Model form uncertainty versus intrinsic atomic variability in amorphous silicon oxides and nitrides

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We quantify uncertainties in density functional theory predictions of several fundamental materials properties of amorphous dielectrics focusing on those that arise from the intrinsic atomic variability of the glass structures and those stemming from approximations in the theory. The intrinsic, or aleatoric, uncertainties are quantified by performing calculations over ensembles of structures obtained by annealing independent liquid samples. We estimate model form, or epistemic, uncertainties by comparing results from two exchange and correlation functionals that exhibit different bonding characteristics: the local density approximation (that typically overbinds), and the generalized gradient approximation (that often underbinds). In the case of density, bulk modulus, and point defect formation energies predictions obtained from systems containing between 72 and 192 atoms, typical of current state-of-the-art calculations, show that the intrinsic variability in the atomic structure leads to uncertainties a factor of two to four times greater than those originating from model form. While model form discrepancies remain important, our results emphasize the importance of using ensembles of structures to make predictions of amorphous materials. The use of such probabilistic atomic-level data as input in

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multiscale materials or device models is critical for predictions with quantified uncertainties but also to uncover how atomic variability affects device performance.

1. Introduction

Predictive modeling and simulation has the potential to revolutionize the design, optimization and certification of materials, devices and structures.[1] Realizing the full potential of these techniques requires rigorous uncertainty quantification in the predictions that would enable simulation data-informed decision-making; see, for example, [2-4]. In this paper we quantify uncertainties and variability in first-principles calculations using density functional theory; this is important because this technique is often used as the foundation of multiscale materials modeling efforts [5-6]. In general, uncertainties in the predictions of a simulation arise either from known variability in an input quantity (aleatoric uncertainty) or due to a lack of knowledge (epistemic uncertainty) [7]. Uncertainties in density functional theory predictions of materials properties have multiple origins and their relative importance depends on the specific application. However, two sources of uncertainties dominate predictions in most cases: i) simplifications in the atomic structure used (e.g. simplified model structures, lack of defects) and ii) those arising from physical approximations made in the theory (epistemic). In the case of DFT predictions of total energies the latter is the choice of exchange and correlation functional [8-9]. In the cases of interest in this paper, involving amorphous systems, the uncertainties associated with the atomistic structures are aleatoric in nature (i.e. they are inherent and cannot be reduced). Other sources of uncertainty in DFT calculations include those associated with numerical approximations (such as basis sets, pseudopotentials, grids for numerical integrations, etc.); these are often called verification uncertainties and an excellent description of them can be found in

Ref. [9]. In this paper we focus on the first two types described (those associated with the atomic structure and those associated with approximations in the theory) since they are of a fundamental nature and pervasive in DFT applications. We characterize how these uncertainties affect the prediction of bulk properties (density and bulk modulus) and point defect formation energy in amorphous dielectrics of technological interest.

In amorphous materials, variability at the atomic-structure level can be classified into two types: i) one is intrinsic, associated with the glassy network, and leads to property variability from point to point in the same sample and from sample to sample; ii) a second kind depends on processing conditions and can lead to significant changes in properties; see Ref. [10] and references therein. The second kind has been particularly challenging to capture in simulations.

Amorphous dielectrics, such as silicon oxides ($a\text{-SiO}_2$) and nitrides ($a\text{-Si}_3\text{N}_4$), are used in a range of electronic applications spanning individual memory [11] and transistor [12] devices, to entire integrated circuits, [13] solar cells [14-15] and micro-electromechanical systems [16-17]. The electronic properties of these materials govern device performance and can only be quantitatively understood by studying accurate atomic scale models including defects. Structurally, these materials are characterized by a random network lacking long-range order and specific short-range connectivity features that are inherently variable, resulting in distributions of properties.

Computational techniques have become a useful and cost-effective way to predict the materials properties of a wide range of materials; in particular, multiscale approaches have been recently used to predict ensembles of low energy $a\text{-SiO}_2$ [6, 18] and $a\text{-Si}_3\text{N}_4$ [10, 19] structures and their properties. At the heart of these predictions is density functional theory (DFT) [20], a quantum mechanical based technique that provides a good balance between accuracy and computational

efficiency for a large variety of ground state properties of condensed matter systems [9]. The input to DFT is an exchange and correlation functional that is only known approximately and, thus, leads to epistemic uncertainties. Here we present a quantitative comparison between the model form uncertainty in DFT and the intrinsic topological variability present in amorphous SiO_2 and Si_3N_4 materials prepared by annealing molten samples.

The remainder of the manuscript is organized in the following manner. Section 2 discusses simulation details focusing on the approximations made in the exchange and correlation functional and an overview of those that are used in the present work. In Section 3 we discuss the results of our distributions of calculated densities, bulk moduli, and formation energies for $a\text{-SiO}_2$ and $a\text{-Si}_3\text{N}_4$ ensembles. Section 4 then summarizes with our conclusions.

2. Methods

2.1 Density functional theory and model form approximations

The DFT method we use involves self-consistently solving the Kohn-Sham equations, equivalent to the many-body Schrodinger equation for ground state total energy calculations except that the $3N$ spatial coordinates of N electrons are replaced with a three spatial coordinate electronic density, $n(\mathbf{r})$. This is achieved by replacing the N interacting electron potential with an effective potential of non-interacting particles. Interactions between electrons other than those in the classical mean field Hartree term and the effect of the anti-symmetric nature of the electronic wave function are accounted for in a density-dependent exchange-correlation functional (E_{xc}). The exact form of this functional is not known but several approximations have been formulated [21-28] whose success depends upon the material system being studied, and often they are

derived for specific systems of interest. Two of the most commonly used and widely applicable functional approximations are the local density approximation (LDA) and the generalized gradient approximation (GGA). LDA assumes that the functional energy (E_{xc}^{LDA}) at any point in space $\mathbf{r}$ is dependent only on the density at that point, and GGA assumes that the energy (E_{xc}^{GGA}) is also dependent on the gradient of the density ($\nabla n(\mathbf{r})$). That is

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{xc}^{LDA}[n(r)] d\mathbf{r} \quad (1)$$

$$E_{xc}^{GGA}[n(\mathbf{r}), \nabla n(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{xc}^{GGA}[n(r)] F_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})] d\mathbf{r} \quad (2)$$

where $\varepsilon_{xc}[n(\mathbf{r})] = \varepsilon_x[n(\mathbf{r})] + \varepsilon_c[n(\mathbf{r})]$ can be split into its respective exchange and correlation contributions, and F_{xc} is known as the enhancement factor. An analytic form for ε_x exists [20, 29], however none exists for ε_c and this is typically fit to a combination of theoretical and experimental data. Although a few common fits exist [22,30-31], we use the fitting of Perdew and Zunger [23] to the first principles homogenous electron gas calculations of Ceperley and Alder [32] for the correlation contribution to this term. The enhancement factor for GGA is not unique and several forms exist, parameterized both empirically from experiments [26] and non-empirically from first-principles [24, 31, 33]. For our calculations we use the non-empirical parameterization of Perdew, Burke and Enzerhof (PBE) [24]. These choices are implemented in most DFT codes and are therefore readily available in the scientific community, as well as being the most commonly used for the dielectric materials [34-37] under investigation in this study. All calculations are performed using SeqQuest [38], a Gaussian basis set code that expands the Kohn-Sham orbitals with double-zeta plus polarization basis sets. For the LDA calculations, silicon atoms are treated with Hamann type norm-conserving pseudopotentials [33] and

Troullier/Martins type pseudopotentials [39] are used for the oxygen and nitrogen atoms. GGA calculations employ a new form of Hamaan pseudopotentials [40] for silicon and again Troullier/Martins type [39] for oxygen and nitrogen. Each calculation was performed on systems sufficiently large that the Γ -point was adequate for Brillouin-zone integration [18].

2.2 Ensembles of amorphous structures and property calculations

Stoichiometric samples of 72-atom and 192-atom a -SiO₂, as well as 112-atom a -Si₃N₄ samples were generated using reactive molecular dynamics annealing followed by DFT relaxation as described in Refs. [18] and [10] respectively. The samples were equilibrated at a temperature higher than the predetermined melting point and ensembles of statistically independent samples were annealed to room temperature using empirical force fields. This resulted in an ensemble of 234 independent MD structures; 60 samples of each size of a -SiO₂ and 114 samples of a -Si₃N₄. The use of cooling rates significantly slower than in prior theoretical studies led to relatively small defect populations and the generation of defect-free, amorphous structures. The resulting structures were fully relaxed using DFT with respect to atomic coordinates and cell parameters (all six degrees of freedom - three lattice parameters and three angles- where treated independently). A stress threshold of 0.5 GPa was used for cell relaxations. A detailed description of structural generation characterization for both a -SiO₂ and a -Si₃N₄ can be found in Refs. [18] and [10], respectively. We note that while all the a -SiO₂ structures were obtained under nominally identical conditions the a -Si₃N₄ are annealed at different densities to mimic different processing conditions.

The bulk moduli of the a -Si₃N₄ ensemble were obtained from energy-volume relationships obtained by isotropically straining the relaxed structures. The simulation cell lengths were

strained in the range -3% to +6% keeping cell angles fixed and relaxing atomic positions. We computed the bulk modulus of each structure by fitting a quadratic equation of state to the resulting energy-volume data. Energy-volume data for each individual structure is provided in the supplementary material.

Point defects in these materials dominate their performance and degradation [9] and significant efforts have been devoted to their identification and characterization. Formation energies per point defect pair are calculated with reference to the average energy of all defect-free amorphous networks. In our stoichiometric systems, defects come necessarily in pairs (in simple terms, breaking or forming a bond changes the number of defective atoms by two). A defect-free α -SiO₂ structure is a continuous random network of SiO₄ tetrahedra connected via doubly coordinated oxygen atoms, whereas for α -Si₃N₄ it is SiN₄ tetrahedra connected via triply coordinated nitrogen atoms. The formation energy per defect pair is then calculated as the energy difference of a defective cell (E_{def}) and the average energy of all defect-free cells ($\langle E_{perf} \rangle$)

$$E_f = \frac{E_{def} - \langle E_{perf} \rangle}{N_{def}}, \quad (3)$$

where N_{def} is the number of defect pairs in the cell. The average of defect-free cells is used rather than the pair-wise convolution of differences to reduce the spread of the resulting distribution. It should then be noted that negative formation energies simply implies that the defect cell energy lies within the low-end tail of energies that are less than the average of all defect-free energies. The use of the average energy as a reference to compute defect energies is a necessary evil due to the lack of one-to-one correspondence between defective and defect-free structures. Also of note is that we do not distinguish between defect types and compute the

overall distribution of defect-pair formation energies; a detailed defect analysis was included in our prior publications. [10,18]

We quantify model form uncertainties by comparing LDA and GGA predictions on a structure-by-structure basis. Specifically, we compute the distribution of the absolute value difference in property prediction between LDA and GGA methods on a structure-by-structure basis $|P_i^{GGA} - P_i^{LDA}|$, where P denotes the property of interest and i the structure. We define the model-form error for each property as the value that corresponds to the 95th percentile of data in ascending order; i.e. for 95% of the structures the absolute value of the difference between LDA and GGA predictions is less than the model-form error.

In order to quantify aleatoric uncertainties in the resulting properties we fit Gaussian distributions to the histograms of calculated properties for each functional. We compute the uncertainty associated with intrinsic atomic variability (Δ_{atomic}) we use the average between four standard deviations for each functional

$$\Delta_{atomic} = (\sigma^{GGA} + \sigma^{LDA}) / 2. \quad (5)$$

If the distribution of property values was Gaussian, this definition of aleatoric variability captures 95% of the data providing a measure equivalent to that used for model-form uncertainty. We use the ratio $\Delta_{atomic} / \Delta_{model}$ to quantify the relative importance of the two types of uncertainties. That is, at unity this ratio tells us that both uncertainties are equally important, where as values greater than one indicates that atomic-variability dominates the uncertainty in the prediction.

3. Aleatoric and epistemic uncertainties in property predictions

The mean and standard deviations of all the properties calculated are shown in Table 1 and subsequent quantifications of all uncertainties for each calculated properties are summarized in Table 2 (round off leads to slight inconsistencies in the values between Tables 1 and 2). The following sub-sections discuss aleatoric and model-form uncertainties in density, bulk modulus and defect formation energies.

3.1 Density predictions

Figures 1(a-c) show the predicted densities for each of the systems under investigation. As is well known, LDA suffers from a lack of core-valence repulsion and thus tends to overbind; GGA tends to over-correct this problem leading to underbinding, and this is observed all three systems. A comparison with experimental values provides further support to this observation; experimental densities for α -SiO₂ (2.20-2.27g/cm³[41-42]) lie between the high-end tails of GGA and low-end tails of LDA. For α -Si₃N₄ a wide range of densities have been reported depending on processing conditions: 2.60-3.20g/cm³[43-45]; this range is consistent with our predictions but extends to lower values which could be the result of porosity in some of the experimental samples.

As expected the model-form uncertainty, Δ_{model} , in density is independent of system size but that associated with intrinsic atomic variability decreases with increasing system size. This size dependence follows approximately the square root of the number of atoms as expected based on statistical mechanics [46]. We find that for the largest systems the intrinsic atomistic uncertainty almost twice as large as that originating from model form. For example, for 95% of the structures

192-atom SiO₂ structures the discrepancy between LDA and GGA was less than 0.13 g/cm³ while range of 0.23 g/cm³ around the mean is required to capture 95% of the structures. For the smaller, 72-atom systems, the aleatoric uncertainty is a factor of three larger than the model-form one.

3.2 Bulk modulus predictions

The bulk modulus is an elastic constant that can be interpreted as a measure of bond stiffness and their density. The distribution of values predicted over the range of samples is quite large and, as expected, our results show that LDA tends to slightly overestimate this property compared to GGA. The wide range is also consistent with experimental values (α -Si₃N₄: 100-190GPa [47]). We note that the wide range of values in the experiments reflects various processing conditions; in the simulations we also varied processing conditions (annealing density)[19] and the range denotes both intrinsic atomistic variability and annealing conditions.

We find that for 95% of the structures the discrepancy between the GGA and LDA predictions is ~21 GPa or less. While this is a relatively large discrepancy, given the very wide range of predicted values in Figure 2, it is not surprising that the uncertainty originating from intrinsic variability in the ensemble of structures is larger than the model form error for this system, see Table 3.

3.3 Defect formation energy predictions

The formation energy per defect pair involves differences between the total, relaxed energies of defective and defect-free systems; such calculations are known to be functional dependent [6].

We note that, as opposed to the case of density and bulk moduli, increasing the simulation cell size is not expected to lead to a reduction in the variability of defect formation energies, as long the defective cell contains a single defect pair. The importance in capturing atomic variability in defect formation energy in predictive modeling of dielectric charging has been recently demonstrated [19]. Interestingly, since the defect formation energy is the difference between two total energy calculations on independent structures increasing system size makes its calculation more complex from a numerical point of view.

Table 1 shows that the mean values of the defect formation energies from LDA and GGA are in reasonable agreement, ranging from 1.7 to 2.7 eV. These differences are relatively small compared with the intrinsic variability. From Table 3 we see that the model form error varies from 2.2 to 6.3 and is approximately a factor of two smaller than the intrinsic variability.

4. Discussion and conclusions

We performed DFT calculations on an ensemble of hundreds of relaxed structures of amorphous dielectrics (ranging in size from 72 to 192 atoms) to determine the density, bulk modulus, and defect formation energy distributions using two commonly used functionals. The uncertainties originating from model uncertainties (GGA vs. LDA) are in line with values from the literature. Interestingly, in all cases we find that the uncertainty originating from the intrinsic atomic variability is comparable or greater than that from the choice of exchange and correlation functional. We stress that model form errors are not unimportant, the comparison of aleatoric and epistemic uncertainties highlight the importance of performing calculations over ensembles of atomistic structures in the case of amorphous materials.

In the prediction of density we find that the intrinsic material variability is a factor of two to three larger than the model form error in two density functional choices for the system sizes investigated here. As expected, the aleatoric variability decreases with increasing system size in bulk property predictions. In the case of bulk moduli predictions the intrinsic variability is slightly larger compared to model form errors.

We note that in this paper we do not quantify errors in the predictions due to inaccuracies in the initial ensemble of amorphous structures used for the DFT calculations. This ensemble was obtained from annealing simulations using MD with empirical potentials and is affected by the quality of the interatomic potential and annealing procedure. This is a state-of-art method and quantifying the uncertainties involved is beyond the scope of this paper. We expect our conclusions regarding the importance of atomic variability to be valid for other amorphous materials and such calculations would be of interest. For crystalline materials with low defect densities the model-form errors in DFT calculations clearly outweigh those originating from atomistic variability and improving the accuracy of DFT methods is clearly critical for a wide range of applications.

The methods presented here can easily be applied to other exchange and correlation functional choices and numerous classes of crystalline and non-crystalline materials where local variability may affect the desired properties. Such predictions can be used as input parameters for stochastic [48] or deterministic simulations [19] with coarser descriptions to assess how variability at atomic scales and uncertainties in fundamental theory affects the quantities of interest.

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(a)

(b)

(c)

Figure 1. Distributions of predicted densities using both LDA and GGA functional for (a) 72-atom α -SiO₂ (b) 192-atom α -SiO₂ and (c) 112-atom α -Si₃N₄.

Figure 2. Functional predicted bulk modulus distributions using LDA and GGA for 112-atom *a*-Si₃N₄. (Experimental *a*-Si₃N₄: 100-190 GPa)

(a)

(b)

(c)

Figure 3. Formation energy per defect pair using LDA and GGA for (a) 72-atom α -SiO₂ (b) 192-atom α -SiO₂ and (c) 112-atom α -Si₃N₄.

TABLES

Table 1. Calculated mean and standard deviations of properties.

Property	μ^{LDA}	μ^{GGA}	σ^{LDA}	σ^{GGA}
ρ^{a-SiO_2} (72-atom) [g/cm ³]	2.26	2.16	0.102	0.092
ρ^{a-SiO_2} (192-atom) [g/cm ³]	2.23	2.14	0.061	0.056
$\rho^{a-Si_3N_4}$ (112-atom) [g/cm ³]	3.09	2.94	0.124	0.119
$B^{a-Si_3N_4}$ (112-atom) [GPa]	148.44	138.47	19.61	18.67
$E_f^{a-SiO_2}$ (72-atom) [eV]	2.61	2.70	1.25	1.13
$E_f^{a-SiO_2}$ (192-atom) [eV]	2.09	1.72	2.66	2.88
$E_f^{a-Si_3N_4}$ (112-atom) [eV]	2.21	2.40	1.98	1.96

Table 2. Summary quantifying the sources of uncertainty for calculated properties.

Property	Δ_{model}	$\Delta_{atomic} = \frac{4\sigma^{GA} + 4\sigma^{DA}}{2}$	$\Delta_{atomic} / \Delta_{model}$
ρ^{a-SiO_2} (72-atom) [g/cm ³]	0.13	0.39	3.07
ρ^{a-SiO_2} (192-atom) [g/cm ³]	0.13	0.23	1.81
$\rho^{a-Si_3N_4}$ (112-atom) [g/cm ³]	0.27	0.49	1.80
$B^{a-Si_3N_4}$ (112-atom) [GPa]	21.24	76.55	3.60
$E_f^{a-SiO_2}$ (72-atom) [eV]	2.17	4.76	2.19
$E_f^{a-SiO_2}$ (192-atom) [eV]	6.25	11.08	1.77

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Graphical

(a)

(b)

13

(c)

Figure 1. Distributions of predicted densities using both LDA and GGA functional for (a) 72-atom α -SiO₂ (b) 192-atom α -SiO₂ and (c) 112-atom α -Si₃N₄.