Error correction in multi-fidelity molecular dynamics simulations using functional uncertainty quantification

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Abstract

We use functional, Fréchet, derivatives to quantify how thermodynamic outputs of a molecular dynamics (MD) simulation depend on the potential used to compute atomic interactions. Our approach quantifies the sensitivity of the quantities of interest with respect to the input *functions* as opposed to its parameters as is done in typical uncertainty quantification methods. We show that the functional sensitivity of the average potential energy and pressure in isothermal, isochoric MD simulations using Lennard-Jones two-body interactions can be used to accurately predict those properties for other interatomic potentials (with different functional forms) without re-running the simulations. This is demonstrated under three different thermodynamic conditions, namely a crystal at room temperature, a liquid at ambient pressure, and a high pressure liquid. The method provides accurate predictions as long as the change in potential can be reasonably described to first order and does not significantly affect the region in phase space explored by the simulation. The functional uncertainty quantification approach can be used to estimate the uncertainties associated with constitutive models used in the simulation and to correct predictions if a more accurate representation becomes available.

Keywords: uncertainty quantification, functional derivative, molecular dynamics, interatomic potential, free energy calculation

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1. Introduction

Uncertainty quantification (UQ) is becoming increasingly important in predictive simulations of materials and devices [1]. While the majority of the early UQ work focused on solid and fluid mechanics, there is growing interest in applying and extending UQ techniques to simulations at the material level, including density functional theory [2, 3], molecular dynamics (MD) [4, 5, 6, 7, 8], and multiscale methods [9, 10, 11]. These efforts highlighted the importance of acknowledging uncertainties in model parameters, from measurement or averaging techniques, as well as intrinsic variability of the systems or processes under investigation. These studies, and most UQ work thus far, examined uncertainties in input parameters and specialized software packages have been developed for this task: examples include DAKOTA [12], PUQ [13], and Π 4U [14]. However, in many applications – especially those involving complex physics – accounting for uncertainty in parameters is not enough, as the functional forms of the constitutive models themselves are approximate. This is particularly true in materials modeling where lack of knowledge leads to unquantified or poorly quantified uncertainties. Examples of input functions with varying degrees of accuracy include exchange and correlation functionals used in density functional theory calculations [2, 15], interatomic potentials for molecular dynamics (MD) [16, 17, 18], generalized stacking faults used in dislocation dynamics [19], and constitutive laws for micromechanical simulations. In this paper we use functional derivatives (FD), recently proposed as a mathematical framework to quantify uncertainties that arise from constitutive models used in simulations [20], to quantify and correct uncertainties that originate from the interatomic potential used in MD simulations.

Functional uncertainty quantification (~~FUQ~~FunUQ) can, in principle, be used to assess the uncertainties originating from approximate input constitutive laws, correct predictions if a more accurate function becomes available, and rank when and where to replace a low-fidelity model used in a simulation with one of higher fidelity in order to reduce prediction error by running additional simulations. This paper introduces a computationally efficient method to compute FDs in MD simulations involving two-body interatomic potentials, extending ideas from thermodynamic integration and free-energy perturbation methods [21, 22]. The FD quantifies how a quantity of interest (QoI) – in this case the total potential energy or pressure computed from an MD simulation in the canonical ensemble – depends on the input function,

here the Lennard-Jones (LJ) two-body pair potential. We further show that the FD with respect to the LJ potential can be used to compute accurate correction to the potential energy and pressure for a family of pair potentials without re-running the simulation. This is true as long as the discrepancy between the potentials remains within reasonable bounds and the phase space explored by the system with the new potential is not significantly different from that of the original.

The remainder of the paper is as follows. Section 2 describes the functional approach to UQ and connections to similar UQ methods, followed by simulation details and methods to calculate the functional derivative numerically in Section 3. In Section 4 we describe specific examples of error correction using ~~FUQ~~ FunUQ with low and high-fidelity models. ~~Sections 5 and 6 discuss results and conclude~~ discusses results and concludes the paper.

2. Functional uncertainty quantification

In general, a simulation predicts a quantity of interest, Q , given some set of input parameters P_i and constitutive functions f_j , themselves functions of an independent variable z and input parameters N_k :

$$Q = Q(P_i, f_j(z, N_k)) \quad (1)$$

In the cases of interest here, Q will be the time averaged potential energy or pressure and $f(z)$ the LJ potential as a function of interatomic distance used in the MD simulation.

The ~~most common form of UQ is~~ problem of forward propagation in UQ is most commonly concerned with uncertainty in simulation outputs arising from uncertainty in the input parameters. This approach, while very valuable, ignores the fact that the functional forms used as constitutive laws are, almost invariably, approximate and lead to errors in the simulation. To quantify uncertainties with respect to input functions we utilize functional derivatives (Fréchet derivatives) of the QoI with respect to the input functions. The FD can be written in differential form as:

$$\frac{\delta Q[f]}{\delta f(z)}(z_i) = \lim_{\epsilon \rightarrow 0} \frac{Q[f(z) + \epsilon \cdot \delta(z - z_i)] - Q[f(z)]}{\epsilon} \quad (2)$$

This characterizes the functional sensitivity of the QoI with respect to the input function. The definition in Eq. 2 uses the Dirac delta function as the

functional variation; as we describe below, to calculate the functional derivative numerically for the MD simulations we use narrow Gaussian distributions centered at z_i .

Besides quantifying uncertainties in the prediction given uncertain input functions, the functional derivative can be used to correct the error that arises from the use of a low-fidelity model (f) if ~~a higher-fidelity one~~ one of higher-fidelity (g) becomes available. ~~The~~ A first order correction is then obtained using the product of the functional sensitivity (the FD) and functional discrepancy ($g(z) - f(z)$). We call this product the functional error and the first order correction for the QoI is:

$$\Delta Q = \int \frac{\delta Q[f]}{\delta f(z)} \cdot (g(z) - f(z)) dz \quad (3)$$

This is an extension of the multi-variate UQ expression to the space of input functions: sum of variables is replaced by an integral, derivatives with respect to individual variables are replaced by the functional derivative, and the functional error takes the place of the difference in the values of input variable. A simple analytical example is included the supplementary material, Section S1.

In the absence of a high-fidelity model Eq. 3 can alternatively be used for uncertainty propagation by replacing the discrepancy with the uncertainty in $f(z)$ and taking the absolute value of the functional derivative [20]. This procedure returns a first order bound of the uncertainty in Q .

Additionally, this equation can be used to rank high-fidelity simulations in order of their functional error to optimally reduce the error in the predicted QoI, recently demonstrated with calculation of the functional derivative for the restoring force in a multi-fidelity radio frequency MEMS switch simulation [20]. This functional derivative was used to rank model evaluations and minimize the necessary computational cost to maximize error correction in the simulation. In Section 3 we extend the formulation to a significantly more challenging problem: molecular dynamics simulations.

Many other approaches in utilizing and optimizing multi-fidelity simulations and describing model discrepancy exist, notably stemming from the work of Kennedy and O'Hagan [23]. Multi-fidelity simulation orchestration with Bayesian approaches optimize (with uncertainty) utilization of multiple levels of model fidelity [24] and include uncertainty from model selection within a simulation framework, most often through model averaging [25, 26, 27]. Model discrepancy approaches most often investigate the difference between

the simulation predictions and observed data (structural uncertainty) [28]. Alternatively, the discrepancy is between the computational model and a surrogate is of interest [29]. In contrast, we describe direct consideration and correction of uncertainty from multiple models with varying fidelity.

3. Functional derivatives in molecular dynamics

3.1. Systems of interest and simulation details

We demonstrate the ~~FUQ-FunUQ~~ method in molecular dynamics simulations where the input function is a pairwise interatomic potential and the QoIs are the potential energy and pressure (long-time averages) of the system. MD simulations use this pairwise potential energy as a function of atomic separation as an input to compute total energy and interatomic forces (obtained as the negative gradient) which are used to integrate Newton's equations of motion to predict the time evolution of the system. We take the Lennard-Jones 12-6 potential as the low-fidelity input function:

$$\phi_0(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6) \quad (4)$$

and test the ability of ~~FUQ-FunUQ~~ to correct the prediction of the QoI for a family of high-fidelity potentials. The LJ potential uses an inverse sixth order term to describe the attractive part of the interactions and an inverse twelfth order term to describe shorter range repulsion. The parameters for the low-fidelity LJ potential are designed to roughly describe copper (~~$\sigma = 2.315\text{\AA}$, $\epsilon = 0.167\text{eV}$~~) [30], the equilibrium bond distance, $\sigma = 2.315\text{\AA}$ and the equilibrium energy well depth, $\epsilon = 0.167\text{eV}$ [30]. These values were fit to the bulk melt temperature and room temperature lattice constant. We note that this is not an accurate potential for Cu as it ignores important many body effects critical to describe elastic constants and defect energetics. Also notable is the discrepancy of the liquid densities as compared to experiment [31]. However, the goal of the paper is to demonstrate the applicability of ~~FUQ-FunUQ~~ to an MD problem. In this spirit, the high-fidelity potentials are similarly designed for demonstration purposes only and do not represent a more accurate representation of an actual material. We construct seven pair potentials by additively modifying the LJ potential with sine functions in Table 1. This family of functions will be denoted Sine 1 to Sine 7.

Table 1: High-fidelity potential sine modification terms

Name	Modification function
Sine 1	$0.44 + 0.46 \sin(0.17(24.2 + r))$
Sine 2	$-0.47 \sin(-0.15(14 + r)) \cdot \exp(-r)$
Sine 3	$0.07 \sin(1.2(-1.2 + r))/r^2$
Sine 4	$-0.01 + 0.2 \sin(0.3(14 + r)) \cdot \exp(-r)$
Sine 5	$0.7 \sin(0.4(11 + r)) \cdot \exp(-r)$
Sine 6	$0.9 \sin(0.4(11 + r)) \cdot \exp(-r)$
Sine 7	$1.1 \sin(0.4(11 + r)) \cdot \exp(-r)$

135 A final high-fidelity model tested is the Morse potential, defined as the
 136 sum of two exponentials:

$$\phi(\textcolor{blue}{r}) = D_0(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}) \quad (5)$$

137 We use $D_0 = 0.161\text{eV}$, $\alpha = 2.09\text{\AA}^{-1}$, and $r_0 = 2.62\text{\AA}$ to similarly roughly
 138 describe copper.

139 For all potentials a smoothing function is used to ensure stable dynamics
 140 near the cutoff. The function is of fourth order to create potential energy
 141 and force curves that both smoothly tend to zero:

$$s(r) = \frac{(\frac{(r-r_c)}{w})^4}{(1 + \frac{(r-r_c)}{w})^4} \quad (6)$$

142 where r_c is the cutoff distance and w is the width of the smoothing. For all
 143 potentials the cutoff is $5.79\text{\AA}$ (2.5σ , commonly used for LJ potentials) and
 144 smoothing width $1.5\text{\AA}$. Each potential curve is created by summing the base
 145 equation and the modification term and subsequently taking the product
 146 with the smoothing function. The force curve is then created with product
 147 rule differentiation of the potential. These potentials are shown in Figure 1.

148 Each system consists of 500 atoms simulated under isothermal, isochoric
 149 conditions (canonical ensemble). Three physical states of the system were
 150 simulated: one solid at ambient temperature and pressure ($300K$ with density
 151 of $9.02g/cm^3$), one liquid slightly above the melt temperature at ambient
 152 pressure ($1300K$ with density of $6.48g/cm^3$) and another liquid at extreme
 153 temperature and pressure ($5000K$ with density of $8.93g/cm^3$, corresponding
 154 to $55GPa$).

Figure 1: Interatomic potentials used with inset taken from the dotted region. High-fidelity models obtained as sine modified LJ potentials are shown in color labeled with numbers, low-fidelity LJ with bold line in black, and Morse (M) with dashed line in gray.

155 All MD simulations were performed using the LAMMPS package [32]. In
 156 order to obtain the quantities of interest, energies, pressures and functional
 157 derivatives, we performed both temporal and ensemble averages as is common
 158 practice in MD simulations. For each condition, we used several simulations
 159 starting with statistically independent velocities obtained from the Maxwell-Boltzmann
 160 distribution at the desired temperature. For each high-fidelity potential
 161 and thermodynamic condition of interest we performed 16 independent
 162 simulations, each 1 ns long, sufficient for good statistical sampling of the
 163 quantities of interest. For each low-fidelity potential and thermodynamic
 164 condition, ~~from which the functional derivatives were calculated,~~ the total
 165 sample time was 64 ns, ~~similarly~~ from 64 independent simulations of 1 ns.
 166 A ~~convergence of this sampling is~~ longer simulation time was necessary
 167 for the low-fidelity simulations in order to properly converge the FD with
 168 the perturbative approach (discussed in the following section). The use of
 169 multiple independent simulations allowed for concurrent computation and
 170 reduced wall-clock time for the study. An example of the convergence of the
 171 FunUQ corrections is shown in the supplementary material, Section S2. We
 172 now consider the calculation of the FD for MD simulations.

173 3.2. Numerical functional derivatives and a perturbative approach for their
174 calculation

175 For the specific case of interest the [general](#) functional derivative expression
176 [from Eq. 2](#) becomes:

$$\frac{\delta Q[\phi]}{\delta \phi}(r_i) = \lim_{\epsilon \rightarrow 0} \frac{Q[\phi_0(r) + \epsilon \cdot \phi'(r - r_i)] - Q[\phi_0(r)]}{\epsilon} \quad (7)$$

177 where $Q[\phi]$ denotes the average QoI – the potential energy or pressure of
178 the system – using interatomic potential ϕ . The unmodified LJ potential
179 is ϕ_0 and ϕ' [is](#) a normalized Gaussian perturbation centered at interatomic
180 distance $r = r_i$ with width σ . [Note that \$\phi_0\$ here is the same low-fidelity](#)
181 [function used for the correction in Section 4 \(there denoted \$\phi_{LF}\$ \).](#)

182 The functional derivative in Eq. 7 can be calculated by performing a set
183 of simulations with the low-fidelity potential modified by perturbations of
184 varying ϵ and computing a numerical derivative for each position r_i . These
185 modified Lennard Jones potentials and resulting average potential energies
186 as a function of size of the perturbation ϵ are shown in Fig. 2(a) and (b),
187 respectively [\(discussed in more detail below\)](#). However, this brute force ap-
188 proach is computationally very intensive considering that we may need to
189 sample the functional derivative at 100 values of r_i . Even with only three
190 values of ϵ for each separation distance one would need to perform 300 sep-
191 arate MD simulations. To alleviate the computational cost of the approach
192 we now derive a perturbative approach to calculate the functional deriva-
193 tive that can be computed with little overhead with respect to the nominal
194 simulation using the low-fidelity potential, ϕ_0 .

195 At the heart of the calculation of the FD is the evaluation of canonical
196 averages of the QoIs with the interatomic potential and a Gaussian pertur-
197 bation. Recognizing that the modified Hamiltonian of the system can be ad-
198 ditively decomposed into the kinetic energy, the original LJ potential energy
199 and the functional variation (or perturbation) for these two-body potentials
200 we can write the canonical ensemble average of quantity Q as:

$$\langle Q \rangle_H = \frac{\int Q \cdot e^{-\beta H_0} \cdot e^{-\beta H'} }{\int e^{-\beta H_0} \cdot e^{-\beta H'} } \quad (8)$$

201 where H_0 is the Hamiltonian with the LJ potential and H' the potential
202 energy resulting from the Gaussian perturbation following form from Eq. 7.
203 Equation 8 can be re-written as the ratio between two canonical averages over

Figure 2: ~~Calculation~~ Numerical calculation of ~~the~~ a functional derivative with examples of a) unmodified LJ potential in bold black and eight examples of modified interatomic potentials ~~a)~~ in blue (two positive and two negative height Gaussian perturbations with fixed width at each of two positions, r_1 and r_2) and b) numerical derivatives with respect to perturbation height ~~b)~~ from the example perturbations in a). Perturbations enlarged for visibility with one example, P_1 , marked in both a) and b).

204 the unmodified Hamiltonian by multiplying by additional factors of $\int e^{-\beta H_0}$
 205 and rearranging:

$$\langle Q \rangle_H = \langle Q \cdot e^{-\beta H'} \rangle_{H_0} \cdot \frac{1}{\langle e^{-\beta H'} \rangle_{H_0}} \quad (9)$$

206 Since both canonical averages are over the unmodified potential only simu-
 207 lation with the low-fidelity potential is required. Therefore, computing the
 208 functional derivatives requires evaluating the Gaussian perturbation poten-
 209 tials on the trajectory obtained with the low-fidelity model. Such expressions
 210 are commonly used to compute free energies in thermodynamic integration
 211 and free energy perturbation approaches [33, 34].

212 Quantities for the canonical average in Eq. 9 are computed every 1 ps with
 213 a total of 64 ns of simulation time with the low-fidelity LJ potential, deemed
 214 well converged (see supplementary material, [Section S2](#)). We evaluate these
 215 averages using a binned coordination number with a total of 2000 bins to
 216 compute H' and Q (as it contains contributions from the perturbation), de-
 217 scribed in more detail in the appendix. ~~Use of~~ By using the coordination
 218 number ~~simply allows to~~ we further reduce computation and avoid modify-
 219 ing the MD code. Performing the calculation directly within the MD force
 220 loop with atomic positions would be equivalent excluding slight discrepancies
 221 from discretization.

222 Using Eq. 7 with the first term in the difference calculated using Eq. 9
 223 we compute the functional derivative with respect to Gaussian perturbations
 224 centered at r_i with width $\sigma = 0.1$ Å and ~~height~~ heights $\epsilon = \pm 0.00075$ and
 225 ± 0.00375 eV (examples at two r_i in Fig. 2(a)). The perturbation width
 226 was chosen to minimize (localize) the perturbation while retaining sufficient
 227 sampling. The heights were similarly minimized, due to the difficulty of con-
 228 verging exponentially weighted averages, while ensuring a measurable effect
 229 from the perturbations. The numerical derivative is then evaluated by com-
 230 puting the slope of the QoI with respect to ϵ (examples in Fig. 2(b)) at a
 231 set of interatomic separations ranging from zero past the potential cutoff in
 232 increments of 0.05 Å.

233 The thick blue lines in Figure 3 show the functional derivatives obtained
 234 in this manner for all physical conditions and both QoIs. These curves were
 235 averaged from multiple calculations of the FD with independent randomized
 236 samplings from the total of 64 ns of simulation time. The functional deriva-
 237 tive displays significant information about the physics of the systems. The
 238 overall shapes correspond to the atomic shells as in the radial distribution
 239 function – notably more pointed for the solid case. At very low separation

Figure 3: Functional derivatives of the potential energy for the a) solid, a)-b) ambient liquid, b)-and c) extreme liquid e)-cases and of pressure for the d) solid, d)-e) ambient liquid, e)-and f) extreme liquid f)-cases. The perturbative method is shown in thick blue lines and the brute force method in red lines with points.

240 distances the FD goes to zero as atoms hit the soft-wall repulsion of the po-
 241 tentials; for the extreme liquid system the atoms occupy smaller separations.
 242 To assess the accuracy of the calculation the functional derivative was
 243 also computed at equally spaced values of r_i using the brute force approach
 244 described above. For each value of r_i we perform four MD simulations with
 245 varying perturbations (identical to those in the perturbative approach) added
 246 to the LJ potential as shown in Fig. 2(a) and obtain the functional derivative
 247 with the same numerical derivatives as the perturbative approach. For each
 248 separate perturbation the simulation was run for 16 ns (split between 16
 249 independent systems). The results of the brute force approach are shown in
 250 red in Fig. 3; the two methods of calculating the functional derivative are
 251 nearly identical with only small numerical discrepancies.

252 4. Error correction using functional derivatives

253 To demonstrate our approach we now use the functional derivative calcu-
 254 lated perturbatively in the previous section to correct the potential energy
 255 and pressure predicted with the low-fidelity LJ potential assuming a more ac-
 256 curate function is available. As discussed in subsection 3.1, a family of seven
 257 high-fidelity potentials were created by modifying the LJ potential with sine
 258 functions; see Figure 1 and Table 1. These results are discussed in sub-section
 259 4.1; the results for the Morse potential are discussed in sub-section 4.2.

260 4.1. Corrections for sine modified potentials

261 In order to use Eq. 3 we need, in addition to the functional derivative,
 262 the discrepancy function ($\phi_{HF}(r) - \phi_{LF}(r)$), the difference between the high
 263 and low-fidelity potentials. Figure 4 illustrates a) the functional derivative
 264 (a), b) the functional discrepancy (b), and c) the product of the two, the
 265 functional error(c), each as a function of interatomic distance for one case,
 266 the ambient liquid with modified potential Sine 1. These results are shown
 267 for each physical case and potential in the supplementary material, Section
 268 S3. Note that the functional error goes to zero both for small and large
 269 values of r ; at small r it goes to zero following the functional derivative (due
 270 to steep repulsion that keeps atoms from coming close to one another), while
 271 for large distances the discrepancy goes to zero as both potentials tend to
 272 zero at the same cutoff.

273 The functional error was numerically integrated using the trapezoid rule
 274 to obtain the total correction for the QoI. In order to verify these correc-

Figure 4: Method of calculating the cumulative functional error with examples of the [a\)](#) functional derivative [a\)](#), [b\)](#) the [functional](#) discrepancy [b\)](#), and [c\)](#) the product of the two [e\)](#) for the ambient liquid with the Sine 1 high-fidelity potential. The shading shows the integrated area contributing to the total correction [of the QoI as in Eq. 3.](#)

tion predictions we performed explicit MD simulations with the high-fidelity modified LJ potentials. Figure 5 compares the a) potential energy ~~a)~~ and b) pressure ~~b)~~ differences explicitly simulated with low and high-fidelity potentials (gray) to the corrections obtained with FUQ-FunUQ (with colors matching those in Fig. 1, as well as the hybrid LJ-Morse potential discussed in sub-section 4.2 in white). These results are shown in detail in Tables B.2 and B.3 in the appendix.

For almost all cases, the FUQ-FunUQ predictions are in excellent agreement with the direct simulations. Excluding only the Sine 6 and 7 potentials for the ambient liquid (discussed below) average error is 0.600% and 1.70% for potential energy and pressure, respectively. We stress that these very accurate corrections are obtained only making use of the ~~the~~ simulation with the unmodified LJ potential; no additional MD simulations are required.

The ability of FUQ-FunUQ to correct the QoIs is impacted greatly by the degree of phase space overlap between the high and low-fidelity simulations. This can be shown simply by the overlap in histograms of probability distributions of differences in potential energy from the initial to final state, a common practice in free energy calculations [35]. In this case, the states refer to the potential used and the distributions are taken from:

$$\Delta U_0 = (U(\phi_{HF}, \Gamma_{LF}) - U(\phi_{LF}, \Gamma_{LF})) \quad (10)$$

$$\Delta U_1 = (U(\phi_{LF}, \Gamma_{HF}) - U(\phi_{HF}, \Gamma_{HF})) \quad (11)$$

where each term is the energy with potential ϕ and set of samples in phase space $\Gamma = (\mathbf{x}_1, \dots, \mathbf{x}_N)$ (each point dependent on the positions of the N atoms) from the high or low-fidelity potential trajectory. Examples are shown in Fig. 6. More concretely, ΔU_0 gives the difference between the potential energy distribution from the low-fidelity potential MD simulation and the potential energy distribution from the same atom positions through time re-evaluated with the high-fidelity potential (without additional MD simulation).

Lack of phase space overlap and difference in probability distributions is most significant for the the ambient liquid with the Sine 6 and 7 potentials, the same two cases with significantly larger error. Further inspection of the MD trajectory shows that the modified potential results in a structural transformation while the unmodified LJ does not. This is shown in snapshots-atomistic structures (created using the OVITO software package [36]) included as insets in Fig. 6 comparing the ~~atomic-structures-for-the~~ ambient liquid with Sine 1 and Sine 7: the liquid undergoes cavitation for

Figure 5: Comparison of correction from ~~FUQ~~-~~FunUQ~~ (colors matching curves in Fig. 1, with ~~exception~~-~~addition~~ of the hybrid potential, shown in white and discussed in subsection 4.2) and direct simulation (gray). Each set of three bars shows the solid, ambient liquid, and extreme liquid cases from left to right for each potential. Results for ~~a)~~ potential energy ~~a)~~ and ~~b)~~ pressure ~~b)~~.

Figure 6: Examples of potential energy probability distributions showing various degrees of overlap: a) solid with Sine 1 b) extreme liquid with Sine 1 c) ambient liquid with Sine 1, and d) ambient liquid with Sine 7. Overlap is close to zero for systems with phase change in only one potential; inset d) shows an example of a void formed as compared to the normal liquid in inset c).

310 Sine 7 (and to a lesser extent with Sine 5 and 6). ~~Insets were created using~~
311 ~~the OVITO software package [36]~~. Thus the low-fidelity LJ explores a vastly
312 different region in phase space as compared to that of the high-fidelity Sine
313 7; however, even under such unfavorable conditions ~~FUQ~~ FunUQ is able to
314 provide some level of correction. In contrast, the solid cases have sharply
315 peaked distributions with strong overlap and correspondingly highly accu-
316 rate predictions, with the caveat of more difficult convergence of the results.
317 Histograms for all physical cases and potentials are within the supplementary
318 material, [Section S3](#).

319 The degree of similarity of phase space exploration can be further sum-
320 marized by plotting the average of ΔU_0 against the average of ΔU_1 . The
321 closer to slope of unity, the more significant the distribution overlap. Figure
322 7 gives results that agree with the histograms in Fig. 6 and supplementary
323 material, [Section S3](#); namely, for cases where the explored phase space for the
324 low and high-fidelity trajectories is less similar and there is little histogram
325 overlap, the prediction error increases, particularly for the ambient liquid.
326 Results in this figure for the Morse (gray symbols) and hybrid LJ-Morse
327 (white) potentials are discussed in sub-section 4.2.

328 4.2. Correction for the Morse potential and hybrid potential calculations

329 Predicting properties for the Morse potential from LJ further highlights
330 the challenge of attempting to correct a prediction made with a low-fidelity
331 model. In this case the discrepancy between the two models is very large
332 for short interatomic distances, leading to near zero phase space overlap and
333 an inaccurate ~~FUQ~~ FunUQ prediction for all physical cases. The red line in
334 Figure 8 shows this discrepancy as a function of interatomic separation with
335 the functional derivatives from both liquid conditions in blue to demonstrate
336 the sensitivity to changes in the potential at these distances. The short range
337 repulsion is described with an exponential for Morse while LJ uses an inverse
338 power of 12. Thus the discrepancy between the two potentials diverges for
339 short distances and the functional derivative correction, being first order,
340 produces extremely large errors. These results are therefore omitted from
341 Figure 5.

342 Our approach can, nevertheless, be useful in such circumstances, but the
343 high-fidelity model cannot be fully replaced by the low-fidelity one. Instead,
344 we create a hybrid potential in Eq. 12 that smoothly switches from the
345 low-fidelity LJ to the high-fidelity Morse between 2.8 and 2.4Å using error

Figure 7: Similarity in potential energy probability distribution peaks for all potentials (colors matching Figures 1 and 5 in sub-section 4.1 with the exception of Morse in gray and hybrid LJ-Morse in white, both discussed in sub-section 4.2). Each physical case separated for readability: a) solid, b) ambient liquid, and c) extreme liquid. Solid, ambient liquid, and extreme liquid shown with squares, circles, and triangles, respectively. The two plots are separated to show detail.

Figure 8: Discrepancy between LJ and Morse potentials (red) and between hybrid LJ-Morse and Morse (green). Both liquid perturbative functional derivatives shown in blue to demonstrate the non-zero sensitivity at low separation distance.

functions, leading to a discrepancy of reasonable magnitude shown in green in Figure 8.

$$\phi_{Hybrid} = \begin{cases} \phi_{LJ}(r) & r \geq 2.8 \\ \phi_{LJ}(r) \cdot [B(r) + 0.5] + \phi_{Morse}(r) \cdot [-B(r) + 0.5] & 2.8 > r > 2.4 \\ \phi_{Morse}(r) & 2.4 \geq r \end{cases} \quad (12)$$

$$B(r) = 0.5 \operatorname{erf}(8(r - 2.6)) \quad (13)$$

With the hybrid potential in Eq. 12 the high-fidelity model is used only where necessary. This is similar in spirit to adaptive sampling methods in multi-scale simulations, with examples in the literature [37, 38, 39] and codes available: the Co-design Embedded Visco-Plasticity Proxy Application (CoEVP) [40] and the Co-design Heterogeneous Multiscale Method Proxy Application (CoHMM) [41].

It is then possible to use [FUQ-FunUQ](#) to correct a low-fidelity simulation run with this hybrid potential to the result with the high-fidelity Morse by using the discrepancy between the two potentials and the functional derivative of the hybrid potential. The hybrid potential reduces the discrepancy and the functional approach provides an accurate correction for all cases, as shown

with the white bars in Figure 5. The hybrid potential solid case correction shows an additional example of increased error (5.9%), again due to poor overlap in explored phase space between the two potentials (see supplementary material, Section S3). Even with these significantly different systems ~~FUQ~~ FunUQ provides the majority of the necessary correction. Further, all predictions for Morse from the hybrid potential (white symbols) lie near the unity line in Fig. 7 (describing good agreement between the phase space of each trajectory) in contrast to Morse from LJ (gray symbols), furthest from the line. We note that the high-fidelity model needs to be used during the actual simulation; however, only approximately 12% of the atomic force calculations fall in the range requiring the high-fidelity model. Thus, if the high-fidelity model was significantly more intensive than the low-fidelity the methodology would still greatly reduce computational cost.

5. Discussion

The perturbative method to obtain the functional derivatives described here is similar to techniques in free energy methods: free energy perturbation and thermodynamic integration [42, 43]. One subset of these methods most comparable to ~~FUQ~~ FunUQ and often used in biology simulations, referred to as computer alchemy, is utilized to calculate free energy changes along non-physical paths as potentials are slowly turned on or off for the various molecules or solvents of interest [44, 45, 46, 47]. These methods share with the work described here the need to sample from the phase space trajectory of an initial state (often a simple reference state for free energy calculations, e.g. the Einstein crystal), to ensure that phase space is not too dissimilar to that of the final state of interest, and to converge exponentially weighted averages. However, while free energy methods generally focus on a single path from initial to final state (or a bidirectional path), using ~~FUQ~~ FunUQ, once the functional derivative is calculated for a given low-fidelity model, the corrections can be made with respect to any other high-fidelity model as long as minimum conditions are satisfied. If the low-fidelity simulation does not explore the regions of phase space relevant for the high-fidelity potential at the conditions of interest the results will be poor; this is most striking when switching potentials results in a structural phase transition. ~~This A check of phase space overlap should be checked as demonstrated here to ensure meaningful results as with free energy methods. was performed here in order to understand cases where FunUQ is unable~~

396 to provide accurate error corrections as is done in free energy calculation
 397 methods. In real applications where FunUQ would be most useful, i.e.
 398 where the high-fidelity function is much more computationally expensive
 399 than the low-fidelity function, checking phase space overlap is expensive
 400 and should be performed by evaluating the high-fidelity model for relatively
 401 few configurations or replacing it with a computationally efficient surrogate
 402 model. Additionally, the functional derivative correction can only be used for
 403 relatively small functional discrepancies such that its effect can be described
 404 to first order. We also note that the perturbative approach used here is appli-
 405 cable only to input functions that appear linearly in the Hamiltonian so the
 406 perturbation can be separated additively. This is not a general limitation of
 407 ~~FUQ~~ FunUQ but of the specific approach used here to obtain the functional
 408 derivatives.

409 This work demonstrates ~~FUQ~~ FunUQ in equilibrium simulations. Con-
 410 tinuing work should include investigation of functional derivatives in non-
 411 equilibrium processes as an analog of the relationships between free energy
 412 perturbation and non-equilibrium work methods in free energy calculations.
 413 The method can be generally used in equilibrium MD simulations and nu-
 414 merous other physics problems including multi-scale simulations. Ongoing
 415 investigations will include using ~~FUQ~~ FunUQ to correct predictions in solid
 416 mechanics with the plasticity model as the input constitutive law.

417 An important advantage of ~~FUQ~~ FunUQ over uncertainty propagation
 418 in parameters is that it enables changes in the actual functional forms used
 419 in the simulation. In our example, we are not limited to Lennard-Jones
 420 potentials with different parameters but can change the shape of the po-
 421 tential (with the limitations discussed above). This feature makes FunUQ
 422 an important tool within continuing UQ research. For example, efforts in
 423 quantifying model uncertainty [25, 26, 48] could be expanded to problems
 424 with higher computational cost and include an increased number of models
 425 by using FunUQ. Our method could also simplify techniques which include
 426 both parametric and model UQ [49] by utilizing similar forms for each portion
 427 of the uncertainty.

428 6. ~~Conclusions~~

429 In summary we demonstrated the ability to calculate functional deriva-
 430 tives of a quantity of interest predicted by a non-trivial physics simulation
 431 with respect to its input laws. This information can be used to quantify the

432 uncertainties originating in the simulation due to the use of the input func-
 433 tion or to correct the prediction if a more accurate model becomes available.
 434 We developed a computationally efficient approach to compute the functional
 435 derivative in a MD simulations performed using the Lennard-Jones poten-
 436 tial and shows that this information can be used to infer thermodynamic
 437 properties corresponding to various other potentials without re-running the
 438 simulation. The functional uncertainty quantification approach is quite gen-
 439 erally applicable and we believe it will be useful to quantify uncertainties in
 440 a variety of materials models.

441 **Appendix A. Thermodynamic quantities using coordination num-** 442 **ber**

443 The calculation of the functional derivative using the perturbative ap-
 444 proach (Eq. 7 and 9) is expanded upon here, beginning with the contribu-
 445 tion to the Hamiltonian from the perturbation. This quantity can be directly
 446 calculated with a sum over all pairs of atoms as the potential energy in any
 447 MD simulation:

$$H' = \sum_{i < j} \phi'(r_{ij}) \quad (\text{A.1})$$

448 This would require modification of the MD code to calculate this quantity
 449 within the force loop or summing over a saved atomic trajectory. This ex-
 450 pression can be replaced:

$$H' = \frac{N}{2} \sum_k \phi'(r_k) \cdot c(r_k) \quad (\text{A.2})$$

451 where $c(r)$ is the average coordination number at a given separation distance
 452 r , discretized into k bins and N the number of atoms. This is neither invasive
 453 to the code, nor requires significant storage or computation past the low-
 454 fidelity simulation.

455 With the potential energy as the QoI, Q is simply the sum of Eq. A.2
 456 and the low-fidelity simulation potential energy. For the pressure we use the
 457 virial expression (without the small ideal gas contribution as it is already
 458 present in the low-fidelity pressure):

$$P' = \frac{1}{3V} \sum_{i < j} \mathbf{f}_{ij} \mathbf{r}_{ij} \quad (\text{A.3})$$

459 Because we examine cases of two-body central forces this can be simplified:

$$P' = \frac{1}{3V} \sum_{i < j} f(r_{ij}) r_{ij} \quad (\text{A.4})$$

460 and with the same motivations as above, we rewrite in terms of the coordi-
461 nation number, again with k bins in separation distance:

$$P' = \frac{N}{2} \frac{1}{3V} \sum_k f(r_k) \cdot r \cdot c(r_k) \quad (\text{A.5})$$

462 This quantity, added to the low-fidelity simulation pressure, provides Q
463 in Eq. 9 for the QoI pressure.

464 **Appendix B. Correction results**

465 Tables B.2 and B.3 show full results for all physical conditions for po-
466 tential energy and pressure, respectively. Figure 5 compares columns ΔQ^{Sim}
467 and ΔQ^{FUQ} ΔQ^{FunUQ} . All results here are calculated with respect to the LJ
468 low-fidelity potential, except the rows marked with (H). Those cases use the
469 low-fidelity hybrid LJ-Morse potential.

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Table B.2: Comparison of potential energy correction from functional derivatives and direct simulation.

Temp.	Potential	Q_{LF}	Q_{HF}	$Q_{LF} +$ ΔQ^{FUQ} ΔQ^{FunUQ}	ΔQ^{Sim}	ΔQ^{FUQ} ΔQ^{FunUQ}	ΔQ % Error
(K)	-	(eV/atom)					-
300	Sine 1	-1.08	-1.28	-1.27	-0.197	-0.196	0.456
300	Sine 2	-1.08	-0.928	-0.927	0.151	0.152	0.784
300	Sine 3	-1.08	-1.03	-1.03	0.0518	0.0522	0.793
300	Sine 4	-1.08	-1.31	-1.31	-0.235	-0.235	0.0132
300	Sine 5	-1.08	-1.33	-1.34	-0.256	-0.259	0.988
300	Sine 6	-1.08	-1.41	-1.41	-0.330	-0.333	0.993
300	Sine 7	-1.08	-1.48	-1.49	-0.403	-0.407	0.995
300	Morse	-1.08	-0.998	-1.02	0.0804	0.0628	21.9
300	Morse (H)	-1.05	-0.998	-1.00	0.0552	0.0520	5.89
1300	Sine 1	-0.704	-0.850	-0.850	-0.146	-0.146	0.0158
1300	Sine 2	-0.704	-0.602	-0.601	0.102	0.103	1.23
1300	Sine 3	-0.704	-0.666	-0.666	0.0377	0.0379	0.588
1300	Sine 4	-0.704	-0.867	-0.868	-0.164	-0.164	0.160
1300	Sine 5	-0.704	-0.878	-0.876	-0.174	-0.172	1.08
1300	Sine 6	-0.704	-0.956	-0.925	-0.252	-0.221	12.1
1300	Sine 7	-0.704	-1.03	-0.974	-0.330	-0.271	18.0
1300	Morse	-0.704	-0.655	-0.662	0.0485	0.0416	14.3
1300	Morse (H)	-0.703	-0.673	-0.673	0.0295	0.0295	0.0295
5000	Sine 1	-0.398	-0.598	-0.598	-0.200	-0.200	0.136
5000	Sine 2	-0.398	-0.243	-0.241	0.155	0.157	0.896
5000	Sine 3	-0.398	-0.346	-0.345	0.0524	0.0527	0.477
5000	Sine 4	-0.398	-0.636	-0.637	-0.238	-0.239	0.441
5000	Sine 5	-0.398	-0.663	-0.665	-0.265	-0.267	0.932
5000	Sine 6	-0.398	-0.738	-0.741	-0.340	-0.343	0.959
5000	Sine 7	-0.398	-0.814	-0.818	-0.416	-0.420	1.01
5000	Morse	-0.398	-0.321	-0.393	0.0774	0.00547	93.1
5000	Morse (H)	-0.366	-0.320	-0.320	0.0454	0.0455	0.376

Table B.3: Comparison of pressure correction from functional derivatives and direct simulation.

Temp.	Potential	Q_{LF}	Q_{HF}	$Q_{LF} +$ ΔQ^{FUQ} ΔQ^{FunUQ}	ΔQ^{Sim}	ΔQ^{FUQ} ΔQ^{FunUQ}	ΔQ % Error
(K)	-	(GPa)					-
300	Sine 1	-0.116	-3.37	-3.25	-3.26	-3.13	3.89
300	Sine 2	-0.116	2.69	2.70	2.81	2.81	0.279
300	Sine 3	-0.116	0.514	0.538	0.630	0.654	3.75
300	Sine 4	-0.116	-4.12	-4.05	-4.01	-3.94	1.73
300	Sine 5	-0.116	-5.03	-5.07	-4.91	-4.95	0.763
300	Sine 6	-0.116	-6.43	-6.48	-6.32	-6.37	0.792
300	Sine 7	-0.116	-7.83	-7.90	-7.72	-7.78	0.805
300	Morse	-0.116	1.43	-1.31	1.54	-1.19	177
300	Morse (H)	0.491	1.27	1.49	0.781	0.998	27.7
1300	Sine 1	0.129	-1.12	-1.13	-1.25	-1.26	1.44
1300	Sine 2	0.129	1.37	1.36	1.24	1.23	0.498
1300	Sine 3	0.129	0.563	0.562	0.434	0.433	0.219
1300	Sine 4	0.129	-1.58	-1.62	-1.71	-1.75	2.34
1300	Sine 5	0.129	-1.87	-2.03	-2.00	-2.16	7.70
1300	Sine 6	0.129	-1.75	-2.65	-1.88	-2.77	47.3
1300	Sine 7	0.129	-1.74	-3.26	-1.87	-3.39	81.5
1300	Morse	0.129	0.0733	-0.359	-0.0558	-0.488	774
1300	Morse (H)	0.124	0.469	0.463	0.344	0.338	1.68
5000	Sine 1	54.4	51.6	51.6	-2.77	-2.77	0.0187
5000	Sine 2	54.4	57.1	57.1	2.72	2.74	0.905
5000	Sine 3	54.4	55.1	55.1	0.741	0.750	1.17
5000	Sine 4	54.4	50.6	50.6	-3.80	-3.81	0.161
5000	Sine 5	54.4	49.6	49.5	-4.81	-4.84	0.704
5000	Sine 6	54.4	48.2	48.2	-6.18	-6.23	0.845
5000	Sine 7	54.4	46.9	46.8	-7.53	-7.61	1.12
5000	Morse	54.4	39.8	36.8	-14.6	-17.5	20.1
5000	Morse (H)	39.0	39.8	39.8	0.796	0.794	0.279

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