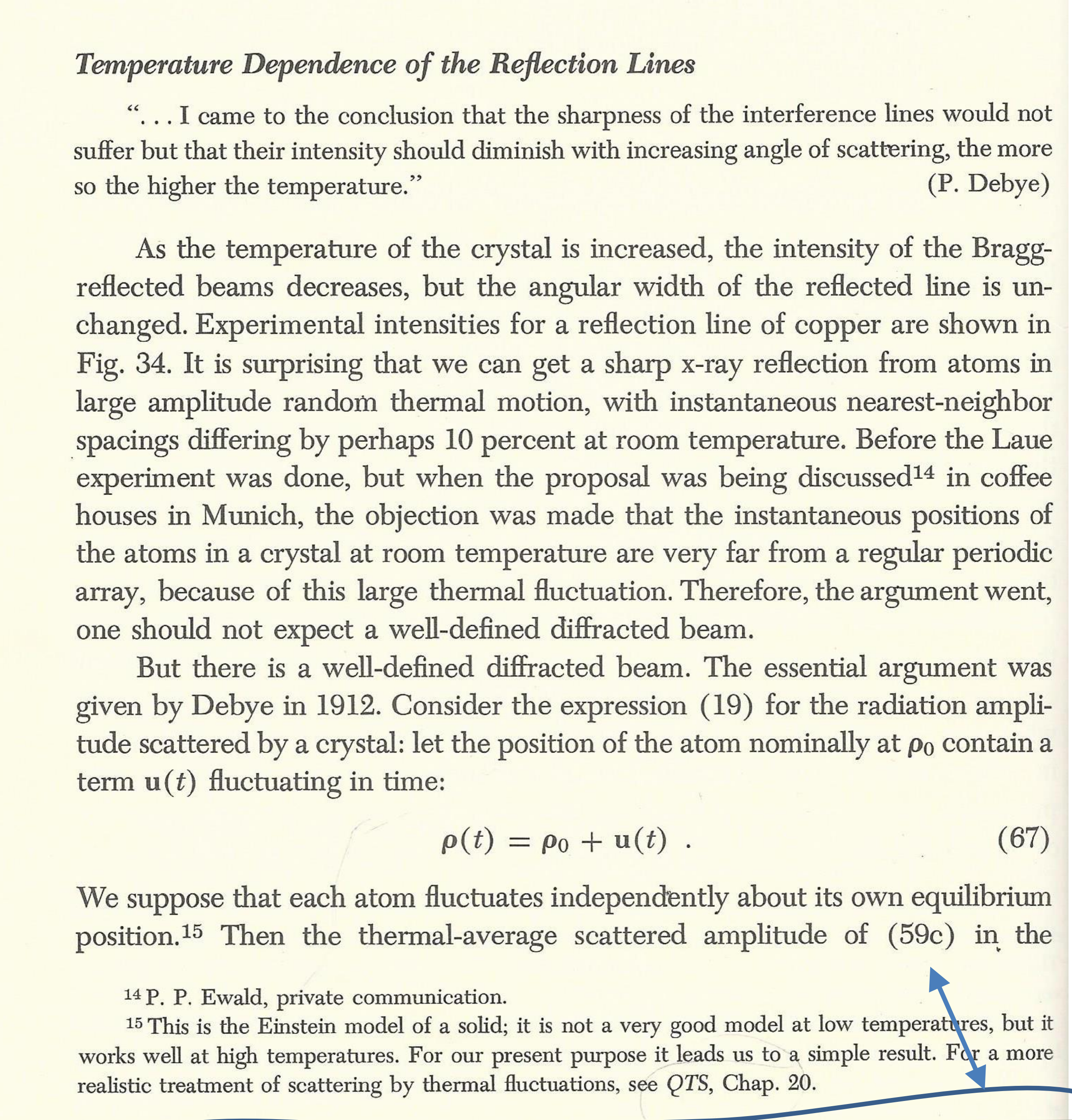
Vibrational Effects on Diffraction: The Debye-Waller Factor
From Kittel, SSP, 4th Edition. See also Prob. 4.8 in Ibach and Luth



Temperature Dependence of the Reflection Lines

"... I came to the conclusion that the sharpness of the interference lines would not suffer but that their intensity should diminish with increasing angle of scattering, the more so the higher the temperature." (P. Debye)

As the temperature of the crystal is increased, the intensity of the Bragg-reflected beams decreases, but the angular width of the reflected line is unchanged. Experimental intensities for a reflection line of copper are shown in Fig. 34. It is surprising that we can get a sharp x-ray reflection from atoms in large amplitude random thermal motion, with instantaneous nearest-neighbor spacings differing by perhaps 10 percent at room temperature. Before the Laue experiment was done, but when the proposal was being discussed[14] in coffee houses in Munich, the objection was made that the instantaneous positions of the atoms in a crystal at room temperature are very far from a regular periodic array, because of this large thermal fluctuation. Therefore, the argument went, one should not expect a well-defined diffracted beam.

But there is a well-defined diffracted beam. The essential argument was given by Debye in 1912. Consider the expression (19) for the radiation amplitude scattered by a crystal: let the position of the atom nominally at $\boldsymbol{\rho}_0$ contain a term $\mathbf{u}(t)$ fluctuating in time:

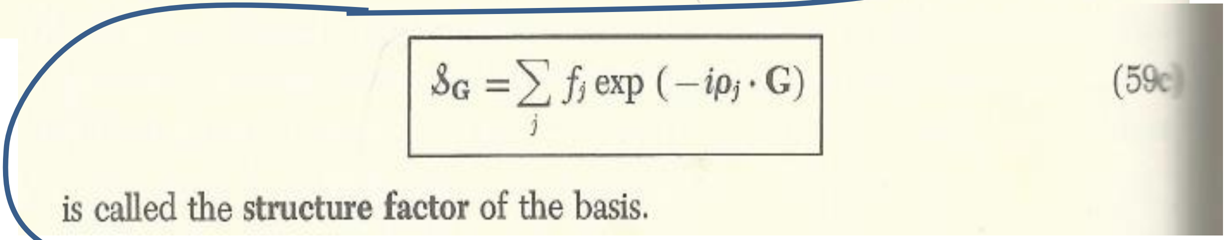
$$\boldsymbol{\rho}(t) = \boldsymbol{\rho}_0 + \mathbf{u}(t) \ . \tag{67}$$

We suppose that each atom fluctuates independently about its own equilibrium position.[15] Then the thermal-average scattered amplitude of (59c) in the

---

[14] P. P. Ewald, private communication.

[15] This is the Einstein model of a solid; it is not a very good model at low temperatures, but it works well at high temperatures. For our present purpose it leads us to a simple result. For a more realistic treatment of scattering by thermal fluctuations, see *QTS*, Chap. 20.



$$\boxed{\mathcal{S}_{\mathbf{G}} = \sum_j f_j \exp\left(-i\boldsymbol{\rho}_j \cdot \mathbf{G}\right)} \tag{59c}$$

is called the **structure factor** of the basis.

direction of a diffraction maximum can be written

$$\langle \mathcal{A} \rangle = \mathcal{A}_0 \langle \exp(-i\mathbf{u}\cdot\mathbf{G}) \rangle \ , \tag{68}$$

where $\mathbf{G}$ is equal to the change in wavevector on reflection and $\langle \cdots \rangle$ denotes thermal average. The appearance of $\mathcal{A}_0$ assures us that all diffraction lines will be sharp.

The exponential factor in (68) reduces the intensity. The series expansion of the exponential is

$$\langle \exp(-i\mathbf{u}\cdot\mathbf{G}) \rangle = 1 - i\langle \mathbf{u}\cdot\mathbf{G} \rangle - \tfrac{1}{2}\langle (\mathbf{u}\cdot\mathbf{G})^2 \rangle + \cdots \ . \tag{69}$$

But $\langle \mathbf{u}\cdot\mathbf{G} \rangle = 0$, because $\mathbf{u}$ is a random thermal motion uncorrelated with the direction of $\mathbf{G}$. Further,

$\longrightarrow \langle u \cos \overset{2}{\theta} \rangle G^2$

$$\langle (\mathbf{u}\cdot\mathbf{G})^2 \rangle = \tfrac{1}{3}\langle u^2 \rangle G^2 \ . \tag{70}$$

The factor $\frac{1}{3}$ arises by geometrical averaging in three dimensions, because only the component of $\mathbf{u}$ along $\mathbf{G}$ is involved. We can limit ourselves to (69) to get a feeling for the physics, but it is useful to note that the function

$$\exp[-\tfrac{1}{6}\langle u^2 \rangle G^2] = 1 - \tfrac{1}{6}\langle u^2 \rangle G^2 + \cdots \tag{71}$$

has the same series expansion as (69) for the first two terms shown here. For a harmonic oscillator it is a fact that all terms in the series (69) and (71) can be shown to be identical. Then the scattered intensity, which is the square of the amplitude, is

$$I = I_0 \exp[-\tfrac{1}{3}\langle u^2 \rangle G^2] \ , \tag{72}$$

where I_0 is the scattered intensity from the rigid lattice as treated earlier. The exponential factor is known as the **Debye-Waller factor.**

Here $\langle u^2 \rangle$ is the mean square displacement of an atom. The thermal average potential energy $\langle U \rangle$ of a classical harmonic oscillator in three dimensions is $\frac{3}{2}k_BT$, whence

$$\langle U \rangle = \tfrac{1}{2}C\langle u^2 \rangle = \tfrac{1}{2}M\omega^2\langle u^2 \rangle = \tfrac{3}{2}k_BT \ , \tag{73}$$

where C is the force constant, M is the mass of an atom, and ω is the frequency of the oscillator. We have used the result $\omega^2 = C/M$. Thus the scattered intensity is

$$I(hkl) = I_0 \exp\left[-\frac{k_BTG^2}{M\omega^2}\right] \ , \tag{74}$$

where hkl are the indices of $\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$. This classical result is a good approximation at high temperatures.