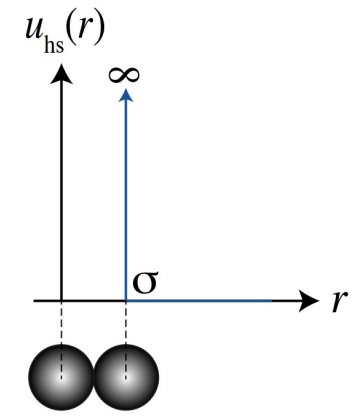
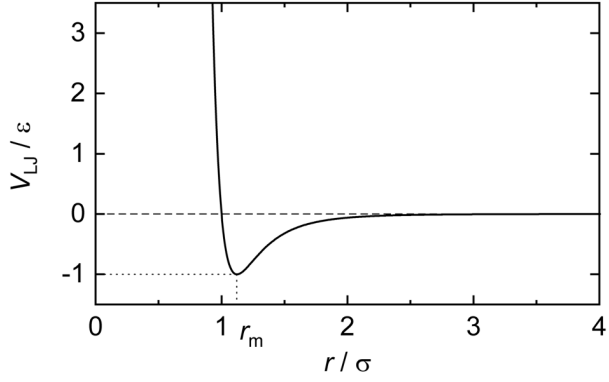
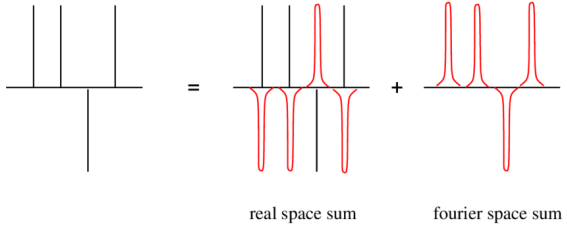
materials design

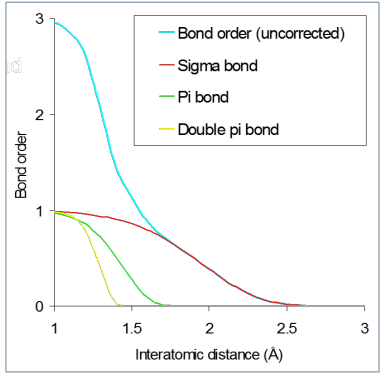
The Past, Present, and Future of Forcefield Technologies

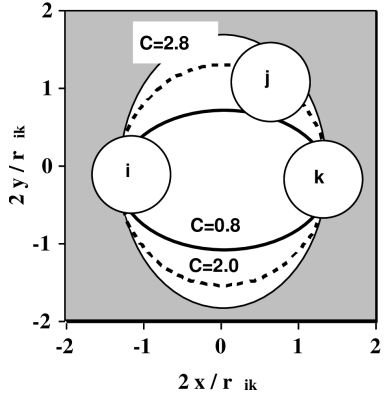
September 19–21, 2023

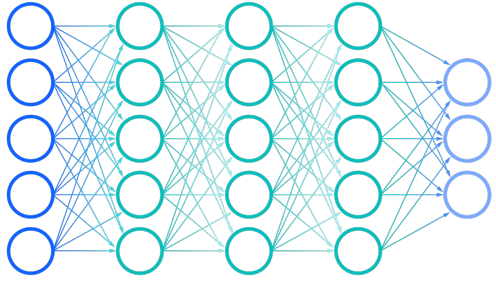












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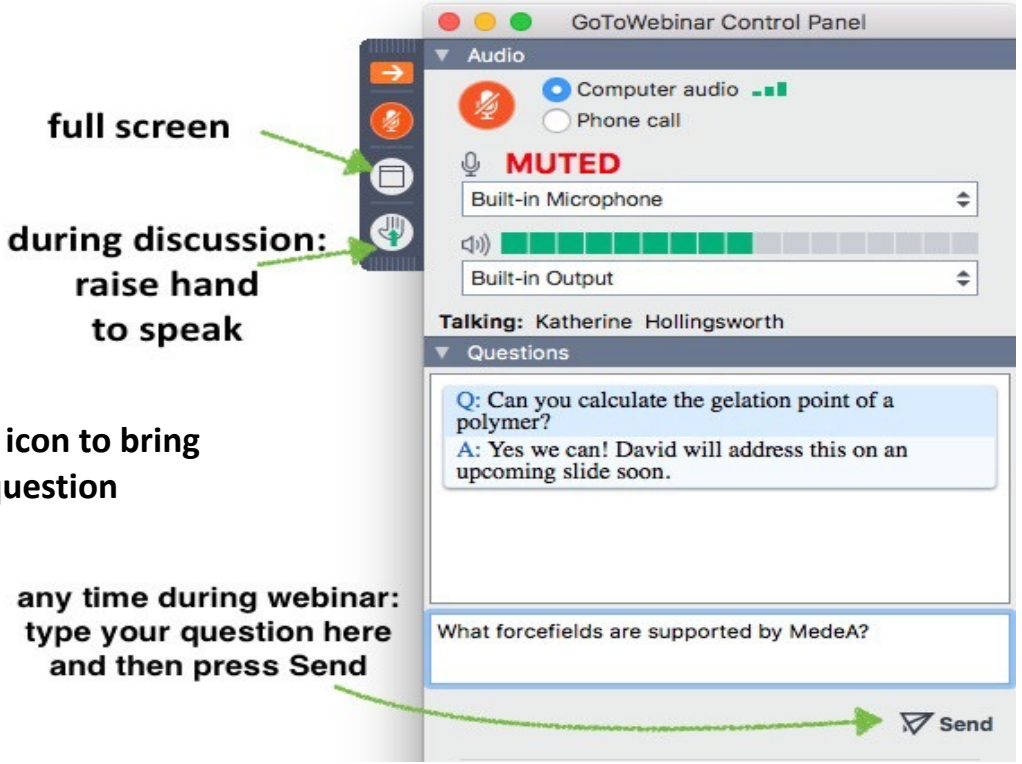

Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

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Webinar Speakers

Katherine Hollingsworth

Presenter: Dr. Garrett Tow

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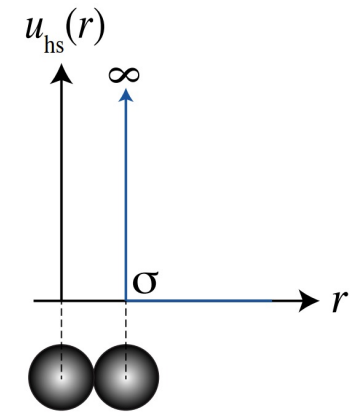
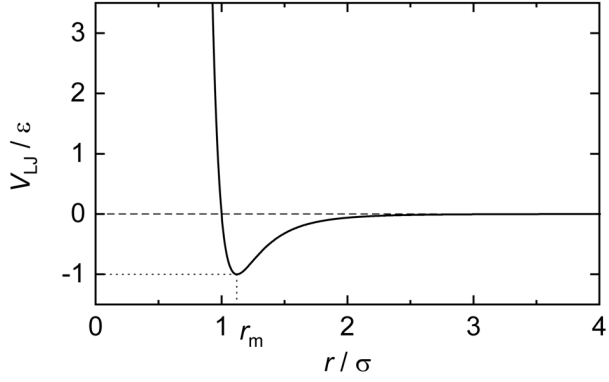
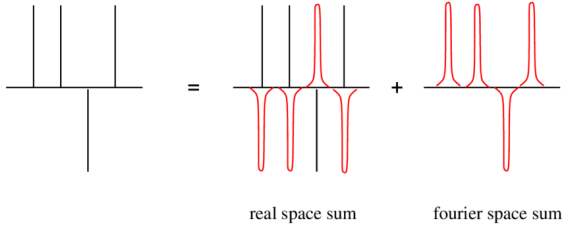
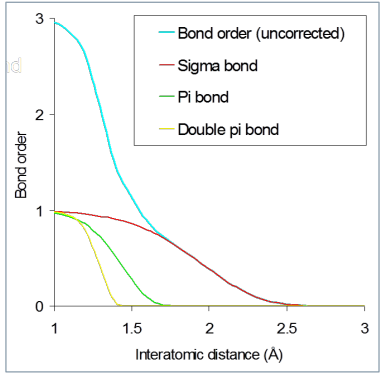
The Past, Present, and Future of Forcefield Technologies

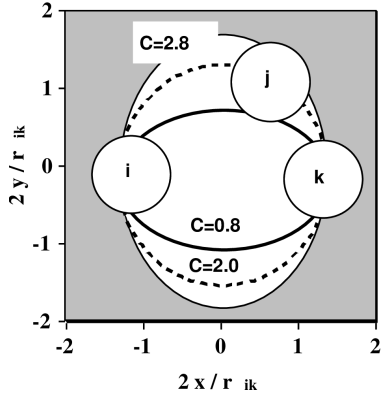
September 19–21, 2023

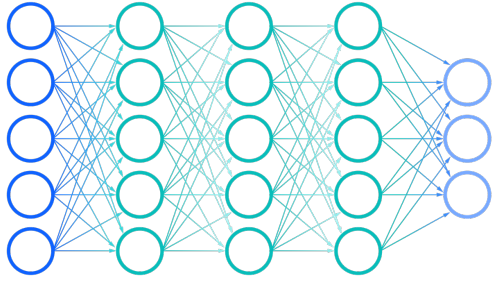






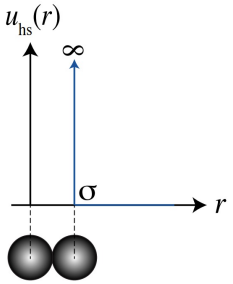


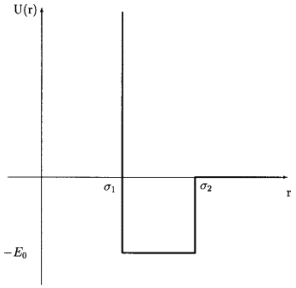


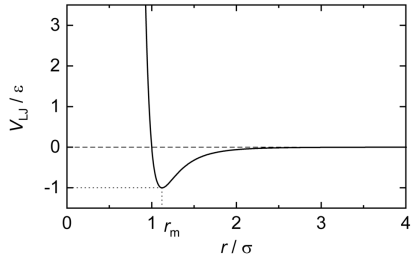


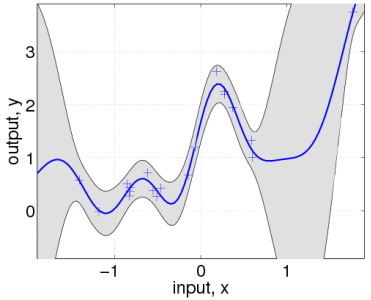
Versatility of Functional Form

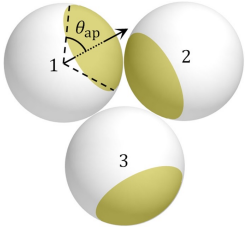
Embellishments and Complexity

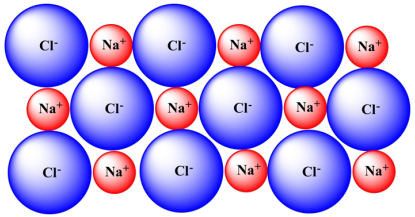


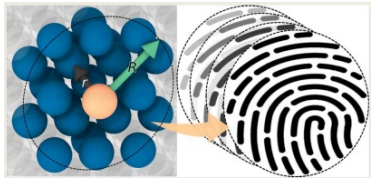


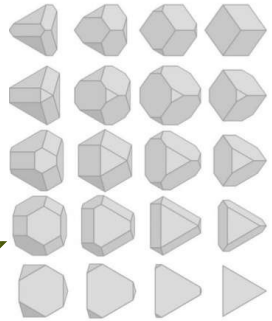


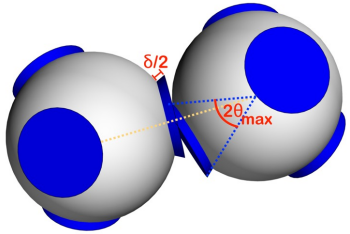


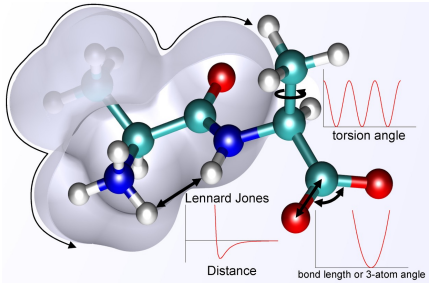


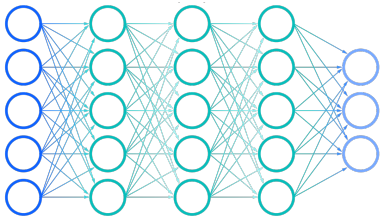












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Forcefield = Hamiltonian

The Hamiltonian is an operator describing the total energy of a system.

Typical forcefield parameters:

- Repulsion–dispersion (ε, σ)
- Energy coefficients for bonded terms $(k_b, k_\theta, k_\varphi)$
- Nominal bond lengths, bond angles, and dihedrals $(b_0, \theta_0, \varphi_0)$
- Partial point charges (q_i)
- Particle masses (m_i)
- Pairwise cutoff distance (r_{cut})
- Analytical tail corrections

Time-Dependent Schrödinger Equation

$$H\,|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\,|\psi(t)\rangle$$

$$H = T + U$$

$$T = \frac{1}{2}\sum_{atoms} mv^2$$

Example forcefield (Hamiltonian) of a molecular model.

$$U = \frac{1}{2}\sum_{bonds} k_b\left(b - b_0\right)^2 + \frac{1}{2}\sum_{angles} k_\theta\left(\theta - \theta_0\right)^2 + \frac{1}{2}\sum_{improper} k_\varphi\left(\varphi - \varphi_0\right)^2 +$$

$$\frac{1}{2}\sum_{torsions} k_\phi\left[1 + \cos\left(n\phi + \delta\right)\right] + \sum_{\substack{atom\\pairs\ i,j}}\left[\frac{q_i q_j}{R_{ij}} + \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}}\right]$$

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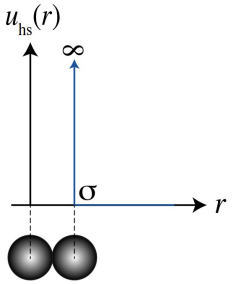
Versatility of Functional Form

Embellishments and Complexity



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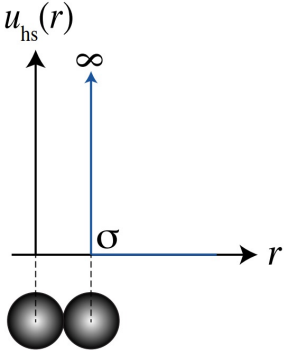
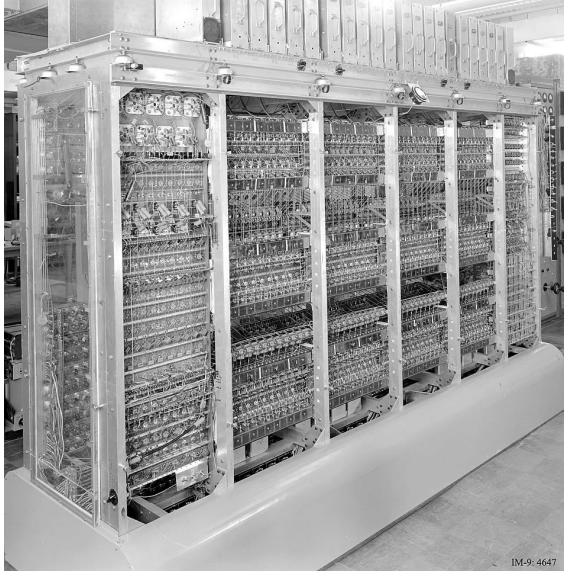
In the Beginning – Hard Spheres

$$V(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} 0 & \text{if} \quad |\mathbf{r}_1 - \mathbf{r}_2| \geq \sigma \\ \infty & \text{if} \quad |\mathbf{r}_1 - \mathbf{r}_2| < \sigma \end{cases}$$





MANIAC

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 6 JUNE, 1953

Equation of State Calculations by Fast Computing Machines

NICHOLAS METROPOLIS, ARIANNA W. ROSENBLUTH, MARSHALL N. ROSENBLUTH, AND AUGUSTA H. TELLER,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

AND

EDWARD TELLER,* *Department of Physics, University of Chicago, Chicago, Illinois*

(Received March 6, 1953)

A general method, suitable for fast computing machines, for investigating such properties as equations of state for substances consisting of interacting individual molecules is described. The method consists of a modified Monte Carlo integration over configuration space. Results for the two-dimensional rigid-sphere system have been obtained on the Los Alamos MANIAC and are presented here. These results are compared to the free volume equation of state and to a four-term virial coefficient expansion.

- 224 particles
- 5 hours to determine P for given V
- Metropolis Monte Carlo

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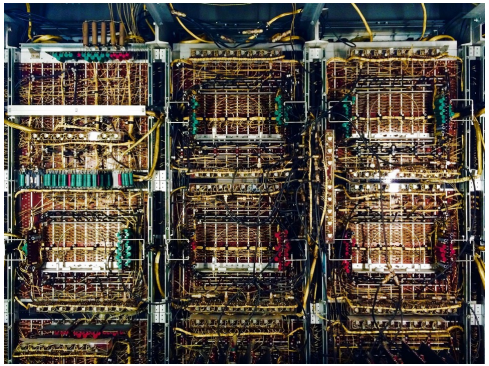
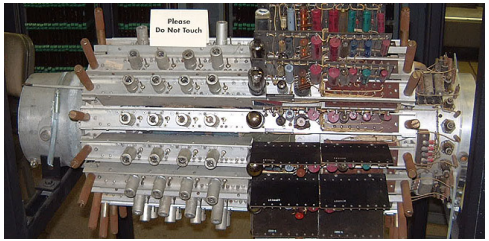
Hard Sphere Molecular Dynamics

UNIVAC I





Mercury delay-line memory of UNIVAC

- 32 particles
- 300 collisions per hour

IBM-704

N	Collisions / hour
32	7000
108	2000
256	1000
500	500

Collisions are determined algebraically

Phase Transition for a Hard Sphere System

B. J. Alder and T. E. Wainwright
University of California Radiation Laboratory, Livermore, California
(Received August 12, 1957)

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Versatility of Functional Form

Embellishments and Complexity

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Square-Well Potentials

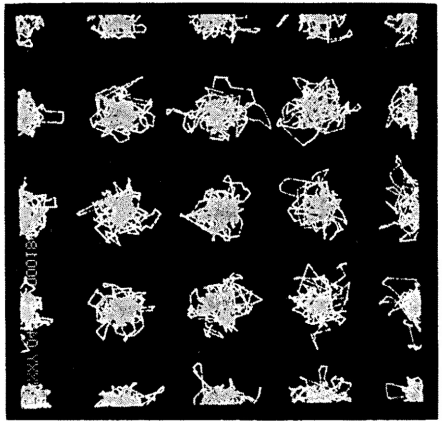


FIG. 2. The traces of 32 hard sphere particles in the periodic boundary conditions in the solid phase for about 3000 collisions.

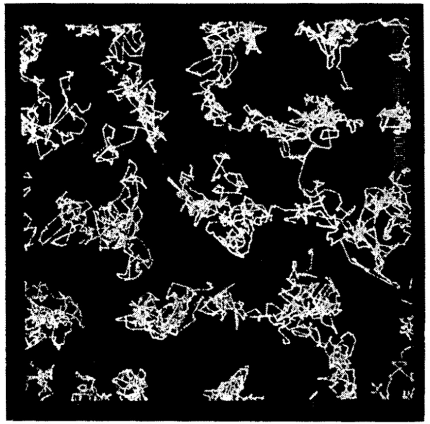


FIG. 3. The traces of the same system as in Fig. 2 after it has transformed to the fluid phase also for 3000 collisions.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 31, NUMBER 2 AUGUST, 1959

Studies in Molecular Dynamics. I. General Method*

B. J. ALDER AND T. E. WAINWRIGHT

Lawrence Radiation Laboratory, University of California, Livermore, California

(Received February 19, 1959)

(1) core collision

$$\Delta\mathbf{v}_i = -\Delta\mathbf{v}_j = \frac{-\mathbf{r}_{ij} b_{ij}}{\sigma_1^2}$$

(2) attractive collision

(a) $C_{ij}^{(2)} > 0$‡

"Capture"

$$\Delta\mathbf{v}_i = -\Delta\mathbf{v}_j = \frac{-\mathbf{r}_{ij}}{2\sigma_2^2}\left[\left(\frac{4\sigma_2^2 V_0}{m} + b_{ij}^2\right)^{\frac{1}{2}} + b_{ij}\right]$$

(b) $C_{ij}^{(2)} < 0$‡

(i) $b_{ij}^2 > \frac{4\sigma_2^2 V_0}{m}$

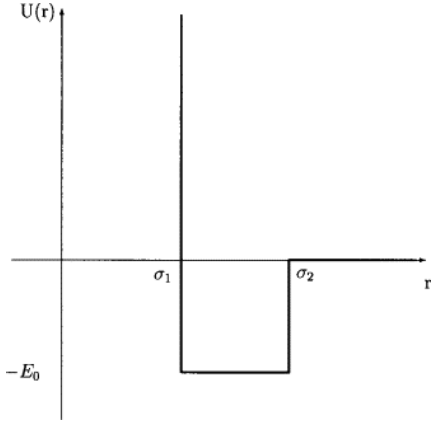
"Dissociation"

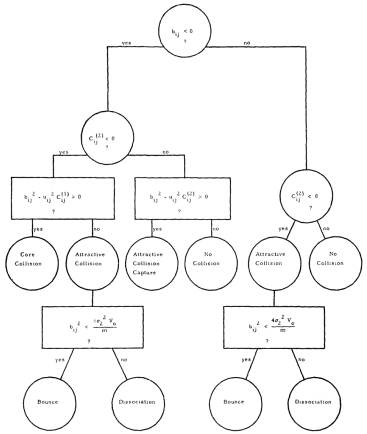
$$\Delta\mathbf{v}_i = -\Delta\mathbf{v}_j = -\frac{\mathbf{r}_{ij}}{2\sigma_2^2}\left[-\left(\frac{-4\sigma_2^2 V_0}{m} + b_{ij}^2\right)^{\frac{1}{2}} + b_{ij}\right]$$

(ii) $b_{ij}^2 < \frac{4\sigma_2^2 V_0}{m}$

"Bounce"

$$\Delta\mathbf{v}_i = -\Delta\mathbf{v}_j = -\frac{\mathbf{r}_{ij} b_{ij}}{\sigma_2^2}.$$





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Versatility of Functional Form

Embellishments and Complexity

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Pairwise Continuous Potentials

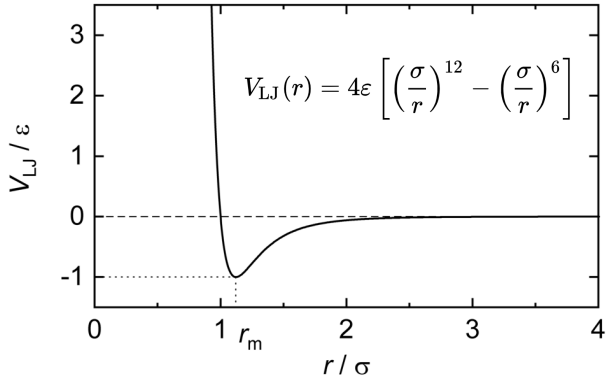
- Lennard-Jones Potential
  - J. E. Lennard-Jones; Cohesion. *Proc. Phys. Soc.* **1931**, *42*, 461.
- Lennard-Jones Particle Simulations
  - M. N. Rosenbluth, A. W. Rosenbluth; Further Results on Monte Carlo Equations of State. *J. Chem. Phys.* **1954**, *22*, 881–884
  - W. W. Wood, F. R. Parker; Monte Carlo Equation of State of Molecules Interacting with the Lennard-Jones Potential. I. A Supercritical Isotherm at about Twice the Critical Temperature. *J. Chem. Phys.* **1957**, *27*, 720–733.
- Simulations of “Real” Materials
  - Born-Mayer Repulsive Potential for Crystalline Copper
    - J. B. Gibson, A. N. Goland, M. Milgram, G. H. Vineyard; Dynamics of Radiation Damage. *Phys. Rev.*, **1960**, *120*, 1229–1253.

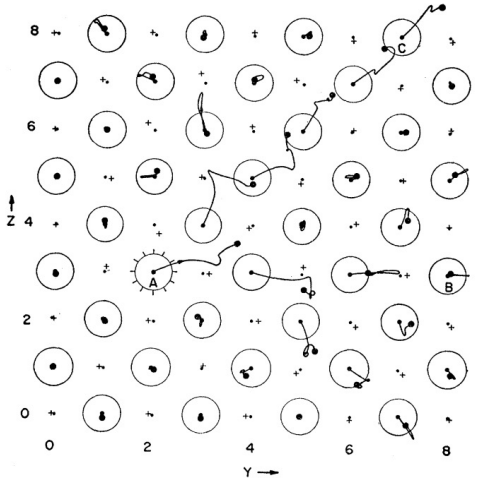
$$\varphi = Be^{-\beta r}$$

  - Lennard-Jones Potential for Liquid Argon
    - A. Rahman; Correlations in the Motion of Atoms in Liquid Argon. *Phys. Rev.* **1964**, *136*, A405–A411.

$$V_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Lennard-Jones Potential





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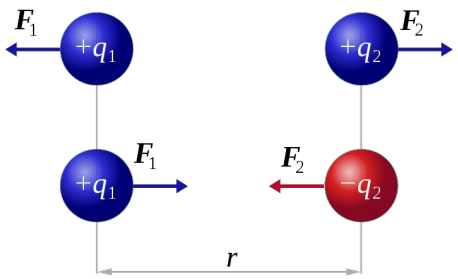
Electrostatics

P. P. Ewald; Die Berechnung optischer und elektrostatischer Gitterpotentiale. *Ann. Phys.* **1921**, *369*, 253–287.

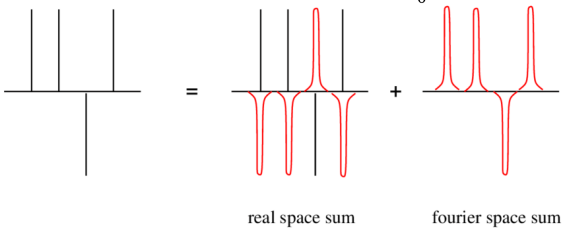
A. A. Barker; Monte Carlo Calculations of the Radial Distribution Functions for a Proton–Electron Plasma. *Aust. J. Phys.* **1965**, *18*, 119–113

S. G. Brush, H. L. Sahlin, E. Teller; Monte Carlo Study of a One-Component Plasma. I. *J. Chem. Phys.* **1966**, *45*, 2102–2118.



$$\left|\boldsymbol{F}_1\right| = \left|\boldsymbol{F}_2\right| = k_e \frac{|q_1 \times q_2|}{r^2}$$

$$k_e = \frac{1}{4\pi\varepsilon_0}$$



Paul Peter Ewald

Paul Peter Ewald in 1934

Born	January 23, 1888 Berlin, Germany
Died	August 23, 1985 (aged 97) Ithaca, New York

The Enemy: $O(N^2)$

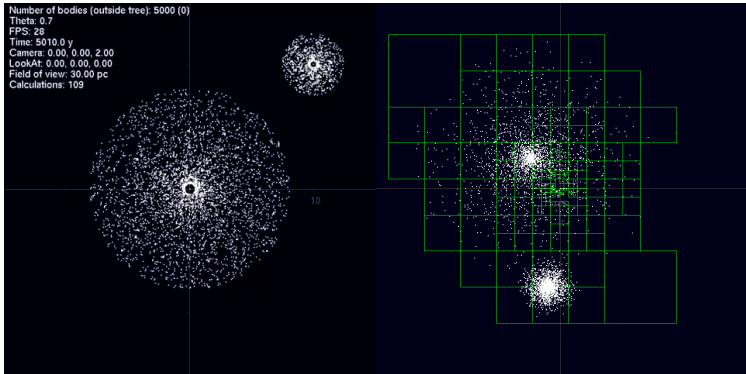
Truncation Methods $O(N)$
- Wolf Summation (discontinuous forces)
- Shifted Force Wolf Summation (poorer energy)
- Modified Shifted Force Wolf Summation
  - *J. Chem. Theory Comput.* **2019**, *15*, 572–583.

Long-Range Solvers $O(N) - O(N \log(N))$
- Particle–Particle Particle–Mesh (PPPM)
- Particle–Mesh Ewald (PME)
- Fast Fourier Poisson Method (FFP)
- Fast Multipole Algorithm (FMA)
- Reduced Cell Multipole Method (RCMM)
- Macroscopic Multipole Method (MMM)
- PPPM/Multipole Expansion (PPPM/MPE)

n-Body Simulations

$$F = G\frac{m_1 m_2}{r^2}$$

Barnes–Hut Treecode

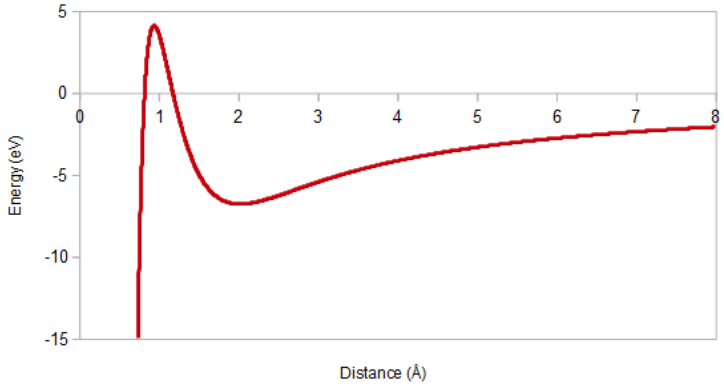


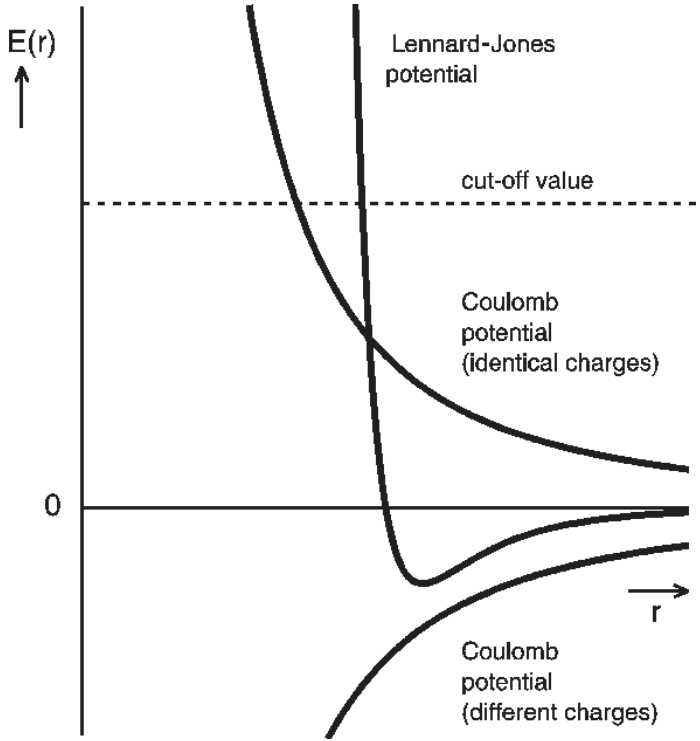
A. Y. Toukmaji, J. A. Board; Ewald Summation Techniques in Perspective: A Survey. *Computer Physics Communications* **1996**, *95*, 73–92.

Using Repulsion to Avoid Coulombic Catastrophe

Buckingham Potential

$$U_{BC}\left(r_{ij}\right) = A_{ij}e^{-\frac{r_{ij}}{\rho_{ij}}} - \frac{C_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}}$$





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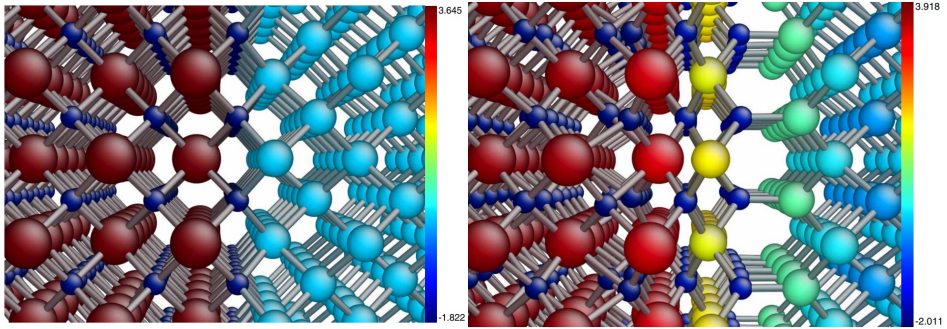
Responsive Electrostatics

Methods
- Charge Equilibration
- Core–Shell
- Drude Oscillator
- Induced Dipole

Implementations
- Self-Consistent Equilibration
  - Matrix Inversion
  - Iterative Procedures
- Extended Lagrangian

Damping
- Thole Damping
- Shielded Coulomb Potential

T.-R. Shan, B. D. Devine, T. W. Kemper, S. B. Sinnott, S. R. Phillpot; Charge-optimized many-body potential for the hafnium/hafnium oxide system. *Phys. Rev. B*, **2010**, *81*, 125328.

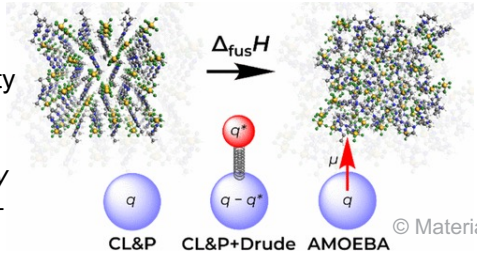


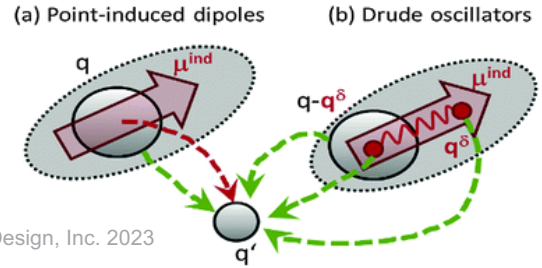
"At a certain level of sophistication it is reasonable to ask whether the models have the physical meaning which is implied or whether we have merely produced convenient parameterisations." ~Sangster **1973**

M. J. L. Sangster; Interionic Potentials and Force Constant Models for Rocksalt Structure Crystals. *J. Phys. Chem. Solids*, **1973**, *34* 355–363.

G. Jacucci, I. R. McDonald, K. Singer; Introduction of the shell model of ionic polarizability into molecular dynamics calculations. *Phys. Lett. A*, **1974**, *50*, 141–143.

M. Klajmon, C. Červinka; Does Explicit Polarizability Improve Simulations of Phase Behavior of Ionic Liquids? *J. Chem. Theory Comput.* **2021**, *17*, 6225–6239.



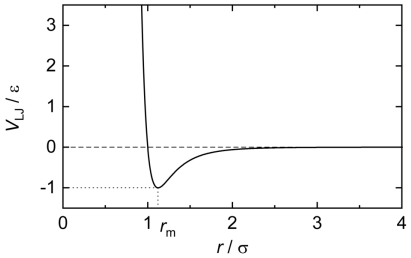


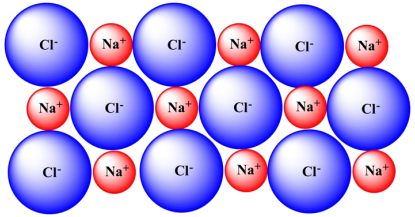
M. Schmollngruber, V. Lesch, C. Schröder, A. Heuerb, O. Steinhauser; Comparing Induced Point-Dipoles and Drude Oscillators. *Phys. Chem. Chem. Phys.*, **2015**, *17*, 14297–14306.

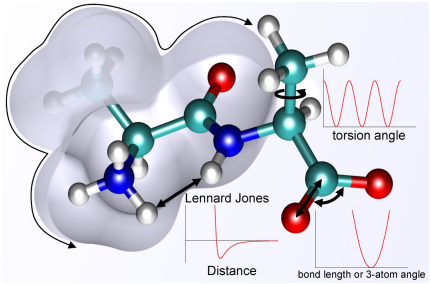
materials design

Versatility of Functional Form

Embellishments and Complexity







materials design

Many-Body Potentials – EAM and MEAM

$$E_i = F_\alpha\left(\sum_{j\neq i}\rho_\beta(r_{ij})\right) + \frac{1}{2}\sum_{j\neq i}\Phi_{\alpha\beta}(r_{ij})$$

Embedding Energy — Atomic Electron Density — Pair Potential

- Embedded-Atom Method (EAM)
  - Considers local coordination effects in addition to pair potential expression.
- Modified EAM (MEAM)
  - Accounts for angular dependence on electron density.
- Multistate MEAM (MS-MEAM)
  - Treats local defects or large strains by reference paths used to determine screening functions.

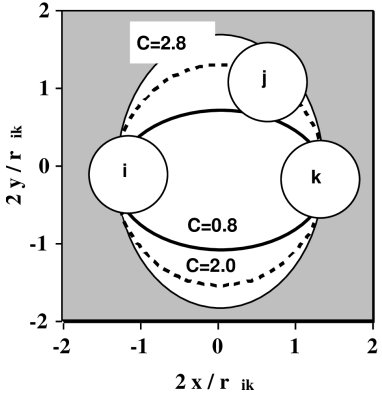
Trained on DFT Data

M. S. Daw, M. I. Baskes; Semiempirical, Quantum Mechanical Calculation of Hydrogen Embrittlement in Metals. *Phys. Rev. Lett.*, **1983**, *50*, 1285–1288.

M. S. Daw, M. I. Baskes; Embedded-Atom Method: Derivation and Application to Impurities, Surfaces, and Other Defects in Metals. *Phys. Rev. B*, **1984**, *29*, 6443–6453.

M. I. Baskes; Modified Embedded-Atom Potentials for Cubic Materials and Impurities. *Phys. Rev. B*, **1992**, *46*, 2727–2742.

M. I. Baskes, S. G. Srinivasan, S. M. Valone, and R. G. Hoagland; Multistate Modified Embedded Atom Method. *Phys. Rev. B*, **2007**, *75*, 094113.



M. I. Baskes; Determination of Modified Embedded Atom Method Parameters for Nickel. **1997**, *50*, 152–158.

materials design

Many Many-Body Potentials

Goal:
Sensitivity to the local coordination environment

Tersoff

$$E = \frac{1}{2}\sum_i \sum_{j \neq i} V_{ij}$$

$$V_{ij} = f_C(r_{ij}+\delta)\left[f_R(r_{ij}+\delta) + b_{ij} f_A(r_{ij}+\delta)\right]$$

$$f_C(r) = \begin{cases} 1 & r < R - D \\ \frac{1}{2} - \frac{1}{2}\sin\left(\frac{\pi}{2}\frac{r-R}{D}\right) & R - D < r < R + D \\ 0 & r > R + D \end{cases}$$

$$f_R(r) = A\exp(-\lambda_1 r)$$

$$f_A(r) = -B\exp(-\lambda_2 r)$$

$$b_{ij} = (1 + \beta^n {\zeta_{ij}}^n)^{-\frac{1}{2n}}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}+\delta) g\left[\theta_{ijk}(r_{ij}, r_{ik})\right] \exp\left[{\lambda_3}^m (r_{ij} - r_{ik})^m\right]$$

$$g(\theta) = \gamma_{ijk}\left(1 + \frac{c^2}{d^2} - \frac{c^2}{\left[d^2 + (\cos\theta - \cos\theta_0)^2\right]}\right)$$

J. Tersoff; New Empirical Approach for the Structure and Energy of Covalent Systems. *Phys. Rev. B*, **1988**, *37*, 6991–7000.

Stillinger–Weber

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\phi_2(r_{ij}) = A_{ij}\epsilon_{ij}\left[B_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{q_{ij}}\right] \exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right)$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk}\epsilon_{ijk}\left[\cos\theta_{ijk} - \cos\theta_{0ijk}\right]^2 \exp\left(\frac{\gamma_{ij}\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right) \exp\left(\frac{\gamma_{ik}\sigma_{ik}}{r_{ik} - a_{ik}\sigma_{ik}}\right)$$

F. H. Stillinger, T. A. Weber; Computer Simulation of Local Order in Condensed Phases of Silicon. *Phys. Rev. B*, **1985**, *31*, 5262–5271.

- 1st Generation Reactive Empirical Bond Order (REBO)
- 2nd Generation REBO
- Adaptive Intermolecular REBO (AIREBO)
- Embedded Ion Method (EIM)
- Environment-Dependent Interatomic Potential (EDIP)
- Angular-Dependent Potential (ADP)
- Bond-Order Potentials (BOP)
- 3-Body Free-Form Potential (Polymorphic)
- Vashishta Family of Potentials
- Charge-Optimized Many-Body Potential (COMB)
- ReaxFF

Class I Forcefields

OPLS / CHARMM / AMBER / TraPPE / GROMOS

OPLS-AA

$$E(\phi) = E_{\text{bond}}(\phi) + E_{\text{angle}}(\phi) + E_{\text{n.b.}}(\phi) + E_{\text{torsion}}(\phi)$$

$$E_{\text{ab}} = \sum_{i}^{\text{on a}} \sum_{j}^{\text{on b}} [q_i q_j e^2 / r_{ij} + 4\epsilon_{ij}(\sigma_{ij}^{12}/r_{ij}^{12} - \sigma_{ij}^{6}/r_{ij}^{6})] f_{ij}$$

$$E_{\text{bond}} = \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2$$

$$E_{\text{angle}} = \sum_{\text{angles}} K_\theta (\theta - \theta_{\text{eq}})^2$$

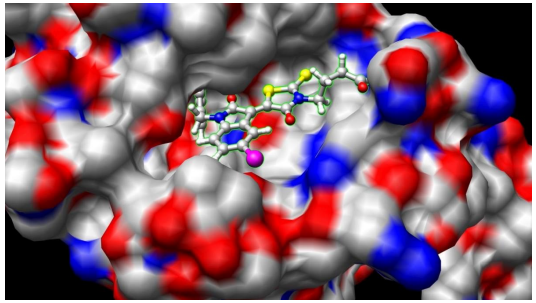
$$E_{\text{torsion}} = \sum_{i} \frac{V_1^i}{2}[1 + \cos(\phi_i + f_i 1)] + \frac{V_2^i}{2}[1 - \cos(2\phi_i + f_i 2)] + \frac{V_3^i}{2}[1 + \cos(3\phi_i + f_i 3)]$$

$$\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}$$

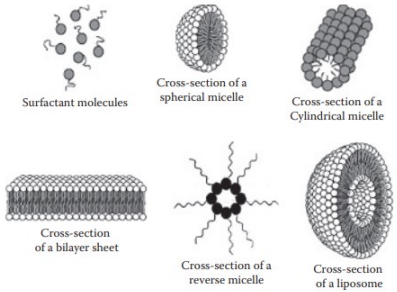
$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$$

W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives; Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.*, **1996**, *188*, 11225–11236.

Computer-Aided Drug Design

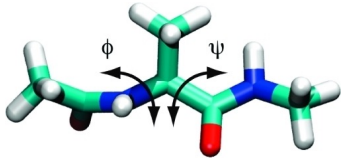


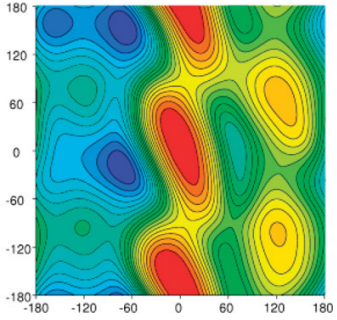
Consumer Products / Aqueous Simulations

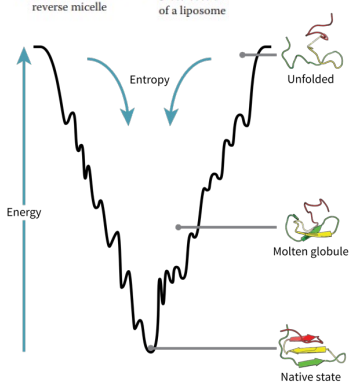


Generalized Sum of Sinusoidal Torsion Terms

$$E = \sum_{i=1,m} K_i[1.0 + \cos(n_i\varphi) - d_i]$$







In the 1980s and 1990s, large amounts of effort went into empirically parameterizing forcefields that cover a large chemical space for condensed phase systems.

materials design

Class II Forcefields

COMPASS / PCFF+

- Accounts for anharmonic and intramolecular coupling interactions.
- Conventionally uses 9-6 LJ form instead of the 12-6 form.
- Sixth-power mixing rules:

$$r^* = [(r_i^{*6} + r_j^{*6})/2]^{1/6}$$

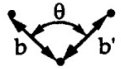
$$\varepsilon = (\varepsilon_i \varepsilon_j)^{1/2} 2(r_i^* r_j^*)^3/[r_i^{*6} + r_j^{*6}]$$

- Attempting to use existing 12-6 LJ parameters in the 9-6 LJ form is not recommended.

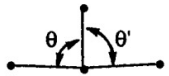
$$\begin{aligned}
E = & \sum_b [{}^2K_b(b - b_0)^2 + {}^3K_b(b - b_0)^3 \\
& + {}^4K_b(b - b_0)^4] + \sum_\theta [{}^2K_\theta(\theta - \theta_0)^2 \\
& + {}^3K_\theta(\theta - \theta_0)^3 + {}^4K_\theta(\theta - \theta_0)^4] \\
& + \sum_\phi [{}^1K_\phi(1 - \cos\phi) + {}^2K_\phi(1 \\
& - \cos 2\phi) + {}^3K_\phi(1 - \cos 3\phi)] \\
& + \sum_{i>j} \frac{q_i q_j}{r_{ij}} + \sum_{i>j} \varepsilon\left[2\left(\frac{r^*}{r_{ij}}\right)^9 - 3\left(\frac{r^*}{r_{ij}}\right)^6\right] \\
& + \sum_b \sum_{b'} K_{bb'}(b - b_0)(b' - b_0') \\
& + \sum_\theta \sum_{\theta'} K_{\theta\theta'}(\theta - \theta_0)(\theta' - \theta_0') \\
& + \sum_b \sum_\theta K_{b\theta}(b - b_0)(\theta - \theta_0) \\
& + \sum_\phi \sum_b (b - b_0)[{}^1K_{\phi b} \cos\phi \\
& + {}^2K_{\phi b} \cos 2\phi + {}^3K_{\phi b} \cos 3\phi] \\
& + \sum_\phi \sum_{b'} (b' - b_0')[{}^1K_{\phi b'} \cos\phi \\
& + {}^2K_{\phi b'} \cos 2\phi + {}^3K_{\phi b'} \cos 3\phi] \\
& + \sum_\phi \sum_\theta (\theta - \theta_0)[{}^1K_{\phi\theta} \cos\phi \\
& + {}^2K_{\phi\theta} \cos 2\phi + {}^3K_{\phi\theta} \cos 3\phi] \\
& + \sum_\phi \sum_\theta \sum_{\theta'} K_{\phi\theta\theta'}(\theta - \theta_0)(\theta' - \theta_0')\cos\phi
\end{aligned}$$

a. bond/bond

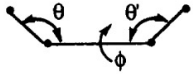
b. bond/angle



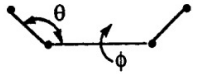
c. angle/angle



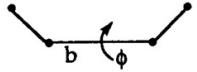
d. angle/angle/torsion



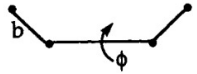
e. angle/torsion



f. bond/torsion (type 1)



g. bond/torsion (type 2)



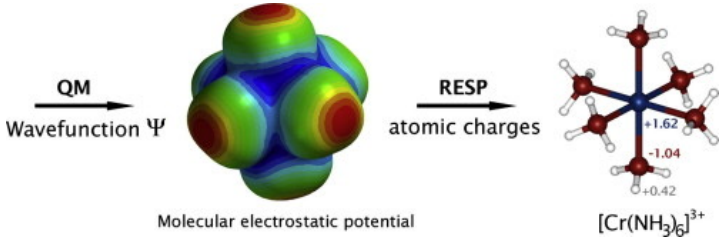
PCFF+ is continuously developed by Materials Design.

J. R. Maple et al.; Derivation of Class II Force Fields. I. Methodology and Quantum Force Field for the Alkyl Functional Group and Alkane Molecules. *J. Comput. Chem.,* **1994**, *15*, 162–182.

materials design

Challenges of Atom Typing

- Defined by intramolecular structure
  - Repulsion–dispersion interactions rely upon standard mixing rules or explicit IJ parameterization.
  - Partial charges are static, but the electrostatic potential is dependent on the local chemical environment.
    - Charge equilibration or polarization methods attempt to address this but add another layer of parameters and significantly increase computational expense.
- Complexity of specification
  - Alternative parameter assignment formalisms have been developed to limit complexity of parameter specification.
  - D.L. Mobley et al., Escaping Atom Types in Force Fields Using Direct Chemical Perception. **2018**, *14*, 6076–6092.



I. Djordjević, S.R. Niketić, *Comp. Theor. Chem.*, **2012**, *1001*, 20–25.

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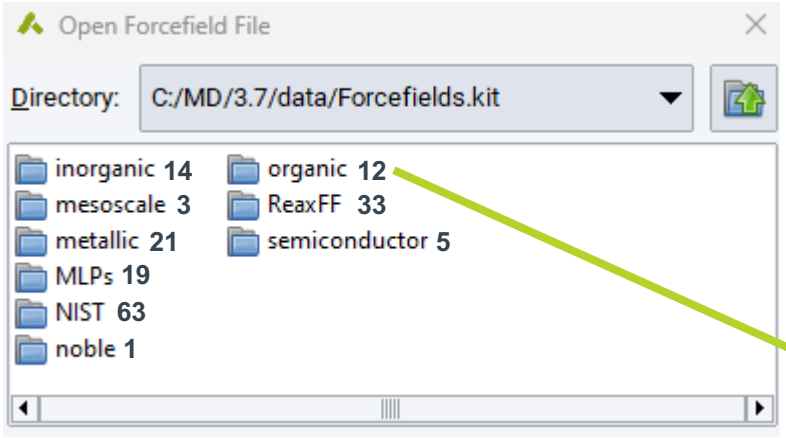
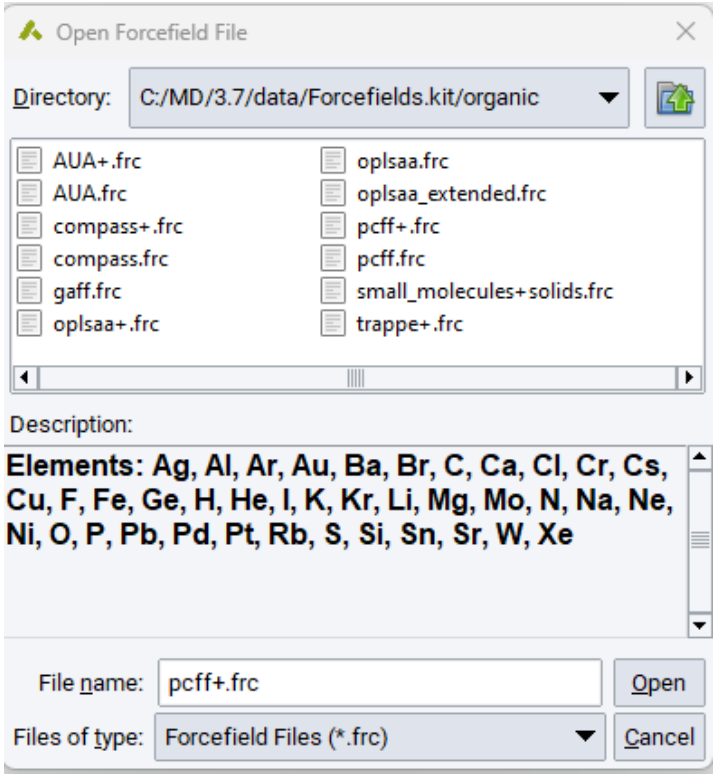
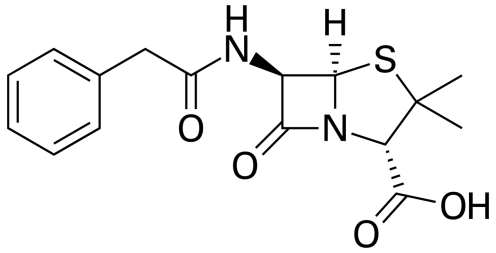
Assigning FF Parameters is Easy … With *MedeA*!





Penicillin G



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* $SC_{16}N_2O_4H_{18}$ (P1) ~ Penicillin

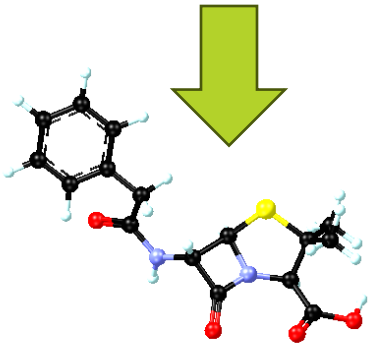
MedeA: provide a SMILES

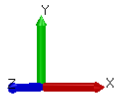
Create a new molecule provided its SMILES string (Simplified Molecular Input Line Entry Specification)

Title: Penicillin

SMILES: O=C(Cc1ccccc1)NC1C(=O)N2C1SC(C2C(=O)O)(C)C

OK Cancel





Atoms

Atom	Name	Element	Atomic Number	Wyckoff Position	Wyckoff Equation	X	Y	Z	Freeze	Occupancy	Spin	FF Atom Type	FF Charge
1	O1	O	8	1a	x,y,z	0.223259	0.525295	0.490271	---	1	0	o_1	-0.45
		C	6	1a	x,y,z	0.316005	0.514904	0.499452	---	1	0	c_1	0.45
		C	6	1a	x,y,z	0.373673	0.593356	0.567263	---	1	0	c2	-0.106
		C	6	1a	x,y,z	0.309836	0.664443	0.628657	---	1	0	cp	0
		C	6	1a	x,y,z	0.232433	0.623576	0.679464	---	1	0	cp	-0.1268
		C	6	1a	x,y,z	0.169662	0.688141	0.731644	---	1	0	cp	-0.1268
		C	6	1a	x,y,z	0.185376	0.794674	0.734357	---	1	0	cp	-0.1268
		C	6	1a	x,y,z	0.26494	0.835666	0.685103	---	1	0	cp	-0.1268
		C	6	1a	x,y,z	0.327496	0.770107	0.632634	---	1	0	cp	-0.1268
10	N1	N	7	1a	x,y,z	0.365496	0.428472	0.44486	---	1	0	n_31	-0.46
11	C9	C	6	1a	x,y,z	0.466	0.427882	0.462566	---	1	0	c4h1	0.057
12	C10	C	6	1a	x,y,z	0.52065	0.332944	0.431602	---	1	0	c_1	0.45
13	O2	O	8	1a	x,y,z	0.526012	0.235751	0.475983	---	1	0	o_1	-0.45
14	N2	N	7	1a	x,y,z	0.564281	0.382925	0.344918	---	1	0	n_30	-0.12
15	C11	C	6	1a	x,y,z	0.514559	0.48453	0.353457	---	1	0	c4h1	0.132
16	S	S	16	1a	x,y,z	0.615575	0.555835	0.355292	---	1	0	sc	-0.25
17	C12	C	6	1a	x,y,z	0.69362	0.47404	0.276577	---	1	0	c0	0.125
18	C13	C	6	1a	x,y,z	0.645179	0.367588	0.27298	---	1	0	c5h1	0.007
19	C14	C	6	1a	x,y,z	0.715168	0.281766	0.296786	---	1	0	c_1	0.562
20	O3	O	8	1a	x,y,z	0.714384	0.227375	0.395707	---	1	0	o_1	-0.45
21	O4	O	8	1a	x,y,z	0.786199	0.260203	0.208161	---	1	0	o_2c	-0.535
22	C15	C	6	1a	x,y,z	0.704141	0.51145	0.156626	---	1	0	c3	-0.159
23	C16	C	6	1a	x,y,z	0.782551	0.475485	0.348298	---	1	0	c3	-0.159
24	H1	H	1	1a	x,y,z	0.417232	0.637783	0.50978	---	1	0	hc	0.053
25	H2	H	1	1a	x,y,z	0.416613	0.552278	0.628259	---	1	0	hc	0.053
26	H3	H	1	1a	x,y,z	0.22106	0.540283	0.678284	---	1	0	hc	0.1268
27	H4	H	1	1a	x,y,z	0.108298	0.655878	0.770401	---	1	0	hc	0.1268
28	H5	H	1	1a	x,y,z	0.135683	0.845583	0.774175	---	1	0	hc	0.1268
29	H6	H	1	1a	x,y,z	0.27786	0.918446	0.687933	---	1	0	hc	0.1268
30	H7	H	1	1a	x,y,z	0.39011	0.801266	0.594747	---	1	0	hc	0.1268
31	H8	H	1	1a	x,y,z	0.331291	0.372701	0.393109	---	1	0	hn2	0.35
32	H9	H	1	1a	x,y,z	0.487048	0.461843	0.542589	---	1	0	hc	0.053
33	H10	H	1	1a	x,y,z	0.470532	0.496725	0.280396	---	1	0	hc	0.053
34	H11	H	1	1a	x,y,z	0.620539	0.355806	0.187589	---	1	0	hc	0.053
35	H12	H	1	1a	x,y,z	0.779183	0.315285	0.142054	---	1	0	ho2	0.423
36	H13	H	1	1a	x,y,z	0.637208	0.505224	0.114364	---	1	0	hc	0.053
37	H14	H	1	1a	x,y,z	0.753551	0.463065	0.112862	---	1	0	hc	0.053
38	H15	H	1	1a	x,y,z	0.726823	0.590729	0.156078	---	1	0	hc	0.053
39	H16	H	1	1a	x,y,z	0.767778	0.450021	0.434401	---	1	0	hc	0.053
40	H17	H	1	1a	x,y,z	0.809247	0.554543	0.350659	---	1	0	hc	0.053
41	H18	H	1	1a	x,y,z	0.833632	0.425207	0.310165	---	1	0	hc	0.053

Periodic structure 41 atoms 43 bonds

materials design

MedeA Automatically Generates LAMMPS-Style Input Files

Data File

```
LAMMPS Description

        41 atoms
        43 bonds
        77 angles
        83 dihedrals
        39 impropers

        15 atom types
        24 bond types
        47 angle types
        40 dihedral types
        27 improper types

# Cell: 14.563000 12.947900 11.810400 90.0000 90.0000 90.0000
    0.000000    14.563000 xlo xhi
    0.000000    12.947900 ylo yhi
    0.000000    11.810400 zlo zhi

Masses

         1 12.01115     # c0
         2 12.01115     # c2
         3 12.01115     # c3
         4 12.01115     # c4h1
         5 12.01115     # c5h1
         6 12.01115     # c_1
         7 12.01115     # cp
         8 1.00797      # hc
         9 1.00800      # hn2
        10 1.00800      # ho2
        11 14.00670     # n_30
        12 14.00670     # n_31
        13 15.99940     # o_1
        14 15.99940     # o_2c
        15 32.06400     # sc

Atoms

1 1 13 -0.45000000 3.251325 6.801469 5.790298 0 0 0      # O1    o_1
2 1 6 0.45000000 4.601975 6.666929 5.898726 0 0 0        # C1    c_1
3 1 2 -0.10600000 5.441805 7.682719 6.699609 0 0 0       # C2    c2
4 1 7 0.00000000 4.512145 8.603138 7.424688 0 0 0        # C3    cp
5 1 7 -0.12680000 3.384923 8.073994 8.024746 0 0 0       # C4    cp
6 1 7 -0.12680000 2.470782 8.909986 8.641007 0 0 0       # C5    cp
7 1 7 -0.12680000 2.699637 10.289356 8.673048 0 0 0      # C6    cp
8 1 7 -0.12680000 3.858314 10.820120 8.091341 0 0 0      # C7    cp
9 1 7 -0.12680000 4.769317 9.971263 7.471657 0 0 0       # C8    cp
10 1 12 -0.46000000 5.322718 5.547815 5.253976 0 0 0     # N1    n_31
11 1 4 0.05700000 6.786354 5.540178 5.463092 0 0 0       # C9    c4h1
12 1 6 0.45000000 7.582232 4.310931 5.097394 0 0 0       # C10   c_1
13 1 13 -0.45000000 7.660312 3.052479 5.621550 0 0 0     # O2    o_1
14 1 11 -0.12000000 8.217620 4.958074 4.073620 0 0 0     # N2    n_30
15 1 4 0.13200000 7.493518 6.273652 4.174465 0 0 0       # C11   c4h1
```

Parameter File

```
bond_coeff              1 1.202 851.14 -1918.5 2160.8  # c_1   o_1
bond_coeff              2 1.4902 253.71 -423.04 396.9  # c     c_1
bond_coeff              3 1.501 321.9 -521.82 572.16   # c     cp
bond_coeff              4 1.417 470.84 -627.62 1327.6  # cp    cp
bond_coeff              5 1.336 390.68 -768.38 923.24  # c_1   n_2
bond_coeff              6 1.4432 319.16 -586.32 961.41 # c     n_2
bond_coeff              7 1.4902 253.71 -423.04 396.9  # c     c_1
bond_coeff              8 1.356 390.68 -768.38 923.24  # c_1   n_30
bond_coeff              9 1.4532 319.16 -586.32 961.41 # c     n_30
bond_coeff             10 1.53 299.67 -501.77 679.81   # c     c
bond_coeff             11 1.823 225.28 -327.71 488.97  # c     s
bond_coeff             12 1.823 225.28 -327.71 488.97  # c     s
bond_coeff             13 1.53 299.67 -501.77 679.81   # c     c
bond_coeff             14 1.4532 319.16 -586.32 961.41 # c     n_30
bond_coeff             15 1.4902 253.71 -423.04 396.9  # c     c_1
bond_coeff             16 1.3683 367.15 -794.79 1055.2 # c_1   o_2
bond_coeff             17 1.53 299.67 -501.77 679.81   # c     c
bond_coeff             18 1.101 345 -691.89 844.6      # c     h
bond_coeff             19 1.0982 372.83 -803.45 894.32 # cp    h
bond_coeff             20 0.9959 495.83 -1092.7 1441.1 # hn2   n_2
bond_coeff             21 1.101 345 -691.89 844.6      # c     h
bond_coeff             22 1.101 345 -691.89 844.6      # c     h
bond_coeff             23 0.952 534.3 -1287.2 1889.1   # ho2   o_2
bond_coeff             24 1.101 345 -691.89 844.6      # c     h
angle_coeff             1 123.15 55.543 -17.212 0.1348 # c     c_1     o_1
angle_coeff             2 125.53 101.88 -41.809 0      # n_2   c_1     o_1
angle_coeff             3 116.93 39.419 -10.995 -8.7733        # c     c_1     n_2
angle_coeff             4 109.5 60 0 0 # *     c_      *
angle_coeff             5 107.73 40.61 -28.812 0       # c_1   c       h
angle_coeff             6 111 44.323 -9.4454 0 # cp    c       h
angle_coeff             7 107.66 39.641 -12.921 -2.4318        # h     c       h
angle_coeff             8 120.05 44.715 -22.735 0      # c     cp      cp
angle_coeff             9 118.9 61.923 34.993 0        # cp    cp      cp
```

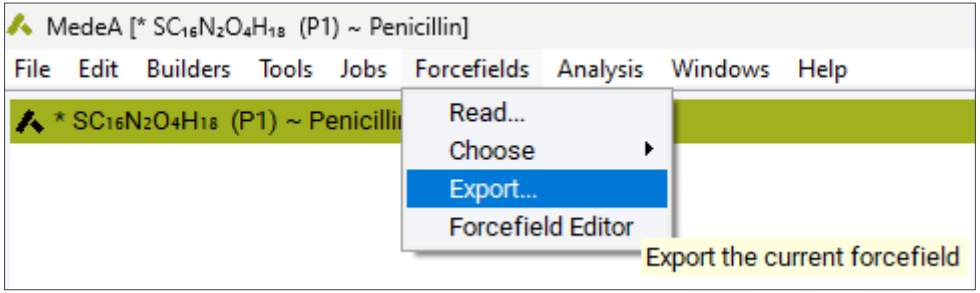
Input File

```
#  This is the control script for LAMMPS.

echo                    both
log                     1.1_Initialize.out

#---------------------------------------------------------
# Stage 1.1: Initialize LAMMPS run for 3-d periodic
#---------------------------------------------------------

units                   real
boundary                p p p
atom_style              full

pair_style              lj/class2/coul/long 9.5
pair_modify             mix sixthpower
pair_modify             tail yes
bond_style              class2
angle_style             class2
dihedral_style          class2
improper_style          class2
special_bonds           lj 0.0 0.0 1.0 coul 0.0 0.0 1.0

box                     tilt large
read_data               structure.dat

include                 parameters.dat

neighbor                2.0 bin
neigh_modify            delay 0 every 1 check yes
kspace_style            pppm 0.00001
```

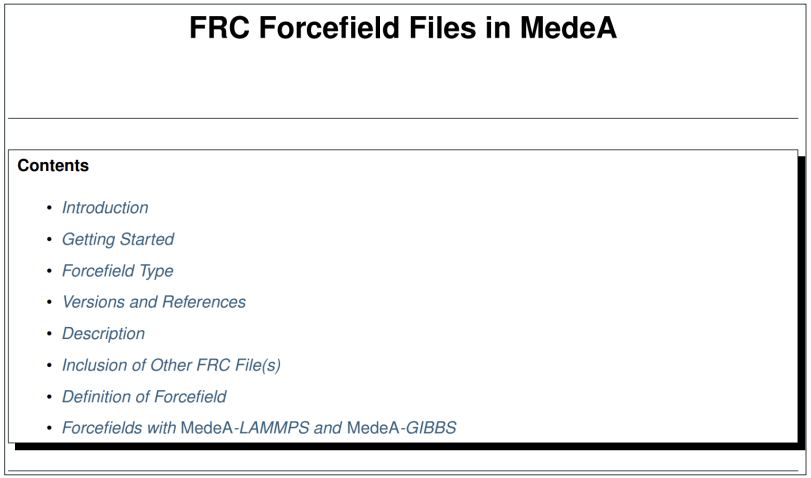
All files are in plaintext and readable. Full transparency.

materials design

Customizing MedeA FRC Files



The FRC file format is well documented!



FRC Forcefield Files in MedeA

Contents

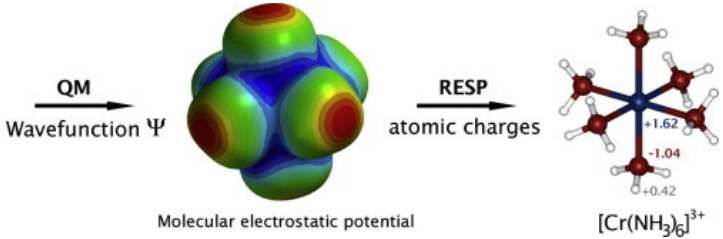
- *Introduction*
- *Getting Started*
- *Forcefield Type*
- *Versions and References*
- *Description*
- *Inclusion of Other FRC File(s)*
- *Definition of Forcefield*
- *Forcefields with* MedeA-*LAMMPS and* MedeA-*GIBBS*

Examples of Oxygen Atom Typing via Templates

```
type oh
  ! oxygen bonded to hydrogen
  template: (>O(-H)(-*))
end_type

type: oc
  !  SP3 oxygen  in ether or acetals
  template (>O(-C)(-C))
  atom_test:1
   aromaticity:NON_AROMATIC
  end_test
end_type

type: oe
  !  SP3 oxygen  in ester
  template (>O(-C(=O))(-C))
  atom_test:1
   aromaticity:NON_AROMATIC
  end_test
end_type
```


materials design

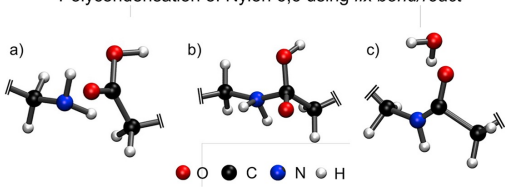
Challenges of Atom Typing



I. Djordjević, S.R. Niketić, *Comp. Theor. Chem.*, **2012**, *1001*, 20–25.

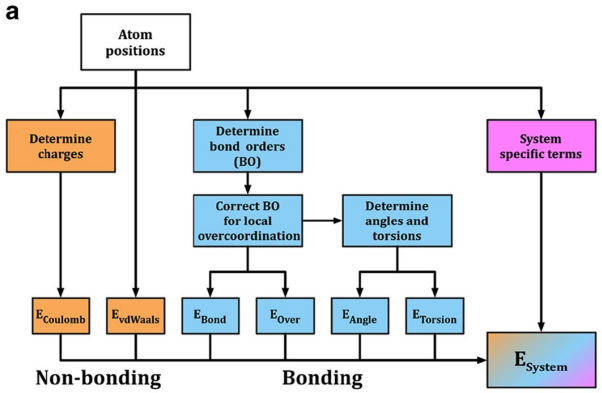
- Reactions require atom type changes
  - Reactions can be facilitated by mapping atom types and bonding topology between reactant and product templates.
  - J.R. Gissinger, B.D. Jensen, K.E. Wise; Modeling Chemical Reactions in Classical Molecular Dynamics Simulations. *Polymer*, **2017**, *128*, 211–217.
  - J.R. Gissinger, B.D. Jensen, K.E. Wise; REACTER: A Heuristic Method for Reactive Molecular Dynamics. *Macromolecules*, **2020**, *53*, 9953–9961.

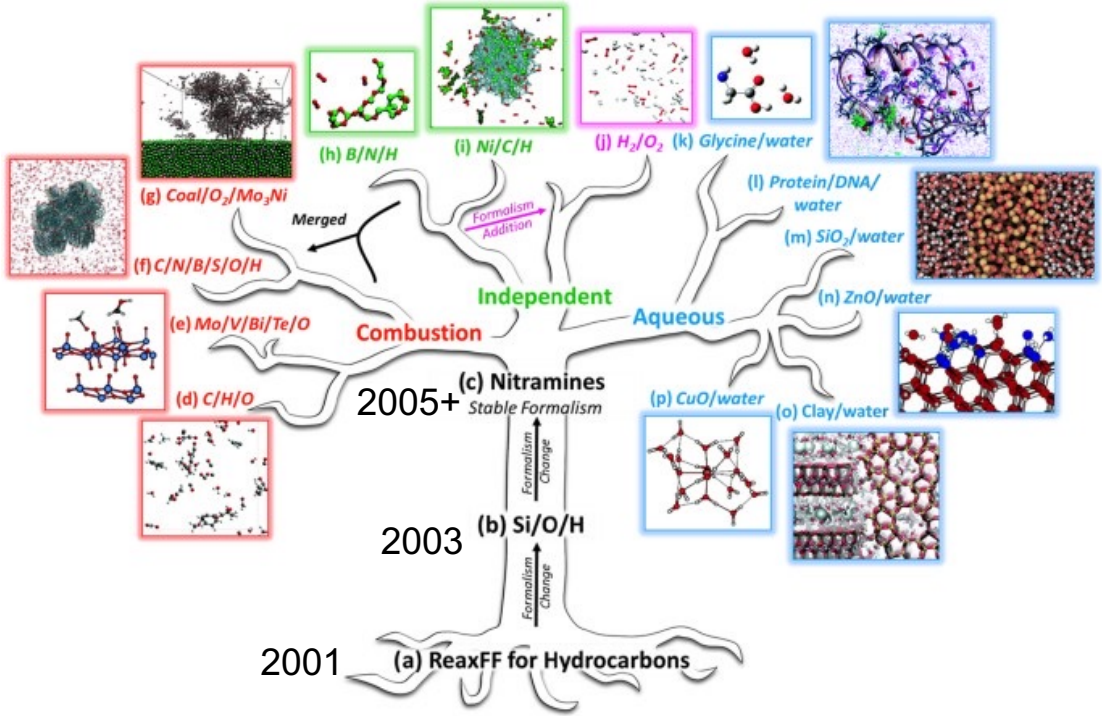
Polycondensation of Nylon 6,6 using *fix bond/react*



ReaxFF

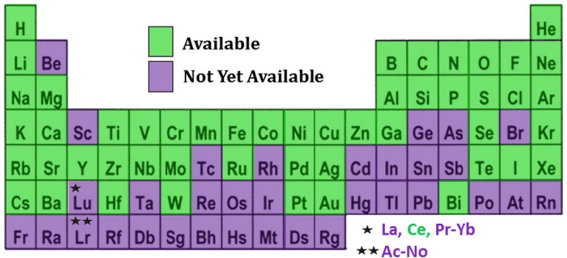
- Charge Equilibration
- Bond Order Term
- Bonded 1-2, 1-3, 1-4 Interactions
  - No Fixed Connectivity





Senftle et al.; The ReaxFF Reactive Force-Field: Development, Applications and Future Directions. *Npj Comput. Mater.* **2016**, *2*, 15011.

b **Current ReaxFF parameter sets:**



- 39 General Parameters
- 32 Atom Parameters
- 16 Bond Parameters
- 6 Off-Diagonal Parameters
- 7 Angle Parameters
- 7 Torsion Parameters
- 4 H-Bond Parameters

100+ Parameters (some not used)

Adri Van Duin

materials design

Versatility of Functional Form

Embellishments and Complexity

materials design

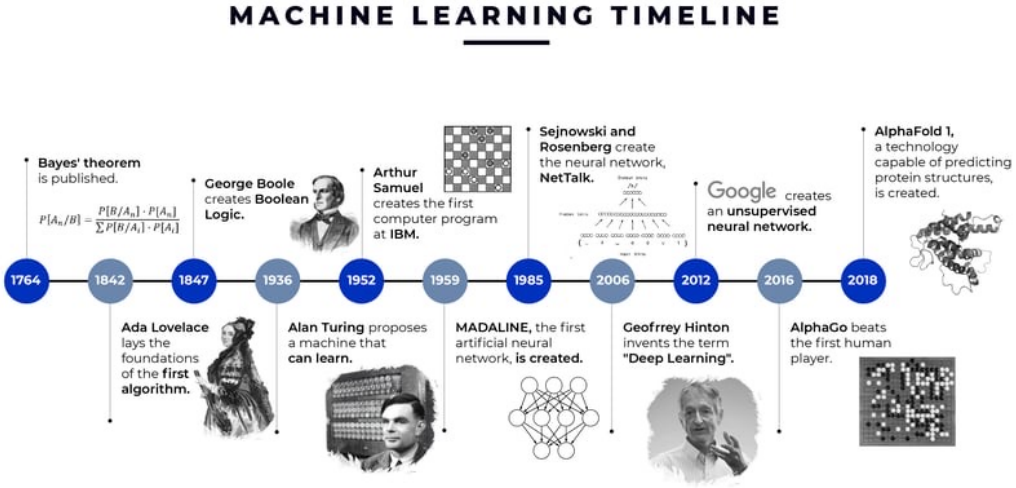
Machine-Learned Potentials

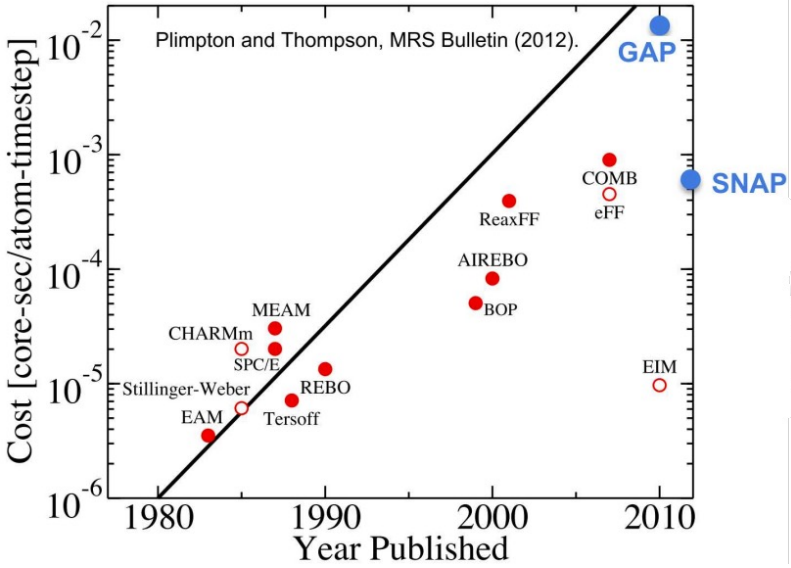
A rose by any other name …

- Machine learning potential (MLP)
- Machine learning interatomic potential (MLIP / ML-IAP)
- Machine learning forcefield (MLFF)

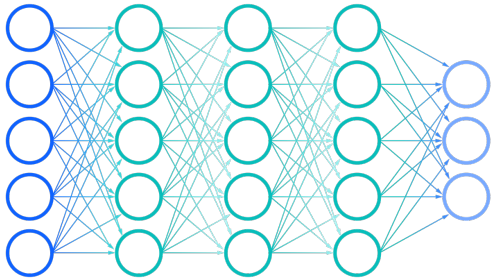
Potentials available in LAMMPS

- Gaussian Approximation Potential (GAP)
- Spectral Neighbor Analysis Potential (SNAP)
- High-Dimensional Neural Network Potential (HDNNP)





https://www.osti.gov/servlets/purl/1639258



https://www.algotive.ai/blog/machine-learning-what-is-ml-and-how-does-it-work

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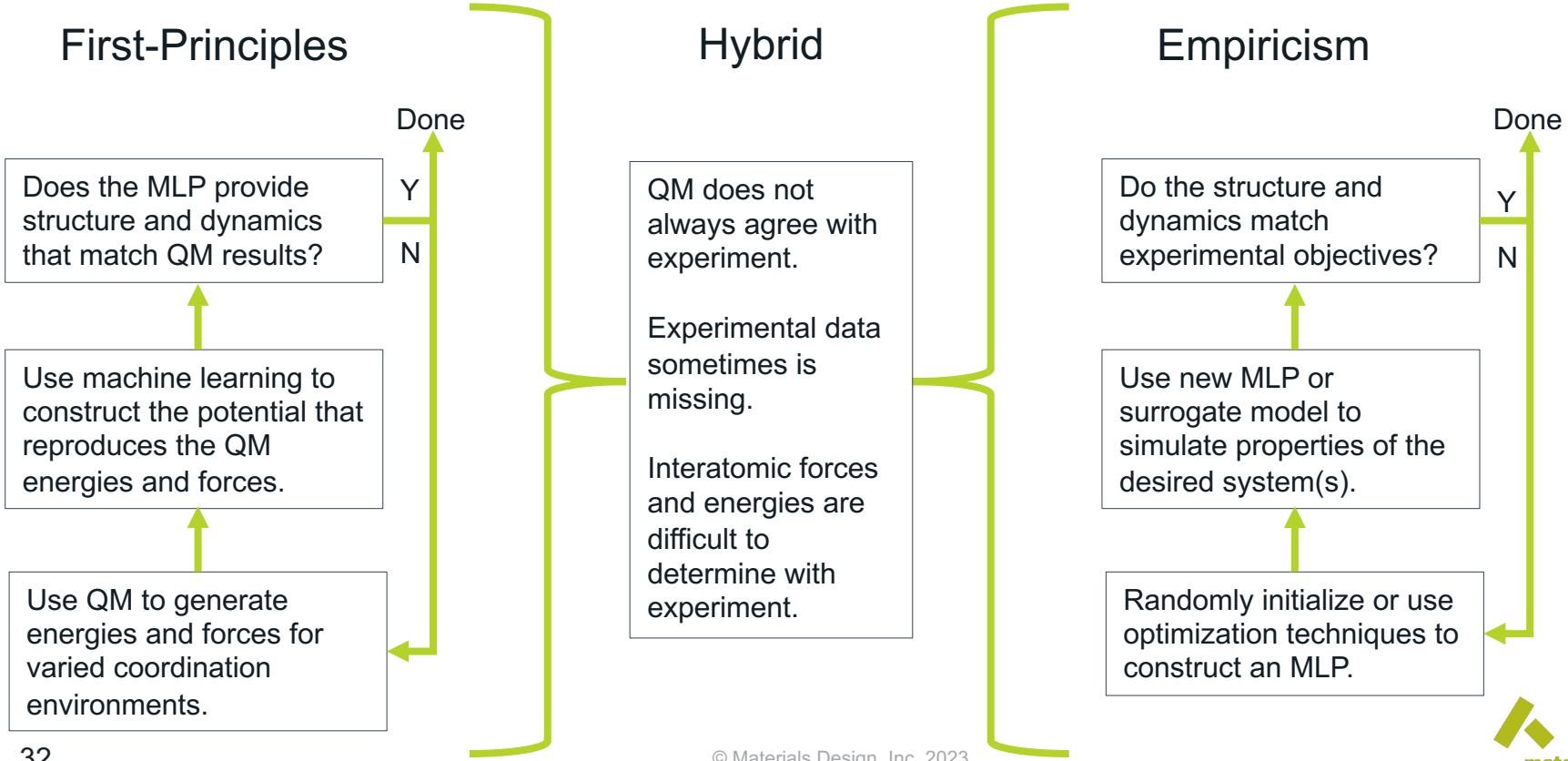
Training Machine-Learned Potentials



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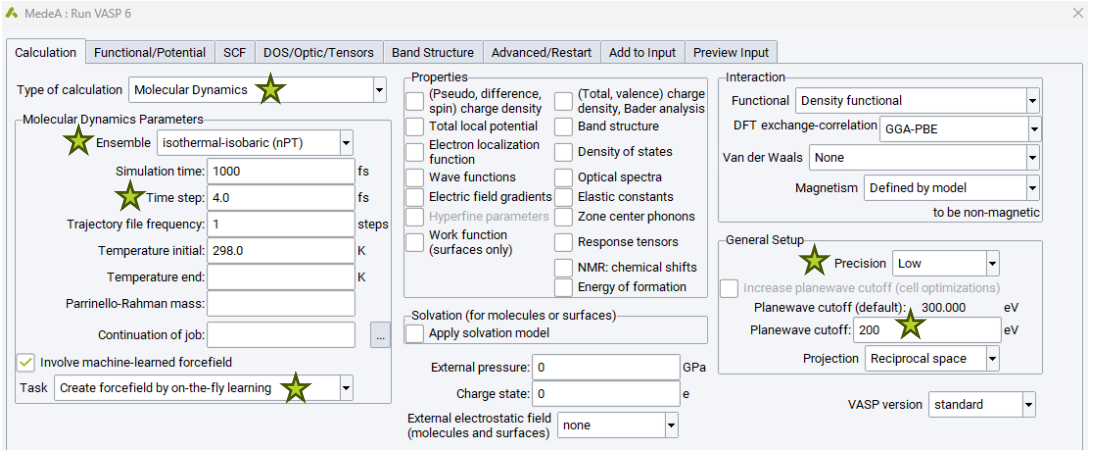
Generating Training Data for MLPs using *MedeA VASP*

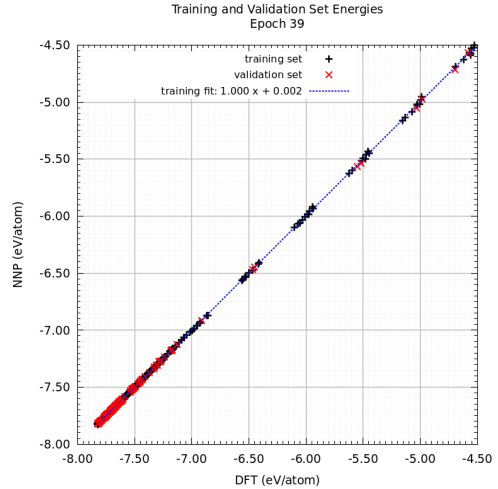
1. Use “sloppy” trajectories to quickly generate both low-energy and high-energy configurations.

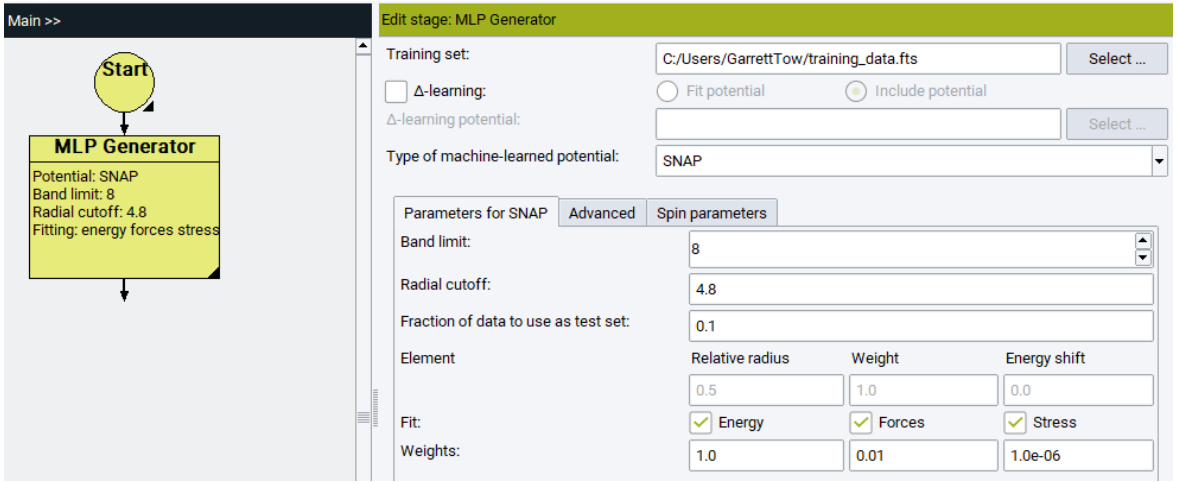
2. Run higher quality single-point energy (SPE) calculations for configurations that are not too correlated.

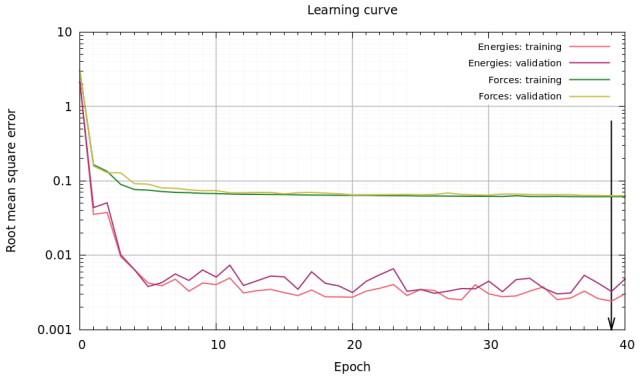
3. Combine all SPE results into a Fitting Training Sets (FTS) file.



Training MLPs is Easy With *MedeA MLPG*!







Potentials Currently Available for Training:

- Spectral Neighbor Analysis Potential (SNAP)
- High-Dimensional Neural Network Potential (HDNNP)
- Atomic Cluster Expansion (ACE)

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Pros and Cons of Machine-Learned Potentials

Pros

- Elemental description; no atom types
- Short-ranged potentials; typically no charges
- No fixed bonds; reactivity allowed
- A potential can model multiple oxidation states
- Near-DFT accuracy but can simulate 10,000+ atom systems

Unclear how much training data is initially needed.
Iterative process that requires adding “missing structures” as needed.

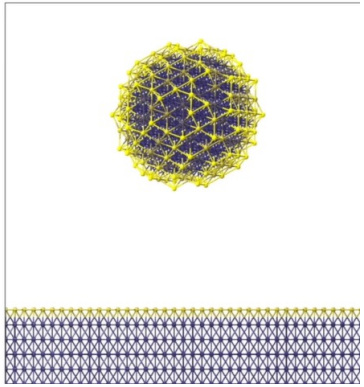
Cons

- Difficult, if not impossible, to physically interpret
- Poor extrapolation beyond training conditions
- Lack of transferability and “mixing rules”

materials design

Machine-Learned Potentials: Surpassing the Limits of the *ab initio* World without leaving it behind

August 1-3, 2023



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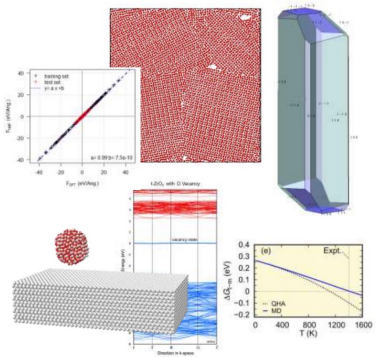
VASP, Machine Learning, and Multi-Scale Physics: Defining the State of the Art in Materials Modeling

Martijn Marsman, University of Vienna and VASP GmbH
Erich Wimmer, Materials Design, Inc.

16-18 August 2022



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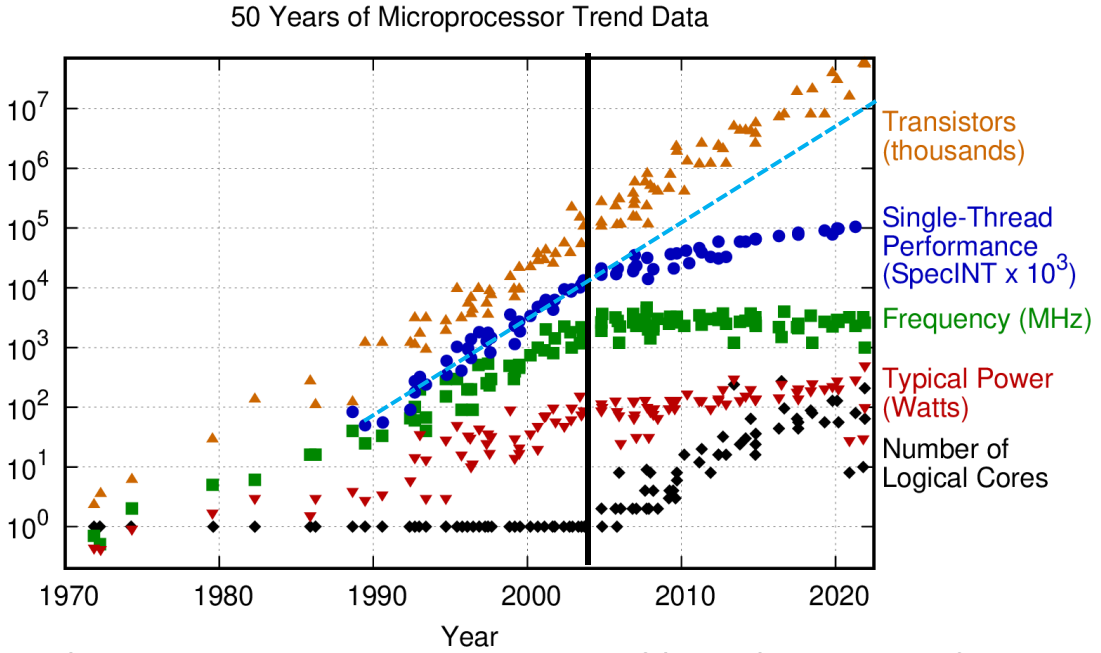
Microprocessor Trends Influence Forcefield Development

- 2004 marks the transition from frequency scaling to parallel computing.
- Single-thread performance keeps slightly improving through:
  - Techniques granting more instructions per clock cycle.
  - Clever power management
  - Dynamic clock frequency
- Currently, processors are being shipped with 128/256 physical/logical cores.



Original data up to the year 2010 collected and plotted by M. Horowitz, F. Labonte, O. Shacham, K. Olukotun, L. Hammond, and C. Batten
New plot and data collected for 2010-2021 by K. Rupp

https://github.com/karlrupp/microprocessor-trend-data

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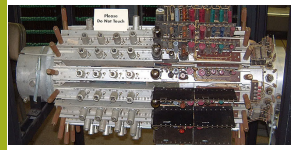
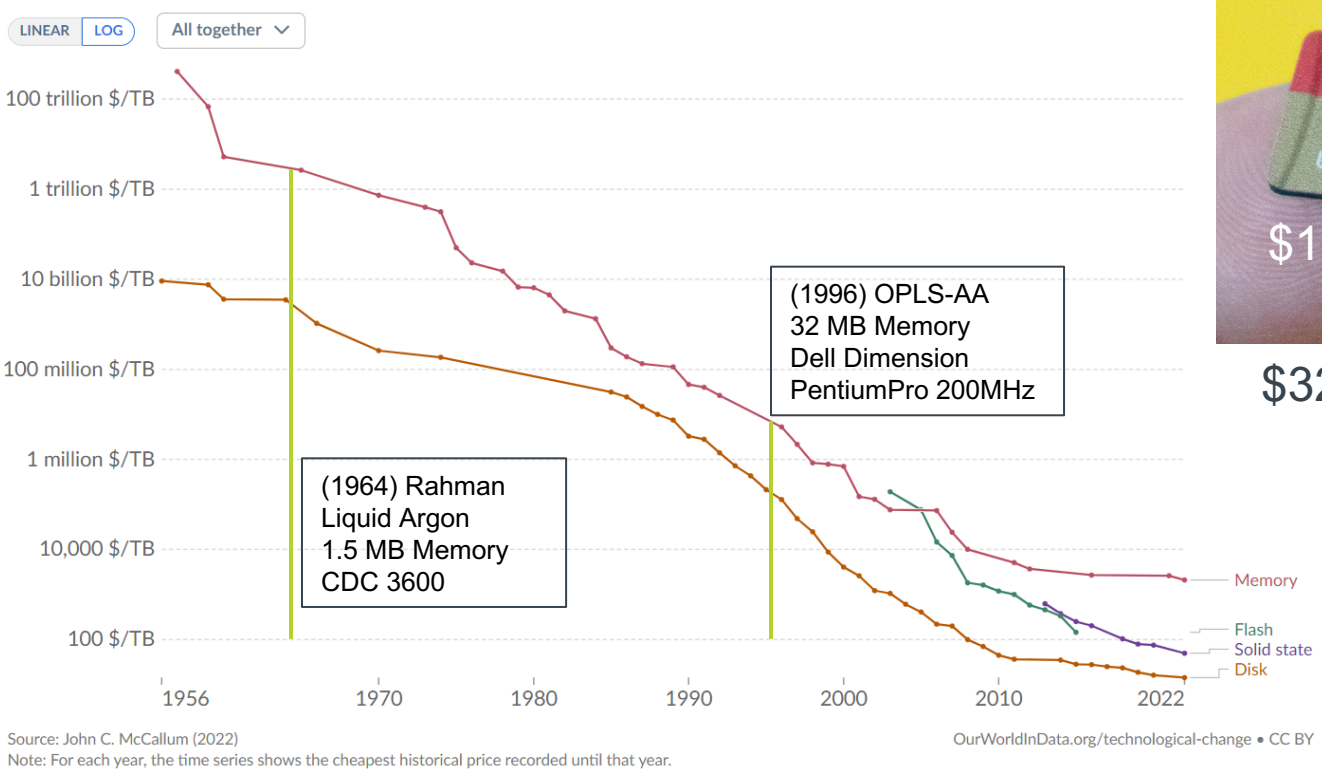
Computing Costs – Memory and Storage



Mercury delay-line memory of UNIVAC 1000 words – 12 characters per word (**1951**)

IBM 350 Disk Drive 3.75 MB (**1956**)



$5–8k

$32

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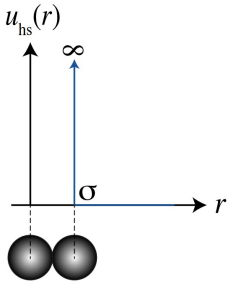
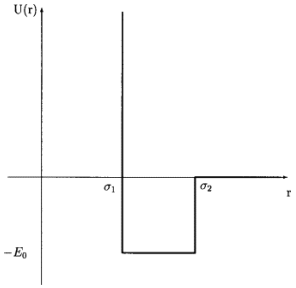
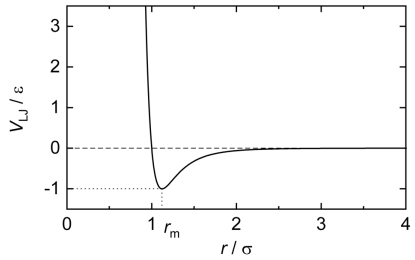
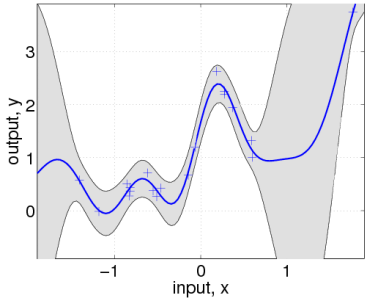
Versatility of Functional Form

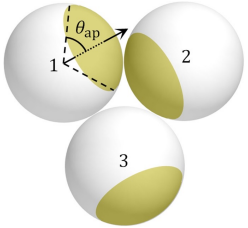
Embellishments and Complexity

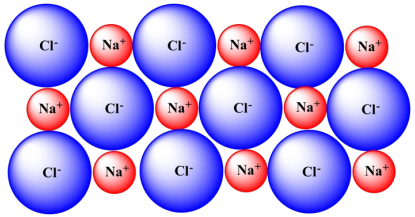


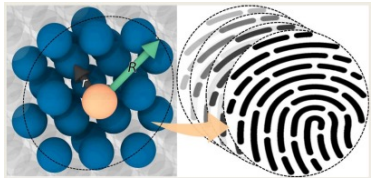


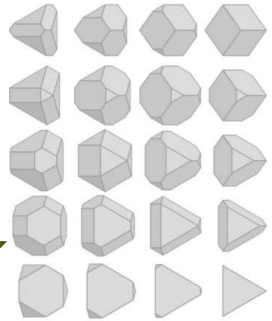


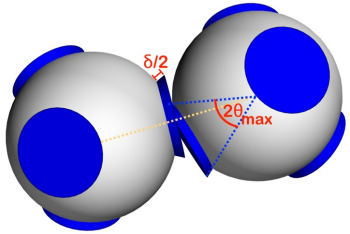


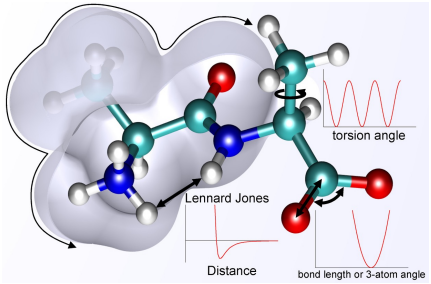


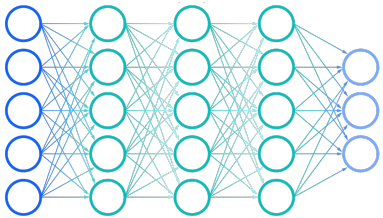












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Relevant *MedeA* Modules

MedeA Environment: Materials Modelling and Simulation Environment

***MedeA EAM*:** A forcefield based simulations provide computationally efficient descriptions of the structural, mechanical, and dynamical properties of metallic systems.

MedeA ReaxFF: A well-established formalism of variable charge, reactive forcefield widely used in forcefield based simulations by the computational materials scientists in both academic and industrial communities.

MedeA Forcefield Optimizer (FFO): Determines optimum forcefield parameters for energy minimization (EM), molecular dynamics (MD), and Monte Carlo (MC) simulations.

***MedeA MLP*:** Machine Learning Potential (MLP) based simulations using *MedeA LAMMPS* carry the accuracy known from first principles calculations to length and time scales, which are orders of magnitude larger, at much lower computational cost. A number of example MLPs from the literature are provided with MedeA MLP. In addition, MLPs created by the *MedeA MLP Generator* (MLPG) can be used.

***MedeA MLPG*:** The Machine Learning Potential Generator (MLPG) forms the centerpiece of Machine Learning materials research by transferring the high accuracy of first principles calculations to the realm of very efficient forcefield simulations. The MLPG builds on training sets consisting of energies, forces, and stresses calculated from first principles for a variety of systems and uses machine learning techniques to create from these training sets parametrized descriptions of the energy/forces/stresses hypersurface. Machine learning potentials generated by the MLPG are ready for immediate use with *MedeA MLP*.

***MedeA VASP*:** The Vienna Ab initio Simulation Package (VASP) is the leading electronic structure program for solids, surfaces, and interfaces. VASP is an extremely well tested, robust, and proven program for calculations based on local and semi-local density functional theory (DFT) applying plane wave basis sets. In addition, VASP provides advanced methods beyond DFT to calculate electronic structure and response, as well as energies of very high accuracy.

Related *MedeA* Webinars

Machine-Learned Potentials: Surpassing the Limits of the ab initio World without leaving it behind:
https://www.materialsdesign.com/webinars/recorded/mlp-surpassing-the-limits-of-ab-initio

On-the-fly Machine Learning Forcefields with MedeA VASP:
https://www.materialsdesign.com/webinars/recorded/MedeA-Training-On-the-fly-Machine-Learning-Forcefields-with-MedeA-VASP

Δ-Machine Learning Beyond DFT: from Phase Transitions to Quantum Paraelectricity and CO Adsorption:
https://www.materialsdesign.com/webinars/recorded/Delta-Machine-Learning-Beyond-DFT%3A-from-Phase-Transitions-to-Quantum-Paraelectricity-and-CO-Adsorption

Training: Generating and Applying Machine-Learned Potentials with MedeA:
https://www.materialsdesign.com/webinars/recorded/UGMtraining-Generating-and-Applying-Machine-Learned-Potentials-with-MedeA

Atomistic Simulations with High-Dimensional Neural Network Potentials:
https://www.materialsdesign.com/webinars/recorded/Atomistic-Simulations-with-High-Dimensional-Neural-Network-Potentials

Atomistic-scale simulations of realistic, complex, reactive materials: the ReaxFF reactive force field and its industrial and academic applications:
https://www.materialsdesign.com/webinars/recorded/ReaxFF-reactive-force-field

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Materials Design UGM 2023

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October 9-11, 2023

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Professor Georg Kresse (University of Vienna, Austria)

Professor Michele Parrinello (Italian Institute of Technology, Italy; ETH Zurich, Switzerland)

Professor Saad Fahaid Khalaf Al-Afnan (KFUPM, Saudi Arabia)

Anders Engström (CEO, Thermo-Calc, Sweden)

Professor Phuti Ngoepe (University of Limpopo, South Africa)

Professor Ralf Drautz (Ruhr-Universität Bochum, Germany)

Kyle Starkey, Leonid Kahle: (Materials Design, USA)

Edwin Knobbe, René Windiks: (BMW, Germany; Materials Design, USA)

Thomas Pigeon (French Institute of Petroleum Energies - IFPEN, France)

Materials Design UGM 2023

Vienna, Austria

Monday, October 9, 2023

More information
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Question and Answer Session

Dr. Garrett Tow

Materials Design

Questions about Materials Design Webinars

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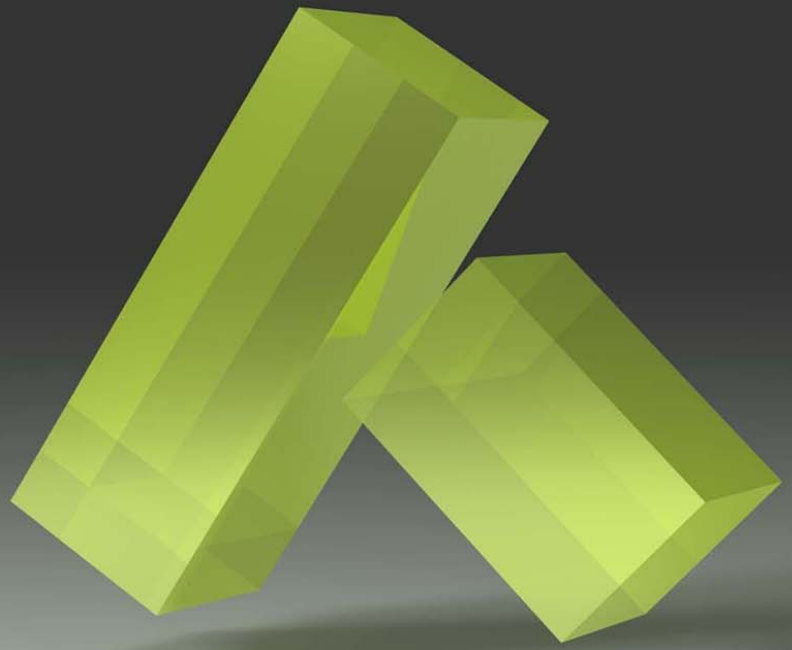


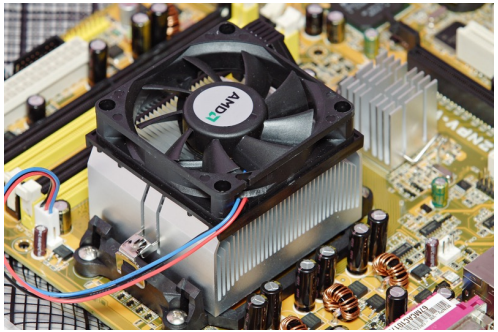
MedeA

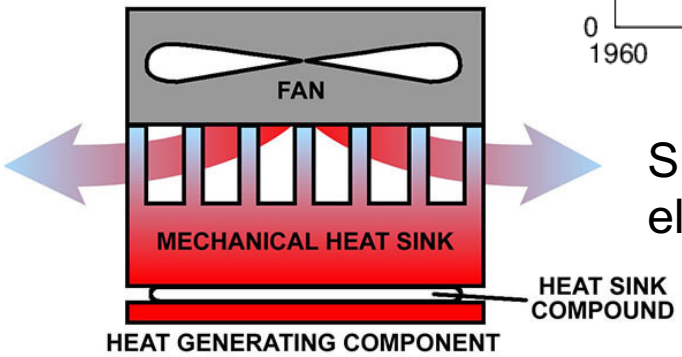
Innovation by Simulation

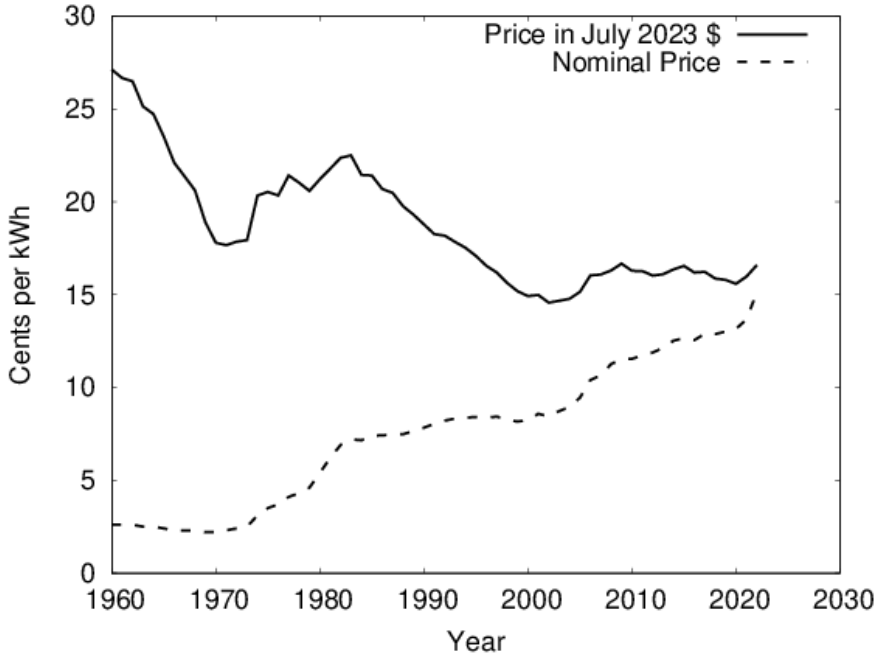
The Price of Power

$P = C * V^2 * F$

P = Power consumption
C = Capacitance switched per clock cycle
V = Voltage
F = Frequency (cycles per second)

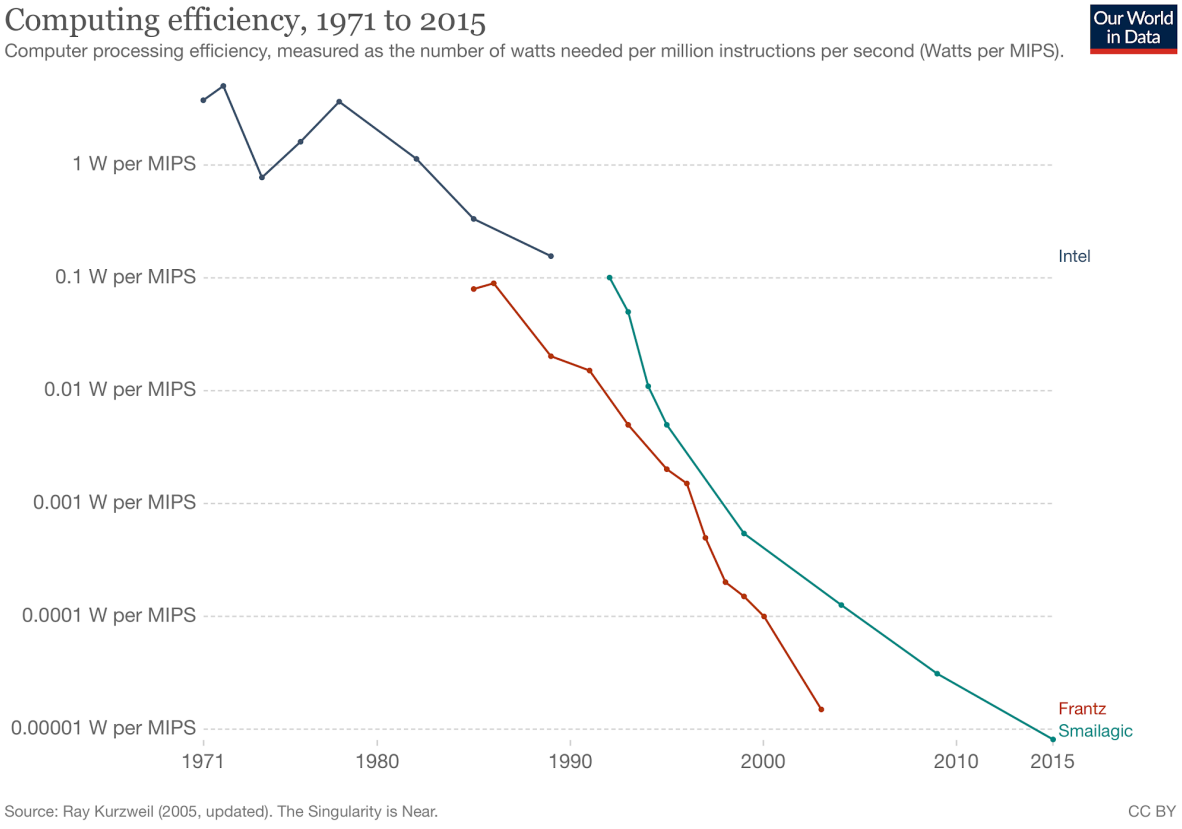






Since 1960, the real price of electricity has dropped by ~40%.

Watts per Million Instructions per Second



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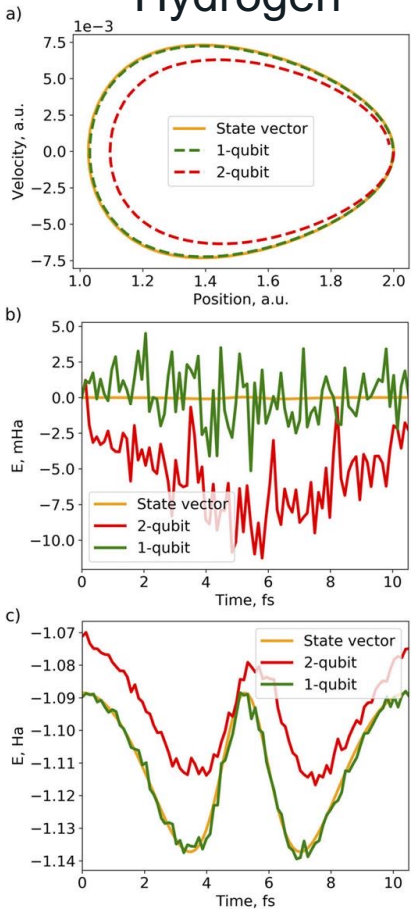
What About Quantum Computing?

- More applicable to QM calculations; classical computing better for classical potentials.
- QM calculations could *eventually* be accelerated by quantum computing.
  - Accelerates the development or on-the-fly refinement of machine-learned potentials.

"Today's quantum computers are generally in the range of 5-100 qubits, whereas solving Shor's algorithm or simulating a useful molecule will require thousands to millions of qubits. Another major issue is fidelity. Due to the sensitive and analog nature of quantum computers, they are inherently error-prone, and errors in each logical operation accumulate through the duration of a quantum circuit. The error rates of today's quantum computers limit them to running only a few logical operations with consistency before accumulated errors lead to a random result. This is impractical as applications with known algorithmic speedups require thousands to millions of operations to be run."

https://resources.nvidia.com/en-us-hpc-ebooks/hpc-for-the-age-of-ai?xs=409135

Hydrogen



This potential energy shift in the two-qubit system is easily explained by the hardware noise from four CNOT gates, which are not present in the one-qubit system; each of the CNOT gates has an error rate on the order of 1%.

D.A. Fedorov et al. *Ab initio* Molecular Dynamics on Quantum Computers. *J. Chem. Phys.* **2021**, *154*, 164103.

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