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On the Classical Interpretation of Thermal Probability Ellipsoids and the Debye–Waller Factor

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Abstract

In many standard text books on crystallography, the Gaussian expression for the Debye–Waller factor is derived from a classical point of view. The physical model normally used is too simple in that it is incompatible with the concept of probability ellipsoids used to depict atomic thermal motion. A classical derivation of the Debye–Waller factor expression is given that corrects some misconceptions.

Introduction

It is well known that the effect of thermal motion on the X-ray diffraction pattern of a crystal is described by the Debye–Waller factor. Thermal motion is incorporated into the structure-factor equation by multiplying the atomic scattering factor of the jth atom by $\exp(-\mathbf{h}^T\mathbf{b}_j\mathbf{h})$, where $\mathbf{b}_j$ is the thermal motion tensor. This exponential function is Gaussian. It can be interpreted as the characteristic function of the probability density distribution of the atomic position, which is therefore also Gaussian. It is now common practice to use this density distribution to depict the thermal motion by drawing a surface of constant probability (an ellipsoid) containing, say, 50% of the total probability density (Johnson, 1965).

A standard derivation of the Gaussian expression for the Debye–Waller factor in text books (James, 1967, p. 22; Warren, 1969, p. 36; Woolfson, 1970, p. 190; Cowley, 1975, p. 246; Dunitz, 1979, p. 45) considers a single atom (or a single mode of vibration of the crystal) that behaves as a classical harmonic oscillator. The atomic position is averaged over space or time and a simple mathematical approximation then leads quickly to the correct result. This derivation is misleading and it gives an incomplete physical picture. Neither a time average nor a space average over identical but independent classical harmonic oscillators gives the Debye–Waller factor and it is only by the mathematical approximation that the correct result appears. Conversely, the Gaussian probability distribution of the atomic position cannot be reconciled with a single classical harmonic oscillator. The latter gives a probability distribution that is far from being Gaussian. In addition, a 90% probability ellipsoid normally has principal axes greater than covalent bond lengths. This cannot be explained in terms of this simple classical model since single atoms appear to have unreasonably large amplitudes of vibration. It is this inconsistency between identical harmonic oscillators and thermal ellipsoids that we wish to comment on in this note. We could find only one current crystallographic text book that uses an adequate physical model for the derivation of the Debye–Waller factor (Willis & Pryor, 1975, p. 92). This is in terms of lattice dynamics: we present here a simple derivation in terms of atomic vibrations.

Text-book derivation

We will consider first the standard text-book derivation of the Debye–Waller factor referred to earlier. The thermal motion modifies each atomic position by a displacement u from the equilibrium position. For a one-dimensional structure, the structure-factor equation becomes

$$F(h)=\sum_{j=1}^{N} f_j \exp[2\pi i h(x_j+u_j/a)]. \qquad (1)$$

This equation also applies in three dimensions if u_j is taken as the displacement of the atom in the direction of the scattering vector $\mathbf{h}$. With $h/a=2\sin\theta/\lambda$, (1) becomes

$$F(h)=\sum_{j=1}^{N} f_j \exp[4\pi i(\sin\theta/\lambda)\,u_j]\exp(2\pi i h x_j) \qquad (2)$$

and the effect of thermal motion is contained in the first exponential. This factor must be averaged over all values of u_j, since it varies with time within a unit cell and will be different from one unit cell to the next. If the jth atom in each cell is vibrating with the same energy, independent of other atoms, the time average is identical to the space average. For a simple harmonic oscillator, u_j varies with time as $A_j \sin \omega_j t$,

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where A_j is the amplitude and ω_j the angular frequency. The time average is therefore given by

$$\langle \exp[4\pi i(\sin\theta/\lambda)u_j]\rangle = \frac{1}{2\pi}\int\limits_{-\pi}^{\pi} \exp[4\pi i(\sin\theta/\lambda)A_j\sin\varphi]\,\mathrm{d}\varphi = J_0[4\pi(\sin\theta/\lambda)A_j], \qquad (3)$$

where J_0 is a Bessel function. This is not the Debye-Waller factor.

This can be converted into the correct result using the approximation normally employed in text-book derivations. The power-series expansions of $J_0(x)$ and $\exp(-x^2/4)$ are the same to terms in x^2. We will also make use of the fact that, for a classical harmonic oscillator, $A_j^2=2\overline{u_j^2}$, where $\overline{u_j^2}$ is the mean square displacement. For small arguments of the function we therefore obtain

$$J_0[4\pi(\sin\theta/\lambda)A_j]\simeq\exp[-8\pi^2(\sin^2\theta/\lambda)\overline{u_j^2}], \qquad (4)$$

which is the Debye-Waller factor. However, for the size of argument normally encountered (which can easily exceed unity), this approximation is not valid and there is no good scientific reason for using it anyway. In addition, the two functions give completely different probability densities of the atomic displacement.

Classical derivation

To obtain the Debye-Waller factor correctly, a more complete physical model must be used. The time taken to record the diffraction pattern will be long compared with the period of vibration of the atoms, so we may regard the X-rays as seeing each atom displaced by an amount u, where $|u|$ is the expected absolute displacement given by the time average. We also expect the oscillators to have a Boltzmann distribution of energy. That is, for a crystal where the vibrational energy is independent of which unit cell the atom is in, the number of atoms per unit volume with a momentum in the interval $\mathrm{d}p_x$, $\mathrm{d}p_y$, $\mathrm{d}p_z$ in the x, y, z directions is

$$\mathrm{d}N \propto \exp(-E/kT)\,\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z, \qquad (5)$$

where E is the energy, k is Boltzmann's constant and T the absolute temperature. We will take the component of momentum in the direction of the displacement u, which is parallel to the scattering vector $\mathbf{h}$. Since the energy of a classical oscillator is proportional to the square of the momentum and also to the square of the expected displacement, we can use (5) to give the probability density of atomic displacement as

$$P(u)\propto\exp(-\alpha u^2), \qquad (6)$$

where α is the constant of proportionality between u^2 and E/kT. This is a Gaussian function that can be normalized to give

$$P(u)=(2\pi\overline{u^2})^{-1/2}\exp(-u^2/2\overline{u^2}), \qquad (7)$$

where $\overline{u^2}$ is the average of u^2 for each atom over the whole range of energies.

We can now obtain the average of (2) over all u_j. The space average of the exponential factor is therefore

$$\langle\exp[4\pi i(\sin\theta/\lambda)u_j]\rangle = (2\pi\overline{u_j^2})^{-1/2}\int\limits_{-\pi}^{\pi}\exp[4\pi i(\sin\theta/\lambda)u_j] \times\exp(-u_j^2/2\overline{u_j^2})\,\mathrm{d}u_j = \exp[-8\pi^2(\sin^2\theta/\lambda^2)\overline{u_j^2}], \qquad (8)$$

which is the Debye-Waller factor.

Thus it is the space average over a large number of oscillators with a Boltzmann distribution of energy that yields the Debye-Waller factor and not the time average over a single oscillator.

It will be seen that the nature of the time average has no effect on the final result. Since atoms in different unit cells are indistinguishable in the diffraction experiment, any statistical distribution of atomic displacement corresponding to the Boltzmann law will be indistinguishable from the time-averaged distribution considered here, assuming the number of atoms is infinite. This assumption is already inherent in the Boltzmann law itself. The Debye-Waller factor is therefore independent of the way the atoms move as a function of time. This is a restatement of the central limit theorem in probability theory.

We hope this corrects misconceptions due to inadequate derivations in a number of current text books.

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