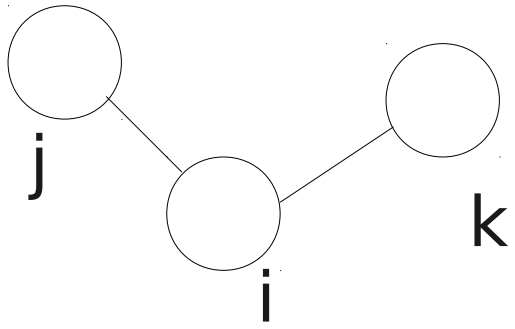
Axilrod-Teller potential

Axilrod BM and Teller E. (1943) "Interaction of the van der Waals Type between Three Atoms", J. Chem. Phys., 11, 299-300.

$$U_{ijk} = E_0 \left[\frac{1 + 3cos\gamma_i cos\gamma_j cos\gamma_k}{(r_{ij} r_{jk} r_{ik})^3} \right]$$

Three-body term



γ_i is the angle between r_{ij} and r_{ik}

Many body effects act to diminish the strength of pairwise dispersion. This is because the third atom may not be *simultaneously* correlated with the other two.

Arises from third order perturbation theory

Is positive for most configurations; Magnitude is about 4-5% of dispersion

Molecules

Molecule	Dipole moment ($x10^{-30}$C.m)	Polarizability ($x10^{-25}$cc)	Boiling Point (^{o}C)
He	0	2.0	-268.9
H_2	0	8.2	-252.9
N_2	0	17.7	-195.8
CO	0.33	19.8	-190
Ar	0	16.6	-185.9
CH_4	0	26.0	-161.5
CF_4	0	0	-128
HCl	3.6	26.3	-85
CO_2	0	26.3	-78
HBr	2.67	30.1	-67
HI	1.4	54.5	-35
NH_3	4.9	22.2	-34.4
SO_2	5.42	43.4	-10
HF	6.37	4.1	19
CCl_4	0	105	76.5
H_2O	6.17	14.8	100

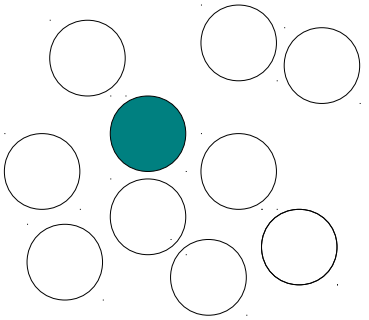
Polarizability arises from atomic and bond polarizations.

It is a tensor.

It can be anisotropic.

Polarizable model

$$U_{pol} = -\frac{1}{2}\sum_i \mu_i . \mathbf{E}_i^0$$



$$\mathbf{E}_i^0 = \sum_{j \neq i} q_j \frac{\mathbf{r}_{ij}}{r_{ij}^3}$$

$$\mu_i = \alpha \mathbf{E}_i$$

$$\mathbf{E}_i = \mathbf{E}_i^0 + \sum_{j \neq i} T_{ij}\mu_j$$

$$T_{ij} = \frac{1}{r_{ij}^3}\left(\frac{3\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2} - 1\right)$$

E_i^0: Field at i due to other fixed charges

μ_i : Induced dipole moment at i

E_i : Total electric field at i

T_{ij} : Electric dipole tensor

U_{pol} is over and above any LJ and Coulombic interactions

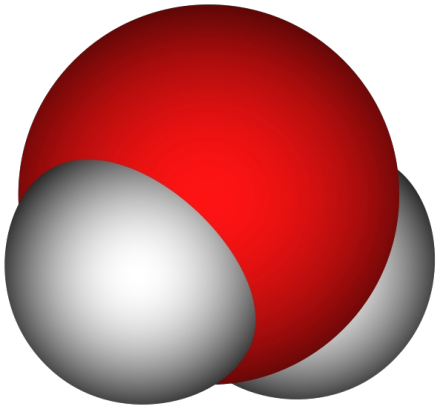
We neither know the field nor the dipole moment. Hence, solved in a self consistent manner (iteratively)

Liem X Dang and many others

Polarizable force fields

- Very important in inhomogeneous situations – interfaces, clusters, ions in solution
- Although intermolecular structure appears not to be much influenced, including polarization in many cases, increases diffusion.
- One can solve the SCF equation using a Car-Parrinello type approach
- Similarly, one can use the extended Lagrangian approach to have a time dependence of the atom charge and make it a dynamical variable (dynamics is fictitious. This is the Rick-Berne model.
- For ionic solids, Paul Madden has showed that polarizable force fields are extremely important to obtain good agreement with experimental Raman spectra.
- Jungwirth & Tobias showed that inclusion of anion polarization is crucial to obtain the correct pattern of segregation of ions at the liquid-vapour interface of aqeuous ionic solutions

Water



Gas Phase data

O-H length = 0.96 A
HOH angle = 104.45°

Dipole moment = 1.85 D

SPC model

q_O = -0.82e

q_H = +0.41e

Bond length = 1.0A

Bond angle = 109.47°

Dipole moment = 2.27 D

Totally different values than experimental data

Spherical cut-off + Reaction field

3-site water models

$$U_{tot}(\{\mathbf{r}\}) = \sum_{\substack{non-bonded \\ i<j}} \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}} + \frac{A}{r_{\mathrm{OO}}^{12}} - \frac{B}{r_{\mathrm{OO}}^{6}}$$

Quantity	TIPS	SPC	TIP3P	SPC/E
r(OH), Å	0.9572	1.0	0.9572	1.0
HOH (deg)	104.52	109.47	104.52	109.47
Ax10^{-3} , kcal/Å^{12}/mol	580	629.4	582	629.4
B, kcalÅ^{6}/mol	525	625.5	595.0	625.5
q(O)	-0.80	-0.82	-0.834	-0.8476
q(H)	+0.40	+0.41	+0.417	+0.4238
Dipole moment (D)	2.25	2.27	2.347	2.35

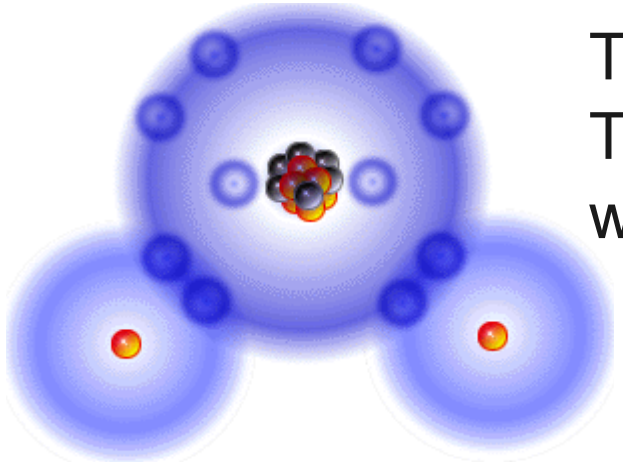
Estimated effective dipole moment of a water molecule in bulk:

2.65 D

Features of water models

- Rigid; No internal dynamics
- One can either use rigid body dynamics with centre of mass coordinate and orientation (using either Euler angles or quaternions) OR use Cartesian coordinates for the three atoms and impose holonomic constraints to maintain molecular geometry (thus giving rise to a constraint force)
- No ”size”, No ”dispersion” for hydrogen
- Hmm.. Water forms hydrogen bonds. There is no magic hydrogen bonding interaction term.
- Hydrogen bond springs forth from the combination of size, charge, LJ and geometry

Water: A ”minor” detail



Two lone pair of electrons
The lone pair orbitals make a tetrahedral angle with each of the bond pair ones

Can we have a 4-site model for water? Yes

Keep the site ”behind” the oxygen atom. This is a ghost site.
It interacts with every site and contributes to the force on each atom.

It also experiences force. However its force is resolved into force components on real atoms.

The real atom coordinates are updated. The ghost atom coordinate is obtained from the coordinates of the three atoms

TIP4P

	TIP4P	TIP4P-Ew	TIP4P/Ice	TIP4P/2005
r(OH),Å	0.9572	0.9572	0.9572	0.9572
HOH, deg	104.52	104.52	104.52	104.52
r(OM),Å	0.15	0.125	0.1577	0.1546
$Ax10^{-3}$, kcal/$Å^{12}$/mol	600.0	656.1	857.9	731.3
B,kcal$Å^6$/mol	610.0	653.5	850.5	736.0
q(M)	-1.04	-1.04844	-1.1794	-1.1128
q(H)	+0.52	+0.52422	+0.5897	+0.5564

No charge on oxygen site
Oxygen contributes to dispersion & size
No size, dispersion for the ghost site

Ghosts have no feet, no size, no dispersion

Rigid versus flexible models

- If molecules are small, assume rigidity
- If molecule can change size/shape, use flexible model
- One can mix rigidity and flexibility. In long molecules, one can freeze the bond lengths and possibly angles, but can have flexibility for larger pieces of the molecule
- Time step for 3-site waters: 2.5 fs for rigid models and 0.5 fs for fully flexible ones.

Parameters

- One can do a quantum chemical calculation of a single molecule, optimize its geometry, obtain site charges using fit to ESP etc..
- These site charges will provide gas phase dipole moment (if present).
- The molecule could be polarized in the condensed phase and hence gas phase parameters may not work.
- So, one can (and should) take these parameters as starting values, obtain condensed phase properties. If necessary tune them so as to obtain good agreement with experimental data.

CHARMM force field (proteins, lipids etc..)

$$U(\vec{R}) = \sum_{\text{bonds}} K_b(b - b_0)^2 + \sum_{\text{UB}} K_{\text{UB}}(S - S_0)^2 +$$
$$\sum_{\text{angle}} K_\theta(\theta - \theta_0)^2 + \sum_{\text{dihedrals}} K_\chi(1 + \cos(n\chi - \delta)) +$$
$$\sum_{\text{impropers}} K_{\text{imp}}(\varphi - \varphi_0)^2 +$$
$$\sum_{\text{nonbond}} \epsilon\left[\left(\frac{R_{\min_{ij}}}{r_{ij}}\right)^{12} - \left(\frac{R_{\min_{ij}}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{\epsilon_1 r_{ij}}$$

Urey-Bradley: Important to get proper frequencies for symmetric and asymmetric stretching modes

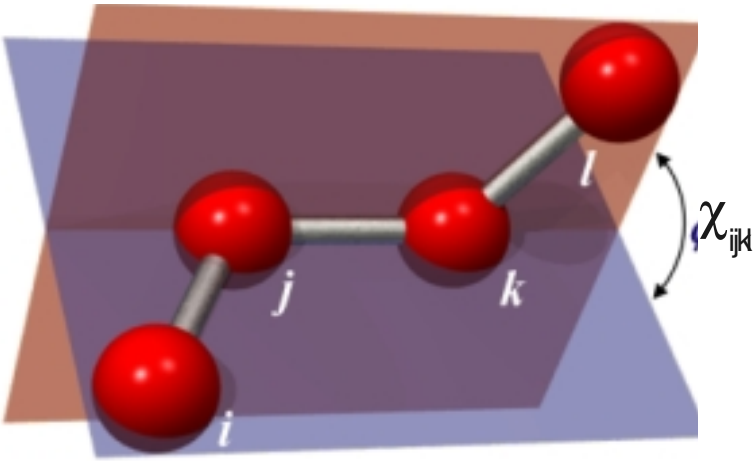
Improper dihedrals: To fix geometry on branching, and to obtain properly frequencies of out-of-plane modes

CHARMM terms

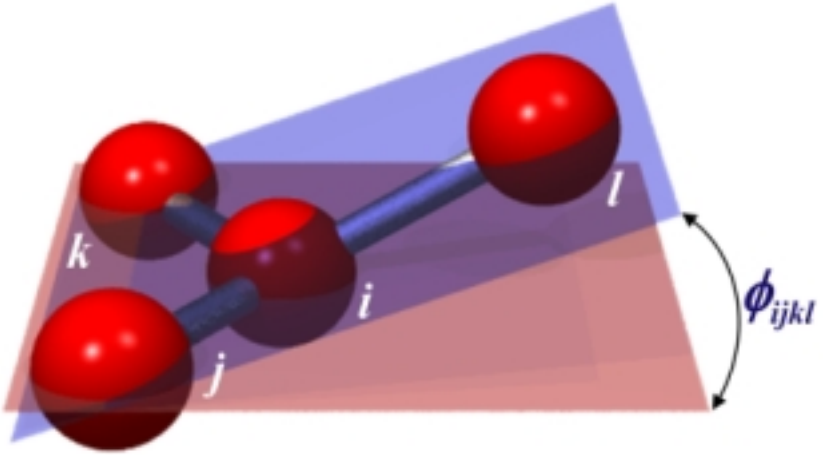
S : Urey-Bradley 1-3 distance

χ : Torsional angle

ϕ : Improper torsional angle



Many of the intramolecular terms and parameters are liberally borrowed from research which tried to model vibrational spectra of molecules using force fields, through normal mode analyses.



Equilibrium bond lengths and angles are usually obtained from crystal structure data

Where experimental vibrational spectra were not known (to obtain force constants), the molecule would be studied using quantum chemical methods to obtain the same.

Biomolecular force fields

The water model consistent with CHARMM is TIP3P.

Other force fields similar to CHARMM are: AMBER, GROMOS, OPLS, ..

They all share more or less the same potential terms, however the parameters could be different.

Some of them have been documented to overstabilize α helices.

Refinement of parameters is an ongoing process.

It is similar to what happens in the parametrization of the exchange and correlation functionals in DFT.

Efforts are underway to include polarizability terms in the force field (Sandeep Patel, Delaware)

Torsion: poly(tetrafluoroethylene)

Poly(tetrafluoroethylene) is PTFE. Commercially called Teflon by DuPont. The molecular formula is: $(-CF_2-)_n$

Is there a temperature dependent phase transition in PTFE?

Experimental data:

Phase I is stable between 30°C to 330°C (melting point). Very high thermal stability. Polymer chains are aligned parallel, closely packed.

However, the orientation of CF_2 groups possess only local correlations, Without long range order.

Crystalline phase: Phase II, exists below room temperature
The chains exhibit coherent helical winding with a pitch of 13 CF_2 groups for a 180° helix turn.

Liquid phase: Interdigitated chains; Higher shear viscosity than in Phase I

What is the torsional potential?

Consider C_4F_{10}

Perform geometry optimizations using good quantum chemical methods for various values of the C-C torsional angle in this molecule.

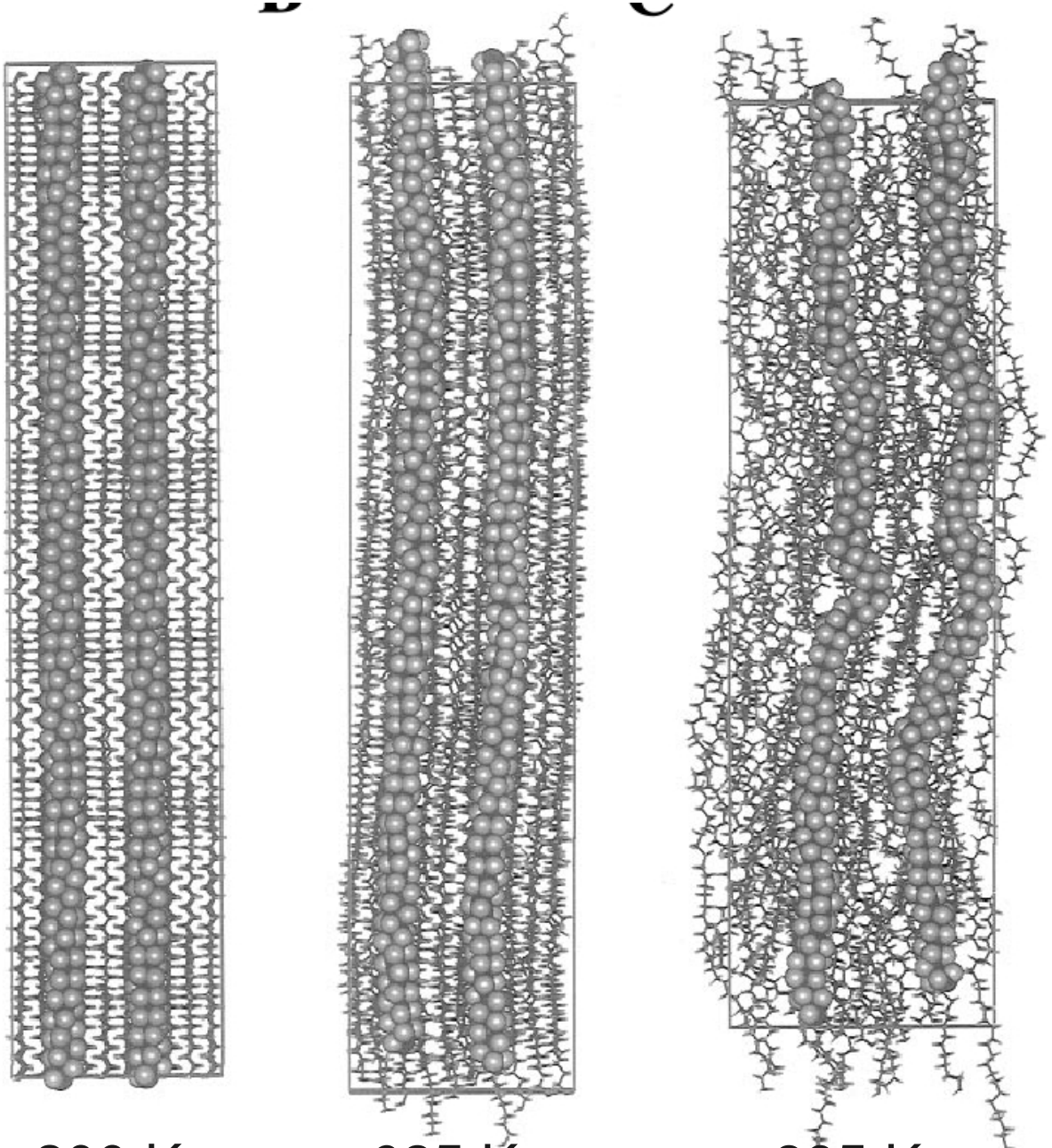
Already known: Lennard-Jones parameters for CF_4

The L-J interactions for different sites on C_4F_{10} are taken to be the same as that in CF_4.

What you have now is the true ”quantum chemical” torsional potential.

Fit it to a cosine power series (or cosine multi-harmonic series)

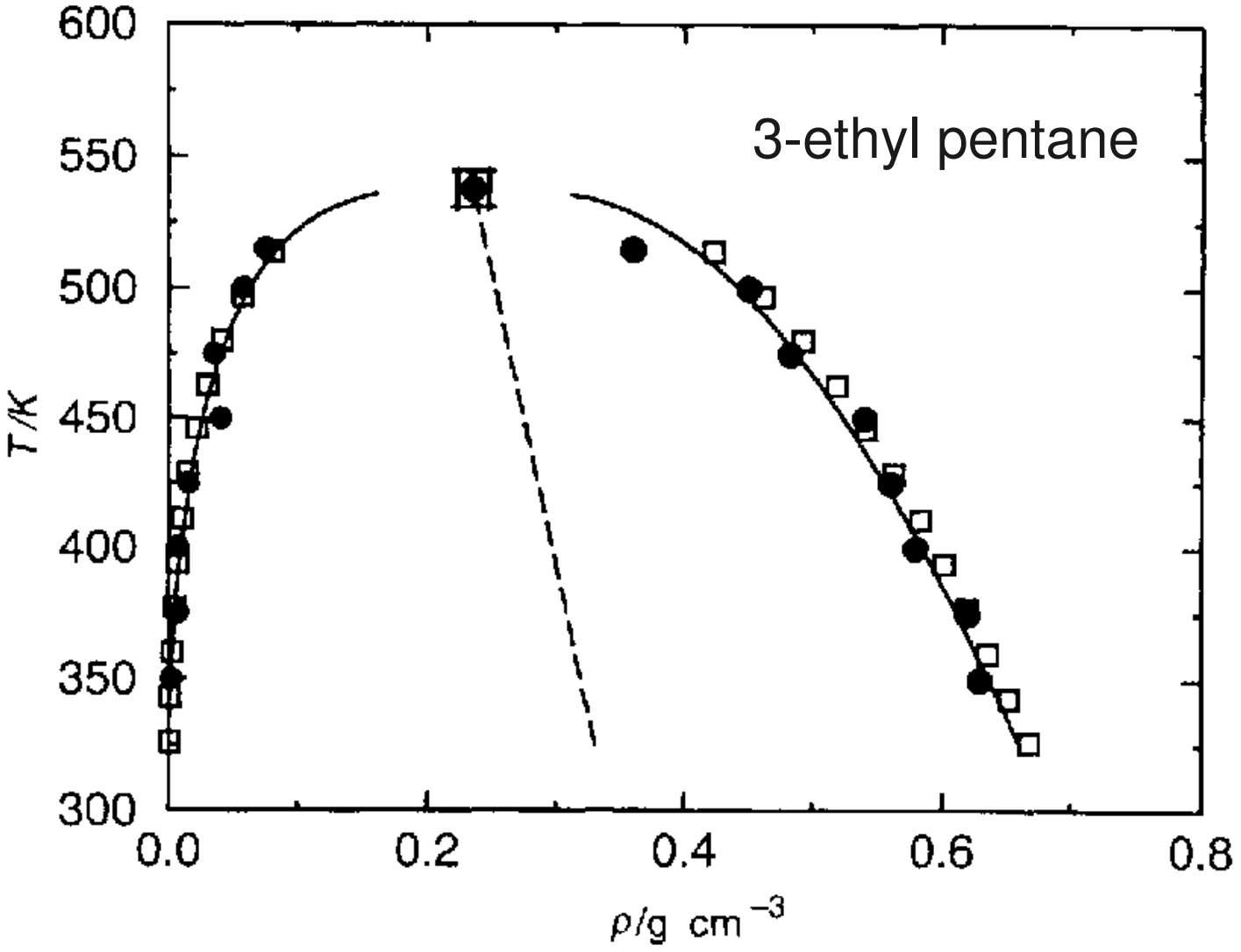
PTFE: Transition



200 K 625 K 895 K

Sprik,
Rothlisberger,
Klein
JPCB (1997)

TRAPPe force field



Hydrocarbons,
Other organics

LJ parameters
obtained by
calculations
of vapour-
liquid
equilibrium
through GEMC
method
and comparing
to experiments

Ilja Siepmann and coworkers

Metals

$$U = \sum_{i<j}^{N} \phi(r_{ij}) + \sum_{i}^{N} V(n_i)$$

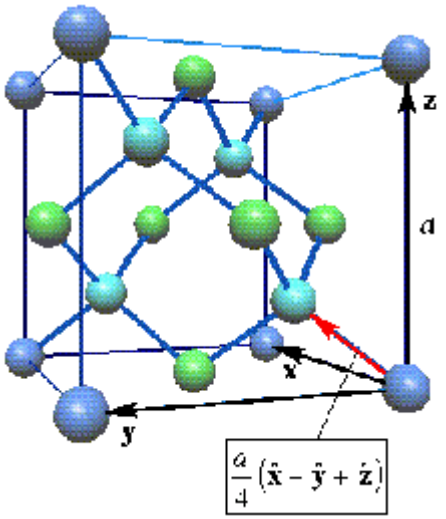
$\phi(r)$ → Two-body part

$V(n_i)$ → Potential energy depending on the ”effective coordination” of atom i; Many-body

$$n_i = \sum_{\substack{j=1 \\ j \neq i}}^{N} \rho(r_{ij})$$

$\rho(r)$ → Short ranged, decreasing function of distance

Examples: Finnis-Sinclair, Embedded Atom, Glue model



Stillinger-Weber

Tetrahedral solids

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

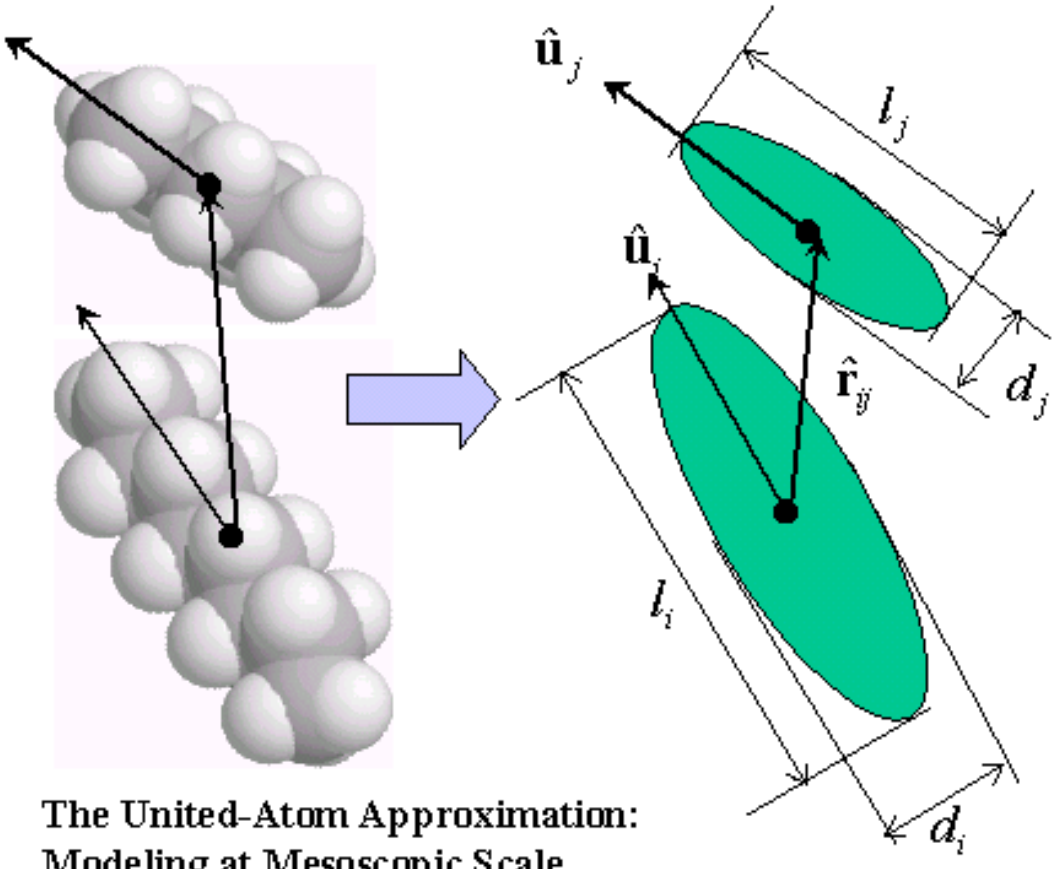
$$\phi_2(r_{ij}) = A_{ij}\epsilon_{ij}\left[B_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{q_{ij}}\right] exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right)$$

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

Three-body term is range dependent

Non-tetrahedral polytypes are seen at high pressures; SW may not work there.

Gay-Berne model

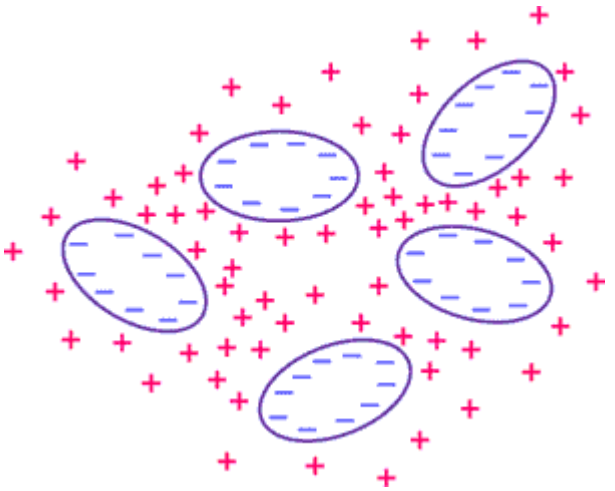


The United-Atom Approximation:
Modeling at Mesoscopic Scale

- Lennard-Jones + Orientation dependent terms
- Able to simulate nematic, discotic nematic, biaxial nematic phases of liquid crystals

Yukawa potential/Colloids

Hydrophobic colloid: Clay
Particles are suspended/dispersed in water
They are charge stabilized



$$U = \frac{1}{2N} U_0 \sum_{i,j} \frac{a}{r_{ij}} e^{-(\lambda r_{ij}/a)}$$

$$\lambda = \kappa a$$

$$U_0 = \frac{Z^2 e^2}{\epsilon a}$$

$$\kappa^2 = \frac{4\pi n Z e^2}{\epsilon k_B T}$$

a : ”diameter” of particle
N : number density
Z : Charge
ε : dielectric constant
κ^{-1} : Screening length (Debye-Huckel)

Numerical potential

- In a system containing many different types of atoms, the interaction potential experienced by a pair of atoms could be a sum of several terms.

- One could write a code which contains a force loop (aka the potential energy calculation routine) for each term.

- This means such term(s) will be calculated in each of these routines. This is expensive.

- Instead, one could identify specific pair types in the system and generate a table of total (i.e., sum) potential energy corresponding to that atom type versus distance on a finely spaced one-dimensional grid.

3.2000000000000002	314.52569214629682
3.3000000000000003	119.76117059907195
3.4000000000000004	4.2885416867260524
3.5000000000000000	-61.936212516303797
3.6000000000000001	-97.613778133392799
3.7000000000000002	-114.46078190846636
3.8000000000000003	-119.85117722611390
3.9000000000000004	-118.43552724741893
4.0000000000000000	-113.14428273048767
4.1000000000000005	-105.81535523135491
4.2000000000000002	-97.590015616183180
4.2999999999999998	-89.164485207323153
4.4000000000000004	-80.950809867787683
4.5000000000000000	-73.180230926617710
4.6000000000000005	-65.969836273236282
4.7000000000000002	-59.365611880455702
4.8000000000000007	-53.370243517088362
4.9000000000000004	-47.961021424231589
5.0000000000000000	-43.101301916804154
5.1000000000000005	-38.747767392248406
5.2000000000000002	-34.854946433348083
5.3000000000000007	-31.377950898201995
5.4000000000000004	-28.274058204579035

STATUTORY WARNING!

In canned codes,the default spline parameters for the evaluation of potential energy could be liberal.

•In the force routine, for a given pair type, once the distance is calculated, you ”lookup” the corresponding energy table and interpolate the potential energy value for the specific distance at hand

•In a similar manner, one can construct a table for the force as well.

•These are more efficient. Typically, cubic splines are employed.

Numerical (continued)..

- If you have obtained the potential energy versus distance quantum mechanically, then you already have a table of numbers
- There is no need to fit it to a functional form.
- You can provide most modern codes this table itself
- This is called a tabulated potential
- Most coarse grainers use tabulated potentials.

The Coulomb potential

• It is special. It is long ranged. Long with respect to how the number of atoms in a spherical shell of radii r and r+dr varies with r. The latter goes as r^2, and 1/r (Coulomb) overtakes it.

• Typical simulation box lengths being in the order of 40 to 50Å , the Coulomb energy does not decay to zero within half box length.

• You don't want to have large interaction cutoffs. At 12 or 13Å , (typical cutoff values), the Coulomb energy is significant.

• One needs to have a cutoff of around 30Å, for the Coulomb energy to become negligible. This is not practical.

Ewald sum

$$\frac{q_i q_j e^2}{r} = q_i q_j e^2 \left(\frac{erf(\alpha r)}{r} + \frac{erfc(\alpha r)}{r} \right)$$

k-space Increasing function of r — Decreasing function of r **Real space**

Fourier representation of 1st term is: $$\frac{1}{2V} \sum_{k \neq 0} \frac{4\pi}{k^2} |\rho(\mathbf{k})|^2 e^{-\frac{k^2}{4\alpha^2}}$$

Fourier component of charge density $$\rho(\mathbf{k}) = \sum_{i=1}^{N} q_i e^{i\mathbf{k}.\mathbf{r}_i}$$

Choose α such that erfc(αr_c) is very small. How small? If you aim for 1 part in 10^4 in the conservation of energy, then erfc(αr_c)/E should be less than 10^{-4}

αr_c >3.5 for the real space part to ”vanish” at r_c

Ewald, continued..

The k-space sum converges fast due to the exponential dependence. So, one can limit the sum up to a value, say, kmax. This convergence should be better than the conservation of total energy.

The k-space part is carried out for all the atoms, including self-interactions.

However, according to the force field, self-interactions are not included. Not included also are Coulombic interactions for pairs of atoms involved in a bond, in a bend, etc..
Hence, these terms must be subtracted off from the total energy.

Self-interaction correction: $$U_{self} = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \sum_{\cdot}^{N} q_i^2$$

"Bonded" correction: $$U_{bonded} = \sum_{\substack{bonded \\ i,j}} q_i q_j e^2 \left(\frac{erfc(\alpha r)}{r}\right)$$

Ewald, continued...

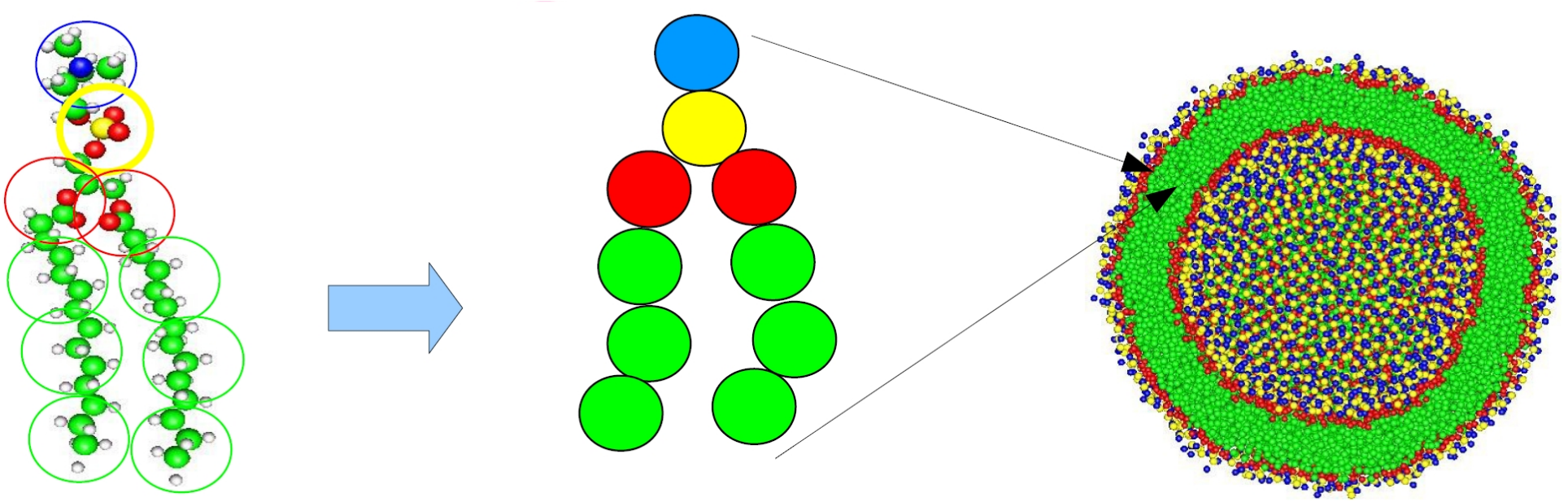
- One can use the method to handle a non-neutral system also.
- In this case, you add a uniform charge distribution over the entire box whose total charge is opposite to that of the charge of the system.
- The site charges interact with this uniform neutralizing background and the interaction energy is

$$U_{neutralizing} = -\frac{\pi q_{tot}^2}{2\alpha^2 V}$$

- The k-space sum can be rewritten as **k**>0 sum, due to the symmetry of the term.
- The positive half reciprocal space must be constructed with care.
- Typically, around 1000-2000 points in k-space are good enough for proper convergence of the reciprocal sum
- Efficiency is guaranteed when the time spent by the code in real space part is equal to that in k-space part
- The Fourier sum can also be performed efficiently using FFTs

Force matching method

Alexander Lyubartsev and many others



Retain only important degrees of freedom.

One could reduce number of atoms by about an order of magnitude

What is the interaction potential for these important degrees of freedom?

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Volume 49, Issue 3, 9 September 1974, Pages 197-198

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g(r) ⟷ V(r)+constant

A uniqueness theorem for fluid pair correlation functions

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Received 5 August 1974. Available online 19 September 2002.

Abstract

It is shown that, for quantum and classical fluids with only pairwise interactions, and under given conditions of temperature and density, the pair potential v(*r*) which gives rise to a given radial distribution function *g*(*r*) is unique up to a constant.

Coarse graining

$H(R_1, R_2, ...R_N, r_1, r_2, ...r_n)$ Hamiltonian for the full system

$$Z = \int dR_1...dR_N dr_1...dr_n exp(-\beta H(R_1, R_2, ...R_N, r_1, r_2, ...r_n)$$

$$= \int dR_1...dR_N exp(-\beta H^{CG}(R_1, R_2, ...R_N)$$

$$H^{CG}(R_1, ...R_N) = -\frac{1}{\beta}\int dr_1...dr_n exp(-\beta H(r_1, r_2, ...r_n)$$

Effective N-body CG potential

It is a potential of mean force. Notice the temperature and density dependence of this ”potential”.

But it is impossible to do simulations with a N-body potential.

We need a pair potential.

$$H^{CG}(R_1, R_2, \ldots, R_N) \approx \sum_{i>j} V_{ij}(R_{ij})$$

Approximations

We can try to fit:

Potential energy
Force on CG site

g(r) between CG sites
Any other ensemble average

$$V^{(n+1)}(r) = V^{(n)}(r) + kT \ln(g^{(n)}(r)/g^{ref}(r))$$

Iterative Boltzmann inversion scheme

- Second virial coefficient
- polarizable model
- teflon: sprik
- ionic liquid/bmimpf6/aimd/classical
- yukawa potential
- ewald summation method
- force matching (Lyubartsev)
- Charmm
- Tabular form
- Siepmann's UA model

Summary

Bonds, Bends: Crystal Structure, Vibrational Spectra, Quantum chemical calculations in gas phase

Torsion : Ratio of trans to gauche states from spectroscopy, torsional barriers from quantum calculations

Charges : Quantum chemical calculations (But be ready to finetune them, if necessary

Lennard-Jones : Start with parameters for atoms which are present In other molecules and depend on other people's σ value.

Adjust the parameters to obtain experimentally Known physical property data for the liquid
density vs temperature & pressure
Surface tension
Diffusion coefficients