Debye's Legacy: Structural Chemistry at the Nanoscale by Innovative Total Scattering Methods

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In order to understand the complexity of nanosized materials and, particularly, the dependence of their functional properties on their variable sizes and shapes, advanced and powerful structural/ microstructural characterization techniques need to be developed. New methods, both at the experimental and computational level, are necessary to correctly interpret the structure-property relationships and to drive the design of nanomaterials toward optimized performances.
X-ray and neutron powder diffraction methods have reached nowadays a high degree of maturity, and constitute the leading technique for investigating complex materials at the atomic length scale. These methods are widely used to investigate the structure and microstructure of microcrystalline samples through the whole pattern modelling of the scattered intensity confined within the Bragg peaks, by the so-called Rietveld approach. However, diffraction patterns collected on nanocrystalline materials show smeared Bragg scattering and a strong diffuse component; here, conventional crystallographic approaches are likely to fail, not being able to suitably extract the information sought for. At variance, the Debye equation (proposed by Peter Debye nearly one century ago – in 1915) directly models the whole scattering of a particle regardless of the presence of any long range order (crystal periodicity). Though really powerful in characterizing nanosized and disordered materials, this equation, if used crudely 'as it is', requires extremely long computational times and has only seldom been used. To overcome this problem, advanced sampling algorithms have been recently developed and, since then, the *Renaissance of the Debye Function* approach took place, providing the material scientist with a powerful tool to investigate structure, size, shape, their distributions, and defects in nanocrystalline materials.
Thanks to this newly available technique, and using tailored experimental and computational algorithms [1], we have been able to extract useful structural and microstructural information for a wide variety of technologically or biomedically relevant materials, ranging from metals, alloys and oxides [2], to bioinspired nanoapatites [4], drug-polymer nanocomposites [4] and highly defective metallorganic polymers [5]. Selected examples will be presented, aiming at highlighting the power of the method and some of the relevant features of the investigated materials (structure, stoichiometry, defectiveness, microstructure and nanoparticle growth mechanisms) and the *quantitative* correlations to their functional properties.

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