

Physics 170:
Statistical Mechanics and Thermodynamics
Lecture 8A

Administrative Notes

Office hours

- Next week (Thanksgiving break):
available Mon-Tues by appointment
- Following week:
available Wed-Fri by appointment

Problem Set 7 due Tuesday, 11/28.

Don't wait till after break to start.

Analyzing Gases: Approaches

Canonical

$$Z \approx \frac{z_1^{3N}}{N!} \rightarrow F(N, \tau, V)$$



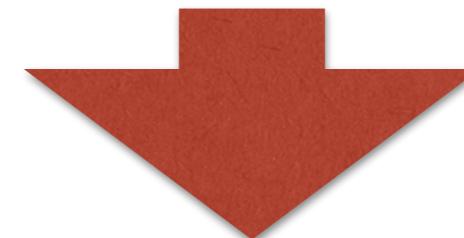
pressure $p(N, \tau, V)$
entropy $\sigma(N, \tau, V)$
heat capacity C_V, C_p
compressibility $\kappa_\tau, \kappa_\sigma$

Heat engines,
speed of sound

Grand Canonical

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{\tau, V} \rightarrow \mu(N) \leftarrow N(\mu) \leftarrow \beta$$

today



Identical particles at
“low” temperature
e.g., electrons in solids

After break

Friday/HW

Identical Particles

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm \psi(\mathbf{r}_2, \mathbf{r}_1)$$

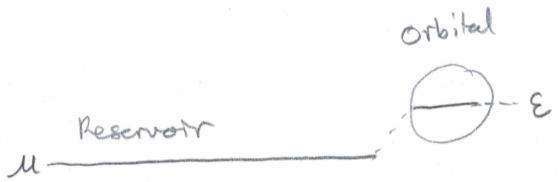
Fermions

- ψ is *antisymmetric* under particle exchange
⇒ Pauli exclusion
- Half-integer spin

Bosons

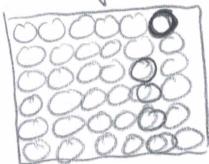
- ψ is *symmetric* under particle exchange
⇒ “like” to be together
- Integer spin

Examples?

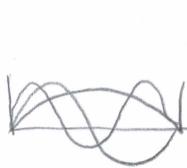


The higher $\mu - E$, the more favorable to transfer particles from reservoir to the orbital of energy E .

Generic system: many orbitals (spatial wavefunctions)



- * electron orbitals in a solid
- * gas: particle-in-a-box eigenstates
... or particles in a harmonic potential



... but start by focusing attention on a single one,

Can think of the others as forming the reservoir.

EXERCISE 8A: GASES OF IDENTICAL PARTICLES*Objectives:*

- Derive the **Bose-Einstein** and **Fermi-Dirac** distributions
- Recognize familiar limiting cases (ideal gas, Planck distribution)
- Analyze an ideal gas with internal degrees of freedom

References: Kittel & Kroemer, Ch. 6 (pp. 151-171)

Past results:

- Grand canonical partition function (Gibbs sum): $\beta = \sum_{\text{asn}} e^{\beta(N\mu - \varepsilon_{s,N})}$
- $\langle N \rangle = \beta^{-1} \partial \ln \beta / \partial \mu$

In our treatment of ideal gases so far, we assumed the classical limit $n\lambda_r^3 \ll 1$, where n is the number density and λ_r is the thermal de Broglie wavelength. Within the framework of the **grand canonical ensemble**, we can analyze the more general case without this constraint. However, it will now matter whether the particles are **fermions** or **bosons**.

1. *Quantum statistics.* Consider a single orbital of energy ε that is coupled to a reservoir of temperature τ and chemical potential μ . (We can consider additional orbitals later. In a non-interacting system, the energy of each orbital will be independent of the occupancy of the others.)
 - a. Suppose that the reservoir contains a single species of **fermions**. Write down the grand canonical partition function for the orbital and calculate the mean particle number $\langle N \rangle_\varepsilon$ occupying the orbital. Also calculate limiting values of $\langle N \rangle_\varepsilon$ for:
 - i. $\varepsilon < \mu$, $|\varepsilon - \mu| \gg \tau$
 - ii. $\varepsilon > \mu$, $|\varepsilon - \mu| \gg \tau$
 - iii. $|\varepsilon - \mu| \ll \tau$

Fermions: $N=0$ or 1

$$\beta = 1 + e^{\beta(\mu - \varepsilon)} = 1 + e^{\beta(\mu - \varepsilon)}$$

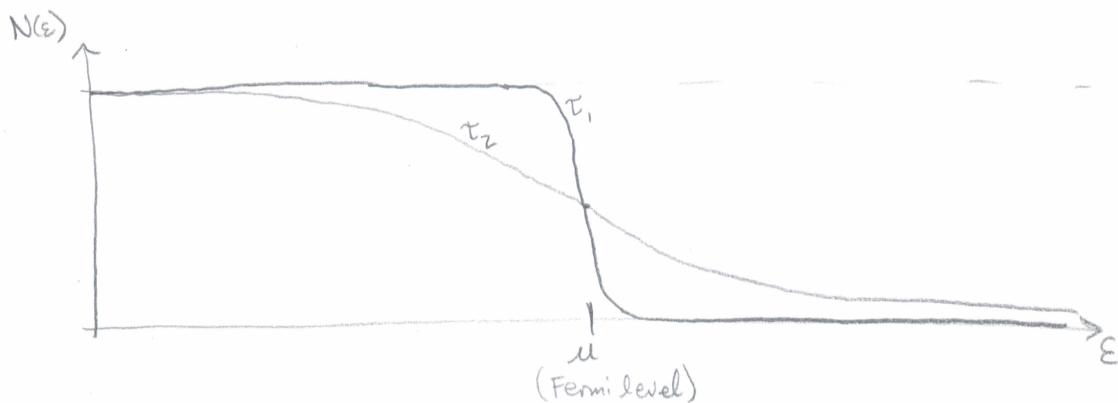
$$\text{i. } \langle N_\varepsilon \rangle = \frac{1}{\beta} \frac{\partial \ln \beta}{\partial \mu} = \frac{1}{\beta} \cdot \frac{\beta e^{\beta(\mu - \varepsilon)}}{1 + e^{\beta(\mu - \varepsilon)}} = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$$

$$\text{i) } \begin{array}{c} \mu \\ -\varepsilon \end{array} \quad \mu - \varepsilon \gg \tau \Rightarrow \langle N_\varepsilon \rangle \approx 1$$

$$\text{ii) } \begin{array}{c} -\varepsilon \\ -\mu \end{array} \quad \varepsilon - \mu \gg \tau \Rightarrow \langle N_\varepsilon \rangle \approx e^{\beta(\mu - \varepsilon)} \rightarrow 0$$

$$\text{iii) } |\varepsilon - \mu| \ll \tau \Rightarrow \langle N_\varepsilon \rangle \approx \frac{1}{1+1} = \frac{1}{2}$$

- b. The occupancy from part a. is the **Fermi-Dirac** distribution function. Sketch it as a function of the energy ε for two different temperatures $\tau_1 < \tau_2$ at the same chemical potential μ . In this context, the chemical potential is called the **Fermi level**. Label the Fermi level on your plot.



Finite temperature ("smears out") the step from occupied to unoccupied, in order to maximize entropy.

- c. Now consider **bosons** instead. Write down the grand canonical partition function and calculate the mean number $\langle N \rangle_\varepsilon$ of bosons occupying the orbital.

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta(N\mu - \varepsilon)}$$

Energy $\varepsilon_N = N \cdot \varepsilon$ for having N bosons in orbital

$$= \frac{1}{1 - e^{\beta(\mu - \varepsilon)}}$$

$$\Rightarrow \langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = -\frac{1}{\beta} \frac{\partial}{\partial \mu} (1 - e^{\beta(\mu - \varepsilon)}) = -\frac{1}{\beta} - \frac{-\beta e^{\beta(\mu - \varepsilon)}}{1 - e^{\beta(\mu - \varepsilon)}}$$

$$\langle N \rangle = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1}$$

- d. What constraint must be placed on the chemical potential for the number of bosons occupying the orbital to make physical sense?

$$\langle N \rangle > 0 \Rightarrow e^{\beta(\varepsilon - \mu)} > 1 \Rightarrow \varepsilon - \mu > 0 \Rightarrow \boxed{\mu < \varepsilon}$$

$\mu - - - - -$

- e. The occupancy from part c. is the **Bose-Einstein** distribution function. Where have you previously seen this function in this course (with $\mu = 0$), and what were the physical interpretations of ε and N ?

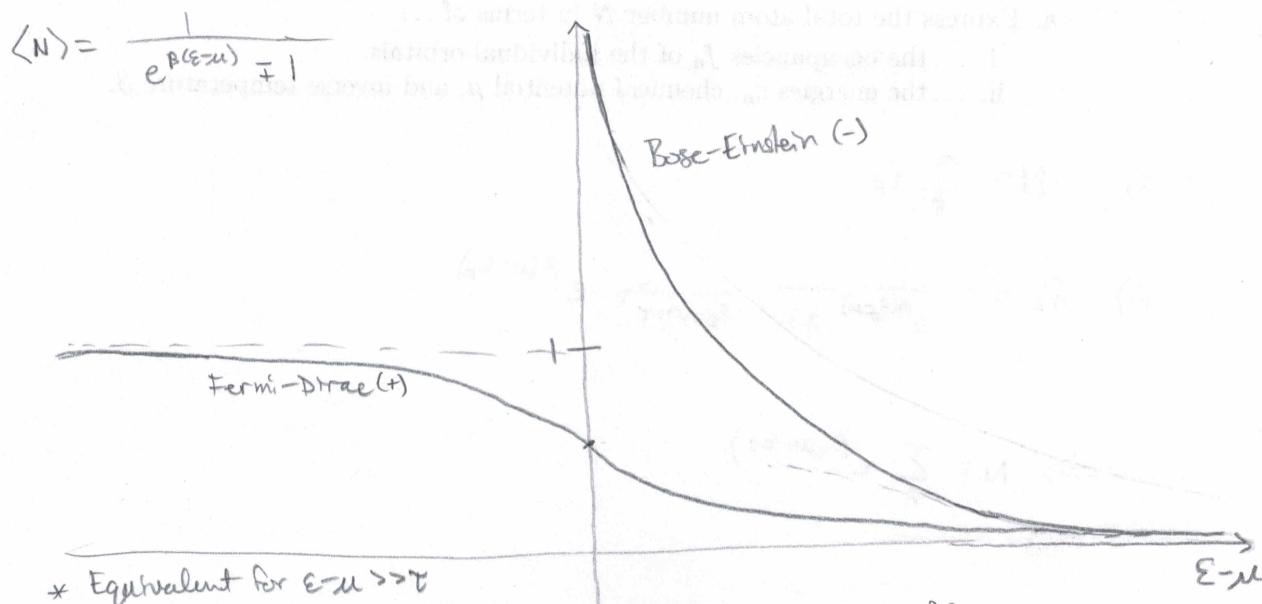
* Planck distribution for photons or phonons in a given optical/vibrational mode.

* Massless particles: $\mu = 0$

ε = photon energy or vibrational quantum

N = # of excitations (photons, phonons)

- f. Sketch the Bose-Einstein distribution function vs. $\varepsilon - \mu$ at fixed temperature τ . Add the Fermi-Dirac distribution function to the same plot. In what limit are the two distributions equivalent? In what regime do they look different? Explain.



* Equivalent for $\varepsilon - \mu \gg \tau$

* Different for $\varepsilon - \mu \lesssim \tau$, b/c # of bosons diverges whereas # of fermions is at most 1.

- g. Consider now a set of many orbitals (such as the particle-in-a-box eigenstates). Let $f(\varepsilon)$ represent the average number of particles in an orbital of energy ε , and let ε_0 represent the energy of the ground state.

- Give a condition on the chemical potential μ for this system to be in the classical regime at temperature τ .
- In the classical regime, what statement can be made about the occupancies $f(\varepsilon)$?



$$\mu - \underline{\quad} = \underline{\quad} \text{ or } \mu - \varepsilon = \varepsilon$$

- $\varepsilon - \mu \gg \tau$ for all ε , so need $\varepsilon_0 - \mu \gg \tau$
- $f(\varepsilon) \ll 1 \quad \forall \varepsilon$ in classical regime, so the quantum statistics don't matter.

$$\text{Recall: } \varepsilon_{\vec{n}} = (n_x^2 + n_y^2 + n_z^2) \cdot \frac{\pi^2 \hbar^2}{2mL^2}$$

2. Revisiting the classical ideal gas. Apply your results from above to the case where the orbitals are the eigenstates $\varepsilon_{\vec{n}}$ of a particle in a three-dimensional box of volume $V = L^3$. Consider a classical gas of N such atoms in the box of volume V .

- Express the total atom number N in terms of ...
 - the occupancies $f_{\vec{n}}$ of the individual orbitals.
 - the energies $\varepsilon_{\vec{n}}$, chemical potential μ , and inverse temperature β .

$$\text{i)} \quad N = \sum_{\vec{n}} f_{\vec{n}}$$

$$\text{ii)} \quad f_{\vec{n}} = \frac{1}{e^{\beta(\varepsilon_{\vec{n}} - \mu)} + 1} \xrightarrow{\varepsilon_{\vec{n}} - \mu \gg \tau} e^{\beta(\mu - \varepsilon_{\vec{n}})}$$

$$\Rightarrow N = \sum_{\vec{n}} e^{\beta(\mu - \varepsilon_{\vec{n}})}$$

- b. Based on a., determine the chemical potential as a function of density N/V and the thermal de Broglie wavelength λ_τ .

Hint: you have previously evaluated the following sum:

$$z_1^3 \equiv \sum_{\mathbf{n}} e^{-\beta \epsilon_{\mathbf{n}}} = \frac{V}{\lambda_\tau^3} \quad (1)$$

$$N = e^{\beta \mu} \sum_{\mathbf{n}} e^{-\beta \epsilon_{\mathbf{n}}} = e^{\beta \mu} \cdot V / \lambda_\tau^3$$

$$\Rightarrow \frac{N \lambda_\tau^3}{V} = e^{\beta \mu} \Rightarrow \boxed{\mu = \tau \ln \left(\frac{N \lambda_\tau^3}{V} \right)}$$

- c. Calculate the Helmholtz free energy $F(N, \tau)$ from the chemical potential. Does it match the result we previously derived for an ideal gas? In what ways is the present derivation different?

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V, \tau}$$

$$dE = \tau d\tau - pdV + \mu dN$$

$$dF = -\tau d\tau - pdV + \mu dN$$

$$\Rightarrow F(N) - F(0) = \int_0^N dN' \mu(N') = \tau \int_0^N dN' [\ln N + \ln(\lambda_\tau^3/V)]$$

$$= \tau \left[N \ln N - N + N \ln(\lambda_\tau^3/V) \right]_0^N$$

$$F(N, \tau, V) = N \tau \left[\ln \left(\frac{N \lambda_\tau^3}{V} \right) - 1 \right]$$

$$\begin{aligned} x \ln x &= \frac{\ln x}{1/x} \\ x \rightarrow 0: \frac{\frac{d}{dx}(\ln x)}{\frac{d}{dx}(1/x)} &= \frac{1}{-1/x^2} \\ &= -x \rightarrow 0 \end{aligned}$$

* Matches previous result

* We did not need hand-waving argument about $N!$ in $Z = z_1^{3N}/N!$
... instead started from \mathcal{Z} which naturally treats particles as identical,
keeping track only of total # in each orbital

(From here we could derive equation of state, etc. \rightarrow same results on firmer footing.)

Rather than just rederiving familiar results, let's add one new ingredient...

3. *Ideal gas with internal degrees of freedom.* Consider a classical gas of identical non-interacting molecules, each of which has internal (vibrational + rotational) energy ε_{int} . The total energy of a single molecule is then $\varepsilon_n + \varepsilon_{\text{int}}$, where ε_n is the energy of the center-of-mass motion.

- a. Since the gas is classical, it should not matter whether the molecules are bosons or fermions. Explain in words why $\beta_{\text{Bose}} \approx \beta_{\text{Fermi}}$ in the classical regime.

In calculating $\sum_{n \in \text{all states & numbers}}$, we only need to include terms with 0 or 1 molecule in a given orbital, since the gas is assumed to be dilute. Thus, we can treat the molecules as though they were fermions and the results will apply equally to a dilute gas of bosons.

- b. Write down the grand canonical partition function β for a single orbital n in terms of the chemical potential μ and energies $\varepsilon_n, \varepsilon_{\text{int}}$.

$$\beta = 1 + \sum_{\text{int}} e^{\beta(\mu - \varepsilon_n - \varepsilon_{\text{int}})}$$

↑
 empty
 orbital

orbital occupied
 by one molecule

- c. Re-express β in terms of the partition function

$$Z_{\text{int}} = \sum_{\text{int}} e^{-\beta \varepsilon_{\text{int}}} \quad (2)$$

associated with the internal degrees of freedom of a single molecule.

$$\beta = 1 + e^{\beta(\mu - \varepsilon_n)} Z_{\text{int}}$$

- d. Find the occupancy f_n of state n at temperature β^{-1} in terms of Z_{int} , μ , and ε_n .

$$f_n = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \left[1 + e^{\beta(\mu - \varepsilon_n)} Z_{\text{int}} \right]$$

$$= \frac{1}{\beta} \cdot \frac{\beta e^{\beta(\mu - \varepsilon_n)} Z_{\text{int}}}{1 + e^{\beta(\mu - \varepsilon_n)} Z_{\text{int}}} = \frac{1}{e^{\beta(\varepsilon_n - \mu)} / Z_{\text{int}} + 1}$$

- e. Recalling that we are assuming the gas to be in the classical regime, simplify your result from d.

$$\varepsilon_n - \mu \gg \tau \Rightarrow f_n \approx \frac{Z_{\text{int}} e^{\beta(\mu - \varepsilon_n)}}{Z_{\text{int}}}$$

- f. Determine the chemical potential as a function of density N/V and Z_{int} . Express it in terms of the result μ_0 for a monatomic ideal gas.

$$N = \sum_n Z_{\text{int}} e^{\beta(\mu - \varepsilon_n)} = Z_{\text{int}} e^{\beta \mu} \sum_n e^{-\beta \varepsilon_n} = Z_{\text{int}} e^{\beta \mu} \cdot V / \lambda_r^3$$

$$\frac{N \lambda_r^3}{Z_{\text{int}} V} = e^{\beta \mu} \Rightarrow \mu = \tau \ln \left(\frac{N \lambda_r^3}{V} \right) - \tau \ln Z_{\text{int}}$$

$$= \mu_0 - \tau \ln Z_{\text{int}}$$

- g. Find the Helmholtz free energy in terms of the value F_0 for a monatomic ideal gas and an additional contribution F_{int} . Give the value and physical interpretation of F_{int} .

$$F = \int_0^N dN' [\mu_0(N') - \tau \ln Z_{\text{int}}]$$

$$F = F_0 - N \tau \ln Z_{\text{int}}$$

F_{int} is just N times the Helmholtz free energy associated with the internal degrees of freedom of a single molecule.

- h. Which of the following properties of the ideal gas are modified by the internal degrees of freedom, and how? Explain.
- i. The equation of state $p(N, \tau, V)$
 - ii. The entropy σ
 - iii. The heat capacities $C_V = \tau(\partial\sigma/\partial\tau)_V$ and $C_p = \tau(\partial\sigma/\partial\tau)_p$ at constant volume and constant pressure
 - iv. The isothermal and adiabatic compressibilities $\kappa_\tau = -V^{-1}(\partial V/\partial p)_\tau$ and $\kappa_\sigma = -V^{-1}(\partial V/\partial p)_\sigma$