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# NANOMECHANICS AND NANOMETALLURGY OF BOUNDARIES

## 100 Years of Scherrer Modifications: Demystifying Diffractogram Width Analyses for Nanocrystalline Materials

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## MISINTERPRETING DIFFRACTION ANALYSES

Grain-morphology evolution in nanocrystalline materials strongly affects the deformation mechanisms collectively responsible for mechanical performance.

Because nanocrystalline materials, with billions of grain boundaries per cubic millimeter, provide a useful 'defect laboratory' by which to study boundary/network-mediated behavior and emergent mechanistic phenomena, **techniques for tracking nanoscale grain sizes *in situ* pose high value experimentally**.

The X-ray diffraction (XRD) analysis of peak widths offers a pragmatic and attractive middle ground between visual inspection and structure refinement to quantify key crystallographic features, such as characteristic size, microstrain, and dislocation density. Unfortunately, overlapping nomenclatures and overlooked nuances complicate rational applications of width analysis.

**OBJECTIVE: This study uses virtual X-ray diffraction from atomistic simulation results to unify and generalize XRD nomenclature to facilitate diffractogram width analysis for nanocrystalline materials.**

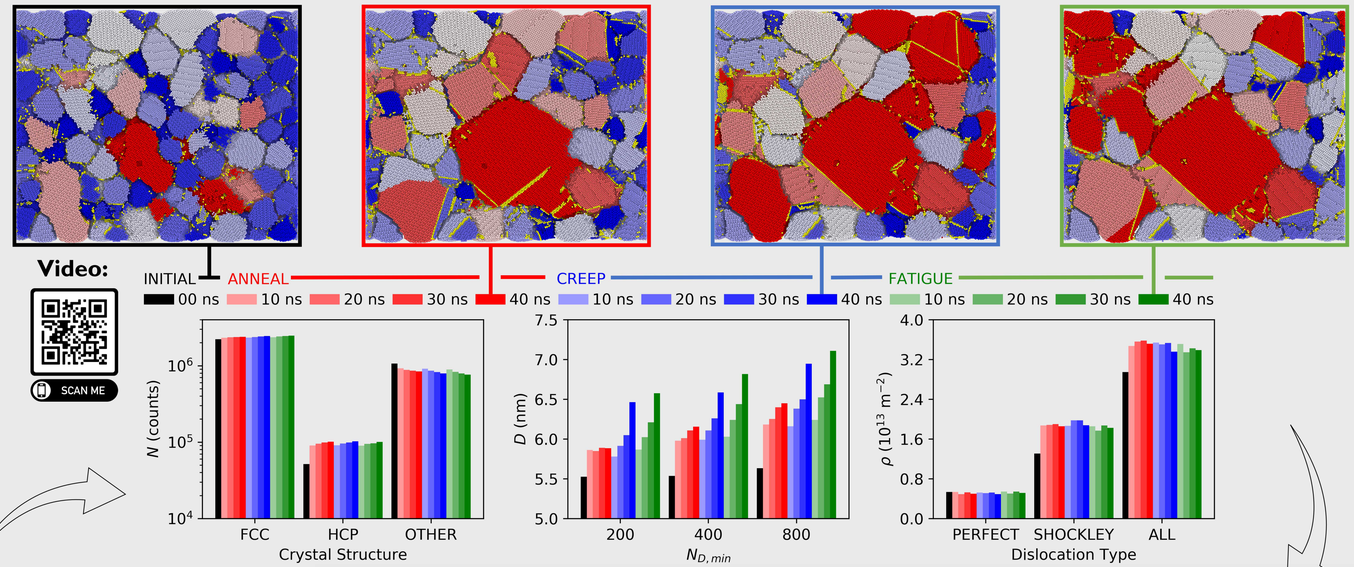
## UNIFYING DIFFRACTOGRAM WIDTH ANALYSES THROUGH ATOMISTIC MODELING

### 1. Atomistically Simulating Grain-Morphology Evolution in Nanocrystalline Nanowires

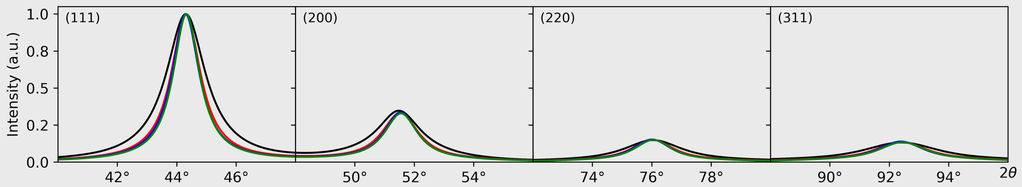
We obtain full volumetric statistics by analyzing molecular-dynamics simulations of nanocrystalline nickel nanowires subjected to anneal, creep and mechanical fatigue [1].

Trends in grain size suggest that both thermal and mechanical mechanisms contribute to grain growth.

We quantify the domain sizes and dislocation densities from the atomistic models to evaluate the accuracy of the predictions from a survey of width analyses.




### 2. Generating Virtual X-ray Diffractograms from Simulations




We simulated virtual diffractograms [2] for the nanocrystalline nickel nanowire at the initial state and every 10-ns increment of anneal, creep and fatigue. Peak widths (β) and peak centers (2θ) are identified through pseudo-Voigt fits. The magnitude of β depends not only on the crystallographic plane (*hkl*) but also on the width type, full-width-half-max width or integral-breadth width.

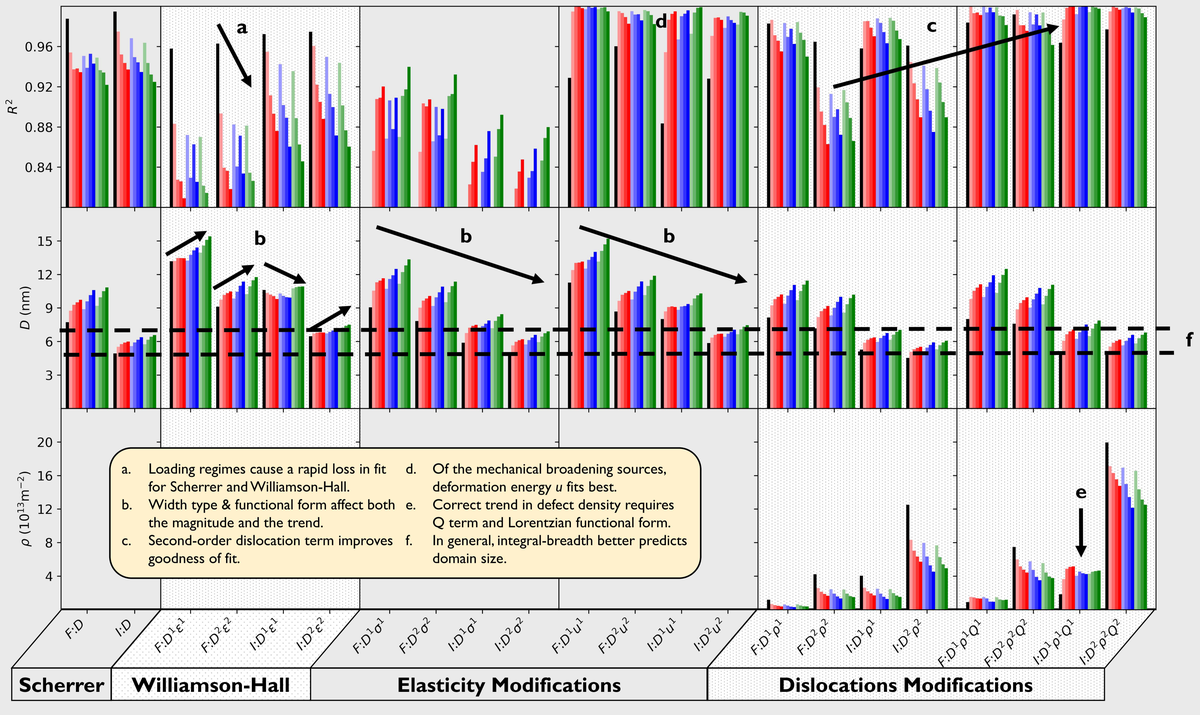
### 3. Tracking Domain Size & Dislocation Evolution *in situ* through Width Analyses

We tested 22 width methods [3-7] on the virtual diffractograms to predict domain size (D) and dislocation density ($\rho$). Methods vary by:

(i) **Width type:** full-width-half-max (*F*) or integral-breadth (*I*)

(ii) **Broadening sources:** domain size (*D*), strain ($\varepsilon$), stress ($\sigma$), energy (u), dislocation density ($\rho$), and dislocation correlation (Q)

(iii) **Functional forms:** Lorentzians ($^1$) or Gaussians ($^2$)




a. Loading regimes cause a rapid loss in fit for Scherrer and Williamson-Hall.
b. Width type & functional form affect both the magnitude and the trend.
c. Second-order dislocation term improves goodness of fit.
d. Of the mechanical broadening sources, deformation energy *u* fits best.
e. Correct trend in defect density requires Q term and Lorentzian functional form.
f. In general, integral-breadth better predicts domain size.

## IN BRIEF

**SUMMARY:** Since the landmark development of the Scherrer method 100 years ago, many specialized versions of diffractogram width analysis have originated to rapidly and non-destructively characterize large volumes of unique nanomaterials. To facilitate the rational applications of width analyses, we present a unified theory and generalized nomenclature enabled by atomistic modeling.

**CONCLUSION: We demonstrate the width-method selection, in terms of width type, broadening source, and functional form can affect not only the magnitudes but also the trends of the crystallographic predictions.**

**OUTLOOK:** The present methodology can be applied to various nanocrystalline materials systems and loading conditions to guide the associated experimental investigations.

## REFERENCES & ACKNOWLEDMENTS

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