Campinas Advanced School of Thermodynamics
Workshop on Molecular Simulations
Session 2 –MD of ethanol with MoSDeF

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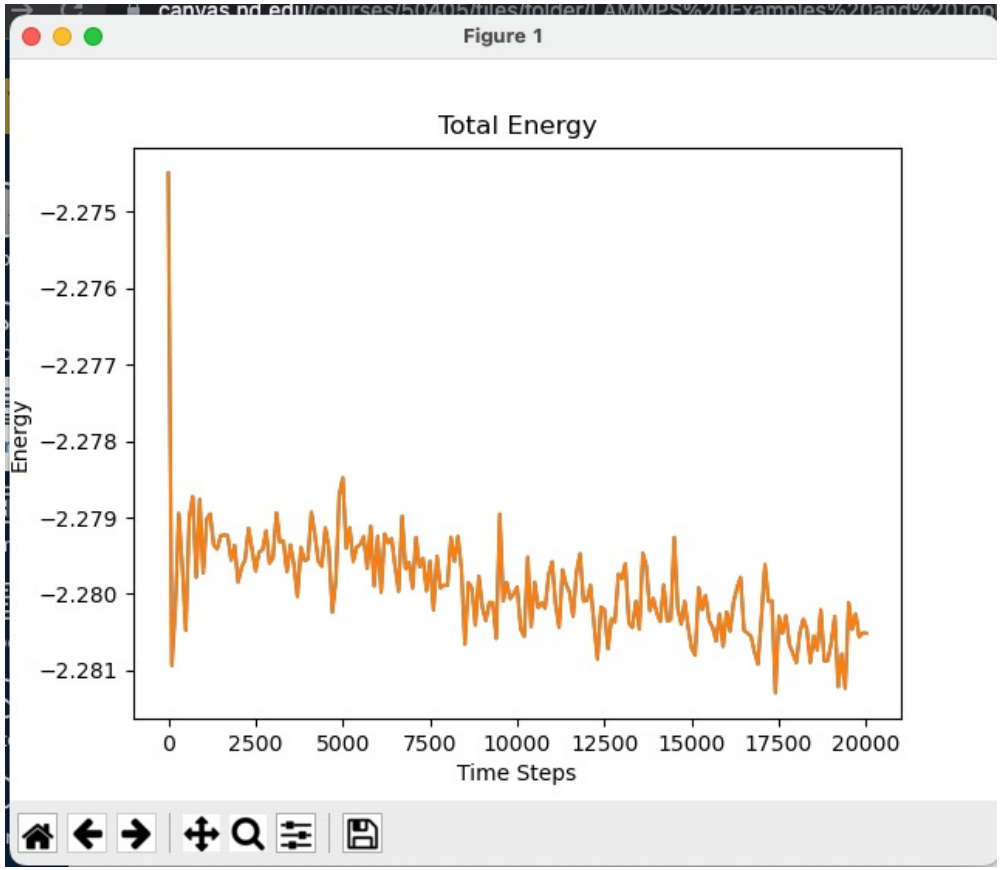
All materials available on MaginnGroup GitHub site

28 October, 2022

UNIVERSITY OF NOTRE DAME

Maginn Group

Computing properties

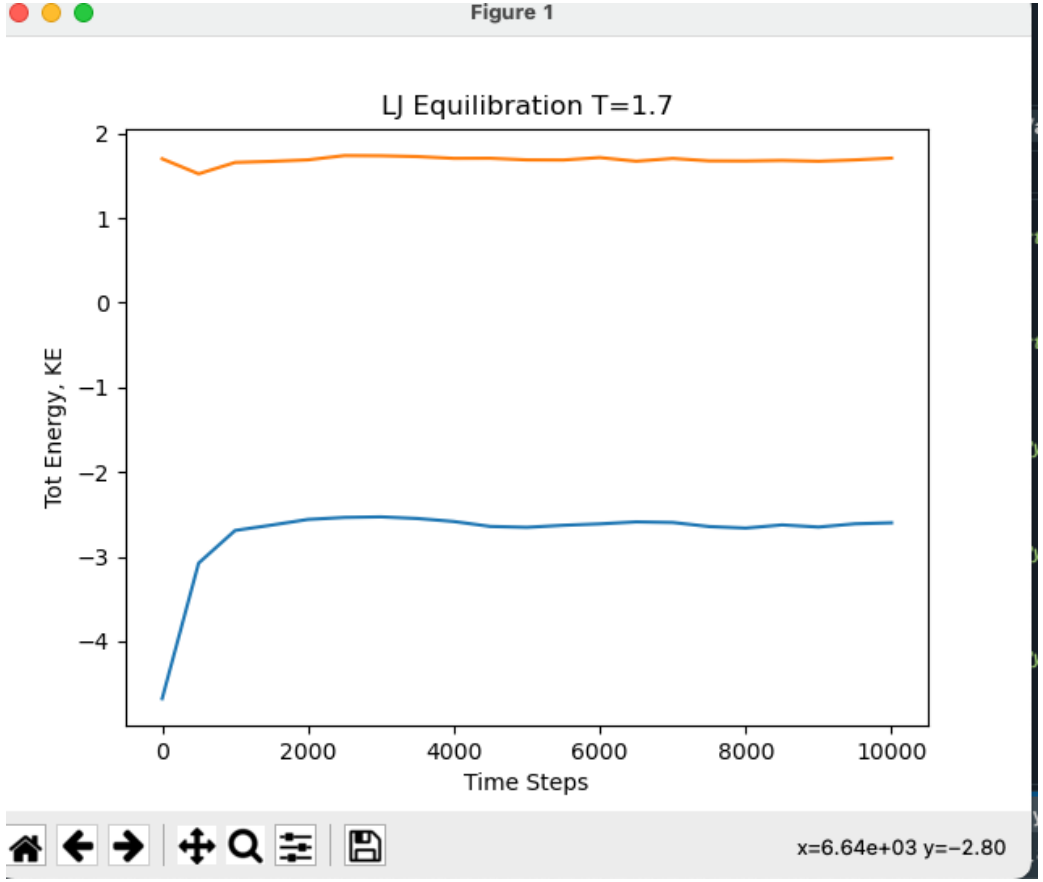


System is clearly “not equilibrated”

Procedure:

1. Run an “equilibration phase” where system relaxes to equilibrium. Throw this out.
2. Restart from the end of equilibration run, compute properties from this.

Longer run

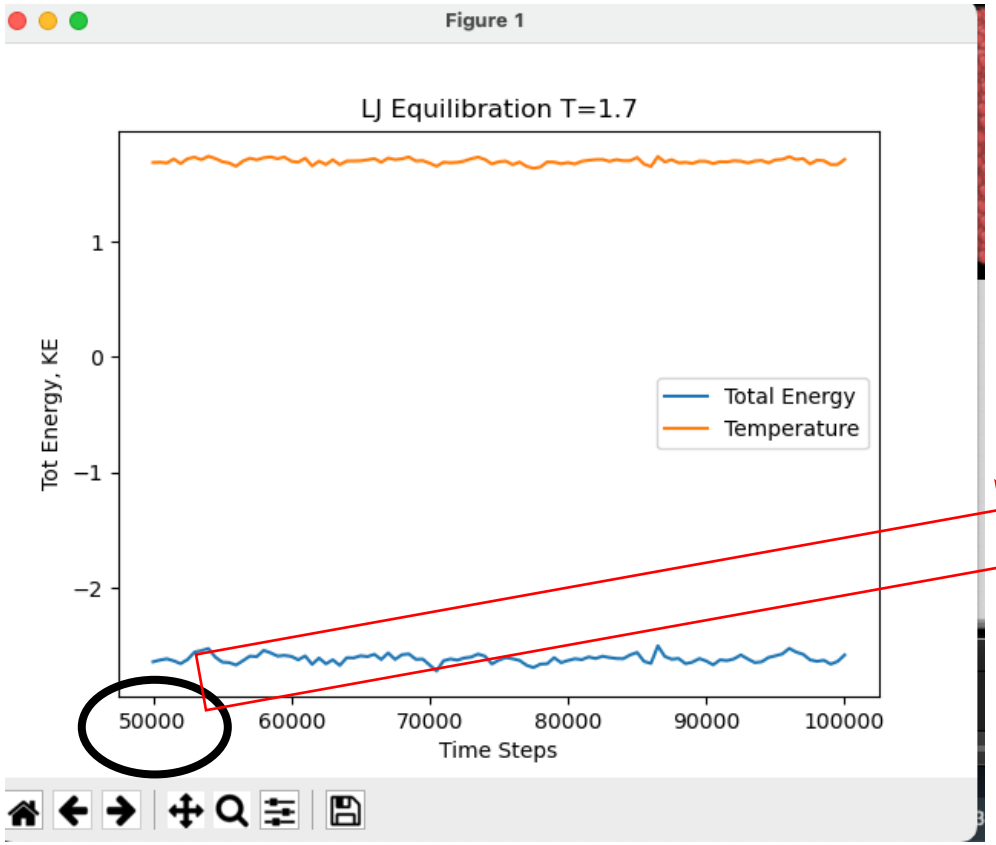


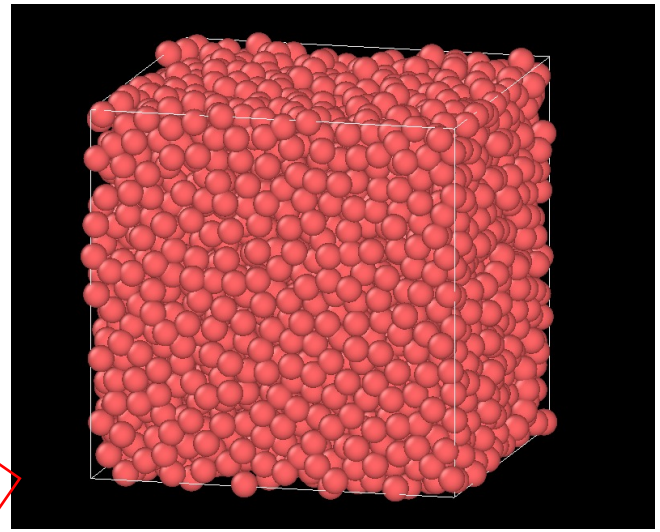
Average Energy -2.730
Average Temperature 1.686

Incorrect! Don't include part that is not equilibrated!

```
# To begin simulation from a restart file, uncomment the line below (adjusting
# the file name, if necessary) and comment the section corresponding to
# information now provided by the restart file.

#read_restart ${NAME}.restart.*

# ##############################################
# start of information provided by restart file
# (If reading data from restart file, comment this section.)

# configure and initialize system
units lj
atom_style atomic
pair_style lj/cut 2.5 # style args(=cutoff)
boundary p p p # x y z (p = periodic boundary conditions)

lattice fcc 0.8442 # style scale(=reduced_density)
region MYBOX block 0 10 0 10 0 10 # ID style args(=xlo,xhi,ylo,yhi,zlo,zhi)
create_box 1 MYBOX # number_of_atom_types region_ID

create_atoms 1 box # atom_type style args

mass 1 1.0 # atom_type mass
velocity all create 3.0 87287 # group_ID style args(=temp,seed)

# set forcefield parameters
pair_coeff 1 1 1.0 1.0 2.5 # atom_i atom_j args(=epsilon,sigma,cutoff)

# end of information provided by restart file
# ##############################################
```

Restart run



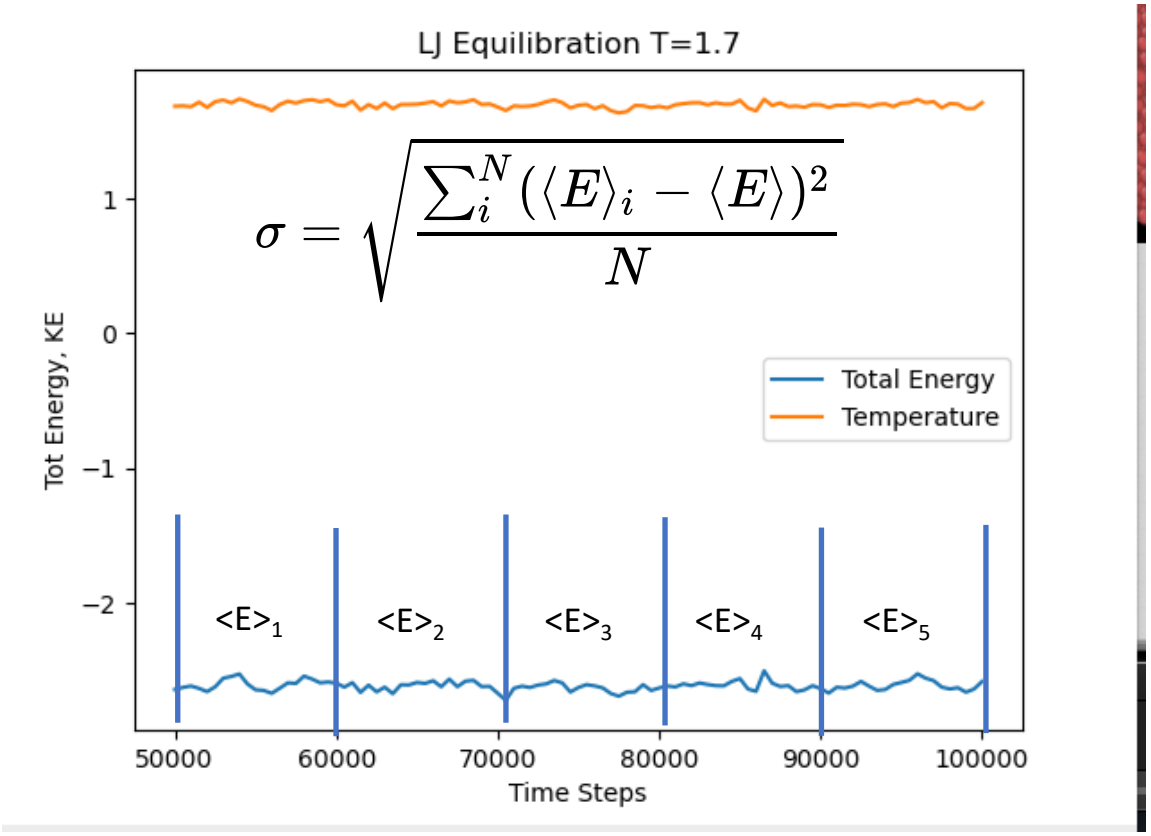


Average Energy -2.6109
Average Temperature 1.694

Proper averages and uncertainties

- Always make sure you take averages over equilibrated trajectories
  - Initial conditions are ”irrelevant”
  - Like to start simulations “close” to equilibrium
  - Use restart files from other simulations close to desired statepoint
- How long should you average?
  - Longer than longest “correlation time” of system
  - Make sure running average is not changing with time
  - Rule of thumb: make sure molecules move several molecular diameters during simulation
- Uncertainties
  - Standard deviation from multiple independent simulations
  - “Block average” standard deviation

Block averages



- Blocks assumed to be independent (longer than correlation time)
- Change block size and check for convergence

Mixtures

Typically relate unlike atom parameters to a combination of like parameters (combination or mixing rule):

$$\epsilon_{ab} = \left(\epsilon_{aa}\epsilon_{bb}\right)^{1/2}$$

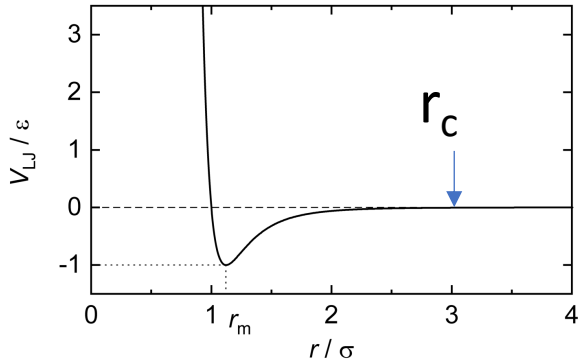
"Lorentz-Berthelot"

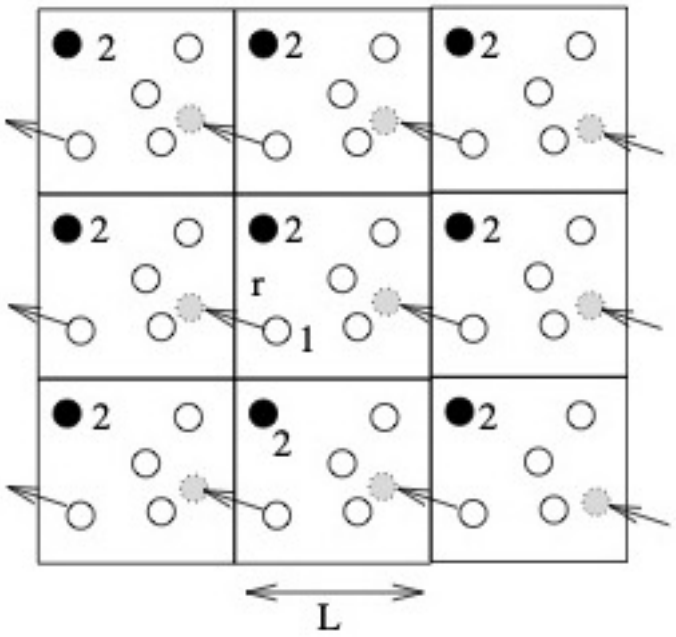
$$\sigma_{ab} = \left(\sigma_{aa} + \sigma_{bb}\right)/2$$

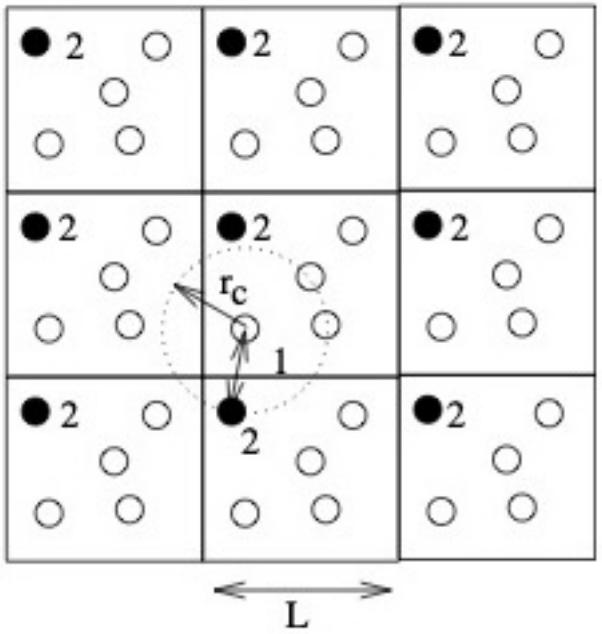
Several other possibilities (purely geometric, "size weighted", "Kong", etc.)

#LAMMPS mixing rules
```
mix geometric
mix arithmetic   (this is Lorentz-Berthelot)
```

Potential Truncation







Cut off potential at no more than ½ box edge length (LJ only – charges are handled differently)

Account for energy beyond r_c

Long range ("tail") corrections

$$E_{tot} = E_{cut} + E_{LRC} = E_{cut} + 2\pi N\rho \int_{r_{cut}}^{\infty} r^2 \mathcal{V}(r) dr$$

For the LJ potential, this is analytic

$$E_{LRC} = 8\pi\rho N\epsilon \left[\frac{\sigma^{12}}{9r_c^9} - \frac{\sigma^6}{3r_c^3} \right]$$

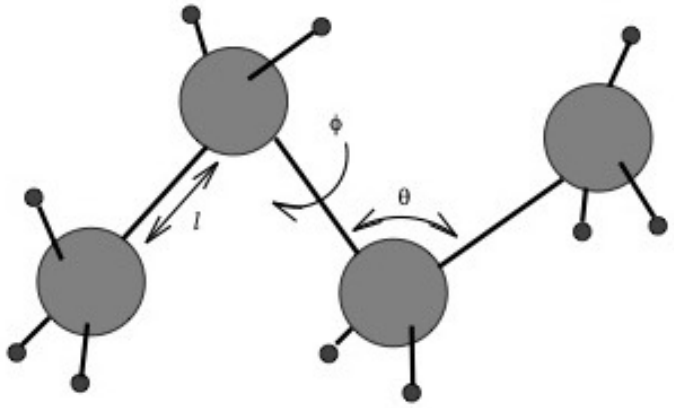
Can also correct pressure
P_{LRC} is analytic

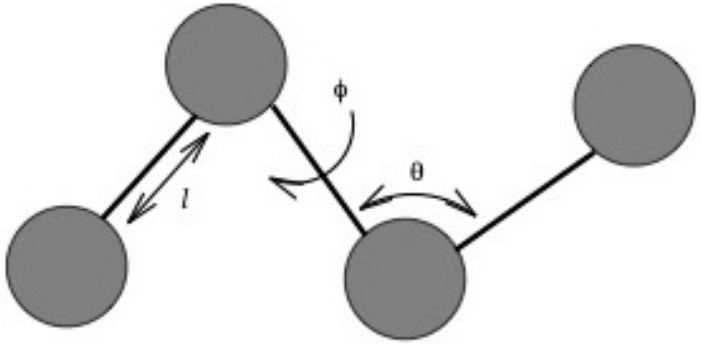
LAMMPS commands

```
pair_style lj/cut 2.5
pair_modify tail yes
```

See Leach: pp 330-334

Simulating multi-atom molecules





"all-atom" butane

"united-atom" butane

We need *intramolecular* force field terms to account for the molecule shape and motion

Intramolecular terms: Bond lengths and angles

Bond length potentials often modeled as a harmonic

$$\mathcal{V}_b(\ell) = k_b(\ell - \ell_0)^2$$

force constant

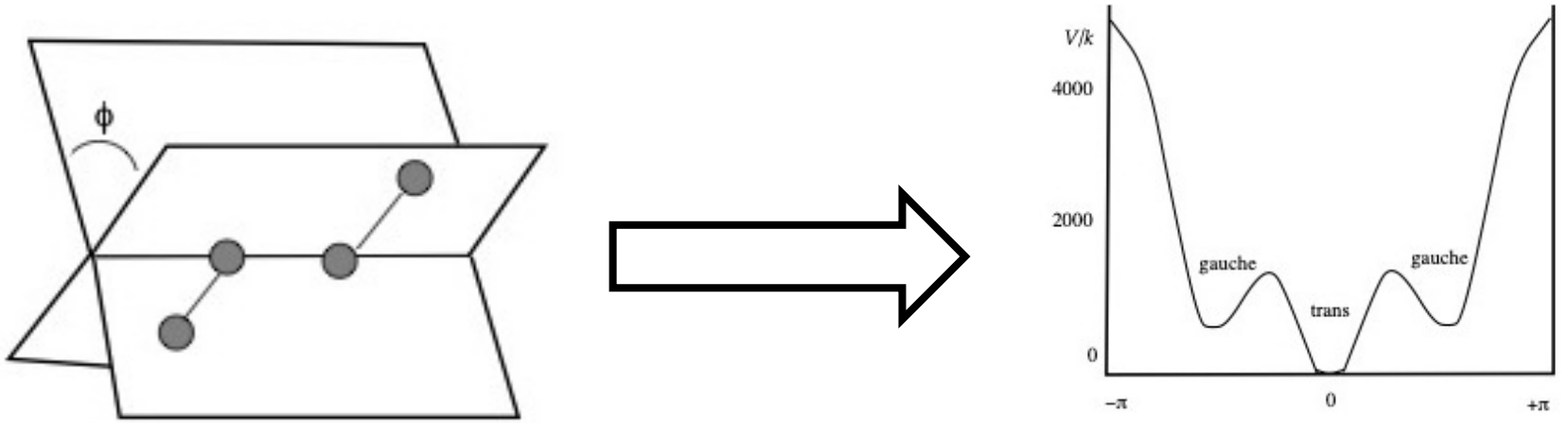
nominal bond length

```
bond_style harmonic
bond_coeff 1 80.0 1.2 # type k_b l_0
```

Harmonic bond angles $\mathcal{V}_\theta(\theta) = k_\theta(\theta - \theta_0)^2$

```
angle_style harmonic
angle_coeff 1 300.0 107.0 # type k_theta theta0
```

Dihedral angles



Optimized Potentials for Liquid Simulation (OPLS) style

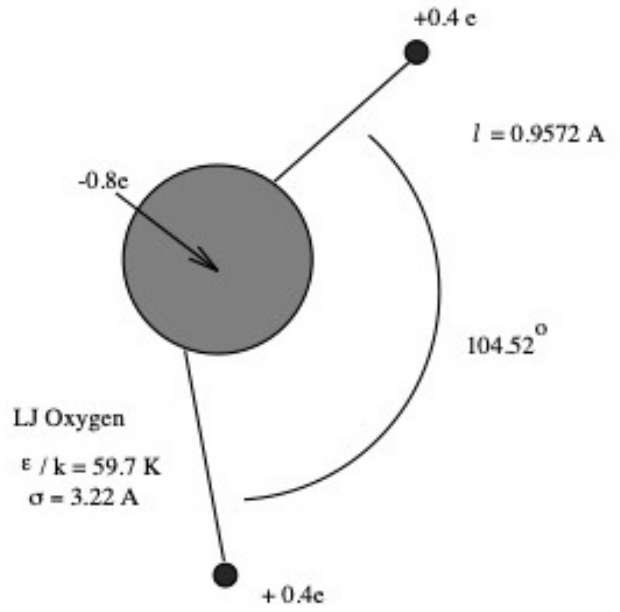
$$\mathcal{V}_\phi = \frac{1}{2}K_1[1+\cos(\phi)] + \frac{1}{2}K_2[1-\cos(2\phi)] + \frac{1}{2}K_3[1+\cos(3\phi)] + \frac{1}{2}K_4[1-\cos(4\phi)]$$

```
dihedral_style opls
dihedral_coeff 1 90.0 90.0 90.0 70.0
```

Chemistry and HArvard Molecular Mechanics (CHARMM) style

$$\mathcal{V}_\phi = k_\phi[1+\cos(n\phi-\delta)]$$

Partial charges



Ex: Water (TIPS model)

- LJ + ”partial charges” on atom centers
- Charges interact via Coulomb potential

$$\mathcal{V}_{zz}(r_{ij}) = \frac{z_i z_j}{4\pi\epsilon_0 r_{ij}}$$

Jorgensen, William L. (1981). "Quantum and statistical mechanical studies of liquids. 10. Transferable intermolecular potential functions for water, alcohols, and ethers. Application to liquid water". *Journal of the American Chemical Society*. American Chemical Society (ACS). **103** (2): 335–340. doi:10.1021/ja00392a016

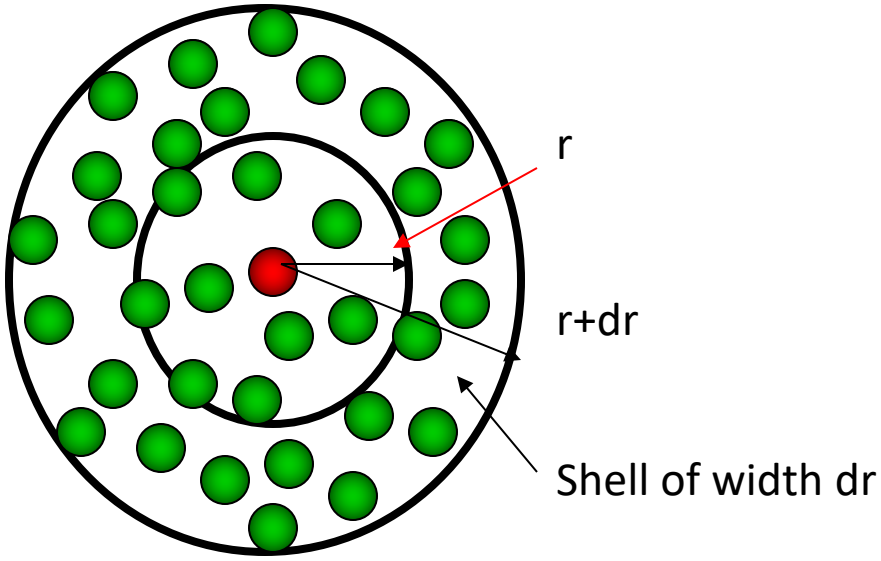
Computing Properties

- What does a fluid "look" like?
- Imagine a snapshot of an atomic liquid

Fluid density in shell is

$$\rho(r)$$

- What are limits on $\rho(r)$?

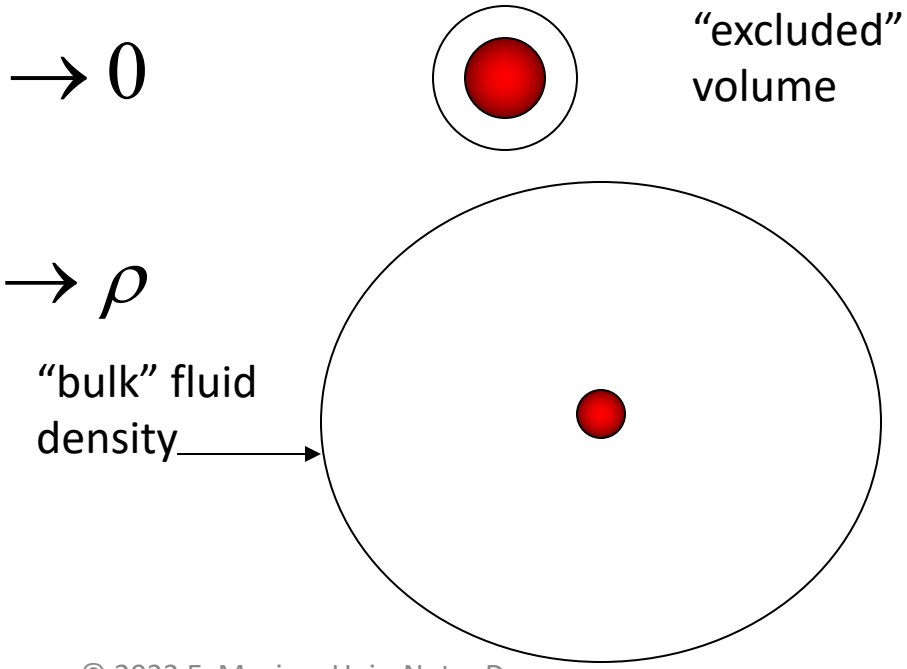


Computing Properties

- What are limits on $\rho(r)$?
- As r-> 0?
- As r-> infinity?

$$r \to 0, \rho(r) \to 0$$

$$r \to \infty, \rho(r) \to \rho$$



Radial Distribution Function

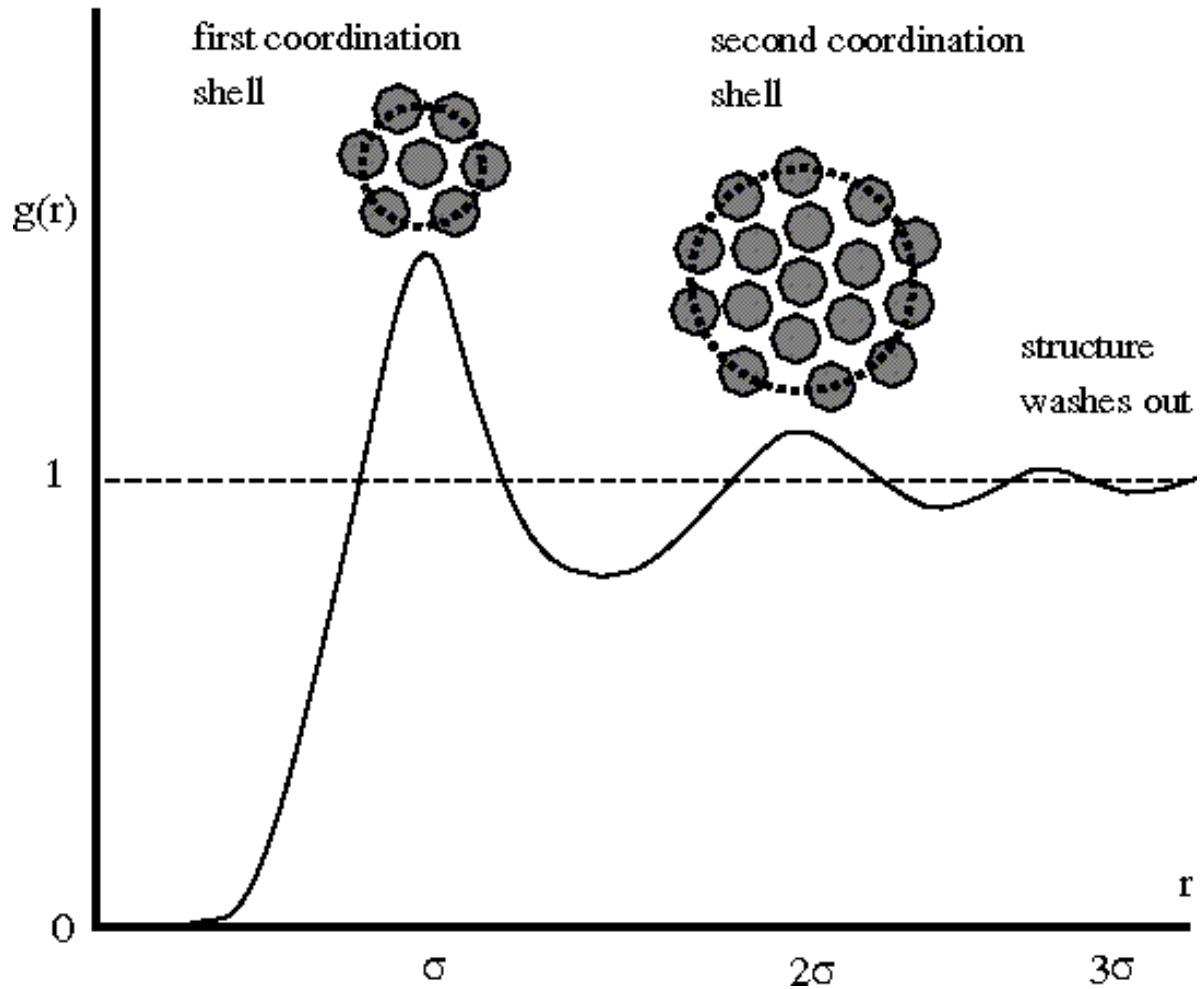
- First statement: fluids have short range “order”
- Last statement: fluids has no long range order.
- Define pair distribution function

$$g(r) \equiv \frac{\rho(r)}{\rho}$$

- Limits:

$$g(0) = 0, g(\infty) = 1$$

Liquid Structure



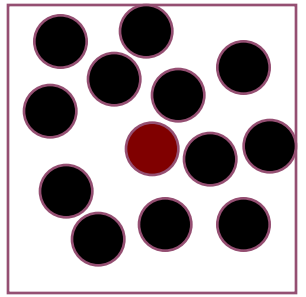
Self-diffusivity

- Right-hand side is macroscopic property
  - applicable at macroscopic time scales

$$\left\langle r^2(t) \right\rangle = 2dDt$$

Einstein equation

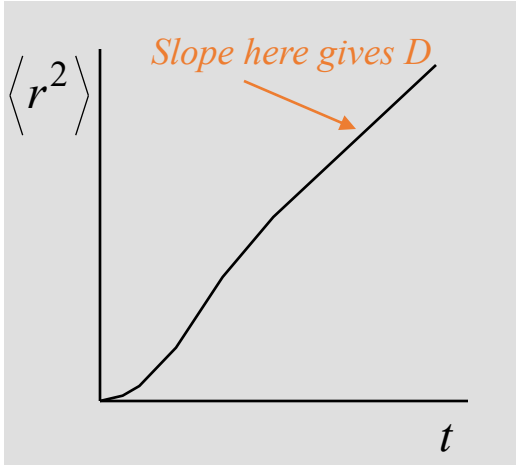
- For any given configuration, each atom represents a point of high concentration (a weak fluctuation)



- View left-hand side of formula as the movement of this atom
  - ensemble average over all initial conditions

$$\left\langle r^2(t) \right\rangle = \int d\mathbf{p}^N \int d\mathbf{r}^N r_1^2(t)\delta(\mathbf{r}_1)\pi(\mathbf{r}^N, \mathbf{p}^N; t=0)$$

  - asymptotic linear behavior of mean-square displacement gives diffusion constant



  - independent data can be collected for each molecule

$$\left\langle r^2(t) \right\rangle = \frac{1}{N}\sum \left\langle r_i^2(t) \right\rangle$$

https://github.com/MaginnGroup/PyLAT

JCIM JOURNAL OF CHEMICAL INFORMATION AND MODELING
Application Note
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pubs.acs.org/jcim

PyLAT: Python LAMMPS Analysis Tools

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PyLAT

This is the github repository for the Python LAMMPS Analysis Tools.

Some of the properties utilize Fortran for speedup. Before using this code, run either the shell script compile.sh or the python script compile.py

Requirements

numpy>=1.14.1

scipy>=1.0.0

The following information can be accessed by running the command "python PyLAT.py -h"

usage:

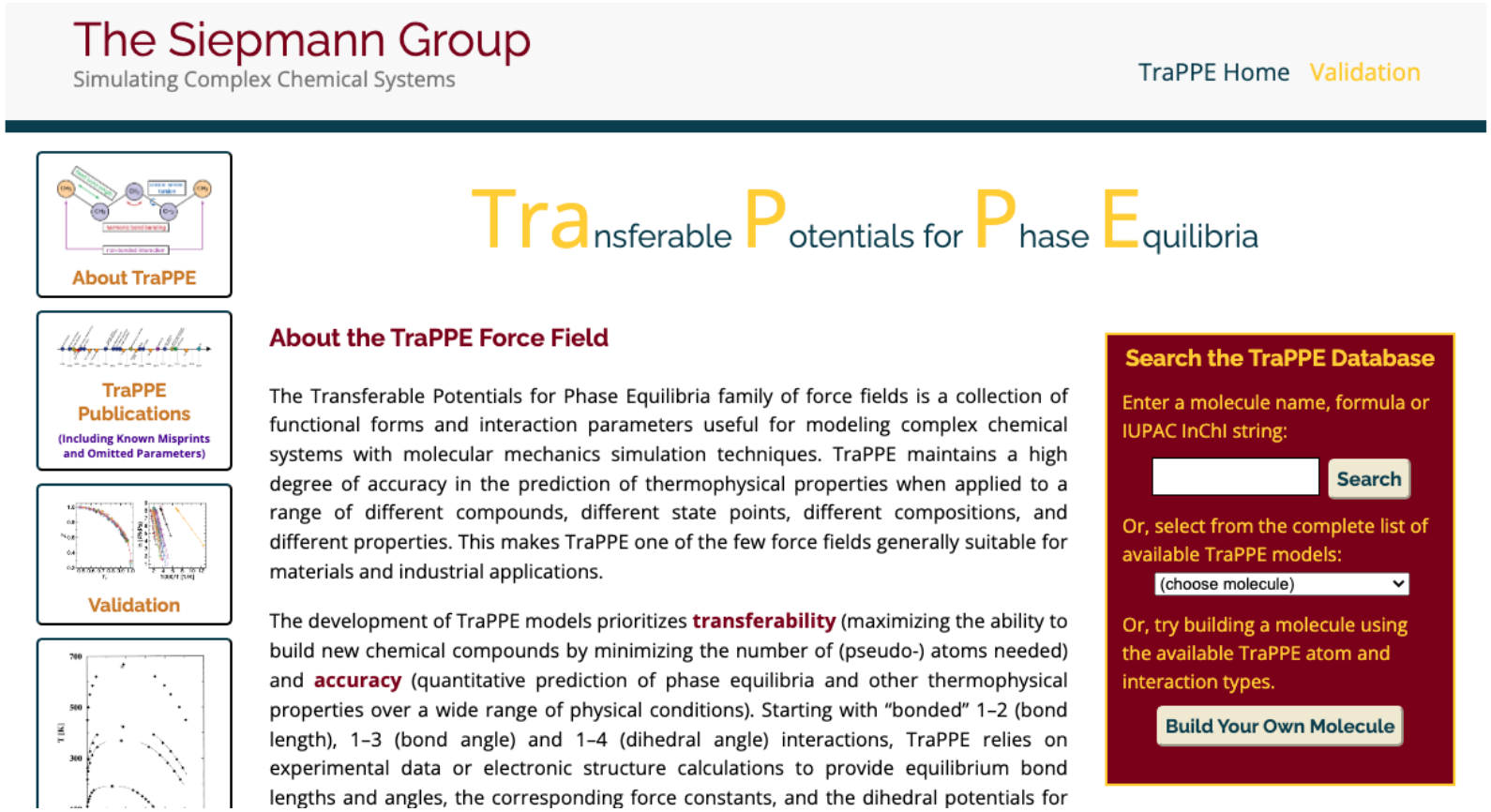
```
            PyLAT.py [-h] [-p PATH] [-i INPUT] [-f OUTPUT] [-g] [-c] [-m] [-d]
            [--NEC] [--GKC] [--IPL] [--DEC] [--DS] [--Visc] --mol MOL
            --nummol NUMMOL [-T TEMP] [-v VERBOSE] [--MSD_skip MSD_SKIP]
            [--MSD_num_init MSD_NUM_INIT] [--D_Tolerance D_TOLERANCE]
            [--RDF_Timesteps RDF_TIMESTEPS] [--RDF_maxr RDF_MAXR]
            [--RDF_binsize RDF_BINSIZE] [--GKC_skip GKC_SKIP]
            [--GKC_Tolerance GKC_TOLERANCE] [--GKC_J_Output]
            [--IPL_skip IPL_SKIP] [--DEC_start DEC_START]
            [--DS_MOL1 DS_MOL1] [--DS_MOL2 DS_MOL2] [--DS_Dist DS_DIST]
            [--DS_Dist_Tol DS_DIST_TOL] [--DS_First_Frame DS_FIRST_FRAME]
            [--DS_Num_Samples DS_NUM_SAMPLES] [--Visc_Dir VISC_DIR]
            [--Visc_Num VISC_NUM] [--Visc_Skip VISC_SKIP]
            [--Visc_Num_Boots VISC_NUM_BOOTS]
            [--Visc_Samples VISC_SAMPLES] [--Visc_Plot]
            [--Visc_Guess VISC_GUESS VISC_GUESS VISC_GUESS VISC_GUESS]
            LOG DAT TRJ [TRJ ...]

Analyze output from LAMMPS simulation

Required files are the log file, the data file and at least one trajectory
file in that order

Also required is the name and number of each molecule type in the system.
To do this, use the --mol and --nummol flags. Use the same order as they
were entered into the data file.
```

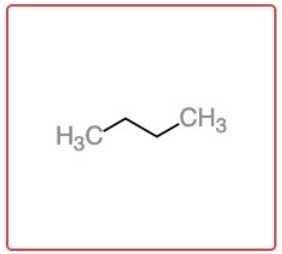
Building complex force fields for LAMMPS

- Generally, need to include a “data file” in addition to input file
  - Contains basic information about the size of the simulation, the initial atomic coordinates, molecular topology, and force field parameters.
- Lots of tools to build these files: we will go into detail about using MoSDeF but there are many other ways to do this

Force field databases

http://trappe.oit.umn.edu/





n-butane (UA)

Chemical Formula: C_4H_{10}

Molecular Weight: 58.12

Smiles String: CCCC

InChI=1S/C4H10/c1-3-4-2/h3-4H2,1-2H3

This model was assembled from previously parameterized TraPPE building blocks and was tested for accuracy as part of the transferability verification process.

Parameters | Simulation Data | Downloads

Functional Forms and Parameters

Nonbonded Interactions

$$u_{NB}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ii}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ii}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad \epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$$

#	(pseudo)atom	type	ε/k_B [K]	σ [Å]	q [e]
1	CH3	[CH3]-CHx	98	3.75	0.0
2	CH2	CHx-[CH2]-CHx	46	3.95	0.0
3	CH2	CHx-[CH2]-CHx	46	3.95	0.0
4	CH3	[CH3]-CHx	98	3.75	0.0

1-2 Bonded Interactions

(TraPPE uses fixed bond lengths)

#	Stretch	Type	Length [Å]
1	1 – 2	CHx-CHy	1.54
2	2 – 3	CHx-CHy	1.54
3	3 – 4	CHx-CHy	1.54

1-3 Bonded Interactions

$$u_{bend}(\theta) = \frac{k_\theta}{2}(\theta - \theta_{eq})^2$$

#	Bend	Type	θ [°]	$k\theta/k_B$ [K/rad^2]
1	1 – 2 – 3	CHx-(CH2)-CHy	114	62500
2	2 – 3 – 4	CHx-(CH2)-CHy	114	62500

1-4 Bonded Interactions

(Read more about TraPPE dihedral conventions)

$$u_{torsion}(\phi) = c_0 + c_1\left[1 + \cos(\phi)\right] + c_2\left[1 - \cos(2\phi)\right] + c_3\left[1 + \cos(3\phi)\right]$$

#	Torsion	Type	c_0/k_B [K]	c_1/k_B [K]	c_2/k_B [K]	c_3/k_B [K]
1	1 – 2 – 3 – 4	CHx-(CH2)-(CH2)-CHy	0.00	355.03	-68.19	791.32

```
# Example of beginning input file using data file
variable       NAME index methane
log            ${NAME}.log
variable       infile index methane.data
variable       mytemp index 328.15

# set up simulation
units          real
atom_style     full
boundary       p p p
pair_style     lj/cut/coul/long 12
kspace_style   ewald 0.0001
pair_modify    tail yes
pair_modify    mix arithmetic
special_bonds  amber

bond_style     harmonic
angle_style    harmonic
#dihedral_style  opls
#improper_style  cvff

read_data      ${infile}
```

LAMMPS Description (1st line of file)

100 atoms (this must be the 3rd line, 1st 2 lines are ignored)
95 bonds (# of bonds to be simulated)
50 angles (include these lines even if number = 0)
30 dihedrals
20 impropers
5 atom types (# of nonbond atom types)
10 bond types (# of bond types = sets of bond coefficients)
18 angle types
20 dihedral types (do not include a bond,angle,dihedral,improper type
2 improper types line if number of bonds,angles,etc is 0)
-0.5 0.5 xlo xhi (for periodic systems this is box size, -
0.5 0.5 ylo yhi for non-periodic it is min/max extent of atoms)
-0.5 0.5 zlo zhi (do not include this line for 2-d simulations)

Masses
1 mass ... N mass (N = # of atom types)

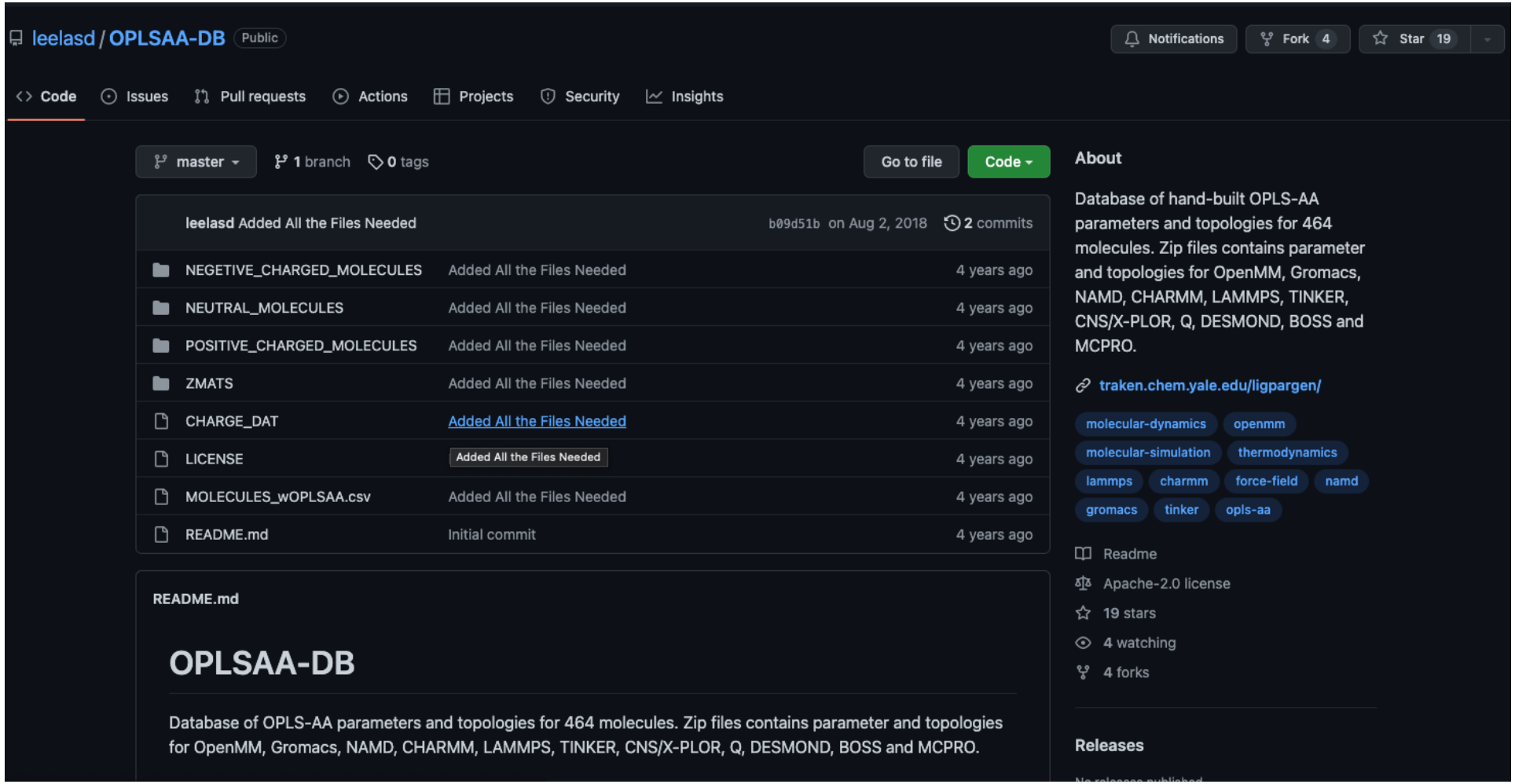
Nonbond Coeffs
1 coeff1 coeff2 ... ... N coeff1 coeff2 ... (N = # of atom types)

```
methane.data - created by mBuild; units = real

2500 atoms
2000 bonds
3000 angles
0 dihedrals
0 impropers

2 atom types
1 bond types
1 angle types

0.000000 40.000000 xlo xhi
0.000000 40.000000 ylo yhi
0.000000 40.000000 zlo zhi

Masses

1          12.010780    # opls_138
2          1.007947     # opls_140

Pair Coeffs # lj
#          epsilon (kcal/mol)                  sigma (Angstrom)
1          0.06600                 3.50000              # opls_138
2          0.03000                 2.50000              # opls_140

Bond Coeffs # harmonic
#          k(kcal/mol/angstrom^2)              req(angstrom)
1          340.0                   1.09                 # opls_138    opls_140

Angle Coeffs # harmonic
#          k(kcal/mol/rad^2)                   theteq(deg)
1          33.0                    107.80000  # opls_140    opls_138    opls_140
```

Atoms # full

1	1	1	-0.240000	36.169297	32.738712	18.053636
2	1	2	0.060000	35.618914	31.986198	17.452327
3	1	2	0.060000	35.460444	33.509299	18.420370
4	1	2	0.060000	36.945195	33.219973	17.423444
5	1	2	0.060000	36.652636	32.239379	18.918402
6	1	1	-0.240000	23.235838	22.713311	15.456040
7	1	2	0.060000	22.294018	22.608173	14.879246
8	1	2	0.060000	23.222708	23.672111	16.013982
9	1	2	0.060000	24.099230	22.702595	14.759470
10	1	2	0.060000	23.327397	21.870364	16.171462
11	1	1	-0.240000	9.485563	13.833860	7.944599
12	1	2	0.060000	8.658834	13.469003	8.588158
13	1	2	0.060000	9.944858	12.976459	7.411044
14	1	2	0.060000	10.251984	14.331392	8.573749
15	1	2	0.060000	9.086575	14.558589	7.205445
16	1	1	-0.240000	31.850319	18.437411	36.362290
17	1	2	0.060000	31.507804	19.006143	37.251108
18	1	2	0.060000	32.687095	18.979813	35.876105
19	1	2	0.060000	31.011002	18.332433	35.644448
20	1	2	0.060000	32.195375	17.431255	36.677498

OPLS – “pre-built”

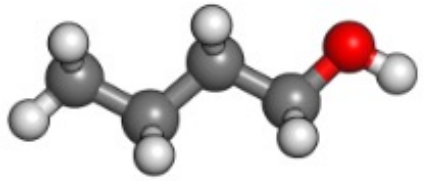


Build your own OPLS

An easy to use tool

http://zarbi.chem.yale.edu/ligpargen/

1. Enter SMILES code: example
   OCCCC = 1-butanol



2. Create PDB file (can do this with many other tools such as Avogadro)

```
REMARK LIGPARGEN GENERATED PDB FILE
ATOM      1  O00 UNK     1       1.000   1.000   0.000
ATOM      2  C01 UNK     1      -0.421   1.000   0.000
ATOM      3  C02 UNK     1      -0.911   1.000   1.441
ATOM      4  C03 UNK     1      -2.436   0.998   1.516
ATOM      5  C04 UNK     1      -2.922   1.000   2.956
ATOM      6  H05 UNK     1       1.284   0.999  -0.930
ATOM      7  H06 UNK     1      -0.768   0.108  -0.531
ATOM      8  H07 UNK     1      -0.768   1.892  -0.531
ATOM      9  H08 UNK     1      -0.506   1.877   1.962
ATOM     10  H09 UNK     1      -0.504   0.125   1.962
ATOM     11  H0A UNK     1      -2.832   0.114   1.004
ATOM     12  H0B UNK     1      -2.834   1.880   1.001
ATOM     13  H0C UNK     1      -2.566   0.114   3.490
ATOM     14  H0D UNK     1      -4.017   0.997   2.985
ATOM     15  H0E UNK     1      -2.568   1.889   3.487
TER
CONECT   1   2
CONECT   2   3
CONECT   3   4
CONECT   4   5
CONECT   1   6
CONECT   2   7
CONECT   2   8
CONECT   3   9
CONECT   3  10
CONECT   4  11
CONECT   4  12
CONECT   5  13
CONECT   5  14
CONECT   5  15
END
```

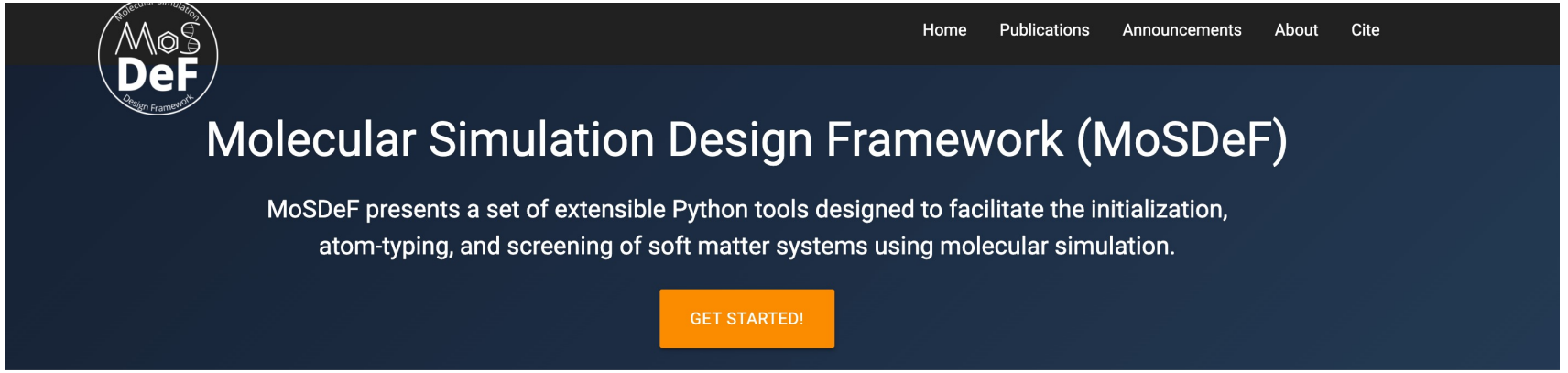
Build your own OPLS

- LigParGen will spit out a LAMMPS datafile for a single molecule in addition to the pdb (and other “data files” for different packages)
- Partial charges computed using one of two methods
- You should always verify the parameters you get!
- A huge source of error and inconsistency in the literature is incorrect force field parameters.
- Lots of other resources

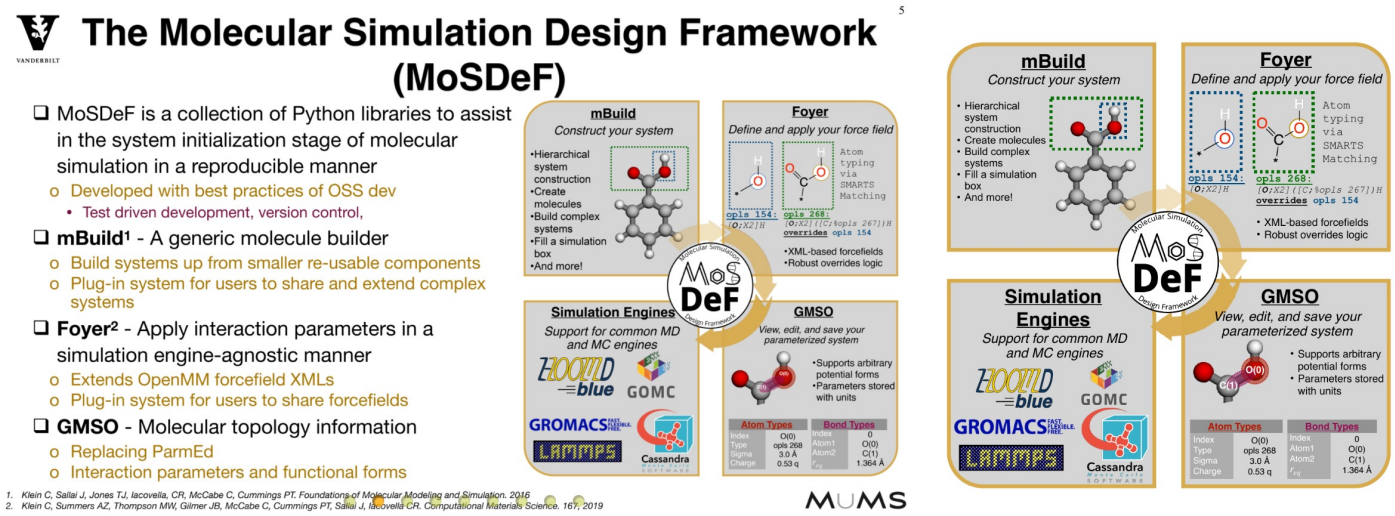
https://github.com/paduagroup/fftool
(inconsistent with LigParGen but conversion tools available)

What about other force fields?

- Lots of tools and converters to go between formats
- Eventually, you will likely need to write or modify scripts
- Great care is required because it is easy to make mistakes!
- For all but the simplest molecules, write scripts
- We will show you how to use a general tool under development called MoSDeF



The MoSDeF tools have been designed to facilitate the hierarchical construction of both atomistic and coarse-grained system configurations, the application of classical force fields (i.e., atom-typing), encapsulation of chemical topology information, and the generation of input files for a variety of molecular dynamics and Monte Carlo simulation engines, including LAMMPS, GROMACS, HOOMD-Blue, Cassandra, and GOMC.



https://github.com/mosdef-hub

mosdef.org