EMC: Enhanced Monte Carlo

A Structure Generator

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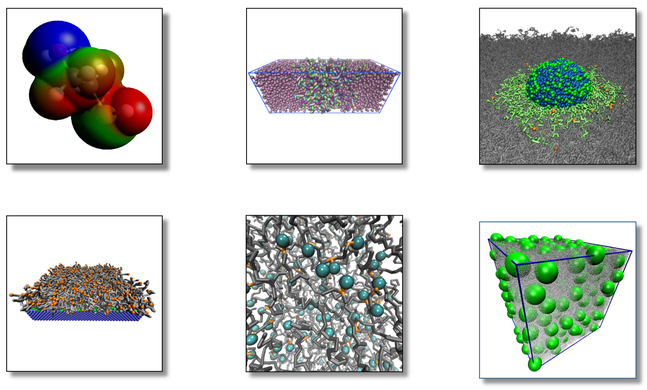
GMC/M: Materials Modeling

BASF
The Chemical Company

Choice Application Areas for Quantum Mechanics or Particle Dynamics



Overview
Advantages and Capabilities

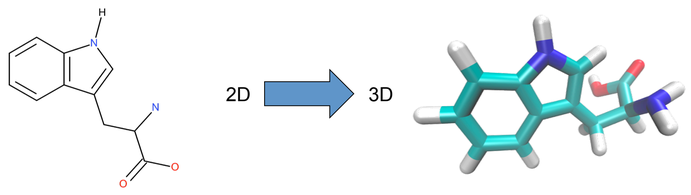
- Freeware under GPL v3.1
  - Source code in C
  - Compiles under MacOS or LINUX with Intel and GNU compilers
  - Command line with scripting interface
- Advantage over commercial solutions
  - Flexible scripting
  - Can build and graft surfaces in condensed media
- Structure builds in
  - Gas phase
  - Condensed phase
- Use of multiple force fields
  - Atomistic typing by EMC
- Ports to PDB, LAMMPS, XYZ
- Applications
  - Atomistic and coarse-grained structures
  - Formulation problems
  - Mechanical, rheological and interfacial properties

Builder Attributes

```
(* EMC: Script *)

variables = {
  input   -> "/Users/pjintve/emc/v9.3.0/lib/fcc_bonded",
  output  -> "dpd"};

// get a crystal unit cell of a completely bonded fcc lattice

variables = {sigma -> 1, lbox -> (4/3)^(1/3),
             kbond -> 400, lbond -> lbox/sqrt(2),
             la -> lbox, lb -> lbox, lc -> lbox};

get       = {input};

// define system variables; sigma and la are defined in input
// r1 represents the nanoparticle's outside perimeter
// r2 represents the nanoparticle's inner core

variables = {n -> 7, l -> n*la, r1 -> 1/2, r2 -> r1-0.6*sigma/l,
             sigma -> 1, cutoff -> 1, delete -> 0.7225,
             temperature -> 1, density -> 3.0,
             fraction -> 0.45, kbond -> 4, lbond -> 1,
             ngraft -> 20, nrepeat -> 20, npolymers -> 10000};

// define an extra grafting site, used to connect polymers to

sites     = {
  site    -> {id -> graft, name -> "grafting", mass -> 1},
  site    -> {id -> m, name -> "monomer", mass -> 1},
  site    -> {id -> t, name -> "terminator", mass -> 1}};
```

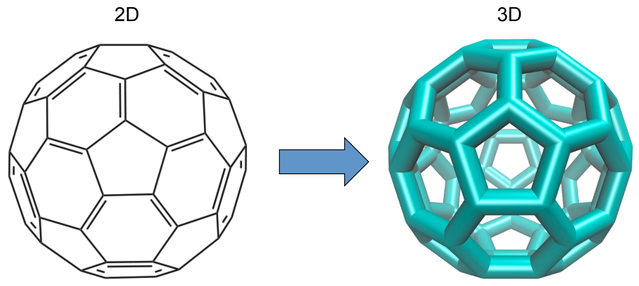
- Script-driven command line execution
- Flexible input
  - Complex chemistry, including branched structures through SMILES
  - Multiple force fields, e.g.
    - COMPASS
    - OPLSUA
    - DPD
    - Colloidal
- Algorithms
  - Inverse Monte Carlo (CCB growth)
  - Local spatial incremental relaxation
  - Composite core exclusion

Molecular Structure Investigations
Coupling 2D to 3D



- Structure input through SMILES
- Example: tryptophan (build based on COMPASS force field)
  - Draw structure with Accelrys Draw (or JChemPaint (Freeware))
  - Obtain SMILES (both Accelrys Draw and JChemPaint convert)
  - Build with EMC (resulting structure dependent on random seed)

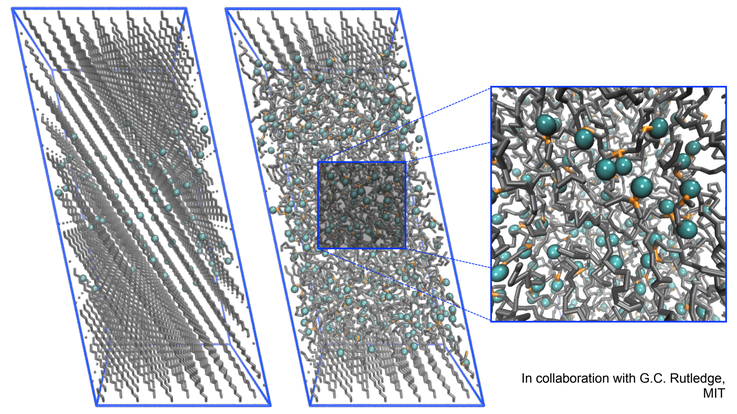
Complex Structure Builds
From this SMILES EMC builds Fullerene



1D

c12c3c4c5c1c6c7c8c2c9c1c3c2c3c4c4c%10c5c5c6c6c7c7c
%11c8c9c8c9c1c2c1c2c3c4c3c4c%10c5c5c6c6c7c7c
%11c8c8c9c1c1c2c3c2c4c5c6c3c7c8c1c23

Branched Semicrystalline Polyethylene
Mechanical Properties of Interphase



In collaboration with G.C. Rutledge, MIT

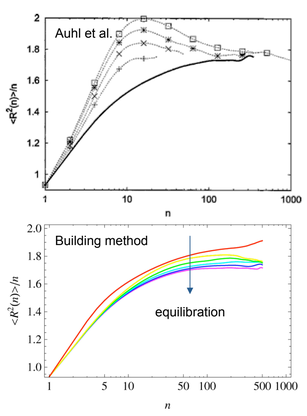
Validation
FENE Model Description

$$
\begin{aligned}
E_{pair}(r) &= \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}+\frac{1}{4}\right], & r<r_c \\ 0, & r\geq r_c \end{cases} \\
r_c &= 2^{\frac{1}{6}}\sigma,\ \sigma=1,\ \epsilon=1 \\
E_{bond}(l) &= \begin{cases} -\frac{1}{2}k\,R_0^2\ln\left[1-(r/R_0)^2\right], & r<R_0 \\ \infty, & r\geq R_0 \end{cases} \\
R_0 &= 1\frac{1}{2}\sigma \\
p(l) &= \frac{e^{-E_{pair}(l)-E_{bond}(l)}}{\int_0^{\infty} e^{-E_{pair}(l)-E_{bond}(l)}\,\mathrm{d}l}
\end{aligned}
$$

- Describes polymeric behavior well
- Allows for comparison with previous work by Auhl et al.
  - Identical model parameters
  - Identical integration conditions
- Short cutoff ranges result in a computationally inexpensive model
- Building procedure consisted of 1000 chains of 500 length
- Systems equilibrated for 35 million time steps

K. Kremer and G. S. Grest, J. Chem. Phys. **92, 5057, 1990.**

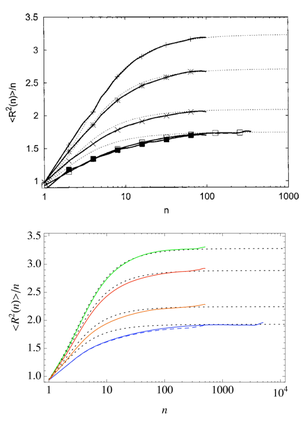
Builder Validation



- Ongoing research
- Comparison between k_θ = 0 equilibration simulations
- 10 million steps for building method after building
- Shape of the curve correct
- Difference of 8% in final curve between built and equilibrated
- Can be fine-tuned with parameters
- Building method fast in constructing
- Linear algorithm

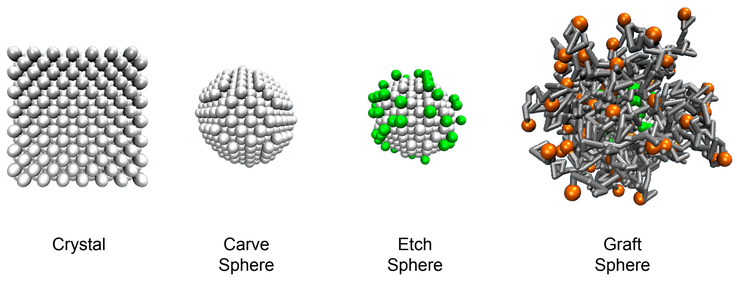
R. Auhl et al., J. Chem. Phys. **119, 12718, 2003.**

Validation
Comparison between Literature and Builder



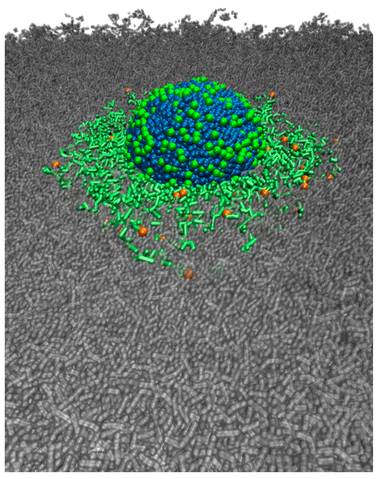
- Building polyethylene-like chains
  - 100, 200, 500 and 5000 repeat units
- Variation of angle bend constant k_θ
- Rouse-like behavior for shorter chains
- Follow exact trend as described in Auhl et al.
- Directly after building
  - Structures already near equilibration
  - Chain physics follow long equilibration runs as performed by Auhl et al.

Curved Surfaces
DPD Building Concept



Curved Surfaces
Final DPD Structure

NanoModel



- EU Project NanoModel
- Structure consists of 3.3 million sites (10K graft on 16 nm SiO_2 in 10K matrix)
- Grown with full force field
- Both polymer graft and matrix are grown concurrently
- Flexible choice of growth methods
  - Pure overlaps with grace
  - Energetic considerations with grace
- Local relaxation at insertion point
- Final structure energetically close to equilibrium (5.11 vs eq 5.21 kT)
- Build of 0.2 million sites ~30 minutes on laptop (5.5 million sites ~2 hours on single processor large machine)

Simulations vs. Experiments

d_{core}	M_{graft}	κ	h_{brush} [nm]			
[nm]	[kg/mol]	[1/nm^2]	exp	DPD	atom	coarse
4	2.0	0.50	–	3.87	3.2	3.5
	2.0	1.00	–	3.93	4.0	4.0
16	9.7	0.39	12.3	13.0	–	–
	9.7	0.53	13.2	13.5	–	–
	20.0	0.69	24.6	23.0	–	–
			DPD		FTI-MC	
			avg	99%	avg	%
12.5	20	0.41	6.13	13.91	5.85	11.2
		0.71	6.27	13.89	6.41	11.9
		0.89	6.47	14.08	6.93	12.2
		1.19	6.66	14.21	8.26	13.2
		1.42	7.01	15.01	8.59	13.6

Experiments: W. Pyckhout, M. Meyer, Forschungszentrum Jülich

FTI-MC: D. Theodorou, E. Voyiatzis, NTU Athens

External