Notes for Lecture 9

Quantum statistical mechanics

Now, we discuss the formalism of the statistical mechanics from the quantum mechanical point of view.

In the quantum regime, the energy quantum has a much more significant effect than in the semi-classical treatment that we have been mostly employing so far would have us to believe. Also, the quantum entanglement has an important consequence: that is, the nature of particles, i.e., whether particles are fermions or bosons, starts to matter tremendously.

Good news is that much of what we established for various ensembles using the semi-classical statistical mechanics can be re-used with little modification for quantum mechanics as well. However, we must recognize that the microstates are more rigorously defined in quantum mechanics, and with that more rigorous definition we can now explore quantum degenerate regimes, which cannot be described in any semi-classical picture.

9.1 Einstein phonons, continued

The simple example of Einstein phonons (Section 8.5) already gives a good taste of important quantum effects.

First, as $T \to 0$ (Eq. 8.63), $C_V \to 0$. Note that this is what one expects from the third law of thermodynamics (point 1 of page 18 of LN 2). The equipartition theorem

(Eq. 6.49) predicts a T-independent heat capacity[1]

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{Q_d}{2}k_B \qquad \text{Du-Long Petit law} \tag{9.1}$$

contradicting the third law.

Second, the entropy $S = (E - F)/T$ can be calculated directly from Eqs. 8.58 and 8.59 (and using, of course, $F = -k_B T \log Z$),

$$S = \frac{1}{T}\big(\hbar\omega + \hbar\omega n_P(\omega) + k_B T \log n_P(\omega)\big) \tag{9.2}$$

$$\rightarrow \begin{cases} k_B \log\left(\frac{k_B T}{\hbar\omega}\right) & T \rightarrow \infty \quad (\text{i.e., } \frac{k_B T}{\hbar\omega} \rightarrow \infty) \\ k_B \beta\hbar\omega e^{-\beta\hbar\omega} \rightarrow 0 & T \rightarrow 0 \quad (\text{i.e., } \frac{k_B T}{\hbar\omega} \rightarrow 0) \end{cases} \tag{9.3}$$

So, at high temperature, the equipartition theorem is seen to be in action, in the following way. First of all, the energy is $k_B T$. And, the above expression for S makes it clear that $\frac{k_B T}{\hbar\omega}$ is the number of states available per oscillator under consideration. Why is this? The number of states for a microcanonical ensemble (i.e., a fixed value of E) can be calculated as the binomial coefficient as $\Omega(E) = \binom{N+M-1}{N-1}$, where N is the number of oscillators (identical but distinguishable since they are all fixed in space)[2], and $M = \frac{E}{\hbar\omega} = N\frac{k_B T}{\hbar\omega}$ is the total number of oscillation quanta. In the limit of $M \gg N$ (classical limit), one can see that this binomial coefficient goes to $\Omega(E) \approx \left(\frac{M}{N}\right)^N = \left(\frac{k_B T}{\hbar\omega}\right)^N$. So, indeed, $\frac{k_B T}{\hbar\omega}$ is $\Omega(E)$ per oscillator.

At low temperature, we see that S shows a **thermally activated behavior** in an Arrhenius law form, $\exp\left(-\frac{E_s}{k_B T}\right)$, where E_s is an energy scale of the problem, which in this case is the oscillation quantum, $\hbar\omega$. This is consistent with the same activated behavior seen for the heat capacity (Eq. 8.63)[3].

We shall see that the following general insight go a long way in guiding us for our exploration of quantum systems.

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[1] $Q_d = 2$ for a single simple harmonic oscillator, since the Hamiltonian $= \frac{1}{2m}p^2 + \frac{1}{2}kx^2$ has two quadratic terms.

[2] Note that the situation here is analogous to those in Sections 8.4.2 and 8.4.3. There, we saw that the problem breaks down to a single magnetic moment problem when using the Gibbs ensemble (constrained H). Here, the problem breaks down to a single oscillator problem when using the canonical ensemble (constrained T). On the other hand, in the micro-canonical ensemble for the current problem (conserved E), the whole system must be considered. This is analogous to the situation in Section 8.4.3, where a conserved M was involved.

[3] And, of course, that result for C_V can be easily re-derived from our expression of S, using $C_V = T\frac{\partial S}{\partial T}$ and $T\frac{d\beta}{dT} = -\beta$.

For a quantum system with an energy scale E_s, the equipartition theorem is valid if $k_B T \gg E_s$, while the system shows a manifestly quantum behavior, i.e., a thermally activated behavior with a small $e^{-\frac{E_s}{k_B T}}$, if $k_B T \ll E_s$.

For the Einstein phonon problem, the activated behavior guarantees that the entropy vanishes as $T \to 0$. This demonstrates **the third law of thermodynamics**[4]. Related to this is the above discussion of the heat capacity, which must also vanish as $T \to 0$.

Clearly, the entropy of the semi-classical ideal gas, Eq. 6.46, does not vanish as $T \to 0$, either! Based on the insight gained above, we expect that once we examine energy scales of the ideal gas problem more properly, this issue will be resolved. We shall do so, soon, in an upcoming lecture.

Another insight can be already learned, if we take a look at the function $n_P(\omega)$ again.

$$n_P(\omega) = \frac{1}{\exp(\beta\hbar\omega) - 1} \tag{8.60}$$

This function is the so-called **Planck distribution function**. What it represents is clearly the "thermal quantum number" of the oscillator, since $E = \left(n_P + \frac{1}{2}\right)\hbar\omega$ (Eq. 8.59).

A simple harmonic oscillator quantum is a particle. More specifically, it is a boson, with zero chemical potential ($\mu = 0$). $n_P(\omega)$ represents the average number of thermally excited bosons, and is equivalent to the **occupation number** for the bosonic state at $\hbar\omega$.

The last part of this makes it clear that the Planck distribution function is a special case ($\mu = 0$)[5] of the Bose-Einstein distribution function $n_{BE}(\omega) = \frac{1}{\exp(\beta(\hbar\omega - \mu)) - 1}$. Why is μ zero? It is because the number of phonons is *fundamentally unrestricted*. An easy way to see this logic is through Section 7.5. In that section, it becomes clear that β is simply a Lagrange multiplier introduced when the energy is allowed to fluctuate but

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[4] However, for the phonon system, the exact manners in which the entropy and the heat capacity vanish as $T \to 0$ are not obtained correctly by the Einstein model. The behavior is captured properly by "Debye's T^3 law," to be covered soon.

[5] So, the classical limit for Einstein phonons does *not* correspond to $\mu \to -\infty$ (Eq. 8.8), since $\mu = 0$ by definition. The same is true for photons. In any case, the classical limit as $n \to \infty$ (large quantum number) or, equivalently, $\hbar \to 0$ is always applicable.

the average energy must be constrained. The chemical potential μ (or rather $-\beta\mu$) comes as an additional Lagrange multiplier, if the total number of particles is allowed to fluctuate, *independently of* the energy, while its average value is constrained. That the number of particles is independent of the total energy for electrons (fermions) or Helium atoms (^{4}He: bosons) is quite obvious[6]. However, the number of oscillation quanta, N, is clearly dependent on energy, and so is *not* an independent variable. There is no additional constraint for N, there is no additional Lagrange multiplier to introduce, and thus there is no μ.

Apart from the particular value of μ, the fact that the oscillation quantum is a boson is easy to understand: clearly many oscillation quanta can coexist! So, without really being aware of it, we have included the effect of quantum statistics in this simple example of Einstein phonons!

9.2 Microstate

The picture of a microstate (μ) as a trajectory in phase space is a Newtonian concept and must be revised in quantum mechanics as the uncertainty principle (and accordingly, quantum fluctuations) becomes more and more important.

Instead, **a microstate in quantum mechanics means a wave function**. Please do not confuse this with a one particle wave function. When we talk about a wave function in statistical physics, it means a **many body (an N-body) wave function**, by default.

9.3 Density matrix—why?

In a standard course of quantum mechanics, the density matrix is often skipped. Instead, most of the time is spent on a state vector, $|\Psi\rangle$, or its wave function such as $\langle \vec{x}_1, \vec{x}_2, ..., \vec{x}_N \,|\, \Psi\rangle$. But, the density matrix is an essential topic of quantum mechanics, and it can be viewed as more general than a state vector. Why?

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[6] This is, of course, because we are assuming low energy scale physics, in the following sense. If one studies high energy physics that is much higher than the mass-energy (mc^2) of particles such as electrons or Helium atoms, then the number of those particles *will* be dependent on energy, and, therefore, *will* be unrestricted!

9.3.1 An example—light polarization

Let us consider a simple experiment involving the photon polarization. Any physics student knows that there is such a thing as "an unpolarized beam of light." How does one describe it? We shall see that the description is possible with the density matrix. We shall see that it is *not* possible to describe such a state with a state vector alone.

Let us describe experiments, first. A beam of light is propagating, and we define the propagation direction as the positive z axis. A polarizer is mounted perpendicular to the beam. Let us say that we have an "x" polarizer, whose output beam has x polarization. If we take the identical polarizer, and rotate it by 90 degrees around the z axis, then we get a "y" polarizer. Clearly, there is an arbitrariness in how we define the x axis, but what matters is that we define the xyz axes so that they form a right-handed Cartesian coordinate system. The polarization corresponding to the polarizer can be defined as a unit-length vector $\alpha\hat{x} + \beta\hat{y}$ (see below). If α and β are real numbers, then we have a linear polarizer, which is basically just the x polarizer rotated by an appropriate amount of angle. However, we can have a circular polarizer or an elliptical polarizer[7]: for such a polarizer, α or β *must* be complex (see below). **An unpolarized beam of light, propagating in the z direction, is defined as a beam of light, whose intensity is reduced by half by any polarizer mounted in the xy plane.** It is also found that when one uses linear polarizers in succession, then the second linear polarizer reduces the intensity further by $\cos^2\alpha$, where α is the angle between the polarization axes of the two polarizers.

Now, let us build a quantum mechanical description for this experiment[8]. Quantum mechanically, the polarizer carries out a "measurement." If we consider an x polarizer, then its measurement operator is given by $|h\rangle\langle h|$, where we defined $|h\rangle$ (h for "horizontal") as the state vector for the x polarized light. Namely, if the initial beam is given by $|\Psi\rangle$, then the final beam after the measurement is given by $|h\rangle\langle h\,|\,\Psi\rangle$, and similarly for other polarizations.

$$|\Psi\rangle \xrightarrow{\textit{measurement}} |h\rangle\langle h\,|\,\Psi\rangle = C_x|h\rangle \qquad \text{by } x \text{ polarizer: } C_x = \langle h\,|\,\Psi\rangle \tag{9.4}$$

$$|\Psi\rangle \xrightarrow{\textit{measurement}} |v\rangle\langle v\,|\,\Psi\rangle = C_y|v\rangle \qquad \text{by } y \text{ polarizer: } C_y = \langle v\,|\,\Psi\rangle \tag{9.5}$$

$$|\Psi\rangle \xrightarrow{\textit{measurement}} |a\rangle\langle a\,|\,\Psi\rangle = C_a|a\rangle \qquad \text{by any polarizer: } C_a = \langle a\,|\,\Psi\rangle \tag{9.6}$$

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[7] These can be made of birefringent wave plates.

[8] You might ask why we do quantum mechanics, when most polarization experiments involve classical light—light with lots of quanta. Wouldn't the classical E&M much easier to deal with? The answer is yes but no. Much of what we do in classical E&M is in fact quantum physics, if the property examined is the property of a single photon (see Sections 9.3.1, 9.3.3). These properties include interference, polarization, transmission, reflection, energy, momentum, diffraction, etc. It is much better to consider these things in quantum mechanical terms.

The last one describes the most general polarization, where the polarization eigenstate $|a\rangle$ is defined as

$$|a\rangle \;=\; \alpha\,|h\rangle + \beta\,|v\rangle \qquad\qquad |\alpha|^2 + |\beta|^2 = 1 \text{ (normalization condition)}, \tag{9.7}$$

$$\alpha = \cos\left(\frac{\theta}{2}\right),\ \beta = e^{i\phi}\sin\left(\frac{\theta}{2}\right), \text{ with real } \theta \text{ and } \phi. \tag{9.8}$$

In the last θ, ϕ form[9] for α and β, we adopted a convention to take α to be real, taking advantage of the fact that the overall phase factor of $|a\rangle$ is unimportant. If α, β are not "special values," then $|a\rangle$ describes an elliptically polarized light. Here are some special values of α, β, which describe linearly polarized light or circularly polarized light: $|a\rangle_{\alpha=1,\beta=0} = |h\rangle$, $|a\rangle_{\alpha=0,\beta=1} = |v\rangle$, $|a\rangle_{\alpha=\frac{1}{\sqrt{2}},\beta=\frac{i}{\sqrt{2}}} \equiv |R\rangle$ (right circularly polarized light), and $|a\rangle_{\alpha=\frac{1}{\sqrt{2}},\beta=\frac{-i}{\sqrt{2}}} \equiv |L\rangle$ (left circularly polarized light). In general, if α and β are both real, then $|a\rangle$ describes a linearly polarized light, with the polarization axis defined by $\alpha\hat{x} + \beta\hat{y}$, and, if $\frac{\beta}{\alpha} = \pm i$, then it describes a circularly polarized light, for which we must conclude that $|\alpha| = |\beta| = 1/\sqrt{2}$.

Now, let us prove that an unpolarized beam of light cannot be described by a wave function. <u>PROOF</u> ✎ Suppose that there *is* a state vector $|\Psi\rangle$ such that $|\langle a|\Psi\rangle| = \frac{1}{\sqrt{2}}$ for any polarization eigenstate $|a\rangle$. Taking $|a\rangle$ as $|h\rangle$ or $|v\rangle$, we must conclude that $|\Psi\rangle = \frac{1}{\sqrt{2}}|h\rangle + \frac{e^{i\phi}}{\sqrt{2}}|v\rangle$, where ϕ is an arbitrary, but fixed, real number. Clearly, $|a\rangle \equiv \frac{1}{\sqrt{2}}|h\rangle + \frac{e^{i\phi}}{\sqrt{2}}|v\rangle$ is a polarization eigenstate! Since, $\langle a|\Psi\rangle = 1$, we have a contradiction. <u>QED.</u> ✐

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[9] Why the particular form of Eq. 9.8? Here, we shall use the spin ½ language, while keeping in mind the fact that the photon spin, the quantum mechanical meaning of photon polarization, is really 1. Using the spin ½ language, with mapping $|h\rangle \to |z\uparrow\rangle$ and $|v\rangle \to |z\downarrow\rangle$, consider the spin rotation operator $R(\theta,\phi) = \exp\left(-i\frac{\phi}{2}\sigma_z\right)\exp\left(-i\frac{\theta}{2}\sigma_y\right)$. $R(\theta,\phi)|z\uparrow\rangle$ gives the up eigenstate for the spin component pointing to the direction defined by polar angle θ and azimuthal angle ϕ. Noting that $\exp\left(-i\frac{\theta}{2}\sigma_y\right) = \cos\left(\frac{\theta}{2}\right) - i\sigma_y\sin\left(\frac{\theta}{2}\right) \doteq \begin{pmatrix}\cos(\theta/2) & -\sin(\theta/2)\\ \sin(\theta/2) & \cos(\theta/2)\end{pmatrix}$, we see that $R(\theta,\phi)|z\uparrow\rangle = e^{-i\frac{\phi}{2}}\left[\cos\left(\frac{\theta}{2}\right)|z\uparrow\rangle + e^{i\phi}\sin\left(\frac{\theta}{2}\right)|z\downarrow\rangle\right]$, which is equal to Eq. 9.8 except for the overall phase factor. So, this is why we used the form of Eq. 9.8, even though there are other equally general ways to write a unit-length 2-dimensional complex vector. From this discussion, it is worth pointing out that *any* general spin ½ state is expressible as $R(\theta,\phi)|z\uparrow\rangle$, which is by definition also a spin up eigenstate as mentioned above. As θ and ϕ changes, the direction pointed to by $R(\theta,\phi)|z\uparrow\rangle$ can be seen as tracing points on a unit sphere in the real 3-dimensional space, e.g., $|z\uparrow\rangle \to (0,0,1)$ and $R(\pi,0)|z\uparrow\rangle = |z\downarrow\rangle \to (0,0,-1)$, and in such visualization of a general spin ½ state as a point on a unit sphere in the real space, the unit sphere is called the "Bloch sphere."

It may be of some interest to summarize the above rather trivial proof in the spin ½ language already introduced in footnote 9. In that language, the following mapping applies:

$$|h\rangle \to |z\uparrow\rangle\,,\ |v\rangle \to |z\downarrow\rangle\,,\ |h'\rangle \to |x\uparrow\rangle\,,\ |v'\rangle \to |x\downarrow\rangle\,,\ |R\rangle \to |y\uparrow\rangle\,,\ |L\rangle \to |y\downarrow\rangle\,.$$

A spinor in this spin ½ representation corresponds to a unique polarization (linear, circular, or elliptical) of photon and vice versa. In the above mapping, the horizontal (vertical) axis is defined as the x (y) axis, and $|h'\rangle \equiv \frac{1}{\sqrt{2}}\left(|h\rangle + |v\rangle\right)$ corresponds to the linear polarization along the x' axis, the x axis rotated 45 degrees around the z axis, and $|v'\rangle \equiv \frac{1}{\sqrt{2}}\left(|h\rangle - |v\rangle\right)$ corresponds to the linear polarization along the y' axis, the y axis rotated 45 degrees around the z axis. And, $|R\rangle = \frac{1}{\sqrt{2}}\left(|h\rangle + i\,|v\rangle\right)$ corresponds to the right circularly polarized light, and $|L\rangle = \frac{1}{\sqrt{2}}\left(|h\rangle - i\,|v\rangle\right)$ to the left circularly polarized light. Lastly, $|a\rangle = \frac{1}{\sqrt{2}}\left(|h\rangle + e^{i\phi}\,|v\rangle\right) = \frac{e^{i\phi/2}}{\sqrt{2}}\left(e^{-i\phi/2}\,|h\rangle + e^{i\phi/2}\,|v\rangle\right)$ is a spinor, which is, up to an overall phase, $|h'\rangle$ rotated by ϕ around the z axis, which corresponds to an elliptical polarization, except when $\phi = n\pi/2$ with n = integer.

How do we represent such a state in quantum mechanics? The answer is the density matrix. We may write

$$\rho_{xy} \equiv \frac{1}{2}\,|h\rangle\langle h| + \frac{1}{2}\,|v\rangle\langle v| \tag{9.9}$$

for the density matrix. Each term in the density matrix is a product of the probability (1/2 for either term in this case) and the projection operator that corresponds to the corresponding measurement. This is not the only way to represent a beam of unpolarized light as a density matrix. One can also choose to measure $|R\rangle$ and $|L\rangle$, and may write

$$\rho_{LR} \equiv \frac{1}{2}\,|R\rangle\langle R| + \frac{1}{2}\,|L\rangle\langle L| \tag{9.10}$$

Of course, a single density matrix must be able to describe all possible measurements, not just those measurements that one may use to construct a density matrix. For example, with ρ_{LR} in hand, one should be able to answer the question: "what is the probability to measure x polarization?" How do we calculate such a probability? Here is the answer.

For a given density matrix, ρ, the probability that a measurement of an operator O will result in an eigenvalue o, with the corresponding eigenstate $|o\rangle$, is given by

$$P_o = \langle o\,|\rho|\,o\rangle \tag{9.11}$$

It is left for your exercise to show that (1) $P_a = \langle a\,|\rho_{xy}|\,a\rangle = \frac{1}{2}$ for any $|a\rangle$ (Eq. 9.7), (2) $P_a = \langle a\,|\rho_{RL}|\,a\rangle = \frac{1}{2}$ for any $|a\rangle$ (Eq. 9.7), and (3) $\rho_{xy} = \rho_{RL}$. Of course, showing (1) and (3) are sufficient to show (2). The condition (3) can be generalized to $\rho_{xy} = \rho_{ab}$ where $|a\rangle = \alpha\,|h\rangle + \beta\,|v\rangle$, normalized, and $|b\rangle = \beta^*\,|h\rangle - \alpha^*\,|v\rangle$ (so that $\langle\, a\,|\, b\,\rangle = 0$ and $\langle\, a\,|\, a\,\rangle = \langle\, b\,|\, b\,\rangle = 1$).

So, now, we know how to write down the representation of an unpolarized light in quantum mechanics!

$$\rho \doteq \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} \qquad \text{density matrix for the polarization of unpolarized light} \tag{9.12}$$

where $\doteq$ means "is represented by" in the sense of the quantum mechanical representation using a certain set of basis.

By the property (3) above, it turns out that, in this particular case, it does not matter what basis we use to represent the density matrix; we always get a diagonal matrix with the two diagonal elements being equal to $\frac{1}{2}$. This is because the unpolarized light is a special case!

It is important to note that just by measuring the polarization in one direction does not get you enough information for obtaining the density matrix. Let us consider an example that illustrates this. Suppose one has a state of photons, and, by measurement, discovers that the light is 60 % x polarized and 40 % y polarized. One may wonder if the matrix, $\left(\begin{smallmatrix} 0.6 & 0 \\ 0 & 0.4 \end{smallmatrix}\right)$, would represent this state in the xy basis. The answer is no, in general. How do we know this? It is easy to see that when one changes the basis to the RL basis, the matrix becomes $\left(\begin{smallmatrix} 0.5 & 0.2 \\ 0.2 & 0.5 \end{smallmatrix}\right)$. So, this state corresponds to an equal mixture of right circularly polarized light and left circularly polarized light. So, why can't we write the matrix as $\left(\begin{smallmatrix} 0.5 & 0 \\ 0 & 0.5 \end{smallmatrix}\right)$ in the RL basis? Clearly, there is an ambiguity here, and we need some more information. As we shall see shortly, the density matrix is a Hermitian matrix with a unit trace and 0 or positive diagonal elements. Thus, for a 2×2 problem like the current one, we need to know three numbers. They can be taken to be the average values of the x polarization, the x' polarization, and the circular polarization. For an unpolarized beam of light, all these numbers are zero, and this is the reason why the diagonal matrix above, $\left(\begin{smallmatrix} 0.5 & 0 \\ 0 & 0.5 \end{smallmatrix}\right)$, is the correct representation for the unpolarized state. In general, the density matrix in the two dimensional Hilbert space can be written as $\rho = \frac{1 + c_1\sigma_1 + c_2\sigma_2 + c_3\sigma_3}{2}$, where 1 means the 2×2 unit matrix, c_i's are real numbers and σ_i's are Pauli matrices[10].

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[10] The properties of coefficients c_i can be further narrowed down: $\rho = \frac{1}{2}\left(1 + \vec{c}\cdot\vec{\sigma}\right) = \frac{1}{2}\left(1 + |\vec{c}|\,\hat{c}\cdot\vec{\sigma}\right)$. From this, it can be shown that $|\vec{c}| \le 1$ (hint: begin by showing that the ensemble average value of $\hat{c}\cdot\vec{\sigma}$ is $|\vec{c}|$). $|\vec{c}| = 1$ defines the "Bloch sphere" (see footnote 9). $|\vec{c}| = 1$ if and only if the state is pure (i.e., $\rho = |a\rangle\langle a|$ for a polarization eigenstate $|a\rangle$; hint: begin by showing that for a pure state (Eq. 9.8) $\vec{c} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$).

That there are off-diagonal elements means that "things are not quite random" or "things are not completely incoherent."

9.3.2 Is the Universe in a pure state?

A pure state in quantum mechanics means a state that is described by a single wave function. We do not know the answer to this question. But, some people may conjecture that the answer is yes. Let us assume so, mostly for the fun of it, in this section.

Let us consider ourselves doing experiments in this Universe. As a rule, we are investigating only a small part of the Universe. We can control parameters that pertain to that small part. Our system under investigation must be reasonably disconnected from the rest of the Universe; otherwise, we cannot be in control of our experiments, and our results will not be reproducible! However, clearly we cannot completely separate our system from the rest of the Universe. There is a weak interaction between them. So, the total wave function of the Universe can be written down as

$$|\Psi_U\rangle = \sum_{i,j} C_{i,j} \, |i\rangle \, |R,j\rangle \tag{9.13}$$

where $|i\rangle$ is the wave function of the system (ortho-normalized), $|R,j\rangle$ is the state of the rest of the universe (ortho-normalized), and i, j are the quantum numbers that describe the system and the rest, respectively.

So, we are measuring a dynamical variable, O, of our system. By definition, this variable is dependent only on the system, not on the rest of the Universe. What is the expectation value for this measurement? Since we have only one overall wave function, the answer is easy.

$$\begin{aligned} \langle O \rangle &= \langle \Psi_U \, | O \, | \, \Psi_U \rangle & (9.14) \\ &= \sum_{i,i',j} C^*_{i',j} C_{i,j} \, \langle i' \, | O \, | \, i \rangle & (9.15) \end{aligned}$$

where in the second step, the ortho-normality condition, $\langle \, \Psi_{R,j} \, | \, \Psi_{R,j'} \rangle = \delta_{j,j'}$ has been used along with the fact that O is j independent, both by assumptions.

Note that, our expression for $\langle O \rangle$ is somewhat complicated. If we assumed that the system is completely disconnected from the rest of the Universe, then we would have gotten no j sum. This motivates us to define a matrix that absorbs the j sum:

$$\rho_{i,i'} \equiv \sum_j C^*_{i',j} C_{i,j} . \tag{9.16}$$

This matrix, which can be readily shown to Hermitian, is now dependent only on the (generally composite) index i for the Hilbert space of the system only. We can define this matrix **the density matrix** of the system. So, we now have

$$\langle O \rangle \;=\; \sum_{i,i'} \rho_{i,i'} \langle i' \,| O \,| i \rangle \;=\; \mathrm{tr}\,\{\rho O\} \tag{9.17}$$

which says that, if we know the density matrix, then we can compute the expectation value for any operator by taking the trace of the matrix product, ρO.

In this view, the density matrix represents the "traced-out" representation of the wave function of the Universe, where "tracing out" means the sum over j (Eq. 9.16), the (generally composite) index for the Hilbert space of the rest of the Universe. The necessity to invoke the density matrix arises from the fact that our system is not isolated.

For the last point, we can note the following. If the system were isolated completely, then the usual quantum mechanics applies. We can then take $i = o$ as the eigenvalue of O, since the eigenstates of any observable form a complete set of states to span the Hilbert space. Then, we would have

$$\langle O \rangle \;=\; \sum_{o} |C_o|^2\, o \tag{9.18}$$

which is the basic quantum mechanics.

9.3.3 Light polarization revisited

From the discussion of the previous paragraph, it is clear that the reason why we would "settle for" a density matrix is our ignorance of the complete wave function, assuming that the Universe is indeed described by a single wave function[11]. Going further, one might argue that such ignorance is even *preferred* in the following sense. One definitely would not like to require complete knowledge of the conjectured single wave function of the Universe to describe at what temperature a kettle of water may boil.

So, depending on your point of view, the density matrix may be viewed either as the poor man's substitute for the full wave function of the Universe, or as an essential instrument with which you can build an excellent quantum mechanical description

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[11] This assumption seems acceptable on the basis of Occam's razor.

for your system, in a general way applicable to various known, or perhaps unknown, scenarios in which your system and the rest of the Universe interact.

After these discussions, it seems helpful to consider a specific situation or two where the full wave function is completely known, in theory, and narrow our focus on a sub-system, for which the wave function is not a good way at all, for doing quantum mechanics. While the following examples describe light polarization in vacuum as in Section 9.3.1, the same language can be applied to the spin polarization of any spin ½ particles such as electrons or protons, if you like, using the correspondence described in the box of page 7.

1. **EPR (Einstein-Podolsky-Rosen) pair of photons.** Suppose you have a machine, using which you can consistently create a pair of photons whose wave function is given by

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|h,v\rangle - |v,h\rangle\right).$$

   In this wave function, the spatial part is omitted for brevity[12], leaving only the polarization part[13]. Now, one of these two photons is flying to the right, to be captured by Alice, and the other to the left, to be captured by Bob. For the argument's sake, let us assume that Alice and Bob are too far away from each other (like at distance, which is a significant fraction of the size of the Universe) to be able to communicate in any reasonable human time scale, while the coherence of the wave function is maintained all the way[14]. You are operating this EPR pair machine to generate a pair of photons at every fixed time interval.

   Either Alice or Bob will then be noticing a steady stream of photons whose polarization, when measured, is either horizontal or vertical. When they keep measuring the polarization of all incoming photons, they will conclude that there are equal number of photons with either polarization. *We* know that the origin of this probabilistic result is due to the wave function written above, but Alice or Bob does not know it, since they cannot communicate by assumption. Question is what would be the best thing that Alice or Bob can do for their quantum mechanical description of the photons that they measure, given their limited knowledge? The answer is the density matrix for a photon, which in

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[12] Also, the spatial part of the wave function will change if we switch to the case of two spin ½ fermions.

[13] The same polarization wave function can be written differently. For example, it can be written as $|\Psi\rangle = \frac{1}{\sqrt{2}}(|R,L\rangle - |L,R\rangle)$.

[14] This is a purely theoretical idea at this moment.

this case is given by

$$\rho \doteq \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$$

in any basis ($|h\rangle$ and $|v\rangle$ or $|R\rangle$ and $|L\rangle$).

Note that from Alice's or Bob's point of view, the full wave function is not known. In fact, they will not know whether the full wave function is (approximately) a two-photon wave function or an N-photon wave function with different values for N. Even for a two photon wave function, there is an ambiguity as to whether the wave function is like the above or something else such as $|\Psi\rangle = \frac{1}{\sqrt{2}} (|h,h\rangle + e^{i\delta} |v,v\rangle)$, with a real value of δ. There are infinite possible full wave functions (including those shown above) that are consistent with the above density matrix. No matter what those wave functions may be, the single photon polarization property such as what Alice or Bob measures, the above density matrix is all one needs.

2. **An unpolarized beam of photons.** Now let us revisit the topic that we discussed already in Section 9.3.1. How do we describe an unpolarized beam of photons? The answer is the density matrix, Eq. 9.12. It is important to realize that, similarly for the EPR example that we just discussed, what we are asking in the question "how do we describe an unpolarized light?" is **the single particle property**, where particle equals photon in the current discussion. For instance, we are not asking the correlation between photon polarizations. Namely, when we are passing photons through a polarizer, what we are really measuring is N times the probability that any single photon in the beam has a certain polarization, where N is (the average of) the total number of photons.

   Thus, regardless of how the unpolarized beam of light is actually made, the same density matrix describes it as long as the polarization is concerned. For instance, you can make an unpolarized beam of light, by generating perfectly polarized beams of light in all conceivable polarization directions and then extracting one photon from each beam, thereby forming a new beam of light. Or, more simply, you can just combine two perfectly polarized beams of light, where the two polarizations are orthogonal (one horizontally polarized and the other vertically polarized, as an example, or one right circularly polarized, and the other left circularly polarized, as another example) and you will also have an unpolarized beam of light! In a more complicated way, you can also do the following. Suppose that you form a beam of light, in which only two photons have the same frequency and each pair of those two photons have the following polarization wave function:

$$|\Psi\rangle = \frac{1}{\sqrt{2}} (|h,v\rangle + |v,h\rangle) .$$

Such a beam of light will also be an unpolarized beam of light. The density matrix, Eq. 9.12, is sufficient for all these examples, as far as describing the polarization of the beam. Of course, if more measurements are made, then one may discover other properties that require going beyond the single particle density matrix, Eq. 9.12. For instance, in the last example, if the beam is monochromatized, then it will show a correlation in the polarization values of two photons of the same frequency.

9.4 Quantum ensemble, Density matrix

Let us recall (Section 5.4) that the ensemble is a device by which we assert that there is a many-to-one mapping from microstates (that we cannot fully measure or control) to a macro state (that we observe consistently, nonetheless).

In classical mechanics, we could distribute microstates as dots in the phase space. In non-equilibrium states, dots have different probabilities even if they have the same total energy value (and same other conserved quantities), while they must, by a fundamental postulate of statistical mechanics (Section 6.1, Eq. 6.5 or 6.4), have the same probabilities of occurrence in equilibrium.

How do we represent an ensemble in quantum mechanics? Clearly a single wave function is not the right answer. A state represented by a single wave function is a state that we know completely, by definition. For an ensemble of states, all we know is that a given state may have a probability to be measured to be in this or that wave function (microstate). So, this is the clue. What represents a measurement? It is the projection operator: $|\Psi_\alpha\rangle\langle\Psi_\alpha|$, where we assume that $|\Psi_\alpha\rangle$'s are all possible members of the ensemble, i.e., all possible microstates. This leads to the definition of the *density matrix*, the quantum equivalent to the probability density function in semi-classical statistical mechanics[15]:

$$\rho(t) \equiv \sum_\alpha p_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha| \tag{9.19}$$

where p_α is the probability for the system to be in state Ψ_α and thus

$$p_\alpha \geq 0, \qquad \sum_\alpha p_\alpha = 1 \tag{9.20}$$

---

[15] The following general points are worth keeping in mind, regarding this definition of the density matrix. (1) Eq. 9.19 represents an *incoherent sum* of pure states, each of which is given by $|\Psi_\alpha\rangle\langle\Psi_\alpha|$. One must keep in mind that not any state, which has a probability p_α to be measured in state Ψ_α, can be written in the form of Eq. 9.19. In general, non-diagonal elements may exist, if the system has coherence (cf. the last paragraph in page 8). (2) $|\Psi\rangle_\alpha$'s are taken to be normalized, but they *do not* need to be mutually orthogonal. Also, they can be over-complete. See property 2 in the next section.

By definition, p_α's are time-independent. However, the states, $|\Psi_\alpha\rangle$'s, are generally time-dependent, satisfying the Schrödinger equation, $i\hbar\frac{\partial}{\partial t}|\Psi_\alpha\rangle = H|\Psi_\alpha\rangle$, where H is the Hamiltonian of the system.

9.5 Properties of the density matrix

1. The density matrix is a Hermitian operator. This is clear because p_α's are real numbers and each projection operator is a Hermitian: $(|\Psi\rangle\langle\Psi|)^\dagger = \langle\Psi|^\dagger|\Psi\rangle^\dagger = |\Psi\rangle\langle\Psi|$.

2. $|\Psi_\alpha\rangle$'s represent observable states, and so they are usually taken as eigenstates of an Hermitian operator such as Hamiltonian. Then, they must form a complete and orthonormal set.

$$\sum_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha| = 1 \tag{9.21}$$

$$\langle\Psi_\alpha|\Psi_{\alpha'}\rangle = \delta_{\alpha,\alpha'} \tag{9.22}$$

   However, note that it is *not* required in general that in the definition of the density matrix, Eq. 9.19, $|\Psi_\alpha\rangle$'s are complete and ortho-normal. In general, they can be over-complete or non-orthogonal. As an example, this is a perfectly fine way of defining a mixed state for photons: 30 % of a pure x-polarization state plus 50 % of a pure right circularly polarized state plus 20 % of a pure left circularly polarized state, i.e., $\rho = 0.3|h\rangle\langle h| + 0.5|R\rangle\langle R| + 0.2|L\rangle\langle L|$, in the notation of Section 9.3.1. Even in such a case, it is always possible to diagonalize ρ with a complete orthonormal basis set, since ρ itself is Hermitian! So, we can take the above two conditions to be true, always.

3. Just as in the semi-classical case, a **pure state** is defined as an ensemble consisting of just one microstate. A **mixed state** is an ensemble consisting of more than one possible microstates. Note that $\rho^2 = \rho$ if and only if a pure state describes the density matrix (proof left for your exercise).

4. For an observable O, the ensemble average is given by

$$\overline{\langle O\rangle} = \mathrm{tr}\{\rho O\} \tag{9.23}$$

   Note that for quantum statistical mechanics, we use the symbol for ensemble average as $\overline{\langle O\rangle}$, to avoid misunderstanding as the mere expectation in quantum mechanics $\langle O\rangle$.

   <u>Proof</u> ✎ `By definition,`

$$\overline{\langle O\rangle} = \sum_\gamma p_\gamma \langle\Psi_\gamma|O|\Psi_\gamma\rangle$$

We need to show that this is identical with tr$\{\rho O\}$. This can be accomplished by inserting the resolution of the identify above (Eq. 9.21).

$$\begin{aligned}
\sum_\gamma p_\gamma \langle \Psi_\gamma | O | \Psi_\gamma \rangle &= \sum_{\gamma,\alpha} p_\gamma \langle \Psi_\gamma | \Psi_\alpha \rangle \langle \Psi_\alpha | O | \Psi_\gamma \rangle \\
&= \sum_{\gamma,\alpha} p_\alpha \langle \Psi_\gamma | \Psi_\alpha \rangle \langle \Psi_\alpha | O | \Psi_\gamma \rangle && \texttt{using Eq. 9.22} \\
&= \sum_\gamma \langle \Psi_\gamma | \rho O | \Psi_\gamma \rangle && \texttt{Eq. 9.19} \\
&= \mathtt{tr}\{\rho O\}
\end{aligned}$$

QED. ✎

5. In the Heisenberg picture of quantum mechanics, matrices evolve in time, and state vectors do not. In that picture,

$$\frac{d\rho}{dt} = 0 \tag{9.24}$$

This is the direct equivalent to Eq. 5.15: it can be called the **quantum Liouville theorem**. This comes from the fact that p_α's are by definition time-independent, and that states are time-independent in the Heisenberg picture (and so is the projection operator for *any* state). Note that for any operator[16] O, the following **Heisenberg equation of motion** holds[17]

$$\frac{dO}{dt} = \frac{i}{\hbar}[H, O] + \frac{\partial O}{\partial t} \tag{9.25}$$

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[16] And even when H is time dependent, while a time dependent Hamiltonian is not of our main interest.

[17] In case some of you are not familiar with the Heisenberg picture, here is a reminder. In the Schrödinger picture, $U(t)|\Psi(t=0)\rangle = |\Psi(t)\rangle$, where $U(t)$ is the time evolution operator determined by the Schrödinger equation. Operators do not get affected by $U(t)$, although they can have explicit time dependence. In the Heisenberg picture, we regard states as fixed in time, i.e., as $|\Psi(t=0)\rangle$, while any operator $O_s(t)$ evolves in time as $O_h(t) = U^\dagger(t) O_s(t) U(t)$, where h means the Heisenberg picture and s means the Schrödinger picture. These two pictures are equivalent, since the matrix element $\langle \Psi_a | O | \Psi_b \rangle$ is independent of which picture we use. Here is the derivation of the Heisenberg equation of motion. DERIVATION ✎

$$\begin{aligned}
U(t+dt)|\Psi(t=0)\rangle &= |\Psi(t+dt)\rangle \approx |\Psi(t)\rangle + dt\frac{d}{dt}|\Psi(t)\rangle \\
&= \left(1 - \frac{i}{\hbar} H dt\right)|\Psi(t)\rangle \\
&= \left(1 - \frac{i}{\hbar} H dt\right) U(t)|\Psi(t=0)\rangle && \texttt{for } \textit{any} \texttt{ state } \Psi(t=0) \\
\therefore \quad U(t+dt) &= \left(1 - \frac{i}{\hbar} H dt\right) U(t) \\
\frac{dU(t)}{dt} &= -\frac{i}{\hbar} H U(t)
\end{aligned}$$

where $U(t)$ is defined as the time evolution operator. This result is very where $\frac{\partial O}{\partial t}$, defined as the Heisenberg picture form of the time derivative of O in the Schrödinger picture, is non-zero only if O has an explicit time dependence. Applying the Liouville theorem above, we get[18]

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}\left[H, \rho\right] \tag{9.26}$$

For any observable O, which does not depend explicitly on time, its time derivative is given by

$$\frac{d\overline{\langle O\rangle}}{dt} = \operatorname{tr}\left\{\frac{\partial \rho}{\partial t} O\right\} \tag{9.27}$$

assuming that $|\Psi_\alpha\rangle$'s are taken as eigenstates of the Hamiltonian, which we now assume to be not explicitly dependent on time. So, this suggests that

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}\left[H, \rho\right] = 0 \tag{9.28}$$

for an equilibrium state. And, we take this as the fundamental postulate here, just as we did in semi-classical statistical mechanics (Section 6.1).

6. For a microcanonical ensemble in equilibrium,

$$p_\mu = \frac{1}{\Omega(\mathcal{E}, V, N)} \tag{9.29}$$

where $\Omega(\mathcal{E}, V, N)$ is the number of microstates, i.e. the number of many body states (i.e., wave functions) $\left|\Psi_\mu\right\rangle$. The entropy is given by[19]

$$S(E, V, N) = k_B \log \Omega(E, V, N) \tag{9.30}$$

`general, valid even when` H *is* `time dependent. From` $O_h(t) = U^\dagger(t) O_s(t) U(t)$,

$$\begin{aligned}\frac{dO_h}{dt} &= \frac{dU^\dagger}{dt} O_s U + U^\dagger \frac{dO_s}{dt} U + U^\dagger O_s \frac{dU}{dt} \\ &= \frac{i}{\hbar} U^\dagger [H, O_s] U + U^\dagger \frac{dO_s}{dt} U\end{aligned}$$

`If` H`'s at different times commute, as is commonly the case,` U `and` H `commute, and the first term becomes` $\frac{i}{\hbar}[H, O_h]$. `If` H`'s at different times do not commute, then` $\frac{i}{\hbar}[H, O]$ `can be computed in the Schrödinger picture and then transformed to the Heisenberg picture. The second term is, by definition,` $\frac{\partial O_h}{\partial t}$. QED. ✎

[18] You may find the following statement in some books: $\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho]$. Such a statement is made within the Schrödinger picture. Here, we use the Heisenberg picture, as it compares well with the semi-classical statistical mechanics picture.

[19] Note the similarity of this definition to the Boltzmann entropy for the semi-classical case, Eq. 6.10. This definition can be extended to non-equilibrium states: we can define the von Neumann entropy, $S = -k_B \operatorname{tr}\{\rho \log \rho\}$. So, the von Neumann entropy is clearly the quantum version of the Gibbs-Boltzmann entropy, Eq. 7.17. Note that due to the Liouville theorem, both Eq. 7.17 and the von Neumann entropy are *time-independent.*

For a canonical ensemble, we have

$$Z(T,V,N) = \sum_{\mu} \exp(-\beta \mathcal{E}_{\mu}) \qquad H\,|\Psi_\alpha\rangle = \mathcal{E}_\mu\,|\Psi_\mu\rangle \tag{9.31}$$

$$p_{\mu} = \frac{\exp\left(-\beta \mathcal{E}_{\mu}\right)}{Z(T,V,N)} \tag{9.32}$$

For a grand canonical ensemble, we have

$$\Phi(T,V,\mu) = \sum_{\alpha} \exp(-\beta(\mathcal{E}_\alpha - \mathcal{N}\mu)) \tag{9.33}$$

$$p_\alpha = \frac{\exp\left(-\beta(\mathcal{E}_\alpha - \mathcal{N}\mu)\right)}{\Phi(T,V,\mu)} \tag{9.34}$$

Here, we use the symbol α or μ interchangeably, to mean the same thing—the index for microstates. **It represents the collection of quantum numbers that characterize the energy eigenstate $|\Psi_\alpha(\mathcal{N})\rangle$ for $\mathcal{N}$ particles.** We shall find that the grand canonical ensemble is of particular importance for quantum statistics. For this reason, α may be preferred to μ, in order to avoid confusion between symbols (μ for microstate and μ for chemical potential).

The case of the Gibbs canonical ensemble is left for your exercise.

9.6 The partition function

As part of the discussion in the previous section, we have just now discussed the various ensembles and the associated partition functions.

In particular, the partition function is already given in Eq. 9.31. Since this is the first time to discuss it in quantum statistical mechanics, let us have a closer look at the way it arises from the density matrix formalism. From the consideration of the canonical ensemble in contact with a reservoir, we know that the probability associated with each microstate in a canonical ensemble is proportional to $\exp(-\beta\mathcal{E}_\alpha)$. So, the density matrix is given by

$$\rho = \sum_{\alpha} \frac{\exp(-\beta\mathcal{E}_\alpha)}{Z} |\Psi_\alpha\rangle\langle\Psi_\alpha| \tag{9.35}$$

where Z is defined as the probability normalization constant, as it should be. By taking the trace of the density matrix with the energy eigenstate basis $|\Psi_{\alpha'}\rangle$, we get

$$\begin{aligned} \mathrm{tr}\,\{\rho\} &= \frac{\sum_{\alpha,\alpha'} \exp(-\beta\mathcal{E}_\alpha)\,\langle\,\Psi_{\alpha'}\,|\,\Psi_\alpha\rangle\,\langle\,\Psi_\alpha\,|\,\Psi_{\alpha'}\rangle}{Z} && (9.36)\\ &= \frac{\sum_{\alpha,\alpha'} \exp(-\beta\mathcal{E}_\alpha)(\delta_{\alpha,\alpha'})^2}{Z} \qquad \text{by Eq. 9.22} && (9.37)\\ &= \frac{\sum_\alpha \exp(-\beta\mathcal{E}_\alpha)}{Z} && (9.38) \end{aligned}$$

Note that $\mathrm{tr}\,\{\rho\} = 1$, by definition, due to the probability sum rule. Or, if you like, by Eq. 9.23, $\mathrm{tr}\,\{\rho\}$ is the ensemble average of the identity operator, and it must be 1. Therefore, we get

$$Z(T,V,N) = \sum_\alpha \exp(-\beta\mathcal{E}_\alpha) \qquad (9.39)$$

While this derivation is trivial, it does show the density matrix formalism at work. It also shows the density matrix is naturally a diagonal matrix in the energy basis. But, note that if we use other basis, say position basis, then it will no longer be diagonal.

9.7 An example—ideal gas, semi-classical view of quantum statistics

While the quantum mechanical problem of non-interacting particles (ideal gas) is most conveniently described in the grand canonical ensemble, studying the canonical ensemble for the same problem has some pedagogical content. So, let us spend a little time doing so.

Here, we do *not* ask what happens to the ideal gas at very low temperature or at very high density[20]. Instead, we ask what is the leading order correction to the semi-classical statistical mechanics due to the quantum statistics?

Let us recall that for calculating the partition function within the semi-classical statistical mechanics (Sections 6.3.4, 8.1), the key step was to consider the partition function of only one particle, as the result for the N particle case is equal to the N-th power of one particle partition function divided by N! (Section 8.1). Then, it might not come as a surprise for you that to answer the above question that we posed, it

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[20] Asking such a question means considering the so-called **quantum degenerate regime**, i.e., the regime of temperature/density where the quantum statistics becomes singularly important. We have already encountered such a regime in Section 9.1 (and Section 8.5), where the Bose-Einstein statistics has the full effect. The quantum degenerate regime is a topic that we will pay our full attention to in later lectures.

is sufficient to consider a two particle density matrix and a two particle partition function.

$$\rho_2 = \frac{\sum_\alpha e^{-\beta\mathcal{E}_\alpha}\left|\mathcal{E}_\alpha\right\rangle\left\langle\mathcal{E}_\alpha\right|}{Z_2} \tag{9.40}$$

$$Z_2 = \sum_\alpha e^{-\beta\mathcal{E}_\alpha} \tag{9.41}$$

We consider two fermions or two bosons. The quantum number, α, for two free particles is given by $\vec{k}_1, \vec{k}_2, s_1, s_2$, where $\vec{k}_1$, $\vec{k}_2$, are wave vectors, and s_1, s_2 are spin quantum numbers. We will assume that $s_1 = s_2$ throughout this section. In this spin subspace, we do not need to consider spin quantum numbers. Then, we have

$$\mathcal{E}_\alpha = \frac{\hbar(k_1^2 + k_2^2)}{2m} \tag{9.42}$$

$$\left|\mathcal{E}_\alpha\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\vec{k}_1, \vec{k}_2\right\rangle + \eta\left|\vec{k}_2, \vec{k}_1\right\rangle\right) \qquad \vec{k}_1 \neq \vec{k}_2,\ \eta = 1 \text{ for boson, } -1 \text{ for fermion} \tag{9.43}$$

$$= \left|\vec{k}_1, \vec{k}_2\right\rangle \qquad \vec{k}_1 = \vec{k}_2,\ \text{boson} \tag{9.44}$$

$$= 0 \text{ (no such state)} \qquad \vec{k}_1 = \vec{k}_2,\ \text{fermion} \tag{9.45}$$

where the exchange symmetry of the two particle case is explicitly taken care of in the last three equations.

Notice that, if we simply ignore the case $\vec{k}_1 = \vec{k}_2$, then the calculation of the partition function becomes very simple, and becomes identical with the classical result. In general, however, we have quite a complicated problem, here, due to the exchange symmetry. To deal with the exchange symmetry, it is convenient to introduce the **occupation number**, $n_{\vec{k}}$. Then we get the following results, which are valid for general values of the number of particles, N, while we are primarily interested in the $N = 2$ case, in this section.

$$\alpha \equiv \{n_{\vec{k}}\} \qquad \sum_{\vec{k}} n_{\vec{k}} = N \qquad n_{\vec{k}} = 0, 1 \text{ (fermion)},\ 0, 1, 2, \ldots \text{ (boson)} \tag{9.46}$$

$$\mathcal{E}_\alpha = \sum_{\vec{k}} \frac{\hbar k^2}{2m} n_{\vec{k}} \tag{9.47}$$

$$\left|\mathcal{E}_\alpha\right\rangle = \frac{1}{\sqrt{N! \prod_{\vec{k}} n_{\vec{k}}!}} \sum_P \eta^{s(P)} \left|P(\vec{\mathbf{k}})\right\rangle \tag{9.48}$$

Here, $\vec{\mathbf{k}}$ is the set of N wave vectors, some repeating $n_{\vec{k}}$ times if $n_{\vec{k}} > 1$, for which $n_{\vec{k}} > 0$. P is the permutation of those wave vectors. The function $s(P)$ is defined as the "sign of the permutation": it gives 1 if the permutation involves an even number of exchanges, and -1 if the permutation involves an odd number of exchanges. $\eta = 1$

for boson, and −1 for fermion, as already introduced above. Eq. 9.48 is written for general N (proof left for your exercise), while it is easy to see that our explicit wave functions given above (Eqs. 9.43,9.44,9.45) are consistent with it.

While the expression for the partition function seems simple, $Z = \sum_\alpha e^{-\beta\mathcal{E}_\alpha}$, it is not simple to evaluate it, since the α index is *not* simple, being highly constrained by the exchange symmetry.

Let us look at the density matrix ρ in the space representation, to figure out how we might achieve the goal of calculating the partition function. We shall carry out this calculation for the $N = 2$ case, while the extension to the general N case will become clear.

$$\begin{aligned}
\langle \vec{r}_1, \vec{r}_2 \,|\rho|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \rangle &= \sum_{\{\vec{k}_1,\vec{k}_2\}} \frac{e^{-\beta\mathcal{E}_\alpha}}{Z_2} \langle \vec{r}_1, \vec{r}_2 \,|\, \mathcal{E}_\alpha \rangle \langle \mathcal{E}_\alpha \,|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \rangle \\
&= \sum_{\vec{k}_1} \sum_{\vec{k}_2} \frac{n_{\vec{k}_1}! n_{\vec{k}_2}!}{2!} \frac{e^{-\beta\mathcal{E}_\alpha}}{Z_2} \langle \vec{r}_1, \vec{r}_2 \,|\, \mathcal{E}_\alpha \rangle \langle \mathcal{E}_\alpha \,|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \rangle \\
&= \sum_{\vec{k}_1} \sum_{\vec{k}_2} \sum_{P,P'} \frac{\eta^{s(P)+s(P')}}{(2!)^2} \frac{e^{-\beta\mathcal{E}_\alpha}}{Z_2} \left\langle \vec{r}_1, \vec{r}_2 \,\middle|\, P(\vec{k}_1, \vec{k}_2) \right\rangle \left\langle P'(\vec{k}_1, \vec{k}_2) \,\middle|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \right\rangle
\end{aligned}$$

Here in the first line, the sum over $\{\vec{k}_1, \vec{k}_2\}$ is restricted to a unique set of two (possibly the same, for bosons) wave vectors, while from the second line on the sums over $\vec{k}_1$ and $\vec{k}_2$ are unrestricted. The over-counting introduced by this change in sum is taken care of by the division by the multinomial coefficient, $N!/\prod_{\vec{k}} n_{\vec{k}}$. To get the last equation, Eq. 9.48 (for $N = 2$) has been used.

It is easy to consider all permutations of two wave vectors.

$$\begin{aligned}
\langle \vec{r}_1, \vec{r}_2 \,|\rho|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \rangle = \frac{1}{(2!)^2} \sum_{\vec{k}_1} \sum_{\vec{k}_2} \frac{e^{-\beta\mathcal{E}_\alpha}}{Z_2} \Big[&\left\langle \vec{r}_1, \vec{r}_2 \,\middle|\, \vec{k}_1, \vec{k}_2 \right\rangle \left\langle \vec{k}_1, \vec{k}_2 \,\middle|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \right\rangle \\
&+ \left\langle \vec{r}_1, \vec{r}_2 \,\middle|\, \vec{k}_2, \vec{k}_1 \right\rangle \left\langle \vec{k}_2, \vec{k}_1 \,\middle|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \right\rangle \\
&+ \eta \left\langle \vec{r}_1, \vec{r}_2 \,\middle|\, \vec{k}_2, \vec{k}_1 \right\rangle \left\langle \vec{k}_1, \vec{k}_2 \,\middle|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \right\rangle \\
&+ \eta \left\langle \vec{r}_1, \vec{r}_2 \,\middle|\, \vec{k}_1, \vec{k}_2 \right\rangle \left\langle \vec{k}_2, \vec{k}_1 \,\middle|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \right\rangle \Big]
\end{aligned}$$

Note that

$$\left\langle \vec{r}_1, \vec{r}_2 \,\middle|\, \vec{k}_1, \vec{k}_2 \right\rangle = \frac{e^{i\vec{k}_1\cdot\vec{r}_1} e^{i\vec{k}_2\cdot\vec{r}_2}}{V} \tag{9.49}$$

where the one body wave function is normalized within the volume of V, with the wave function normalization factor $\frac{1}{\sqrt{V}}$. Inserting this wave function to the above expression for ρ, and also noting that $\vec{k}_1$ and $\vec{k}_2$ are dummy indices that can be swapped, we get

$$\langle \vec{r}_1, \vec{r}_2 \,|\rho|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \rangle = \frac{2}{(2!V)^2} \sum_{\vec{k}_1} \sum_{\vec{k}_2} \frac{e^{-\beta \mathcal{E}_\alpha}}{Z_2} \left[e^{i\vec{k}_1 \cdot (\vec{r}_1 - \vec{r}^{\,\prime}_1)} e^{i\vec{k}_2 \cdot (\vec{r}_2 - \vec{r}^{\,\prime}_2)} + \eta e^{i\vec{k}_1 \cdot (\vec{r}_1 - \vec{r}^{\,\prime}_2)} e^{i\vec{k}_2 \cdot (\vec{r}_2 - \vec{r}^{\,\prime}_1)} \right]$$

Since $\mathcal{E}_\alpha = \frac{\hbar(k_1^2 + k_2^2)}{2m}$, this expression requires us to evaluate one summation

$$I = \sum_{\vec{k}} \exp\left(-\beta \frac{\hbar^2 k^2}{2m} + i\vec{k} \cdot \vec{q} \right)$$

Note that, using a periodic boundary condition for a cubic volume, V, we get

$$\vec{k} = \frac{2\pi}{L} m_i \qquad\qquad m_i = \text{integer};\ i = x, y, z \tag{9.50}$$

Thus,

$$\sum_{\vec{k}} = \sum_{k_x, k_y, k_z} = \frac{V}{(2\pi)^3} \int d^3\vec{k} \tag{9.51}$$

where the volume of the system is given by $V = L^3$. Thus, the above summation becomes

$$\begin{aligned} I &= \frac{V}{(2\pi)^3} \int dk_x dk_y dk_z \, \exp\left(-\beta \frac{\hbar^2 k^2}{2m} + i\vec{k} \cdot \vec{q} \right) \\ &= \frac{V}{(2\pi)^3} \left(\sqrt{\frac{2m\pi k_B T}{\hbar^2}} \right)^3 \exp\left(-\frac{m k_B T}{2\hbar^2} q^2 \right) \\ &= V \lambda^{-3} \exp\left(-\frac{\pi}{\lambda^2} q^2 \right) \end{aligned}$$

where λ is the thermal de Broglie wave length defined in Eq. 6.43. Using this, we get

$$\begin{aligned} \langle \vec{r}_1, \vec{r}_2 \,|\rho|\, \vec{r}^{\,\prime}_1, \vec{r}^{\,\prime}_2 \rangle = \frac{1}{2! Z_2 \lambda^6} \Big\{ & \exp\left(-\frac{\pi}{\lambda^2} \left[(\vec{r}_1 - \vec{r}^{\,\prime}_1)^2 + (\vec{r}_2 - \vec{r}^{\,\prime}_2)^2 \right] \right) \\ & + \eta \exp\left(-\frac{\pi}{\lambda^2} \left[(\vec{r}_1 - \vec{r}^{\,\prime}_2)^2 + (\vec{r}_2 - \vec{r}^{\,\prime}_1)^2 \right] \right) \Big\} \end{aligned} \tag{9.52}$$

Note that the density matrix is not diagonal in the position basis. From $\mathrm{tr}\{\rho\} = 1$, we get

$$Z_2 = \frac{1}{2! \lambda^6} \int d^3\vec{r}_1 d^3\vec{r}_2 \left(1 + \eta \exp\left[-\frac{2\pi}{\lambda^2} (\vec{r}_1 - \vec{r}_2)^2 \right] \right) \tag{9.53}$$

These two results are easily generalized to the arbitrary N case as

$$\langle \vec{r}_1,...,\vec{r}_N \,|\rho|\, \vec{r}'_1,...,\vec{r}'_N\rangle = \frac{1}{Z\,N!\lambda^{3N}}\sum_P \eta^{s(P)}\exp\left(-\frac{\pi}{\lambda^2}\sum_{i=1}^N(\vec{r}_i-\vec{r}'_{P(i)})^2\right) \tag{9.54}$$

$$Z = \frac{1}{N!\lambda^{3N}}\int\prod_i d^3\vec{r}_i\;\sum_P \eta^{s(P)}\exp\left(-\frac{\pi}{\lambda^2}\sum_{i=1}^N(\vec{r}_i-\vec{r}_{P(i)})^2\right) \tag{9.55}$$

Let us look at Z_2 in more detail.

$$Z_2 = \frac{1}{2!\lambda^6}\left[V^2+V\eta\left(\frac{\lambda}{\sqrt{2}}\right)^3\right] = \frac{V^2}{2!\lambda^6}\left[1+\eta\frac{\lambda^3}{V2\sqrt{2}}\right] \tag{9.56}$$

The first term corresponds to the semi-classical result $Z = \frac{V^N}{N!\lambda^{3N}} = \left(\frac{e}{n\lambda^3}\right)^N$, which results from the case when the permuation is the identity transformation (Eq. 9.55). As the indices are permuted, some $V \to \lambda^3$. Therefore, generally,

$$Z = \left(\frac{e}{n\lambda^3}\right)^N\left[1+a_1(n\lambda^3)+a_2(n\lambda^3)^2+...+a_{N-1}(n\lambda^3)^{N-1}\right] \tag{9.57}$$

$$= \left(\frac{e}{n\lambda^3}\right)^N\left[1+\eta\frac{N-1}{2^{5/2}}n\lambda^3+\;...\right] \tag{9.58}$$

While what we have done so far is valid for any temperature or any density, clearly, they are most useful when $n\lambda^3 \ll 1$. In fact, we have just proven that in the limit of $n\lambda^3 \to 1$, we recover the semi-classical result!

Let us look at the pressure (for large N)

$$\begin{aligned} P &= -\left(\frac{\partial F}{\partial V}\right)_T = k_BT\left(\frac{\partial \log Z}{\partial V}\right)_T = k_BTn - \eta\frac{n^2}{2^{5/2}}\lambda^3+... \\ &= nk_BT\left[1-\eta\frac{n\lambda^3}{2^{5/2}}+\;...\right] \end{aligned} \tag{9.59}$$

This implies that the first quantum correction to pressure is positive for fermions and negative for bosons. Thus, one might say that fermions tend to repel one another, while bosons tend to attract one another, *just due to statistics.*

This can be verified by examining the $N = 2$ density matrix, Eq. 9.52. The diagonal terms are given by

$$\langle \vec{r}_1,\vec{r}_2 \,|\rho|\, \vec{r}_1,\vec{r}_2\rangle = \frac{1}{2!Z_2\lambda^6}\left\{1+\eta\exp\left(-\frac{2\pi r^2}{\lambda^2}\right)\right\}. \qquad r \equiv |\vec{r}_1-\vec{r}_2| \tag{9.60}$$

This shows that the probability to find two particles at distance r is (1) uniform for semi-classical ideal gas, (2) enhanced for bosons ($\eta = 1$), and (3) reduced for fermions

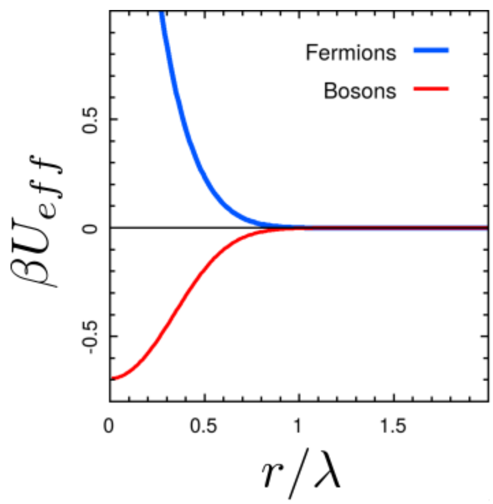
($\eta = -1$). The effect is, as expected, significant only for distance on the order of λ or smaller.

More quantitatively, one can interpret[21] the above density matrix as occurring due to an effective two-body potential, $U_{eff}(r)$, such that

$$\langle \vec{r}_1, \vec{r}_2 \,|\rho|\, \vec{r}_1, \vec{r}_2 \rangle = \frac{1}{Z_2 2! \lambda^6} \exp\left(-\beta U_{eff}(r)\right), \tag{9.61}$$

$$U_{eff}(r) \equiv -k_B T \log\left\{1 + \eta \exp\left(-\frac{2\pi r^2}{\lambda^2}\right)\right\}. \tag{9.62}$$

Here is the figure comparing this potential plotted for the Fermion case ($\eta = -1$) and the Boson case ($\eta = 1$).



While the effective potential is quite negligible if $r \gg \lambda$, the quantum degeneracy kicks in when $r \approx \lambda$ and for $r < \lambda$, the effective potential is repulsive and divergent for fermions (blue), while it is attractive for bosons (red).

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[21] Here, what we are doing is "remapping" our quantum mechanical result to the semi-classical picture of two particles interacting via $U_{eff}(r)$. Consider what would happen to Eq. 6.44 for two semi-classical particles if they interacted via $U_{eff}(r)$? The answer is that Z_2 is proportional to the integration $\int d^3\vec{r}_1 d^3\vec{r}_2\, e^{-\beta U_{eff}(r)}$ up to a multiplicative factor $(1/(2!\lambda^6))$. Looking at this result, one can ask—what would be the probability of finding the two semi-classical particles at $\vec{r}_1$ and $\vec{r}_2$, respectively? The answer is Eq. 9.61. I strongly encourage you to go through this derivation yourself, based on hints contained in this footnote.

9.8 Rotational mode

A quantum rigid body has the Hamiltonian

$$H_{rot} = \frac{\vec{L}^2}{2I} \tag{9.63}$$

where I is the rotational inertia, and $\vec{L}$ is the angular momentum.

The analysis of this problem (see below) with the quantized angular momentum proceeds much like for the single oscillator, except that the partition function cannot be summed exactly. Nevertheless, the (constant volume) heat capacity shows the same qualitative behavior—it is exponentially suppressed at low T, while it goes to the classical value k_B at high T.

The characteristic temperature scale for the quantum rotation can be defined as

$$\theta_{rot} = \frac{\hbar^2}{2Ik_B} \tag{9.64}$$

Using k_B = 25.85 meV / 300 K, $\hbar c$ = 1973 eV Å, and using typical values for Ic^2 (keeping in mind that $I = Ma^2$, where M is the atomic mass and a is the atomic dimension), one can estimate that $\theta_{rot} \sim 1$ K. So, the crossover from the quantum regime to the classical regime occurs at very low temperature in this case, quite different from the vibrational case, in which the crossover to the classical regime happens at room temperature or higher.

$$Z = \sum_{l=0}^{\infty}(2l+1)\exp\left(-\beta\frac{l(l+1)\hbar^2}{2I}\right) = \sum_{l=0}^{\infty}(2l+1)\exp\left(-\frac{\theta_{rot}}{T}\,l(l+1)\right) \tag{9.65}$$

In the classical regime, the l sum can be turned into an integral, with the continuous variable $x \equiv l(l+1)$. Then, we get

$$Z \approx \int_0^\infty dx \exp\left(-\frac{\theta_{rot}}{T}x\right) = \frac{T}{\theta_{rot}} \qquad T \gg \theta_{rot} \tag{9.66}$$

$$E \approx -\frac{\partial \log Z}{\partial \beta} = k_B T \qquad T \gg \theta_{rot} \tag{9.67}$$

$$C_V \approx k_B \qquad T \gg \theta_{rot} \tag{9.68}$$

The latter two results are as expected from the equipartition theorem. The rotational kinetic energy is given by $K\frac{I}{2}\dot{\theta}^2 + \frac{I}{2}\sin^2\theta\,\dot{\phi}^2 = L$, from which the Hamiltonian can be written as $H_{rot} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}$, with $p_\theta = \frac{\partial L}{\partial \dot\theta} = I\dot\theta$ and $p_\phi = \frac{\partial L}{\partial \dot\phi} = I\sin^2\theta\,\dot\phi$. Thus, the Hamiltonian consists of two quadratic terms, giving rise to the equipartition energy $\frac{k_BT}{2} \times 2$.

In the quantum regime, the partition function is can be approximated with the first few terms.

$$Z \approx 1 + 3\exp\left(-\frac{2\theta_{rot}}{T}\right) \qquad T \ll \theta_{rot} \tag{9.69}$$

$$E \approx 6k_B\theta_{rot}\exp\left(-\frac{2\theta_{rot}}{T}\right) \qquad T \ll \theta_{rot} \tag{9.70}$$

$$C_V \approx 3k_B\left(\frac{2\theta_{rot}}{T}\right)^2\exp\left(-\frac{2\theta_{rot}}{T}\right) \qquad T \ll \theta_{rot}. \tag{9.71}$$