Physics 114 **Statistical Mechanics** **Spring 2018**

Seminar 10

Overview:

We have done lots of work on the ideal gas. It is "semiclassical" in the sense that we count states in a box using quantum ideas, but then we assume it is dilute enough that every quantum volume λ_{th}^3 contains at most 1 particle. This week, we take on *quantum gasses*. They are noninteracting, so we want to call them "ideal", but are dense enough so *Fermi-Dirac* or *Bose-Einstein* statistics are needed to count how many particles occupy a quantum state indexed by the wave number $\vec{k}$. This is a challenging topic, with many interesting applications, and we break it up into two weeks. This week, we begin with the general idea of how to count the expected number of fermions or bosons, $\bar{n}_k$ in any state $\vec{k}$. To find thermo averages, say energy $\bar{E}$, we must integrate the product $E(\vec{k}) \times g(\vec{k}) \times \bar{n}_k$, where $g(\vec{k})$ is the density of quantum states which we we first met, in the case of an ideal gas, a few weeks ago.

Other quantities we've met, which become exceptionally useful, are grand canonical ensemble and its grand potential. We also find that *activity* which is also known as *fugacity*, $z = f = e^{\beta\mu}$, is an elegant way to parametrize the state of a bose or fermi ideal gas. New pieces of mathematics this week are the *polylogarithm* and *zeta function*, discussed in Appendices of B&B. While this week we learn the nuts and bolts of dealing with bosons and fermions, we bias our work toward the boson gas. (We will save the topic of Bose-Einstein condensation for next week though.) Bosons are particles with integer spins, and one can have an infinite number of these in any quantum state. Photons are massless bosons, and a very important application this week is photons in thermal equilibrium, also known as *black body radiation.* Another important application (which we'll take up next week) is quantized vibrations, or *phonons* in solids.

Required Reading:

G&T Sections

- 6.3-6.5.1 *this overlaps with reading we did for Seminar 8*
- 6.5.2 *this is also some review, but I'm asking you to think for the first time about relativistic particles*
- Section 6.7

B&B Sections

- Chs. 23 and 29
- Problem 29.6 ... we don't have time to do it this week, but it is an amazing problem that teaches us yet another way to think about where Fermi-Dirac and Bose-Einstein statistics come from

- Section 30.1
- Appendices C4 and C5

Schroeder Sections

- 7.2 and 7.4

Recommended Reading:

- A paper by H. Leff that compares a classical and Boson ideal gas, `PhotonGasAJP.pdf` is in our Resources folder.

Concept checklist from Readings:

- **About counting Bosons and Fermions ...** There is a paradigm shift in how we think of *counting states* this week. Instead of saying we have N particles, and talking about the state *each particle* is in, we make *single-particle states* the primary focus. We ask about how many (identical) particles exist in each of these states.
- Due to their half-integer or integer spins (in a way which one text admits most physicists accept but don't understand) fermionic wave functions are odd under exchange of particles, whereas bosonic wave functions are even. Thus, you cannot have two fermions in a state with identical quantum numbers. Not so for bosons; an arbitrary number can occupy the same quantum state.
- Though our ultimate goal is to understand systems with large numbers of bosons or fermions, the texts take us through some "toy" problems where we have only a few particles. Problems like Schroeder 7.8, 7.17 or G&T 6.15 are worthwhile, because they go to the heart of the kind of state counting needed for *fermions* or *bosons*.
- How many quantum states do we have within small range, dk, around the quantum state k? Here, k is a label, though in many applications it is the magnitude of the *wave number*, $k = p/\lambda$. As we've seen before (twice!) the number density of states near k is called the *density of states* (DOS), written as $g(k)$. Sometimes we are interested in using $g(k)$ to find $g(\epsilon)d\epsilon$, the number of states within $d\epsilon$ of energy ϵ. This can be found by setting $g(k)dk = g(\epsilon)d\epsilon$ and knowing $\epsilon(k)$ for our system of interest.
- In past seminars, we've used $\epsilon = \hbar^2 k^2/2m$ for semiclassical gas particles. Particularly relevant this week is the relation between k and ϵ for *photons*: $\epsilon = \hbar ck$.

- Don't we already know how to deal with identical particles? Isn't $Z(N) = Z_1^N/N!$? Not necessarily ... see Schroeder Section 7.2 for a good argument. We consider the semiclasical result $Z_1 = V/\lambda_{th}^3$. (His notation is $v_Q \equiv \lambda_{th}^3$, the *quantum volume*). If it is *not* the case that $Nv_Q << V$, then the quantum particles are too close to each other for a semiclassical treatment. It is likely that two particles could try to share the same single-particle state. This is forbidden for fermions. While it is OK for bosons, it ruins the counting argument that leads to $Z(N) = Z_1^N/N!$, because that argument assumes there is *at most one* particle in each state.

- Let's tune our thinking to the Grand Canonical ensemble. For a semiclassical gas, $\mu = -kTln(Z_1/N)$. Such a gas has a negative μ with a very large magnitude. If this is *not* true of μ, we need the kind of quantum counting arguments that we learn this week.

- How many particles do we expect to exist in *any single quantum state labelled by k*? This is the *occupation number* $\bar{n}_k$. Finding this quantity lends itself to *Grand Canonical* statistics. Now, we must take into account the distinctive statistics of bosons and fermions. Fermions can only have $n_k = 0$ or 1 particles in state k. Bosons can have an infinite number.

- All three of our texts tackle the calculation of $\bar{n}_k$. Below I use language which most closely follows G&T 6.4, but Schroder 7.2 and B&B Ch. 29 are also fine references!

- We write the grand partition function as $Z_G = \Sigma_k Z_{G,k}$ where

$$Z_{G,k} = \Sigma_{n_k} e^{-\beta n_k(\epsilon_k - \mu)}$$

  Chasing through the two cases (fermions, bosons) leads to:

$$Z_{G,k} = (1 \pm e^{-\beta n_k(\epsilon_k - \mu)})^{\pm 1} \;\; with \; + \; for \; fermions \; ; \;\; - \; for \; bosons$$

- To get the bosonic result, the sum in $Z_{G,k}$ from $n_k = 0$ to ∞ leads to a geometric series, and the convergence of the series requires that the *chemical potential* $\mu < 0$ for bosons, just as is true for a semiclassical ideal gas.

- The Landau potential for each energy state is $\Omega_k = -kTlnZ_{G,k}$ and the expected occupation number is $\bar{n}_k = -\frac{\partial \Omega_k}{\partial \mu}$. These lead to

$$\bar{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1} \;\; with \; + \; for \; fermions \; ; \;\; - \; for \; bosons$$

- As a pure function of the variable ϵ and parametrized by μ, these two expressions are known as the *Fermi-Dirac and Bose-Einstein distribution functions*:

$$f_{FD}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}+1} \;;\quad f_{BE}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}-1}$$

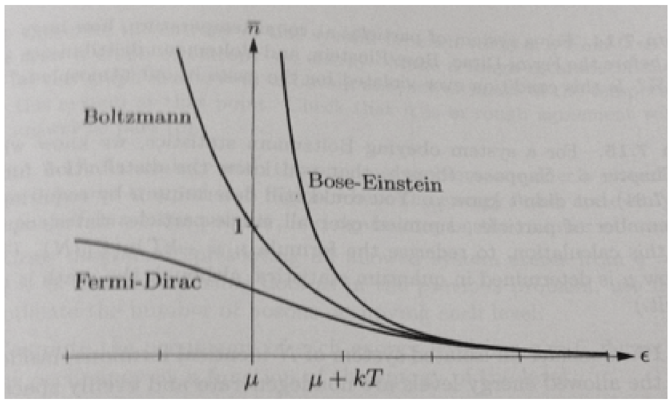

Figure 1: $f(\epsilon)$ vs. ϵ; classical behavior when $\beta(\epsilon-\mu) >> 1$

- When we have many single-particle states close together, we can find thermodynamic averages by treating sums over states k as integrals. We use $\bar{n}_k\ g(\epsilon_k)$ as the *weighting factor* for the quantity we want to average. For example, the mean energy would be

$$\bar{E} = \int_0^\infty \epsilon_k \bar{n}(\epsilon_k) g(\epsilon_k) d\epsilon_k$$

while the expected number of particles is

$$\bar{N} = \int_0^\infty \bar{n}(\epsilon_k) g(\epsilon_k) d\epsilon_k$$

- B&B Section 30.1 treat quantum counting in a formal, general way. For example, you know that from quantum mechanics that there are $2S+1$ spin states for a particle with spin S. Thus, B&B Section 30.1 reminds us that these are part of the quantum labeling of any state, and end up as a multiplicative factor in the Landau free energy.

- B&B also provide us with generic integrals we need to do, and the mathematical names for the functions that result. (In the interest of full disclosure: Mathematica can do these needed integrals, without your knowing their names :-)

- The kinds of definite integrals that we need to calculate averages of energy to a power: E^{n-1}, are a gamma function, $\Gamma(n)$ times a *polylogarithm* function, $Li_n(z)$ which is defined as

$$Li_n(z) = \Sigma_{k=1}^{\infty} \frac{z^k}{k^n}.$$

- The polylogarithm $Li_n(z)$ embraces both fermion and boson cases, through the sign of the argument z. B&B claim this in Eq. (30.14), and prove in Appendix C.5.
- The argument z is the *activity* or *fugacity* $z = e^{\beta\mu}$. (We met this quantity in Seminar 8, when we discovered e.g. that for the semiclassical gas, $\bar{N} = zZ_1$.) When $\mu = 0$, $z = 1$ and the polylogarithm becomes a *Riemann zeta function*, $\zeta(z)$. B&B Appendix C.4 has details on this very useful, special case.

- **Photons ...** have energy $\epsilon = pc = \hbar ck = \hbar\omega = hf$ where these symbols have their usual meaning. E.g. p is momentum and wavelength is $\lambda = c/\nu = h/p$. When we consider a photon confined to a large box, its wavelength, hence momentum, is quantized.

- Photons can be treated as a (non-classical) gas and we can do pure thermodynamics and kinetic theory of gasses to get some good information. For example, B&B Section 23.1 shows us that if energy density is u:

$$u = AT^4 \ ; \quad P = u/3 \ ; \quad Power/unit\ wall\ area = \frac{1}{4}uc = \sigma T^4$$

where $\frac{1}{4}Ac \equiv \sigma$ is a constant of proportionality known as the *Stefan-Boltzmann constant.*

- If we want to find the value of σ and more, we do stat . We use the 3D density of states $g(k) = 2 \times \frac{V\pi k^2 dk}{2\pi^3}$ where the extra 2 is for the two polarization states. This can be recast as $g(\epsilon_k)$ or $g(\omega)$ in order to find the average energy:

$$\bar{E} \equiv U = \int_0^\infty \hbar\omega \ \bar{n}_{BE}(\omega) g(\omega) d\omega$$

where $\bar{n}_{BE}(\omega)$ is the Bose Einstein occupation number distribution with $\mu = 0$:

$$\bar{n}(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

- Doing the integral above gives $U = AT^4$ as thermo predicts. The integral is set up to go over angular frequency ω, but we change variable to get an expression for A that is proportional to $\int_0^\infty \frac{x^3}{e^x - 1} dx = \zeta(4)\Gamma(4) = \pi^4/15$. Thus we have an exact value for $A = \frac{\pi^2 k_B^4}{15c^3\hbar^3}$. The Stefan-Boltzmann constant is thus $\sigma \approx 5.67 \times 10^{-8} W m^{-2} K^{-4}$.

- Though we will not have time to focus strongly on it in this seminar, please do the excellent reading of B&B sections 23.3, 23.3 and 23.8 (which overlaps with some of Schroder 7.4) to learn topics which astrophysicists and laser/atomic physicists need:
  - spectral energy density
  - absorptivity, emissivity and how they are related by Kirchoff's law
  - Einstein A and B coefficients.
- A *black body* is a system (a kiln, a star, ...) containing photons at thermal equilibrium. Please be able to work with the *black body distribution*, which is the quantity under the integral sign in the equation for energy:

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{(e^{\beta\hbar\omega} - 1)}$$

  Please know that this is the energy density near frequency ω. Know how to change variable to find $u(\lambda)$. In terms of either variable, this function has a characteristic shape ... zero at high and low frequencies and peaked in the middle at a place, ω_{max} or λ_{max}, which you can find by setting the derivative of u equal to zero. This peak occurs where $\hbar\omega_{max}/kT = 2.821....$ This has a name: *Wein's displacement law*.

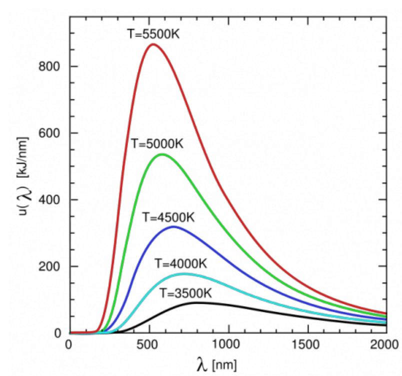

Figure 2: $u(\lambda)$ vs. λ; classical behavior when $\hbar c/\lambda << kT$

- At long λ (small ω) this spectrum can be described classically, with equipartition applying to modes of E&M radiation. In this regime, $u \propto \lambda^{-4}$, which is known as the *Rayleigh-Jeans* law. At short λ, the spectrum goes to zero because when $\hbar c/\lambda >> kT$ there is insufficient thermal energy to occupy such high energy modes. This limit, which was termed the "ultraviolet catastrophe" because Rayleigh-Jeans blows up there, benefits greatly from knowing the stat mech of photons. As with the classical paramagnet problem done last week, stat mech shows that quantum mechanics is real! Both high and low wavelength limits are beautifully fit by using the BE distribution function.

- Please be able to combine stat mech and thermodynamics, as in G&T Problem 6.25 or the assigned problems Schroeder 7.44, 7.45. These ask you to derive good stuff like entropy and free energy of photons in equilibrium. Below are a couple of tables (from the optional reading by Leff) that give a snapshot of how the photon and matter ideal gasses compare.

Table II. Comparison of equations for classical ideal and photon gases.

Classical ideal gas	Photon gas
N is specified and fixed	$N = rVT^3$
$U = \frac{3}{2}NkT$	$U = bVT^4 = 2.7NkT$
$P = NkT/V$	$P = \frac{1}{3}bT^4 = 0.9NkT/V$
$S = Nk[\ln(T^{3/2}V/N) + \ln(2\pi mk/h)^{3/2} + \frac{5}{2}]$	$S = \frac{4}{3}bVT^3 = 3.6Nk$

Table III. Numerical comparison of classical ideal and photon gas functions. Here the ideal gas is 1.00 mol of monatomic argon at $P = 1.01\times 10^5$ Pa, $V = 2.47\times 10^{-2}$ m^3, and $T = 300$ K.

Function	Classical ideal gas	Photon gas
N	6.02×10^{23} atoms	1.35×10^{13} photons
U	3.74×10^3 J	1.51×10^{-7} J
P	1.01×10^5 Pa	2.04×10^{-6} Pa
S	155 J/K	6.71×10^{-10} J/K

Presentation: We don't have a lot of time for presentation this week. But a cool and often neglected piece of math is summarized in Appendices C4 and C5 of B&B : the Riemann zeta function and polylogarithm. Please *prepare* a presentation on at most two sheets of paper (or a small number of slides) that teach us about these functions. Also, describe an application of each of these functions to what we are studying this week.

Warmup Problems: *Due before seminar, Monday or Tuesday*

1: Counting states for three cases: Schroeder Problem 7.10

2: Black body stuff:
Schroeder problem 7.37
Schroeder problem 7.38

Leftover problems from last week, Seminar 9:

- Wednesday Section A: Problems 5, 6, 7
- Wednesday Section B: Problems 5, 6, 7, 8

- Thursday Section: Problems 6, 7, 8
  also Daniel's presentation, also Jaron solving Seminar 8, problem 7.

Regular problems:

Note: Some of the problems I've assigned are two textbook problems. Some just one problem but, as in the case of Problem 6, Schroeder 7.49, it is long. Please introducers and solvers ... talk together and share the work. The introducer can do some of the solving!

1: Finding μ from N for bosons:
(Introducer, please compare for us the situation with bosons vs. classical particles. If you want, get us inspired by doing the short, easy Schroeder Problem 7.15?)
Schroeder problem 7.17

2: The Cosmic Microwave Background B&B Problem 23.3

3: Ortho and parahydrogen B&B Problem 29.5

4: Relativisitic particles:
G&T 6.18
G&T 6.20

5 : Energy, Entropy and Pressure of a photon gas:
Schroeder problem 7.44
Schroeder problem 7.46

6: Early universe with electrons and positrons:
Schroeder problem 7.49