1.6   Local dynamics

An EXAFS photoelectron samples the modulus of the instantaneous interatomic distance between absorber (1) and back-scatterer (2) atoms

$$r \equiv |\mathbf{r}| = |\mathbf{R}_c + \mathbf{u}_2 - \mathbf{u}_1| \tag{1.46}$$

Here the $\mathbf{u}_1$ and $\mathbf{u}_2$ denote the thermal displacements from the equilibrium positions at a given temperature and $\mathbf{R}_c$ is the equilibrium distance between mean positions of the two atoms (see Fig. 1.2). If we decompose the atomic relative displacement $\Delta\mathbf{u}$
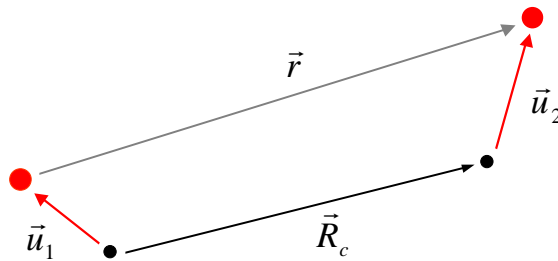

Fig. 1.2. Comparison between crystallographic equilibrium distance R_c and instantaneous interatomic distance r probed by EXAFS.

into projections parallel and perpendicular to the bond direction, we have [29]

$$r = R_c + \Delta u_\parallel + \frac{\Delta u_\perp^2}{2R_c} - \frac{\Delta u_\parallel \Delta u_\perp^2}{2R_c^2} + \dots \tag{1.47}$$

This approximate analytical relation for r has been obtained through a Taylor expansion, considering small relative displacements with respect to the interatomic distance

$$x = \frac{|\mathbf{u}_2 - \mathbf{u}_1|}{R_c} \ll 1 \tag{1.48}$$

1.6.1   Cumulants and local dynamical properties

The first three cumulants C_i^* represent average value, variance and asymmetry of the EXAFS one-dimensional distribution of distances $\rho(r)$. Through Eq. (1.47), they can be connected to the local dynamical behavior of the system, i.e. to the atomic relative displacements parallel and perpendicular to the interatomic bond.

First cumulant

The thermal average of Eq. (1.47) leads to

$$C_1^* \equiv \langle r \rangle = R_c + \frac{\langle \Delta u_\perp^2 \rangle}{2R_c} + \dots \tag{1.49}$$

where it has been considered that $\langle \Delta u_\| \rangle = 0$. This is easily understood since thermal displacements $\mathbf{u}_i$ are referred (at any temperature) to the equilibrium positions [30], which are defined as the centers of the probability distributions of atoms.

Second cumulant

Properly combining Eqs. (1.47) and (1.49), we obtain

$$C_2^* \equiv \langle (r - \langle r \rangle)^2 \rangle = \langle \Delta u_\|^2 \rangle + \frac{1}{R_c} \langle \Delta u_\perp^2 \Delta u_\| \rangle - \frac{1}{R_c^2} \langle \Delta u_\perp^2 \Delta u_\|^2 \rangle +$$
$$+ \frac{1}{4R_c^2} \Big[\langle \Delta u_\perp^4 \rangle - \langle \Delta u_\perp^2 \rangle^2 \Big] + \dots \tag{1.50}$$

In the case of harmonic crystal, this equation correctly reduces to Eq. (4) of Ref. [13] (which lacks the second term on the right-hand side). Anyway, it is customary to truncate Eq. (1.50) to the first dominant term, which corresponds to the parallel mean square relative displacement [15]

$$C_2^* \simeq \langle \Delta u_\|^2 \rangle \equiv MSRD_\| \tag{1.51}$$

Third cumulant

Proceeding as above, we find that the third cumulant is given by:

$$C_3^* \equiv \langle (r - \langle r \rangle)^3 \rangle = \langle \Delta u_\|^3 \rangle + \frac{3}{2R_c} \Big[\langle \Delta u_\|^2 \Delta u_\perp^2 \rangle - \langle \Delta u_\|^2 \rangle \langle \Delta u_\perp^2 \rangle \Big] + \dots \tag{1.52}$$

The lowest order term $\langle \Delta u_\|^3 \rangle$ corresponds to the parallel mean cubic relative displacement (MCRD$_\|$). For an ideally harmonic crystal [31] it would be zero: in this case Eq. (1.52) correctly reduces to Eq. (7) of Ref. [13] (which lacks the first term on the right-hand side). Therefore it is well understood that the third cumulant is mainly due to crystal anharmonicity. The second order term on the right-hand side of Eq. (1.52) is instead due to the harmonic part of the crystal potential: the third cumulant is then always different from zero, also for an harmonic crystal [13], so that in principle the distribution $\rho(r)$ is never gaussian.

1.6.2   Mean square relative displacements

The parallel and perpendicular MSRDs are defined as

$$MSRD_\| = \langle \big| (\mathbf{u}_2 - \mathbf{u}_1) \cdot \hat{\mathbf{R}}_c \big|^2 \rangle \tag{1.53a}$$

$$MSRD_\perp = \langle \big\| (\mathbf{u}_2 - \mathbf{u}_1) \big\|^2 \rangle - \langle \big| (\mathbf{u}_2 - \mathbf{u}_1) \cdot \hat{\mathbf{R}}_c \big|^2 \rangle \tag{1.53b}$$

They both can be decomposed into the sum of un-correlated mean square displacements (MSDs) and a correlation term

$$
\begin{aligned}
\langle \Delta u_{\parallel}^2 \rangle &= \langle |(\mathbf{u}_2 \cdot \hat{\mathbf{R}}_c)|^2 \rangle + \langle |(\mathbf{u}_1 \cdot \hat{\mathbf{R}}_c)|^2 \rangle - 2\langle (\mathbf{u}_2 \cdot \hat{\mathbf{R}}_c)(\mathbf{u}_1 \cdot \hat{\mathbf{R}}_c) \rangle \\
&= \langle u_{2_{\parallel}}^2 \rangle + \langle u_{1_{\parallel}}^2 \rangle - 2\langle u_{2_{\parallel}} u_{1_{\parallel}} \rangle
\end{aligned}
\tag{1.54a}
$$

$$
\begin{aligned}
\langle \Delta u_{\perp}^2 \rangle &= \langle \|\mathbf{u}_2\|^2 - |(\mathbf{u}_2 \cdot \hat{\mathbf{R}}_c)|^2 \rangle + \langle \|\mathbf{u}_1\|^2 - |(\mathbf{u}_1 \cdot \hat{\mathbf{R}}_c)|^2 \rangle + \\
&\quad -2 \langle \mathbf{u}_2 \cdot \mathbf{u}_1 - (\mathbf{u}_2 \cdot \hat{\mathbf{R}}_c)(\mathbf{u}_1 \cdot \hat{\mathbf{R}}_c) \rangle \\
&= \langle u_{2_{\perp}}^2 \rangle + \langle u_{1_{\perp}}^2 \rangle - 2\langle \mathbf{u}_{2_{\perp}} \cdot \mathbf{u}_{1_{\perp}} \rangle
\end{aligned}
\tag{1.54b}
$$

In these equations we have set

$$
\begin{aligned}
\|\mathbf{u}_i\|^2 &= u_{i_{\parallel}}^2 + u_{i_{\perp}}^2 \\
\mathbf{u}_i \cdot \mathbf{u}_j &= u_{i_{\parallel}} u_{j_{\parallel}} + \mathbf{u}_{i_{\perp}} \cdot \mathbf{u}_{j_{\perp}} \qquad \text{for} \qquad i \neq j
\end{aligned}
$$

The comparison between EXAFS MSRDs and the absolute mean square displacements (MSDs)[‡] obtained from x-ray diffraction (XRD) allows the valuation of correlation of atomic motion parallel and perpendicular to interatomic bond.

On the basis of statistics theorems [30], it is possible to place bounds upon the correlation terms of Eqs. (1.54a) and (1.54b)

$$
-\sqrt{\langle u_{2_{\parallel}}^2 \rangle \langle u_{1_{\parallel}}^2 \rangle} \leq \langle u_{2_{\parallel}} u_{1_{\parallel}} \rangle \leq \sqrt{\langle u_{2_{\parallel}}^2 \rangle \langle u_{1_{\parallel}}^2 \rangle}
$$

$$
-\sqrt{\langle u_{2_{\perp}}^2 \rangle \langle u_{1_{\perp}}^2 \rangle} \leq \langle \mathbf{u}_{2_{\perp}} \cdot \mathbf{u}_{1_{\perp}} \rangle \leq \sqrt{\langle u_{2_{\perp}}^2 \rangle \langle u_{1_{\perp}}^2 \rangle}
$$

One can then place upper and lower bounds to parallel and perpendicular MSRDs [30]

$$
\langle \Delta u_{\parallel}^2 \rangle_{low} \equiv \left(\sqrt{\langle u_{2_{\parallel}}^2 \rangle} - \sqrt{\langle u_{1_{\parallel}}^2 \rangle} \right)^2 \leq \langle \Delta u_{\parallel}^2 \rangle \leq \left(\sqrt{\langle u_{2_{\parallel}}^2 \rangle} + \sqrt{\langle u_{1_{\parallel}}^2 \rangle} \right)^2 \equiv \langle \Delta u_{\parallel}^2 \rangle_{upp}
$$

$$
\langle \Delta u_{\perp}^2 \rangle_{low} \equiv \left(\sqrt{\langle u_{2_{\perp}}^2 \rangle} - \sqrt{\langle u_{1_{\perp}}^2 \rangle} \right)^2 \leq \langle \Delta u_{\perp}^2 \rangle \leq \left(\sqrt{\langle u_{2_{\perp}}^2 \rangle} + \sqrt{\langle u_{1_{\perp}}^2 \rangle} \right)^2 \equiv \langle \Delta u_{\perp}^2 \rangle_{upp}
$$

It is then possible to put lower and upper bounds upon the parallel and perpendicular mean square relative displacements without any knowledge of their correlation: lower and upper bounds correspond to highly correlated and anti-correlated relative motion, respectively.

[‡]According to Ref. [30], the perpendicular mean square displacement $\mathrm{MSD}_{\perp} \equiv \langle u_{\perp}^2 \rangle$ refers to a projection on the plane perpendicular to the interatomic bond. This is consistent with the use of the term "perpendicular" in Eq. (1.47) and followings. Elsewhere [32] the so-called $U_{\perp}$ are used, referring however to a single direction contained in the perpendicular plane. In the case of rotational symmetry around the bond direction, $\langle u_{\perp}^2 \rangle = 2U_{\perp}$.