1 Why is "Thermal Average" needed & how is it done ?

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Real objects atoms/ions are in motion. From a classical point of view this means that their positions are not fixed. From a quantum mechanical point of view the object may be exploring different eigenstates with the probability $P_n \propto \exp -\beta E_n$, where n is a label of the eigenstate with energy E_n and as usual $\beta = \dfrac{1}{kT}$ We will deal with the consequence of this for the specific case of the structure factor. The structure factor of a collection of atoms whose positions are given by r_n, is defined as :

$$S(\vec{q}) = \sum_n e^{i\vec{q}.\vec{r_n}} \tag{1}$$

The instantaneous position has a mean part and a time varying part (the notation should be self explanatory)

$$\vec{r_n} = \vec{R_n} + \vec{u_n}(t) \tag{2}$$

Now if the time dependent part $\vec{u_n}$ is ignored, then we get back the definition of the static structure factor, which is frequently evaluated for various lattice and basis sets. Recall that even in a solid the amplitude of the the thermal vibrations of the atoms sitting in lattice sites can be $\sim 10\%$ of the inter-atomic spacing. Important experimental observables like intensity of X-rays scattered in a particular direction depends of $|S(\vec{q})|^2$. How will the averaged time dependence affect the observed scattered intensity? Will it broaden a peak or do something else? This question was clearly answered by Debye and Waller. The result is generally called the "Debye-Waller" factor.

$$\langle S(\vec{q})\rangle = \underbrace{\left(\sum e^{i\vec{q}.\vec{R_n}}\right)}_{\text{static structure factor}} \frac{\sum e^{i\vec{q}.\vec{u_n}} e^{-\beta H}}{\sum e^{-\beta H}} = \underbrace{\left(\sum e^{i\vec{q}.\vec{R_n}}\right)}_{\text{static structure factor}} \frac{\int d\vec{p}\; d\vec{u_n} e^{i\vec{q}.\vec{u_n}} e^{-\beta H}}{\int d\vec{p}\; d\vec{u_n} e^{-\beta H}} \tag{3}$$

Here we have assumed that the thermal average of all the u_n will be identical. Since this is fluctuating part of the position co-ordinate, this is not a particularly wrong assumption. So the problem ultimately reduces to doing a thermal average of an exponential quantity or an operator. From here on, we can drop the explicit t dependence of $\vec{u_n}$, it is implied.

1.1 Classical case

$$\left\langle e^{i\vec{q}.\vec{u}}\right\rangle = \frac{\int d\vec{p}\; d\vec{u} e^{i\vec{q}.\vec{u}} e^{-\beta H}}{\int d\vec{p}\; d\vec{u} e^{-\beta H}} \tag{4}$$

We can take the relevant part of the Hamiltonian to be , with the understanding that $u_x = x, u_y = y, u_z = z$

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 \left(x^2 + y^2 + z^2\right) \tag{5}$$

It is straightforward to see that the momentum co-ordinates are simply going to separate out and cancel, so the relevant part will be

$$\left\langle e^{i\vec{q}.\vec{u}}\right\rangle = \left(\frac{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 x^2} e^{iq_x x} dx}{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 x^2} dx}\right) \left(\frac{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 y^2} e^{iq_y y} dy}{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 y^2} dy}\right) \left(\frac{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 z^2} e^{iq_z z} dz}{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 z^2} dz}\right) \tag{6}$$

The first term on the RHS can be written, by completing the square on the gaussian integral in the numerator

$$\frac{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 x^2} e^{iq_x x} dx}{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 x^2} dx} = \frac{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 \left[x^2 - 2i\frac{q_x}{\beta m\omega^2} + \left(\frac{q_x}{\beta m\omega^2}\right)^2\right]} dx}{\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m\omega^2 x^2} dx} \times e^{-\dfrac{{q_x}^2}{\beta m\omega^2}} \tag{7}$$

Hence

$$\left\langle e^{i\vec{q}.\vec{u}}\right\rangle = e^{-\frac{{q_x}^2}{\beta m\omega^2}} \times e^{-\frac{{q_y}^2}{\beta m\omega^2}} \times e^{-\frac{{q_x}^2}{\beta m\omega^2}} \tag{8}$$

Now recall the classical equipartition theorem applied to potential energy of the vibrational degrees of freedom,

$$\frac{1}{2}m\omega^2\left\langle x^2\right\rangle = \frac{1}{2}m\omega^2\left\langle y^2\right\rangle = \frac{1}{2}m\omega^2\left\langle z^2\right\rangle = \frac{1}{2}kT \tag{9}$$

and by isotropy

$$\left\langle x^2\right\rangle = \left\langle y^2\right\rangle = \left\langle x^2\right\rangle = \left\langle \frac{u^2}{3}\right\rangle \tag{10}$$

Combining the results from equations 10, 9 and 8, we get

$$\boxed{\left\langle e^{i\vec{q}.\vec{u}}\right\rangle^2 = e^{-\frac{q^2\left\langle u^2\right\rangle}{3}}} \tag{11}$$

This means that the effect of temperature will be to suppress the value of $S(\vec{q})$, but not to broaden it. This is exactly what one observes in the temperature dependence of the height of the X-ray diffraction peaks, obviously here $\vec{q} = \vec{G}$ must be satisfied, where $\vec{G}$ is some reciprocal lattice vector.

1.2 The quantum mechanical case

A legitimate question is whether the result will continue to hold if the thermal averaging was carried out quantum mechanically under similar assumptions. The key assumption we used was that the oscillations are simple harmonic. However a classical result with harmonic oscillators is not necessarily true if treated quantum mechanically. In this case however this result, quite remarkably, holds exactly. We will prove a general identity for thermal average of an operator that is linear in position and momentum co-ordinates or equivalently in a and $a^\dagger$.

If

$$C = \lambda a + \mu a^\dagger \tag{12}$$

Then the following result, called the Bloch identity, holds:

$$\left\langle e^C\right\rangle = \frac{\sum_n e^{-\beta E_n}\left\langle n|e^C|n\right\rangle}{\sum_n e^{-\beta E_n}} = e^{\frac{\langle C\rangle^2}{2}} \tag{13}$$

provided $|n\rangle$ are harmonic oscillator states and $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$ as usual. Notice that these are the QM equivalents of the assumption we used in the classical case.

One can guess that expanding out the exponential will help, but this is quite non-trivial since a and $a^\dagger$ do not commute. To prove equation 13 we need to prove a sequence of results first. Since the operator C is a sum of two parts, we first ask how to relate e^{A+B} with e^Ae^B, remembering that A, B are non-commuting operators.

1.2.1 How different are e^{A+B} and e^Ae^B?

To address this question we recall a key result about *any* two operators A and B

$$\boxed{e^A\ B\ e^{-A} \ = \ B \ + \ [A,B] \ + \ \frac{1}{2!}[A,[A,B]] \ + \ \frac{1}{3!}[A,[A,[A,B]]] \ + \ \ldots} \tag{14}$$

In the special case the commutator $[A,B]$ is a number, it is easy to see that all terms after the first two in RHS will vanish. This turns out to be the case for x and p or a and $a^\dagger$.
The result 14 can be proved in the following way. Start by defining a function of a *numerical variable* u and trying to write out its Taylor expansion around $u = 0$

$$f(u) \ = \ e^{uA}\ B\ e^{-uA} \tag{15}$$

$$f'(u) \ = \ e^{uA}\ AB\ e^{-uA} \ - \ e^{uA}\ BA\ e^{-uA} = e^{uA}\ (AB - BA)\ e^{-uA} \tag{16}$$

$$f''(u) \ = \ e^{uA}\ A(AB - BA)\ e^{-uA} \ - \ e^{uA}\ (AB - BA)A\ e^{-uA} = e^{uA}\ [A,[A,B]]\ e^{-uA} \tag{17}$$

$$f'''(u) \ = \ e^{uA}\ A[A,[A,B]]\ e^{-uA} \ - \ e^{uA}\ [A,[A,B]]A\ e^{-uA} = e^{uA}\ [A,[A,[A,B]]]\ e^{-uA} \tag{18}$$

One can see that the pattern will continue with each successive derivative. The Taylor expansion then requires the successive values

$$
\begin{aligned}
f(0) &= B && (19)\\
f'(0) &= [A,B] && (20)\\
f''(0) &= [A,[A,B]] && (21)\\
f'''(0) &= [A,[A,[A,B]]] && (22)
\end{aligned}
$$

Now, if we assume that the expansion will remain convergent at $u = 1$, then by writing out the Taylor expansion one gets

$$f(1) = e^A B e^{-A} \;=\; f(0) + f'(0) \;+\; \frac{1}{2!} f''(0) \;+\; \frac{1}{3!} f'''(0) \;+\; \ldots \tag{23}$$

By substituting the values of the derivatives the result 14 follows. If the commutator $[A, B] =$ some number, then it follows that

$$\boxed{e^A \; B \; e^{-A} \;=\; B \;+\; [A,B]} \tag{24}$$

Now let us get back to the question that we started this section with. Let us define another similar function and proceed as follows:

$$
\begin{aligned}
f(u) &= e^{uA} e^{uB} && (25)\\
\therefore \quad \frac{df}{du} &= Af + fB &&\\
&= Af + e^{uA} B e^{uB} &&\\
&= Af + \underbrace{e^{uA} B e^{-uA}}_{B+u[A,B]} \underbrace{e^{uA} e^{uB}}_{f} &&\\
&= (A \;+\; B \;+\; u[A,B]) f && (26)
\end{aligned}
$$

We can then "integrate" this differential equation with the boundary condition $f(0) = 1$ between 0 and 1.

$$
\begin{aligned}
\frac{df}{du} &= (A \;+\; B \;+\; u[A,B])\, f && (27)\\
\therefore \quad \int_0^1 df \frac{1}{f} &= (A+B) \int_0^1 du \;+\; [A,B] \int_0^1 u du && (28)\\
\therefore \quad f(1) &= e^A e^B = e^{A+B} e^{\frac{1}{2}[A,B]} && (29)
\end{aligned}
$$

Putting $A = \lambda a^\dagger$ and $B = \mu a$, and noting $[\lambda a^\dagger, \mu a] = -\lambda\mu$ we obtain

$$\boxed{\left\langle e^C \right\rangle \;=\; \left\langle e^{\lambda a^\dagger \;+\; \mu a} \right\rangle \;=\; \left\langle e^{\lambda a^\dagger} \; e^{\mu a} \right\rangle \; e^{\lambda\mu/2}} \tag{30}$$

1.2.2 How to calculate $\left\langle e^{\lambda a^\dagger} \; e^{\mu a} \right\rangle$

$$e^{\lambda a^\dagger} \; e^{\mu a} = \sum_{m,n=0}^{\infty} \frac{\lambda^m \mu^n}{m! \, n!} (a^\dagger)^m \; (a)^n \tag{31}$$

Since the matrix elements will be taken in harmonic oscillator eigenstates only $m = n$ terms will exist. So we will need to evaluate

$$\left\langle \; e^{\lambda a^\dagger} \; e^{\mu a} \; \right\rangle = \sum_{n=0}^{\infty} \frac{\lambda^n \mu^n}{n! \, n!} \left\langle \; {a^\dagger}^n \; a^n \; \right\rangle \tag{32}$$

1.2.3 The evaluation $\left\langle {a^\dagger}^n a^n \right\rangle$

First note that the evaluation of $\left\langle a^\dagger a \right\rangle$ is straightforward.

$$\left\langle a^\dagger a \right\rangle = \frac{\sum\limits_{p=0}^{\infty} e^{-\beta p \hbar\omega} \left\langle p \mid a^\dagger a \mid p \right\rangle}{\sum\limits_{p=0}^{\infty} e^{-\beta p \hbar\omega}} = \frac{\sum\limits_{p=0}^{\infty} p \; z^p}{\sum\limits_{p=0}^{\infty} z^p} = \frac{1}{\frac{1}{1-z}} z \frac{\partial}{\partial z}\left(\frac{1}{1-z}\right) = \frac{z}{1-z} = \frac{1}{e^{\beta\hbar\omega}-1} \tag{33}$$

where in the intermediate steps we wrote $z = e^{-\beta\hbar\omega}$. To calculate the required thermal averaged quantity, we first need to get the following expectation value.

- What is the expectation value $\left\langle p \mid {a^\dagger}^n a^n \mid p \right\rangle$? This is *not* a thermal average.

$$a^n \mid p\rangle \quad = \quad \begin{cases} \sqrt{p}\sqrt{p-1}\sqrt{p-2}\ldots\sqrt{p-n+1} \mid p-n\rangle & \text{if} \quad p >= n \\ 0 & \text{if} \quad p < n \end{cases} \tag{34}$$

$$\therefore \langle p \mid {a^\dagger}^n a^n \mid p\rangle \quad = \quad \begin{cases} \dfrac{p!}{(p-n)!} & \text{if} \quad p >= n \\ 0 & \text{if} \quad p < n \end{cases} \tag{35}$$

So now,

$$\left\langle {a^\dagger}^n a^n \right\rangle = \frac{\sum\limits_{p=0}^{\infty} e^{-\beta p \hbar\omega} \left\langle p \mid {a^\dagger}^n a^n \mid p \right\rangle}{\sum\limits_{p=0}^{\infty} e^{-\beta p \hbar\omega}} \tag{36}$$

$$= \frac{\sum\limits_{p>=n}^{\infty} \dfrac{p!}{(p-n)!} \; z^p}{\sum\limits_{p=0}^{\infty} z^p} \tag{37}$$

$$= (1-z)\left[n!\, z^n + (n+1)!\, z^{n+1} + \frac{(n+2)!}{2!} z^{n+2} + \ldots\right] \tag{38}$$

$$= (1-z) n!\, z^n \left[1 + (n+1)z + \frac{(n+1)(n+2)}{2!} z^2 + \frac{(n+1)(n+2)(n+3)}{3!} z^3 + \ldots\right] \tag{39}$$

$$= (1-z) n!\, z^n \left(\frac{1}{1-z}\right)^{n+1} \tag{40}$$

$$= n! \left(\frac{z}{1-z}\right)^n \tag{41}$$

Comparing equations 33 and 41 we arrive at an important intermediate result

$$\boxed{\left\langle {a^\dagger}^n a^n \right\rangle = n! \left\langle a^\dagger a \right\rangle^n} \tag{42}$$

Returning to equation 30 we can now write:

$$\boxed{\left\langle e^C \right\rangle \; = \; \left\langle e^{\lambda a^\dagger \, + \, \mu a} \right\rangle \; = \; \left\langle e^{\lambda a^\dagger} \; e^{\mu a} \right\rangle \; e^{\lambda\mu/2} = e^{\lambda\mu/2} \sum_{n=0}^{\infty} \frac{\lambda^n \mu^n}{n!\, n!} \left\langle \; {a^\dagger}^n \; a^n \; \right\rangle = e^{\lambda\mu/2} \sum_{n=0}^{\infty} \left(\frac{\lambda^n \mu^n}{n!}\right) \left\langle \; a^\dagger \; a \; \right\rangle^n} \tag{43}$$

Now what is $\left\langle C^2 \right\rangle$?

$$
\begin{aligned}
C^2 &= \left(\lambda a^\dagger + \mu a\right)\left(\lambda a^\dagger + \mu a\right) && (44)\\
&= \lambda^2 a^\dagger a^\dagger + \lambda\mu\left(aa^\dagger + a^\dagger a\right) + \mu^2 aa && (45)\\
\therefore \left\langle C^2\right\rangle &= \lambda^2 \underbrace{\left\langle a^\dagger a^\dagger\right\rangle}_{=0} + \lambda\mu\left\langle 2a^\dagger a + 1\right\rangle + \mu^2 \underbrace{\left\langle aa\right\rangle}_{=0} && (46)\\
\therefore \left\langle e^{C^2/2}\right\rangle &= e^{\lambda\mu/2} e^{\lambda\mu\left\langle a^\dagger a\right\rangle} && (47)\\
&= e^{\lambda\mu/2} \sum_{n=0}^{\infty}\left(\frac{\lambda^n\mu^n}{n!}\right)\left\langle a^\dagger a\right\rangle^n && (48)
\end{aligned}
$$

Comparing this with equation 43, the Bloch identity follows. After which we recall the connection between position and momentum operators with a and $a^\dagger$

$$
\begin{aligned}
a &= \sqrt{\frac{m\omega}{2\hbar}}\, x \;+\; i\sqrt{\frac{1}{2\hbar m\omega}}\, p && (49)\\
\therefore x &= \sqrt{\frac{\hbar}{2m\omega}}\, \left(a \;+\; a^\dagger\right) && (50)
\end{aligned}
$$

Considering $C = iq_x x$, where iq_x is a number and x is the "operator", we can see that this is obviously in the form $\lambda a^\dagger + \mu a$.
The relation,

$$
\left\langle e^{iq_x x}\right\rangle = e^{-{q_x}^2\left\langle x^2\right\rangle/2} \tag{51}
$$

must hold. Squaring the sides and adding the parts coming from y and z, the full result follows as before.