Impact of thickness of the samples on S(α, β) measurements of nuclear graphite

Kemal Ramić, Iyad Al-Qasir, Luke Daemen, José Ignacio Marquez Damian, Chris W. Chapman, Travis Greene, Goran Arbanas, Jesse Brown, Anne Campbell, Douglas Abernathy, Matthew Stone, Garrett Granroth, Will Wieselquist

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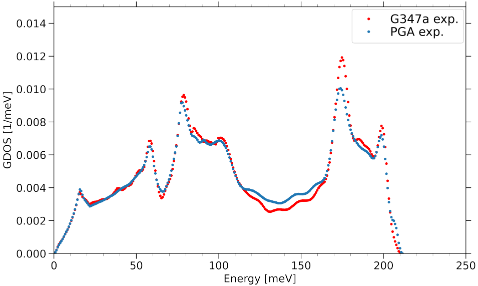
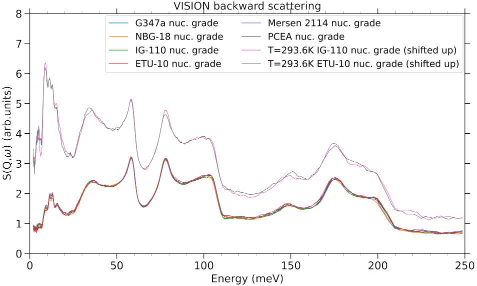
Experimental evidence of no impact of porosity on the phonon spectra

- Derived phonon spectra from ARCS $S(\alpha, \beta)$ measurements:



- $S(\alpha, \beta)$ measurements at VISION instrument:



- Multiple grades, with porosities from 10% to 25%, and grain sizes from 13 to 1600 μm, have been measured and show no appreciable differences in phonon spectra.
- Typical sample thickness of 2-4 mm was used to minimize multiple scattering.

ReGra 2025 confusing principles/arguments

- During ReGra it was suggested that the reason why there isnt any observed influence of pores on the measured S(α, β) spectra is because the samples were too thin, and MFP (mean free path, which is energy dependent) for thermal neutron (i.e. E=25 meV) is on the order os 2.5 cm hence the neutrons couldn't "see" the pores.
- It was also argued that multiple scattering effect is somehow captured in ENDF porosity TSLs, when it is absolutely clear that ENDF files are supposed to contain only single interaction nuclear data, and transport codes handle the "transport", in this case multiple scattering.
- From ReGra report (`https://www.osti.gov/servlets/purl/2998877`):

> **We note that the various ENDF reactor grade porosity cases do not agree with ARCS data or specific heat measurements. However, it was also argued that special care was needed to correctly extract the heat capacity from the porosity TSL files and that would lead to an agreement with the measured heat capacity. This statement still needs to be independently verified. Finally, the high precision ARCS measurements were small sample measurements so that multiple scattering was absent. In a reactor, there multiple scattering is an important effect that seems to be captured by the ENDF reactor graphites even if the details appear incorrect.**

Why pores do not affect the phonon spectra?

- Phonons: wavelength $\sim$ 1–10 Å; pores: diameter $\sim$ 1–10 μm ($\sim 10^4$–10^5 Å) $\Rightarrow$ scale mismatch.
- Pores act as macroscopic boundaries, not microscopic scatterers $\Rightarrow$ bulk PDOS set by graphite crystallites.
- Only pore-surface atoms differ; upper bound gives $f_{\text{surface}} \approx 0.013\%$ $\Rightarrow$ negligible INS impact.
- Surface carbon atom remain strongly sp^2-bonded $\Rightarrow$ no new low-energy "rattling" modes.

Table 1: Calculation of Surface Atom Fraction in Porous Nuclear Graphite

Parameter	**Symbol**	**Value**	**Source/Calculation**
Theoretical Graphite Density	ρ_{ideal}	2.26 g/cm^3	Literature value
Bulk Nuclear Graphite Density	ρ_{bulk}	1.80 g/cm^3	Typical nuclear grade
Volumetric Porosity	ϕ	20.4%	$1 - (\rho_{bulk}/\rho_{ideal})$
Average Pore Radius	R_p	1.0 μm	Conservative estimate
Carbon Atomic Mass	M_C	12.01 amu	Standard
Surface Area per Carbon Atom	A_{atom}	5.24 Å^2	Geometric ($\frac{\sqrt{3}}{2}a^2$)
Calculations (per cm^3 of material)			
Volume of Solid	V_{solid}	0.796 cm^3	$1 - \phi$
Volume of Pores	V_{pores}	0.204 cm^3	ϕ
Number of Pores	N_{pores}	4.87×10^{10}	$V_{pores}/(\frac{4}{3}\pi R_p^3)$
Total Pore Surface Area	A_{pores}	6120 cm^2	$3 \times V_{pores}/R_p$
Number of Surface Atoms	$N_{surface}$	1.17×10^{19}	A_{pores}/A_{atom}
Number of Bulk Atoms	N_{bulk}	9.04×10^{22}	$(V_{solid}\rho_{ideal}N_A)/M_C$
Fraction of Surface Atoms	$f_{surface}$	0.013%	$N_{surface}/(N_{surface} + N_{bulk})$

INS PDOS: Single-Scattering Is the Goal

- INS measures energy exchange $E_f = E_i \pm \hbar\omega$; for polycrystals, $S(Q, \omega)$ is proportional to the PDOS under standard conditions.
- Data analysis assumes the **Born approximation**: each detected neutron undergoes **one** scattering event $\Rightarrow$ clean link between measured $d^2\sigma/d\Omega dE'$ and $S(Q, \omega)$.
- **Multiple scattering** (2+ events before exit) convolves uncorrelated processes $\Rightarrow$ smears PDOS features and adds background.
- Experimental design therefore enforces high transmission: the **"10% scattering / 90% transmission rule"** (Beer–Lambert: $I/I_0 = e^{-\Sigma t}$).
- For $I/I_0 = 0.9$: $\Sigma t \approx 0.105$; Poisson gives $P_1 \approx (\Sigma t)e^{-\Sigma t} \approx 0.09$ vs. $P_2 \approx (\Sigma t)^2 e^{-\Sigma t}/2 \approx 0.0045$.
- Result: single-scattering signal $\sim 20\times$ stronger than double-scattering $\Rightarrow$ multiple scattering is a small correction, not a distortion.

Why “Thin” INS Samples Still Represent Bulk Graphite

- “Thin” refers to **neutron optics** (small Σt), not a physically tiny specimen: For example, graphite $t \sim 2\,\text{mm}$, with diameter $\sim 10\,\text{mm}$ is typical.
- Such a sample is **macroscopically large** and contains a huge number of grains/crystallites $\Rightarrow$ strong statistical averaging.
- Example volume: $V_{\text{sample}} = \pi(5\,\mathrm{mm})^2(2\,\mathrm{mm}) \approx 157\ \mathrm{mm}^3$.
- Typical grain size $\sim 20\ \mu\mathrm{m} = 0.02\ \mathrm{mm} \Rightarrow V_{\text{grain}} \approx (0.02\ \mathrm{mm})^3 = 8 \times 10^{-6}\ \mathrm{mm}^3$.
- Number of grains illuminated:

$$N_{\text{crystallites}} \approx \frac{V_{\text{sample}}}{V_{\text{grain}}} \approx \frac{157}{8 \times 10^{-6}} \approx 2 \times 10^{7}$$

- Beam sizes (mm^2–cm^2) sample **tens of millions** of randomly oriented grains $\Rightarrow$ PDOS is a true bulk polycrystal average, not a surface artifact.

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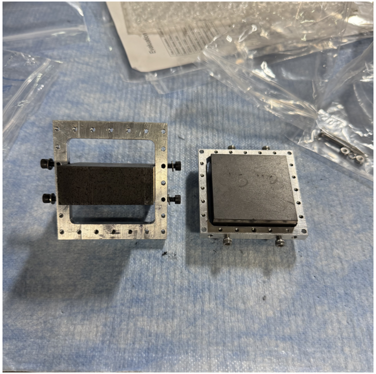
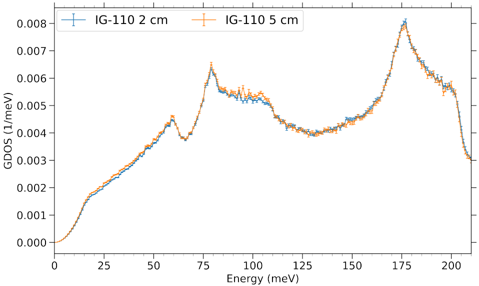
ARCS measurement of thicker samples

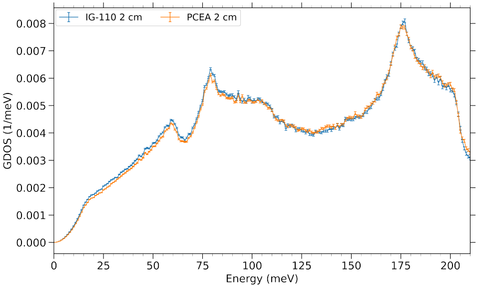
- We measured two samples in two orientations:
    1. IG-110 nuc. graphite with porosity of 21.6%, and average grain size of 20 μm
    2. PCEA nuc. graphite with porosity of 18%, and average grain size of 360 μm

    + Thin orientation, thickness 2 cm
    + Thick orientation, thickness 5 cm
- Due to limited time availability we only measured two incident energies, 130 and 300 meV
- We had a previous measurement of 4 mm thick G347A nuc. graphite with porosity of 17.8%, and average grain size of 50 μm, at the same incident energies



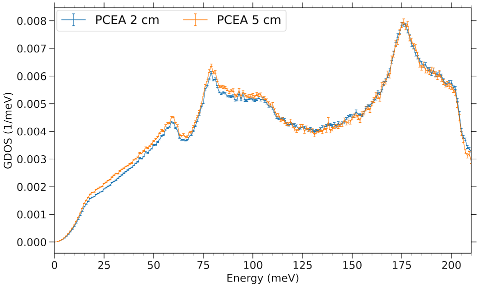
ARCS measurement of IG-110 nuc. graphite

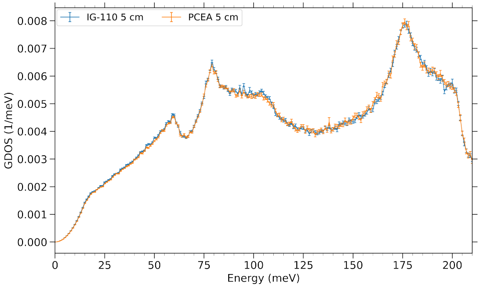




- No impact of thickness or the porosity of the sample on the measured phonon spectra.

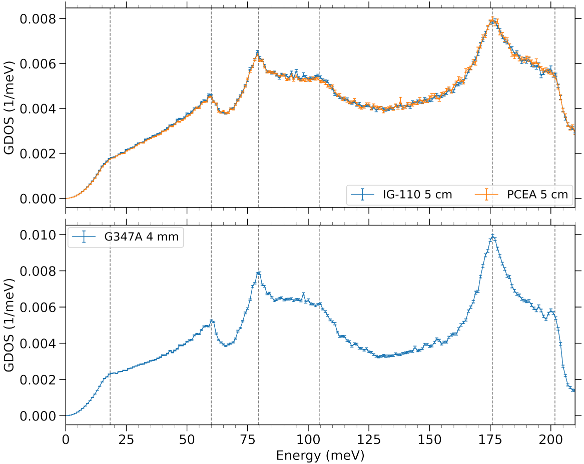
ARCS measurement of PCEA nuc. graphite





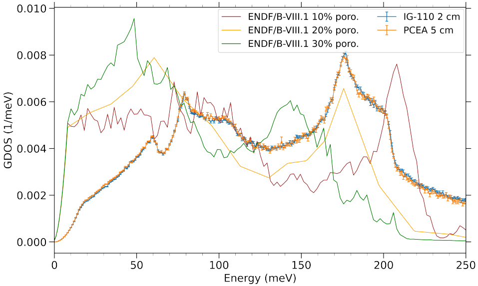
- No impact of thickness or the porosity of the sample on the measured phonon spectra.

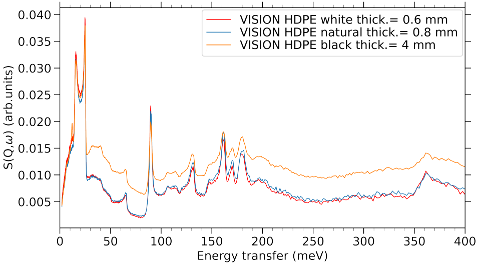
ARCS measurement of PCEA nuc. graphite



- As explained before, thickness of the sample has no appreciable impact on the experimentally derived phonon spectra for graphite beyond some smearing.

Comparison with ENDF-B/VIII.1 porosity TSLs





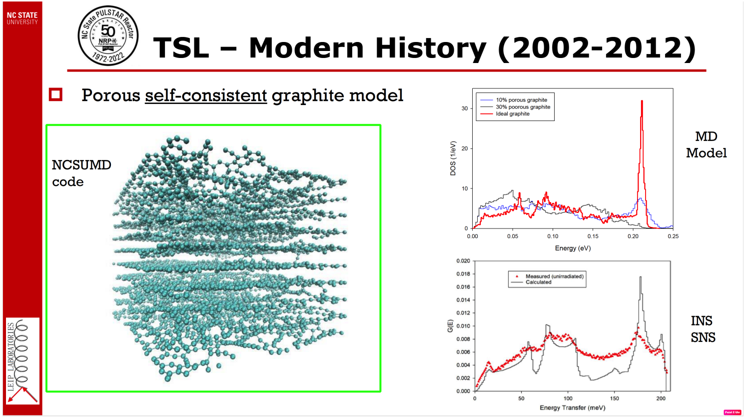
- Porosity TSLs **DO NOT** conserve scattering reaction rate and bulk neutron transport properties as was presented during ReGra, and **DO NOT** capture the multiple scattering effect. They are a product of a misunderstanding of how to model pores, as well as imperfect inter-atomic potential, leading to a confusion that porosity impacts phonon spectra; which has been explained in detail in our recent publication "Porosity in nuclear graphite and its impact on nuclear reactor science and criticality safety applications" `https://doi-org.ornl.idm.oclc.org/10.1016/j.carbon.2025.120619`.

- Additionally, thickness of the sample doesn't play a major role in S(α, β) measurements, beyond introducing multiple scattering which smears the features and introduces background.

Modeling issues in 10%, 20%, and 30% porosity TSLs

Two main issues in the modeling of porosity TSLs:

1. Choice of representing of pores by randomly removing atom to match the desired porosity level

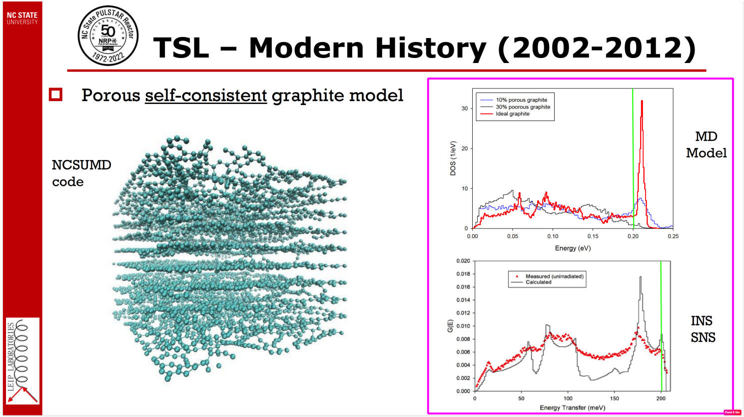


* Slide 26, “Thermal Scattering Law Research and Development at North Carolina State University”, A. Hawari, TPR 2024

Modeling issues in 10%, 20%, and 30% porosity TSLs

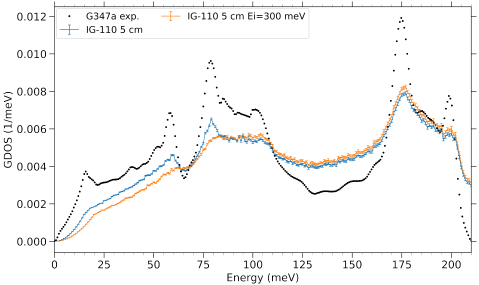
Two main issues in the modeling of porosity TSLs:

2. Inadequate inter-atomic potential used for molecular dynamics

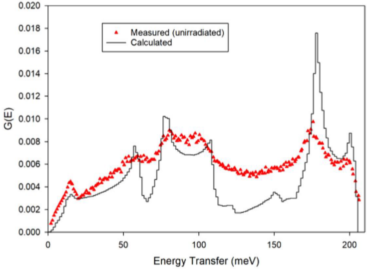


* Slide 26, “Thermal Scattering Law Research and Development at North Carolina State University”, A. Hawari, TPR 2024

INS measurement of nuc. graphite resolution impact



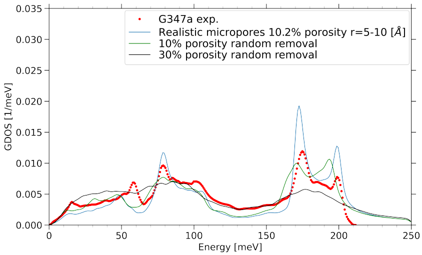
INS
SNS



- Good measurements requires significant planning and good choice of Incident energies to get the best possible phonon spectra resolution.

Summary & Conclusions

- S(α, β) measurements of nuclear graphite consistently show that porosity has no measurable effect on graphite's thermal scattering behavior.
- New measurements have demonstrated that thickness of the sample in S(α, β) measurements, does not play a large role beyond smearing the spectra and introducing unnecessary background.
- ENDF/B-VIII.1 porosity TSLs **DO NOT** conserve scattering reaction rate and bulk neutron transport properties as was presented during ReGra, and **DO NOT** capture the multiple scattering effect (nor they should by definition).
- ENDF/B-VIII.1 porosity TSLs employed an inappropriate understanding of how to model pores, as well as imperfect inter-atomic potential, leading to a confusion that porosity impacts phonon spectra, and by extension incoherent inelastic and coherent elastic scattering cross section, and hence impacting k_{eff}.



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Porosity in nuclear graphite - micrometer pores

Pores in nuclear graphite are voids of different shapes and sizes, from nanometer to micrometer sizes.

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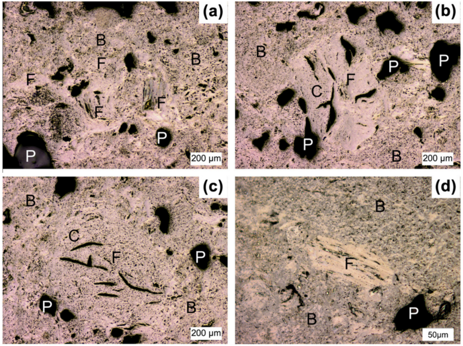


Fig. 5. Optical micrographs of PCEA graphite: (a) bright field image showing filler particles with various shapes, (b) bright field micrograph of filler with relatively high degree of crystallite alignment surrounded by binder matrix, (c) bright field micrograph of roughly spherical filler particle, and (d) bright field image of relatively small acicular filler particle. P-Porosity, F-Filler, B-Binder, C-Shrinkage crack.

* Page 193, J. Kane et al. / Journal of Nuclear Materials 415 (2011) 189–197

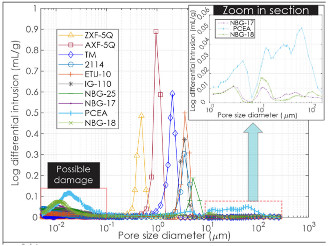
Porosity in nuclear graphite - micrometer pores

Mercury porosimetry results showing pore size distribution - porosity distribution as a function of pore size diameter and mercury intrusion.

Table 4
Apparent density and open, closed, and total porosity for selected graphite grades calculated using helium pycnometry, weight, and volume measurements.

Grade	Type	Grain size (μm)	App. Dens. (g/cm^3) Weight and dimensions	Solid dens. (g/cm^3) He pycnometry	OPV (%)	CPV (%)	TP (%)
ZXF-5Q	Micro-fine	1	1.80	2.11	14.9	5.4	20.3
AXF-5Q	Ultra-fine	5	1.73	2.09	17.6	5.8	23.4
TM	Super-fine	10	1.72	2.09	17.6	5.9	23.5
2114	Super-fine	13	1.81	2.08	12.9	6.8	19.7
ETU-10	Super-fine	15	1.73	2.09	17.1	6.0	23.1
IG-110	Super-fine	20	1.76	2.05	13.9	8.0	21.9
NBG-25	Fine	60	1.81	2.06	12.3	7.5	19.8
NBG-17	Medium-fine	800	1.85	2	7.8	10.2	18.0
PCEA	Medium-fine	800	1.76	1.99	11.5	10.2	21.7
NBG-18	Medium-coarse	1600	1.85	2.02	8.1	9.7	17.8

OPV – open porosity volume, CPV – close porosity volume and TP – total porosity.



* Page 17, J.D. Arregui-Mena et al. / Materials Characterization 190 (2022) 112047

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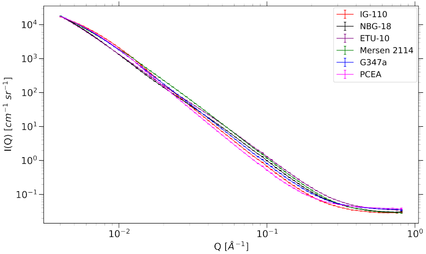
What about nanopores?

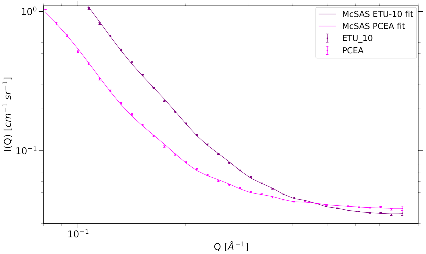
- We measured SANS I(Q) at GP-SANS beamline at HFIR ORNL of six different grades of nuclear graphite:



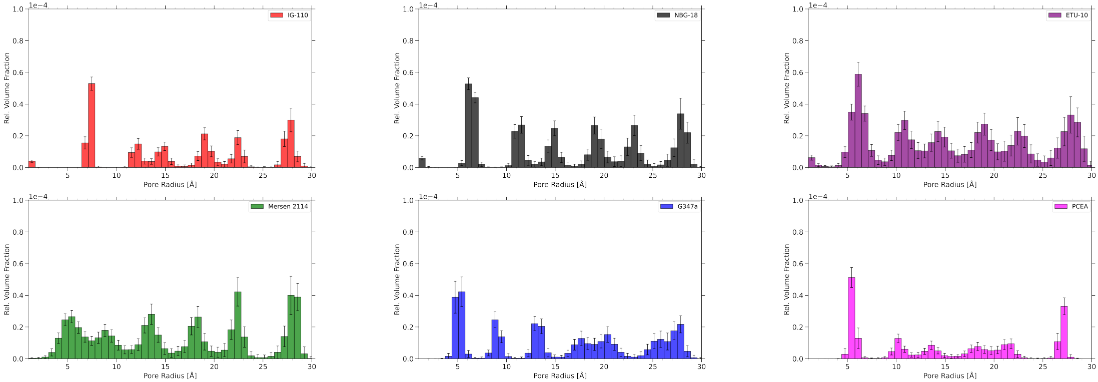
- SANS is a tool that can be used to determine the size of the smallest nanopores. The largest pore sizes accessible via conventional SANS are dictated by the lowest measurable scattering vector, with the maximum accessible radius approximately given by

$$r_{\max} \approx \frac{\pi}{Q_{\min}}. \quad (1)$$

- Since our $I(Q)$ data ranges in Q from 0.004 $Å^{-1}$ to 0.81 $Å^{-1}$, the maximum accessible pore radius is around 75 Å, and the minimum accessible radius is about 4 Å.
- We utilized the McSAS software —a form-free, Monte Carlo–based regression tool — to fit the SANS data over 0.08–0.8 $Å^{-1}$, a range that captures the narrow-pore distribution. By fitting the measured $I(Q)$ using a spherical pore model, McSAS enabled us to retrieve a pore size distribution spanning radii from approximately 1 to 30 Å.

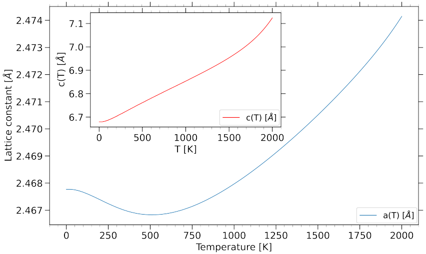


What about nanopores?



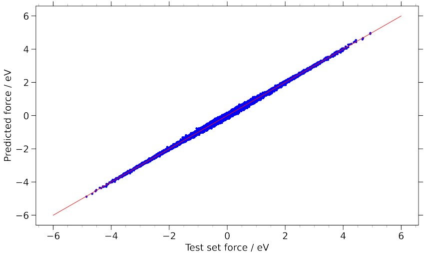
More accurate modeling of the pores methodology

- First, we need a more accurate inter-atomic potential for molecular dynamics (MD).
- We first calculated temperature dependent lattice constants of graphite using quasi-harmonic approximation method.



- Then we perfromed ab-initio MD calculations with VASP to generate the training data for DeepMD framework for generating machine learned potentials to be used with LAMMPS.

- We trained a machine learned potential using “se_e2_a” descriptor, a trade-off between the accuracy and speed.



- More information can be found in our publication “Porosity in Nuclear Graphite and its Impact on Nuclear Reactor Science and Criticality Safety Applications” submitted to Carbon, and available as pre-print at `https://papers.ssrn.com/sol3/papers.cfm?abstract_id=5271524`.

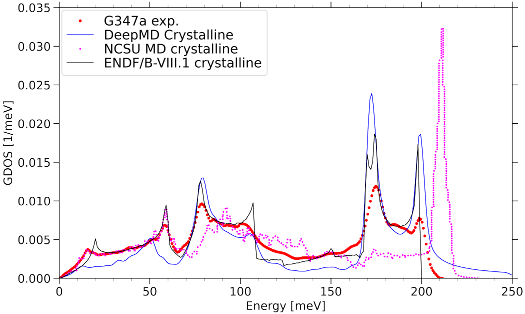
More accurate modeling of the pores methodology

- We employed a custom Python script to generate porous supercell structures as follows: starting from a perfect crystalline supercell of graphite, spherical “voids” were carved out by removing all atoms within a chosen radius of randomly selected center points. We enforced a minimum spacing between pore centers and from pores to cell boundaries to avoid overlap or truncated pores.

Table 2: Summary of the graphite structures used in MD simulations. Nominal porosity is the fraction of atoms removed to create pores. Pore radii given as a range indicate multiple pores of varying size; ‘—’ indicates random atom removal (no well-defined pore radii).

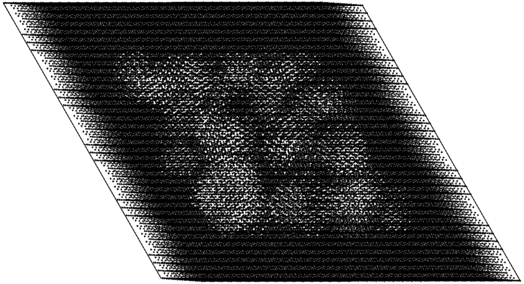
Structure	Cell Size	Nom. Porosity (%)	Pore Radius (Å)	# Pores	# Atoms
Crystalline	$35 \times 35 \times 12$	0.0	—	0	59 k
(1) Realistic Nanopores	$35 \times 35 \times 12$	10.2	5–10	62	52 k
(2) Single Large Pore	$35 \times 35 \times 12$	7.5	22.1	1	54 k
(3) Many Nanopores	$40 \times 40 \times 16$	16.9	3.5–6	52	85 k
(4) 30% Random Removal	$40 \times 40 \times 20$	30.0	—	—	89 k
(5) 10% Random Removal	$35 \times 35 \times 12$	10.0	—	—	53 k

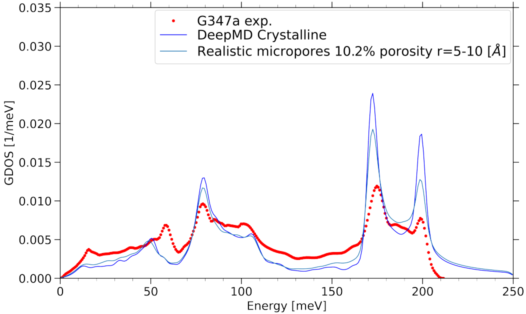
Crystalline structure



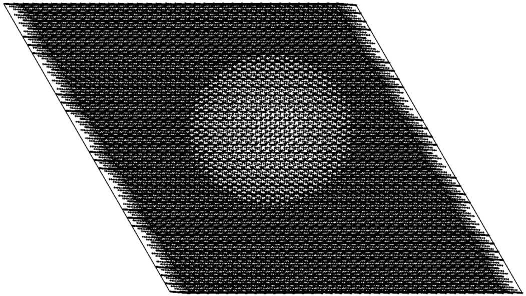
- The experimental phonon spectra (e.g. from INS measurements) and ENDF/B-VIII.1 phonon spectra show the characteristic split optic peaks near 170–200meV.
- The NCSU MD phonon spectra for crystalline graphite deviates above 60meV, merging those peaks into one and slightly misplacing others.
- Our DeepMD-based phonon spectra aligns much more closely with the ENDF (DFT) and experimental curves, capturing both high-energy peaks and generally following the experimental spectrum within small discrepancies (a slight intensity mismatch in parts of the acoustic band below 60meV).
- It should be emphasized that our trained DeepMD potential is not intended to perfectly match the experiment or serve as the basis for a new ENDF TSL evaluation. Rather, our goal is simply to demonstrate that pore presence does not alter phonon spectra. Other DeepMD descriptors offer higher accuracy than `se_e2_a`, but `se_e2_a` was chosen here due to lower computational cost.

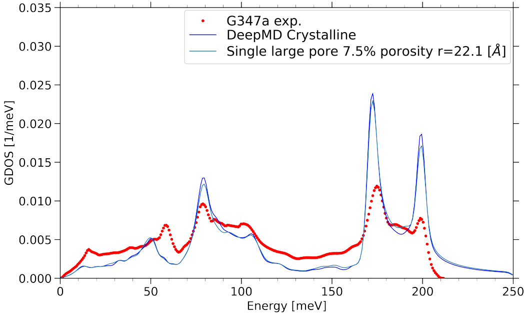
Realistic Nanopores, Supercell: 35 × 35 × 12, Porosity 10.2 % , radius 5–10 Å



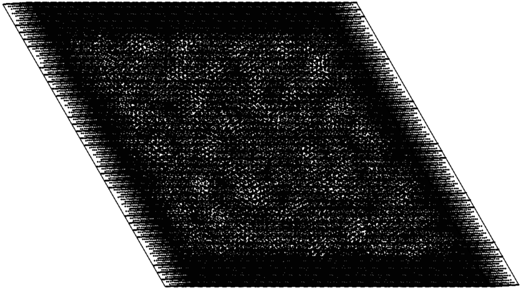


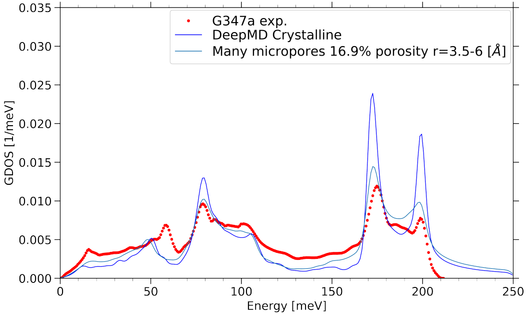
Single Large Nanopore, Supercell: 35 × 35 × 12, Porosity 7.5 %, radius 22.1 Å



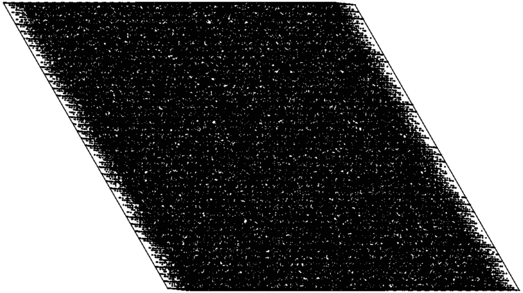


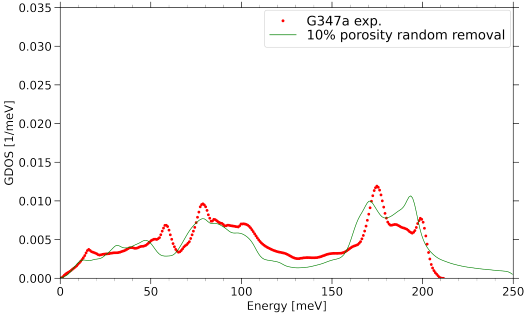
Many Nanopores, Supercell: $40 \times 40 \times 16$, Porosity 16.9 %, radius 3–6 Å



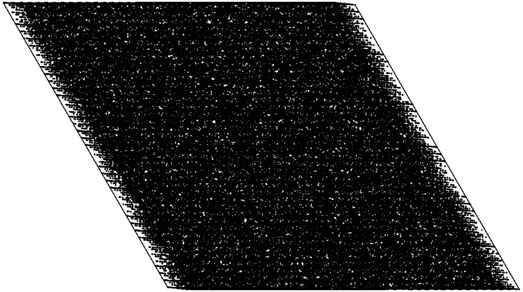


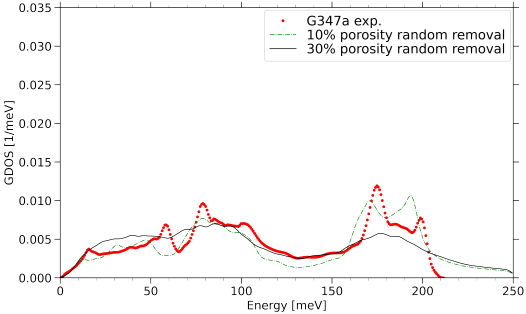
10% and 30% Random Removal





10% and 30% Random Removal





Random removal of atoms starts distorting the phonon spectra in a unphysical way same as for porosity TSLs!!!