

Origins of intrinsic stress in disordered carbon materials: A first-principles study

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The origin of intrinsic stress in amorphous and structurally disordered carbon films remains a fundamental challenge. Numerous previous studies have focused on deposition parameters and their relationship with stress, resulting in the hypothesis that a high sp^3 -C fraction is a key factor governing compressive stress. However, the precise role of geometrical parameters in stress generation is still unknown. Here, we show that intrinsic stress is mainly dominated by two geometrical parameters: standardized bond length and density, followed by sp^3 -C fraction. We found that the high sp^3 -C fraction independently contributes to tensile stress, contrary to previous experimental results. A data-driven assisted investigation of various amorphous carbon models prepared using first-principles calculations quantitatively revealed the effect of each parameter by isolating their contributions. As a result, a generalized formula is proposed to correlate the intrinsic stress and fundamental structural parameters.

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I. INTRODUCTION

Amorphous carbon (a-C), or diamondlike carbon (DLC), is widely valued for its hardness, chemical stability, and versatility as a protective coating across engineering, electronics, and biomedicine [1–7]. A distinctive advantage of a-C lies in its tunable physical properties, which can be systematically tailored by adjusting the ratio of sp^2 to sp^3 carbon bonding hybridization and the incorporation of hydrogen. The commonly employed ternary phase diagram delineates compositions based on the atomic fractions of sp^3 carbon, sp^2 carbon, and hydrogen [8]. Within this framework, hydrogen-free carbon films containing 10%–20% sp^3 bonding are generally referred to as amorphous carbon (a-C), while those with 20%–90% sp^3 fraction are designated as tetrahedral amorphous carbon (ta-C). Despite their technological appeal, a-C films often exhibit high intrinsic stress that leads to delamination, representing a major obstacle to industrial deployment. The fundamental structural origins of this stress, however, remain unresolved.

Intrinsic stress in a-C films has long been hypothesized to arise primarily from the high concentration of sp^3 -hybridized carbon (sp^3 -C). Numerous experimental studies have reported a positive correlation between elevated sp^3 fractions and compressive stress [9–11]. The subplantation model provides a physical explanation, suggesting that the formation of sp^3

bonds is most likely when carbon impinges on the surface with kinetic energies near 100 eV [12]. Experimental data further support this, showing a marked increase in compressive stress as ion energy approaches this range [13,14]. Complementary mathematical models have also been proposed to describe the development of compressive stress under ion bombardment conditions [15,16].

The direct causal relationship, however, between sp^3 -C fraction and intrinsic stress remains a subject of ongoing debate. Some studies argue that while ion bombardment may induce compressive stress, this stress is not necessarily consequence of sp^3 -C stabilization itself [17,18]. Supporting this view, post-thermal annealing has been shown to relieve stress in a-C films with only minimal reduction in sp^3 -C fraction [19,20]. Despite these insights, most prior investigations have focused on deposition conditions and process parameters, relatively few have addressed the fundamental structural factors underlying stress generation. Deeper understanding at the atomic scale is required to inform the design of stress-relieving carbon film process. Previous study has established that strain and mechanical response in disordered network materials can be rationalized in terms of network connectivity and mean coordination, as formalized within topological rigidity theory. This conceptual framework has been used to relate stress accumulation to bonding hybridization states, particularly the fraction of sp^3 -coordinated carbon atoms [21].

This work is intended to build upon this established conceptual picture by providing a quantitative, atomically resolved perspective on intrinsic stress generation in nonhydrogenated a-C. Rather than inferring stress behavior from coordination alone, we directly link first-principles stress tensors to local structural and geometrical descriptors, enabling a more detailed assessment of the microscopic origins of stress. By employing explainable machine-learning analysis, we

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systematically isolate and evaluate the individual contributions of bond-length distortions, bond-angle distributions, density, and sp^3 fraction to the predicted stress. This approach allows us to explicitly identify which local geometric features dominate intrinsic stress buildup, with particular attention to the debated role of sp^3 -C, whose contribution cannot be uniquely determined from mean coordination considerations.

Here, we present a comprehensive first-principles investigation into the atomic origins of intrinsic stress in amorphous and defect-containing carbon networks. Using density functional theory (DFT), we constructed a series of realistic carbon models, by introducing random defects into crystalline carbon and performing anneal-quenching simulations to mimic the disordered atomic arrangements typical of a-C [22]. These models allowed us to systematically examine how key geometric parameters, such as sp^3 -C fraction, density, and bond length, independently influence stress formation and elucidate the effects of each parameter. We also incorporated data-driven techniques to explore hypothesis of the stress generation mechanism. Beyond process optimization, machine learning (ML) offers promising capabilities in elucidating complex mechanisms previously regarded as opaque. In a recent study, a predictive model of plasma-enhanced chemical vapor deposition (PECVD) processes was combined with explainable artificial intelligence (XAI) techniques to reveal synergistic effects among process variables influencing carbon film depositions [23–26]. In this study, analysis of the ML prediction model from geometrical parameters to intrinsic stress employing XAI was adopted to explore the parameters influencing stress value and refine the hypothesis to accelerate the research.

By merging systematic first-principles simulations with advanced data-driven analytics, this study aims to establish a comprehensive understanding of intrinsic stress formation in amorphous carbon films. Our results clarify the controversial role of sp^3 -C in stress generation and reveal additional more important geometric factors that govern stress evolution.

II. METHODS

A. DFT calculations for carbon models and their analysis

All calculations were performed within the framework of spin-polarized DFT, using the Vienna *ab initio* simulation package (vasp) [27–29]. Ion-electron interactions were described using projector augmented wave (PAW) approach [30]. The exchange-correlation energy was described by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [31]. Plane-wave basis sets with a kinetic energy cutoff of 816 eV were used to represent the electronic wave functions. Long-range van der Waals interactions, especially relevant in layered structures such as graphite, were included using DFT-D3 method with Becke-Johnson damping function [32]. Brillouin zone integrations were conducted using appropriately chosen Monkhorst-Pack grids [33], whose k spacing was confirmed to be sufficient to acquire energetic convergence.

All structure preparation and postprocessing were conducted using Python-based libraries, including the Atomic Simulation Environment (ASE) [34]. Each atom was

classified as sp -, sp^2 -, sp^3 - hybridized based on its coordination number, with a bond cutoff distance of 1.85 Å [35]. Since carbon typically forms up to four covalent bonds, only up to the fourth nearest neighbors were considered bonded, even if within the cutoff distance. The intrinsic stress for each structure was quantified using the average of the diagonal elements of the Cauchy stress tensor, calculated during the final cell optimization:

$$\sigma = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3}. \quad (1)$$

This indicates the internal pressure applied to all boundaries of the supercell. This approximation shows less than 6% deviation on average from stress values estimated using Young's modulus [36] and strain for a selected subset of structures. For simplicity, the comparative data based on Young's modulus are not shown here. Only normal stress, which is expected to affect film delamination, is discussed in this research. The validity of using anisotropic cells for stress calculations has been discussed previously [37].

B. Data-driven analysis of stress generation mechanisms

To quantitatively describe the influence of various geometrical parameters on stress generation and explore the hypothesis of the mechanisms to foster this research, a data-driven modeling approach was employed. A dataset comprising 100 amorphous carbon supercells (48 atoms each) was constructed by randomly placing carbon atoms in cube-like cells with densities 1.5 to 3.1 g/cm³, encompassing the range from porous carbon to diamondlike structures. To investigate the intrinsic structural effects on stress, the cell size and shape were fixed throughout the calculations. Random initial placements was carried out while avoiding atom-atom distance <1.2 Å to ensure stability. All structures underwent *ab initio* molecular dynamics (AIMD) heating (5000 K, 1 ps), quenching (16000 K/ps) with 1 fs time step, and final relaxation. The quenching rate was chosen to ensure stable numerical convergence without inducing artificial structural instabilities. Importantly, the conclusions of this work do not rely on the absolute value of the quenching rate, but on qualitative and comparative trends observed across consistently treated simulations. An example of the calculation workflow is illustrated in Fig. 1.

AIMD simulations were performed under the NVT ensemble using the velocity Verlet algorithm with a Nosé-Hoover thermostat [38–40]. A $(1 \times 1 \times 1)$ Γ -point k mesh and a looser convergence threshold were used for AIMD compared to static DFT relaxations.

To establish the relationship between structural features and stress, a regression model was developed using the number of sp^3 -carbon atoms, cell density, averaged bond length and bond angles as input variables, and intrinsic stress as the output. A total of 100 structures were used after screening. The dataset was split into 80 training data and 20 test samples. Input and output values of the training set were standardized (zero mean, unit variance), and the model was fitted using Gaussian process regressor [41] with a kernel composed of the ConstantKernel, radial basis function (RBF) and WhiteKernel implemented in scikit-learn [42]. This model was chosen for

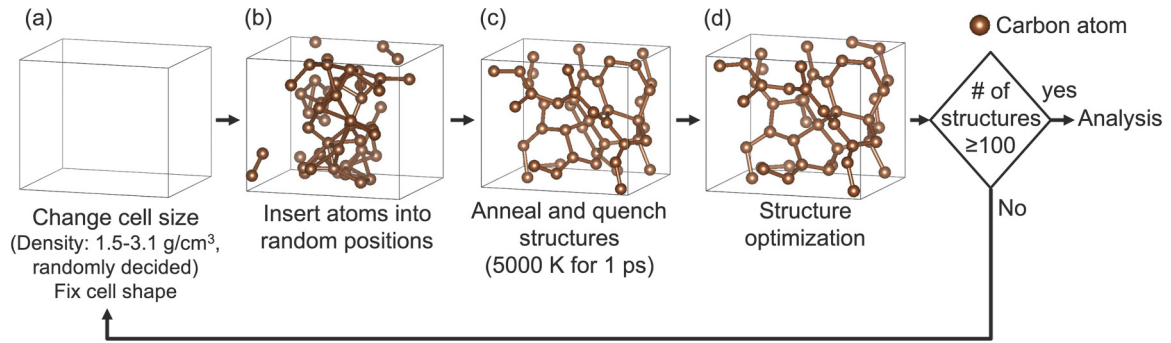


FIG. 1. Schematic workflow for preparing the dataset used in data-driven modeling. (a) An empty simulation cell with adjustable size and fixed cell shape. The atomic density is randomized by varying the cell volume before inserting 48 carbon atoms. (b) An example of an initial carbon structure generated by randomly placing atoms within the cell. (c) The structure obtained after annealing and quenching the initial configuration via AIMD. (d) The final structure after geometry relaxation.

its superior prediction accuracy even for smaller size datasets and relatively higher robustness against noises. Model performance was evaluated using mean absolute error (MAE) and root mean squared error (RMSE), and interpreted using XAI technique, as summarized in Fig. 2. Among various XAI

methods, Shapley additive explanations (SHAP) [43] were employed in this study to enable a quantitative discussion on the contribution of each input feature to the model output. SHAP values quantify the marginal contribution of an individual input parameter to the predicted stress as deviations from a reference prediction. For a given a-C structure, the SHAP value associated with the standardized bond length is defined as the difference between the stress predicted by the trained machine-learning model when the bond length takes its actual value for that structure and when it is replaced by its dataset-averaged value.

Importantly, this difference is evaluated in a conditional manner by averaging over all possible combinations of the remaining input parameters, such as density and sp^3 -C fraction, as sampled in the dataset.

In this way, SHAP provides a *post hoc* decomposition of the model prediction, in which each SHAP value represents the feature's independent, marginal contribution to the output, averaged over the realistic correlations inherent in amorphous carbon structures. This procedure enables the disentanglement of the individual effects of bond length, density, and sp^3 fraction on intrinsic stress without imposing artificial constraints on the atomic configurations. Specifically, a SHAP value for one feature and instance implies that feature independently changed the output by that SHAP value during the prediction process.

C. Generation of defective carbon structures

To discuss the effect of bond length and bonding hybridization on stress generation, defective carbon models with systematically varied sp^3 -C fraction with fixed density were prepared. They were generated by introducing vacancies or interstitial atoms into bulk crystalline supercells of diamond and graphite. Specifically, optimized C_{48} diamond supercells were used to generate 100 unique defective C_{43} models by randomly removing 5 carbon atoms. Similarly, 100 defective graphite models were prepared by inserting 5 carbon atoms into the interlayer space at random positions.

All structures were then fully relaxed using DFT while fixing the unit cell dimensions. Atomic positions were optimized until the residual force on each atom was less than 0.001 eV/Å. The underlying rationale is that introducing or removing atoms alters the coordination number and hybridization state

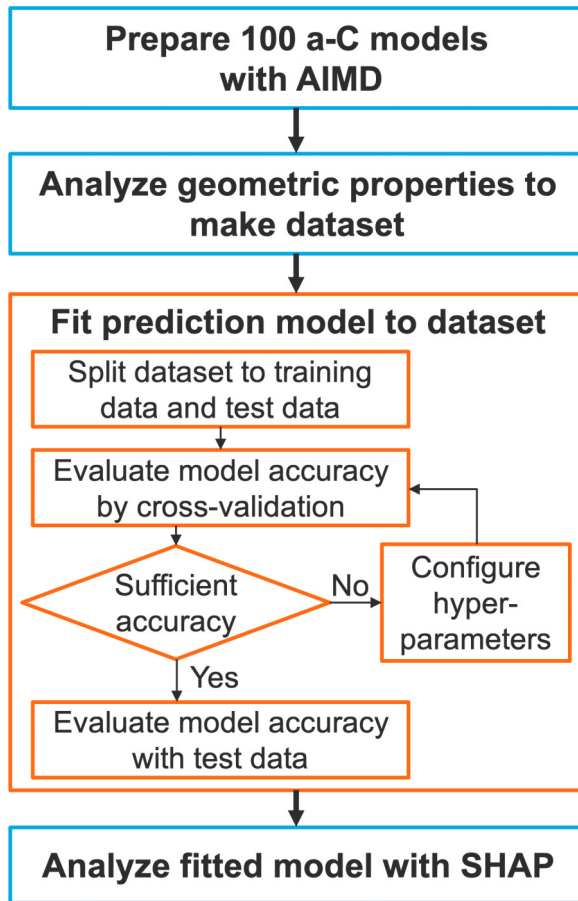


FIG. 2. Flowchart illustrating the data-driven discovery of trends from first-principles calculations. The workflow involves generating 100 amorphous carbon (a-C) models via AIMD, extracting geometric properties to construct the dataset, training and optimizing a predictive model through cross validation, and finally interpreting the model using SHAP analysis.

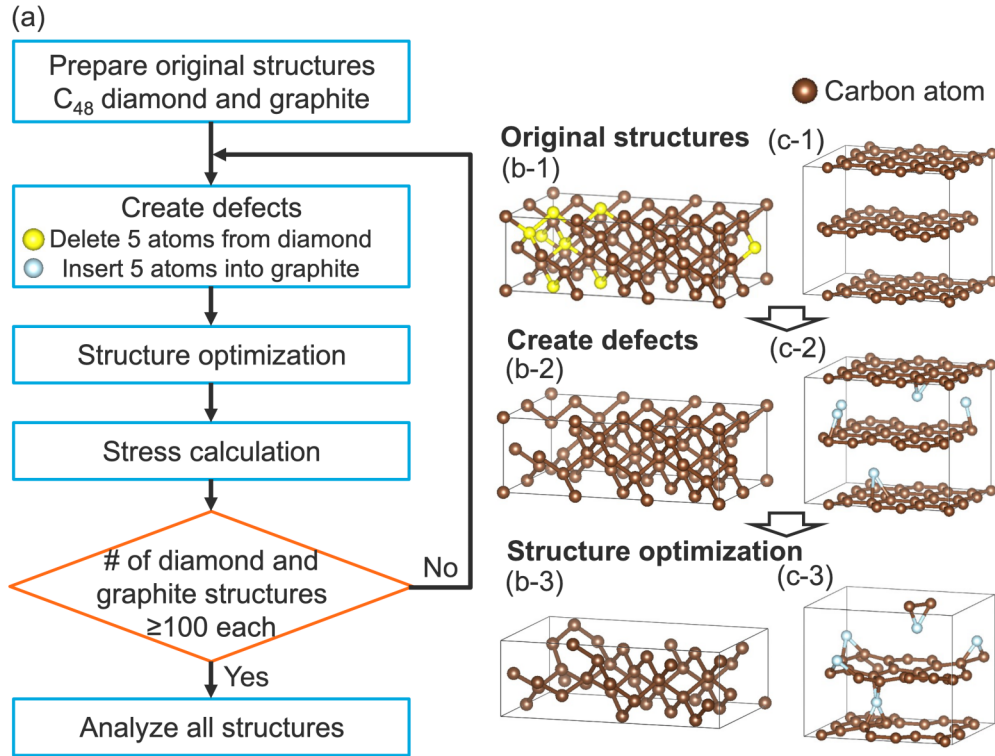


FIG. 3. Schematic illustration of the procedure for generating defective carbon structures through geometry optimization. (a) Flowchart of the preparation process for defective carbon models starting from diamond and graphite structures. (b-1) An example of the original structure of a C_{48} diamond structure, where five atoms (highlighted in yellow) are selected for removal to introduce vacancy defects. (b-2) The structure after vacancy creation by atom removal. (b-3) The resulting C_{43} defective diamond structure after geometry relaxation. (c-1) The original C_{48} graphite structure. (c-2) An example of graphite with five inserted atoms (shown in light blue) representing defect introduction. (c-3) The corresponding C_{43} defective graphite structure after geometry relaxation.

of surrounding atoms, leading to structurally relaxed configurations. Figure 3 provides an overview of the defect generation process. For Brillouin zone sampling, k -mesh spacing of 0.5 and $0.3 \text{ \AA}^{-1}$ were used for defective diamond and graphite models, respectively.

D. Generation of amorphous carbon models via AIMD

To ensure the generality of the stress-related findings, several a-C models with fixed densities were also prepared. An anneal-quench protocol based on AIMD was adopted. Pre-relaxed carbon structures were linearly heated from 0 K to 3000–10 000 K over 500 fs, annealed at the target temperature for 1 ps (1 fs time step), and then quenched to 0 K at rates of either 2500 or 16 000 K/ps, followed by full geometric relaxation. These quenching rates simulate the quenching with varied relaxation time for modeling of a wide variety of carbon structures. These preparations are outlined in Fig. 4. Other calculation configurations were the same as those used to prepare the dataset for the previous hypothesis exploration step.

III. RESULTS

A. Data-driven analysis of stress determinants

A data-driven approach was adopted to obtain geometrical parameters which have a strong influence on stress

generation. In this calculation, in total six parameters, sp^3 -C fraction, mean bond length, density, mean bond angles for sp , sp^2 , sp^3 -C each, were employed as features for constructing a prediction model. A total of 100 carbon structures were analyzed. These structures were randomly partitioned into training and test datasets, and a Gaussian process regressor (GPR) model was trained to predict stress values based on the six input parameters.

To account for variations in bonding hybridization which can affect the mean bond length of each instance, standardized bond length was introduced, defined as the deviation from the groupwise average, namely, an ideal bond length L_{ideal} . This ideal L_{ideal} value is computed as a weighted average of the expected bond lengths corresponding to different carbon hybridizations, given by

$$L_{\text{ideal}} = \sum_{i=1}^3 (i+1)n_{sp^i}d_{sp^i} / \sum_{i=1}^3 (i+1)n_{sp^i} \quad (2)$$

where $d_{sp} = 1.37 \text{ \AA}$, $d_{sp^2} = 1.42 \text{ \AA}$, and $d_{sp^3} = 1.54 \text{ \AA}$ are the average bond lengths for hybridized carbon atoms and n_{sp^i} represents the number of each hybridized atom type in the structure. This standardization enables direct comparison across structurally diverse carbon models with variations in bonding character. As for the mean bond angles, each of them was also standardized by subtracting the ideal bond angle for each hybridized atom: 180° for sp -C, 120° for sp^2 -C,

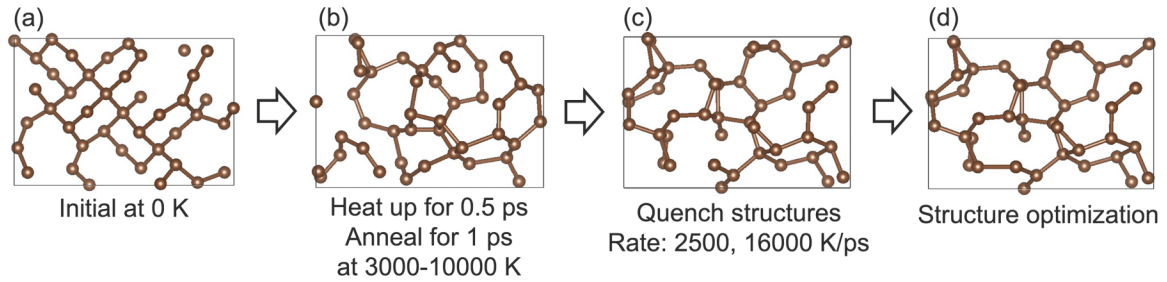


FIG. 4. Schematic illustration of the procedure modeling amorphous carbon structures via anneal-quench method. (a) An example of an initially selected, prerelaxed defective carbon structure at 0 K. (b) The structure after heating to target temperature and annealing for 1 ps using AIMD. (c) The structure after quenching back to 0 K at a rate of 2500 or 16 000 K/ps. (d) The final structure obtained after geometry relaxation of the quenched configuration.

and 109.5° for sp^3 -C. Figure 5 presents the predictive performance of the model, plotting the DFT-calculated stress (X axis) against the model-predicted stress (Y axis).

Blue (filled) and orange (hollow) points represent training and test data, respectively. A perfect model would yield points aligned along the $Y = X$ line. The predictive performance of model was also quantified using mean absolute error (MAE) and root mean squared error (RMSE), as summarized in Table I. The MAE for the test dataset is approximately 1.2 GPa, which is significantly smaller than the typical stress range observed in this study (~ 10 GPa). This level of accuracy is sufficient for reliable interpretability analysis aimed at elucidating trends in the influence of individual structural features on stress. The generalizability of the prediction model was further evaluated using 10-fold cross validation. Specifically, the training dataset was partitioned into 10 subsets; in each iteration, one subset was used as the test set while the remaining subsets were used to train the model. This

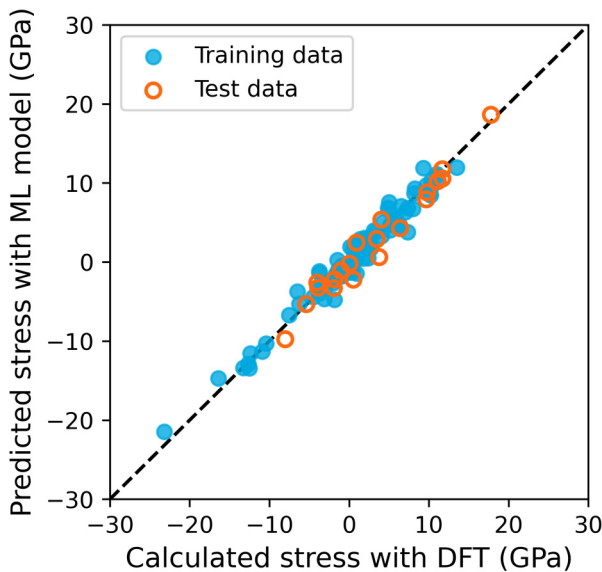


FIG. 5. Accuracy plot of GPR model trained on DFT-calculated stress data. The X axis shows stress values obtained from DFT calculations, while the Y axis shows the corresponding values predicted by the ML model. Blue and orange points represent training and test data, respectively. Deviations from the diagonal $Y = X$ line indicate prediction errors.

procedure was repeated until each subset had been used once for evaluation. The resulting MAE and RMSE were 1.37 and 1.69 GPa, respectively, with standard deviation of 0.335 and 0.406 GPa across the 10 folds. These relatively small variations indicate stable model performance and suggest that the differences among the training, test, and cross-validation errors are not statistically significant. The remaining prediction error is likely attributable to intrinsic uncertainties in the dataset, including approximately 6% deviations between stress values estimated from Young's modulus-based calculations and those obtained directly from the Cauchy stress tensor, which may limit the achievable prediction accuracy.

To further interpret the contribution of each parameter, SHAP analysis was performed. SHAP values quantify the contribution of each input feature to deviations from the average stress prediction, expressed in GPa. Sum of SHAP values for all features of one instance equals to the deviation of the instance's predicted stress from the average. Figure 6(a) shows the mean absolute SHAP values of each feature and Figs. 6(b-1)–6(b-3) show the SHAP values for features which suggested big influences on stress generation: bond length, density, and sp^3 -C fraction. Each marker in Figs. 6(b-1)–6(b-3) corresponds to one structure.

Key observations from SHAP analysis indicate that longer standardized bond lengths contribute to tensile stress, whereas shorter bond lengths increase compressive stress. Similarly, higher density affects increased compressive stress, while lower density leads to tensile stress. Although the sp^3 -C

TABLE I. Prediction accuracy of the Gaussian process regression (GPR) model. The upper and lower rows present the mean absolute error (MAE) and root mean squared error (RMSE), respectively, between the GPR-predicted stress and corresponding DFT values. Errors are shown for both training and test datasets. The rightmost column presents the mean MAE and RMSE obtained from 10-fold cross validation on the training data, providing a measure of the model's generalizability.

	MAE (GPa)	RMSE (GPa)
Training data	1.01	1.28
Test data	1.19	1.46
10-fold cross validation on the training data	1.37	1.69

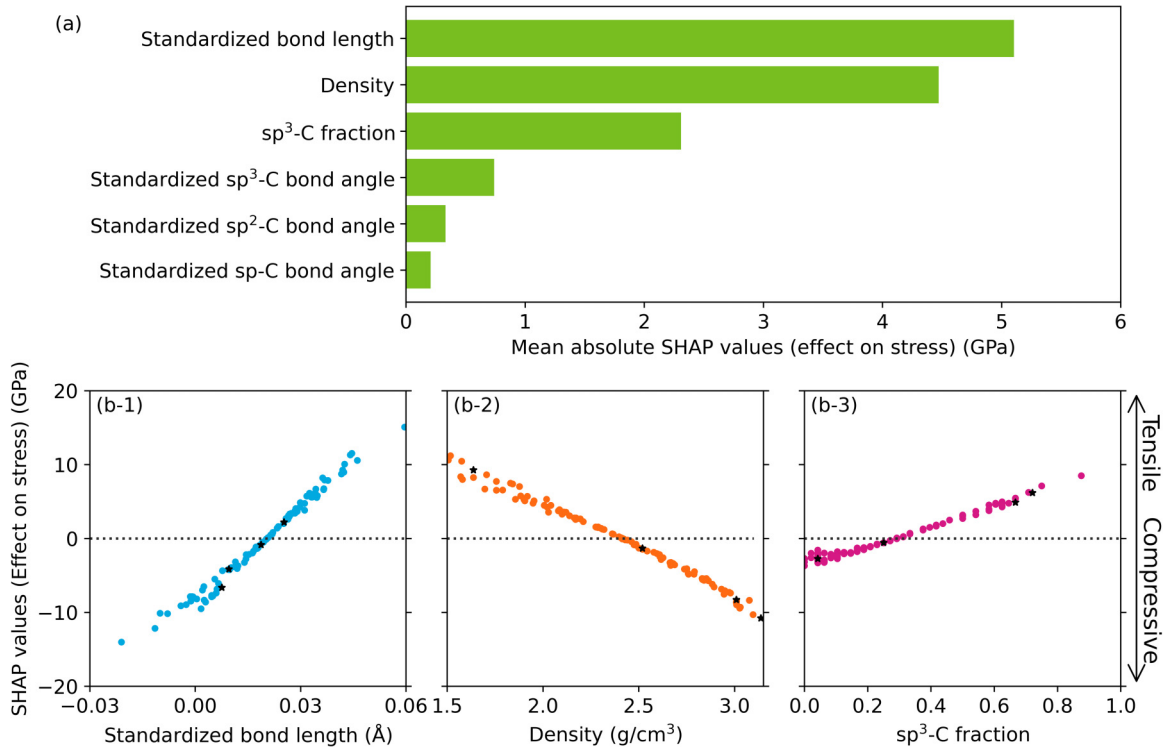


FIG. 6. SHAP analysis of input features contributing to stress prediction by the GPR model. (a) Mean absolute SHAP values representing the overall contribution of each input feature to the predicted stress, sorted in descending order: standardized mean bond length, density, sp^3 -C fraction, and mean bond angles for sp^3 , sp^2 , sp -hybridized carbon. (b-1) SHAP values of standardized bond length. The X axis shows the bond length values standardized by subtracting the ideal mean bond length [as defined in Eq. (2)]; the Y axis shows their corresponding SHAP values, shared with (b-2) and (b-3). Each point represents one structure, indicating the feature's contribution to deviation from the average predicted stress (~ 1 GPa). (b-2) SHAP values of density. (b-3) SHAP values of sp^3 -C fraction. Results obtained from larger supercells containing 86–96 carbon atoms (one 86-atom cell and three 96-atom cells) are shown using star markers, while the original 48-atom configurations are shown using circle markers. The consistency of the SHAP trends between the two system sizes demonstrates the robustness of the identified structure-stress relationships with respect to supercell size.

fraction exhibits a comparable trend to bond length which increases tensile stress, it has minimal impact on compressive stress at low values. Contributions of bond angles to stress are relatively small.

Averaging SHAP values over all samples provides a measure of feature importance. Among the three, bond length showed the highest impact, followed by density and then sp^3 -C fraction. Interestingly, even though only these three parameters were adopted as input features for the training of a prediction model, MAE for the test data remained 1.19 GPa. The fact that the model achieved the same accuracy using only three input features supports the dominance of these parameters in stress generation and suggests minor contributions from other geometric features in the sampled a-C structures.

Because intrinsic tensile and compressive stress of film can be interpreted as the net force applied to the cell for the direction normal to its surface and bond angles have less correlation to this force, SHAP values for bond angles might be far smaller than other features. They are expected to affect shear stress, as the bond angle deviation from stable state can be related to torsion of the structure, while it is not discussed in this paper. The effect of the other three dominant parameters will be discussed in the following sections.

To assess the robustness of the present analysis with respect to finite-size effects, calculations were performed using

larger amorphous carbon supercells containing 86–96 carbon atoms. These configurations were generated following the same melt-quench protocol and analyzed using the identical machine-learning and SHAP workflow as applied to the 48-atom cells.

Importantly, the resulting SHAP value distributions and feature rankings obtained from the 96-atom models exhibit the same qualitative trends as those reported for the 48-atom systems in Fig. 6. In particular, the dominant contributions associated with local coordination environments and bonding distortions remain unchanged, indicating that the key structure-stress relationships identified in this work are not artifacts of the smaller cell size.

While larger simulation cells are expected to be necessary to fully capture long-range elastic relaxation and interface effects present in real amorphous carbon materials, these results demonstrate that a 48-atom supercell is sufficient to reliably extract the local intrinsic stress trends and their microscopic origins within the scope of the present atomistic analysis.

Summarizing the results obtained through data-driven analysis of stress generation, one hypothesis can be proposed: three geometrical parameters, bond length, sp^3 -C fraction and density are the dominant cause of the intrinsic stress. This hypothesis is required to be scientifically validated by calculating stress of structures with systematically changed

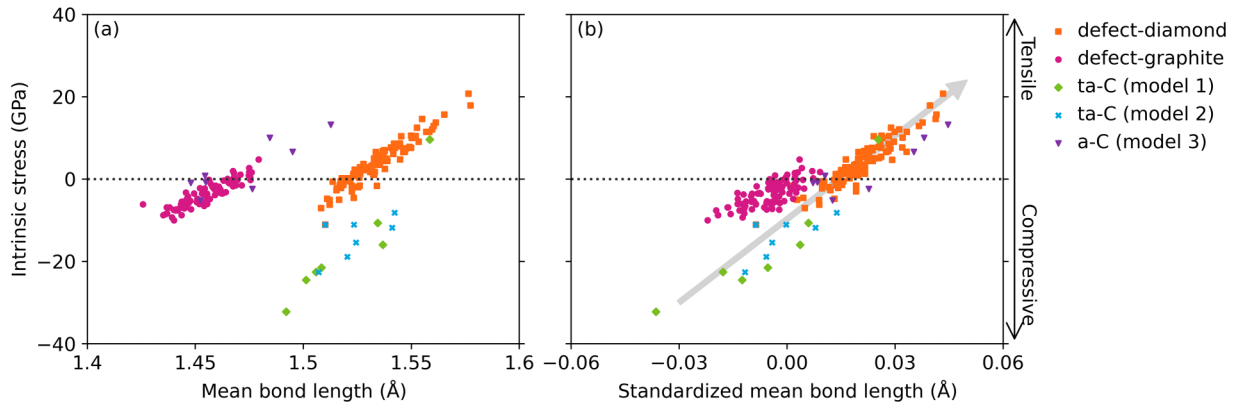


FIG. 7. Relationship between intrinsic stress and bond length in various carbon structures. (a) X axis shows the average bond length within each structure, and Y axis shows the intrinsic stress, with positive values indicating tensile stress. Square and circle markers represent defective diamond and graphite structures, respectively, while the remaining markers correspond to amorphous carbon (a-C) and tetrahedral amorphous carbon (ta-C) structures. Multiple structures labeled as model 1, 2, or 3 originate from the same initial configuration but differ in annealing conditions. (b) Same plot as in (a), but with X-axis values standardized by subtracting the ideal mean bond length defined in Eq. (2). The Y axis is identical to that in (a).

parameter to find the physics behind the phenomena and prove mutual orthogonality. The independent influence of bond length on stress generations is shown and discussed in the subsequent section.

B. Stress and bond length relationship

Figure 7 illustrates the relationship between intrinsic stress and bond length across various amorphous and defective carbon structures.

In Fig. 7(a), the intrinsic stress is plotted as a function of the mean bond length, which is defined as the average of all interatomic distances within each atomic network. Data points are grouped into five structural categories: defective diamond, defective graphite, tetrahedral amorphous (ta-C: models 1 and 2), and amorphous carbon (model 3). All structures originated from pure diamond, namely, defective diamond and ta-C, have the same density of 3.14 g/cm^3 , making it possible to compare multiple structures while eliminating the effect of density. This applies to another set of structures, defective graphite and a-C, whose density is fixed to 2.34 g/cm^3 . A clear monotonic trend is observed, where structures with shorter mean bond lengths are associated with compressive stress, while those with longer bond lengths tend to exhibit more tensile stress. While the slopes of the trends are comparable, the intercepts vary across structural categories, reflecting differences in bonding configurations and intrinsic stress baselines. More specifically, the defective graphite models and a-C (model 3) structures cluster with relatively short bond lengths (most of which are shorter than 1.48 Å), while defective diamond models and ta-C models are generally positioned at longer bond lengths ($>1.48 \text{ Å}$), consistent with higher sp^3 fraction.

To account for variations in bonding hybridization, standardized mean bond length, defined as the deviation from L_{ideal} , is introduced as described in the previous section and Eq. (2).

The resulting standardized analysis, as shown in Fig. 7(b), reveals a nearly linear and universal correlation between bond length deviation and intrinsic stress, indicating that stress

is primarily governed by local geometric distortion relative to the hybridization-specific equilibrium bond lengths. This trend can be rationalized in terms of interatomic potentials: For example, within a Lennard-Jones or harmonic potential framework, bond stretching away from equilibrium induces a restoring force that manifests as tensile stress in the network, while over compressed bonds generate repulsive forces leading to compressive stress. Theoretically, zero stress should have arisen at the standardized bond length of 0 Å , which was not confirmed; this might be explained by the inaccuracy during an approximation when L_{ideal} was calculated. The ideal bond lengths of each hybridized carbon atoms are defined as constant value of $d_{\text{sp}} = 1.37 \text{ Å}$, $d_{\text{sp}^2} = 1.42 \text{ Å}$, and $d_{\text{sp}^3} = 1.54 \text{ Å}$, which are, in reality, expected to be variables depending on environmental parameters such as the external pressure and the charge density of coordinated atoms. Another possibility is that other geometrical parameters, such as density, are affecting stress to the same extent to all structures.

These results collectively demonstrate that mean bond length, both raw and standardized, serves as a physically meaningful and predictive descriptor of intrinsic stress in amorphous and defective carbon models. The persistence of the linear stress–bond length correlation across five structurally distinct models highlights a common geometric origin of stress generation in disordered carbon systems. In contrast to more complex or nonlocal descriptors, bond length offers a simple yet robust parameter for evaluating mechanical behavior. The generality of this bond length–stress relationship suggests that similar principles may apply to other network-forming materials, including amorphous oxides, nitrides, and chalcogenides.

C. Stress and sp^3 -C fraction relationship

To clarify the effect of bonding hybridization on stress generation, the relationship between intrinsic stress and sp^3 -carbon (sp^3 -C) fraction is illustrated in Fig. 8.

Square and circle markers denote the stress values of defective diamond and graphite models, respectively, as

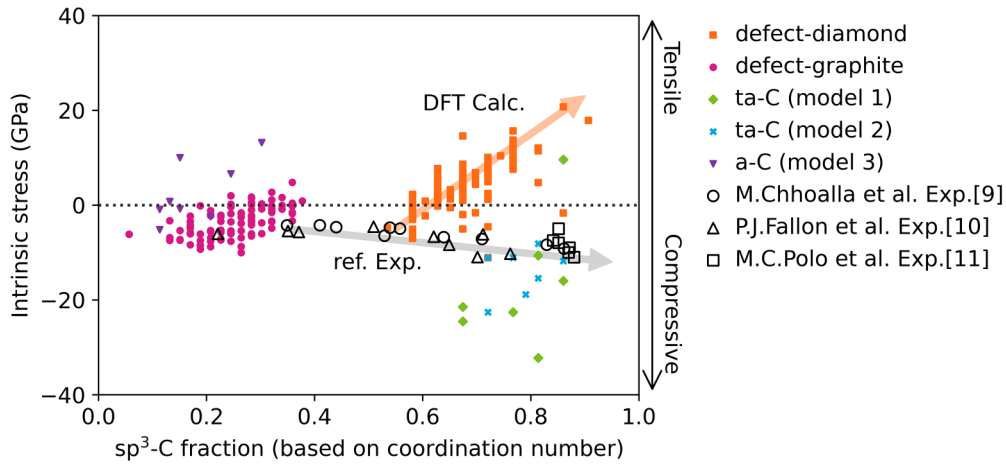


FIG. 8. Relationship between intrinsic stress and sp^3 -C fraction in various defective or amorphous carbon models. X axis represents the sp^3 -C fraction of each structure, determined based on the coordination number of individual carbon atom. The Y axis shows the intrinsic stress. Square and circle markers indicate defective diamond and defective graphite structure, respectively, while the remaining markers correspond to amorphous carbon (a)–(c) and tetrahedral amorphous carbon (ta-C) models. Structures labeled as model 1, 2, or 3 originate from the same initial configuration but differ in annealing conditions. Empty markers represent experimental results reported in the literature.

previously introduced in Fig. 7. Triangles, diamonds, and cross markers represent the results for a-C and ta-C models, while hollow symbols correspond to experimental data reported in the literature [9–11]. All simulation results exhibit a trend of increasing tensile stress with increasing sp^3 -C fraction, suggesting a positive correlation between sp^3 bonding and tensile character under fixed-density conditions, while intercepts are different for structures originated from diamond and graphite. This trend is rationalized by considering that sp^3 -hybridized carbon occupies less volume than its sp^2 counterpart. In our simulations, the primitive unit cell volumes of diamond and graphite are 5.7 and 9.4 Å³, respectively. Therefore, an increase in sp^3 -C fraction leads to volumetric contraction under fixed boundary conditions, giving rise to tensile stress.

However, the trend that increasing sp^3 -C fraction correlates with tensile stress contrasts with experimental observations, which consistently show a correlation between high sp^3 -C fraction and increased compressive stress. This discrepancy likely arises from the differing roles of density in each case. In simulations, density was fixed for each model set, making sp^3 -C fraction the primary variable influencing stress. In contrast, experimental films deposited under typical conditions exhibit coupled variations in density and sp^3 -C fraction, where higher sp^3 -C fractions are usually associated with higher film density. As controlling density independently during deposition is experimentally challenging, the apparent compressive stress observed at high sp^3 -C fractions in experiments may, in fact, be driven by increased density rather than bonding configuration alone. This matches the hypothesis arisen from data-driven analysis where high density works independently to increase compressive stress. To verify the effect of density from scientific perspectives and identify the cause of the discrepancy between calculation and experimental results, density was also systematically varied and stress for each structure was calculated. This result will be further discussed in the following section.

D. Stress and density relationship

Figure 9 illustrates how intrinsic stress in a-C and ta-C evolves with (a) density and (b) sp^3 -carbon fraction. Data from three computational models are plotted alongside experimental results from Chhowalla *et al.* [9] and Fallon *et al.* [10].

To isolate independent effect of density, a set of three representative ta-C or a-C structures, originating from annealing at 5000 K and quenching at 16 000 K/ps, were selected from models 1–3. For each structure, isotropic scaling of lattice parameters was applied (multiplication factors from 0.9–1.1), inducing controlled variations in density while preserving atomic topology. The resulting structures were geometrically relaxed, and their intrinsic stress and sp^3 -carbon fraction were calculated. This protocol produced a set of data points, shown in Figs. 9(a) and 9(b), where the same marker shape denotes the same stress state across both density and sp^3 -C axes.

As shown in Fig. 9(a), a nearly linear relationship was observed between increasing density and compressive stress. This behavior holds across all models and matches well with the trend seen in experimental data, particularly at higher densities (~ 2.8 – 3.3 g/cm³). In addition, our simulation results in the low-to-mid density range (<2.5 g/cm³) show moderate tensile towards weak compressive stress, while denser structures (>3.0 g/cm³) exhibit increasingly large compressive stress values.

The increase in compressive stress at high density can be explained as follows: as atoms are densely packed into a fixed volume, configurational entropy is reduced, and internal strain accumulates. In a fully relaxed system, such strain would naturally drive volumetric expansion, which is restricted under periodic boundary conditions, hence resulting in compressive stress.

Figure 9(b) further supports these results by showing the corresponding sp^3 -C fractions. A general correlation is observed: compressive stress increases with higher sp^3 fraction. By comparing the paired data across Figs. 9(a) and 9(b), we can distinguish the role of density from bonding

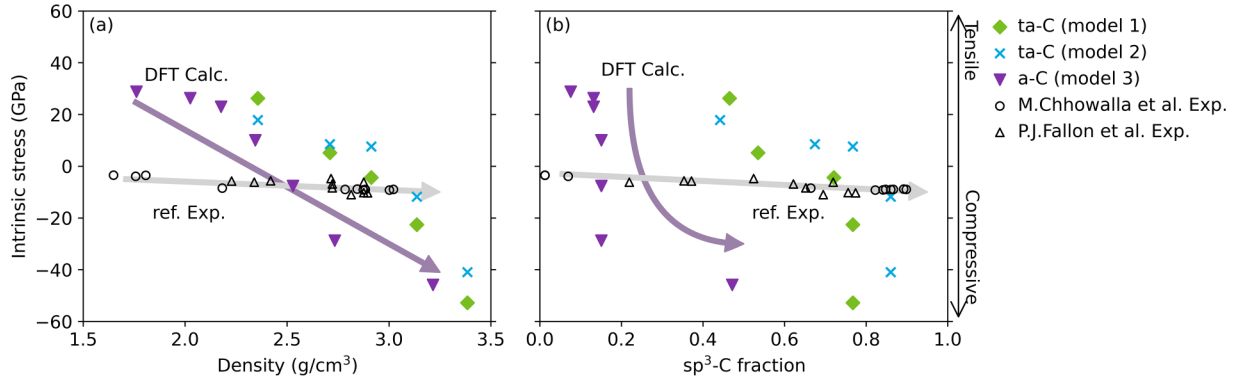


FIG. 9. Stress and density relationship. Calculated stress of isotropically scaled amorphous carbon structures with systematically varied densities and sp^3 -C fraction. (a) Stress versus density relationship. The X axis shows the density of each structure, and the Y axis shows the intrinsic stress. Data points with identical marker (model 1, 2, or 3) represent structures originating from the same annealed, prerelaxed configuration, scaled isotropically to different cell sizes. Empty markers indicate experimental data from literature. (b) Corresponding sp^3 -C fractions for the structures shown in (a), allowing for direct comparison between density, stress, and hybridization.

configuration. Focusing on the triangle symbols representing a-C structures (model 3), there exists a parameter range where density increases substantially, resulting in a sharp rise in compressive stress, while the sp^3 fraction remains nearly constant. This decoupling confirms that high density alone can significantly drive compressive stress, even in the absence of major bonding changes. These findings suggest that while sp^3 hybridization contributes to stress buildup in a-C, density plays a dominant and independent role in determining the magnitude of intrinsic stress.

The discrepancy in the absolute stress value in Fig. 9 might be mainly attributed to an intentionally limited extent of structural optimization, although theoretical limitations of GGA-PBE functional could be another reason. In this calculation, to compare structures with very similar sp^3 -C fractions for revealing pure density effect, structures were modeled without full relaxation using AIMD after expanding or shrinking cell size. Therefore, realistically, preparing these structures would be difficult, whereas the trend is valid as a subject of discussion.

IV. DISCUSSION

Based on this calculation, the opposite trend observed between calculation and experimental results in stress and sp^3 -C fraction shown in Fig. 8 is now confirmed only to be associated with the strong influence of density in experimentally deposited films.

To elucidate the mechanisms of intrinsic stress in a-C networks, we decompose the total stress change ($\Delta\sigma$) into contributions from three fundamental structural parameters: sp^3 -C fraction (f_{sp^3}), bond length (l), and the atomic density (ρ). This relationship can be expressed as

$$\Delta\sigma = \frac{\partial\sigma}{\partial f_{sp^3}} \Delta f_{sp^3} + \frac{\partial\sigma}{\partial l} \Delta l + \frac{\partial\sigma}{\partial \rho} \Delta\rho, \quad (3)$$

where Δf_{sp^3} , Δl , and $\Delta\rho$ are the corresponding variations in those structural quantities. Our first-principles calculations, composed of data-driven hypothesis exploration and systematic approaches, reveal that both $\partial\sigma/\partial f_{sp^3}$ and $\partial\sigma/\partial l$ are

positive, implying that increases in sp^3 fraction and bond elongation promote tensile stress. This is due to the smaller volume of sp^3 -C compared to that of sp^2 -C and bond stretch generating a restorative elastic force that contributes to tensile stress. In contrast, the derivative $\partial\sigma/\partial\rho$ is negative, indicating that atomic density leads to compressive stress as discussed so far. Deviations of stress which cannot be explained by these three terms in Eq. (3) would still exist, yet they are likely sufficiently small according to data-driven analysis, where stress value can be predicted only from these three parameters.

This decomposition challenges the longstanding notion that high sp^3 -C fraction is the primary origin of compressive stress. Our results suggest that sp^3 bonding intrinsically favors tensile stress, and that compressive stress arises predominantly from densification effects.

Collectively, these results substantiate the hypothesis that intrinsic stress in a-C films can be quantitatively modeled and interpreted using only three geometrical descriptors, which was suggested through data-driven analysis. The minimal influence of other factors further reinforces the effectiveness and interpretability of this low-dimensional parameter space.

V. CONCLUSIONS

In this work, we performed a comprehensive first-principles investigation combined with data-driven modeling to elucidate the origins of intrinsic stress in amorphous and defective carbon networks. SHAP results suggested the significant importance of bond length on stress generation, followed by those of density and sp^3 -C fraction. Elongated bonds and sp^3 -rich structures were correlated to large SHAP values, i.e., big impact to increase tensile stress, while high density was indicated as a key factor originating high compressive stress. Our systematic analysis substantiated the hypothesis by isolating the effects of each parameter. A stress decomposition framework used in this research allowed us to isolate and quantify the individual contributions of each descriptor to overall stress generation. This work thus provides a unified, interpretable model for understanding and predicting stress in carbon-based thin films.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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