

## Temperature dependence on the diffracted x-rays

**1. Initial expectation:** Since heat adds energy to the crystal, the atoms will probably vibrate causing the lattice constants,  $a_i$ , to oscillate somewhat randomly over time. This should cause the  $\mathbf{G}$ 's to oscillate since they depend on the  $a_i$ , and this will then cause the  $\Delta\mathbf{k}$ 's and hence the final  $\mathbf{k}$ 's to oscillate slightly, which will cause the diffracted  $\lambda$ 's to oscillate and this should show up as a broadening of the lines ( $\lambda$ 's or  $\theta$ 's) [due to the Doppler effect].

**2. Start with the structure factor,  $S_G$ :**  $S_G = \sum_j f_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j)$  where the  $f_j$  are the atomic form factors that shouldn't be affected by temperature. This is because the electrons around the atom can't just accept any energy so their density should remain constant even if the atom itself is oscillating.

### 3. Introduce thermal motion of the atoms:

Since the crystal is oscillating:  $\mathbf{r}_j(t) = \mathbf{r}_{j0} + \mathbf{u}(t)$

where the vector  $\mathbf{u}(t)$  is due to the thermal oscillations, so

$\langle S_G \rangle = \sum_j f_j \exp(-i\mathbf{G} \cdot \mathbf{r}_{j0}) \langle \exp(-i\mathbf{G} \cdot \mathbf{u}) \rangle$ , where  $\langle \rangle$  indicates time average

### 4. Apply a Taylor series expansion to the exponential with $\mathbf{u}(t)$ :

$$\langle \exp(-i\mathbf{G} \cdot \mathbf{u}) \rangle = \langle 1 - i\mathbf{G} \cdot \mathbf{u} + \frac{1}{2}(\mathbf{G} \cdot \mathbf{u})^2 + \dots \rangle = \langle 1 \rangle - \langle i\mathbf{G} \cdot \mathbf{u} \rangle + \frac{1}{2} \langle (\mathbf{G} \cdot \mathbf{u})^2 \rangle + \dots$$

The first order term  $\langle i\mathbf{G} \cdot \mathbf{u} \cos(\theta) \rangle = 0$  since it can be both positive and negative at any instant and hence will average to zero. In fact, all odd order terms (the imaginary terms) will also be zero for the same reason.

The second order term,  $-\frac{1}{2} \langle G^2 u^2 \cos^2 \theta \rangle = -\frac{1}{2} G^2 \langle u^2 \rangle \langle \cos^2 \theta \rangle$  is not zero since it is an average of squared (always positive) terms. [As long as the  $G$ ,  $u$ , and angle oscillate in time **independently**, then the above equality holds. This equality would not hold if the  $G$ ,  $u$ , and angle did oscillate together. For example,  $\langle \cos^2(\theta) \rangle$  does not equal  $\langle \cos(\theta) \rangle^2$  since  $\langle \cos^2(\theta) \rangle$  is greater than zero, but  $\langle \cos(\theta) \rangle$  equals zero. Demonstration of  $\langle a^2 b^2 c^2 \rangle$  compared to  $\langle a^2 \rangle \langle b^2 \rangle \langle c^2 \rangle$ : let  $a = 1, 2, 3$ ;  $b = 1, 3, 5$ ;  $c = 2, 4, 8$ . If  $a_1$  goes with  $b_1$  goes with  $c_1$ , etc. then  $\langle a^2 b^2 c^2 \rangle = [(1^2 * 1^2 * 2^2) + (2^2 * 3^2 * 4^2) + (3^2 * 5^2 * 8^2)] / 3 = 4,993$ ; but  $\langle a^2 \rangle = [1^2 + 2^2 + 3^2] / 3 = 4.667$ ;  $\langle b^2 \rangle = [1^2 + 3^2 + 5^2] / 3 = 11.667$ ;  $\langle c^2 \rangle = [2^2 + 4^2 + 8^2] / 3 = 28.0$  so  $\langle a^2 \rangle \langle b^2 \rangle \langle c^2 \rangle = 4.667 * 11.667 * 28 = 1,524$  – which is not the same as  $\langle a^2 b^2 c^2 \rangle = 4,993$ . However, if each of the  $a$ 's are independent of each of the  $b$ 's and  $c$ 's, then there are 27 combinations of  $a_i^2 * b_j^2 * c_k^2$  and they average out to 1,524 – which is equal to  $\langle a^2 \rangle \langle b^2 \rangle \langle c^2 \rangle$ !]

Note: we can evaluate the average of  $\cos^2(\theta)$ :

$$\langle \cos^2(\theta) \rangle = \frac{\int \cos^2(\theta) dV}{\int dV} = \frac{\iiint \cos^2(\theta) dr r d\theta r \sin(\theta) d\phi}{\iiint dr r d\theta r \sin(\theta) d\phi}$$

[ $dV = dx * dy * dz$  in rectangular; in spherical  $dV =$  small distance in radial direction,  $dr$ ; times a small distance in the  $\theta$  direction around the  $x$  axis,  $r d\theta$ ; times a small distance around the  $z$  axis,  $r \sin(\theta) d\phi$ ; to give  $dV = dr * r d\theta * r \sin(\theta) d\phi$ ]

The integrals over  $d\phi$  and over  $dr$  are exactly the same in the numerator and in the denominator, so they give values that cancel. Also, if we let  $\cos(\theta) = x$ , then  $dx = -\sin(\theta) d\theta$  so using this substitution:

$$\begin{aligned} \langle \cos^2(\theta) \rangle &= \int_0^\pi \cos^2(\theta) \sin(\theta) d\theta / \int_0^\pi \sin(\theta) d\theta \\ &= \int_{-1}^{+1} x^2 dx / \int_{-1}^{+1} dx = (2/3) / 2 = \mathbf{1/3} . \end{aligned}$$

Note that this average is over a 3-D volume; compare this to the time average of  $\cos^2(\omega t)$  which is  $1/2$ .

$$\begin{aligned} \text{Therefore: } \langle \exp(-i\mathbf{G}\cdot\mathbf{u}) \rangle &\approx \langle 1 \rangle - \langle i\mathbf{G}\cdot\mathbf{u} \rangle - \frac{1}{2}\langle (\mathbf{G}\cdot\mathbf{u})^2 \rangle = 1 - \frac{1}{2}\langle (1/3)G^2\langle u^2 \rangle \rangle \\ &\approx \exp(-G^2\langle u^2 \rangle/6), \end{aligned}$$

[where the last step used the inverse Taylor Series – that is recognizing the series as being the same as the exponential function series] and so

$$\langle S_G \rangle = \sum_j f_j \exp(-i\mathbf{G}\cdot\mathbf{r}_{j0}) \exp(-G^2\langle u^2 \rangle/6)$$

and since the exp factor does not depend on the particular  $j$ , it can be factored out so

$$\langle S_G \rangle = S_{G0} \exp(-G^2\langle u^2 \rangle/6) \quad (\text{where } S_{G0} \text{ is the structure factor without thermal motion}).$$

### 5. Look at intensity: [The symbol $\propto$ means proportional to.]

$$I \propto A^2 \propto S_G^2, \text{ therefore } I_G = I(hk\ell) = I_0 \exp(-(1/3)\langle u^2 \rangle G^2)$$

{NOTE: the (1/6) in the exp becomes (1/3) due to  $S_G$  being squared:  $(e^a)^2 = e^{2a}$ .} where  $I_0$  is the intensity without thermal vibration. The exponential factor is called the **Debye-Waller factor**.

### 6. Investigate what this means:

All the thermal vibrations do is to **reduce the intensity** of the diffracted x-ray beam. It **does NOT influence the  $\theta$  or the  $\mathbf{k}$**  (and hence the  $\lambda$ ) of the diffracted beam - contrary to our initial expectations. And this DOES agree with experiment! The missing energy will appear as a diffuse background of x-rays.

### 7. Look at $\langle u^2 \rangle$ from a classical harmonic oscillator viewpoint:

For a spring (harmonic oscillator), Potential Energy =  $\frac{1}{2}kx^2$  where  $k$  is the spring constant.

Also from Newton's Second law:  $F_{\text{spring}} = -kx = ma = m d^2x/dt^2$  which has a solution of the form:  $x(t) = A \sin(\omega t + \theta_0)$ , and using this in the equation

$$-kx = m d^2x/dt^2 \quad \text{gives} \quad -k = -m\omega^2, \quad \text{or} \quad \omega^2 = k/m.$$

Here we will use **C to denote the effective spring constant** rather than  $k$  which we are already using for the wavevector, so here  $\omega^2 = C/m$ . We will also use  **$\Omega$  for the frequency of oscillation of the atoms** since we have used  $\omega$  for the frequency of the x-rays, so here  **$\Omega^2 = C/m$** ).

$$\text{Therefore, } \langle PE \rangle = \frac{1}{2}C\langle u^2 \rangle = \frac{1}{2}\Omega^2 m \langle u^2 \rangle.$$

From Thermodynamic considerations:

$$\langle KE \rangle = (3/2) k_B T \quad (\text{where } k_B \text{ is Boltzmann's constant} = 1.38 \times 10^{-23} \text{ Joules/Kelvin})$$

and from the equipartition of energy theorem,  $\langle KE \rangle = \langle PE \rangle$ , so

$$\frac{1}{2}\Omega^2 m \langle u^2 \rangle = (3/2) k_B T, \quad \text{or} \quad \langle u^2 \rangle = 3k_B T / m\Omega^2.$$

Therefore, using this expression of  $\langle u^2 \rangle$  in the Intensity gives:

$$I(hk\ell) = I_0 \exp(-(1/3)[3k_B T / m\Omega^2]G^2) = I_0 \exp(-k_B G^2 T / m\Omega^2).$$

This should be a **good approximation for high T** where classical theory works well.

## 8. Plug in some values to see how this works for high Temps:

We'll use Cooper: density  $\approx 9$  gm/cc; mass = 60 amu  $\approx 1 \times 10^{-25}$  kg; density = m/V so  $V = \text{mass}/\text{density} = a^3$  so  $a \approx 2 \times 10^{-10}$  m;

$K = 2\pi/a \approx 3 \times 10^{10} \text{ m}^{-1}$ ; speed of sound  $\approx 4,600 \text{ m/s} = \lambda f = \Omega/k$  or  $\Omega = (4,600 \text{ m/s}) \cdot (3 \times 10^{10} \text{ m}^{-1}) \approx 1.3 \times 10^{14} \text{ rad/sec}$

melting temperature  $\approx 1,350 \text{ K}$

$$\begin{aligned} I(T)/I_0 &\approx \exp(-\{[1.38 \times 10^{-23} \text{ J/Kelvin}] \cdot [3 \times 10^{10} \text{ m}^{-1}]^2 \cdot T\} / \{(10^{-25} \text{ kg}) \cdot (1.3 \times 10^{14} \text{ s}^{-1})^2\}) \\ &= \exp(-[7.3 \times 10^{-6} / \text{Kelvin}] T) . \end{aligned}$$

If  $T=300\text{K}$  (room temp),  $I(300\text{K})/I_0 = .998$ ; If  $T=1,350\text{K}$  (melting temp),  $I(1350\text{K})/I_0 = .990$ ;

Also,  $u_{\text{rms}} = \sqrt{\langle u^2 \rangle} = \sqrt{(3k_B T/m\Omega^2)} \approx 2.7 \times 10^{-12} \text{ m}$  at room  $T$  of 300 Kelvins

(which is about 1% of the value of  $a$ , the lattice constant).

At  $T = 1,100 \text{ K}$ , then  $u_{\text{rms}} \approx 6 \times 10^{-12} \text{ m}$

(which is almost 3% of the lattice constant)

## 9. For low temperatures, we must employ the quantum theory:

For a harmonic oscillator (using the standard  $k$  for spring constant and  $\omega$  for angular speed):

$$E = (n_x + 1/2)\hbar\omega_x + (n_y + 1/2)\hbar\omega_y + (n_z + 1/2)\hbar\omega_z;$$

at  $T=0$ ,  $E = (3/2)\hbar\omega$ . We still have the following results:

$$\langle \text{PE} \rangle = \langle \text{KE} \rangle = 1/2 E = (3/4)\hbar\omega .$$

In addition,  $\langle \text{PE} \rangle = 1/2 C \langle u^2 \rangle$  and  $\omega^2 = k/m$  so, using  $\Omega$  for  $\omega$  and  $C$  for  $k$ , we get  $C = \Omega^2 m$  and so

$$\langle u^2 \rangle = 2\langle \text{PE} \rangle / C = 2(3/4)\hbar\Omega / \Omega^2 m = 3\hbar / 2\Omega m \quad (\text{for } T=0 \text{ Kelvins}).$$

$$\text{Therefore, } I(hk\ell) = I_0 \exp(-(1/3)[3\hbar/2\Omega m]G^2) = I_0 \exp(-[(\hbar G^2/2\Omega m)])$$

## 10. Plugging in the same values for $G$ , $m$ , and $\Omega$ as above for low $T$ gives:

$$I/I_0 \approx .996 . \quad u_{\text{rms}} = \sqrt{\langle u^2 \rangle} = \sqrt{(3\hbar/2\Omega m)} \approx 3.5 \times 10^{-12} \text{ m} \text{ using the values in part 8.}$$

11. Also note that  $I(hk\ell)$  is affected less for small  $G$  (small values for  $h, k, \ell$ ) than for large  $G$  (large values for  $hk\ell$ ).

$$I(hk\ell) = I_0 \exp(-k_B G^2 T / m \Omega^2) \text{ (high } T) \text{ and } I(hk\ell) = I_0 \exp(-[(\hbar G^2 / 2\Omega m)]) \text{ (low } T) .$$

Recall for a cubic lattice that the distance between planes in the lattice is:  $d_{hk\ell} = Na / (h^2 + k^2 + \ell^2)^{1/2}$ .

While the atoms do oscillate as seen above, they do not oscillate independently; the planes of the atoms oscillate with the atoms and so the distance between the planes of atoms stays about the same. We'll see this in the 2<sup>nd</sup> part of the course. If the distance between the planes stays the same, then the diffraction condition (Bragg's Law) shouldn't vary with temperature – as verified by experiment.