NE-M1-PRI12ENP – Integrated Nuclear Engineering Project

Molecular Modeling of Materials for Nuclear Engineering Applications

Lecture 2 – Introduction to Statistical Thermodynamics

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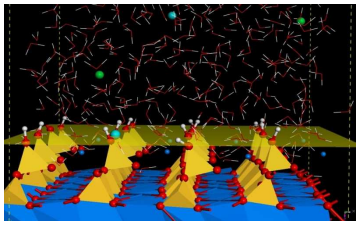

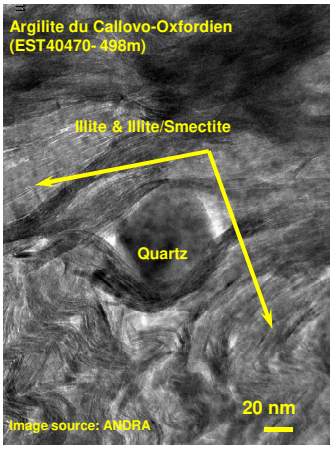

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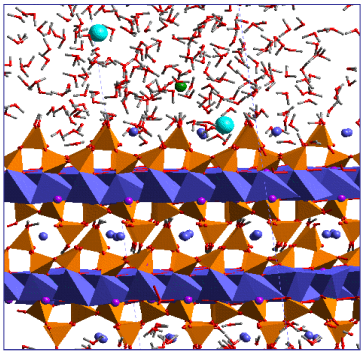
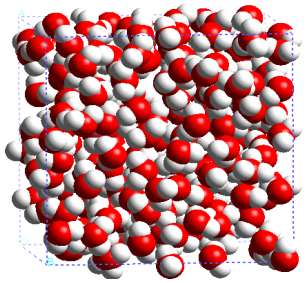
What is Computational Molecular Modeling?

- Use powerful computers to calculate properties of materials, represented by *N* interacting particles (atoms, molecules, ions, etc.)
- *Time* ~ 0.1 - 1.0 ns
- *L* ~ 10 - 100 nm
- *N* ~ 1,000 – 1,000,000 atoms



- Use **statistical mechanics** to dynamically model such processes as *hydration, adsorption, intercalation, expansion, diffusion, and the behavior of water and ions.*
- **Objective**: Quantitative understanding of the *molecular- and nano-scale structure and dynamical behavior of materials*

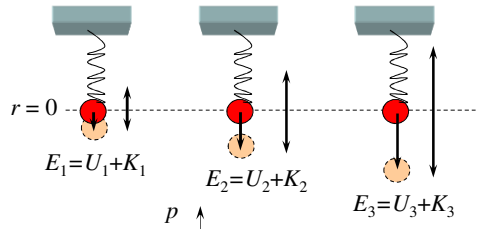
Thermodynamic State *vs* Mechanical State

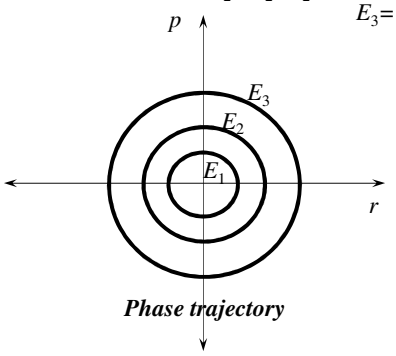


- **Thermodynamic system in equilibrium** is described by a very limited number of macroscopic variables – *T, P, V, x*

- Mechanical system of *N* particles (atoms, molecules) free to move in 3 dimensions is described by 3*N* coordinates at every instant ($N \sim N_A \sim 6 \cdot 10^{23}$)
- ***Motions of such a huge number of objects can be described only statistically***
- ***Very many (equivalent?) mechanical states correspond to the same thermodynamic equilibrium state***

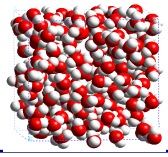
Motion in Phase Space





Single particle

$N = 1$
r coordinate
$p = mv$ momentum
$F = ma = k(r - r_0)$ equation of motion
$U = ½\, k(r - r_0)^2$ potential energy
$K = ½\, mv^2 = p^2/2m$ kinetic energy
2D phase space (1D motion)



Macroscopic system

$N = N_A \sim 6 \cdot 10^{23}$ atoms
$\mathbf{q} = \{\mathbf{q}_1(t), \mathbf{q}_2(t), ..., \mathbf{q}_N(t)\}$ generalized coordinates
$\mathbf{p} = \{\mathbf{p}_1(t), \mathbf{p}_2(t), ..., \mathbf{p}_N(t)\}$ generalized momenta
6*N*-D phase space

Classical Hamiltonian

$\mathbf{q} = \{\mathbf{q}_1(t), \mathbf{q}_2(t), ..., \mathbf{q}_N(t)\}$	generalized coordinates
$\mathbf{p} = \{\mathbf{p}_1(t), \mathbf{p}_2(t), ..., \mathbf{p}_N(t)\}$	generalized momenta
$H(\mathbf{p},\mathbf{q},t) = K(\mathbf{p},\mathbf{q},t) + U(\mathbf{p},\mathbf{q},t)$	Hamiltonian (total energy)
$K(\mathbf{p},\mathbf{q},t) = \sum \frac{m_i \mathbf{v}_i^2}{2} = \sum \frac{\mathbf{p}_i^2}{2m_i}$	kinetic energy
$U(\mathbf{p},\mathbf{q},t) = U(\mathbf{q})$	potential energy

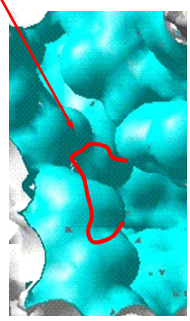
$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$ canonical equations of motion

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \sum \frac{\partial H}{\partial q_i}\dot{q}_i + \sum \frac{\partial H}{\partial p_i}\dot{p}_i \quad \Rightarrow \quad \frac{dH}{dt} = \frac{\partial H}{\partial t}$$

$$H = \text{const} \quad \text{if} \quad \frac{\partial H}{\partial t} = 0 \quad \Rightarrow \text{ conservation of energy}$$

Phase Trajectory and Ergodicity
Equivalence of Time- and Ensemble- Averages

phase trajectory on a constant-energy surface



A – some observable macroscopic property

$\mathbf{\Gamma}(t) \equiv \mathbf{\Gamma}(\mathbf{p}(t), \mathbf{q}(t))$ point in the phase space

$$A_{\text{obs}} = \langle A \rangle_{\text{time}} = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} A(\mathbf{\Gamma}(t))$$ averaging over a ***dynamic trajectory***

$$A_{\text{obs}} = \langle A \rangle_{\text{ens}} = \sum_{\mathbf{\Gamma}} A(\mathbf{\Gamma}) \cdot \rho_{\text{ens}}(\mathbf{\Gamma})$$ averaging over a ***statistical ensemble of atomic configurations***

$$A_{\text{obs}} = \langle A \rangle_{\text{time}} \equiv \langle A \rangle_{\text{ens}}$$

Equivalence of time- and ensemble- averages – ***ERGODICITY***

The mechanical system is ***ergodic***, if over long periods of time all points on the phase surface can be equally accessible

Partition Function

$$\rho(\mathbf{\Gamma}) = \rho(\mathbf{p},\mathbf{q}) = \frac{1}{Z(T,V)} \exp[-H(\mathbf{p},\mathbf{q}) / k_B T]$$

probability of a mechanical state Γ corresponding to an equilibrium thermodynamic state *T,V*

partition function or ***statistical integral***

$$Z = \int \exp[-H(\mathbf{p},\mathbf{q}) / k_B T] d\mathbf{p} d\mathbf{q} = \Lambda(T,V) \int \exp[-K(\mathbf{p}) / k_B T] d\mathbf{p} \cdot \int \exp[-U(\mathbf{q}) / k_B T] d\mathbf{q}$$

$$Z = Q_{\text{id}} \int \exp[-U(\mathbf{q}) / k_B T] d\mathbf{q} = Q_{\text{id}} \int \exp[-U(\mathbf{r}) / k_B T] d\mathbf{r} = Q_{\text{id}} \cdot Q_{\text{conf}}$$

When cartesian coordinates and cartesian momenta are used, the kinetic energy factor of the total energy represented by the hamiltonian *H* in the expression for *Z* reduces to a constant depending upon the size, temperature and volume of the system:

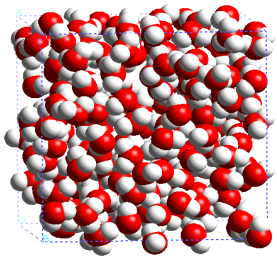
Helmholtz free energy of the thermodynamic system

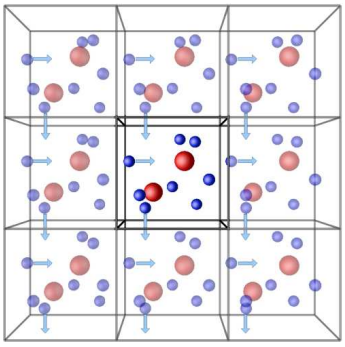
$$A(T,V) = -k_B T \ln Z = -k_B T \ln Q_{\text{conf}} + \text{const}(N,T,V)$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \qquad S = -\left(\frac{\partial A}{\partial T}\right)_V$$

Two Principal Approaches to Classical Molecular Modeling

- **MD - time averages** over a dynamic trajectory in the phase space of the simulated system
- **MC - ensemble averages** over a computer-generated random Markov chain of molecular configurations
- Periodic boundary conditions (PBC)



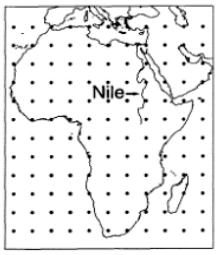


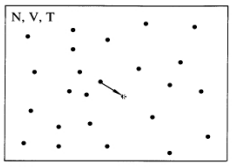
http://isaacs.sourceforge.net/phys/pbc.html

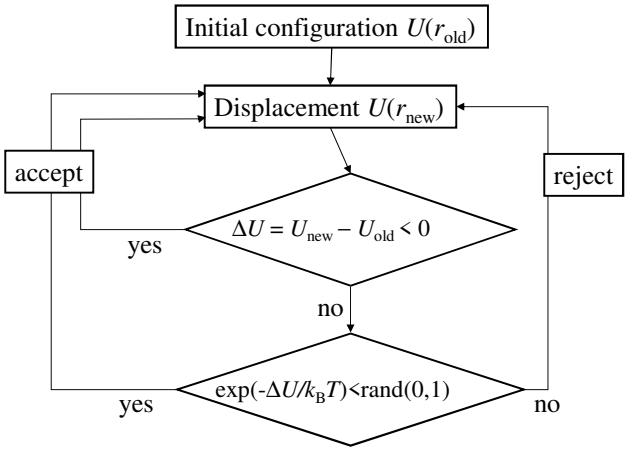
Monte Carlo Simulations – Ensemble Averages

$$Q_{\text{conf}} = \int \exp[-U(\mathbf{r})/k_{\text{B}}T]d\mathbf{r}$$ 3N-dimensional integral

(*Metropolis et al.*, 1953)

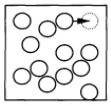






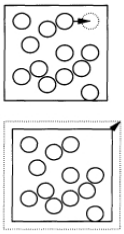
Monte Carlo Simulations in Different Ensembles

N V T – canonical ensemble (*Metropolis et al.*, 1953)



$p = \exp(-\beta U)$ $\beta = 1/k_{\text{B}}T$

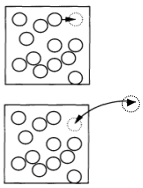
N P T – isothermal-isobaric ensemble (*Wood*, 1968; McDonald, 1969)



$p = \exp(-\beta H) = \exp[-\beta(U + PV) + N \ln V]$

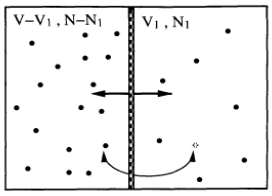
Monte Carlo Simulations in Different Ensembles

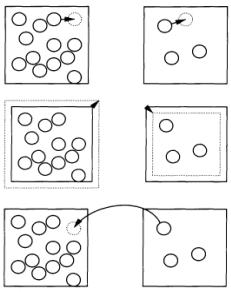
$\mu V T$ – grand canonical ensemble (*Norman & Filinov*, 1969)



$$p = \exp(-\Psi) = \exp[-\beta (U - \mu N) - \ln N! - 3N \ln\Lambda + N \ln V]$$

Gibbs ensemble (*Panagiotopoulos*, 1987)





Molecular Dynamics Simulations

Use powerful computers to ***numerically solve Newtonian equation of motion*** for *N* interacting particles:

$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + ½\, \mathbf{a}_i \Delta t^2;$

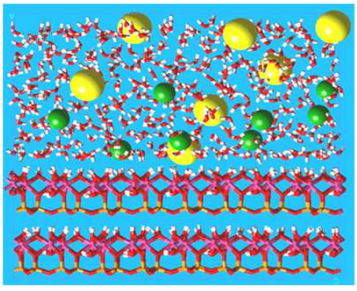
$\Delta t \sim 10^{-15}$ sec

$\mathbf{a}_i = \mathbf{F}_i/m = [\, -\partial U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)/\partial\, \mathbf{r}_i\,] / m$;

$i=1,2,\ldots,N$

$N \sim 1{,}000 - 100{,}000$

$U = \Sigma\Sigma\, U_{ij} + \Sigma\Sigma\Sigma\, U_{ijk} + \ldots$



N V E – microcanonical ensemble – most natural for MD, isolated system
N V T – canonical ensemble – the system can exchange energy with the environment (thermostat)
N P T – isothermal-isobaric ensemble – volume of the system can also change (barostat)
$\mu V T$ – grand canonical ensemble – the system can exchange mass with the environment (???)

Molecular Modeling: Intermolecular Interactions

MD

$\boldsymbol{r}_i(t+\Delta t) = \boldsymbol{r}_i(t) + \boldsymbol{v}_i(t)\Delta t + \tfrac{1}{2}\boldsymbol{a}_i\Delta t^2$; $\Delta t \sim 10^{-15}$ sec

$\boldsymbol{a}_i = \boldsymbol{F}_i/m = [\,-\partial U(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N)/\partial \boldsymbol{r}_i\,]/m$; $i=1,2,\ldots,N$

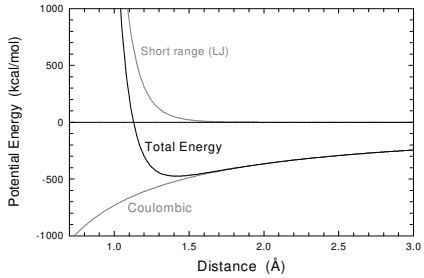
MC

$$Z = \int \exp[-H(\mathbf{p},\mathbf{q})/k_B T]\,d\mathbf{p}\,d\mathbf{q}$$

$$\rho(\Gamma) = \rho(\mathbf{p},\mathbf{q}) = \frac{1}{Z}\exp[-H(\mathbf{p},\mathbf{q})/k_B T]$$

$$\langle A \rangle = \int A(\mathbf{p},\mathbf{q})\rho(\mathbf{p},\mathbf{q})\,d\mathbf{p}\,d\mathbf{q}$$

$$H(\mathbf{p},\mathbf{q}) = U(\mathbf{q}) + K(\mathbf{p})$$

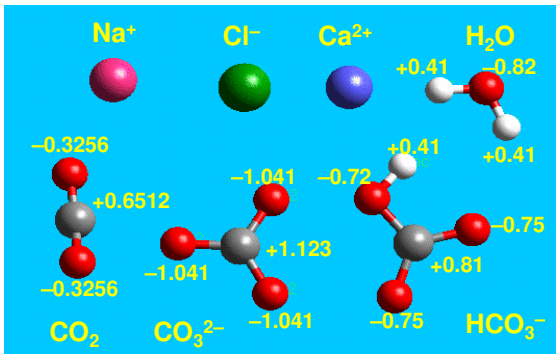


$U = \Sigma\Sigma\, U_{ij}$

$U_{ij} = \Sigma\Sigma(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j/\varepsilon_0 r_{ij}) + \Sigma\, \tfrac{1}{2}k_b\,(r_{ij} - r_0)^2 + \Sigma\, \tfrac{1}{2}k_\theta\,(\theta_{ij} - \theta_0)^2$

Short-range repulsion v-d-Waals Coulombic bond stretching bond bending

Potential Models of Simple Aqueous Species

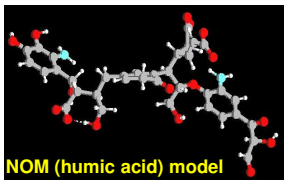


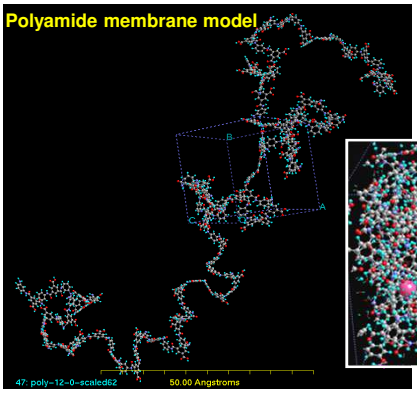
$U_{ij} = \Sigma\Sigma(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j/\varepsilon_0 r_{ij}) + \Sigma\, \tfrac{1}{2}k_b\,(r_{ij} - r_0)^2 + \Sigma\, \tfrac{1}{2}k_\theta\,(\theta_{ij} - \theta_0)^2$

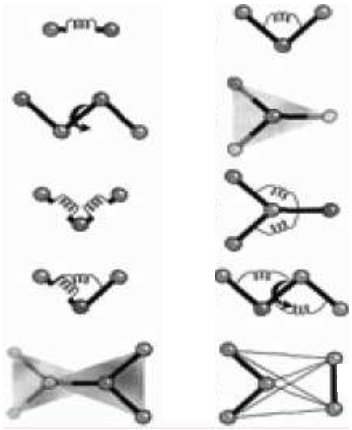
Short-range repulsion v-d-Waals Coulombic bond stretching bond bending

Rigid models (fixed geometry) are also useful sometimes

Models of Complex Organic Molecules



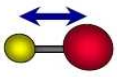




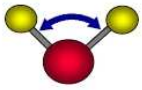
Potential Energy of Intermolecular Interaction

Typical Models

$$U = k_2(r - r_o)^2$$



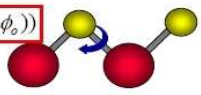
Bond Stretch



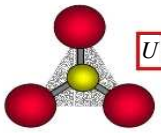
$$U = k_2(\theta - \theta_o)^2$$

Angle Bend

$$U = k(1 + \cos(n\phi - \phi_o))$$



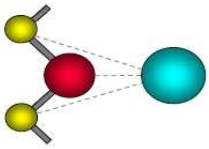
Torsion



$$U = k(1 + \cos(n\chi - \chi_o))$$

Out-of-Plane Stretch

Nonbonded



$$U_{nonbond} = \sum_{i>j}^{N} \frac{q_i q_j}{r_{ij}} + \sum_{i>j}^{N} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \right)$$

Potential Energy of Intermolecular Interaction

$$U_{Total} = \underbrace{U_{Coul} + U_{VDW}}_{\text{Nonbonded}} + \underbrace{U_{Bond\ Stretch} + U_{Angle\ Bend} + U_{Torsion}}_{\text{Bonded}} + \dots$$

Parameterization using structure and properties

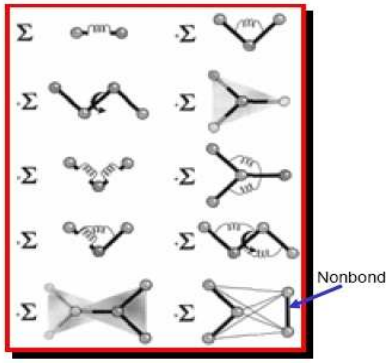
$$U_{Coul} = \frac{e^2}{4\pi\varepsilon_o} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}$$

Lennard-Jones Potential

$$U_{VDW} = \sum_{i \neq j} D_o \left[\left(\frac{R_o}{r_{ij}} \right)^{12} - 2 \left(\frac{R_o}{r_{ij}} \right)^{6} \right]$$

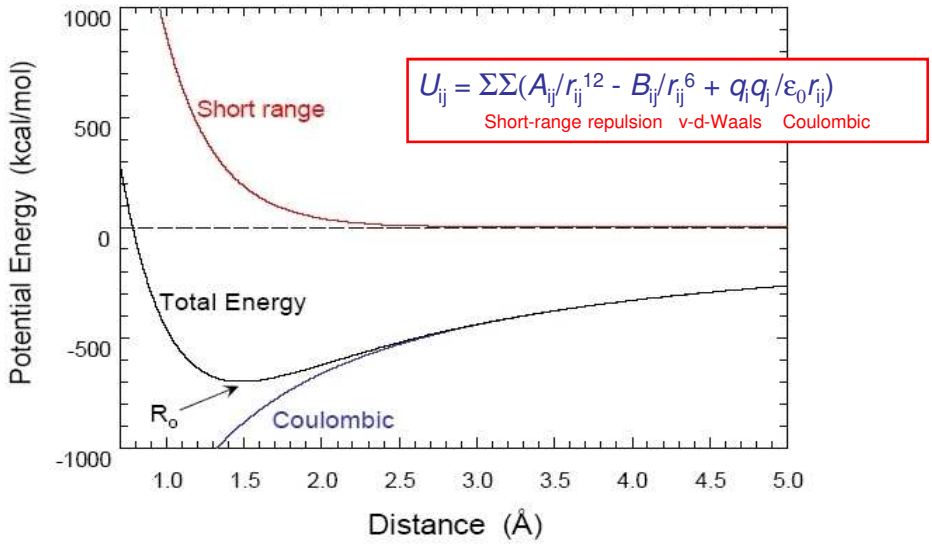
Buckingham Potential (Ionic solids)

$$U_{ij} = k \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-r_{ij} / \rho_{ij}) - \frac{C_{ij}}{r_{ij}^6}$$



Amber, Charmm, CFF, CVFF, CLAYFF
Dreiding, MM1, MMFF, Tripos, UFF

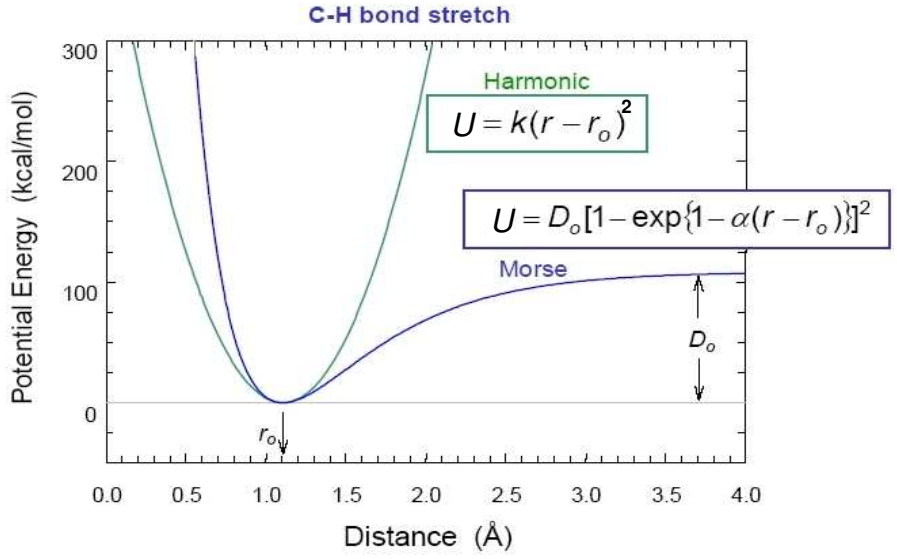
Typical Nonbonded Terms



$U_{ij} = \Sigma\Sigma(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j/\varepsilon_0 r_{ij})$

Short-range repulsion v-d-Waals Coulombic

Typical Bonded Terms



Force Field Parameters Determination

Empirical (from experimental data)

- Structural information (bond distances, angles, crystal cell parameters – from X-ray, neutron and electron diffraction)
- Spectroscopic information (vibrational frequencies, NMR chemical shifts, atomic coordination)
- Crystal properties (elastic constants or bulk modulus, refractive indices, dielectric constants, piezoelectric constants)
- Obtain only equilibrium-based values
- Parameters implicitly include temperature effects
- Force fields based on models of simple molecular fragments for specific applications (organic, bio-organic, zeolites, clays, etc.)

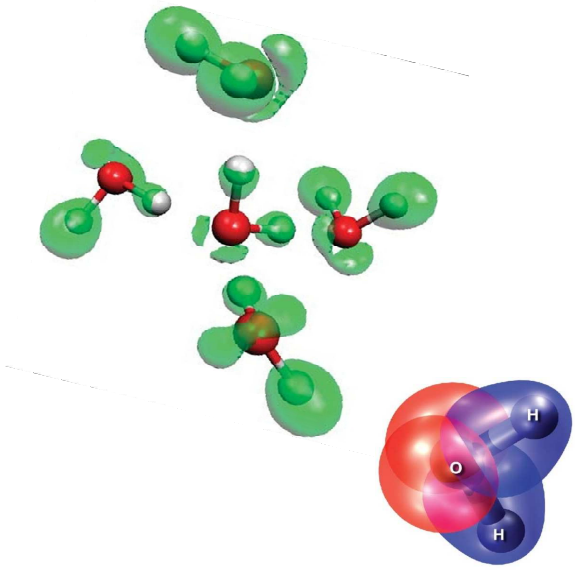
Force Field Parameters Determination (2)

- ***Ab initio - electronic structure calculations***
- Parameterize interactions that cannot be evaluated through experimental means
- Control geometries of clusters to obtain energies for non-equilibrium ranges
- Require extended basis sets (and GC or MP2) for accuracy
- Incorporate electron correlation (VDW) with DFT (cf. Hartree-Fock)

Partial charge assignments

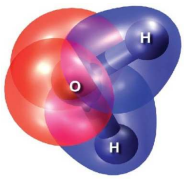
- Experimental deformation densities based on precision X-ray diffraction analysis
- Mulliken electron population analysis from quantum-mechanical (MO) calculation
- CHELPG method of fitting charges to MO-based electrostatic potential
- QEq method based on bond geometry and electronegativities of various atoms

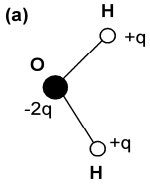
Classical Molecular Models of Water



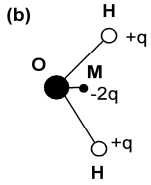
Acronym (date)	Reference	Status	Type	Sites	$\mu_g(D)$	$\mu_l(D)$
BF (1933)	7	empirical	R	4	2.0	2.0
R (1951)	21	empirical	R	5	1.84	1.84
BNS (1971)	22	empirical	R	5	2.17	2.17
ST2 (1973,1993)	23	empirical	R	5	2.35	2.35
CF (1975,1978,1995)	24	empirical	F	3	1.86	1.98
MCY (1976)	25	ab initio	R	4	2.19	2.19
DCF (1978,1980,1993)	26	empirical	F,D,P	3	1.855	-
PE (1979)	27	empirical	P	I	1.855	2.50
SPC (1981)	14	empirical	R	3	2.27	2.27
TIP3P (1981,1983)	15	empirical	R	3	2.35	2.35
RWK (1982)	28	empirical	F	4	1.85	1.89
TIP4P (1983)	15	empirical	R	4	2.18	2.18
BJH (1983)	29	empirical	F	3	1.87	1.99
SPC/F (1985)	30	empirical	F	3	2.27	2.42
MCYL (1986)	31	ab initio	F	4	2.19	2.26
SPC/E (1987)	32	empirical	R	3	2.35	2.35
WK (1989)	33	empirical	R	4	2.60	2.60
SPCP (1989)	34	empirical	P	3	1.85	2.90
CKL (1990)	35	empirical	F,P	4	1.88	2.20
MCHO (1990)	36	ab initio	P	6	2.12	≈3.0
NCC (1990)	37	ab initio	P	6	1.85	2.80
NEMO (1990,1995)	38	ab initio	P	5	2.04	2.89
PTIP4P (1991)	39	empirical	P	4	1.85	2.80
SPC/FP (1991)	40	empirical	F,P	3	1.85	2.44
PSRWK (1991)	41	empirical	P	4	1.88	2.63
KJ (1992)	42	empirical	P	4	1.85	-
NCCvib (1992)	37b	ab initio	F,P	6	1.85	3.11
ASP-W (1992,1998)	43	ab initio	P	3	1.85	2.90
RPOL (1992)	44	empirical	P	3	2.02	2.62
CPMD (1993,1999)	45	DFT+CP	F,D,P	nucl.+el.	1.87	2.95
PPC (1994)	46	ab initio	P	4	2.14	2.51
SPC/FQ (1994)	47	empirical	P	3	1.85	2.83
TIP4P/FQ (1994)	47	empirical	P	4	1.85	2.62
KKY (1994)	48	empirical	F,D	3	2.38	2.21
SQPM (1995)	49	valence bond	P	4	1.85	2.62
SCPDP (1996)	50	empirical	P	4	1.85	2.87
TAB/10D (1998)	51	SCF+MD	P	5	1.85	2.65
NSPCE (1998)	52	empirical	R	3	2.18	2.18
NCF (1998)	53	empirical	F	3	1.85	1.90
MCDHO (2000)	54	ab initio	F, P	4	1.85	3.01
TIP5P (2000)	55	empirical	R	5	2.29	2.29
SPC/HW (2001)	56	empirical	R	3	2.41	2.41
DEC (2001)	57	empirical	R	3	1.85	1.85
SWFLEX (2001)	58	empirical	P	4	1.85	2.59
POLARFLEX (2001)	59	valence bond	F,P	3	1.85	2.55
POL5 (2001)	60	ab initio	P	5	1.85	2.71

The Structure of H_2O Molecule and Classical Intermolecular Potentials

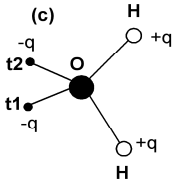




SPC
SPC/E
TIP3P



MCY
TIPS2
TIP4P



BNS
ST2
TIP5P

$$U_{ij} = \Sigma\Sigma(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i q_j/\varepsilon_0 r_{ij}) +$$

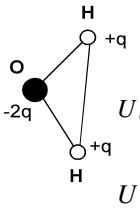
Short-range repulsion Van der Waals Coulombic

$$+ \Sigma\, ½\, k_b(r_{ij} - r_0)^2 + \Sigma\, ½\, k_\theta(\theta_{ij} - \theta_0)^2$$

bond stretching bond bending

- ***Ab-initio*** **quantum mechanical potentials**
- **Empirical and semi-empirical potentials**

H_2O: Central Force and BJH Flexible Potentials



$$U_{OO}(r) = \frac{604.6}{r} + \frac{111889}{r^{8.86}} - 1.045\left\{\exp\left[-4(r-3.4)^2\right] - \exp\left[-1.5(r-4.5)^2\right]\right\}$$

$$U_{OH}(r) = -\frac{302.2}{r} + \frac{26.07}{r^{9.2}} - \left\{\frac{41.79}{1+\exp\left[40(r-1.05)\right]}\right\} - \left\{\frac{16.74}{1+\exp\left[5.493(r-2.2)\right]}\right\}$$

$$U_{HH}(r) = \frac{151.1}{r} + \left\{\frac{418.33}{1+\exp\left[29.9(r-1.968)\right]}\right\}$$ (Stillinger & Rahman, 1978)

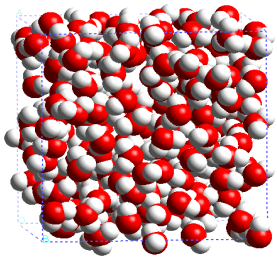
$$U_{\text{intra}} = \sum L_{ij}\rho_i\rho_j + \sum L_{ijk}\rho_i\rho_j\rho_k$$ (Bopp et al., 1983)

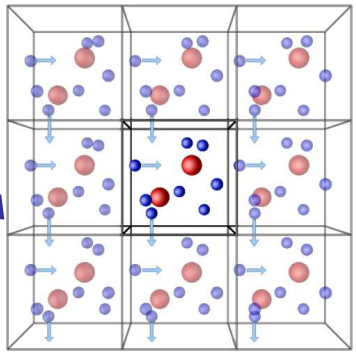
$\rho_1 = (r_1 - r_e)/r_1$ r_e=0.9572 Å
$\rho_2 = (r_2 - r_e)/r_2$
$\rho_3 = \alpha - \alpha_e = \Delta\alpha$ α_e=104.52°
r_1, r_2 - *instantaneous OH$_i$ lengths*
α - *instantaneous HOH angle*

$\rho_1\rho_2(\rho_1+\rho_2)$	-55.7272	$(\rho_1^2+\rho_2^2)$	2332.27
$(\rho_1^2+\rho_2^2)\Delta\alpha$	237.696	$\rho_1\rho_2$	-55.7272
$(\rho_1^4+\rho_2^4)$	5383.67	$(\rho_1+\rho_2)\Delta\alpha$	126.242
$\rho_1\rho_2(\rho_1^2+\rho_2^2)$	-55.7272	$(\Delta\alpha)^2$	209.860
$(\rho_1^3+\rho_2^3)\Delta\alpha$	349.151	$(\rho_1^3+\rho_2^3)$	-4522.52

Periodic Boundary Conditions

- **MD - time averages** over a dynamic trajectory in the phase space of the simulated system
- **MC - ensemble averages** over a computer-generated random Markov chain of molecular configurations
- Periodic boundary conditions (PBC)

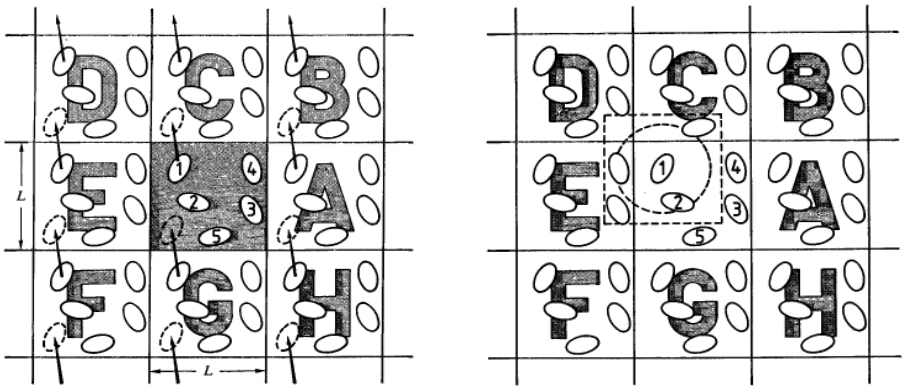




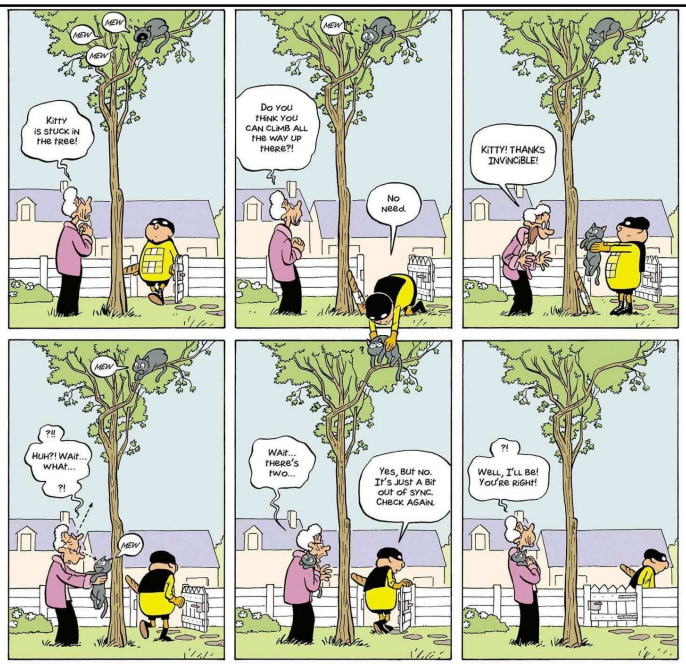
http://isaacs.sourceforge.net/phys/pbc.html

Minimum Image Convention and Spherical Cutoff

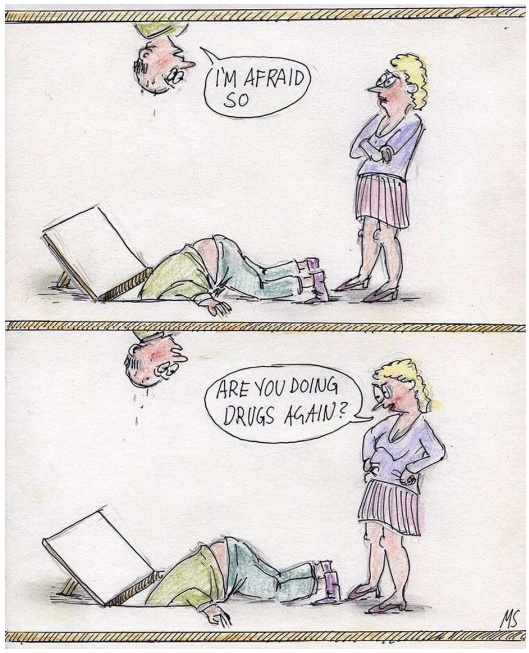
Short-range interactions



Periodic Boundary Conditions and Minimum Image Convention Better Explained (I)



Periodic Boundary Conditions and Minimum Image Convention Better Explained (II)

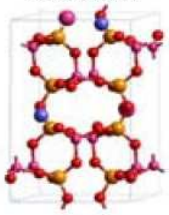


Long-Range (Electrostatic) Interactions

Ewald summation

$$U_{elect} = \sum_{i>j}^{N} \frac{q_i q_j e^2}{r_{ij}}$$

Labradorite



$$U_{recip} = \frac{1}{2}\frac{4\pi}{V}\sum_{G}\frac{1}{G^2}\exp\left(-G^2/4\eta\right)\sum_{i}\sum_{j} q_i q_j \exp(-iGr_{ij})$$

$$U_{real} = \frac{1}{2}\sum_{i}\sum_{j} q_i q_j \operatorname{erfc}(-\eta^{1/2} r_{ij})/r_{ij}$$

G is reciprocal lattice vector
Ewald method scales as $N^{3/2}$

$\eta_{opt} = (nw\pi^3/V^2)^{1/3}$

w is ratio of computational cost

Alternative Methods
N > 10,000 atoms; scale as N log N
Fast multipole, Petersen *et al.* (1994)
Particle mesh, Essmann *et al.* (1995)

Total Potential Energy of a System

$$U_{Total} = \underbrace{U_{Coul} + U_{VDW}}_{\text{Nonbonded}} + \underbrace{U_{Bond\ Stretch} + U_{Angle\ Bend} + U_{Torsion}}_{\text{Bonded}} + \ldots$$

Parameterization using structure and properties

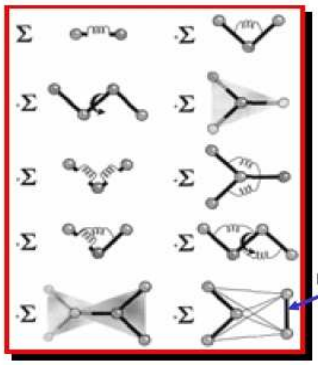
$$U_{Coul} = \frac{e^2}{4\pi\varepsilon_o}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}}$$

Lennard-Jones Potential

$$U_{VDW} = \sum_{i\neq j} D_o\left[\left(\frac{R_o}{r_{ij}}\right)^{12} - 2\left(\frac{R_o}{r_{ij}}\right)^{6}\right]$$

Buckingham Potential (Ionic solids)

$$U_{ij} = k\frac{q_i q_j}{r_{ij}} + A_{ij}\exp(-r_{ij}/\rho_{ij}) - \frac{C_{ij}}{r_{ij}^6}$$



Amber, Charmm, CFF, CVFF, CLAYFF
Dreiding, MM1, MMFF, Tripos, UFF

Molecular Mechanics & Energy Minimization

$$U = \Sigma\Sigma\, U_{ij}(\mathbf{q}_{ij}) + \Sigma\Sigma\Sigma\, U_{ijk}(\mathbf{q}_{ijk}) + \ldots$$

min $\Rightarrow \partial\, U(\mathbf{q}_1,\mathbf{q}_2,\ldots\, \mathbf{q}_N) / \partial\, \mathbf{q}_i = 0;$

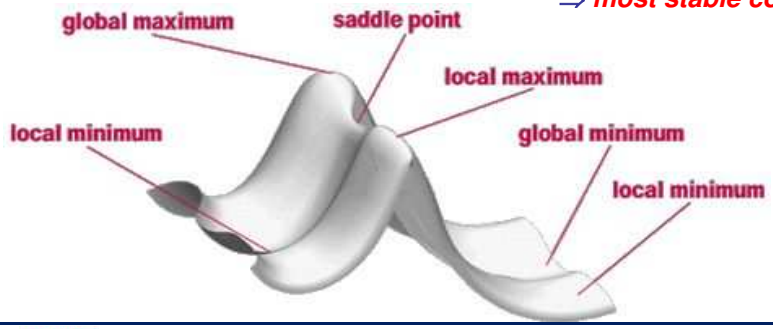
$\partial^2\, U(\mathbf{q}_1,\mathbf{q}_2,\ldots\, \mathbf{q}_N) / \partial\, \mathbf{q}_i \partial\, \mathbf{q}_j > 0;$

$i,j = 1,2,\ldots,N$

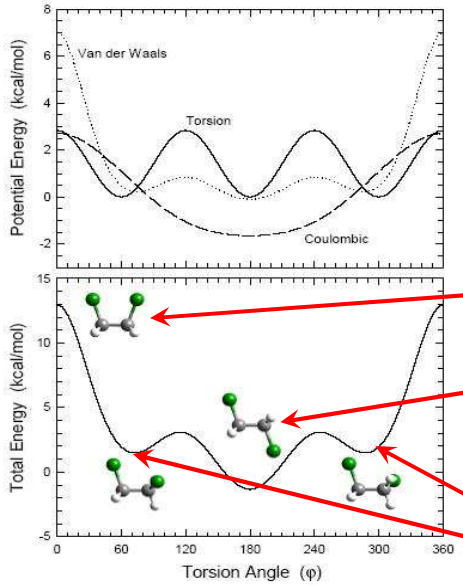
Also called ***structure optimization***

The goal is to find a set of coordinates (atomic positions) that result in the ***lowest possible energy*** *of the system*

$\Rightarrow$ ***most stable configuration***



Molecular Mechanics & Energy Minimization (2)



Component contributions to the total potential energy for ***dichloroethane*** as a function of the ***torsion angle defined by Cl-C-C-Cl***.

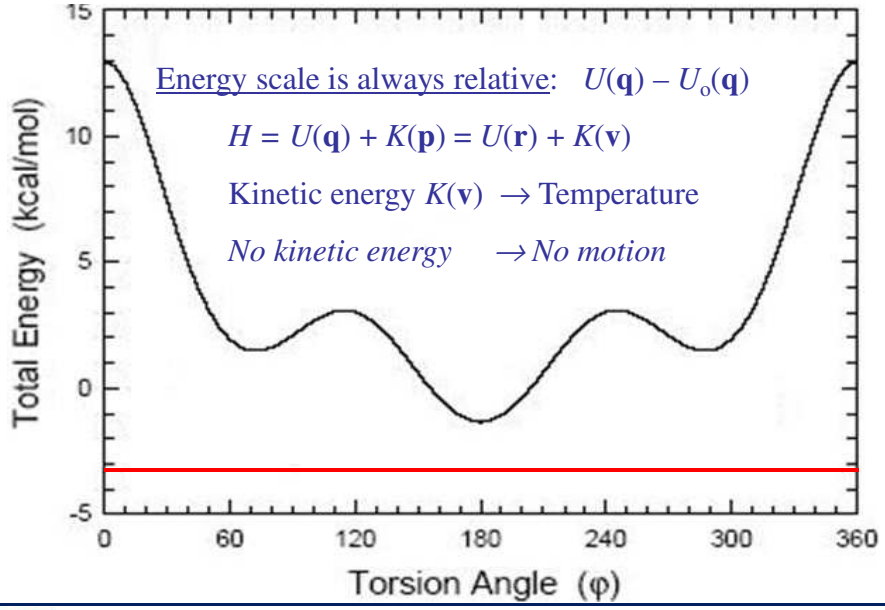
Structural models corresponding to the three stable conformers:

The least stable transition structure

Global minimum

Two local minima

Molecular Mechanics (3)



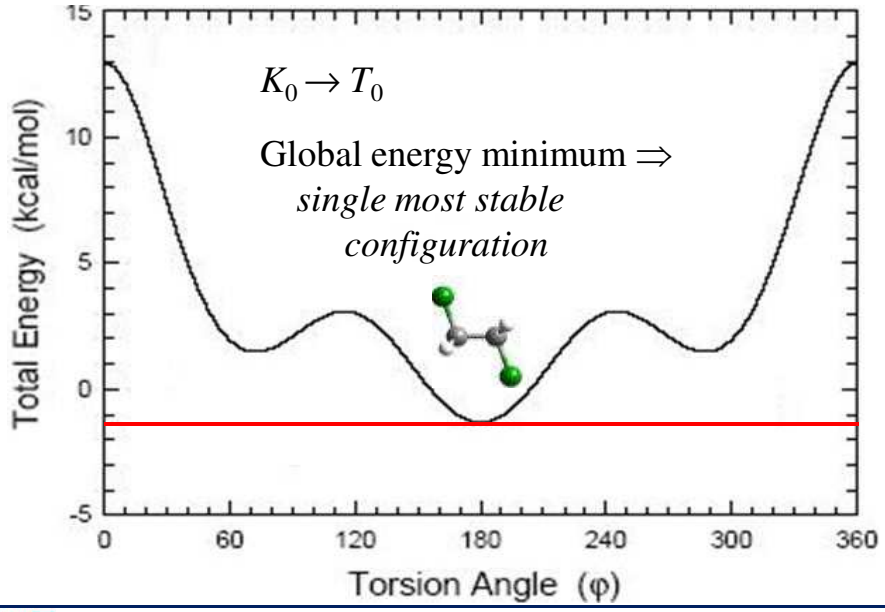
Energy scale is always relative: $U(\mathbf{q}) - U_o(\mathbf{q})$

$H = U(\mathbf{q}) + K(\mathbf{p}) = U(\mathbf{r}) + K(\mathbf{v})$

Kinetic energy $K(\mathbf{v})$ $\rightarrow$ Temperature

No kinetic energy $\rightarrow$ *No motion*

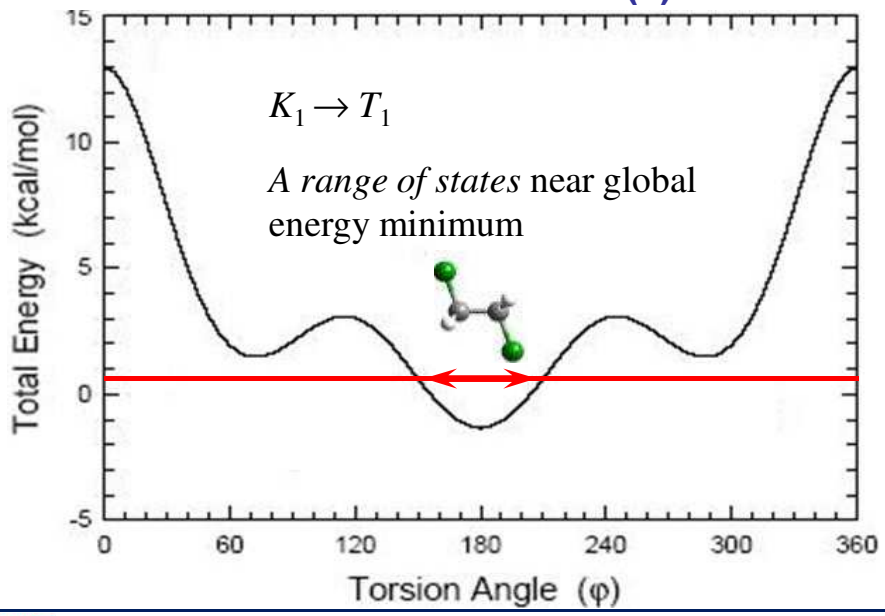
Molecular Mechanics (4)



$K_0 \rightarrow T_0$

Global energy minimum $\Rightarrow$
single most stable configuration

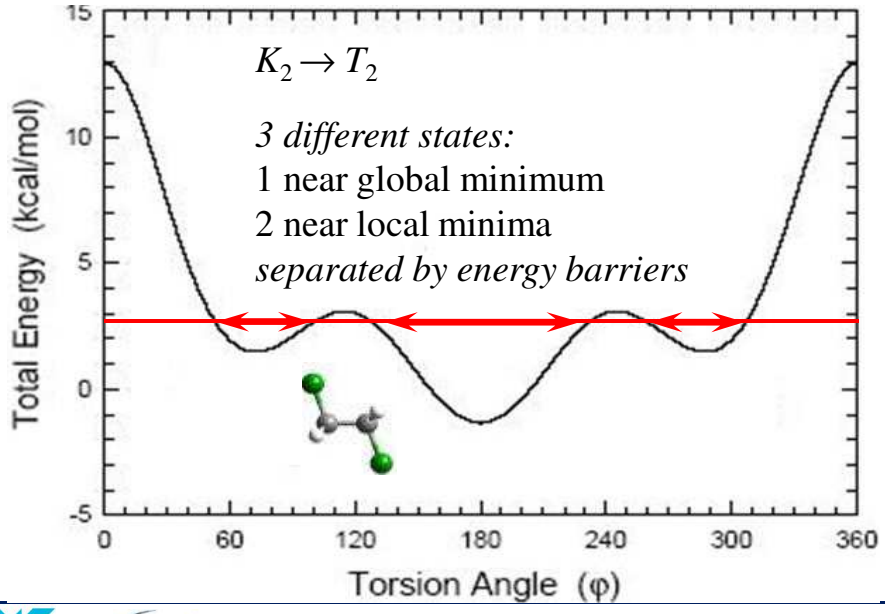
Molecular Mechanics (5)



$K_1 \rightarrow T_1$

A range of states near global energy minimum

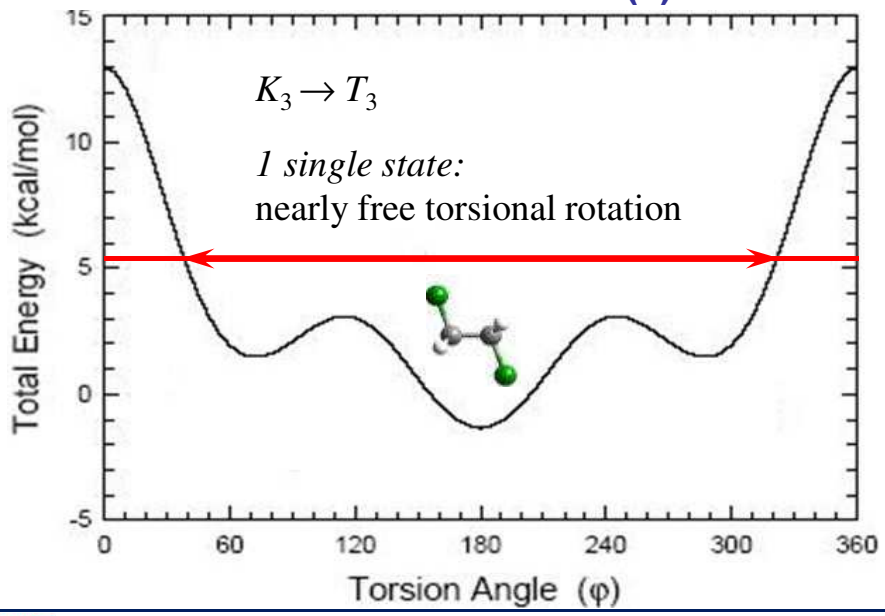
Molecular Mechanics (6)



$K_2 \rightarrow T_2$

3 different states:
1 near global minimum
2 near local minima
separated by energy barriers

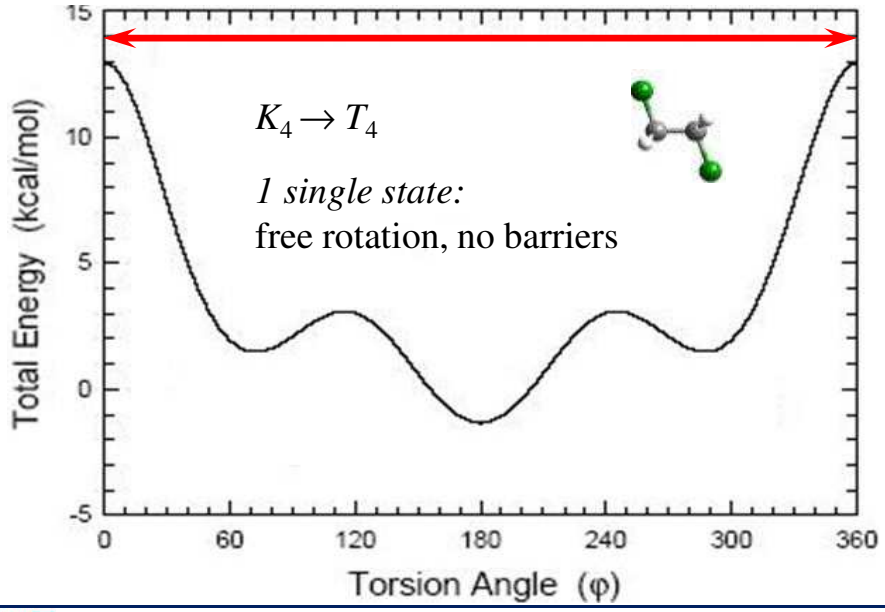
Molecular Mechanics (7)



$K_3 \rightarrow T_3$

1 single state:
nearly free torsional rotation

Molecular Mechanics (8)



$K_4 \rightarrow T_4$

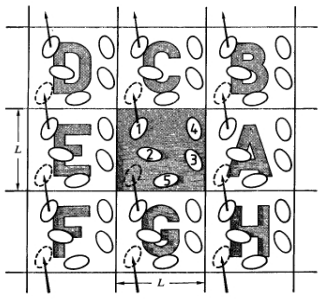
1 single state:
free rotation, no barriers

Classical MC & MD Molecular Modeling - Details

- *N* ~ 1,000-1000,000 atoms / *t* ~ 1-10 ns / n ~ 10^6-10^7 conf.
- Typically, constant *T*,*P* or *T*,*V* statistical ensembles
- Many molecular modeling software packages currently available.
- Most important: develop efficient numerical tools for the analysis of MD-generated trajectories or MC-generated ensembles of configs.
- *Coordinates* → Equilibrium thermodynamic properties
  → Atom-atom radial distribution functions
  → Coordination numbers, hydration numbers
  → Fluid structure, hydration shells
  → Molecular cluster formation and sorption environments
- *Velocities* → Diffusion
  → Velocity autocorrelation functions
  → Power spectra; dynamic details of atomic motions
- Comparison and interpretation of spectroscopic measurements: NMR, IR, Raman, X-ray.
- Molecular mechanisms controlling the behavior of aqueous species in solution and at substrate interfaces.

Methods of Molecular Computer Simulations: Molecular Dynamics (MD) and Monte Carlo (MC)

- **MD - time averages** over a dynamic trajectory in the phase space of the simulated system
- **MC - ensemble averages** over a computer-generated random Markov chain of molecular configurations
- Periodic boundary conditions (PBC)



MD MC

$$T = \frac{2}{3Nk_B}\left\langle \sum_{i=1}^{N} \frac{m_i \mathbf{v}_i^2}{2} \right\rangle$$

$$D = \lim_{t\to\infty} \frac{1}{6Nt}\left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle$$

$$P = \frac{Nk_B T}{V} - \left(\frac{1}{3V}\right)\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle$$

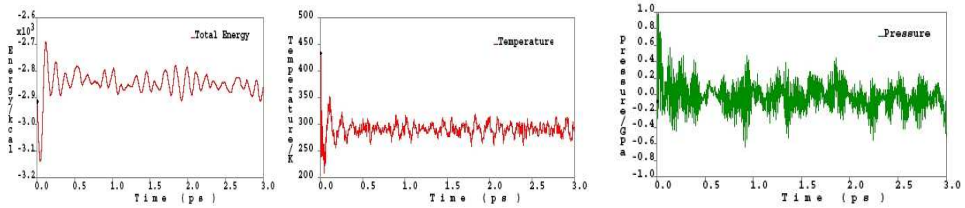
$$H_{conf} = \langle U \rangle + P\langle V \rangle$$

$$V_m = \langle V \rangle N_A / N$$

$$g_{ij}(r)$$

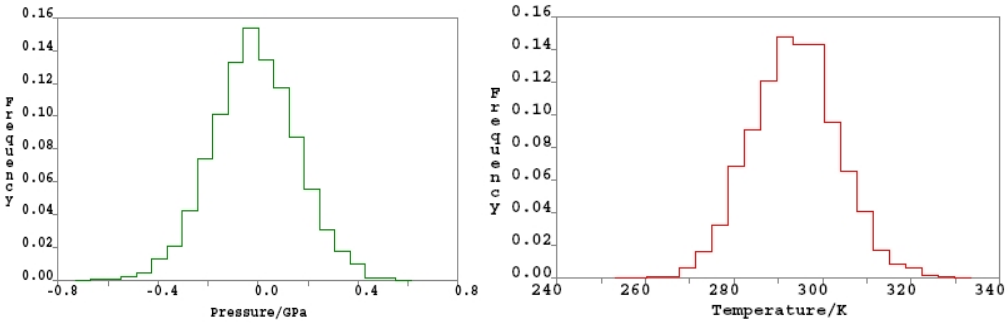
Possible Sources of Errors in Molecular Simulations

- System size, periodicity, correlation length
- Initial configuration: coordinates, velocities (MD), doubling temperature
- Equilibration
- MD: time scale, time step, numerical integration, total simulation time
- MC: acceptance rate, efficiency probing the configuration space
- Accumulation statistics, convergence, statistical errors



Statistical Distributions

MD simulation of 2.2*m* NaCl Aqueous Solution at 1 bar and 300 K



*These distributions are due to the **natural** fluctuations of the thermodynamic properties, corresponding to an equilibrium state of the simulated system*

Fluctuation Properties

$$C_V = R\left(\frac{2}{3} - N\frac{\langle T^2\rangle - \langle T\rangle^2}{\langle T\rangle^2}\right)^{-1}$$ Heat capacity

$$C_P = \left(\frac{\langle H^2\rangle - \langle H\rangle^2}{Nk_B T^2}\right)$$

Averages of fluctuation properties converge much slower than other thermodynamic averages

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\langle V^2\rangle - \langle V\rangle^2}{Nk_B T\langle V\rangle}\right)$$ Isothermal compressibility

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\langle H_{conf}V\rangle - \langle H_{conf}\rangle\langle V\rangle}{Nk_B T^2\langle V\rangle}\right)$$ Thermal expansivity

$$g_K = \frac{\left\langle\left|\sum \boldsymbol{\mu}_i\right|^2\right\rangle - \left\langle\left|\sum \boldsymbol{\mu}_i\right|\right\rangle^2}{N\boldsymbol{\mu}^2}$$ Kirkwood factor

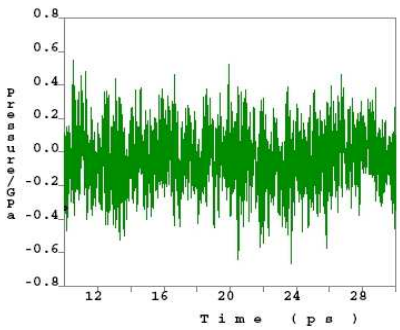
$$\varepsilon = 1 + \frac{4\pi\rho\boldsymbol{\mu}^2 y g_K}{3k_B T}$$ Dielectric constant

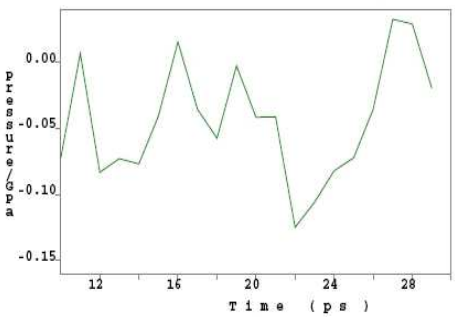
Statistical Errors

Method of block averages

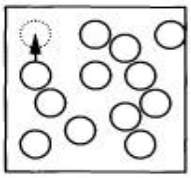
If $\langle A\rangle_i$ is the mean value of the property A computed over the block i, then the statistical error δA of the mean value $\langle A\rangle$ over the whole trajectory (or chain of configurations) can be estimated as

$$(\delta A)^2 = \frac{1}{M(M-1)}\sum_{i=1}^{M}\left[\langle A^2\rangle_i - \langle A\rangle_i^2\right]$$





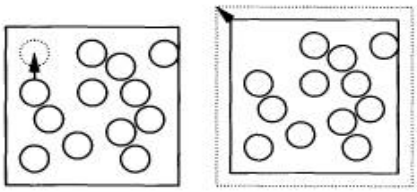
Monte Carlo Simulations in Different Ensembles



$N\,V\,T$ – canonical ensemble

$p = \exp(-\beta U)$ $\quad \beta = 1/k_B T$

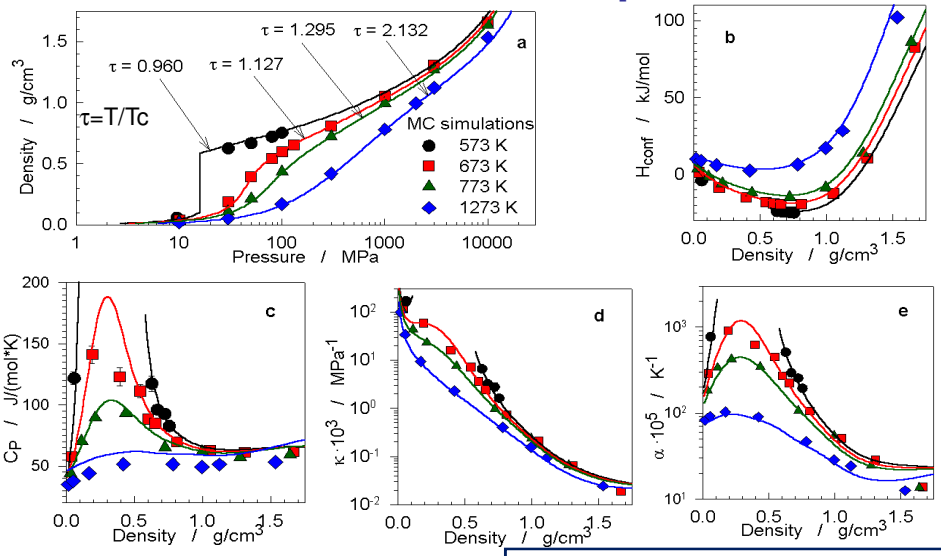
$N\,P\,T$ – isothermal-isobaric ensemble



$p = \exp(-\beta H) = \exp[-\beta (U + PV) + N \ln V]$

- Most efficient acceptance ratio for new configurations ~ 50%
- Relative frequency of various types of moves also important

Thermodynamic Properties of Water
MC Simulations with TIP4P potential



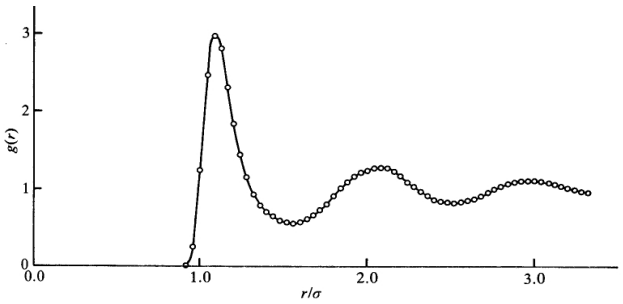
Kalinichev, *Rev. Mineral.Geochem.*, **42**, 83-129 (2001)

Fluid Structure
Radial Distribution Functions (RDFs)

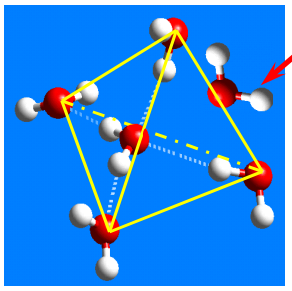
- ***Pair distribution function*** or ***radial distribution function g(r)*** – probability to find an atom *i* at a certain distance *r* from another atom *j*
- Normalized to a completely random distribution of atoms in space

$$g(r) = \rho^{-2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r}_i)\delta(\mathbf{r}_j - \mathbf{r}) \right\rangle = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

- Comparable to exp. data on X-ray or neutron diffraction
- In practice, $\delta(\mathbf{r}\text{-}\mathbf{r}_{ij})$ is replaced by a function which is non-zero in a very narrow range of **r**, and $g(\mathbf{r})$ is calculated as a histogram
- $g(\mathbf{r})$ = 1 for ideal gas

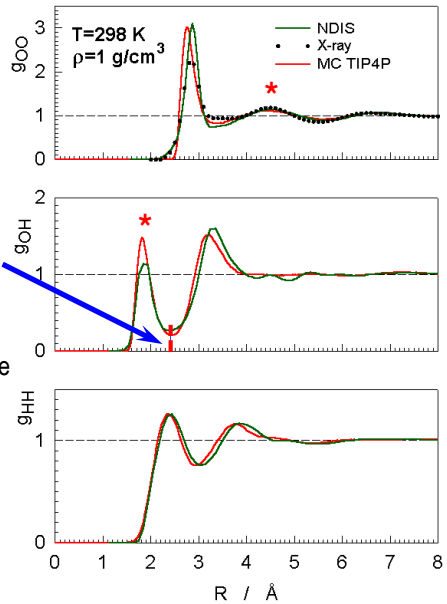


Structure of Water: Atom-Atom Radial Distribution Functions (RDFs)



Interstitial H_2O molecule

Distance criterion for H-bonding



- **Ice:** Tetrahedrally ordered O in the diamond-like network
- H positions are disordered
- Proton diffusion
- Proton hopping
- **Liquid:** Only short-range tetrahedral ordering remains

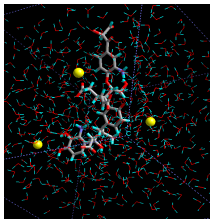
Radial Distribution Functions and Running Coordination Numbers

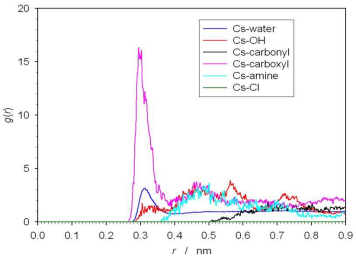
- Importance of $g(r)$ normalization
- Height of the $g(r)$ peaks is not necessarily an indication of high population
- Average density or concentration of species is equally important

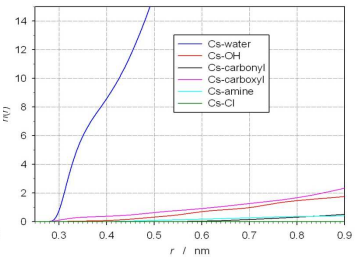
$$g_{ij}(r) = \frac{1}{N_j \rho_i} \left\langle \sum_i \sum_j \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$

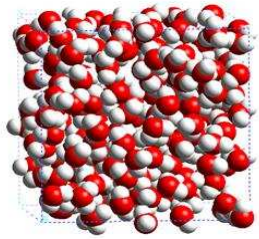
3 Cs^+ ions in aqueous solution with humic acid (NOM anion)

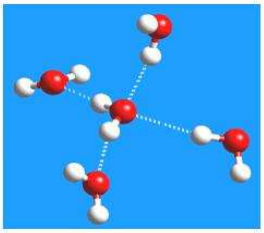


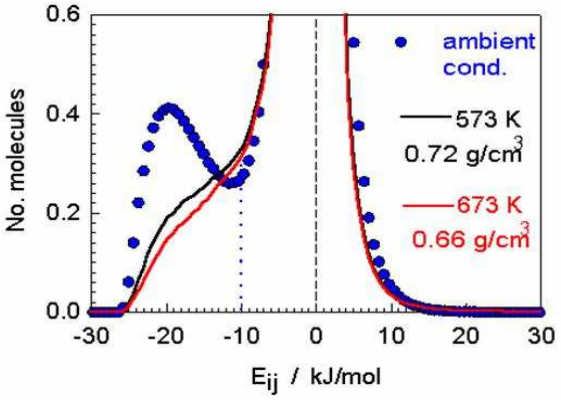




Micro-Thermodynamic Properties: Pair Energy Distributions



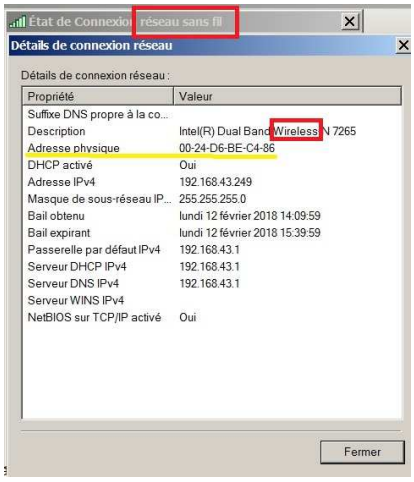




Getting physical address (MAC address) of your Wi-Fi card

When you are connected to any Wi-Fi (wireless) network ⇒ Go to you "Network Parameters" menu ⇒ ⇒ Go to "Status" ⇒ Go to "Details of the wireless connection"

Your table should look something like this:



Questions for the final paper / report on one of the topics: 1 – clays; 2 – cement; 3 – TiO_2 surfaces; 4 – corrosion; 5 – organics, etc. (Please use only as a guidance)

- What molecular modeling method was used and why?
- Was it a fully atomistic simulations, or some simplified models were used?
- What other approximations were used in the modeling?
- What was the number of particles in the simulations? Was it big enough for the specific problem? Was it small enough to make the simulations computationally efficient?
- How long-range electrostatic interactions were handled in the simulations? Was it important for the given problem?
- What kind of boundary conditions were applied to the simulation box? Why?
- What properties of the system were calculated from the molecular simulation?
- Make a qualitative assessment of the accuracy for the calculated properties given the number of atoms in the simulated system and the duration of the simulation.
- What other properties would you additionally calculate from the same simulations for the same system?
- Formulate 2 or 3 strong points of the given molecular simulation paper and 2 or 3 weak points of the paper.