Application of Green's function and molecular dynamics to dislocations and lattice vibrations in small metal grains and grain boundaries

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Introduction

Nanocrystalline (nc) FCC metals contain a high density of interface structures that result in these materials having unique mechanical and structural properties [1]. Due to the difficulty with the experimental characterisation of such systems, atomistic simulation has played an important and guiding role in the elucidation of these structures. Morever when the atomistic simulation of nc structures is used in conjunction with methods that simulate conventional experimental techniques such as X-ray diffraction (XRD), thermal neutron inelastic scattering, and transmission electron microscopy, explicit synergetic relations between modelling and experiment become possible.

In the present submission we provide two examples of such synergetic atomistic modelling approaches. In the first case we calculate the phonon properties of bulk nc structres separating the contribution from grain interiors and grain boundary regions [2,3]. This is motivated by inelastic thermal neutron scattering experiments that probe the phonon (or vibrational) density of states (VDOS), which have estabilished anomalous behaviour for nc materials when compared to the perfect crystalline VDOS. In the second case we calculate the two-theta XRD profile directly from the computer generated nc structures [4], at typical synchrotron photon energies, to investigate the role of the high density of grain boundaries that exists in the nc regime. This work is motivated by recent in-situ plastic deformation experiments performed at the Swiss synchrotron light source on nc Ni, which though a series of loading and unloading experiments have demonstrated that upon unloading beyond yield, any broading due to plasticity is predominantly recovered [5, see also presentation SRMS5-161].

Methods and Materials

The phonon or vibrational density of states (VDOS) is calculated using two different approaches. In the first instance, the average VDOS for the grain interior and grain boundary regions is obtained via the Fourier transform of the velocity-velocity auto-correlation function [2], the latter of which is given by

$$\langle \widetilde{v}(0) \cdot \widetilde{v}(t) \rangle = \frac{1}{N} \sum_{i} \widetilde{v}_i(0) \cdot \widetilde{v}_i(t), \qquad (1)$$

and obtained directly from finite temperature molecular dynamics simulations. In Eqn. (1), the averages are performed separately over the grain interior and grain boundary regions to obtain the associated VDOS via the Fourier transform. Although this method is relatively efficient and yields energy spectra that can be compared to experiment, it does not allow for an efficient investigation of the VDOS for one or a few atom. To do this, the local VDOS is calculated directly from the imaginary part of the onsite Greens function:

$$G_{ii}^{\mu v}(\omega) = \left[\left(\widetilde{I}\omega^2 - \widetilde{\Delta} \right)^{-1} \right]_{ii}^{\mu v}, \qquad (2)$$

where $\widetilde{\Delta}$ is the force matrix (derived from an empirical potential) and the Greek indices represent phonon polarization directions. Thus to obtain the onsite Green's function a secular Eqn. must be diagonalised, which becomes an intractable problem for systems containing a large number of atoms. However by employing order N recursion techniques, the onsite Greens function can be calculated directly and efficiently, and thus the VDOS can be investigated for particular atoms of interest [3].

For an atomic configuration consisting of N atoms, a (Debye) powder X-ray spectrum can be calculated via,

$$I(k) = |f|^2 \left(N + \sum_{i \neq j}^{N} \frac{\sin kr_{ij}}{kr_{ij}} \right), \qquad (3)$$

where r_{ij} represents the distance between atoms i and j, f is the atomic form factor (assumed to be the same for each atom and in the present work independent of the scattering vector), and k is the scattering vector magnitude. Eqn 3 is the spherically averaged structure factor of the atomic configuration and involves a double summation over all atoms resulting in a order N^2 dependence. However by recasting Eqn. 3 as

$$I(k) = |f|^2 \left(N + \int_0^{\infty} l(r) \frac{\sin kr}{kr} dr \right), \qquad (4)$$

the problem is simplified to the calculation of the pair-distribution function, $l(r)$, which can be much more efficiently evaluated allowing systems up to 10s of millions of atoms to be investigated [4].

Results

Fig.s 1A and 1B displays the on-site Greens function derived VDOS for respectively the grain interior and grain boundary regions for computer generated nc Ni with a mean grain diameter of 5nm. Each VDOS is taken from the the average of 1000 grain interior and 1000 grain boundary atoms, where the shaded region indicates the energy dependent standard deviation over the sampled local environments. Fig. 1A demonstrates that despite the small grain size, the grain interiors on average do not exhibit vibrational modes that differ significantly from the fcc crystalline case, whereas Fig. 1B indicates that the grain boundary vibrational spectrum is considerably different. In the low frequency regime, a non-quadratic power law with exponent ~1.5 is measured, which via the Debye density of states form $(\sim \omega^{d-1})$, correlates well with the measured dimensionality, ~2.5, of the computer generated GB region [2].
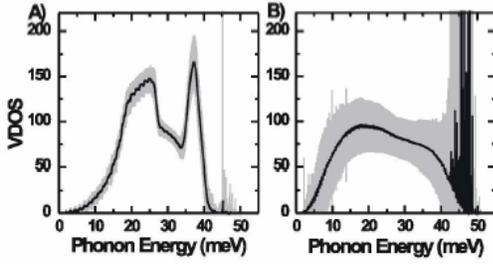
Fig 1

Nanocrystalline Ni VDOS for A) grain interior and B) grain boundary region where the standard deviation derived from an environment ensemble.

In the high frequency regime, a singular structure is observed in the grain boundary VDOS (see fig. 1B). Detailed inspection of the grain boundary structure reveals that such singular structure represents high-frequency localised modes at the interface region [3].
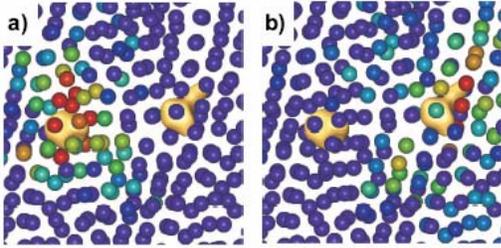

Fig 2

High angle GB with viewing angle parallel to the GB normal where atoms are coloured according to their VDOS oscillator strength evaluated at phonon enegies a) 44.791 meV and 44.318 meV.

Fig. 2A and 2B display the atomic structure of a grain boundary with atoms coloured according to their local VDOS oscillator strength at two phonon energies at which VDOS singular peaks are observed to occur. Here red (blue) represent the maximum (minimum) oscillator strength. Inpection of Fig. 2 indicates that the corresponding vibrational modes are well localised in the grain boundary and in both cases correspond to regions of reduced coordination [3].

Fig. 3A displays the calculated XRD specrum by applying eqn 4 to computer generated nc Ni structures consisting of each of approximatley 1.5 million atoms. An incident photon energy of 17.5KeV is used which is similar to that used in in-situ deformation experiments at the Swiss synchrotron light source. Two grain sizes are considered: 5 nm and 12nm. Closer inspection of Fig. 3A reveals that well defined peak profiles are obtained and are suitable for traditional peak profile analysis in terms of peak position and integral-peak width. Fig. 3B displays the integral peak width versus peak position (in terms of the scattering vector) – the traditional Williamson-Hall plot, where an estimation of the grain size is given by the y-intercept, and the root-mean-square (RMS) strain by the gradient. Such an analysis yields for the 5nm sample a grain size of ~5.3 and a RMS strain of ~0.34, and for the 12nm sample a grain size of ~10.1 and a RMS strain of ~0.1 [4]. Fig. 3B) also includes experimentally derived Williamson-Hall data, and demonstrates that the simulated spectra lacks the strong anisotropy seen in experiment. This suggests that comparison of the current simulated XRD data with experimentally derived XRD data must be taken with care since the microstructure of the experimental samples is not fully represented by the computer-generated structures.
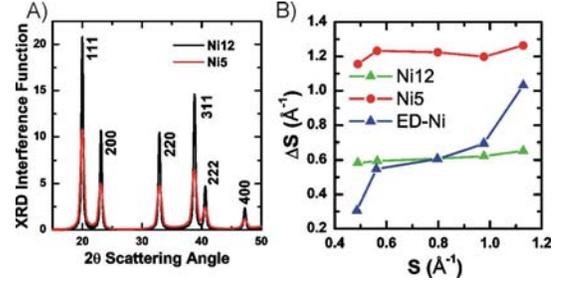

Fig 3

Calculated XRD spectra A) and resulting Williamson-Hall plot B) for computer generated nanocrystalline Ni structures with mean grain size of 12nm and 5nm. Incident photon energy is 17.5KeV.

Discussion

Inelastic neutron scattering experiments have revealed that fcc nanocrystalline structures exibit anomolous bulk phonon properties. The present work estabilishes that such anomolous behaviour arises from the low and high frequency vibrational properties of the grain boundary region [2,3], while within the grain interiors, the vibrational properties remain similar to that of bulk crystalline behaviour. Moreover simulation has revealed that the low frequency non-quadratic behaviour may arise from a reduced effective dimensionality in the grain boundaries since the VDOS is expected to scale at low frequencies as ω^{d-1}, where d is the spatial dimension. On the other hand, in the high frequency regime, the anomolous behaviour arises from localised vibrational modes with in the grain boundary region.

Knowledge of the grain boundary VDOS allows one to directly calculate the thermal mean-square-displacement (MSD) of grain boundary atoms within the harmonic approximation. Use of the VDOS displayed in fig. 1B results in a thermal MSD of $\sim85.10^{-4}$ Å^2. On the other hand, by calculating the XRD profile from atomic coodinates derived from both instantaneous and averaged atomic configurations it becomes possible to extract bulk Debye-Waller factors and therefore bulk values for the MSD. Doing so gives $\sim42.10^{-4}$ Å^2 for the 12nm and $\sim46.10^{-4}$ Å^2 for the 5nm grain size sample which are not so different from the calculated MSD ($\sim43.10^{-4}$ Å^2) and also the experimental MSD ($\sim42.10^{-4}$ Å^2) for bulk crystalline fcc Ni. The smaller values (when compared to the grain boundary) and relative insentivity to grain size of the XRD derived bulk MSD values reflects the fact that the Bragg peaks present in the calculated XRD patterns primarily probe the nc grain interiors, and not that of the grain boundary.

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