THE PHENOMENOLOGICAL FUNCTION USED FOR THE SIZE-RELATED STRAIN

We adopted a phenomenological function to model size-related strain effects, rather than directly linking the strain curve to basic physics, because of the following reasons:

1. the main aim of this manuscript is to propose a quite general approach available for any monoatomic fcc-derived non-crystallographic nanoclusters. Strain - in the approximation of uniform strain - is important in these structures and it is very likely to have a strong dependence on cluster size due to the major importance of surface energy at small sizes.
2. Little is known about the strain-size dependence for small nanoclusters, from the physical point of view. On one side, there is little reliable experimental information; at least, we are not aware of a precisely determined description of strain-size dependence for any specific system. On the other side, theoretical calculations (as in D'Agostino et al.) are rare and difficult to generalize to different combinations of materials with surfactants and substrates. Therefore it is not presently possible to introduce one function (or a set thereof for various known cases) depending on physically meaningful parameters which can give direct information on the system. It is plausible - and there are indications given in cited literature - to have a smooth monotonic dependence of the lattice parameter with the NP size which asymptotically becomes constant at large sizes. Tiny hints are found in literature about possible step-like effects at some critical size (see Vogel, for Au clusters with a threshold of 575 atoms), possibly due to interaction with bulky surfactants or lock-in for composite crystals.
3. Needing to be adaptable to a wide range of sample materials and conditions and due to the poorness of the theoretical information available, our only choice was to try to extract from diffraction data an approximate knowledge of a set of physically meaningful strain values at different sizes. These can be useful to who studies specific systems in order to test and improve his physical model. Two possible choices were in front of us.

The first would be to use one average strain parameter for every cluster dimension (and structure type). It was discarded as it would increase tenfold the number of free model parameters - and decrease the reliability of the results especially for broad distributions, where the smaller sizes would be strongly penalized as the scattering power goes with the sixth power of the diameter. The second was to find a flexible function depending on few parameters which could acceptably approximate plausible physical dependences for most system according to the general considerations above reported.

4. According to the aforesaid considerations, we chose a form with 4 free parameters (Ξ, Ω, n_0, w, Eqs. 9,10) which can be bent to reproduce acceptably many plausible behaviours. It is evident that we can distinguish three main cases:

I) constant strain with respect to cluster size (as expected for narrow size distributions),

II) a smooth asymptotic behaviour as shown in the papers of Palozs and Vogel,

III) a step-like form as for more complex situations (composite nanoparticles).

In fact, we have performed tests to see that the chosen function approximates fairly well different realistic behaviours for all three cases. Case I) is trivial: set $\Xi=\Omega$ and the function becomes a constant. About case III) our function is intrinsically suited (see Fig. 2). Case II is more delicate because it includes a vast class of functions. We report now two examples of how we can closely approximate at least two different classes of functions of physical interest, with a convenient parameter choice. In both examples we consider a log-normal distribution (with parameters as from Tab. 3) of icosahedral-type particles. No noise and no background were introduced. Diffraction patterns were simulated with different strain-size functions and the best approximation by our function was determined.

- Consider a rational strain function

  $$a = 1 - 0.097887\,(2n^2+3n+1) / (7.618034\,n^2 + 6\,n + 2.723607),$$

  which is typical for quadratic first-neighbour interactions (see Eq.29 of our manuscript). Setting in Eqs.9,10 $n^0=0$, $w= 4.918087$, $\Omega = 0.976849$, $\Xi = 0.964244$ we obtain an excellent approximation, shown in Fig. 1a,b. In particular, the diffraction profiles coincide to over 6 digits, the strain values to three digits.
- As another example, consider an exponential strain function,

  $$a = 0.974301 - 0.012509 \exp(-n/5).$$

Setting in our function $n^0=0$, $w= 1.789804$, $\Omega = 0\ .974147$, $\Xi= 0.\ 964592$, again we get an excellent approximation, as shown in Fig. 2a,b. The strain curves differ more than the 3rd digit only in the region ($n>12$), where the considered distribution is already zero.

D'Agostino G., Pinto A. and S. Mobilio, Phys. Rev. B **48** (1993) 14447-14453

Vogel M., Bradley J., Vollmer O. and Abraham I., J. Phys. Chem. **B 102** (1998) 10853-10859

Palosz B., Grzanka E., Gierlotka S., Stel'makh S., Pielaszek R., Bismayer U., Neuefeind J., Weber H.-P., Proffen Th., Von~Dreele R. and W. Palosz, Z. Kristallogr. **217** (2002) 497-509

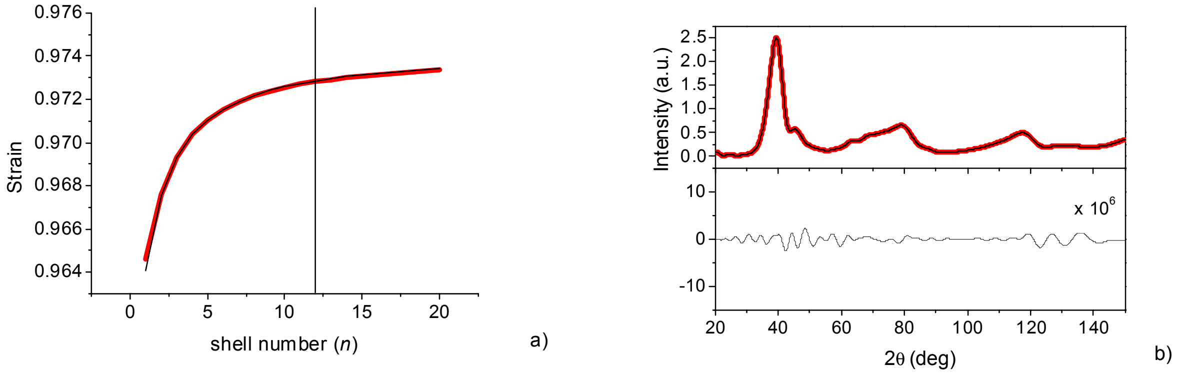

Fig.1. a), the strain-size dependence: red, the function used to generate the simulation (rational strain behaviour $a = 1 - 0.097887\ (2n^2+3n+1)\ /\ (7.618034\ n^2 + 6\ n + 2.723607)$); black, the fit with our function, see text. The mark at n=12 shows the upper limit for the size distribution in the relative calculated diffraction patterns.
b) the corresponding diffraction patterns and their difference (calculated for I-type clusters of Au, lambda=0.15418 nm, size distribution as from Tab. 3 of the manuscript; no noise or background added). The same colour code (red for the original function, black for our fit) is used (upper half). Difference plot (below) is magnified by 10^6.

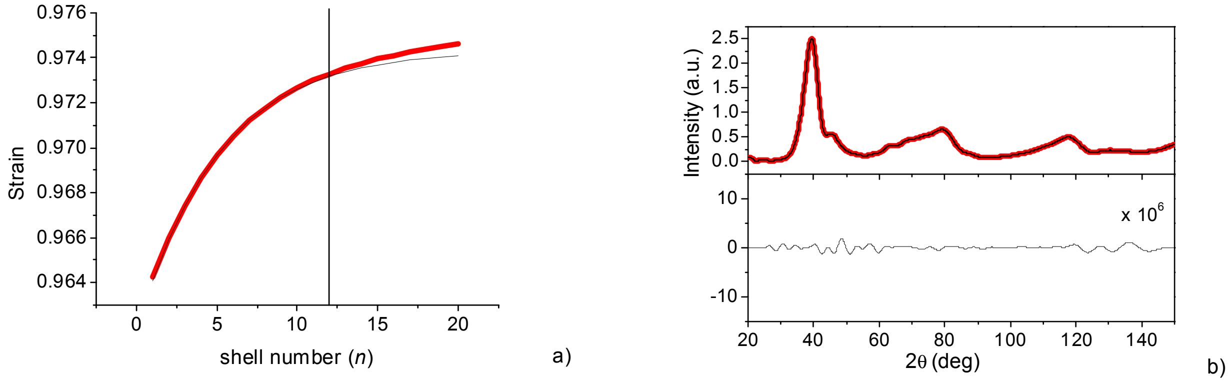

Fig.2. a), the strain-size dependence: red, the original function (an exponential strain, $a = 0.974301 - 0.012509\ \exp(-n/5)$), black, the fit with our function, see text. The mark at n=12 shows the upper limit for the size distribution in the relative calculated diffraction patterns.
b) the corresponding diffraction patterns and their difference (calculated for I-type clusters of Au, lambda=0.15418 nm, size distribution as from Tab. 3 of the manuscript; no noise or background added). The same colour code is used (red for the original function, black for our fit). Difference plot (below) is magnified by 10^6.