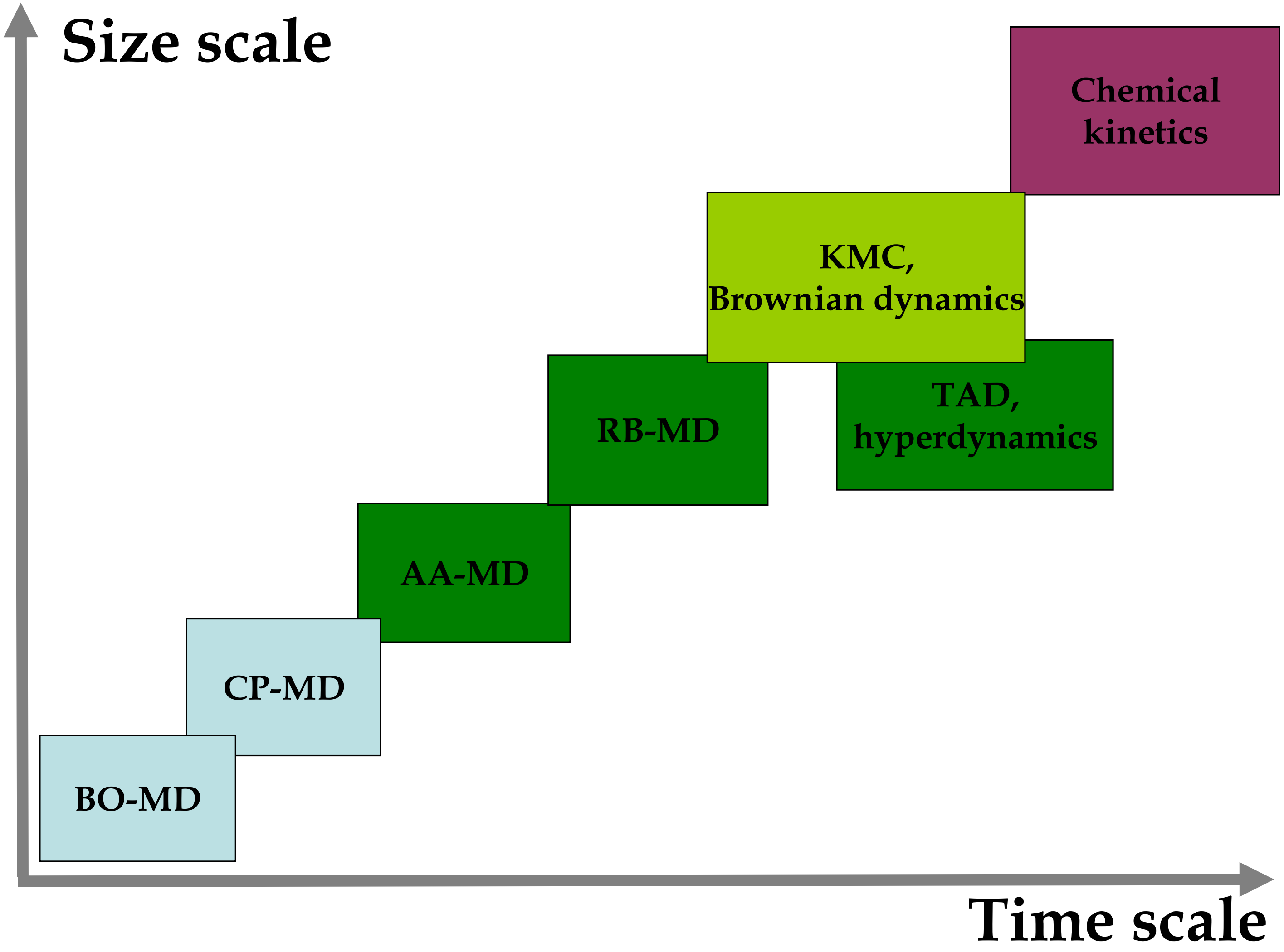
Computational Materials Theory and Methods

Lecture 2:
Classical Molecular Mechanics

Alexey V. Akimov
University at Buffalo, SUNY

Time and size scales for different methods of dynamics



Size scale

Chemical kinetics

KMC,
Brownian dynamics

TAD,
hyperdynamics

RB-MD

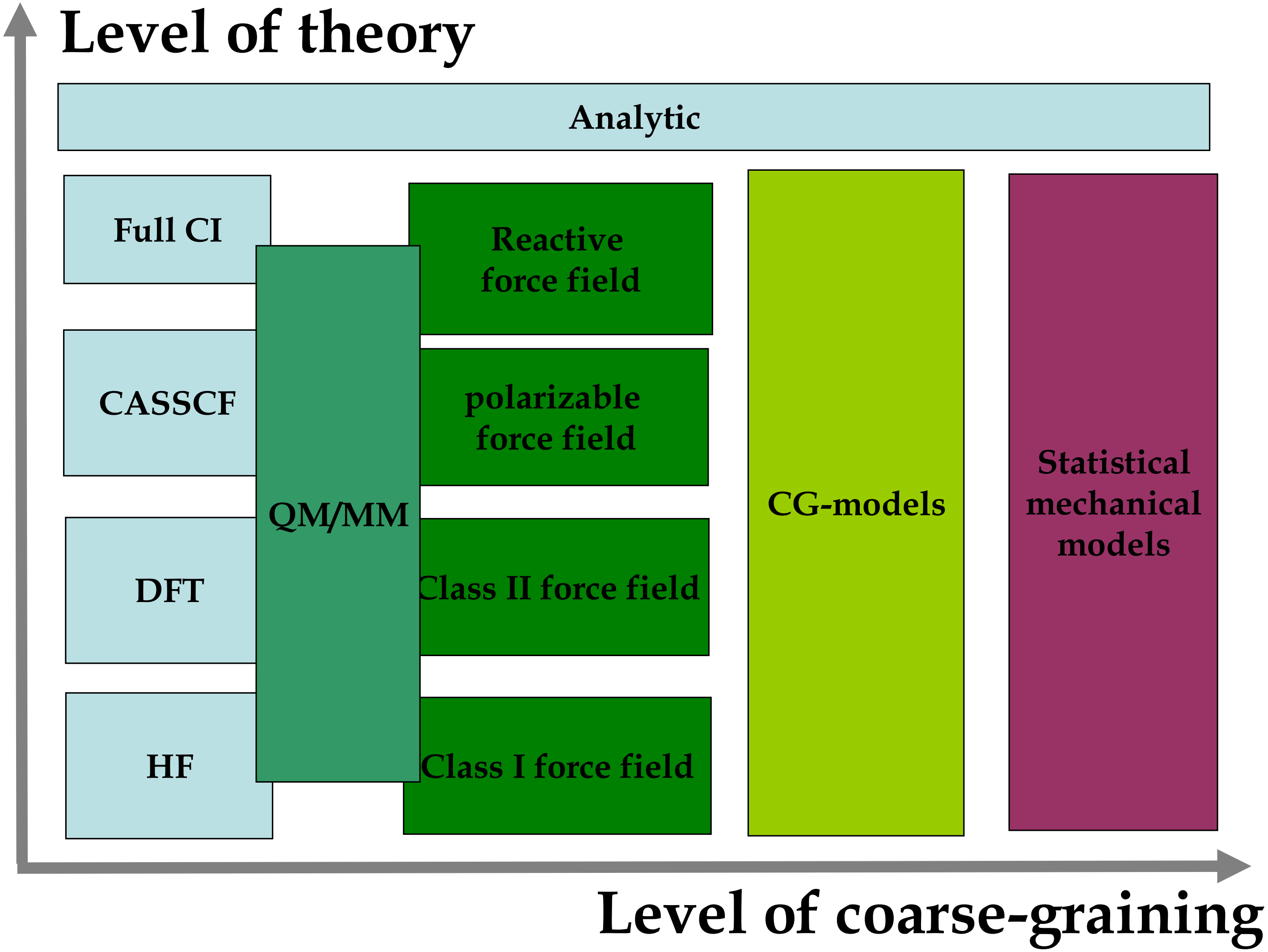
AA-MD

CP-MD

BO-MD

Time scale

Accuracy and methodology

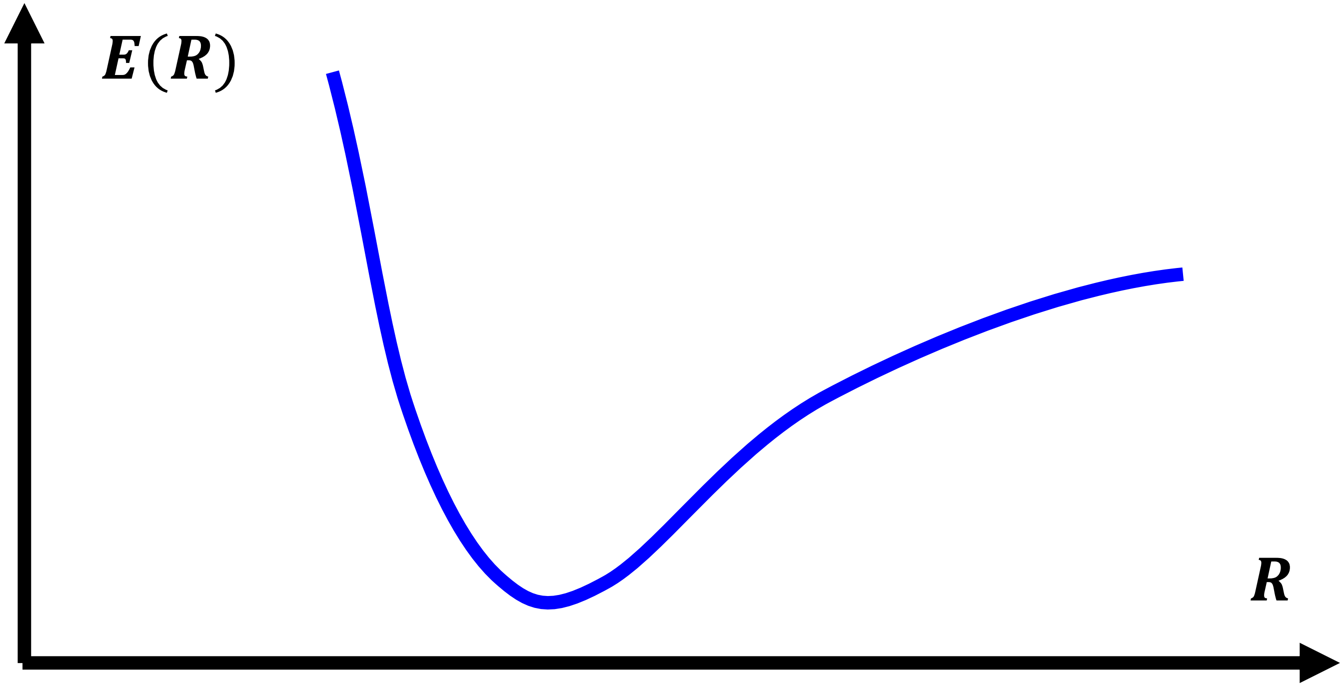


Potential energy surface (PES)

Stationary Schrodinger Equation

$$\hat{H}\Psi(r;R) = E(R)\Psi(\mathbf{r};\mathbf{R})$$

- Computationally **expensive**!
- Can we **fit the curves** with a simple analytical function?



Within the Born-Oppenheimer Approximation

Force fields (Molecular Mechanics)

Force field

functional

parameters

$$f(q_1, q_2, ..\, q_N; P_1, P_2, \ldots P_M)$$

- Numerically efficient
- Has suitable derivatives
- Is continuous
- Physically meaningfull

- Based on atom and interaction types
- Minimal amount is desirable
- Transferable or system-specific
- Reproduce ab initio or experiment (thermodynamic properties, spectra, chemical reactivity, etc.)

$$E_{tot} = E_{bonded} + E_{non-bonded}$$

describes covalent bonding

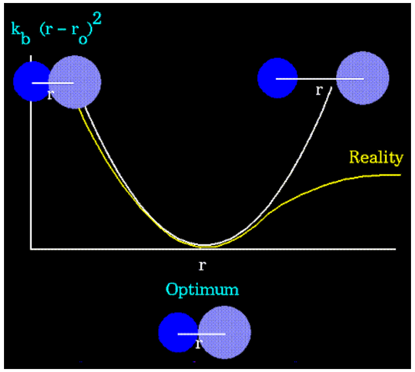
non-covalent interactions

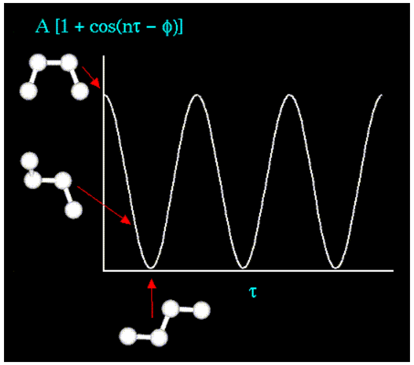
Bonded interactions

$$E_{bonded} = E_{bonds} + E_{angles} + E_{dihedrals} + E_{oop}$$

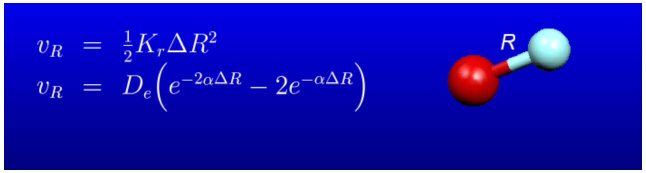
In quantum mechanics: bonds are everywhere “bond order”

In molecular mechanics: bonded atoms must be specified by the user



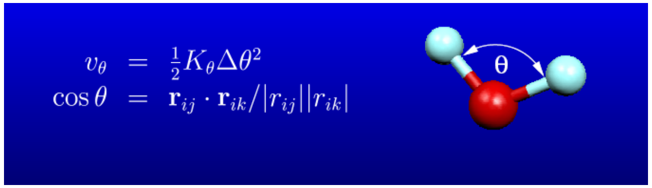


bonded, 2-particle: bond stretching



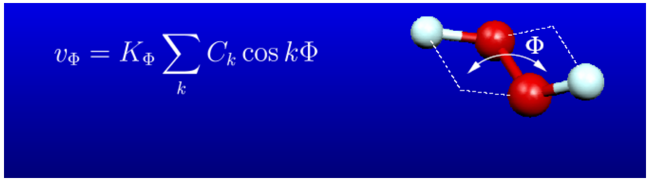
$$\begin{aligned} v_R &= \tfrac{1}{2} K_r \Delta R^2 \\ v_R &= D_e\left(e^{-2\alpha\Delta R} - 2e^{-\alpha\Delta R}\right) \end{aligned}$$

bonded, 3-particle: angle bending



$$\begin{aligned} v_\theta &= \tfrac{1}{2} K_\theta \Delta\theta^2 \\ \cos\theta &= \mathbf{r}_{ij} \cdot \mathbf{r}_{ik} / |r_{ij}||r_{ik}| \end{aligned}$$

bonded, 4-particle: torsion/dihedral, out-of-plane/improper dihedrals



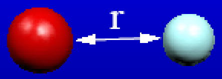
$$v_\Phi = K_\Phi \sum_k C_k \cos k\Phi$$

Non-bonded interactions

Charges are usually constant,
but there are **geometry-dependent charge schemes** (e.g. qEQ)
Accounts for the polarizability

$$v_{disp}(r_i, r_j) = -\frac{C_6}{|\mathbf{r}_i - \mathbf{r}_j|^6}$$

$$v_{el}(r_i, r_j) = \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$

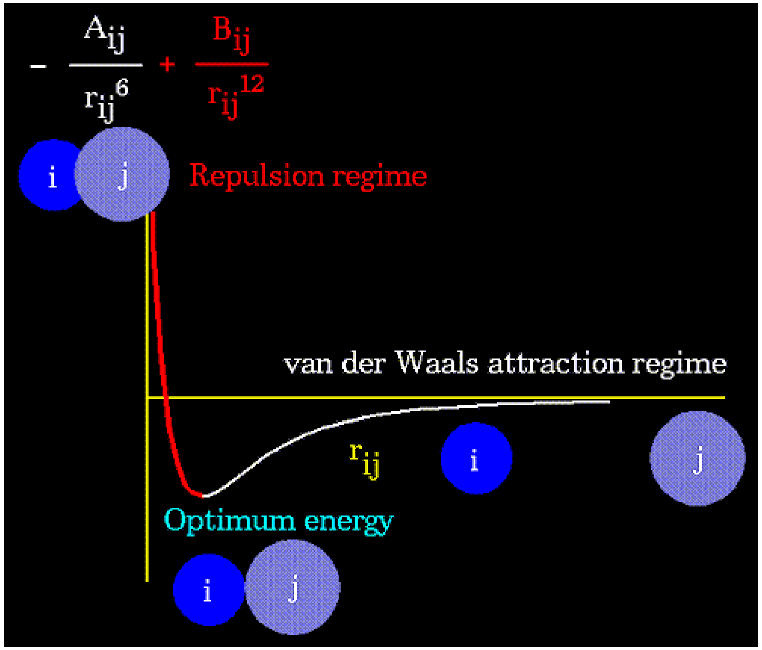


Rappe, A. K.; Goddard, W. A.
J. Phys. Chem. **1991**, *95*, 3358–3363.

Ogawa, T.; Kurita, N.; Sekino, H.; Kitao, O.; Tanaka, S.
Chem. Phys. Lett. **2004**, *397*, 382–387.

Chen, J.; Martinez, T. J. *Chem. Phys. Lett.* **2007**, *438*, 315–320.

non-bonded 2-particle vdw and Coulomb interactions



$$-\frac{A_{ij}}{r_{ij}^{6}} + \frac{B_{ij}}{r_{ij}^{12}}$$

In periodic systems, the lattice summation methods are used, such as **Ewald sum** method.

Karasawa, N.; Goddard III, W. A.
J. Phys. Chem. **1989**, *93*, 7320–7327.

Atom types

Universal FF (UFF)

Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard III, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.

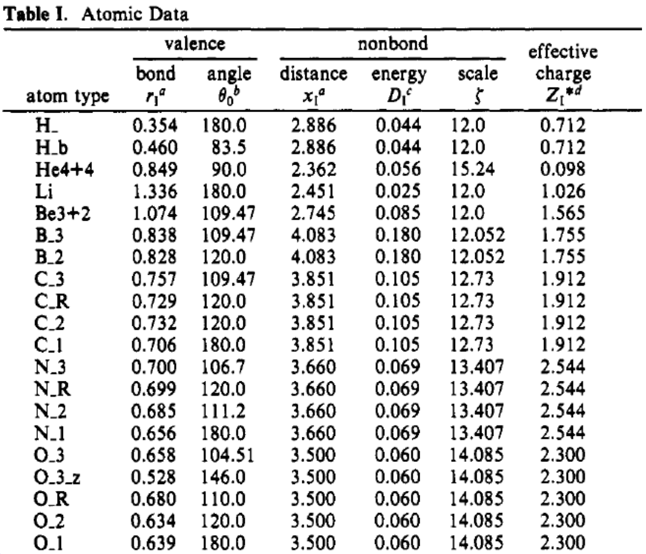


Table I. Atomic Data

	valence		nonbond			
atom type	bond $r_I{}^a$	angle $\theta_0{}^b$	distance $x_I{}^a$	energy $D_I{}^c$	scale ζ	effective charge $Z_I{}^{*d}$
H_	0.354	180.0	2.886	0.044	12.0	0.712
H_b	0.460	83.5	2.886	0.044	12.0	0.712
He4+4	0.849	90.0	2.362	0.056	15.24	0.098
Li	1.336	180.0	2.451	0.025	12.0	1.026
Be3+2	1.074	109.47	2.745	0.085	12.0	1.565
B_3	0.838	109.47	4.083	0.180	12.052	1.755
B_2	0.828	120.0	4.083	0.180	12.052	1.755
C_3	0.757	109.47	3.851	0.105	12.73	1.912
C_R	0.729	120.0	3.851	0.105	12.73	1.912
C_2	0.732	120.0	3.851	0.105	12.73	1.912
C_1	0.706	180.0	3.851	0.105	12.73	1.912
N_3	0.700	106.7	3.660	0.069	13.407	2.544
N_R	0.699	120.0	3.660	0.069	13.407	2.544
N_2	0.685	111.2	3.660	0.069	13.407	2.544
N_1	0.656	180.0	3.660	0.069	13.407	2.544
O_3	0.658	104.51	3.500	0.060	14.085	2.300
O_3_z	0.528	146.0	3.500	0.060	14.085	2.300
O_R	0.680	110.0	3.500	0.060	14.085	2.300
O_2	0.634	120.0	3.500	0.060	14.085	2.300
O_1	0.639	180.0	3.500	0.060	14.085	2.300

Generalized Amber FF

Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. *J. Comput. Chem.* **2004**, *25*, 1157–1174.

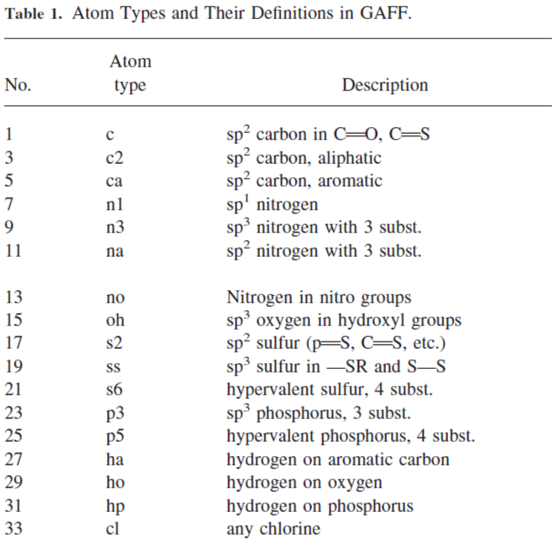


Table 1. Atom Types and Their Definitions in GAFF.

No.	Atom type	Description
1	c	sp^2 carbon in C═O, C═S
3	c2	sp^2 carbon, aliphatic
5	ca	sp^2 carbon, aromatic
7	n1	sp^1 nitrogen
9	n3	sp^3 nitrogen with 3 subst.
11	na	sp^2 nitrogen with 3 subst.
13	no	Nitrogen in nitro groups
15	oh	sp^3 oxygen in hydroxyl groups
17	s2	sp^2 sulfur (p═S, C═S, etc.)
19	ss	sp^3 sulfur in —SR and S—S
21	s6	hypervalent sulfur, 4 subst.
23	p3	sp^3 phosphorus, 3 subst.
25	p5	hypervalent phosphorus, 4 subst.
27	ha	hydrogen on aromatic carbon
29	ho	hydrogen on oxygen
31	hp	hydrogen on phosphorus
33	cl	any chlorine

MERCK FF 94

Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 490–519.

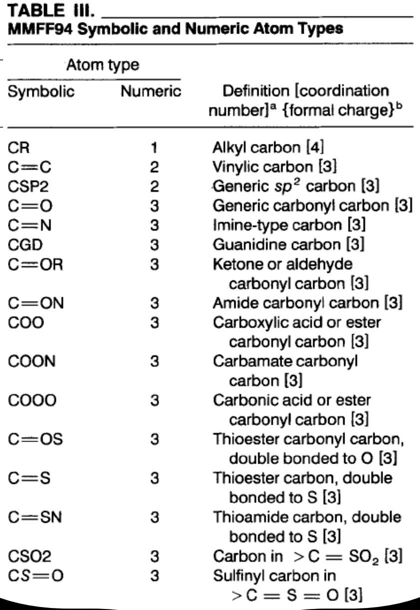


TABLE III.
MMFF94 Symbolic and Numeric Atom Types

Atom type		
Symbolic	Numeric	Definition [coordination number]ᵃ {formal charge}ᵇ
CR	1	Alkyl carbon [4]
C═C	2	Vinylic carbon [3]
CSP2	2	Generic *sp*^{2} carbon [3]
C═O	3	Generic carbonyl carbon [3]
C═N	3	Imine-type carbon [3]
CGD	3	Guanidine carbon [3]
C═OR	3	Ketone or aldehyde carbonyl carbon [3]
C═ON	3	Amide carbonyl carbon [3]
COO	3	Carboxylic acid or ester carbonyl carbon [3]
COON	3	Carbamate carbonyl carbon [3]
COOO	3	Carbonic acid or ester carbonyl carbon [3]
C═OS	3	Thioester carbonyl carbon, double bonded to O [3]
C═S	3	Thioester carbon, double bonded to S [3]
C═SN	3	Thioamide carbon, double bonded to S [3]
CSO2	3	Carbon in $>C=SO_2$ [3]
C*S*═O	3	Sulfinyl carbon in $>C=S=O$ [3]

General purpose FFs

Specialized FFs

Parameterization: Specialized FFs

MERCK FF 94

- Accurate
- Focus on organic molecules
- Many parameters!

$$E_{MMFF} = \sum EB_{ij} + \sum EA_{ijk} + \sum EBA_{ijk} + \sum EOOP_{ijk;l} + \sum ET_{ijkl} + \sum EvdW_{ij} + \sum EQ_{ij}$$

$$EB_{ij} = 143.9325 \frac{kb_{IJ}}{2} \Delta r_{ij}^2 \times \left(1 + cs\, \Delta r_{ij} + 7/12 cs^2 \Delta r_{ij}^2\right)$$

$$EA_{ijk} = 0.043844 \frac{ka_{IJK}}{2} \Delta \vartheta_{ijk}^2 (1 + cb\, \Delta \vartheta_{ijk})$$

$$EBA_{ijk} = 2.51210 (kba_{IJK}\, \Delta r_{ij} + kba_{KJI}\, \Delta r_{kj})\, \Delta \vartheta_{ijk}$$

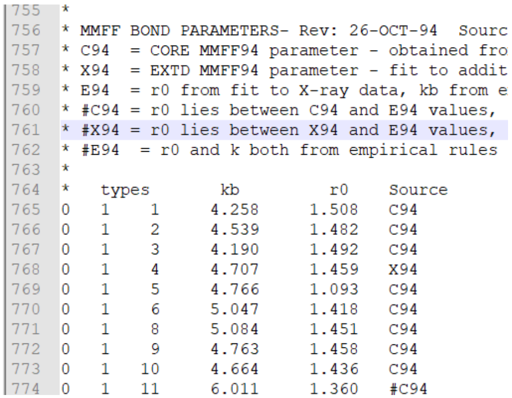
$$EOOP_{ijk;l} = 0.043844 \frac{koop_{IJK:L}}{2} \chi_{ijk;l}^2$$

$$ET_{ijkl} = 0.5 (V_1 (1 + \cos \Phi) + V_2 (1 - \cos 2\Phi) + V_3 (1 + \cos 3\Phi))$$

$$E_{vdW_{ij}} = \varepsilon_{IJ} \left(\frac{1.07 R_{IJ}^*}{R_{ij} + 0.07 R_{IJ}^*} \right)^7 \left(\frac{1.12 R_{IJ}^{*7}}{R_{ij}^7 + 0.12 R_{IJ}^{*7}} - 2 \right)$$

$$EQ_{ij} = 332.0716 q_i q_j / \left(D (R_{ij} + \delta)^n \right)$$

$$q_i = q_I^0 + \sum \omega_{KI}$$



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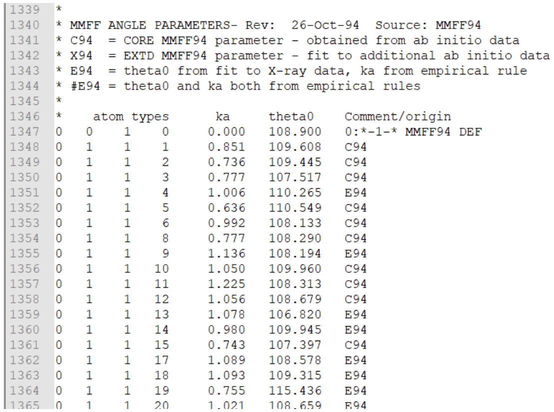
*
* MMFF BOND PARAMETERS- Rev: 26-OCT-94  Sourc
* C94  = CORE MMFF94 parameter - obtained fro
* X94  = EXTD MMFF94 parameter - fit to addit
* E94  = r0 from fit to X-ray data, kb from e
* #C94 = r0 lies between C94 and E94 values,
* #X94 = r0 lies between X94 and E94 values,
* #E94  = r0 and k both from empirical rules
*
*   types       kb        r0    Source
0   1    1     4.258     1.508   C94
0   1    2     4.539     1.482   C94
0   1    3     4.190     1.492   C94
0   1    4     4.707     1.459   X94
0   1    5     4.766     1.093   C94
0   1    6     5.047     1.418   C94
0   1    8     5.084     1.451   C94
0   1    9     4.763     1.458   C94
0   1   10     4.664     1.436   C94
0   1   11     6.011     1.360   #C94
```



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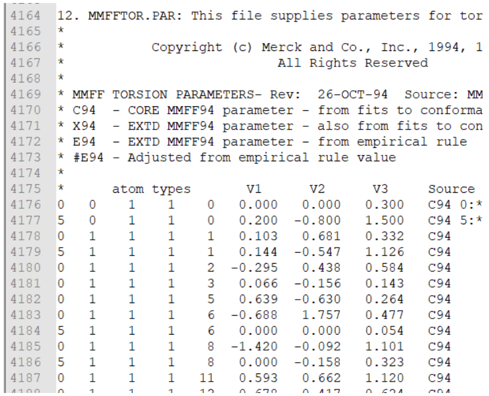
*
* MMFF ANGLE PARAMETERS- Rev:  26-Oct-94  Source: MMFF94
* C94  = CORE MMFF94 parameter - obtained from ab initio data
* X94  = EXTD MMFF94 parameter - fit to additional ab initio data
* E94  = theta0 from fit to X-ray data, ka from empirical rule
* #E94 = theta0 and ka both from empirical rules
*
*    atom types       ka     theta0    Comment/origin
0   0    1    0     0.000   108.900   0:*-1-* MMFF94 DEF
0   1    1    1     0.851   109.608   C94
0   1    1    2     0.736   109.445   C94
0   1    1    3     0.777   107.517   C94
0   1    1    4     1.006   110.265   E94
0   1    1    5     0.636   110.549   C94
0   1    1    6     0.992   108.133   C94
0   1    1    8     0.777   108.290   C94
0   1    1    9     1.136   108.194   E94
0   1    1   10     1.050   109.960   C94
0   1    1   11     1.225   108.313   C94
0   1    1   12     1.056   108.679   C94
0   1    1   13     1.078   106.820   E94
0   1    1   14     0.980   109.945   E94
0   1    1   15     0.743   107.397   C94
0   1    1   17     1.089   108.578   E94
0   1    1   18     1.093   109.315   E94
0   1    1   19     0.755   115.436   E94
0   1    1   20     1.021   108.659   E94
```



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12. MMFFTOR.PAR: This file supplies parameters for tor
*
*             Copyright (c) Merck and Co., Inc., 1994, 1
*                                 All Rights Reserved
*
* MMFF TORSION PARAMETERS- Rev:  26-OCT-94  Source: MM
* C94  - CORE MMFF94 parameter - from fits to conforma
* X94  - EXTD MMFF94 parameter - also from fits to con
* E94  - EXTD MMFF94 parameter - from empirical rule
* #E94 - Adjusted from empirical rule value
*
*       atom types        V1      V2      V3     Source
0   0   1   1   0   0.000   0.000   0.300   C94 0:*
5   0   1   1   0   0.200  -0.800   1.500   C94 5:*
0   1   1   1   1   0.103   0.681   0.332   C94
5   1   1   1   1   0.144  -0.547   1.126   C94
0   1   1   1   2  -0.295   0.438   0.584   C94
0   1   1   1   3   0.066  -0.156   0.143   C94
0   1   1   1   5   0.639  -0.630   0.264   C94
0   1   1   1   6  -0.688   1.757   0.477   C94
5   1   1   1   6   0.000   0.000   0.054   C94
0   1   1   1   8  -1.420  -0.092   1.101   C94
5   1   1   1   8   0.000  -0.158   0.323   C94
0   1   1   1  11   0.593   0.662   1.120   C94
```

Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 490–519.

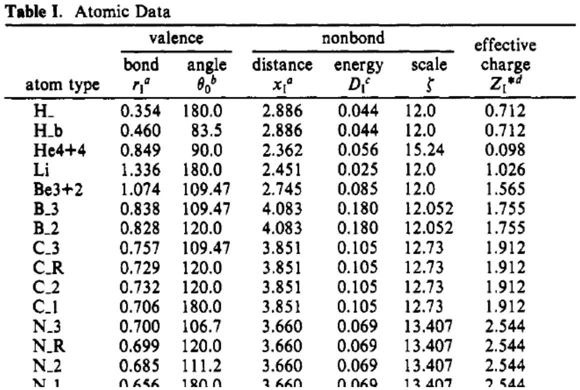
Parameterization: General-purpose FFs

Universal FF (UFF)

- **Not so accurate!**
- **General purpose (e.g. organometallic)**
- **Way fewer parameters!**

Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard III, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.

$$E = E_R + E_\theta + E_\phi + E_\omega + E_{\mathrm{vdw}} + E_{\mathrm{el}}$$



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N_1	0.656	180.0	3.660	0.069	13.407	2.544

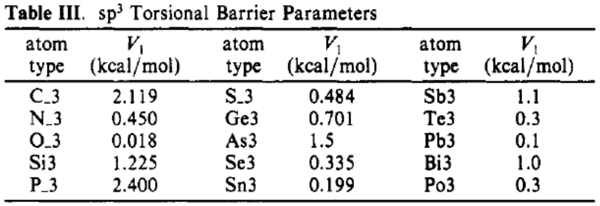


Table III. sp^3 Torsional Barrier Parameters

atom type	V_1 (kcal/mol)	atom type	V_1 (kcal/mol)	atom type	V_1 (kcal/mol)
C_3	2.119	S_3	0.484	Sb3	1.1
N_3	0.450	Ge3	0.701	Te3	0.3
O_3	0.018	As3	1.5	Pb3	0.1
Si3	1.225	Se3	0.335	Bi3	1.0
P_3	2.400	Sn3	0.199	Po3	0.3

$$E_R = \tfrac{1}{2}k_{IJ}(r - r_{IJ})^2$$

$$E_R = D_{IJ}[e^{-\alpha(r-r_{IJ})} - 1]^2$$

$$r_{IJ} = r_I + r_J + r_{BO} + r_{EN}$$

$$k_{IJ} = \left(\frac{\partial^2 E_r}{\partial R^2}\right)_0 = 2G\,\frac{Z_I{}^* Z_J{}^*}{R^3} = 664.12\frac{Z_I{}^* Z_J{}^*}{r_{IJ}{}^3}$$

$$r_{BO} = -\lambda(r_I + r_J)\ln(n)$$

$$r_{EN} = r_I r_J(\sqrt{\chi_I} - \sqrt{\chi_J})^2/(\chi_I r_I + \chi_J r_J)$$

$$E_\theta = \frac{K_{IJK}}{n^2}[1 - \cos(n\theta)]$$

$$E_\theta = K_{IJK}[C_0 + C_1 \cos\theta + C_2 \cos 2\theta]$$

$$E_\phi = \tfrac{1}{2}V_\phi[1 - \cos n\phi_0 \cos n\phi]$$

$$V_{sp^2} = 5\sqrt{U_j U_k}(1 + 4.18 \ln(\mathrm{BO}_{jk}))$$

$$E_{\mathrm{vdw}} = D_{IJ}\left\{-2\left[\frac{x_{IJ}}{x}\right]^6 + \left[\frac{x_{IJ}}{x}\right]^{12}\right\}$$

$$x_{IJ} = \sqrt{x_I \times x_J}$$

$$D_{IJ} = (D_I D_J)^{1/2}$$

$$E_{\mathrm{el}} = 332.0637(Q_i Q_j/\epsilon R_{ij})$$

Polarization: Charge equilibration method

Rappe, A. K.; Goddard, W. A. *J. Phys. Chem.* **1991**, *95*, 3358–3363.

$$E_A(Q) = E_{A0} + Q_A\left(\frac{\partial E}{\partial Q}\right)_{A0} + \tfrac{1}{2}Q_A^2\left(\frac{\partial^2 E}{\partial Q^2}\right)_{A0} + \ldots$$

$$E_A(+1) = E_{A0} + \left(\frac{\partial E}{\partial Q}\right)_{A0} + \tfrac{1}{2}\left(\frac{\partial^2 E}{\partial Q^2}\right)_{A0}$$

$$E_A(0) = E_{A0}$$

$$E_A(-1) = E_{A0} - \left(\frac{\partial E}{\partial Q}\right)_{A0} + \tfrac{1}{2}\left(\frac{\partial^2 E}{\partial Q^2}\right)_{A0}$$

$$\left(\frac{\partial E}{\partial Q}\right)_{A0} = \tfrac{1}{2}(\mathrm{IP} + \mathrm{EA}) = \chi_A^0$$

electronegativity

$$\left(\frac{\partial^2 E}{\partial Q}\right)_{A0} = \mathrm{IP} - \mathrm{EA}$$

$$\mathrm{IP} - \mathrm{EA} = J_{AA}^0$$

self-Coloumb (idempotential)

TABLE I: Atomic Parameters[a]

element	χ, eV	J, eV	R, Å	ζ, au
Li	3.006	4.772	1.557	0.4174
C	5.343	10.126	0.759	0.8563
N	6.899	11.760	0.715	0.9089
O	8.741	13.364	0.669	0.9745
F	10.874	14.948	0.706	0.9206
Na	2.843	4.592	2.085	0.4364
Si	4.168	6.974	1.176	0.7737
P	5.463	8.000	1.102	0.8257
S	6.928	8.972	1.047	0.8690
Cl	8.564	9.892	0.994	0.9154
K	2.421	3.84	2.586	0.4524
Br	7.790	8.850	1.141	1.0253
Rb	2.331	3.692	2.770	0.5162
I	6.822	7.524	1.333	1.0726
Cs	2.183	3.422	2.984	0.5663
H	4.5280[b]	13.8904[b]	0.371	1.0698

$$E_A(Q) = E_{A0} + \chi_A^0 Q_A + \tfrac{1}{2}J_{AA}^0 Q_A^2$$

$$E_Q(Q_1 \ldots Q_N) = \sum_A (E_{A0} + \chi_A^0 Q_A) + \tfrac{1}{2}\sum_{A,B} Q_A Q_B J_{AB}$$

$$\chi_A(Q_1 \ldots Q_N) = \frac{\partial E}{\partial Q_A} = \chi_A^0 + \sum_B J_{AB} Q_B$$

$$\chi_1 = \chi_2 = \ldots = \chi_N$$

$$Q_{\mathrm{tot}} = \sum_{i=1}^{N} Q_i$$

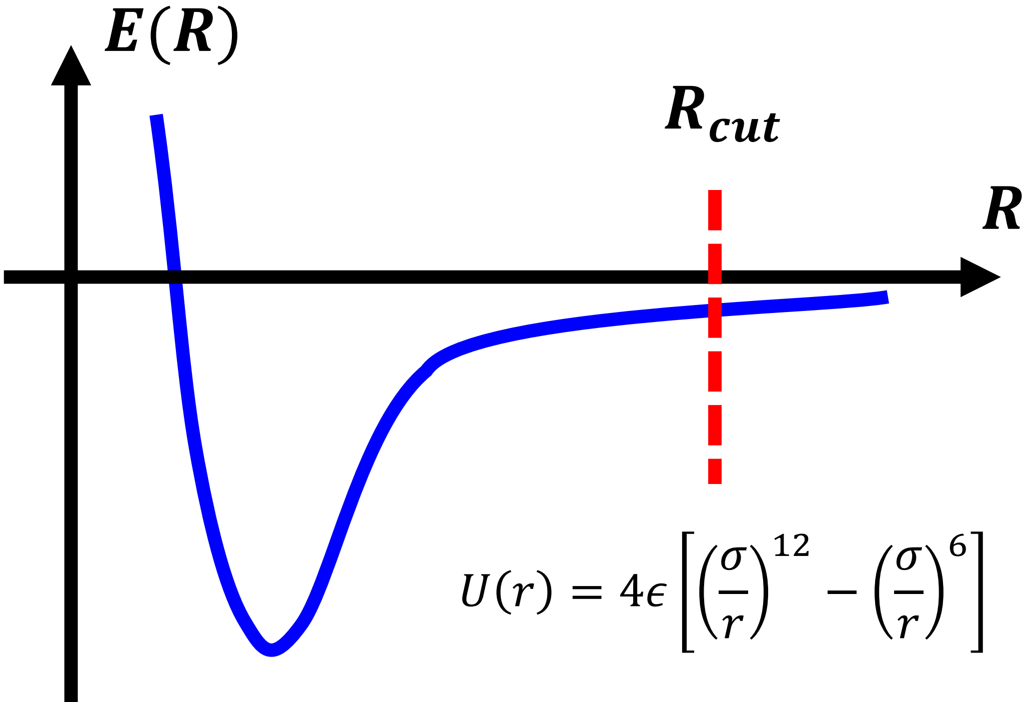
Handling vdW interactions with PBC

$$U(\{\boldsymbol{R}\}, \boldsymbol{L_x}, \boldsymbol{L_y}, \boldsymbol{L_z}) = \frac{1}{2} \sum_{n_x, n_y n_z} \sum_{i,j} U(|\boldsymbol{R_i} - \boldsymbol{R_j} - \boldsymbol{L_x} n_x - \boldsymbol{L_y} n_y - \boldsymbol{L_z} n_z|)$$

$\boldsymbol{L_x}, \boldsymbol{L_y}, \boldsymbol{L_z}$	Simulation cell vectors
$\{\boldsymbol{R}\}$	Atomic coordinates

- All combinations of integers n_x, n_y, n_z
- **That is an infinite number of cells!**
- Exclude self-interactions

Dealing with the infinite number of terms

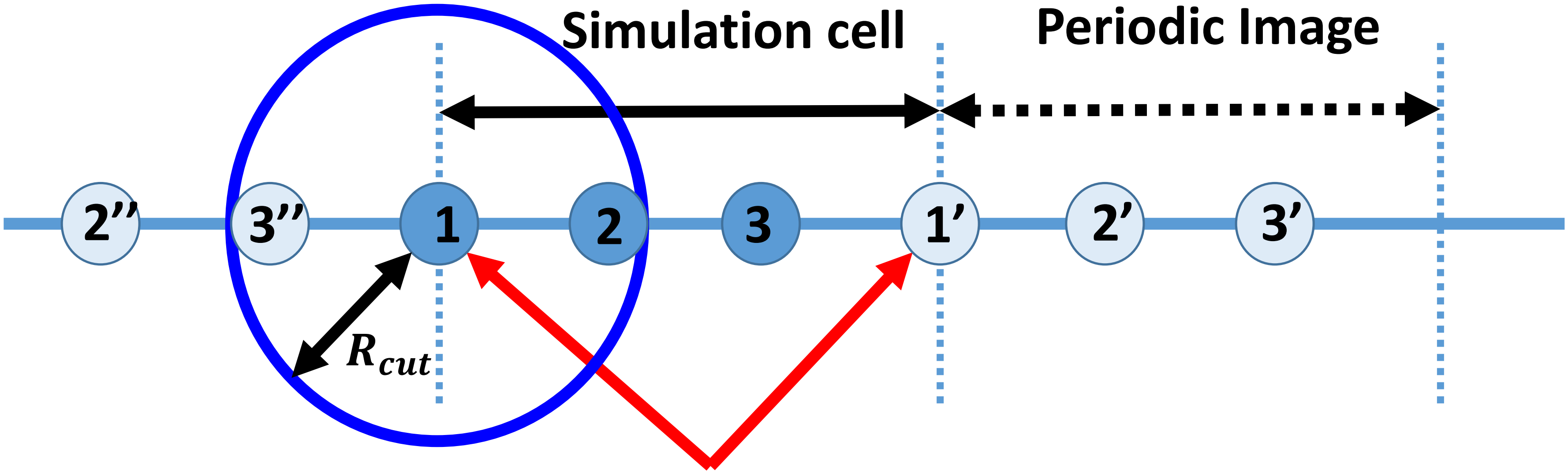


$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Van der Walls interactions are **short-ranged**

Disregard all the interactions for the particles separated more than by R_{cut}

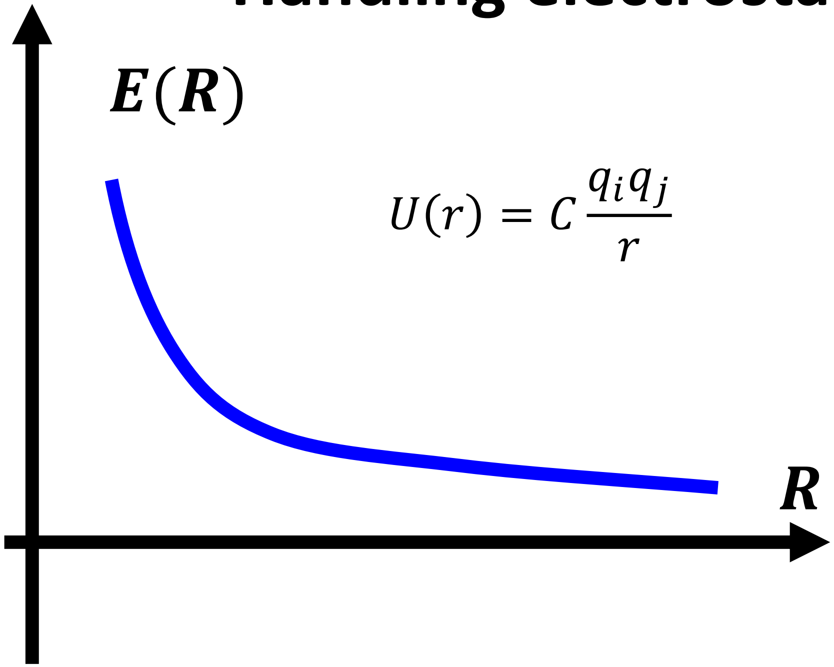
Handling non-bonded interactions with PBC



Same atom/molecule

If simulation cell size L is larger than $2R_{cut}$, it is sufficient to have only one shell of periodic images

Handling electrostatic interactions with PBC



$$U(r) = C\frac{q_i q_j}{r}$$

Electrostatic interactions
are **long-ranged**

Can not use the cutoff technique

Direct summation is slowly converging

$$\frac{1}{r} = \frac{\mathrm{erf}\,c(r)}{r} + \frac{1 - erf\,c(r)}{r}$$

Converges fast
in real space

Converges fast
in reciprocal space

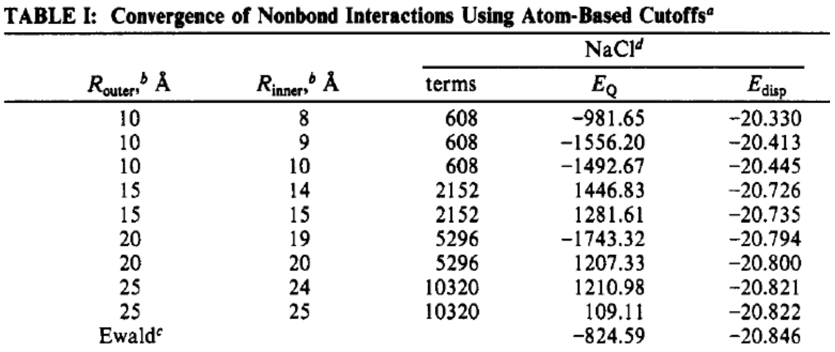
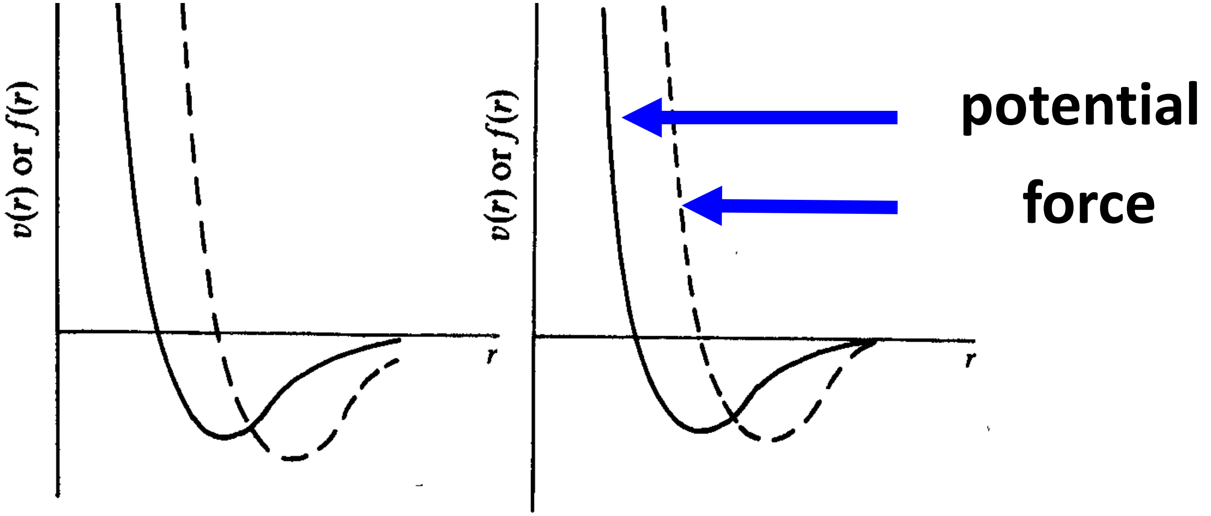


TABLE I: Convergence of Nonbond Interactions Using Atom-Based Cutoffs[a]

		NaCl[d]		
R_{outer},[b] Å	R_{inner},[b] Å	terms	E_{Q}	E_{disp}
10	8	608	−981.65	−20.330
10	9	608	−1556.20	−20.413
10	10	608	−1492.67	−20.445
15	14	2152	1446.83	−20.726
15	15	2152	1281.61	−20.735
20	19	5296	−1743.32	−20.794
20	20	5296	1207.33	−20.800
25	24	10320	1210.98	−20.821
25	25	10320	109.11	−20.822
Ewald[c]			−824.59	−20.846

Continuity of forces



Truncation of the potential makes it discontinuous at $R = R_{cut}$.

Solution: shift by the corresponding energy

shifted potential

$$v^{\mathrm{S}}(r_{ij}) = \begin{cases} v(r_{ij}) - v_{\mathrm{c}} & r_{ij} \leqslant r_{\mathrm{c}} \\ 0 & r_{ij} > r_{\mathrm{c}} \end{cases}.$$

But the forces are still discontinuous!

Solution: Modify the potential such that the force is also continuous at $R = R_{cut}$

shifted-force potential

$$v^{\mathrm{SF}}(r_{ij}) = \begin{cases} v(r_{ij}) - v_{\mathrm{c}} - \left(\dfrac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}}\right)_{r_{ij}=r_{\mathrm{c}}} (r_{ij} - r_{\mathrm{c}}) & r_{ij} \leqslant r_{\mathrm{c}} \\ 0 & r_{ij} > r_{\mathrm{c}} \end{cases}$$

$$SW(R, R_{on}, R_{off}) = \begin{cases} 1, R < R_{on} \\ \left(\dfrac{R_{off} - R}{R_{off} - R_{on}}\right)^3 \left[1 + 3\left(\dfrac{R - R_{on}}{R_{off} - R_{on}}\right) + 6\left(\dfrac{R - R_{on}}{R_{off} - R_{on}}\right)^2\right], R_{on} \le R \le R_{off} \\ 0. R > R_{off} \end{cases}$$

Classification of the FFs

$$E(q_1, q_2, \dots) = E(0, 0, \dots) + \sum_{i \in DOF} \frac{\partial E}{\partial q_i} q_i + \frac{1}{2} \sum_{i,j \in DOF} \frac{\partial^2 E}{\partial q_i \partial q_j} q_i q_j + \cdots$$

Class I FFs: (diagonal terms): e.g. all bonds, all angles, etc.
Class II FFs: (+ cross-terms): e.g. add bond-angle interactions (e.g. like in MMFF94)

Bond-order ("reactive") FFs:

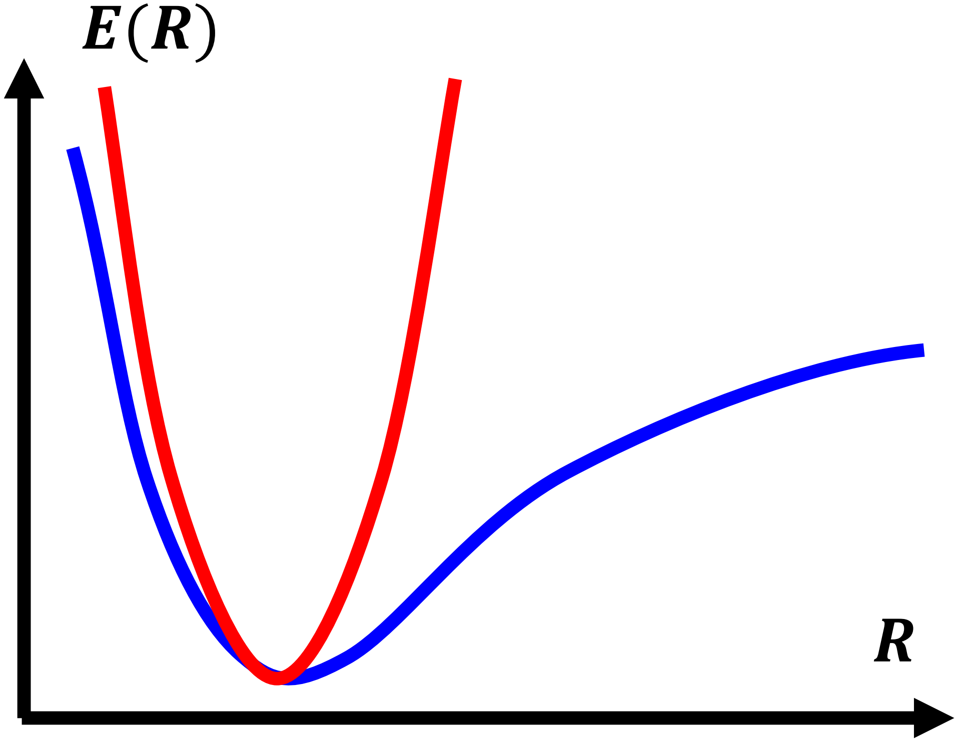
$$E(q_1, q_2, \dots) = \sum_{(i,j)} a_{ij} bo_{ij} + \sum_{\substack{(i_1,j_1),\\(i_2,j_2)}} a_{i_1 j_1} a_{2 j_2} bo_{i_1 j_1} bo_{i_2 j_2} + \cdots$$

$$bo_{ij} = Ae^{-\alpha r_{ij}}$$

Bond order

not the way it is defined in QM!

Reactive FFs



Why bond order?

Harmonic potential:

$$U(x) = \frac{1}{2}kx^2$$

$$U(x \to \infty) \to \infty$$

Bond breaking is impossible!

$$bo_{ij} = Ae^{-\alpha r_{ij}}$$

Morse potential:

$$U(x) = D\left[e^{-2\alpha\left(r_{ij}-r_{ij}^0\right)} - 2e^{-\alpha\left(r_{ij}-r_{ij}^0\right)}\right] = D[bo_{ij}^2 - 2bo_{ij}]$$

$$A = e^{\alpha r_{ij}^0}$$

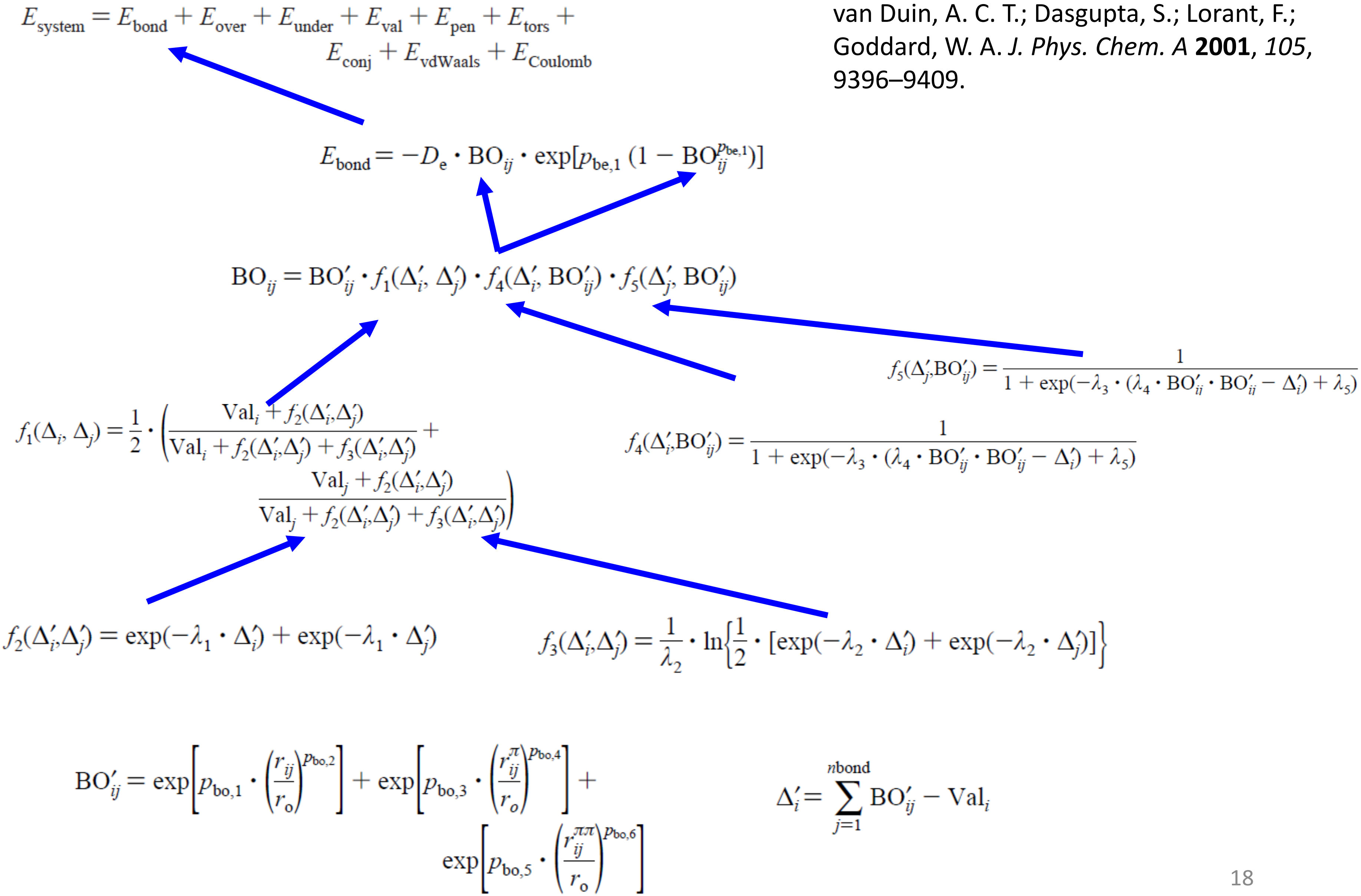
$$U(x \to \infty) \to 0$$

Physically correct limit: No interaction for infinitely separated atoms

Bond breaking is possible!

ReaxFF

van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A. *J. Phys. Chem. A* **2001**, *105*, 9396–9409.



$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

$$E_{\text{bond}} = -D_e \cdot \text{BO}_{ij} \cdot \exp\left[p_{\text{be},1}\left(1 - \text{BO}_{ij}^{p_{\text{be},1}}\right)\right]$$

$$\text{BO}_{ij} = \text{BO}'_{ij} \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, \text{BO}'_{ij}) \cdot f_5(\Delta'_j, \text{BO}'_{ij})$$

$$f_5(\Delta'_j, \text{BO}'_{ij}) = \frac{1}{1 + \exp(-\lambda_3 \cdot (\lambda_4 \cdot \text{BO}'_{ij} \cdot \text{BO}'_{ij} - \Delta'_j) + \lambda_5)}$$

$$f_1(\Delta_i, \Delta_j) = \frac{1}{2} \cdot \left(\frac{\text{Val}_i + f_2(\Delta'_i, \Delta'_j)}{\text{Val}_i + f_2(\Delta'_i, \Delta'_j) + f_3(\Delta'_i, \Delta'_j)} + \frac{\text{Val}_j + f_2(\Delta'_i, \Delta'_j)}{\text{Val}_j + f_2(\Delta'_i, \Delta'_j) + f_3(\Delta'_i, \Delta'_j)} \right)$$

$$f_4(\Delta'_i, \text{BO}'_{ij}) = \frac{1}{1 + \exp(-\lambda_3 \cdot (\lambda_4 \cdot \text{BO}'_{ij} \cdot \text{BO}'_{ij} - \Delta'_i) + \lambda_5)}$$

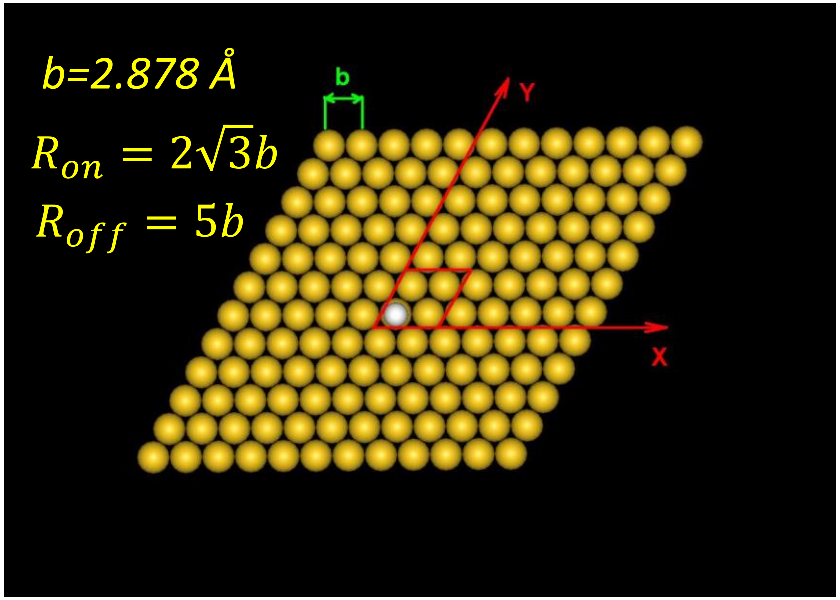
$$f_2(\Delta'_i, \Delta'_j) = \exp(-\lambda_1 \cdot \Delta'_i) + \exp(-\lambda_1 \cdot \Delta'_j)$$

$$f_3(\Delta'_i, \Delta'_j) = \frac{1}{\lambda_2} \cdot \ln\left\{\frac{1}{2} \cdot \left[\exp(-\lambda_2 \cdot \Delta'_i) + \exp(-\lambda_2 \cdot \Delta'_j)\right]\right\}$$

$$\text{BO}'_{ij} = \exp\left[p_{\text{bo},1} \cdot \left(\frac{r_{ij}}{r_o}\right)^{p_{\text{bo},2}}\right] + \exp\left[p_{\text{bo},3} \cdot \left(\frac{r_{ij}^{\pi}}{r_o}\right)^{p_{\text{bo},4}}\right] + \exp\left[p_{\text{bo},5} \cdot \left(\frac{r_{ij}^{\pi\pi}}{r_o}\right)^{p_{\text{bo},6}}\right]$$

$$\Delta'_i = \sum_{j=1}^{n\text{bond}} \text{BO}'_{ij} - \text{Val}_i$$

Constructing your own FF: Example 1



$b=2.878\ \text{Å}$

$R_{on} = 2\sqrt{3}b$

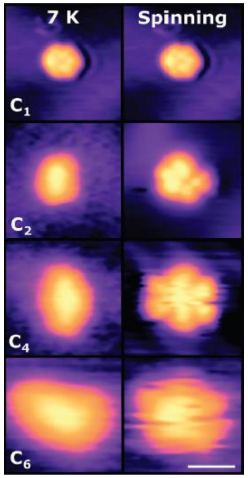
$R_{off} = 5b$

Physisorption: All atoms, except S

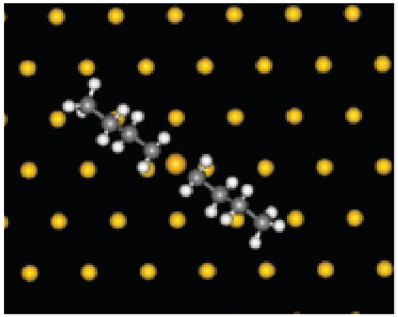
$$E_{phys,nonbonded} = \sum_{\substack{i,j \\ i\in molecule \\ j\in surface}} D_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] SW\left(r_{ij}\right)$$

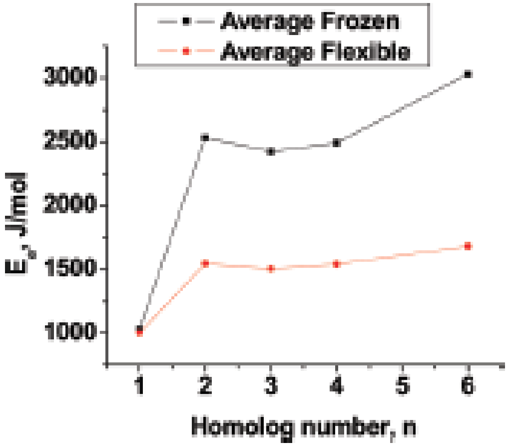
Chemisorption: S atom

$$E_{chem} = \sum_{\substack{i,j \\ i\in molecule \\ j\in surface}} D_{ij}\left[\left(e^{-\alpha\left(r_{ij}-r_{ij}^{0}\right)}-1\right)^{2}-1\right] SW\left(r_{ij}\right)$$



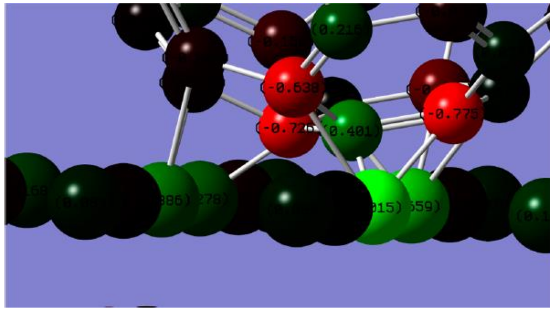
The temperature when $C_n, n \geq 2$ started rotating didn't depend too much on the alkyl size n





Constructing your own FF: Example 2

Akimov, A. V.; Williams, C.; Kolomeisky, A. B. *J. Phys. Chem. C* **2012**, *116*, 13816–13826.



$$E = E_{\mathrm{vdw}} + E_{\mathrm{elec}}$$

$$E_{\mathrm{elec}} = \sum_{i \in \mathrm{real}} \left(\chi_i q_i + \frac{1}{2} J_i q_i^2 + q_i \sum_{\substack{j \in \mathrm{real} \\ j \neq i}} \frac{q_j}{r_{ij}} + q_i \sum_{j \in \mathrm{image}} \frac{\tilde{q}_j}{\tilde{r}_{ij}} \right)$$

$$E_{\mathrm{vdw}} = D\left[\left(\frac{\sigma_{\mathrm{C-Au}}}{r} \right)^{12} - 2\left(\frac{\sigma_{\mathrm{C-Au}}}{r} \right)^{6} \right]$$

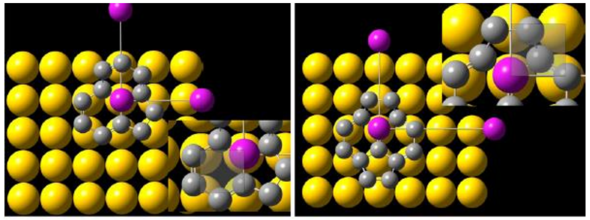
$$q_i = \beta\rho_i - \gamma \sum_{\substack{j \neq i \\ j \in C}} \rho_j S_2(r_{ij})$$

$$\rho_i = \sum_{k \in Au} e^{-\alpha r_{ik}} S_1(r_{ik})$$

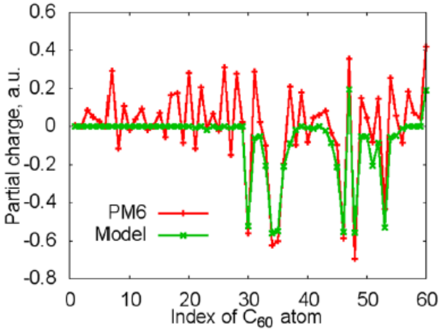
$$\beta > 0$$

$$\gamma > 0$$

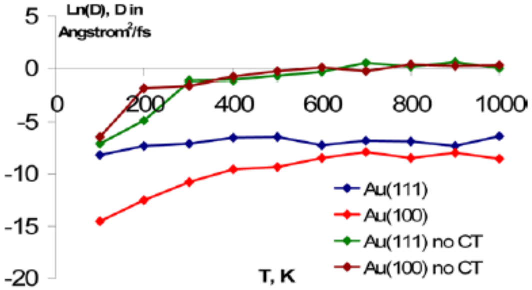
Parameterization (PM6)



Validation



C60/Au diffusion coefficients



Materials modeling FFs

Embedded atom method (EAM)

Daw, M. S.; Baskes, M. I. Phys. Rev. Lett. 1983, 50, 1285−1288

Systems with non-directional bonds (metals, alloys)

Modified EAM (MEAM)

Baskes, M. I. Phys. Rev. Lett. 1987, 59, 2666−2669
Baskes, M. I.; Nelson, J. S.; Wright, A. F. Phys. Rev. B 1989, 40, 6085−6100.

Introduced bond directionality (silicon, etc.)

MEAM92

Baskes, M. I. Phys. Rev. B 1992, 46, 2727−2742.

Extended set of elements (metals and non-metals)

Brenner, Tersoff-Brenner, REBO

Brenner, D. W. Phys. Rev. B 1990, 42, 9458−9471

Reactive potentials for hydrocarbons

ReaxFF

Van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A. J. Phys. Chem. A 2001, 105, 9396−9409

Charge-optimized many-body (COMBx)

Yu, J.; Sinnott, S.; Phillpot, S. Phys. Rev. B 2007, 75, 085311

Polarizable reactive potentials

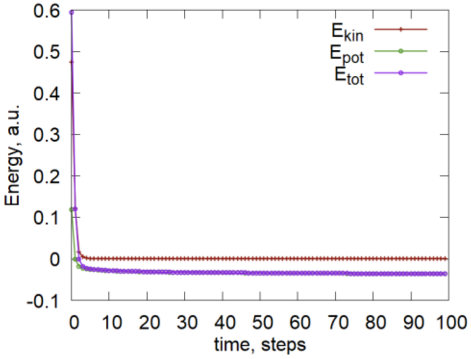
Learn more: Akimov, A. V.; Prezhdo, O. V. *Chem. Rev.* **2015**, *115*, 5797–5890.

Exercises: Running AA MD of H2O cluster

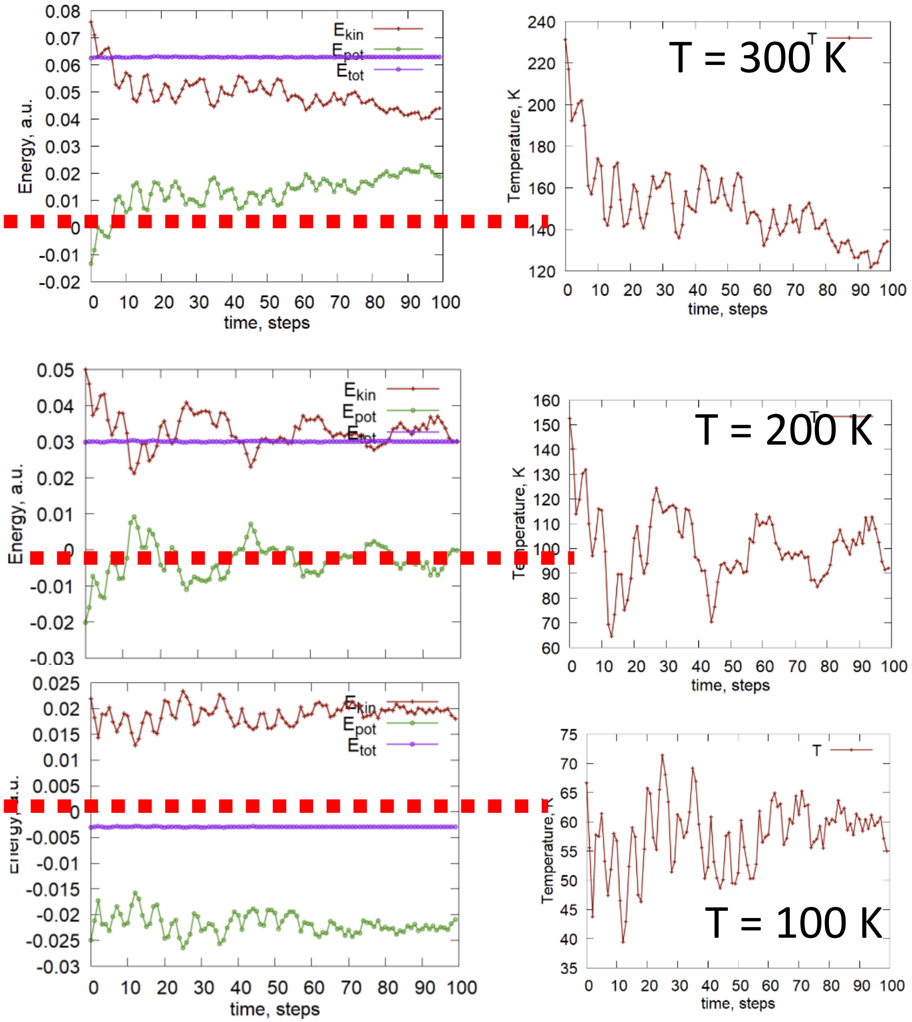
Tut2.1

params["input_structure"] = "/23waters-aa.ent"

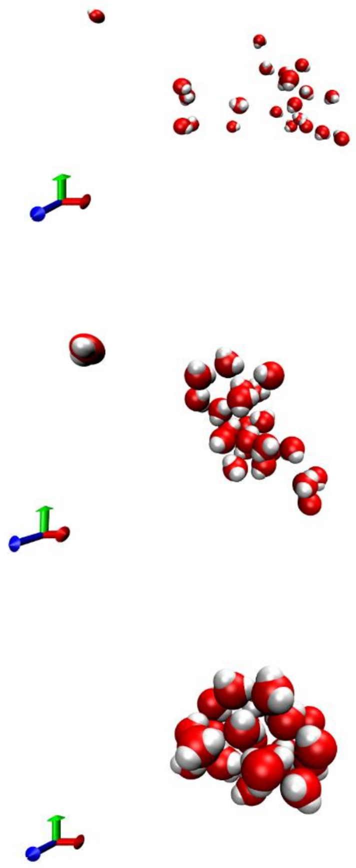
First, we cool the system down - optimization



Then, put some kinetic energy



time = 5 ps



Exercises: Running RB MD of H2O cluster

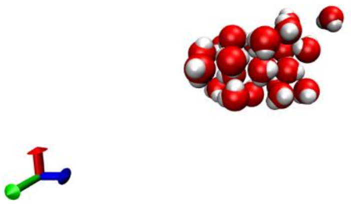
Tut2.1

params["input_structure"] = "/23waters.ent"

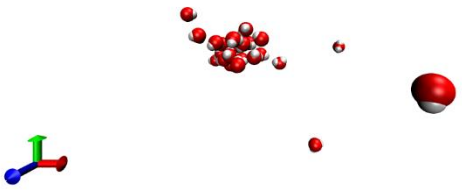
Now, do the same, but remove internal degrees of freedom

$$E_{tot} = \cancel{E_{bonded}} + E_{non-bonded}$$

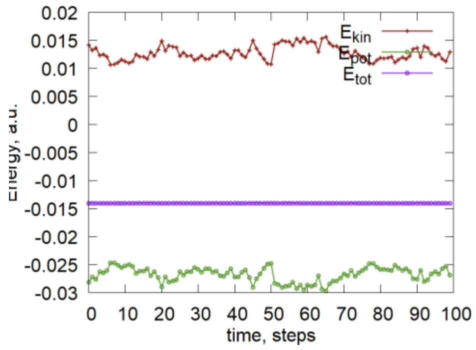
T = 100 K

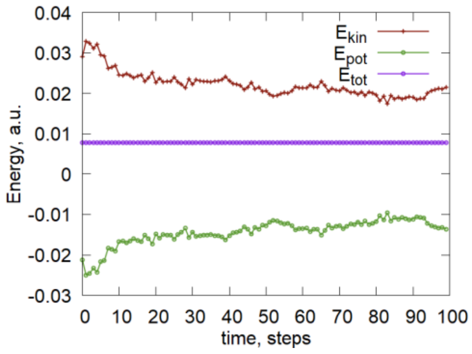


T = 200 K



Using rigid-body molecular dynamics (RB-MD)





Internal degrees of freedom act as “energy buffer”

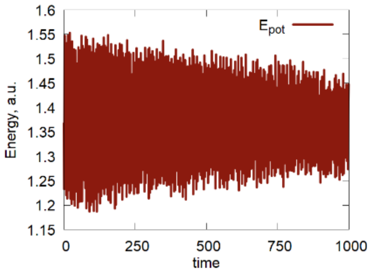
The kinetics in AA and RB bay be very different!

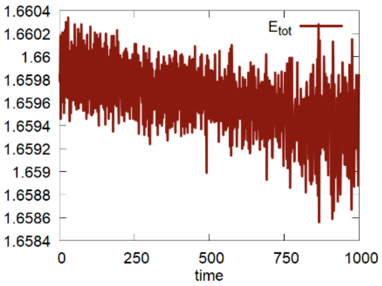
Exercises: Running aa MD of SubPc/C60 cluster

Tut2.2

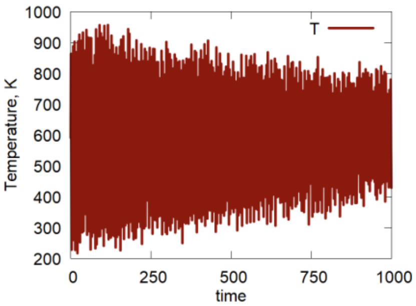
This is the same as before, but using a predefined library
Use: **run_aa_md.py**

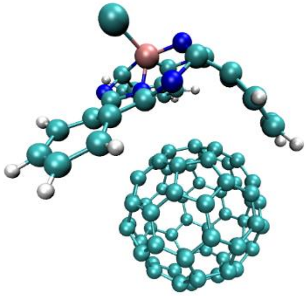
Energy is well conserved



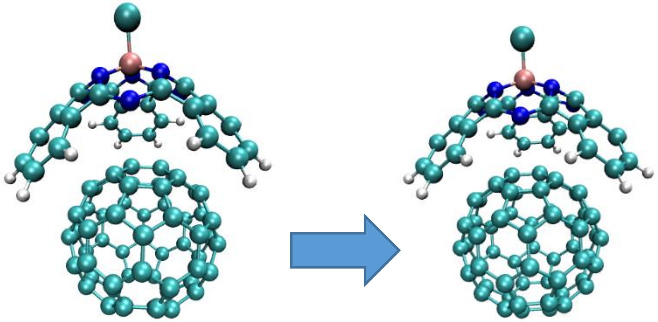


High T – behaves wildly



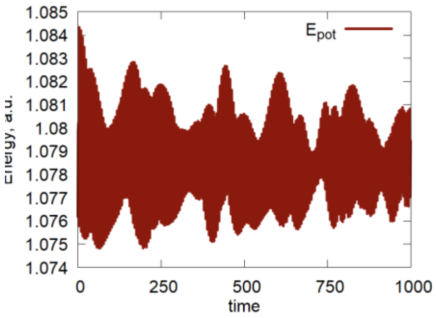


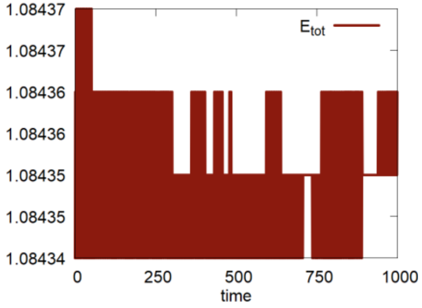
Assign T = 300 K after cooling



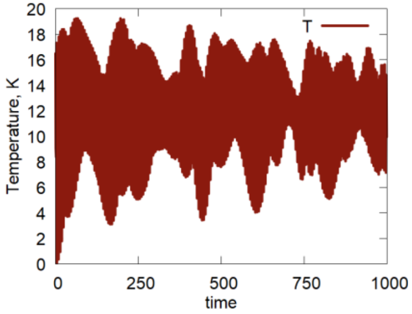
Optimized

10 ps of MD





Internal degrees of freedom
“absorb” energy leading
to low temperature



Exercises: Running aa MD of SubPc/C60 cluster

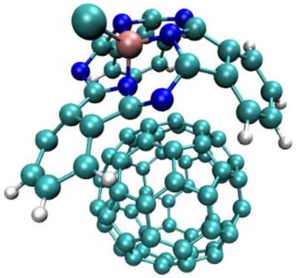
Tut2.2

This is the same as before, but using **another class**
Use: **run_aa_md_state.py**

Gives the same as before (NVE ensemble)

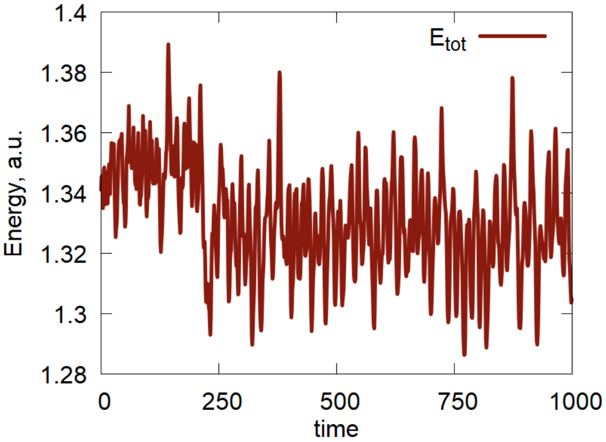
"ensemble":"NVT"

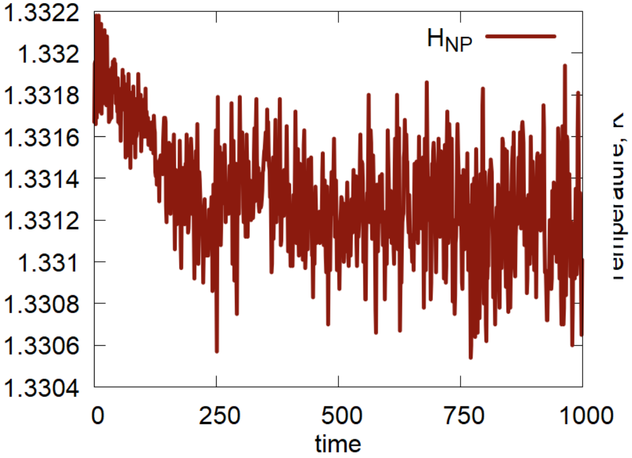
ST.set_thermostat(therm)

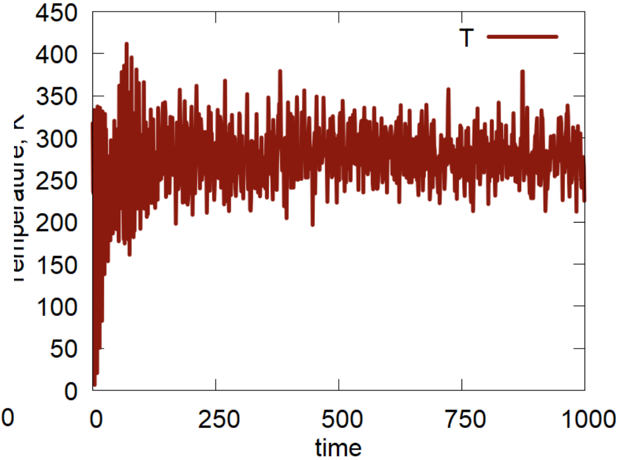


10 ps of MD

One N center inversion occurs

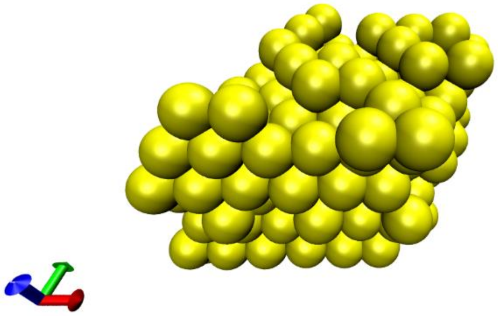


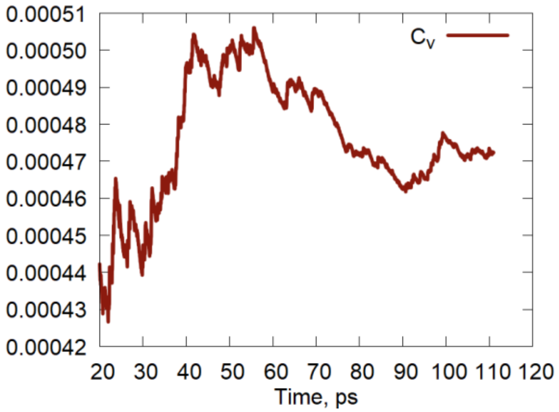


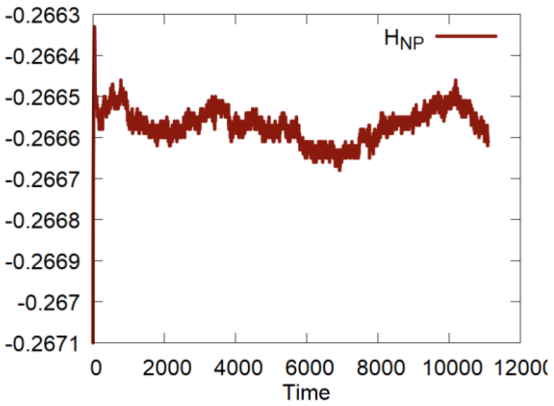


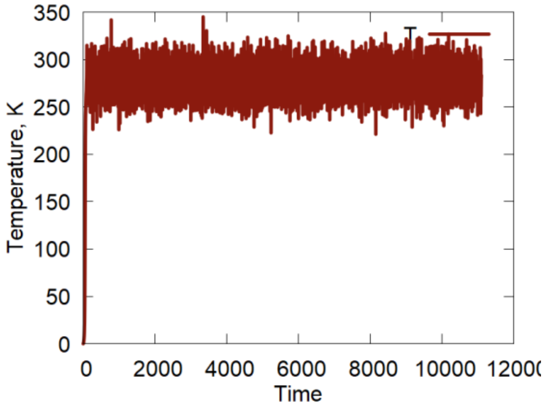
Exercises: Computing specific heat capacity of gold

Tut2.3









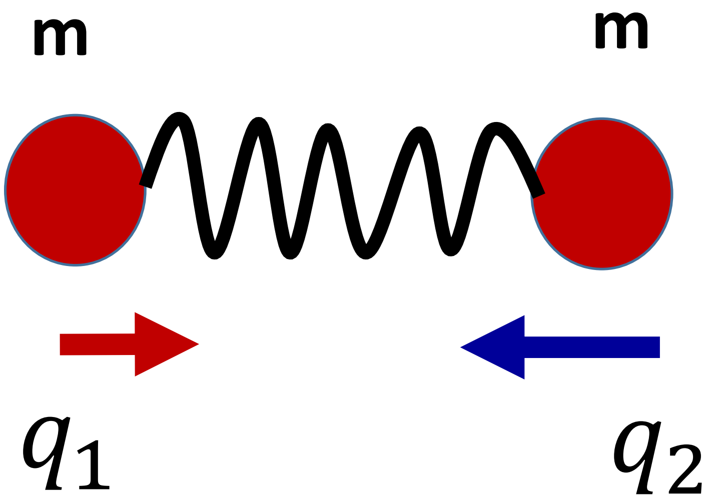
$$C_V = \frac{4.72{*}10^{-4}\ Ha^2}{3.17 * 10^{-6}\frac{Ha}{K} * 278.0^2 K^2} = 1.93 * 10^{-3}\frac{Ha}{K}$$

$$m = \frac{216}{N_A} mol * 197\frac{g}{mol} = \frac{42552}{N_A} g = 7.07 * 10^{-20} g$$

$$c = \frac{C_v}{m} = \frac{1.93 * 10^{-3}\frac{Ha}{K}}{7.07 * 10^{-20} g} * 4.36 * 10^{-18}\frac{J}{Ha} = 1.19 * 10^{-1} = \mathbf{0.119}\frac{\boldsymbol{J}}{\boldsymbol{g * K}}$$

Reference value: $\mathbf{0.129}\ \frac{\boldsymbol{J}}{\boldsymbol{g * K}}$

Normal modes analysis



$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} = -\frac{\partial V}{\partial q_i}$$

$$T = \frac{1}{2}\mathrm{m}(\dot{q}_1^2 + \dot{q}_2^2)$$

$$\mathrm{V} = \mathrm{k}(\mathrm{q}_1 - \mathrm{q}_2)^2$$

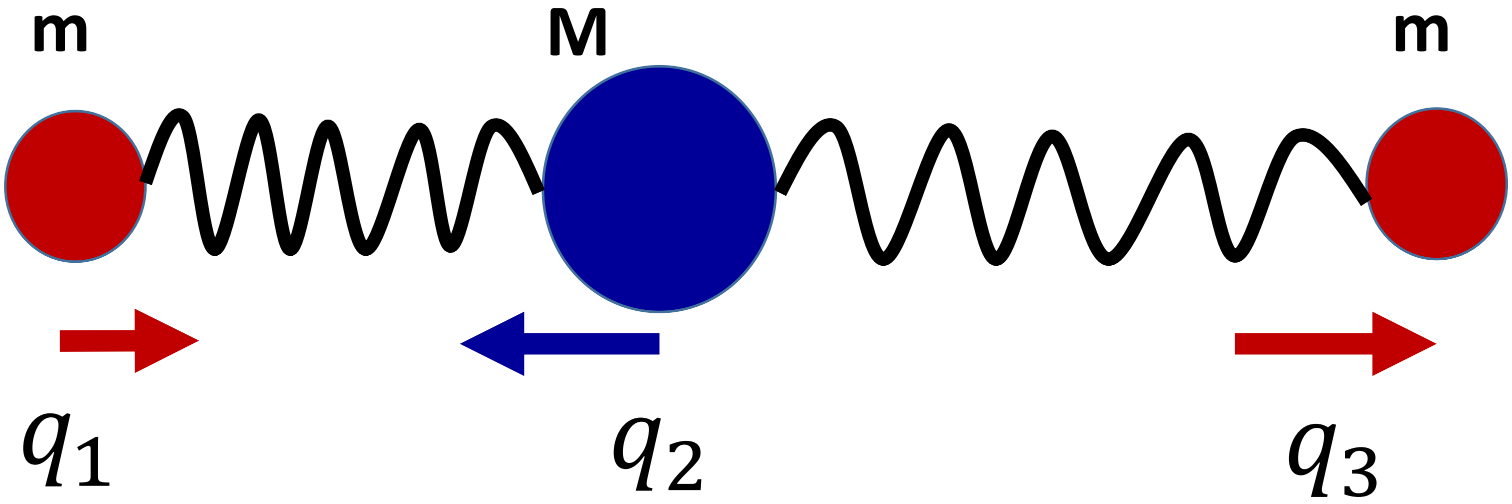
$$m\ddot{q}_1 = -2k(q_1 - q_2)$$

$$m\ddot{q}_2 = 2k(q_1 - q_2)$$

$$det\begin{pmatrix} 2k - m\omega^2 & -2k \\ -2k & 2k - m\omega^2 \end{pmatrix} = (2k - m\omega^2)^2 - 4\mathrm{k}^2 = -4\mathrm{km}\omega^2 + m^2\omega^4 = 0$$

$$m\omega^2 = 4k \Rightarrow \omega = 2\sqrt{\frac{k}{m}}$$

Normal modes analysis



q_i are the displacements of all atoms in Cartesian coordinate system

$$T = \frac{1}{2}\mathrm{m}(\dot{q}_1^2 + \dot{q}_3^2) + \frac{1}{2}M\dot{q}_2^2$$

Kinetic energy

$$\mathrm{U} = \frac{1}{2}\mathrm{k}(\mathrm{q}_1 - \mathrm{q}_2)^2 + \frac{1}{2}k(q_3 - q_2)^2$$

Potential energy

Apply Lagrangian Equations of motion

$$m\ddot{q}_1 = k(q_2 - q_1)$$

$$M\ddot{q}_2 = k(q_1 - q_2) + k(q_3 - q_2)$$

$$m\ddot{q}_3 = k(q_2 - q_3)$$

Search the solutions in the form:

$$q_i = A_i \exp(i\omega t + \delta_i)$$

$$-m\omega^2 q_1 = k(q_2 - q_1)$$

$$-M\omega^2 q_2 = k(q_1 - q_2) + k(q_3 - q_2)$$

$$-m\omega^2 q_3 = k(q_2 - q_3)$$

$$(-m\omega^2 + k)q_1 - kq_2 = 0$$

$$-kq_1 + (-M\omega^2 + 2k)q_2 - kq_3 = 0$$

$$-kq_2 + (-m\omega^2 + k)q_3 = 0$$

Apply Lagrangian Equations of motion

$$-m\omega^2 q_1 = k(q_2 - q_1)$$

$$-M\omega^2 q_2 = k(q_1 - q_2) + k(q_3 - q_2)$$

$$-m\omega^2 q_3 = k(q_2 - q_3)$$

$$(-m\omega^2 + k)q_1 - kq_2 = 0$$

$$-kq_1 + (-M\omega^2 + 2k)q_2 - kq_3 = 0$$

$$-kq_2 + (-m\omega^2 + k)q_3 = 0$$

$$\begin{pmatrix} m\omega^2 - k & k & 0 \\ k & M\omega^2 - 2k & k \\ 0 & k & m\omega^2 - k \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

Non-trivial solution is when

$$\det \begin{pmatrix} m\omega^2 - k & k & 0 \\ k & M\omega^2 - 2k & k \\ 0 & k & m\omega^2 - k \end{pmatrix} =$$

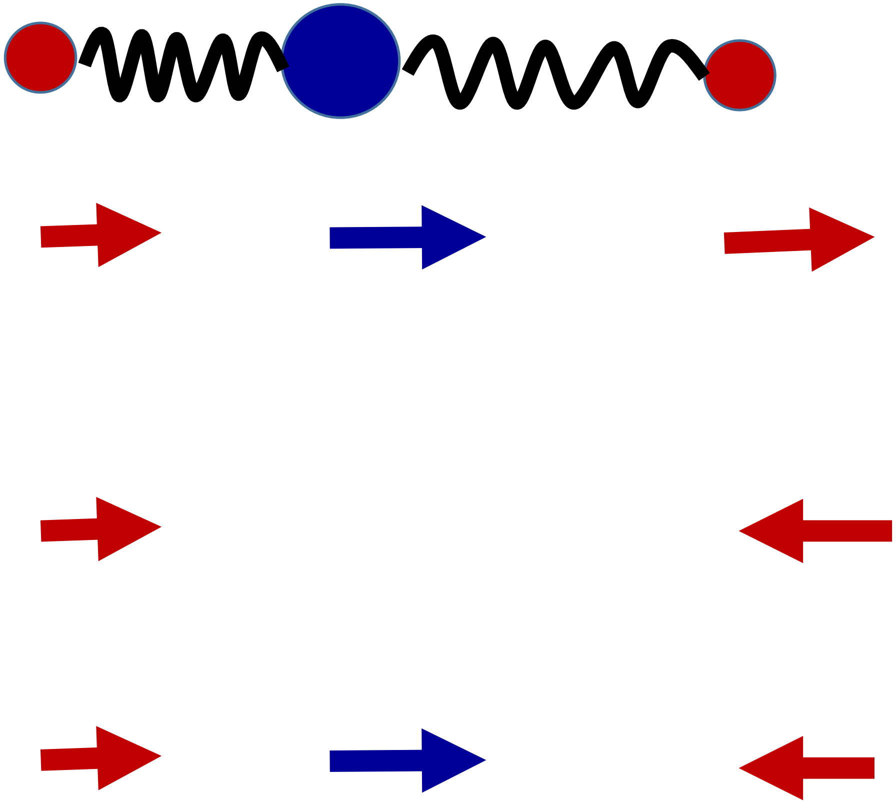
$$= (m\omega^2 - k)[(M\omega^2 - 2k)(m\omega^2 - k) - k^2] - k[k(m\omega^2 - k)] =$$

$$= (m\omega^2 - k)[(M\omega^2 - 2k)(m\omega^2 - k) - 2k^2] = 0$$

$$(M\omega^2 - 2k)(m\omega^2 - k) - 2k^2 = Mm\omega^4 - 2km\omega^2 - kM\omega^2 = \omega^2[Mm\omega^2 - k(2m + M)]$$

Possible solutions

Normal modes



$$\omega_1 = 0$$

(translation)

$$\omega_2 = \sqrt{\frac{k}{m}}$$

$$\omega_3 = \sqrt{\frac{k(2m + M)}{Mm}}$$

In a general form

$$T = \frac{1}{2}\sum_i m_i \dot{q}_i^2$$

Kinetic energy

$$\mathrm{V} = \mathrm{V}\left(q_{eq}\right) + \sum_i \frac{\partial V}{\partial q_i} q_i + \frac{1}{2}\sum_{i,j} \frac{\partial^2 V}{\partial q_i \partial q_j} q_i q_j$$

Potential energy

$$q_i = A_i \exp(i\omega t + \delta_i)$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0$$

$$-m_i \omega^2 q_i + \sum_i \frac{\partial^2 V}{\partial q_i \partial q_k} q_k = 0 \quad ➡ \quad \det\left|M\omega^2 - \mathrm{H}\right| = 0$$