



A typical simple interatomic potential has harmonic
radial and angular bonds, dihedral angle interactions,
van der Waals nonbonding interactions, and
Coulomb terms; e.g.,
$$V_{total} = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_{\theta} (\theta - \theta_{eq})^2 + \sum_{bonds} V_n [1 + \cos(n\phi + \gamma)] + \sum_{i < j} \{ \varepsilon_{ij} [(\frac{r_{ij}}{r_{ij}})^{12} - (\frac{r_{ij}}{r_{ij}})^6] + \frac{q_i q_j}{\theta_{ij}} \}$$

Or perhaps you prefer Born/Mayer/Buckingham potential types- $U_{ij} = A \exp(-Br) - C/r^6 + Q_i Q_j/r$ and 'Many-Body' or 'Embedded Atom' terms- $U_{EA}(r_i) = Function(\rho_i)$ and smooth rollover depending upon local atomic coordination *e.g., detect local neighborhood, bridge between sp² and sp³ bonding schemes, surface vs bulk interaction parameters*



$$\begin{split} V(r) &= 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \\ \mathbf{f}_i &= \frac{48\varepsilon}{\sigma^2} \sum_{j \neq i}^N \left(\mathbf{r}_i - \mathbf{r}_j \right) \left[\left(\frac{\sigma}{r_{ij}}\right)^{14} - \frac{1}{2} \left(\frac{\sigma}{r_{ij}}\right)^8 \right] \\ \text{In order to simplify the notation, } \varepsilon \text{ is chosen as the unit of energy } \varepsilon/k_\text{B} \text{ is chosen as the unit of Temperature, and } \sigma \text{ as the unit of length. Then the unit of time is given by } \sqrt{m\sigma^2/48\varepsilon}. \text{ Newton's equation for each particle then becomes dimensionless}, \\ \frac{d^2\mathbf{r}_i}{dt^2} &= \mathbf{g}_i = \sum_{j\neq i}^{\mathsf{N}} (\mathbf{r}_i - \mathbf{r}_j) \left(\frac{1}{r_{ij}^{14}} - \frac{1}{2r_{ij}^8}\right). \end{split}$$

The Lennard-Jones (6-12) two parameter potential is truly minimal, but amazingly versatile. The scaled accelerations g_i are rapidly calculated.





$$\begin{split} \rho g(r) &= \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{\substack{j=1 \\ (j \neq i)}}^{N} \delta(r - r_{ij}) \right\rangle & S(\mathbf{k}) &= \frac{1}{N} \left\langle \rho(\mathbf{k})\rho(-\mathbf{k}) \right\rangle \\ &= \frac{1}{N} \left\langle \sum_{ij} e^{i\mathbf{k}\cdot(\mathbf{r}_i - r_j)} \right\rangle \\ &= \frac{1}{N} \left\langle \sum_{ij} \cos(\mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle \end{split}$$
$$\rho(\mathbf{k}) &= \sum_{i=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_i} & S(k) = 1 + \rho g(k). \end{split}$$
Two body correlation functions g(r), FT of density $\rho(\mathbf{k})$, and the scattering Structure Factor S(k) are immediately useful outputs Courtesy Furio Ercolessi: http://www.fisica.uniud.it/~ercolessi/

$$\begin{split} V &= \frac{1}{2} \sum_{ij} \phi(r_{ij}) + \sum_{ijk} g(r_{ij}) g(r_{ik}) \left(\cos \theta_{jik} + \frac{1}{3} \right)^2 \\ \text{Stillinger-Weber potential is nice for tetrahedral semiconductors, but number of parameters is growing.} \\ \text{F. Stillinger and T. A. Weber, Phys. Rev. B 31, 5262 (1985).} \\ V &= \frac{1}{2} \sum_{ij} \phi_R(r_{ij}) + + \frac{1}{2} \sum_{ij} B_{ij} \phi_A(r_{ij}) + \\ G_{ij} &= \sum_k f_c(r_{ik}) g(\theta_{jik}) f(r_{ij} - r_{ik}) \\ \text{Tersoff potential has variable-strength pair-wise interactions :} \\ \text{B}_{ij} (G_{ij}) - \text{ while flexible, has a frightening number of parameters. Think of sp2 vs sp3 bonding in hydrocarbons.} \\ \text{J. Tersoff, Phys. Rev. B 37, 6991 (1988); D. W. Brenner, Phys. Rev. B 42, 9458 (1990).} \end{split}$$



By making random jumps (actually biased random sampling)
in configuration space, we can survey widely separated
regions of configuration space. The configuration average of
a quantity is one of the basic outcomes.
\$\$\langle A \rangle = \frac{1}{Z} \int A\(\mathbf{x}\) e^{-\frac{B\(\mathbf{x}\)}{T}} d\mathbf{x}\$\$
\$\$\langle A \rangle_{est} = \frac{\sum_{l=1}^{M} A\(\mathbf{x}_l\) e^{-\frac{B\(\mathbf{x}_l\)}{T}}}{\sum_{l=1}^{M} e^{-\frac{B\(\mathbf{x}_l\)}{T}}}\$\$
\$\$\langle A \rangle_{est} = \frac{\sum_{l=1}^{M} A\(\mathbf{x}_l\)}{M}\$\$
Thermal Average => Random Sum => Importance-Sampled Sum

The Metropolis algorithm is as follows:

The first conformation is randomly generated. At each point in the construction of the chain of conformations a move is attempted to the current conformation. The move is rejected immediately if the local chain conformation is not compatible with the attempted move or if it violates the excluded volume condition. If these two conditions are satisfied then the so called Metropolis criterion is applied. If the difference between the energy of the resulting conformation and the energy of the current conformation, ΔE , is negative (i.e. the energy of the resulting conformation is smaller than the energy of the current conformation), then the resulting conformation is accepted and it becomes the new conformation in the chain. If ΔE is positive, however, a (pseudo)random number between 0 and 1, 0<R<1, is generated and the resulting conformation is only accepted if $exp(-\Delta E/kT) >$ \$. If $exp(-\Delta E/kT) < R$ then the resulting conformation is refused. Whenever the conformation resulting from the attempted move is refused for any of the three possible reasons, then the new conformation of the chain is the same current conformation. For sequence selection the same algorithm is used but the "moves" correspond to switching the position of two monomers while the conformation is kept fixed

The probability of accepting a trial move is given by:

$$P_{\text{accept}} = \min(1, e^{-\Delta E/T})$$

Metropolis, N., Rosembluth, A., Rosembluth, M. & Teller, A. ,J. Chem. Phys. 21, 1087-1092, (1953)

"Measurements"

Generate configurations of, say, the Ising model using a Monte Carlo algorithm, such as Metropolis. Then what do we do with them? Numerically measure quantities of interest, such as:

energy	$E = -rac{J}{V} \sum_{(i,j)} S_i S_j$	V = volume (# sites)
magnetization.	$M = \frac{1}{V} \sum_{t}^{V \times V} S_{t}$	
correlation function	$\Gamma(n) = \frac{1}{V} \sum_{i} S_i S_{i+n} -$	$-\left(\frac{1}{V}\sum_{i}S_{i}\right)^{2}$
correlation length	$\Gamma(n) \sim e^{-n/\xi}$	
specific heat	$C/V = \frac{1}{V} \frac{\partial E}{\partial T} = \Big\langle (E - $	$-\left\langle E ight angle ight angle ^{2}ig angle =\left\langle E^{3} ight angle -\left\langle E ight angle ^{2}$
susceptibility	$\chi/V = \frac{1}{V} \frac{\partial M}{\partial T} = \Big\langle (M$	$-\langle M\rangle\rangle^2 \rangle = \langle M^2\rangle - \langle M\rangle^2$

Quantities such as these are measured for <u>each</u> configuration, and the averages and statistical errors calculated.

Courtesy Paul Coddington, Northeast Parallel Architectures Center

















Target systems include such 'classics' as Fe_xAg, anion diffusion in solid-oxide fuel cells, and textured/functionalized wet bioactive surfaces.

e.g.,we model selected crystal surfaces of HAP where atoms are deposited by a patterned laser beam and then heated to diffuse and aggregate into mesoscopic pillars (5-20 micron diameter).



Water, and ions like Zn are then inserted to chemically modify the surface, molecules such as peptides bind to this surface, providing an attractive environment for osteoblasts (bone-builders) to attach and function.

The whole process must be modeled in stages, each one with a specific approach from a coarse KMC, a finer Molecular Dynamics, to a Quantum Mechanical one.



Quantum Mechanics Full-scale Many-body treatment – Configuration Interaction (CI) expansion- O(N!) limits to small systems Limited Multideterminant Expansion- MC-SCF – MBPT: Certain types of correlations summed- MP2, MP3, CCSD, CCSDT,... O(N^p) p=6,7 ? Optimized Single Determinant- HF, UHF- O(N³) Density Functional Theory (DFT)- from LDA to LSDA, PBE, GGA, MGGA, and on and on...O(N or N² or N³, depending on cleverness) Semiempirical QM: PPP, Hückel, Tight-Binding, and on and on...- Fast, parameterized, limited predictions

The time-dependent Schrödinger equation is really simple.

$$i\hbar \frac{d\Psi(\mathbf{r}, t)}{dt} = \hat{H}\Psi(\mathbf{r}, t),$$

If H is a time-independent operator, then

$$\Psi(\mathbf{r},t) = e^{-i\hat{H}t/\hbar}\Psi(\mathbf{r},0).$$



How to go from 4^{N} variables to $4^{?}$

Some form of mean-field theory is the answer-

 $H \sim \sum_{i} h_{i} + higher-order-correlations$ (Hartree-Fock, Dirac-Slater-Gaspar, Kohn-Sham...)

Then try to solve $(h_i - \varepsilon_i) \Psi_i = 0$, i=1,2,...Nand assemble density $\rho(r)$, two-point density matrix $\rho(r, r')$ iteratively-Self-Consistent-Field



The ground state energy E is a functional of the density *n*.

$$E[n] - T[n] + U[n] + \int V(\vec{r})n(\vec{r})d^3r$$

Introducing an auxiliary set of 'one-electron wavefunctions' and occupation numbers to define *n*:

$$n(\vec{r}) \stackrel{\text{def}}{=} n_s(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2$$

Kohn & Sham then derived an Effective Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) - \epsilon_i\phi_i(\vec{r}),$$

Which is determined from any external potential V, the local e-e Coulomb repulsion, and "all the rest" in the form of $V_{\rm XC}$

$$V_s = V + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + V_{XC}[n_s(\vec{r})],$$







