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WPPM macros for TOPAS

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Supplementary Information

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1. Deduction of the equations for the mean and square mean strain referred to a crystal structure having mean lattice parameter a'

In a general distortion problem, provided atoms do not "disappear" (as it is the case for planar defects and dislocations) we can distinguish between three different configurations, as shown in Figure 1:

- The *as-built* configuration: that where atoms occupy positions corresponding to a particle carved from an infinite and perfect structure.
- The *mean-relaxed* configuration: a configuration equal to the as-built one but changing the lattice parameters to the mean ones obtained through the indexing of the diffraction pattern.

- The *relaxed* configuration: the "real" atomic configuration for the particle, where the presence of the surface distorts the perfect crystalline structure respect to the infinite or bulk counterpart.

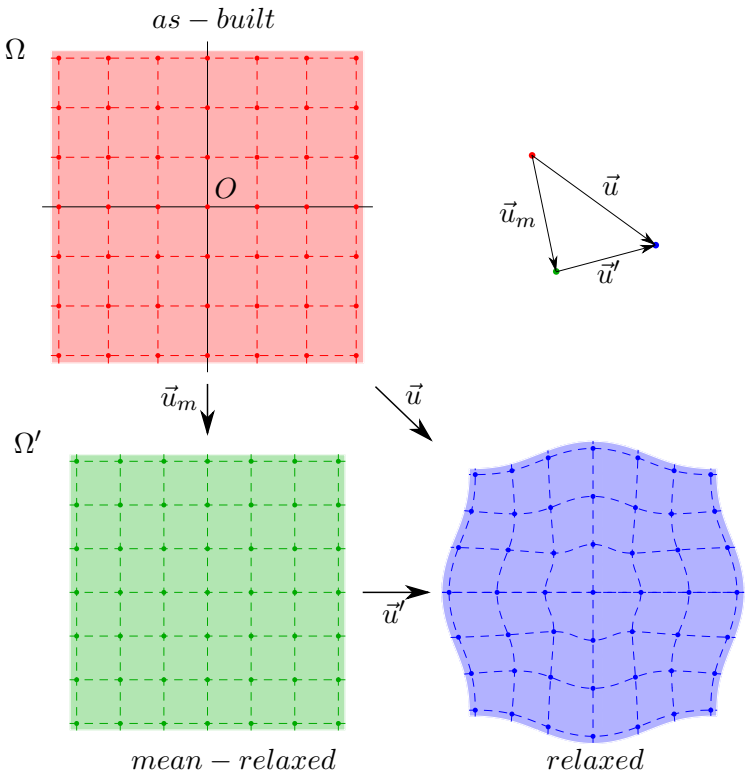

Fig. 1. Schematic representation of the different configurations in a general distortion of a crystallite, with constant number of atoms. The *as-built* configuration is transformed into the *mean-relaxed* one by the displacement field $\vec{u}_m$ and then to the *relaxed* or final configuration through $\vec{u}'$. The geometrical relation between the differents displacement fields is shown at the top-right.

The most common scope of XRPD techniques is to determine the mean-relaxed configuration. Peak profiles details are on the other hand related to the strain or distortion of the relaxed configuration relative to the mean-relaxed one (Warren, 1990). The model proposed in (Perez-Demydenko & Scardi, 2017), nevertheless, refers the strain, specifically the mean values of $< \Delta L_{hkl} >$ and $< \Delta L^2_{hkl} >$ (eqs. (22) and (23) of that study, respectively), to the as built configuration. Therefore some further work should be made to correct those expressions.

From the view point of a continuous displacement field which distorts a continuous piece of matter (we neglect the points in Figure 1 and focus only in the shape changes) a point of the as-built body at $\vec{r}$, upon deformation will move to position $\vec{r}\,'$ given by:

$$\vec{r}\,' = \vec{r} + \vec{u}_m(\vec{r}) + \vec{u}\,'(\vec{r} + \vec{u}_m(\vec{r})), \tag{1}$$

i.e. we can imagine the whole distortion problem as two successive distortions: a first one that moves points in the as-built configuration to the mean-relaxed one, and a second that moves points from the latter to the relaxed configuration. The first distortion is characterized by the displacement field $\vec{u}_m$ defined in Ω. To be compatible with a simple shrinkage or expansion of the lattice, which is what is intended by an indexing of a cubic powder pattern, $\vec{u}_m$ should be given by:

$$\vec{u}_m = \left(\frac{a'}{a} - 1\right)\vec{r} = \alpha\,\vec{r}, \tag{2}$$

where a' is the lattice parameter after indexing and a that of the corresponding bulk or infinite structure. The second distortion is characterized by the displacement field $\vec{u}\,'$, which is defined only in the region occupied by the mean-relaxed configuration, Ω'. According to what was said before we should compute $< \Delta L_{hkl} >$ and $< \Delta L_{hkl}^2 >$ using $\vec{u}'$ and performing the mean over Ω' for its permitted values of L (since Ω and Ω' have different volumes, they will have different maximum permitted values of L for each hkl, in general).

Since the total displacement field defined in Ω, which moves a point from the as-built configuration to the relaxed one, is $\vec{u}(\vec{r}) = \vec{r}\,' - \vec{r}$, eq. (1) can be written as

$$\vec{u}(\vec{r}) = \vec{u}_m(\vec{r}) + \vec{u}\,'(\eta(\vec{r})), \tag{3}$$

where the function $\eta(\vec{r}) = \vec{r} + \vec{u}_m(\vec{r}) = (\alpha + 1)\vec{r}$, $\eta(\vec{r}) \in \Omega' \;\forall\; \vec{r} \in \Omega$. Writing eq. (3) for points at $\vec{r}$ and $\vec{r} + L\hat{s}$, both in Ω, taking the component parallel to the diffraction

vector $\hat{s}$ and subtracting we obtain:

$$\Delta L_{\hat{s}}(\vec{r}, L) = \Delta L_{m,\hat{s}}(\vec{r}, L) + \Delta L'_{\hat{s}}(\eta, \vec{r}, L), \tag{4}$$

where

$$\Delta L_{\hat{s}}(\vec{r}, L) = u_{\hat{s}}(\vec{r} + L\hat{s}) - u_{\hat{s}}(\vec{r}), \tag{5a}$$

$$\Delta L_{m,\hat{s}}(\vec{r}, L) = u_{m,\hat{s}}(\vec{r} + L\hat{s}) - u_{m,\hat{s}}(\vec{r}), \tag{5b}$$

$$\Delta L'_{\hat{s}}(\eta, \vec{r}, L) = u'_{\hat{s}}(\eta(\vec{r} + L\hat{s})) - u'_{\hat{s}}(\eta(\vec{r})). \tag{5c}$$

Let's denote as $\Omega_{-L\hat{s}}$ the domain Ω displaced by the vector $-L\hat{s}$; a "ghost" domain as termed in (Wilson, 1962). It can be seen that in order to have both $\vec{r}$ and $\vec{r} + L\hat{s}$ in Ω for a given L, we should have $\vec{r} \in \Omega^*_{-L\hat{s}}$ where $\Omega^*_{-L\hat{s}} = \Omega \cap \Omega_{-L\hat{s}}$. We now could substitute each term in eq. (4) by its mean over $\Omega^*_{-L\hat{s}}$, but still it would not be clear that the last term, $< \Delta L'_{\hat{s}}(\eta, \vec{r}, L) >_{\Omega^*_{-L\hat{s}}}$, is what we are looking for. Some further comments are useful for this. First, it can be noted that the vector going from $\eta(\vec{r}+L\hat{s})$ to $\eta(\vec{r})$ is also parallel to $\hat{s}$ and have length:

$$L' = \|\eta(\vec{r} + L\hat{s}) - \eta(\vec{r})\| = \|(\alpha + 1)L\hat{s}\| = (\alpha + 1)L = (a'/a)L. \tag{6}$$

This means that η, or the displacement field $\vec{u}_m$, transforms any $\hat{s}$-parallel segment of length L in Ω to a segment of length L' of Ω', also parallel to $\hat{s}$. Second, besides knowing that $\eta : \Omega \to \Omega'$, it can be demonstrated that $\eta : \Omega^*_{-L\hat{s}} \to \Omega'^*_{-L'\hat{s}}$. Therefore, we can write eq. (5c) and its mean in $\Omega^*_{-L\hat{s}}$ as

$$\Delta L'_{\hat{s}}(\eta, \vec{r}, L) = \Delta L'_{\hat{s}}(\vec{r}', L') = u'_{\hat{s}}(\vec{r}' + L'\hat{s}) - u'_{\hat{s}}(\vec{r}'), \tag{7}$$

$$< \Delta L'_{\hat{s}}(\eta, \vec{r}, L) >_{\Omega^*_{-L\hat{s}}} = < \Delta L'_{\hat{s}}(\vec{r}', L') >_{\Omega'^*_{-L'\hat{s}}} = < u'_{\hat{s}}(\vec{r}' + L'\hat{s}) - u'_{\hat{s}}(\vec{r}') >_{\Omega'^*_{-L'\hat{s}}}, \tag{8}$$

where $\vec{r}' = \eta(\vec{r}) \in \Omega'^*_{-L'\hat{s}} \, \forall \, \vec{r} \in \Omega^*_{-L\hat{s}}$ and $\vec{r}' + L'\hat{s} = \eta(\vec{r} + L\hat{s}) \in \Omega' \, \forall \, \vec{r} \in \Omega^*_{-L\hat{s}}$.

From eqs. (5b) and (2) we have that

$$\Delta L_{m,\hat{s}}(\vec{r},L) =< \Delta L_{m,\hat{s}}(\vec{r},L) >_{\Omega^*_{-L\hat{s}}} = \alpha L. \tag{9}$$

Supposing that what we know are the mean value of $< \Delta L_{hkl} >$ and $< \Delta L^2_{hkl} >$, referred to the as-built configuration, $< \Delta L_{\hat{s}}(\vec{r},L) >_{\Omega^*_{-L\hat{s}}}$ and $< \Delta L^2_{\hat{s}}(\vec{r},L) >_{\Omega^*_{-L\hat{s}}}>$, the corrected value from eq. (4) will be then given by

$$< \Delta L'_{\hat{s}}(\vec{r}',L') >_{\Omega'^*_{-L'\hat{s}}} =< \Delta L_{\hat{s}}(\vec{r},L) >_{\Omega^*_{-L\hat{s}}} -\alpha L, \tag{10}$$

$$< \Delta L'^2_{\hat{s}}(\vec{r}',L') >_{\Omega'^*_{-L'\hat{s}}} =< \Delta L^2_{\hat{s}}(\vec{r},L) >_{\Omega^*_{-L\hat{s}}} -2 < \Delta L_{\hat{s}}(\vec{r},L) >_{\Omega^*_{-L\hat{s}}} \alpha L + \alpha^2 L^2. \tag{11}$$

Knowing which means are we referring to, eqs. (10) and (11) can be written shortly as

$$< \Delta L'_{\hat{s}}(L') >_{\Omega'} =< \Delta L_{\hat{s}}(L) >_{\Omega} -\alpha L, \tag{12}$$

$$< \Delta L'^2_{\hat{s}}(L') >_{\Omega'} =< \Delta L^2_{\hat{s}}(L) >_{\Omega} -2 < \Delta L_{\hat{s}}(L) >_{\Omega} \alpha L + \alpha^2 L^2. \tag{13}$$

Dividing eq. (12) by L' and eq. (13) by L'^2 we obtain the corresponding mean- and mean-square strains along a distance L' in Ω' parallel to $\hat{s}$:

$$< \varepsilon'_{\hat{s}}(L') >_{\Omega'} = \frac{a}{a'} \left(< \varepsilon_{\hat{s}}(L) >_{\Omega} -\alpha\right), \tag{14}$$

$$< \varepsilon'^2_{\hat{s}}(L') >_{\Omega'} = \left(\frac{a}{a'}\right)^2 \left(< \varepsilon^2_{\hat{s}}(L) >_{\Omega} -2 < \varepsilon_{\hat{s}}(L) >_{\Omega} \alpha + \alpha^2\right). \tag{15}$$

It is important to note that the Ls in the right- and left- members in eqs. (12,13,14,15) are not the same, they are related through the equation $L' = (\alpha+1)L = (a'/a)L$. The maximum permitted for both depends upon $\hat{s}$, but for L the limiting volume is Ω whereas for L' it is Ω'.

If the distortion model with which we are working is defined by a continuous displacement field, the means in eqs. (10) and (11) can be computed through integrations, as all possible distances L and L' can be considered, respectively, in Ω and Ω'. If on the

other hand, the distortion model is given by a Molecular Dynamic simulations yielding (mean) relaxed atomic positions from the as-built one, not all distances are allowed in principle. In this case the means can only be computed directly [1] through summations over pairs of unit cells or atoms, in the as-built and relaxed atomic configurations. Pair distances can be expressed in units of the unit cell parameter. In these units, it can be seen from eq. (6) that the segments L and L' will have the same length, i.e. an $L = \mathrm{d}_{uc}a$ in the as-built configuration will transforms into an $L' = \mathrm{d}_{uc}a'$ in the mean-relaxed configuration. Therefore, when distances over discrete atomic positions have to be considered, eqs. (10) and (11) transform to

$$< \Delta L'_{\hat{s}}(\vec{r}', a'\mathrm{d}_{uc}) >_{\omega'^*_{-a'\mathrm{d}_{uc}\hat{s}}} = < \Delta L_{\hat{s}}(\vec{r}, a\mathrm{d}_{uc}) >_{\omega^*_{-a\mathrm{d}_{uc}\hat{s}}} - \alpha a\mathrm{d}_{uc}, \tag{16}$$

$$\begin{aligned} < \Delta L'^2_{\hat{s}}(\vec{r}', a'\mathrm{d}_{uc}) >_{\omega'^*_{-a'\mathrm{d}_{uc}\hat{s}}} = & < \Delta L^2_{\hat{s}}(\vec{r}, a\mathrm{d}_{uc}) >_{\omega^*_{-a\mathrm{d}_{uc}\hat{s}}} - \\ & - 2 < \Delta L_{\hat{s}}(\vec{r}, a\mathrm{d}_{uc}) >_{\omega^*_{-a\mathrm{d}_{uc}\hat{s}}} \alpha a\mathrm{d}_{uc} + \alpha^2 (a\mathrm{d}_{uc})^2, \end{aligned} \tag{17}$$

where the discrete ω domains refers to the atomic positions inside their corresponding continuous Ω domains. We could as well write these equations shortly as:

$$< \Delta L'_{\hat{s}}(a'\mathrm{d}_{uc}) >_{\omega'} = < \Delta L_{\hat{s}}(a\mathrm{d}_{uc}) >_{\omega} - \alpha a\mathrm{d}_{uc}, \tag{18}$$

$$< \Delta L'^2_{\hat{s}}(a'\mathrm{d}_{uc}) >_{\omega'} = < \Delta L^2_{\hat{s}}(a\mathrm{d}_{uc}) >_{\omega} - 2 < \Delta L_{\hat{s}}(a\mathrm{d}_{uc}) >_{\omega} \alpha a\mathrm{d}_{uc} + \alpha^2 (a\mathrm{d}_{uc})^2. \tag{19}$$

For the strains we would obtain like before:

$$< \varepsilon'_{\hat{s}}(a'\mathrm{d}_{uc}) >_{\omega'} = \frac{a}{a'} \left(< \varepsilon_{\hat{s}}(a\mathrm{d}_{uc}) >_{\omega} - \alpha \right), \tag{20}$$

$$< \varepsilon'^2_{\hat{s}}(a'\mathrm{d}_{uc}) >_{\omega'} = \left(\frac{a}{a'} \right)^2 \left(< \varepsilon^2_{\hat{s}}(a\mathrm{d}_{uc}) >_{\omega} - 2 < \varepsilon_{\hat{s}}(a\mathrm{d}_{uc}) >_{\omega} \alpha + \alpha^2 \right). \tag{21}$$

[1] A continuous displacement field could be built by means of an interpolations from the known displacement values at the atomic positions. Then eqs. (10) and (11) could be applied also in this case.

2. Mean radial displacement according to the surface relaxation model presented in (Perez-Demydenko & Scardi, 2017)

The displacement field for the surface relaxation model proposed in (Perez-Demydenko & Scardi, 2017) has the form $\vec{u}(\vec{r}) = u(\vec{r})\hat{r}$ with $u(\vec{r})$ given by:

$$u(\vec{r}) = \sigma\, s'_{\hat{r}}\, r + \beta\, f_{R,r_o}(r). \tag{22}$$

Here $s'_{\hat{r}} = s_{11} - 2(s_{11} - s_{12} - s_{44}/2)(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2)$ and (l_1, l_2, l_3) are the components of the position versor $\hat{r}$. Since the function f_{R,r_o} does not depend on the orientation, the average of eq. (22) over a sphere of radius r will be:

$$< u(\vec{r}) >_r = \frac{1}{4\pi r^2} \iint \sigma\, s'_{\hat{r}}\, r \mathrm{d}^2\vec{r} + \beta\, f_{R,r_o}(r). \tag{23}$$

Using spherical coordinates $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$ and $x = r\cos\theta$ the inverse of the Young modulus is given by $s'_{\hat{r}} = s_{11} - 2(s_{11} - s_{12} - s_{44}/2)(\sin^4\theta\cos^2\phi\sin^2\phi + \sin^2\theta\cos^2\theta)$, which means that

$$\begin{aligned} \frac{1}{4\pi r^2} \iint \sigma\, s'_{\hat{r}}\, r \mathrm{d}^2\vec{r} &= \frac{1}{4\pi r^2} \int_0^{\pi} \int_0^{2\pi} \sigma\, s'_{\hat{r}}\, r\, r^2 \sin\theta \mathrm{d}\theta \mathrm{d}\phi \\ &= \frac{1}{5}(3s_{11} + 2s_{12} + s_{44}) r\sigma. \end{aligned} \tag{24}$$

Substituing this eq. into eq. 23 we obtain for the mean radial displacement $< u(\vec{r}) >_r = (1/5)(3s_{11} + 2s_{12} + s_{44})r\sigma + \beta f_{R,r_o}(r)$.

References

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