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Variable Charge Equilibration in LAMMPS

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Charge equilibration

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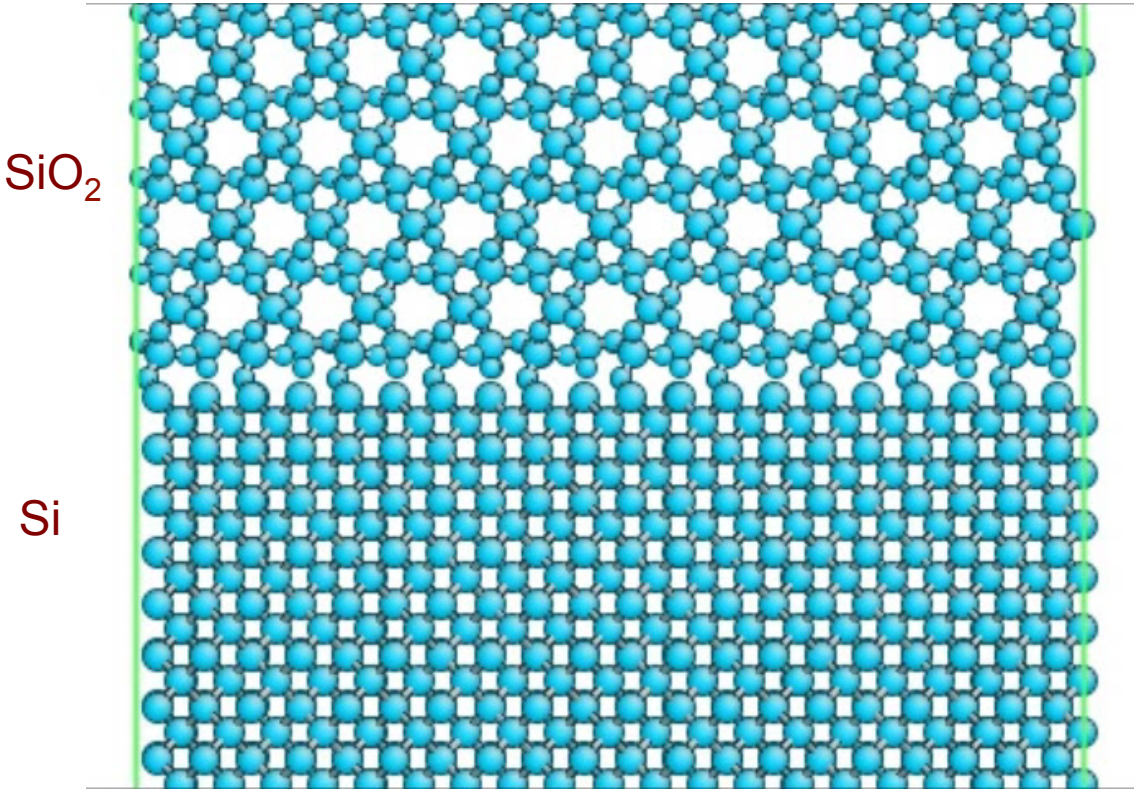
- Si/α-quartz SiO_2 interface with COMB (pair_style comb)



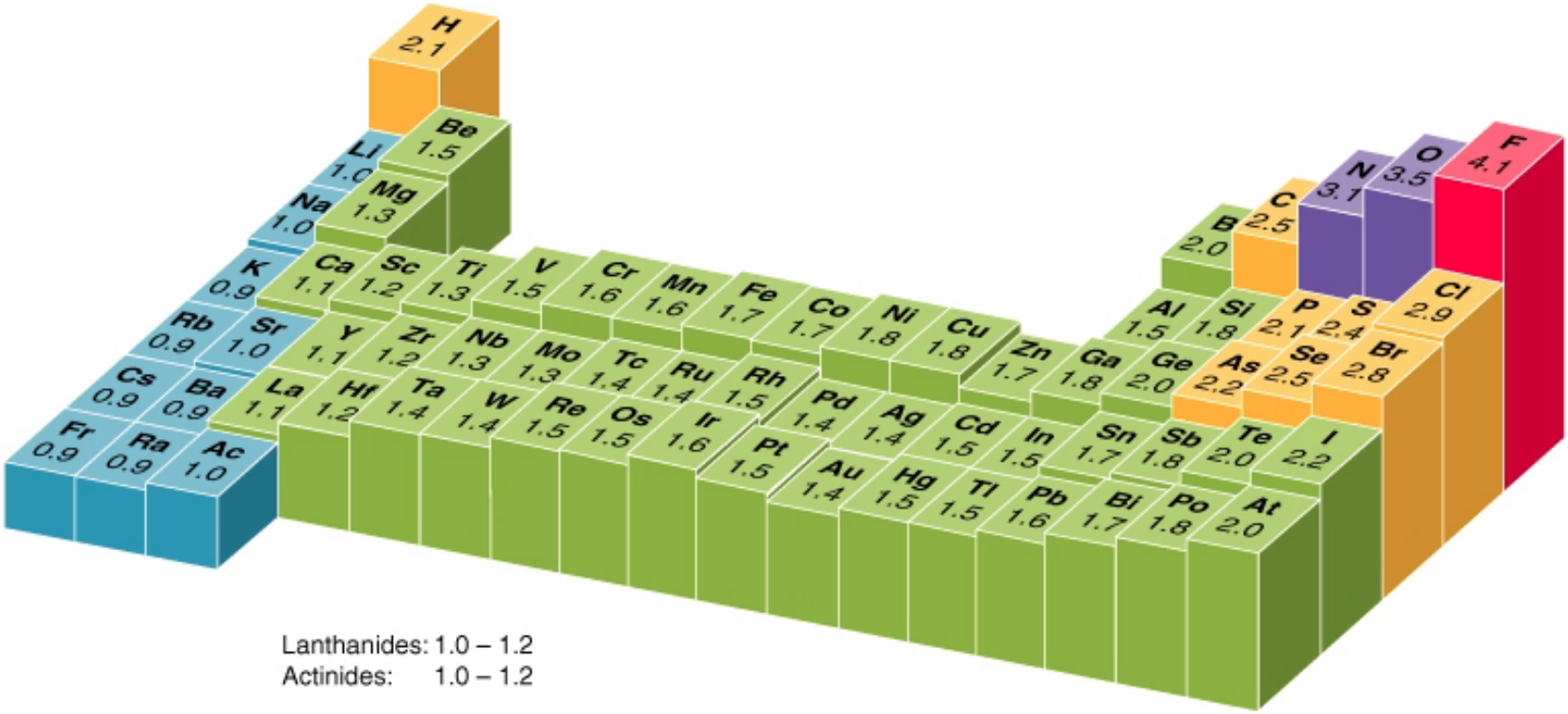
- Variable charge pair_styles in LAMMPS include:
  - COMB (**comb**, **comb3**), ReaxFF (**reax**, **reax/c**), embedded ion method (**eim**), and Streitz-Mintmire (**coul/sm**)

Overview: fix qeq/variants

Charge solver / Charge model	Matrix inversion	Damped dynamics
Point charge $\frac{q_i q_j}{r_{ij}}$	**qeq/point**	**qeq/dynamic**
Shielded $\frac{q_i \cdot q_j}{[r_{ij}^3 + (1/\gamma_{ij})^3]^{1/3}}$	**qeq/shielded** qeq/reax	
Slater 1*s* $q_i \cdot \zeta^3 \pi^{-1} e^{(-2\zeta r_{ij})} \cdot q_j$	**qeq/slater**	qeq/comb

Electronegativity

- First proposed by Linus Pauling in 1932
- A chemical property that describes the tendency of an atom to attract electrons (or electron density) towards itself



Electronegativity

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- When two or more atoms combine to form a molecule, their electronegativities are equalized – Sanderson's postulate [a]
- Electronegativity, X, of any chemical species is the negative of its chemical potential, μ [b]
  - $$\mathrm{X}_i = -\mu_i = -\frac{\partial E(\rho)}{\partial \rho} = e\frac{\partial E(q_i)}{\partial q_i}$$
- At equilibrium, electron density will transfer between atoms so that chemical potential (electronegativity) at all atomic sites are equal

Electronegativity equalizaton ➔ charge transfer

[a] R. T. **Sanderson**, *Chemical Bonds and Bond Energy*; Academic, New York (1976)
[b] R. G. **Parr**, R. A. **Donnelly**, M. **Levy**, W. E. **Palke**, *J. Chem. Phys.* 68, 3801 (1978)

Electronegativity

- Since electronegativity is the derivative of energy with respect to electron density (charges), it is useful to express electronegativity through expressing energy as a function of charge
- Most basic expression is the sum of atomic ionization energy and electrostatics
  - $E(q_i) = \chi \cdot q_i + \frac{1}{2} \cdot \eta \cdot q_i^2 + \sum_{i<j} q_i \cdot J_{ij} \cdot q_j$
  - $\mu(q_i) = q_i + \eta \cdot q_i + \sum_{i<j} J_{ij} \cdot q_j$
  - Used in ReaxFF and Streitz-Mintmire potentials
    - Differ in charge models, J_{ij}

$$\frac{q_i \cdot q_j}{[r_{ij}^3 + (1/\gamma_{ij})^3]^{1/3}}$$

$$q_i \cdot \xi^3 \pi^{-1} e^{(-2\xi r_{ij})} \cdot q_j$$

A. K. **Rappe**, W. A. **Goddard** III, *J. Phys. Chem.* 95 8 (1991)
A. C. T. **van Duin**, S. **Dasgupta**, F. **Lorant**, W. A. **Goddard** III, *J. Phys. Chem. A* 105 9396 (2001)
F. H. **Streitz** and J. W. **Mintmire**, Phys. Rev. B 50, 11996 (1994)

Matrix Inversion Method

- Solving equilibrium charges for a system of *N* atoms
  - A problem of *N* variables
- Based on electronegativity equalization principle
  - $\mu_i = \mu_{i+1} = \cdots = \mu_N$
  - *N – 1* conditions
  - Adding the condition of conservation on total charge
    - $q_{tot} = \sum_i q_i$
- The charge equilibration equations become
  - $\mathrm{CD} = -\mathrm{D}$

Rappe, A. K., Goddard III, W. A, *J. Phys. Chem.* 95 8 (1991)

Matrix Inversion Method

- Solving charges with CD = -D

$$\begin{bmatrix} J_{i,j}-J_{1,j} & J_{i+1,j}-J_{1,j} & \cdots & J_{N,j}-J_{1,j} & 1 \\ J_{i,j+1}-J_{1,j+1} & J_{i+1,j+1}-J_{1,j+1} & \cdots & J_{N,j+1}-J_{1,j+1} & 1 \\ \vdots & \vdots & \vdots & \vdots & 1 \\ J_{i,N}-J_{1,N} & J_{i+1,N}-J_{1,N} & \ddots & J_{N,N}-J_{1,N} & 1 \\ q_i & q_{i+1} & \cdots & q_N & 1 \end{bmatrix} \begin{bmatrix} \eta_i-\eta_1 \\ \eta_{i+1}-\eta_1 \\ \vdots \\ \eta_N-\eta_1 \\ -q_{tot} \end{bmatrix} = -\begin{bmatrix} \eta_i-\eta_1 \\ \eta_{i+1}-\eta_1 \\ \vdots \\ \eta_N-\eta_1 \\ -q_{tot} \end{bmatrix}$$

- Solve the sparse matrix problem with a linear conjugate gradient minimization method
  - Fast converging method for solving *q*, but only applicable to linear equations
  - $\mu(q_i) = q_i + \eta \cdot q_i + \sum_{i<j} J_{ij} \cdot q_j$

Damped Dynamics Method

- More complicated expression of energy as a function of charge
  - COMB
  - $$E(q_i) = E^p(q_i) + \sum_{i<j} q_i \cdot J_{ij} \cdot q_j + \sum_{i<j} V_{ij}\left(r_{ij}, q_i, q_j\right)$$

    $$E^p(q_i) = \chi \cdot q_i + \frac{1}{2} \cdot \eta_1 \cdot q_i^2 + \frac{1}{3} \cdot \eta_2 \cdot q_i^3 + \frac{1}{4} \cdot \eta_3 \cdot q_i^4$$

    $$V_{ij} = A(q) \cdot Ae^{-\lambda \cdot r_{ij}} + B(q) \cdot Be^{-\alpha(q) \cdot r_{ij}}$$

- Solving charges with EEM requires iterative, damped dynamics

Yu J., Sinnott S. B., Phillpot, S. R., *Phys. Rev. B* 75 085311 (2007)
Shan T.-R., Devine B. D., Kemper T. W., Sinnott S. B., Phillpot S. R., *Phys. Rev. B* 81 125328 (2010)

Damped Dynamics Method

- Analogous to classical Newtonian dynamics
  - $$m_i \ddot{r}_i = -\frac{\partial}{\partial r_i} E(\{r_i\},\{q_i\})$$
  - $$s_i \ddot{q}_i = -\frac{\partial}{\partial q_i} E(\{r_i\},\{q_i\})$$

$$q_{tot} = \sum_i q_i$$

S. W. **Rick**, S. J. **Stuart**, B. J. **Berne**, *J. Chem. Phys.* 101 6141 (1994)

Damped Dynamics Method

- Analogous to classical Newtonian dynamics
  - $$m_i \ddot{r}_i = -\frac{\partial}{\partial r_i} E(\{r_i\},\{q_i\})$$
  - $$s_i \ddot{q}_i = -(\frac{\partial}{\partial q_i} E(\{r_i\},\{q_i\}) - \frac{1}{N}\sum_i \frac{\partial}{\partial q_i} E(\{r_i\},\{q_i\}))$$

S. W. **Rick**, S. J. **Stuart**, B. J. **Berne**, *J. Chem. Phys.* 101 6141 (1994)

Damped Dynamics Method

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  - $$m_i \ddot{r}_i = -\frac{\partial}{\partial r_i} E(\{r_i\},\{q_i\})$$
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  - $$s_i \ddot{q}_i = -\mu_i + \bar{\mu} - \eta_d \dot{q}_i$$

- Also know as the Extended Lagrangian method
  - Damped dynamics with fixed damping
  - Large damping facilitates convergence, but leads to instability more easily

S. W. **Rick**, S. J. **Stuart**, B. J. **Berne**, *J. Chem. Phys.* 101 6141 (1994)

Summary and Outlooks

- Fix qeq/variants allows easy expansion and inclusion of more charge models and QEq solvers

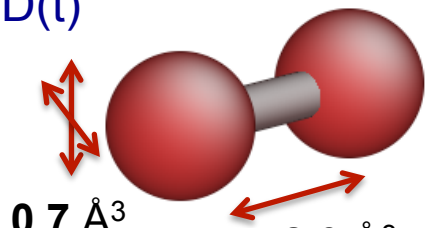
Charge solver / Charge model	Matrix inversion	Damped dynamics	Advanced Damped dynamics
Point charge $\frac{q_i q_j}{r_{ij}}$	**qeq/point**	**qeq/dynamic**	
Shielded $\frac{q_i \cdot q_j}{[r_{ij}^3 + (1/\gamma_{ij})^3]^{1/3}}$	**qeq/shielded** qeq/reax		
Slater 1*s* $qi \cdot \zeta^3 \pi^{-1} e^{(-2\zeta r_{ij})} \cdot q_j$	**qeq/slater**	qeq/comb	
SQE [1] QTPIE [2]			

[1] D. **Mathieu**, J. Chem. Phys. 127 224103 (2007)
[2] J. **Chen** and T. J. **Martinez**, Chem. Phys. Lett. 438 315 (2007)

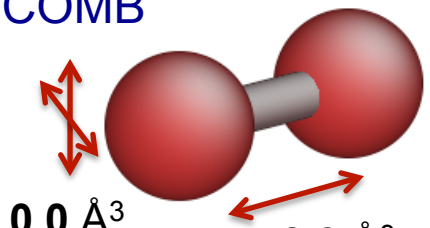
Summary and Outlooks

- Molecular polarization can be decomposed into
  - Atomic polarization
  - Change in permanent dipole moment between bonded atoms
  - Exchange of charge between bonded atoms (QEq)

CCSD(t)



QEq w/ COMB



- Expand "fix qeq/variants" to "fix polarization" based on the fluctuating charge-fluctuating point dipole model [1]
  -

$$\vec{\mu}_i = P_i \vec{E}(\vec{r}) = P_i \left[\vec{E}_i^q + \sum_{j=1, j\neq i}^{N} T_{ij} \vec{\mu}_j \right],$$

$$\vec{E}_i^q = \frac{1}{4\pi\varepsilon_0} \sum_{j\neq i}^{N} q_j \frac{\partial J_{ij}^{qq}}{\partial r} \frac{\vec{r}}{|\vec{r}_{ij}|},$$

$$T_{ij} = \frac{1}{4\pi\varepsilon_0 |\vec{r}_{ij}|^3} \left(1 - 3\frac{\vec{r}_{ij} \cdot \vec{r}_{ij}}{|\vec{r}_{ij}|^2} \right) \times \left[1 - e^{-2\zeta_i r} \left(1 + 2\xi_j r_{ij} + 2\xi_j^2 r_{ij}^2 \right) \right].$$

[1] H. A. **Stern**, G. A. **Kaminski**, J. L. **Banks**, R. H. **Zhou**, B. J. **Berne**, and R. A. **Friesner**, J Phys. Chem. B 103, 4730 (1999)