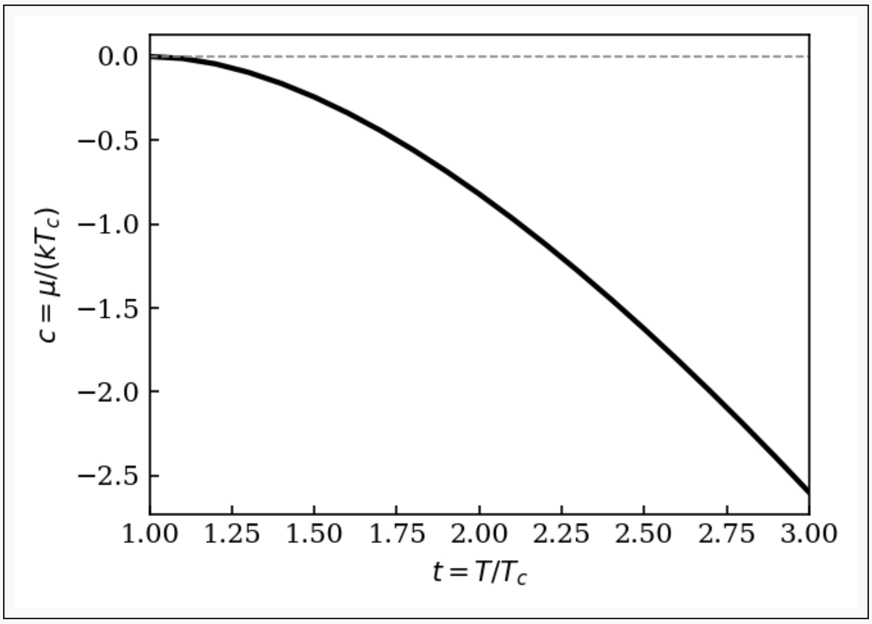

Figure 1: $c = \mu/(kT_c)$ vs $t = T/T_c$ for $t = 1, 1.1, ..., 3$. At $t = 1$, $\mu = 0$. For $t > 1$, $\mu < 0$ and becomes more negative as t increases.

Part (3): Heat capacity below T_c

With $\mu = 0$, Equation 13 reads

$$U = K \int_0^\infty \mathrm{d}\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta\varepsilon} - 1} \tag{18}$$

Set $y = \beta\varepsilon$:

$$U = K(kT)^{5/2} \underbrace{\int_0^\infty \mathrm{d}y \frac{y^{3/2}}{e^{y} - 1}}_{\text{constant}} \implies U \propto T^{5/2} \tag{19}$$

At constant volume, $C_V = \frac{\partial U}{\partial T} \propto T^{3/2}$, so $\alpha = 3/2$.

Part (4): Heat capacity above T_c

With the same K, $N = K(kT_c)^{3/2} I(t, c)$ where $I(t, c)$ is the integral in Equation 12 and $J(t, c) = \int_0^\infty x^{3/2}/\left(e^{(x-c)/t} - 1\right) \mathrm{d}x$,

$$U = K(kT_c)^{5/2} J(t, c) = NkT_c \frac{J(t, c)}{I_0} \tag{20}$$

For each t, $c(t)$ is fixed by $I(t, c) = I_0$. Differentiating $U = NkT_c(J/I_0)$ with respect to T and using $\mathrm{d}t/\,\mathrm{d}T = 1/T_c$:

$$C_V = \frac{\partial U}{\partial T} = NkT_c \cdot \frac{1}{I_0}\frac{\mathrm{d}J}{\mathrm{d}t} \cdot \frac{1}{T_c} = Nk\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{J}{I_0}\right) \tag{21}$$

The derivative was evaluated numerically using a central difference at each t.

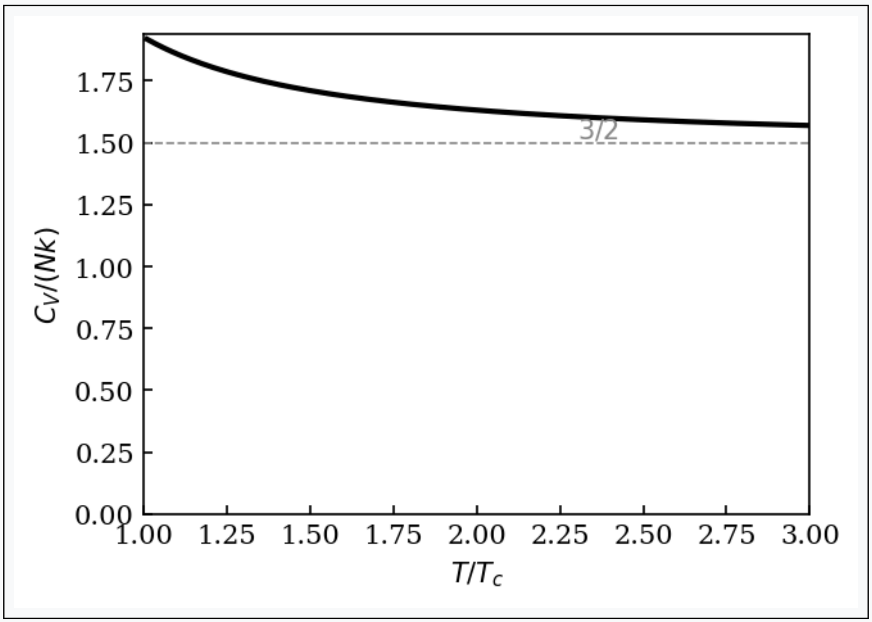

Figure 2: $C_V/(Nk)$ vs T/T_c for $T > T_c$. The curve rises from the jump at T_c and approaches $3/2$ at large T/T_c, as expected for a non-relativistic monatomic gas in the classical limit (equipartition: $\frac{3}{2}kT$ per particle).