Physics 114 Statistical Mechanics Spring 2021

Week 10 Conceptual Overview

Concept checklist from Readings:

- **About counting Bosons and Fermions ...** There is a paradigm shift in how we think of *counting states* this week that carries over from the week we first learned to use the Grand Canonical Ensemble. 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 ... 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 think back 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* $\bar{n}_k$. We know that finding this quantity lent itself to *Grand Canonical* statistics. This week, we add to this that we must 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 suggested 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 $Z_G = \Pi_k Z_{G,k}$ where

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

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

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

- 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*:

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

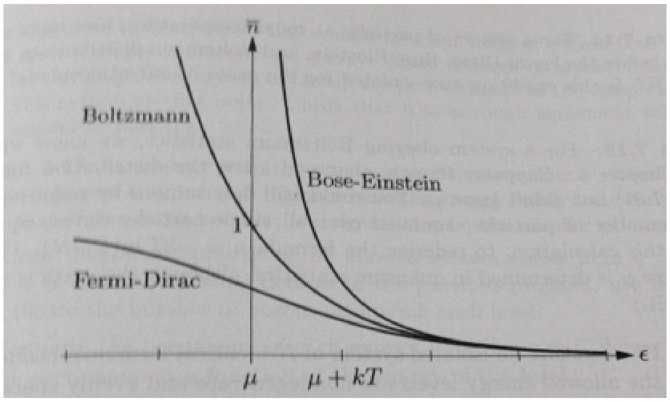


Figure 1: $f(\epsilon)$ vs. ϵ; classical behavior when $\beta(\epsilon - \mu) >> 1$

- 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 mech. 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, our assignment includes B&B sections 23.3, 23.3 and 23.8 (This material is also present in Schroder 7.4). These are 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.*

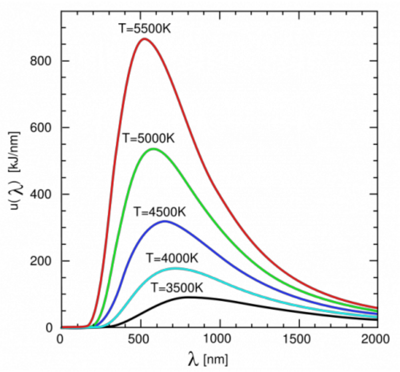
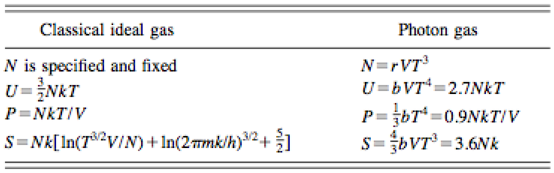


Figure 2: $u(\lambda)$ vs. λ; classical behavior when $\hbar c/\lambda << kT$

- 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.

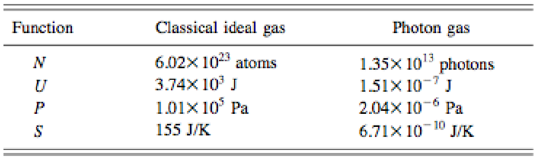
- Please be able to combine stat mech and thermodynamics to derive stuff like entropy and free energy of photons in equilibrium. An example that requires this is G&T Problem 6.25 (or if you read Schroeder, his problems 7.44, 7.45) Below are a couple of tables (from the optional reading by Leff) that 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 $P=1.01\times10^5$ Pa, $V=2.47\times10^{-2}$ 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

- **Quantized vibration in solids ...** Recall the Einstein model of solids. Now we have a new perspective on it. The q quanta of energy shared among the N oscillators are like q bosons. The expected energy per oscillator, e, is the ground state energy, $\hbar\omega/2$, plus the energy of $\bar{n}$ bosons ... each one carrying energy $\bar{\omega}$. That is:

$$Z_1 = e^{-\beta\hbar\omega/2}\frac{1}{1-e^{-\beta\hbar\omega}}$$

$$=> \quad e = (1/2+\bar{n})\hbar\omega \quad with \quad \bar{n} = \frac{1}{e^{\beta\hbar\omega}-1}$$

These new bosons are quanta which carry vibrational energy. Like photons, they have $\mu = 0$.

- We introduce a relevant, new temperature $T_E = \hbar\omega/k_B$. If we do the familiar calculation of C_v for the Einstein solid, we notice that for for $T >> T_E$ we are in the high T limit known as "Dulong-Petit" . This limit is just what we'd get from *equipartition*: $C_v = 3Nk_B$. (Notation alert: We have wave vectors k floating around now, so I have tried to write Boltzmann's constant as k_B ... but look out for typos.)

- The problem with the Einstein crystal's C_v is that it falls to zero much too fast as $T \to 0$. Not a theoretical problem, but an experimental one. Experiments give $C_v \propto T^3$ as $T \to 0$.

- The *Debye model* is an improvement. The same kind of summing over modes as we've done a couple times before, is now applied to lattice vibrations. Now our quantized vibrations are not independent oscillators as in the Einstein model, but the *normal modes* of a lattice of N atoms. Every quantized wave vector $\vec{k}$ is converted to a frequency based on the average speed of sound, $\bar{c}$, in the lattice:

  $$k\bar{c} = \omega$$

  This allows us to get the density of states:

  $$g(\omega)d\omega = \frac{3V\omega^2 d\omega}{2\pi^2 \bar{c}^3}$$

- U can be found in the usual way, by integrating $\hbar\omega$ weighted by $\bar{n}(\omega)g(\omega)$ over all ω. However, we need to think about the limits of integration. Unlike E&M radiation in a box, solid vibrations have a shortest wavelength λ_D equal to the typical spacing between atoms. This is shown in problem G&T 6.65, which is assigned this week. It's equivalent to arguing that there is a high frequency cutoff ω_D, so we don't count more modes than there are. There can only be $3N$ *normal modes* of vibration in a 3d crystal with N atoms.

- This high energy low wavelength cutoff leads us to define an equivalent temperature, the *Debye temperature* $T_D = \hbar\omega_D/k_B$. We thus get:

  $$U = N\ 9\frac{(k_B T)^4}{(k_B T_D)^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

- At low T, $C_v \propto T^3$ which is what experiments show. Schroeder reminds us that in a metal, there is another contribution at low temperatures proportional to T, which is something we discussed above, the contribution from the "free electron gas" (i.e. the conduction electrons). At high T, the law of Dulong and Petit, $C_v = 3Nk$ is obeyed, just as for an Einstein solid. Hooray!

- B&B Section 24.3 gives us a glimpse of a situation where we can no longer treat phonons like particles-in-boxes. Now, is *not* the case that the *dispersion relation* is $\omega \propto k$. Nor is the density of states $g(\omega) \propto \omega^2$ in 3d. This analysis probably familiar to you from a Phys 111 seminar, where you looked at the *normal modes* of a system of masses, connected by springs. In this section, we can read the variable q as being like the wave number, k. We see the relationship between ω and q in Eq. (24.33) and Fig. 24.5 for a 1d chain of masses. Because $sin(qa/2) \propto (aq/2)$ for small q, the small-q limit is just like an Einstein or Debye model. For large q, the situation is different. Also different is $g(\omega)$. The low-ω limit is like a particle in a box. But higher ω behavior in Fig. 24.7 shows that $g(\omega)$ depends on the detailed way atoms are bound together in the copper solid.