

# PHYSICS 231

## Debye Waller factor

The intensity of Bragg scattering is reduced, due to motion of atoms about their equilibrium positions, by the Debye-Waller factor, generally written as  $e^{-2W}$ , where, for a monatomic (*i.e.* Bravais) lattice,

$$e^{-2W} = \langle \exp(i\mathbf{G} \cdot \mathbf{u}_l) \rangle^2. \quad (1)$$

Here  $\mathbf{G}$  is a reciprocal lattice vector, and  $\mathbf{u}_l$  is the displacement of the  $l$ -th atom. The average in Eq. (1) is easily found if one makes the harmonic approximation because one can then use the result

$$\langle e^A \rangle = e^{\frac{1}{2}\langle A^2 \rangle}, \quad (2)$$

where  $\langle \dots \rangle$  denotes a quantum statistical mechanical average at a temperature  $T \equiv \beta^{-1}$  for a simple harmonic oscillator (or set of oscillators), and  $A$  is a linear combination of the displacements and momenta of the oscillators (or, equivalently, a linear combination of creation and destruction operators,  $c_i^\dagger$  and  $c_i$ ), *i.e.*

$$A = \sum_i (a_i c_i + b_i c_i^\dagger), \quad (3)$$

where the  $a_i$  and  $b_i$  are constants. We now proceed to prove Eq. (2).

The most commonly given proofs of Eq. (2) uses Wick's theorem, which relates the average of a product of operators to sums of products of pairwise averages. It is taught in classes on many-body theory and field theory. However D. Mermin, J. Math. Phys. **7**, 1038 (1966), has a derivation which does not require Wick's theorem and which we follow here. To begin with, consider just a single oscillator, and let us evaluate

$$\langle e^{ac+bc^\dagger} \rangle, \quad (4)$$

$c$  and  $c^\dagger$  are creation and annihilation operators for an oscillator with Hamiltonian

$$\mathcal{H} = \epsilon(c^\dagger c + \frac{1}{2}). \quad (5)$$

We start with the well known formula

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}, \quad (6)$$

assuming that the commutator  $[A, B]$  is a  $c$ -number. A derivation of this is given in the Appendix. Applying Eq. (6) to Eq. (4) gives

$$\langle e^{ac+bc^\dagger} \rangle = \langle e^{ac} e^{bc^\dagger} \rangle e^{-\frac{1}{2}ab}. \quad (7)$$

We can also apply Eq. (6) to Eq. (4) but with the opposite identification of  $A$  and  $B$  to give

$$\langle e^{ac+bc^\dagger} \rangle = \langle e^{bc^\dagger} e^{ac} \rangle e^{\frac{1}{2}ab}. \quad (8)$$

Eqs. (7) and (8) are consistent only if

$$g(a, b) \equiv \langle e^{ac} e^{bc^\dagger} \rangle \quad (9)$$

$$= e^{ab} \langle e^{bc^\dagger} e^{ac} \rangle \quad (10)$$

$$= e^{ab} \langle e^{\beta\mathcal{H}} e^{ac} e^{-\beta\mathcal{H}} e^{bc^\dagger} \rangle, \quad (11)$$

where the last line follows from the cyclic invariance of the trace. Expanding out the  $\exp(ac)$  in the last line one can sandwich factors of  $e^{\beta\mathcal{H}}$  and  $e^{-\beta\mathcal{H}}$  around each factor of  $c$  and so

$$g(a, b) = e^{ab} \langle e^{ac(\beta)} e^{bc^\dagger} \rangle, \quad (12)$$

where

$$c(\beta) \equiv e^{\beta\mathcal{H}} c e^{-\beta\mathcal{H}} \quad (13)$$

$$= e^{-\beta\epsilon} c, \quad (14)$$

where the last line is derived in the Appendix. Hence we have

$$g(a, b) = e^{ab} g(ae^{-\beta\epsilon}, b). \quad (15)$$

Iterating this procedure another  $n$  times we have

$$g(a, b) = e^{ab(1+e^{-\beta\epsilon}+\dots+e^{-n\beta\epsilon})} g(ae^{-(n+1)\beta\epsilon}, b), \quad (16)$$

and so taking the limit  $n \rightarrow \infty$  we have

$$g(a, b) = e^{ab(1-e^{-\beta\epsilon})^{-1}} g(0, b). \quad (17)$$

Now trivially,

$$g(0, b) = \langle e^{bc^\dagger} \rangle = 1, \quad (18)$$

since all terms in the expansion of the exponential give zero except the first. Hence

$$g(a, b) = e^{ab[n(\epsilon)+1]}, \quad (19)$$

where

$$n(\epsilon) = \frac{1}{e^{\beta\epsilon} - 1}, \quad (20)$$

is the Planck distribution, and so from Eqs. (7), (9) and (19), we obtain

$$\langle e^{ac+bc^\dagger} \rangle = e^{ab[n(\epsilon)+\frac{1}{2}]} = e^{\frac{1}{2}\langle (ac+bc^\dagger)^2 \rangle}. \quad (21)$$

The derivation goes over straightforwardly to the case where there are many operators and so we obtain Eq. (2).

As a result of Eq. (2), the Debye Waller factor for a lattice with one atom per unit cell is given by

$$\langle \exp(i\mathbf{G} \cdot \mathbf{u}_l) \rangle^2 = e^{-2W}, \quad (22)$$

where

$$W = \frac{1}{2} \langle (\mathbf{G} \cdot \mathbf{u}_l)^2 \rangle. \quad (23)$$

This expression is evaluated by transforming to  $k$ -space, so

$$W = \frac{1}{2N} \sum_{\mathbf{k},s} \langle (\mathbf{G} \cdot \mathbf{u}_s(\mathbf{k}))^2 \rangle, \quad (24)$$

where  $s$  denotes a branch. Writing

$$\mathbf{u}_s(\mathbf{k}) = \vec{\varepsilon}_s(\mathbf{k}) \sqrt{\frac{\hbar}{2M\omega_{\mathbf{k},s}}} (c_{\mathbf{k},s} + c_{-\mathbf{k},s}^\dagger), \quad (25)$$

where  $\vec{\varepsilon}_s(\mathbf{k})$  is the polarization vector and  $M$  is the mass of the ion, we have

$$W = \frac{\hbar}{2M} \frac{1}{N} \sum_{\mathbf{k},s} \frac{[\mathbf{G} \cdot \vec{\varepsilon}_s(\mathbf{k})]^2}{\omega_{\mathbf{k},s}} \left[ n_{\mathbf{k},s} + \frac{1}{2} \right], \quad (26)$$

where  $n_{\mathbf{k},s} \equiv n(\hbar\omega_{\mathbf{k},s})$ . Our final result, then, is that the intensity of a Bragg peak is reduced, due to the motion of the atoms, by the Debye Waller factor,  $e^{-2W}$ , where  $W$  is given by Eq. (26).

Note:

- $W \neq 0$  even at  $T = 0$  because of the zero point motion of the atoms.
- In three dimensions,  $W$  is finite so the intensity of Bragg peaks is finite, as observed.
- In two dimensions,  $W$  is finite at  $T = 0$  but infinite at finite- $T$ . (You should show that the integral diverges logarithmically as  $k \rightarrow 0$ .) Since the amplitude of the Bragg peak is proportional to  $e^{-2W}$  then there are no (delta-function) Bragg peaks in two dimensions. In other words there is no long range crystalline order at finite- $T$  in two dimensions. Because of thermal fluctuations, positional order is eventually lost at long distances, though locally there will be a good crystalline arrangement. This was known in the 1930's through the work of Landau (see Landau and Lifshitz, *Statistical Mechanics*), and Peierls, (*Quantum Theory of Solids*) and was made rigorous in the 1960's through the work of Mermin, Wagner, and Hohenberg, see especially N.D. Mermin. *J. Math. Phys.* **8** 1061 (1967). Since the divergence is weak, and since it turns out that there is long range *orientational* order, see Halperin and Nelson, *Phys. Rev.* **19**, 2467 (1979), the delta function Bragg peaks are replaced by cusp-like divergences of the form  $|\mathbf{q} - \mathbf{G}|^{-[2-\eta_{\mathbf{G}}(T)]}$ , where  $\eta_{\mathbf{G}}(T)$  is an exponent which varies with  $T$  and  $G$ .
- In one dimension, not only is there no Bragg peak (long range positional order) at finite- $T$  but now, additionally, zero point fluctuations destroy long range order even at  $T = 0$ . You should show that the divergence is power law at finite- $T$  but only logarithmic at  $T = 0$ .
- These last results just depend on there being at least one acoustic phonon branch with a linear dispersion relation. It is quite easy to see that they do *not* depend on the assumption made above of one atom per unit cell. However, all our calculations have used the harmonic approximation. One might worry that the conclusions would be changed if we relax this.

Although, it might seem impossibly difficult to get exact results when anharmonic interactions are included, this turns out not to be the case, and the work of Mermin, Wagner and Hohenberg shows *rigorously* that the above conclusions about lack of translational order in low dimensions, found within the harmonic approximation, are correct.

## Appendix

First of all we will derive Eq. (14), *i.e.*

$$e^{\beta\mathcal{H}}ce^{-\beta\mathcal{H}} = e^{-\beta\epsilon}c, \quad (27)$$

where  $\mathcal{H}$  is the free particle Hamiltonian in Eq. (5). Defining

$$F(\tau) = e^{\tau\mathcal{H}}ce^{-\tau\mathcal{H}}, \quad (28)$$

and differentiating with respect to  $\tau$  gives

$$\frac{dF}{d\tau} = e^{\tau\mathcal{H}}[\mathcal{H}, c]e^{-\tau\mathcal{H}} \quad (29)$$

$$= -\epsilon e^{\tau\mathcal{H}}ce^{-\tau\mathcal{H}} \quad (30)$$

$$= -\epsilon F(\tau). \quad (31)$$

Solving this equation with the boundary condition  $F(0) = c$  gives Eq. (14).

Finally, we derive Eq. (6). Let us write

$$e^{(A+B)\tau} = e^{A\tau}e^{B\tau}f(\tau), \quad (32)$$

where  $\tau$  is a  $c$ -number. Then

$$f(\tau) = e^{-B\tau}e^{-A\tau}e^{(A+B)\tau}, \quad (33)$$

and, differentiating with respect to  $\tau$  gives

$$\frac{df}{d\tau} = -e^{-B\tau}[B, e^{-A\tau}]e^{(A+B)\tau}. \quad (34)$$

We evaluate the commutator  $[B, e^{-A\tau}]$  using the result

$$[B, A^n] = n[B, A]A^{n-1}, \quad (35)$$

valid if  $[B, A]$  is a  $c$ -number, which is obtained by successively moving the factor of  $B$  through the  $n$  factors of  $A$  one place at a time. Hence

$$[B, F(A)] = [B, A]F'(A), \quad (36)$$

where  $F$  is any function, and the prime denotes a derivative. For the case of interest here, this gives

$$[B, e^{-A\tau}] = -[B, A]\tau e^{-A\tau}. \quad (37)$$

Substituting into Eq. (34) then gives

$$\frac{df}{d\tau} = -[B, A]\tau e^{-B\tau}e^{-A\tau}e^{(A+B)\tau}, \quad (38)$$

$$= -[B, A]\tau f(\tau). \quad (39)$$

Integrating, and using the boundary condition that  $f(0) = 1$ , which is obvious, gives the desired result, Eq. (6).