Accelerating *Ab Initio* Molecular Dynamics with On-the-Fly Machine Learning

Jonathan Vandermause,[1,2] Steven B. Torrisi,[2] Simon Batzner,[3] Alexie Kolpak,[4] and Boris Kozinsky[1]

[1] *John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA*

[2] *Department of Physics, Harvard University, Cambridge, MA 02138, USA*

[3] *Center for Computational Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

[4] *Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

(Dated: January 10, 2019)

Abstract

Ab initio molecular dynamics is a powerful tool for accurately probing the dynamics of molecules and solids, but it is limited to system sizes on the order of 1000 atoms and time scales on the order of 10 ps. We present a scheme for rapidly training a machine learning model of the interatomic force field that approaches the accuracy of *ab initio* force calculations but can be applied to larger systems over longer time scales. Gaussian Process models are trained on-the-fly, with density-functional theory calculations of the atomic forces performed whenever the model encounters chemical configurations outside of the training set. We demonstrate the flexibility of our approach by testing it on a range of single- and multi-component systems.

I. LITERATURE

1. On-the-fly force fields with GPs and KRR [1–3]
2. Gaussian Approximation Potentials (GAP) [4–6]
3. The SOAP kernel [7]
4. Other covariant kernels (two- and three-body) [5, 6, 8, 9]
5. Vector-valued GPs and ICM [10]
6. DFT and Quantum Espresso [11, 12]

II. SMOOTH TWO-BODY KERNEL

We find that a covariant two-body kernel gives good accuracy for bulk metals with a vacancy [6, 9]. The covariant kernel implemented here is derived from a rotationally invariant local energy kernel k_{inv} that directly compares interatomic distances:

$$k_{\text{inv}} = \sigma^2 \sum_{i,j} \exp\left(-\frac{(r_i - r_j)^2}{2\ell^2}\right) f_{\text{cut}}(r_i) f_{\text{cut}}(r_j), \tag{1}$$

where the sum ranges over all atoms in the atomic environments. f_{cut} is a cutoff function that ensures that the local energy and its derivative go smoothly to zero at finite radius r_{cut} [5]:

$$f_{\text{cut}} = \begin{cases} 1 & r \leq r_{\text{cut}} - d, \\ \frac{\cos(\pi \frac{r - r_{\text{cut}} + d}{d}) + 1}{2} & r_{\text{cut}} - d < r \leq r_{\text{cut}}, \\ 0 & r > r_{\text{cut}}. \end{cases} \tag{2}$$

The cutoff function smooths the model by eliminating sharp discontinuities associated with atoms entering and leaving the cutoff sphere surrounding the central atom.

The local energy kernel described by Eq. (1) induces a covariant matrix-valued force kernel $\frac{\partial^2 k_{\text{inv}}}{\partial \xi_i \partial \chi_j}$ suitable for the direct prediction of atomic forces, where ξ_i and χ_i denote the i^{th} Cartesian coordinate of the central atom of the first and second atomic environments, respectively. In the table below, we summarize all the terms needed to efficiently calculate the force kernel and its derivatives with respect to the model hyperparameters ℓ, σ, and d.

Energy Kernel	$k_{\text{inv}}(\rho_1, \rho_2; \ell, \sigma, d)$	$\sigma^2 \sum_{i,j} k(r_i, r_j) f_{\text{cut}}(r_i) f_{\text{cut}}(r_j)$
-	$k(r_i, r_j; \ell)$	$\exp\left(-\frac{(r_i - r_j)^2}{2\ell^2}\right)$
-	$f_{\text{cut}}(r; d)$	$\frac{\cos(\pi \frac{r - r_{\text{cut}} + d}{d}) + 1}{2},\ r_{\text{cut}} - d < r \leq r_{\text{cut}}$
Force Kernel	$\frac{\partial^2 k_{\text{inv}}}{\partial \xi_i \partial \chi_j}$	$\sigma^2 \sum_{i,j} (k_0 + k_1 + k_2 + k_3)$
-	$k_0(r_i, r_j; \ell, d)$	$k \frac{\partial f_{\text{cut}}(r_i)}{\partial \xi_i} \frac{\partial f_{\text{cut}}(r_j)}{\partial \chi_j}$
-	$k_1(r_i, r_j; \ell, d)$	$\frac{\partial k}{\partial \xi_i} f_{\text{cut}}(r_i) \frac{\partial f_{\text{cut}}(r_j)}{\partial \chi_j}$
-	$k_2(r_i, r_j; \ell, d)$	$\frac{\partial k}{\partial \chi_j} \frac{\partial f_{\text{cut}}(r_i)}{\partial \xi_i} f_{\text{cut}}(r_j)$
-	$k_3(r_i, r_j; \ell, d)$	$\frac{\partial^2 k}{\partial \xi_i \partial \chi_j} f_{\text{cut}}(r_i) f_{\text{cut}}(r_j)$
-	$\frac{\partial k}{\partial \xi_i}$	$\frac{k(r_i - r_j)\xi_i}{\ell^2 r_i}$
-	$\frac{\partial k}{\partial \chi_j}$	$\frac{k(r_j - r_i)\chi_j}{\ell^2 r_j}$
-	$\frac{\partial^2 k}{\partial \xi_i \chi_j}$	$\frac{k\xi_i\chi_j(\ell^2 - (r_j - r_i)^2)}{\ell^4 r_i r_j}$
-	$\frac{\partial f_{\text{cut}}(r_i)}{\partial \xi_i}$	$\frac{\pi \xi_i}{2 d r_i} \sin(\pi \frac{r_{\text{cut}} - r_i}{d}),\ r_{\text{cut}} - d < r \leq r_{\text{cut}}$
ℓ Derivative	$\frac{\partial^3 k_{\text{inv}}}{\partial \ell \partial \xi_i \partial \chi_j}$	$\sigma^2 \sum_{i,j} \left(\frac{\partial k_0}{\partial \ell} + \frac{\partial k_1}{\partial \ell} + \frac{\partial k_2}{\partial \ell} + \frac{\partial k_3}{\partial \ell}\right)$
-	$\frac{\partial k}{\partial \ell}$	$\frac{k(r_i - r_j)^2}{l^3}$
-	$\frac{\partial^2 k}{\partial \ell \partial \xi_i}$	$\frac{k\xi_i(-2\ell^2 + (r_i - r_j)^2)(r_i - r_j)}{l^5 r_i}$
-	$\frac{\partial^2 k}{\partial \ell \partial \xi_i \partial \chi_j}$	$\frac{k\xi_i\chi_j\left(-2\ell^4 + 5\ell^2(r_i - r_j)^2 - (r_i - r_j)^4\right)}{l^7 r_i r_j}$
d Derivative	$\frac{\partial f_{\text{cut}}(r_i)}{\partial d}$	$\frac{\pi(r - r_{\text{cut}})}{2d^2} \sin\left(\frac{\pi(r_{\text{cut}} - r)}{d}\right)$
-	$\frac{\partial^2 f_{\text{cut}}(r_i)}{\partial d \partial \xi_i}$	$\frac{\pi \xi_i \left(\pi(r - r_{\text{cut}}) \cos\left(\frac{\pi(r - r_{\text{cut}})}{d}\right) + d \sin\left(\frac{\pi(r - r_{\text{cut}})}{d}\right)\right)}{2d^3 r_i}$
σ Derivative	$\frac{\partial^3 k_{\text{inv}}}{\partial \sigma \partial \xi_i \partial \chi_j}$	$2\sigma \sum_{i,j} (k_0 + k_1 + k_2 + k_3)$

TABLE I. Quantities used to calculate the smoothed two-body force kernel and its derivatives.

III. ON-THE-FLY LEARNING

IV. COMPUTATIONAL DETAILS

[1] Z. Li, J. R. Kermode, and A. De Vita, Physical review letters **114**, 096405 (2015).

[2] V. Botu and R. Ramprasad, International Journal of Quantum Chemistry **115**, 1074 (2015).

[3] V. Botu and R. Ramprasad, Physical Review B **92**, 094306 (2015).

[4] A. P. Bartók, M. C. Payne, R. Kondor, and G. Csányi, Physical review letters **104**, 136403

(2010).

[5] A. P. Bartók and G. Csányi, International Journal of Quantum Chemistry **115**, 1051 (2015).

[6] V. L. Deringer and G. Csányi, Physical Review B **95**, 094203 (2017).

[7] A. P. Bartók, R. Kondor, and G. Csányi, Physical Review B **87**, 184115 (2013).

[8] A. Glielmo, P. Sollich, and A. De Vita, Physical Review B **95**, 214302 (2017).

[9] A. Glielmo, C. Zeni, and A. De Vita, Physical Review B **97**, 184307 (2018).

[10] M. A. Alvarez, L. Rosasco, N. D. Lawrence, *et al.*, Foundations and Trends® in Machine Learning **4**, 195 (2012).

[11] W. Kohn, Reviews of Modern Physics **71**, 1253 (1999).

[12] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, *et al.*, Journal of physics: Condensed matter **21**, 395502 (2009).