Notes for Lecture 10

Scattering, Quantum statistical mechanics

It is important that what we discussed so far is related to measurements. Of course, the equation of state is something that one can measure. Indeed, measurements and characterizations of the equation of state came first, and then our theoretical understanding of it came next. We also saw that, in homework problems, the measured data of the specific heat of solids can give access to the entropy and other fundamental thermodynamic functions. In closing the semi-classical statistical mechanics, maybe it is fit to describe another important class of experiments – wave scattering. One should always keep in mind that experimental data carry all information regarding the interactions present in the system. Just because the theory cannot handle all the interactions should not deter a phenomenological understanding which can be developed from a critical set of data and good theoretical ideas.

After touching upon this topic, we will go ahead to the quantum statistical mechanics.

10.1 Scattering of wave

The starting point of any scattering discussion can be taken as

$$\psi(\vec{x}) \;=\; \exp(i\vec{k}\cdot\vec{x}) + f(k,\theta)\frac{\exp(ikr)}{r} \tag{10.1}$$

Here, we shall confine ourselves to an elastic scattering, so $k = |\vec{k}|$ is used in the second term. In other words, we are considering a diffraction. While this form

of wave function should be familiar from the elementary non-relativistic quantum mechanics, this wave function can be viewed as generally applicable for any wave that gets scattered. That is, whether the incoming wave consists of light particles, electrons, or even atoms/molecules, the above formula says that it comes in in a plane wave form (by an experimental setup) and then scatters off with the quantum amplitude $f(k,\theta)$[1] in a form of a spherical wave with angle dependence included by the θ dependence of θ.

In the above expression, the implicit assumption is that the sample by which the wave is scattered is small in comparison to the experimental dimensions. Importantly, the sample to the detector distance (r) is large compared to the sample size so that it makes sense to say that the sample is placed at the origin and acts as a point source, as the above equation implies.

So the above equation satisfactorily describes the experiment. But, here we are interested in the theory of it.

For doing the theory, let us suppose that our sample consists of N fixed scattering centers.[2] We can then apply the above formula to each scattering center. With the origin fixed somewhere inside the sample, the individual scatterer will cause

$$\psi_j(\vec{x}) \;=\; \exp(i\vec{k}\cdot\vec{x}) + \exp(i\vec{k}\cdot\vec{x}_j)\, f_j(k,\theta_j)\, \frac{\exp\left(ik|\vec{x}-\vec{x}_j|\right)}{|\vec{x}-\vec{x}_j|} \tag{10.2}$$

In the second term, the $\exp(i\vec{k}\cdot\vec{x}_j)$ term accounts for the extra phase that is accumulated before the light scatters off of the scattering center at $\vec{x}_j$ as opposed to the origin.[3] The angle θ_j means the angle of the outgoing vector $\vec{x}-\vec{x}_j$. Now, let us assume that each scattering center is identical. So, we put $f_m(\theta_j) \equiv f_j(\theta_j)$ with the subscript m is used to mean "molecule."[4] In addition, using the same assumption as described above, we can put $\theta_j \approx \theta$ and $|\vec{x}-\vec{x}_j| \approx r$ where r, θ as defined in Eq. 10.2. Also, note[5] that $\exp(ik|\vec{x}-\vec{x}_j|) \approx \exp(ikr)\exp(-i\vec{k'}\cdot\vec{x}_j)$. Thus, summing up[6] the diffracted part of the wave we get the total scattering amplitude $f(k,\theta)$ of Eq. 10.2

[1] You can, and should try to, show that $d\sigma/d\Omega = |f(k,\theta)|^2$.

[2] So, here we are assuming that during the scattering event, the movement of atoms is much less than the wavelength of the probing wave.

[3] Some more discussions of this problem can be found at this URL (homework 3 solutions).

[4] If a molecule consists of an array of atoms, then one can extend this current consideration to see that $f_m = \sum_l \exp(i\vec{k}\cdot(\vec{x}_{a,l,j}-\vec{x}_j)) f_{a,l,j}$, where $f_{a,l,j}$ is an *atomic form factors* for the l-th atom, and f_m is the so-called a *structure factor*.

[5] This was shown in class. Also, see footnote 3.

[6] You may wonder whether this simple summing up is good enough, worrying that there may be multiple scattering events. Indeed such multiple scattering is known to be important for electron diffraction. For X-ray scattering, it is less of a concern.

in terms of $f_m(k,\theta)$'s as

$$f(k,\theta) \;=\; f_m(k,\theta)\sum_j e^{-i(\vec{k}'-\vec{k})\cdot\vec{x}_j} \;=\; f_m(k,\theta)\sum_j e^{-i\vec{q}\cdot\vec{x}_j} \tag{10.3}$$

$$\vec{q} \;\equiv\; \vec{k}'-\vec{k} \tag{10.4}$$

For a unit incoming flux of the wave, the intensity of the diffracted wave measured by the detector at distance r and angle θ is given by

$$I \;=\; \frac{|f(k,\theta)|^2}{r^2} \;=\; \frac{|f_m(k,\theta)|^2}{r^2}\sum_{j,l} e^{-i\vec{q}\cdot(\vec{x}_j-\vec{x}_l)} \tag{10.5}$$

Finally, the ensemble average must be taken to take into account of the statistical distribution of microstates

$$I \;=\; \frac{|f(k,\theta)|^2}{r^2} \;=\; \frac{|f_m(k,\theta)|^2}{r^2}\left\langle\sum_{j,l} e^{-i\vec{q}\cdot(\vec{x}_j-\vec{x}_l)}\right\rangle \tag{10.6}$$

Recall from Eq. 6.14 that (with a change of notation $\vec{q}\to\vec{x}$, and dropping the t dependence as we are concerned with an equilibrium property here)

$$f_2(\vec{p},\vec{x},\vec{p}\,',\vec{x}') = \left\langle\sum_{j\neq l}\delta(\vec{p}-\vec{p}_j)\delta(\vec{x}-\vec{x}_j)\delta(\vec{p}\,'-\vec{p}_l)\delta(\vec{x}\,'-\vec{x}_l)\right\rangle$$

is the *two particle density function*. Integrating over momentum variables, we get the **two particle distribution function** or the **pair distribution function**

$$n_2(\vec{x},\vec{x}') \;=\; \left\langle\sum_{j\neq l}\delta(\vec{x}-\vec{x}_j)\delta(\vec{x}'-\vec{x}_l)\right\rangle \tag{10.7}$$

From this, it follows that

$$\left\langle\sum_{j\neq l} e^{-i\vec{q}\cdot(\vec{x}_j-\vec{x}_l)}\right\rangle \;=\; \int d^3\vec{x}\, d^3\vec{x}'\, e^{-i\vec{q}\cdot(\vec{x}-\vec{x}')}\, n_2(\vec{x},\vec{x}') \tag{10.8}$$

So, the diffraction intensity is proportional to the Fourier transform of the two particle distribution function. Note that the two particle distribution function is of order N^2. So, we can drop the diagonal sum ($j=l$) in Eq. 10.5, which gives N. Assuming that the translation invariance holds[7],

$$n_2(\vec{x},\vec{x}') \;=\; n_2(\vec{x}-\vec{x}') \tag{10.9}$$

[7]This should hold in normal situations. However, if considering a system of liquid residing in a crystalline environment, this assumption will be broken. In that case, the crystal translation invariance must be incorporated instead.

So, the diffraction intensity is finally expressed as

$$I(k,r,\theta) \;=\; \frac{|f_m(k,\theta)|^2\, V}{r^2}\, \widetilde{n}_2(\vec{q}) \tag{10.10}$$

where, to recapitulate, k is the magnitude of the wave number of the probe wave, r, θ define the position of the outgoing wave detector relative to the sample, V is the sample volume, and $\widetilde{n}_2(\vec{q})$ is the Fourier transform of $n_2(\vec{x}, \vec{x}')$ with respect to $\vec{x} - \vec{x}'$.

So, assuming that one has access to the f_m quantity, it is possible to measure directly the two particle density function just by doing a scattering experiment!

10.2 Thermodynamic functions from pair distribution

In semi-classical statistical mechanics, if $n_2(\vec{x}, \vec{x}')$ is known completely, then all thermodynamic functions can be derived. Here, we will show that E can be derived. In a homework problem, you will show that P can de derived from $n_2(\vec{x}, \vec{x}')$.

Recall from the discussion of Section 7.2.2, we have

$$E = \left.\frac{\partial \log Z}{\partial(-\beta)}\right|_{T,V}$$

The partition function is given by, in the presence of the interaction (from Eq. abc),

$$\log Z \;=\; -3N \log \lambda(T) - \log N! + \log\left[\int d\vec{\mathbf{q}}\, \exp(-\beta H_{int})\right] \tag{10.11}$$

where $H_{int} = \sum_{i<j} U_{ij}$. The derivative of the $\lambda(T)$-containing term gives the equipartition energy for the kinetic energy, which is $\frac{3}{2} N k_B T$. Effecting the differentiation of

the last term, we get

$$E = \frac{3}{2}Nk_BT + \frac{\int d\vec{\mathbf{q}}\, H_{int}\exp(-\beta H_{int})}{\int d\vec{\mathbf{q}}\,\exp(-\beta H_{int})} \tag{10.12}$$

$$= \frac{3}{2}Nk_BT + \frac{1}{2}\sum_{i\neq j}\frac{\int d\vec{\mathbf{q}}\, U_{ij}\exp(-\beta H_{int})}{\int d\vec{\mathbf{q}}\,\exp(-\beta H_{int})} \tag{10.13}$$

$$= \frac{3}{2}Nk_BT + \frac{1}{2}\sum_{i\neq j}\frac{\int d\vec{\mathbf{q}}\, U(\vec{q}_i,\vec{q}_j)\exp(-\beta H_{int})}{\int d\vec{\mathbf{q}}\,\exp(-\beta H_{int})} \tag{10.14}$$

$$= \frac{3}{2}Nk_BT + \frac{1}{2}\sum_{i\neq j}\int d^3\vec{x}d^3\vec{x}'U(\vec{x},\vec{x}')\frac{\int d\vec{\mathbf{q}}\,\delta(\vec{x}-\vec{q}_i)\delta(\vec{x}'-\vec{q}_j)\exp(-\beta H_{int})}{\int d\vec{\mathbf{q}}\,\exp(-\beta H_{int})} \tag{10.15}$$

$$= \frac{3}{2}Nk_BT + \frac{1}{2}\int d^3\vec{x}d^3\vec{x}'U(\vec{x},\vec{x}')\sum_{i\neq j}\frac{\int d\vec{\mathbf{q}}\,\delta(\vec{x}-\vec{q}_i)\delta(\vec{x}'-\vec{q}_j)\exp(-\beta H_{int})}{\int d\vec{\mathbf{q}}\,\exp(-\beta H_{int})} \tag{10.16}$$

$$= \frac{3}{2}Nk_BT + \frac{1}{2}\int d^3\vec{x}d^3\vec{x}'U(\vec{x},\vec{x}')n_2(\vec{x},\vec{x}') \tag{10.17}$$

where, in the last step, we simply used the fact that the pair distribution function is the ensemble average of the two particle density in the real space, $\sum_{i\neq j}\delta(\vec{x}-\vec{q}_i)\delta(\vec{x}'-\vec{q}_j)$. Thus, assuming that we know the form of the two particle potential, $U(\vec{x},\vec{x}')$, we can simply derive the energy from the two particle distribution function.

10.3 Quantum statistical mechanics

Let us look back on what we did so far with semi-classical mechanics. We first defined a density function in the phase space. We discussed general properties such as the Liouville theorem and the Poincaré recurrence. We also discussed some limited phenomenological theory of the time reversal symmetry breaking (i.e. how an irreversible process actually arises) – Boltzmann equation and his H theorem. Then, we made a leap into the statistical mechanics, deciding not to worry too much about how the time reversal symmetry breaking occurs. Instead we asserted that the system settles for the most probable state (see Eqs. 7.11 through 7.13) and this maximum entropy principle was taken as an axiom. From this, all other laws of thermodynamics were derived (except the third law, which cannot be derived from semi-classical physics).

Now, starting in quantum mechanics, we do pretty much the same. We are actually well prepared for it, since many of what we did in semi-classical statistical mechanics applies also to the quantum statistical physics (e.g., all the thermodynamic relations

and how we go from the partition function to the grand partition function, etc.). Let us mention what needs to be changed in quantum statistical mechanics.

10.3.1 Micro state

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

Instead, a micro state 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.

10.3.2 Ensemble, density matrix

Let us recall (Section 5.3) that the ensemble is a device by which we assert that there is a many-to-one mapping from micro states (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 5.6), 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 (micro state). 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 micro states. This leads to the definition of the *density matrix*, the quantum equivalent to the probability density function in semi-classical statistical mechanics:

$$\rho(t) \equiv \sum_\alpha p_\alpha |\Psi_\alpha\rangle \langle\Psi_\alpha| \tag{10.18}$$

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

$$p_\alpha \geq 0, \qquad \sum_\alpha p_\alpha \;=\; 1 \tag{10.19}$$

10.3.3 Properties of the density matrix

1. The density matrix is a Hermitian operator. This is clear because each projection operator is a Hermitian: $(|\Psi\rangle\langle\Psi|)^\dagger = \langle\Psi|^\dagger |\Psi\rangle^\dagger = |\Psi\rangle\langle\Psi|$.

2. We must keep in mind that $|\Psi\rangle_\alpha$ represent an observable state, and so it is necessarily an eigenstate of a Hermitian operator such as Hamiltonian or momentum, etc. As such, they must form a complete and orthonormal set.

$$\sum_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha| \;=\; 1 \tag{10.20}$$

$$\langle\Psi_\alpha|\,\Psi_\beta\rangle \;=\; \delta_{\alpha,\beta} \tag{10.21}$$

   However, notice that, even if $|\Psi\rangle$'s are chosen not to be a complete and orthonormal set by some "mistake," the density matrix can always be diagonalized with the complete orthonormal basis due to it being a Hermitian matrix (item 1).

3. Just as in the semi-classical case, a **pure state** is defined as an ensemble consisting of just one micro state. A **mixed state** is an ensemble consisting of more than one possible micro states. Note that $\rho^2 = \rho$ if and only if we have a pure state (left as your exercise to show it).

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

$$\overline{\langle O\rangle} \;=\; \mathrm{tr}\,\{\rho O\} \tag{10.22}$$

   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 $\langle O\rangle$.
   PROOF ✎ `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` $\mathrm{tr}\,\{\rho O\}$`. This can be`

accomplished by inserting the resolution of the identify above (Eq. 10.20).

$$\begin{aligned}\sum_\gamma p_\gamma \langle \Psi_\gamma | O | \Psi_\gamma \rangle &= \sum_{\gamma,\alpha} p_\gamma \langle \Psi_\gamma | \Psi_\alpha \rangle \langle \Psi_\alpha | O | \Psi_\gamma \rangle \\ &= \sum_{\gamma,\alpha} p_\alpha \langle \Psi_\gamma | \Psi_\alpha \rangle \langle \Psi_\alpha | O | \Psi_\gamma \rangle \qquad \text{using Eq. 10.21} \\ &= \sum_\gamma \langle \Psi_\gamma | \rho O | \Psi_\gamma \rangle \qquad \text{Eq. 10.18} \\ &= \mathtt{tr}\{\rho O\}\end{aligned}$$

QED. ✎

5. In the Heisenberg picture of quantum mechanics

$$\frac{d\rho}{dt} = 0 \tag{10.23}$$

This is the direct equivalent to Eq. 5.23. I.e., this is 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. Note that for any operator[8] O,

$$\frac{dO}{dt} = \frac{i}{\hbar}[H, O] + \frac{\partial O}{\partial t} \tag{10.24}$$

where $\frac{\partial O}{\partial t}$ is non-zero only if O has an explicit time dependence.[9] Namely, $\frac{\partial O}{\partial t}$ is the time derivative of O in the Schrödinger picture. Applying the Liouville

[8] And even when H is time dependent.

[9] PROOF ✎

$$\begin{aligned}U(t+dt) &= \left(1 - \frac{i}{\hbar} H dt\right) U(t) \\ \frac{dU(t)}{dt} &= -\frac{i}{\hbar} H U(t)\end{aligned}$$

where $U(t)$ is defined as the time evolution operator. Defined this fundamental a way, H *can* be time dependent. From $O_h(t) = U^\dagger(t) O_s(t) U(t)$ (where h means Heisenberg picture and s means Schrödinger picture), we get

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

If H commutes at different times, the first term becomes $\frac{i}{\hbar}[H, O_h]$. The second term is, by definition, $\frac{\partial O_h}{\partial t}$. QED. ✎

theorem above, we get

$$\frac{\partial \rho}{\partial t} \;=\; -\frac{i}{\hbar}\,[H,\rho] \tag{10.25}$$

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

$$\frac{d\overline{\langle O\rangle}}{dt} \;=\; \mathrm{tr}\left\{\frac{\partial \rho}{\partial t}\,O\right\} \tag{10.26}$$

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

$$\frac{\partial \rho}{\partial t} \;=\; -\frac{i}{\hbar}\,[H,\rho] \;=\; 0 \tag{10.27}$$

for an equilibrium state. And, we take this as the fundamental postulate here, just as we did in semi-classical statistical mechanics (Section 5.6).

6. For a micro canonical ensemble in equilibrium,

$$p_\alpha \;=\; \frac{1}{\Omega(E,V,N)} \tag{10.28}$$

where $\Omega(E,V,N)$ is the number of micro states, i.e. the number of many body states ("wave functions") $|\Psi_\alpha\rangle$. The entropy is given by[10]

$$S(E,V,N) \;=\; k_B\,\log\Omega(E,V,N) \tag{10.29}$$

For a canonical ensemble, we have

$$Z(T,V,N) \;=\; \sum_\alpha \exp(-\beta E_\alpha) \qquad\qquad H\,|\Psi_\alpha\rangle = E_\alpha\,|\Psi_\alpha\rangle \tag{10.30}$$

$$p_\alpha \;=\; \frac{\exp\left(-\beta E_\alpha\right)}{Z(T,V,N)} \tag{10.31}$$

For a grand canonical ensemble, we have

$$\mathcal{Q}(T,V,\mu) \;=\; \sum_\alpha \exp(-\beta(E_\alpha - N\mu)) \tag{10.32}$$

$$p_\alpha \;=\; \frac{\exp\left(-\beta(E_\alpha - N\mu)\right)}{\mathcal{Q}(T,V,N)} \tag{10.33}$$

[10]This is the so-called Gibbs entropy. This definition can be extended to non-equilibrium states: by generalizing the Boltzmann's H function, we can define the von Neumann entropy, $S = -k_B\,\mathrm{tr}\,\{\rho\log\rho\}$.