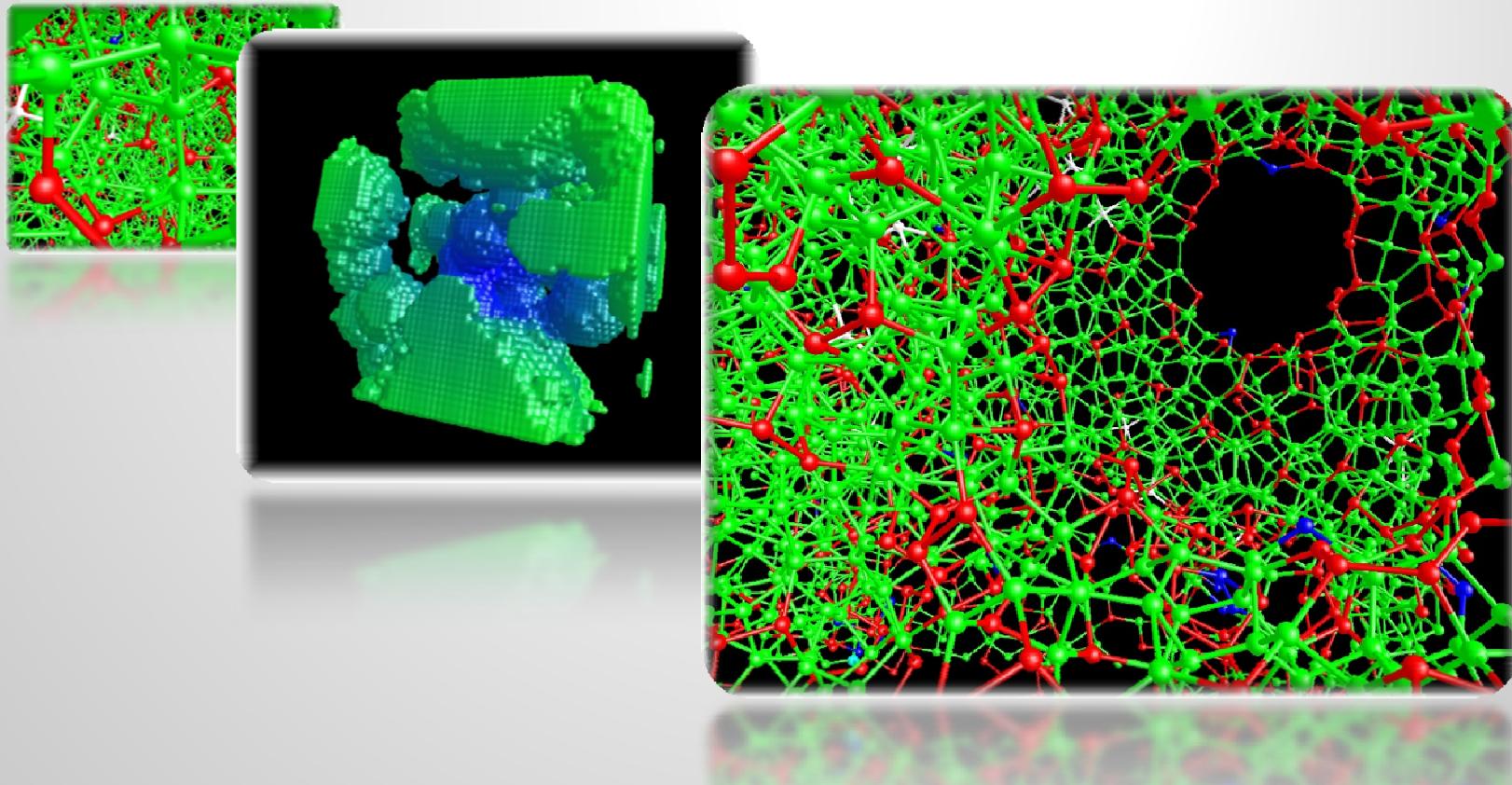


Hybrid Reverse Monte Carlo Modelling of Disordered Materials

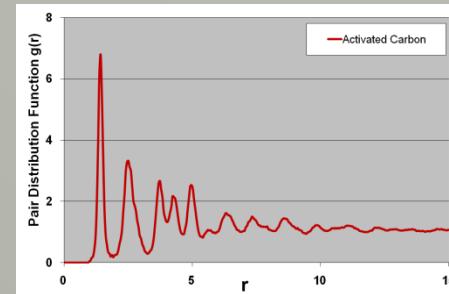
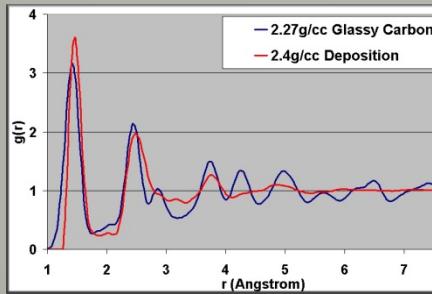
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Introduction

- Disordered materials have many applications ranging from pore size selective filtration to protective coatings.
- Modelling such materials via empirical potential methods (MD/MC) may be difficult since the production conditions may be obscure.



- Via experimental diffraction, the **structure factor $S(q)$** and its Fourier transform counterpart, the **pair distribution function $g(r)$** , have much variations even amongst similar amorphous carbons.

Reverse Monte Carlo (RMC) Method

- Analogous to energy minimization Monte Carlo.
- Minimizes ‘least-squares’ difference between system and experimental diffraction data.
- Structure factor $S(q)$ can come from electron, x-ray or neutron diffraction.
- Simulation pair distribution function $g(r)$ is calculated and is related to $S(q)$ by a Fourier transform.

$$\chi^2 = \sum_q \frac{(S(q)_{theory} - S(q)_{expt.})^2}{\sigma(q)^2}$$

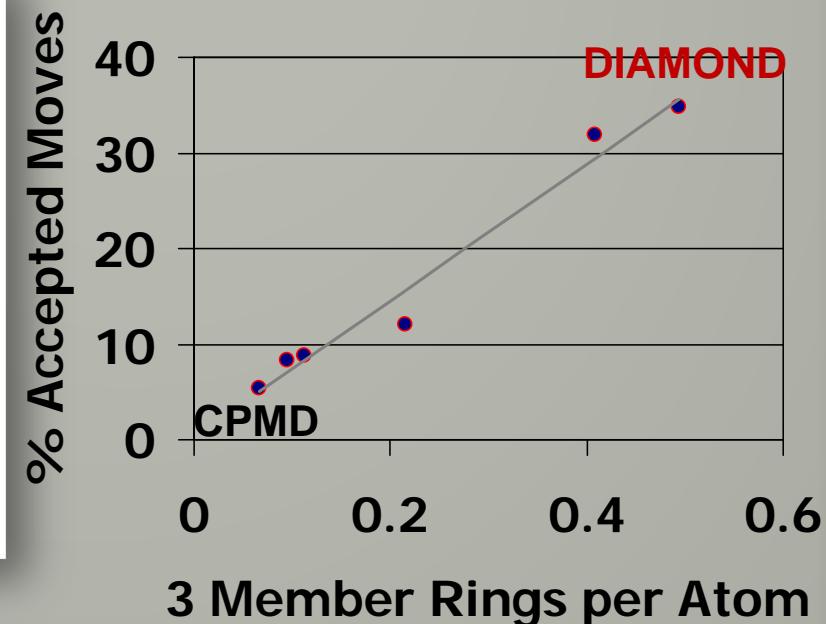
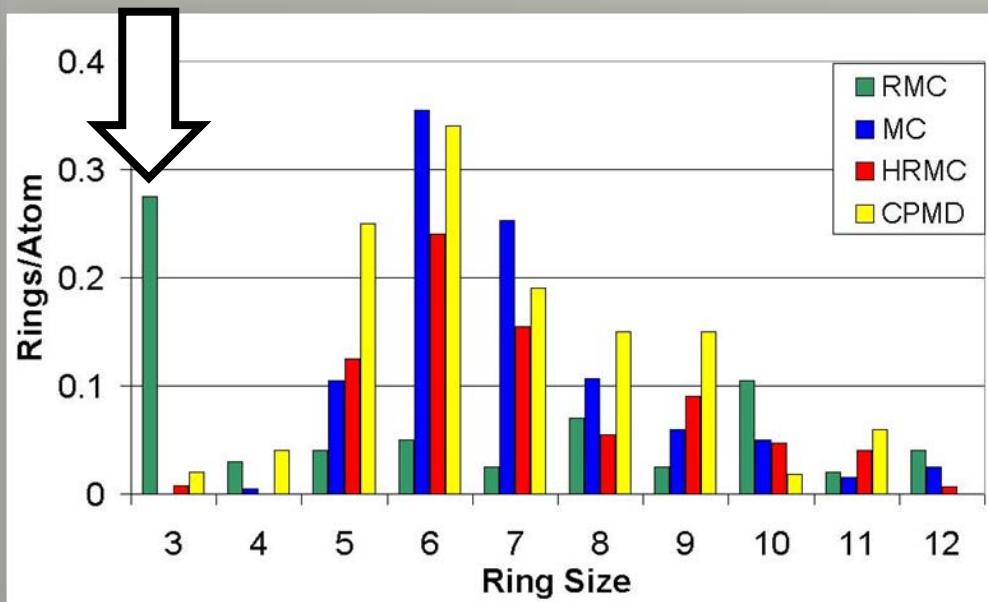
if $X_{new} < X_{old}$ accepted

if $X_{new} > X_{old}$ $P = \exp\left(\frac{-(\chi^2_{new} - \chi^2_{old})}{2}\right)$

- R. L. McGreevy and L. Pusztai, Mol. Sim. 1 (1988) 359.

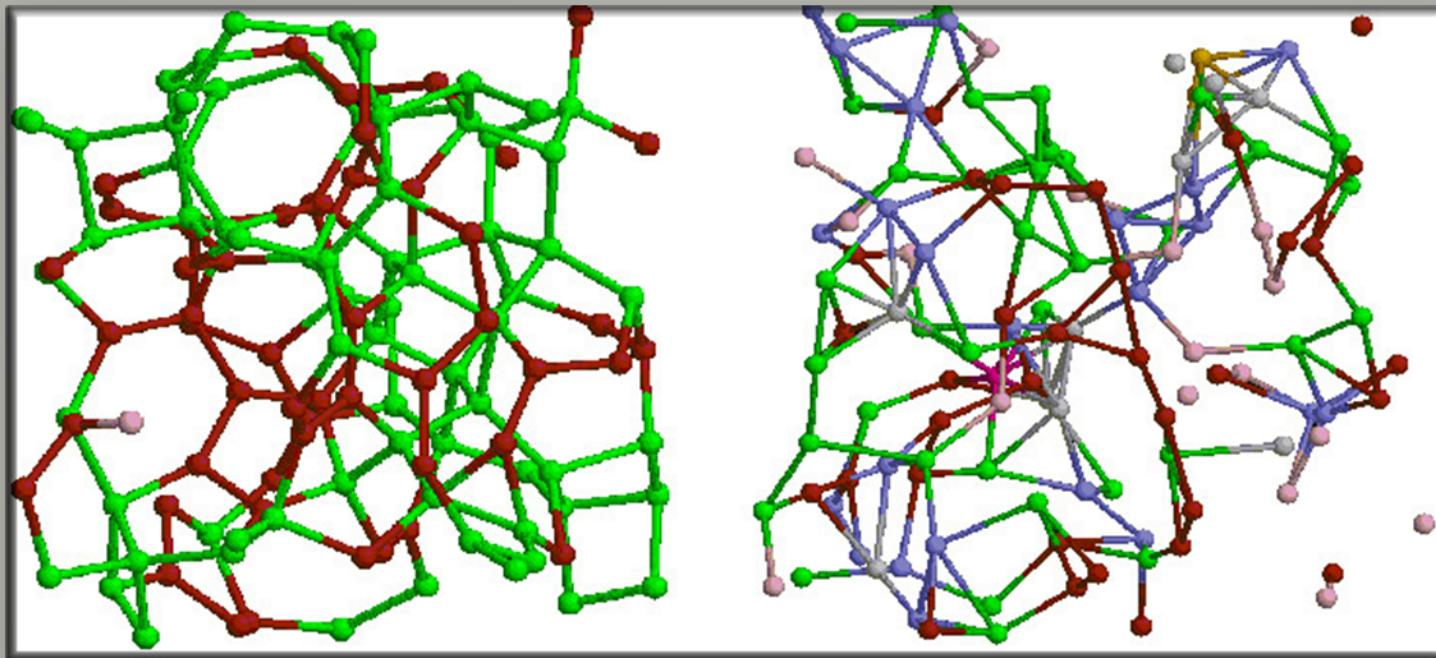
Reverse Monte Carlo (RMC) Method

- Great fits but unphysical structures.
- Inherent and artificial small atomic ring creation in RMC leads to highly strained networks.



Reverse Monte Carlo (RMC) Method

- Both carbon atomic networks have a common $g(r)$.



MC EDIP potential (left), RMC (right).
Coordination - **Green = 4, Red = 3, Pink = 2**

Reverse Monte Carlo (RMC) Method

- A unique $g(r)$ does not exist for systems that cannot be described accurately by pair-wise additive two body potentials.
- Covalent bonded amorphous materials like silicon and carbon (for example) require additional constraints in addition to diffraction data to constrain bond angles.

Hybrid Reverse Monte Carlo (HRMC) Method

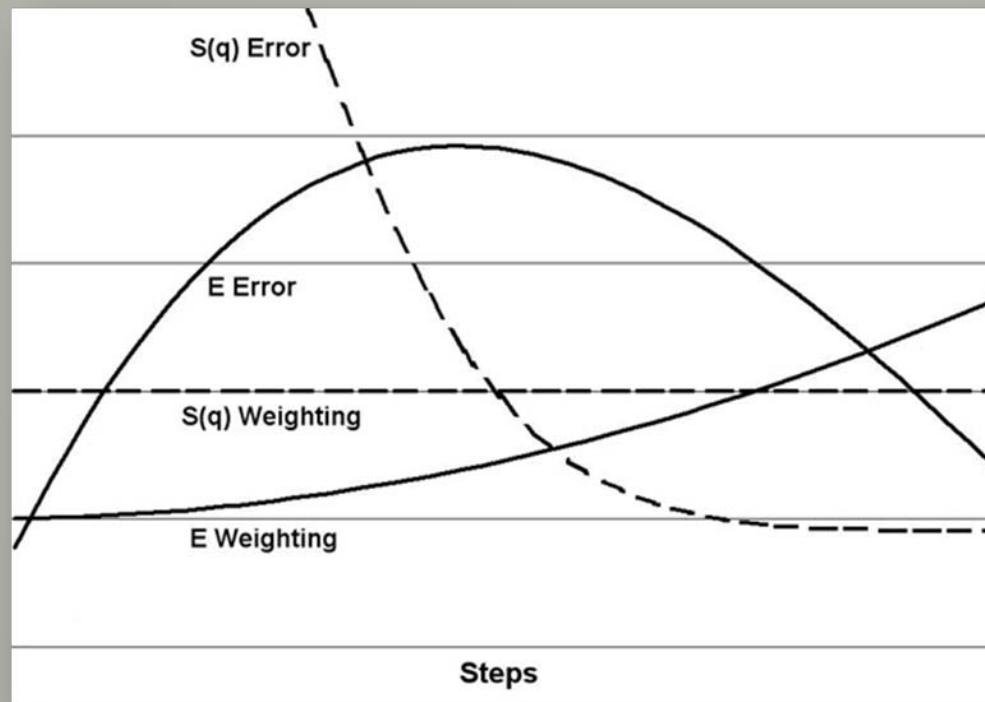
- Combination of RMC and empirical potential MC, which minimizes energy in addition to diffraction data fits.

$$X_{\text{total}}^2 = (X_{\text{sq}}^2 + X_{\text{gr}}^2)/2 + E / kT$$

- Eliminate small atomic ring problem plaguing the RMC methodology.
- Currently, potentials include EDIP carbon, silicon and silicon carbide, Stillinger-Weber silicon, germanium and a bond-order potential for silicon carbide.

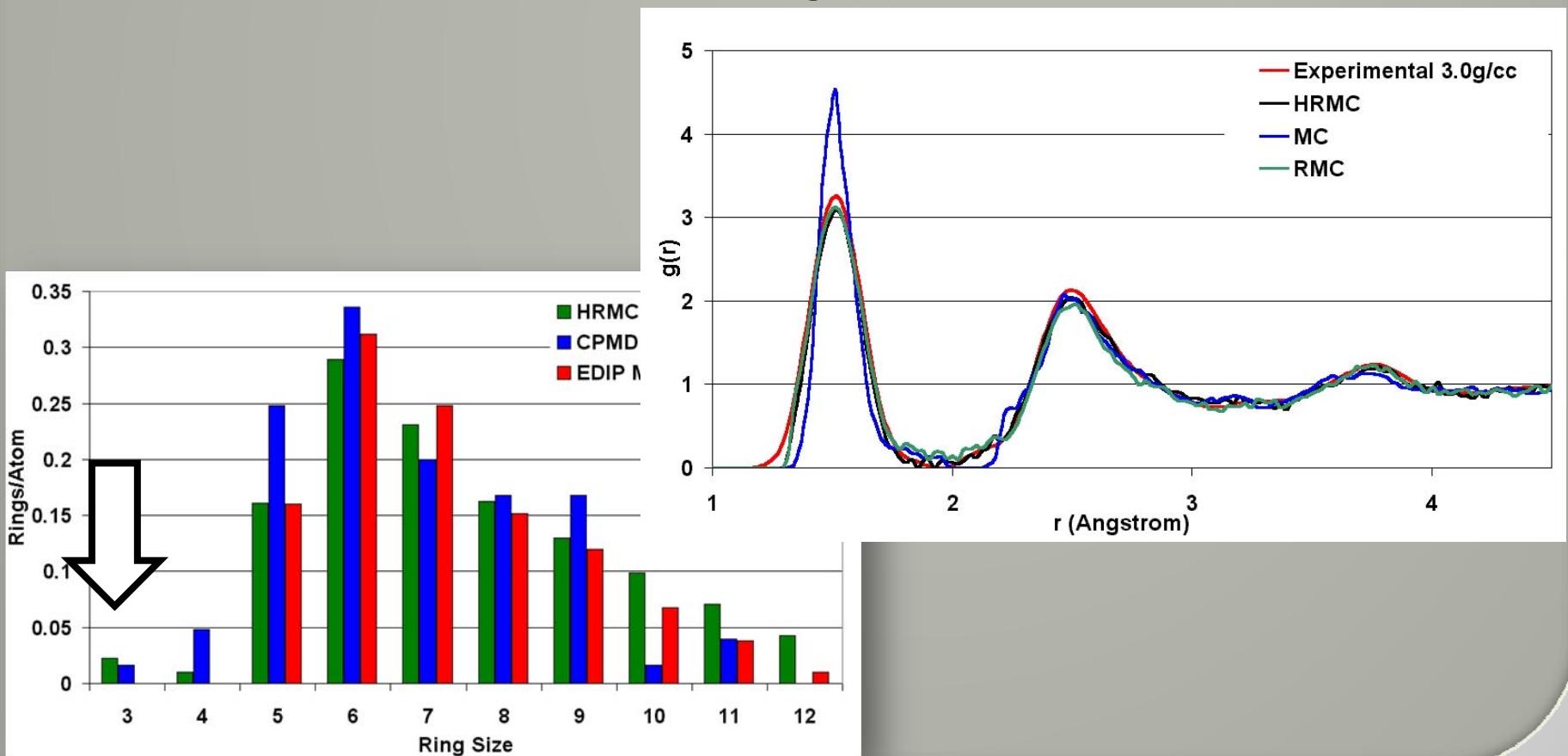
Hybrid Reverse Monte Carlo (HRMC) Method – Quench scheme

- Minimizing multiple contributions to cost function.
- Advantage is taken of the lack of uniqueness of the $g(r)$ (and $S(q)$). $S(q)$ is fit at high T when the energy constraint has a low weighting.

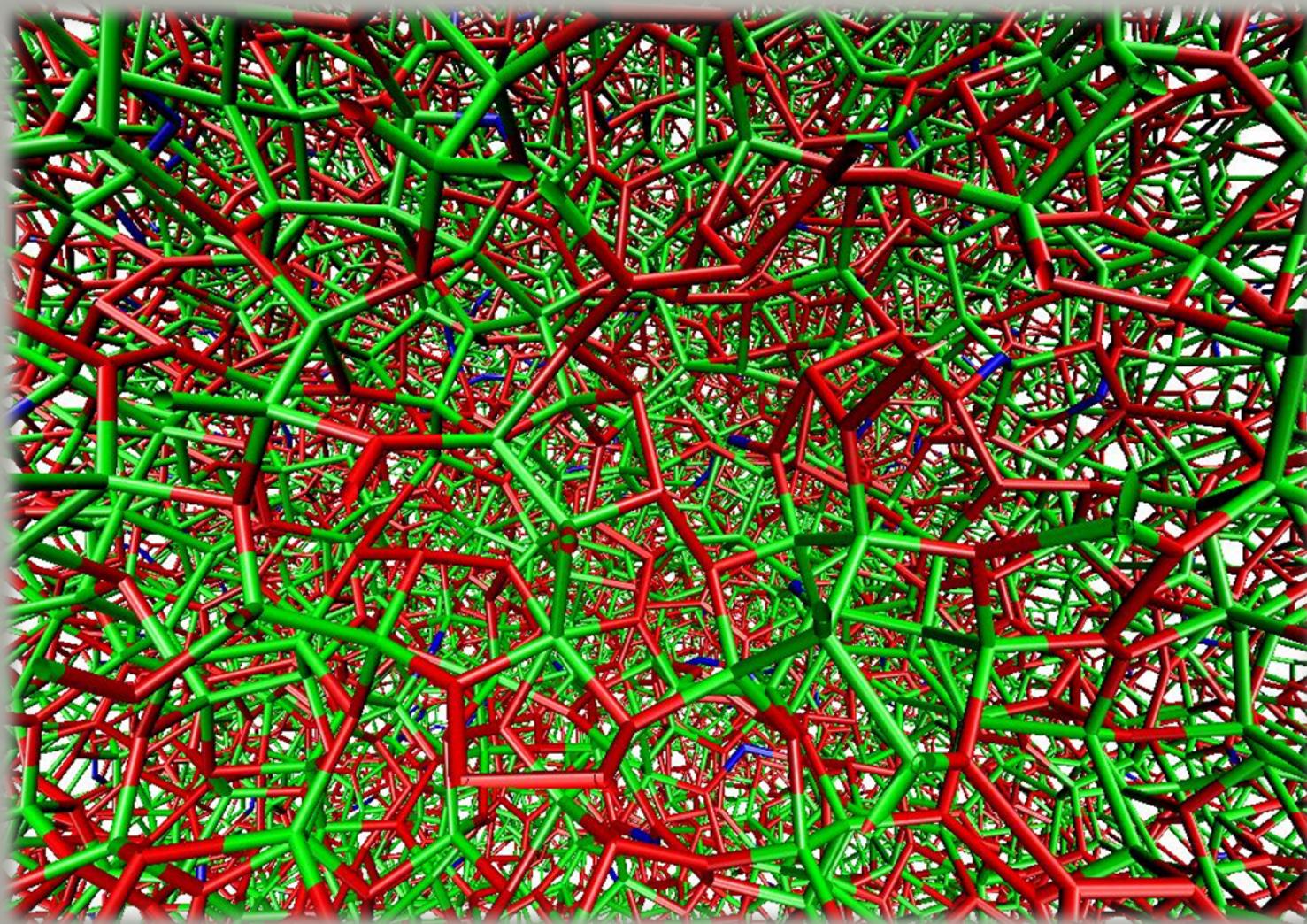


Hybrid Reverse Monte Carlo (HRMC) Method – Tetrahedral Amorphous Carbon (3.0g/cm³)

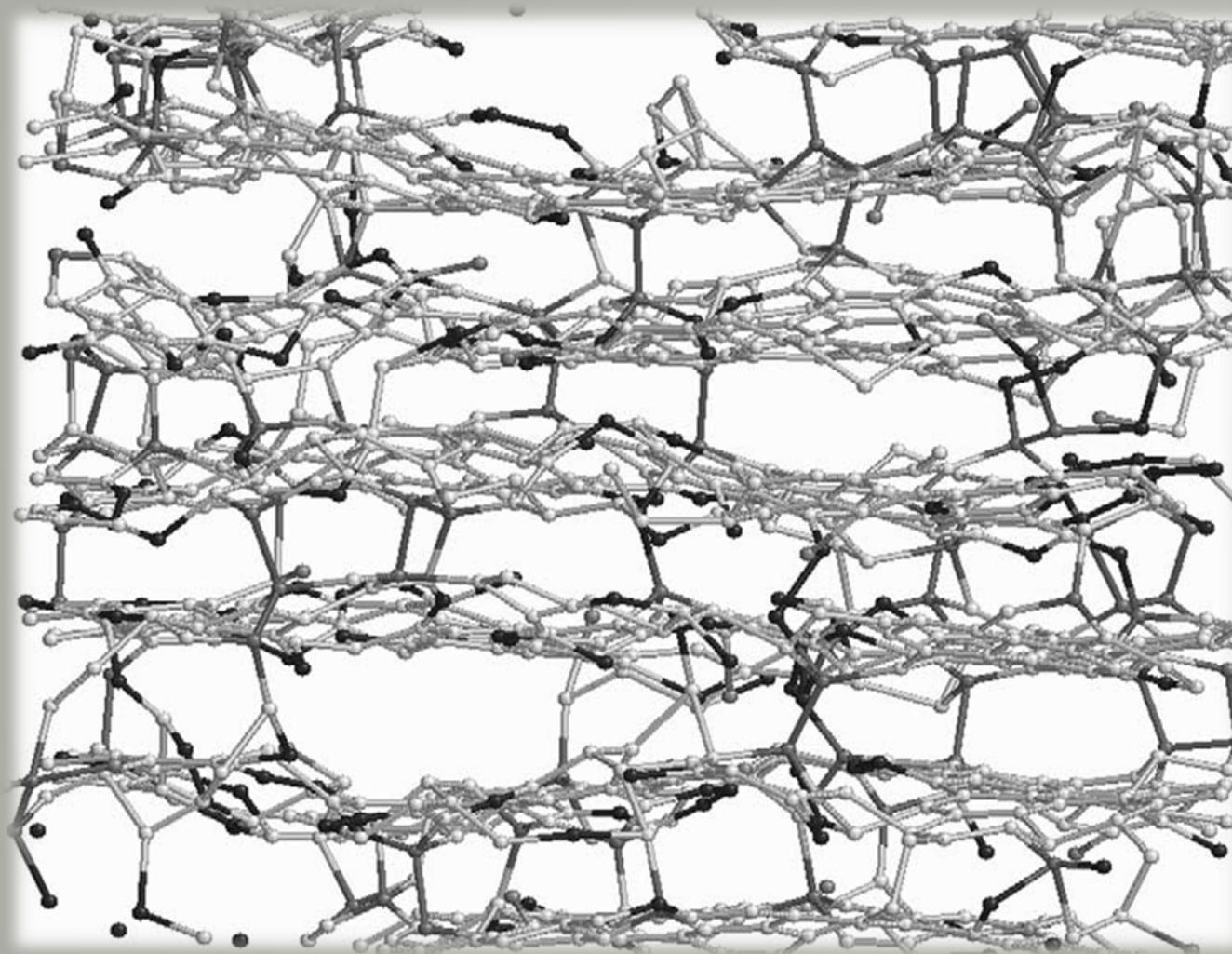
- EDIP potential, 24389 atoms.
- EDIP MC overshoot in g(r) fixed via HRMC.



Hybrid Reverse Monte Carlo (HRMC) Method – Tetrahedral Amorphous Carbon (3.0g/cm³)



Hybrid Reverse Monte Carlo (HRMC) Method – Carbon Char (2.2g/cm³)

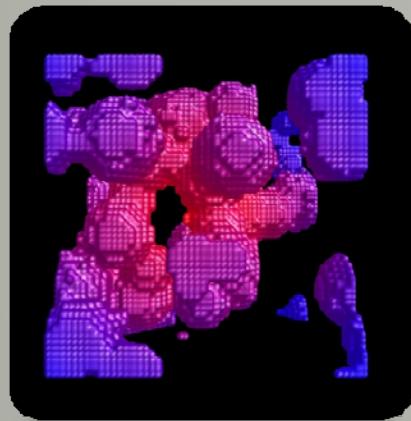


Coordination
4 - grey
3 - white
2 - dark

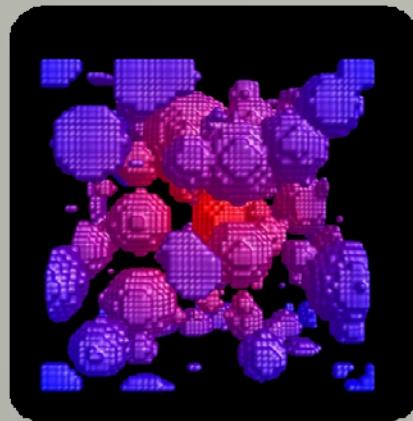
- sp³ cross linking between graphitic sheets.

Hybrid Reverse Monte Carlo (HRMC) Method – Porosity/Surface Area Constraint

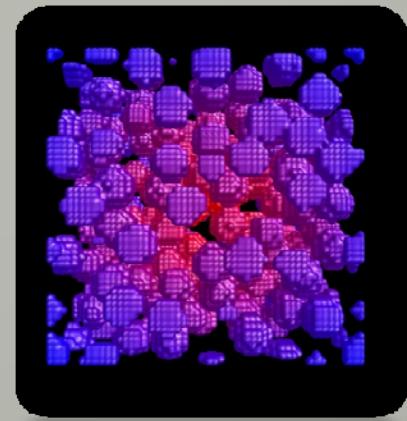
- Spherical overlap model of pores which analytically calculated porosity and surface area.
- Monte Carlo based moves changing sphere positions and radii to produce arbitrary geometry.



0.2 (250 m²/g)



0.2 (500 m²/g)

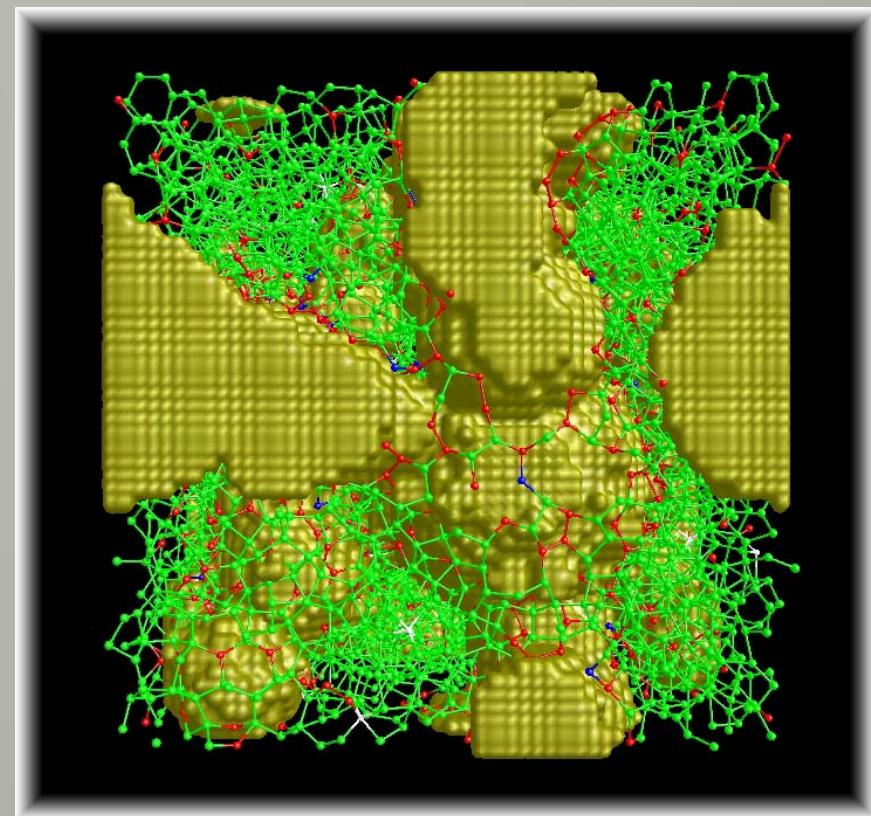
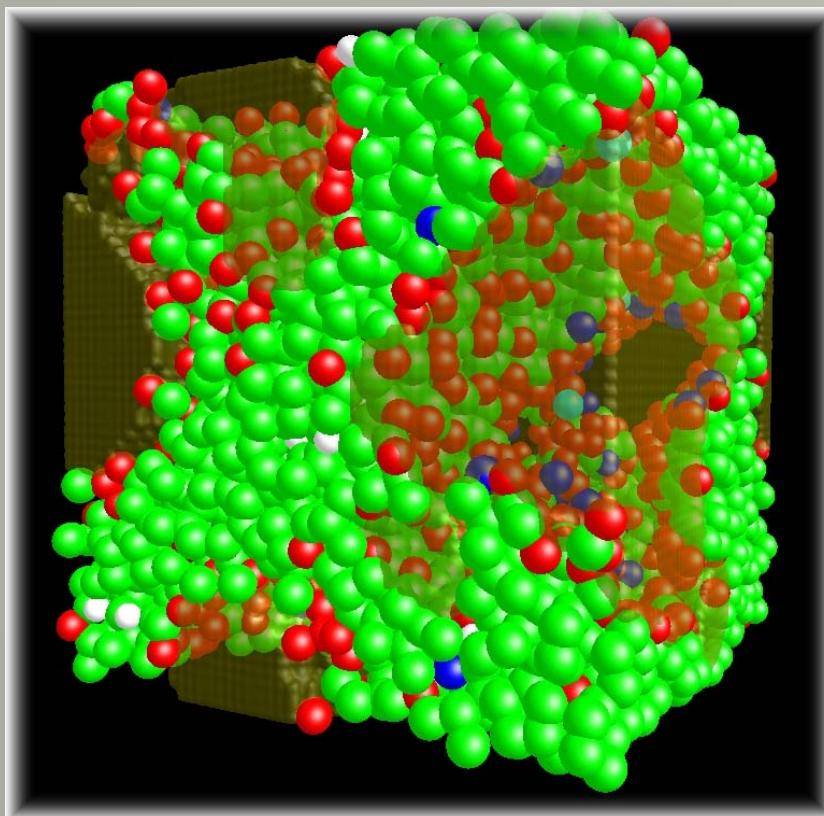


0.2 (1000 m²/g)

- Porosity cells are generated and then input into HRMC.
- Any atomic moves into pore cells are rejected

Hybrid Reverse Monte Carlo (HRMC) Method – Porous Amorphous Silicon

- Stillinger-Weber potential (4865 atoms, 0.39, 84m²/g).
Pore model made from 200 overlapping spheres.



Extensions / Conclusion

- Porosity/surface area decoupled from energetics.
Dynamic constraint preferable.
- Bonding in silicon carbide, C-C, Si-Si versus C-Si bonding.
- Generality - if some measurable physical quantity can be calculated efficiently from xyz positions, it can be used as a constraint.
- Acknowledgement -
Tim Petersen, Dougal McCulloch, Ian Snook, Irene Yarovsky, Brendan O'Malley, Salvy Russo.