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Conference on Structure and Dynamics in Soft Matter and Biomolecules: From Single Molecules to Ensembles

4 - 8 June 2007

Computer Simulation of Structural Glasses

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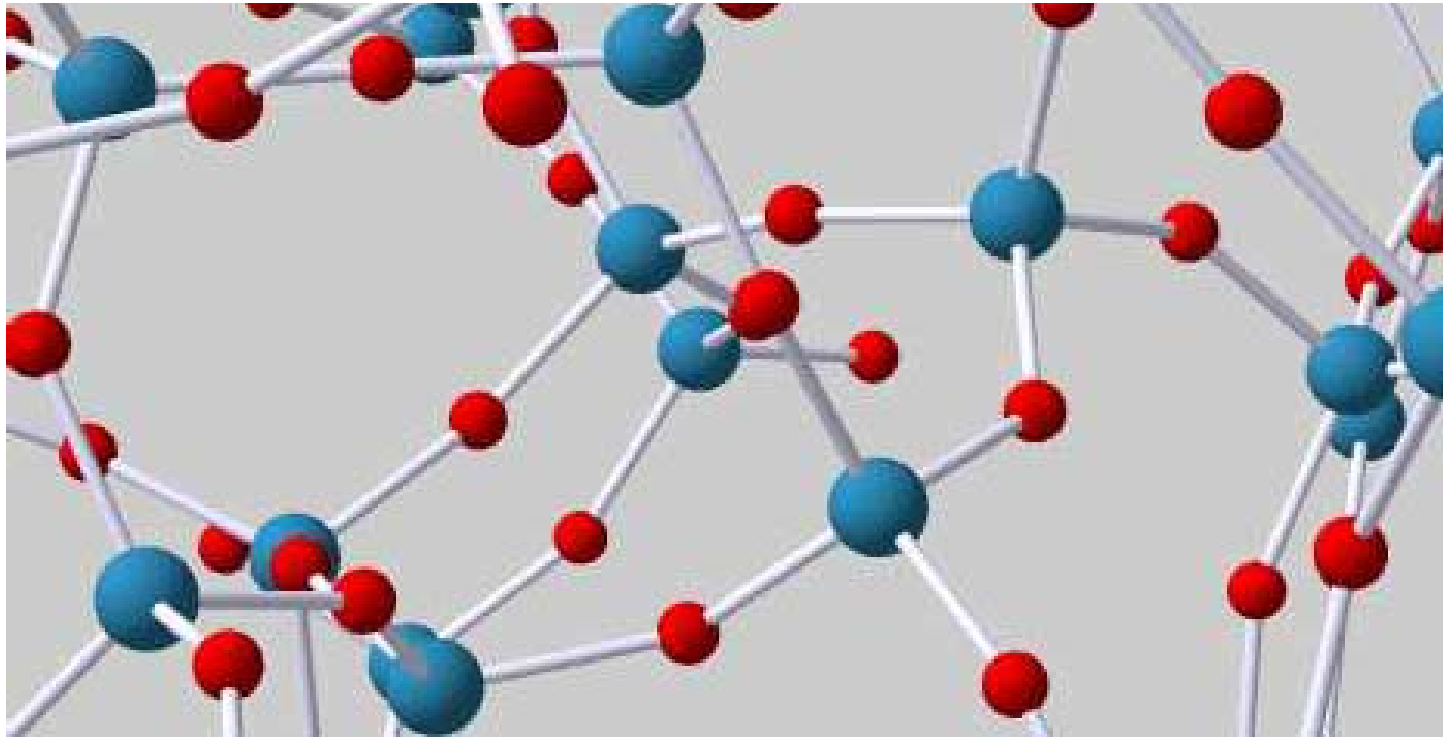
Computer simulation of structural glasses



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The Netherlands

Trieste, June 5, 2007

Organization of this talk

1. **Disordered Materials**
2. **Molecular Dynamics**
3. **Activation-Relaxation Technique (ART)**
4. **Bond-exchange à la Wooten-Winer-Weaire**
5. **Results**

work done in collaboration with Normand Mousseau, Richard Vink, Liesbeth Huisman, Kees Storm, Werner van der Weg, Partha Biswas,
...

Disordered materials were not always appreciated:

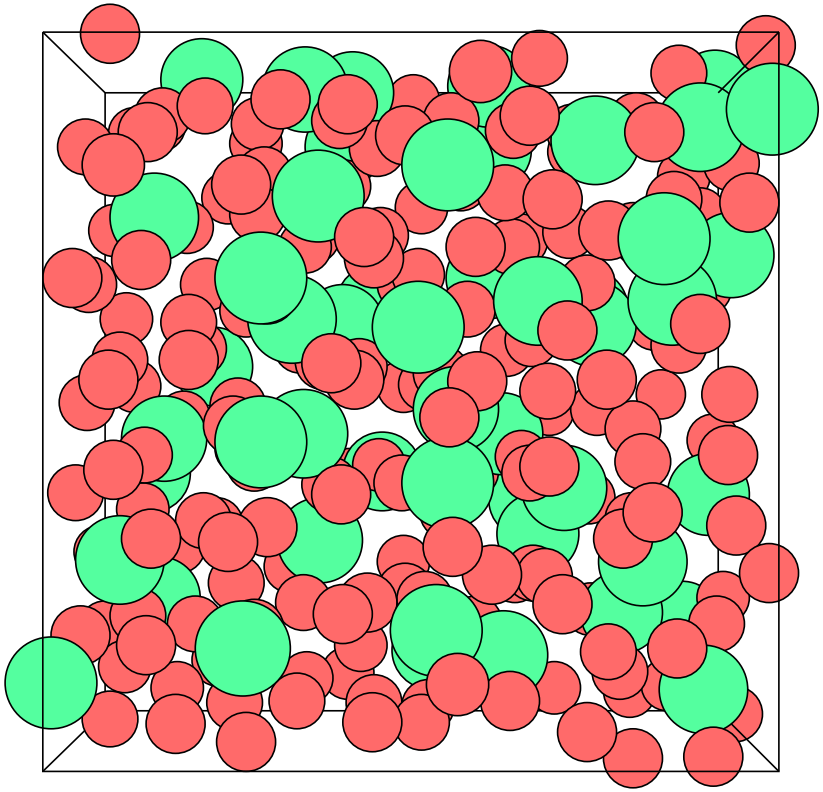
"To many persons here a block of ice may seem of no more interest and beauty than a block of glass; but in reality it bears the same relation to glass that orchestral harmony does to the cries of the marketplace. The ice is music, the glass is noise; the ice is order, the glass confusion."

(J. Tyndall, "Heat – A Mode of Motion", Longmans, Green, London, 1863)

Still, many disordered materials are important:

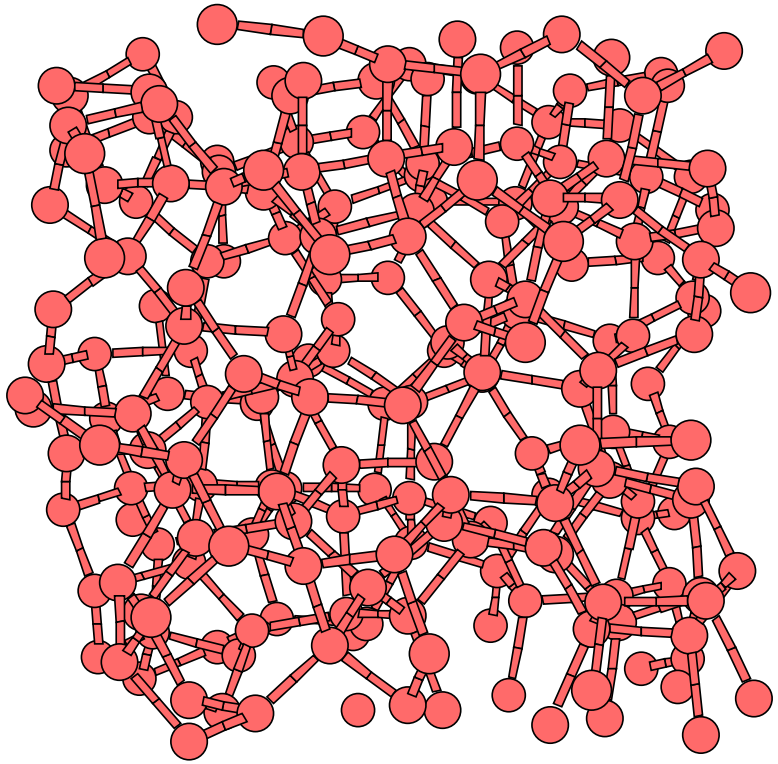
amorphous silicon (a-Si): Staebler-Wronski effect
SiO_2 glass: Stability if used for storage of nuclear waste
metallic glasses: aging of stainless steel
proteins: Folding

Metalic glasses



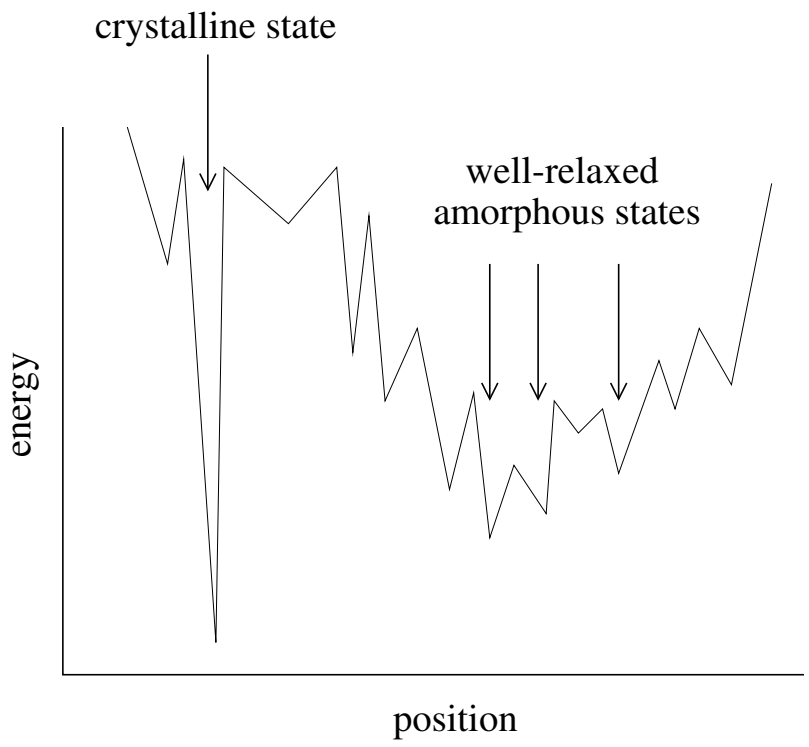
Computer configuration of $Ni_{80}P_{20}$
Well approximated by Dense Random Packed (DRP) model

Network-forming glasses



Computer configuration of a-Si
Well approximated by Continuous Random Network (CRN) model

Glassy and amorphous materials



Questions:

- **nature of dynamics: is it local?**
- **glass transition**
- **anomalous relaxation + "aging"**
- **Structure + microscopic details**
- **"universality"?**

Hand-built Dense Random Packing (DRP) models

- Bernal (1960): pour thousands of steel balls into a flexible container, placed on an irregular surface;
- Knead to maximise the density;
- Pour wax or paint over the balls to fix the configuration.
- Modern approach: colloidal particles, confocal microscopy

Hand-built Continuous Random Network (CRN) models:

- Bell and Dean (1966), Polk (1971), Polk and Boudreaux (1973)

Weak points:

- not many atoms (~ 500), $\Rightarrow$ many atoms at the surface
- building rules rather arbitrary

Molecular Dynamics

Principle of Molecular Dynamics (MD): integrate Newton's law

$$\vec{X}(t+\Delta t) = \vec{X}(t) + \Delta t \cdot \frac{\partial \vec{X}}{\partial t} + \frac{1}{2}(\Delta t)^2 \cdot \frac{\partial \vec{X}}{\partial t} + \ldots$$

or in a more practical representation:

$$\begin{aligned} \vec{x}(t+\Delta t) &= \vec{x}(t) + \Delta t \cdot \vec{v}(t) \\ \vec{v}(t+\Delta t) &= \vec{v}(t) + \Delta t \cdot \vec{F}(t)/m \end{aligned}$$

More accurate schemes:

- **leap-frog**
- **Verlet**
- **velocity-Verlet**
- **Gear algorithms**
- $\ldots$

Size limitations in MD

- **For simple short-range potential (e.g., Lennard Jones):**
  N can be as large as millions of atoms
  One force calculation takes $\sim N\mu$s of CPU-time

- **If Coulombic forces are present:**
  Either the program scales as N^2, or a complicated scheme (Ewald summation, multipole expansion) is required;
  Slowing down by one or two orders of magnitude

- **If gravitational forces are present:**
  even worse, no shielding

- **For** *ab-initio* **computations:**
  $N \sim 1000$ atoms
  One force calculation takes minutes to days of CPU-time

Time limitations in MD

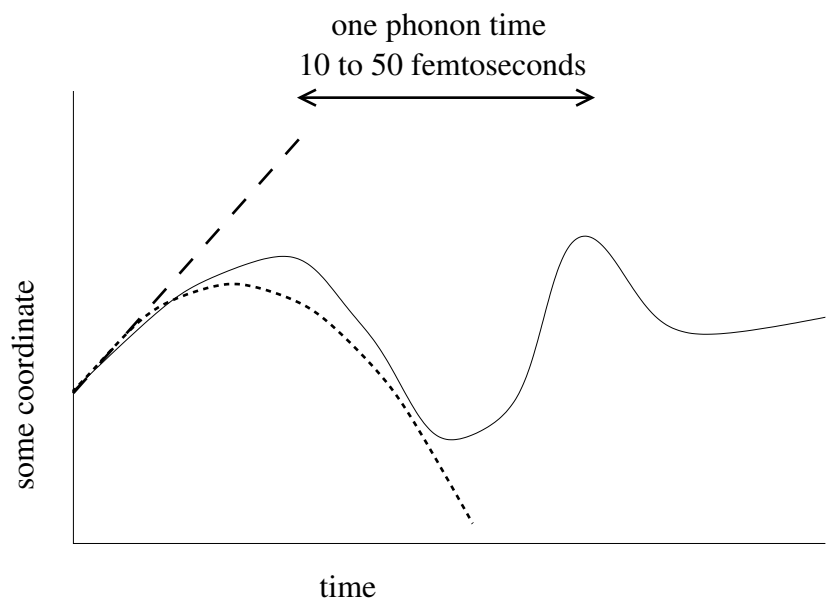
Molecular Dynamics simulates "natural" dynamics of system
Allows for studying dynamical properties:

- Self-diffusion
- Structural relaxation
- Adaptation under strain and stress

Nature limits the time step:

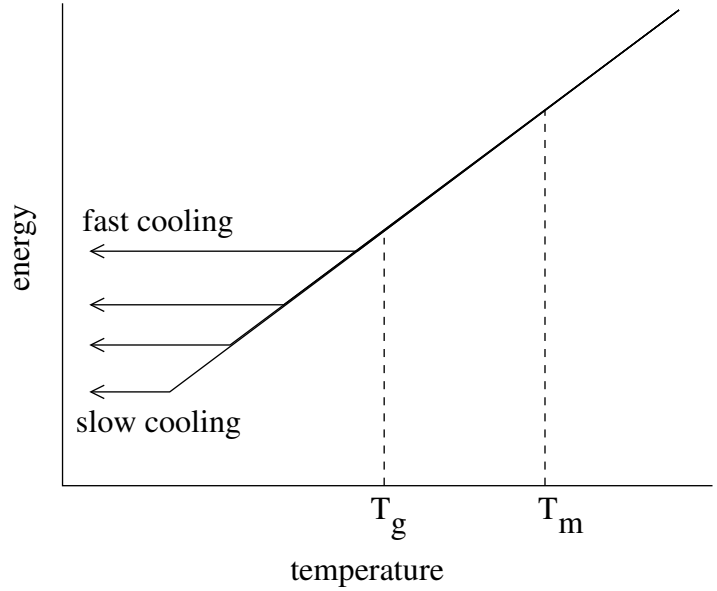
Time step Δt is limited by phonon frequency

$\Delta t \sim$ 1 to 10 femtoseconds.



Experimental cooling rates

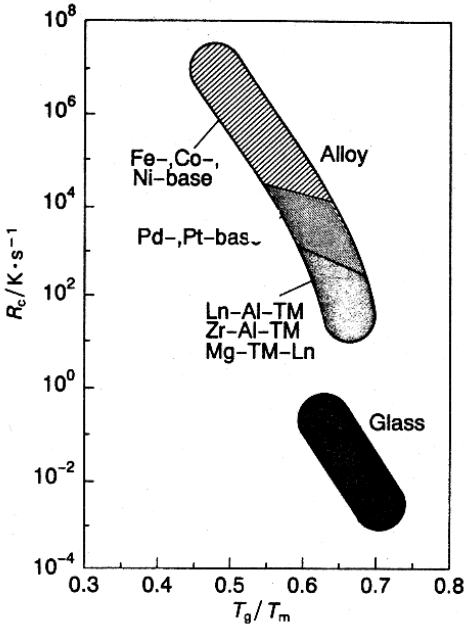
Structure of glasses depends on cooling rate



Two important temperatures:
T_g **is the temperature where the viscosity crosses** 10^{12} **Poise**
T_m **is the melting temperature (from the crystalline phase).**
Between T_g **and** T_m**: undercooled liquid**

Cooling rates

Experimental cooling rates:



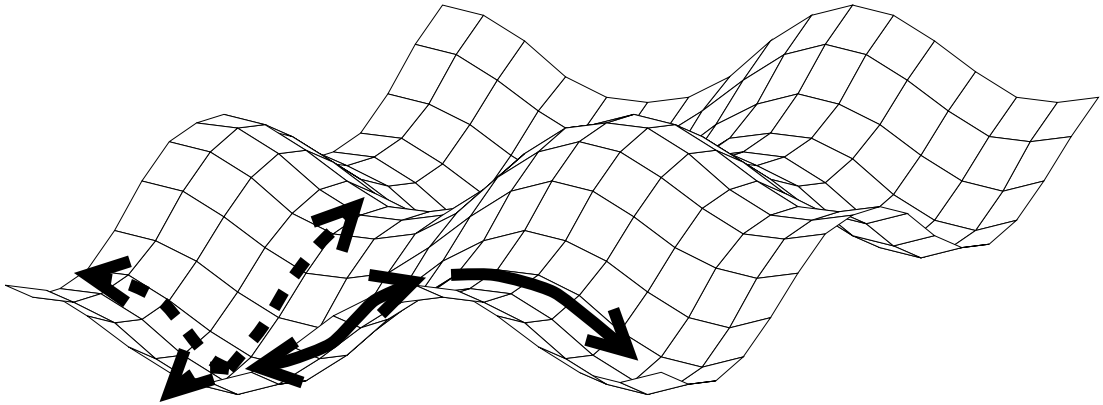
For metallic glasses, simulations need:
$\sim$ (1000 K) / (10^5 K/s) = 0.01 second = 10^{13} time steps

For network glasses:
$\sim$ (1000 K) / (10^{-1} K/s) = 10^4 second = 10^{19} time steps

Achievable: up to 10 μs or 10^{10} time steps
$\Rightarrow$"true" relaxation outside reach of MD.

Cause of slow evolution

Activated dynamics makes MD slow

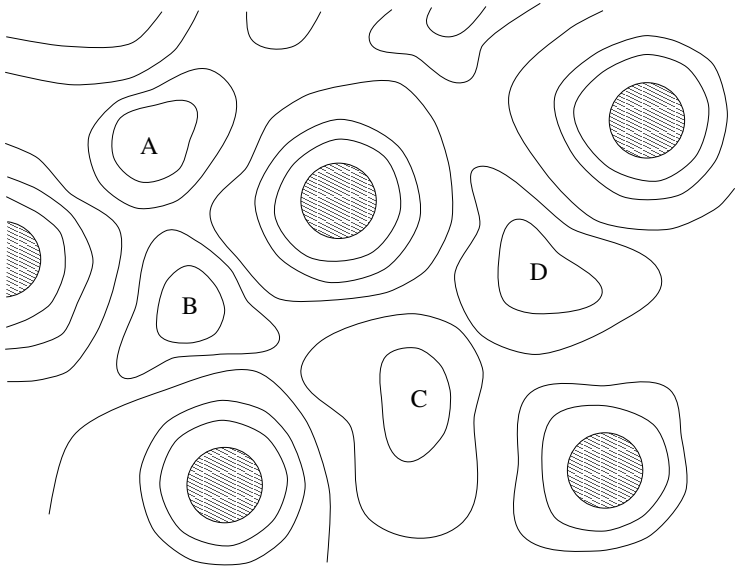


- **At low temperatures, the long-time dynamics is activated.**
- **The time evolution can be characterized by a sequence of hops between local energy minima (basins).**
- **Rate of hop i with energy barrier B_i:**

$$r_i = \nu_i \exp\left(-B_i/k_b T\right)$$

- **This forms the basis for transition state theory (TST).**

Complex energy landscapes



- **No symmetry, curved trajectories**
- **high dimensions: if n atoms are involved, the trajectory is located in a $3n$-dimensional sub-space.**
- **How can we explore the energy landscape?**

We want a method that brings the configuration from one minimum (say, B) to another (e.g., A or C).

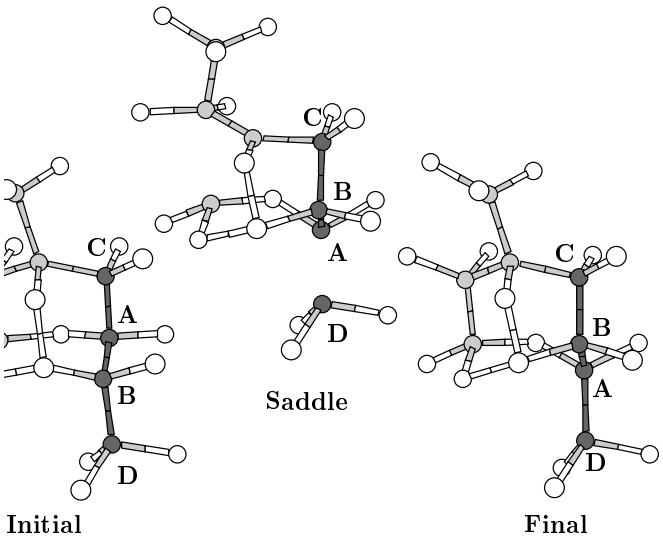
Activation-relaxation technique (ART), Barkema & Mousseau 1996

- **Converge to a first-order saddle point (*activation*),**
- **go down on the other side (*relaxation*).**

Minimum – Saddle point – Minimum trajectory

$\Updownarrow$

Complex atomistic rearrangement



These mechanisms are not imposed *a priori*, but are determined by the constructed trajectory.

- **events can involve few or hundreds of atoms**
- **activation energies can be meV to many eV**

Obtaining well-relaxed structures with ART

1. **Generate one ART event**

2. **If the energy decreases, accept it**

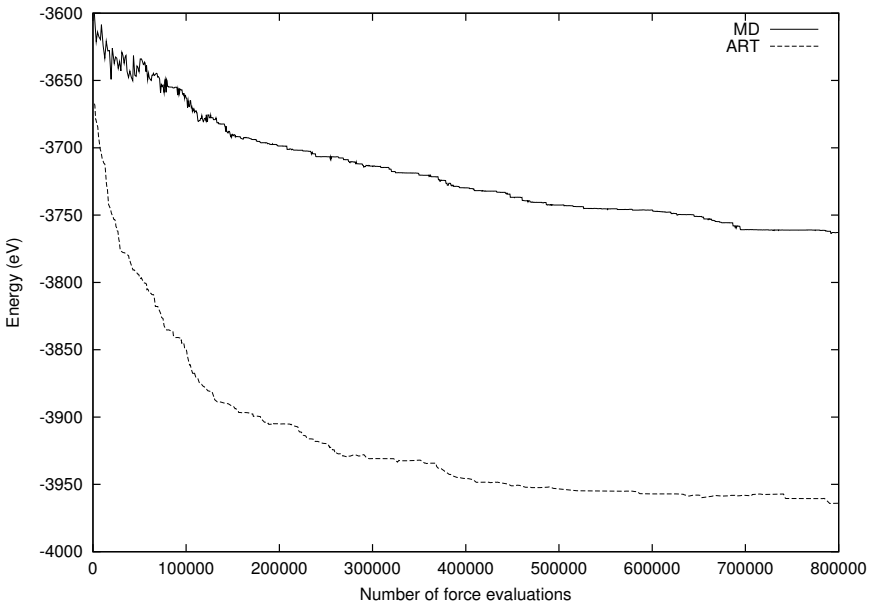
3. **If the energy increases, accept it with probability**

   $$P_{acc} = \mathbf{Min}\left[1, \exp\left(-\Delta E / k_b T\right)\right]$$

   (Metropolis acceptance ratio)

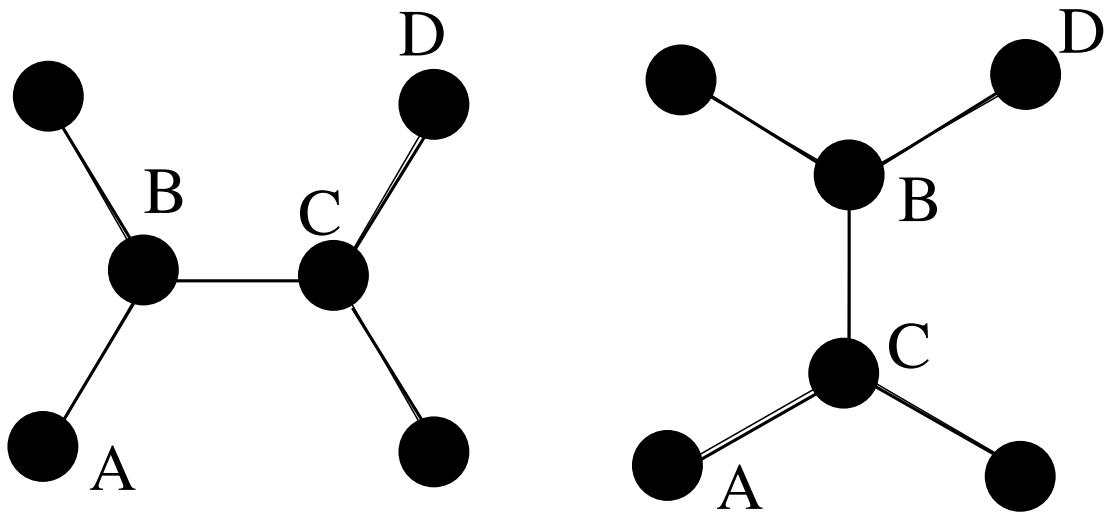
4. **Iterate 1-3**

Much more efficient than MD:



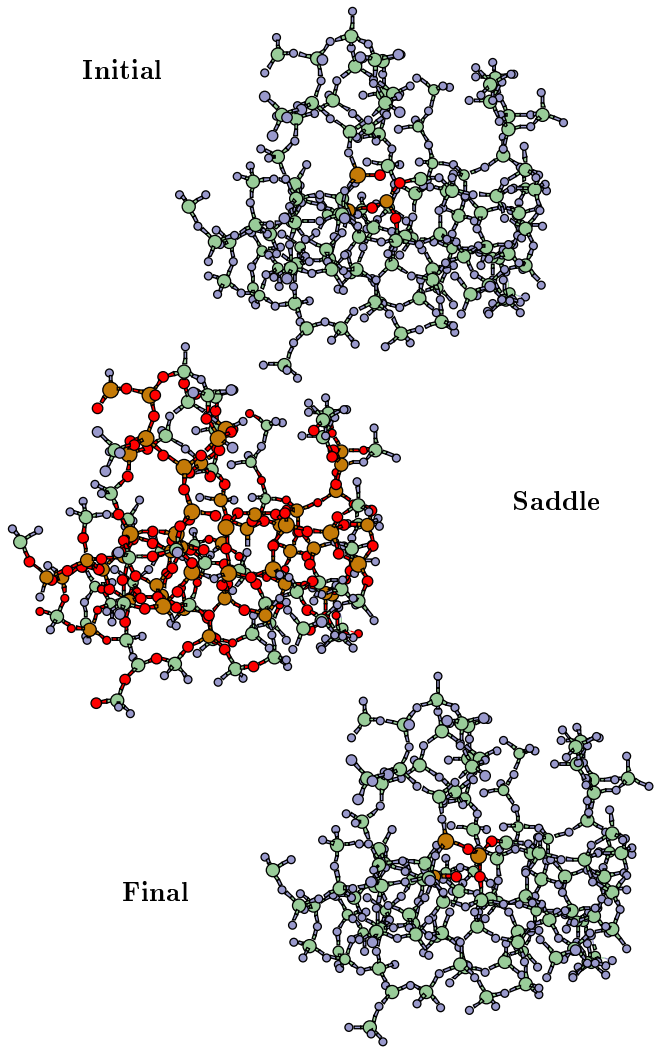
Elementary mechanismns in network glasses

Analysis of ART-events in a-Si:
dominant mechanism is a so-called bond transposition



- **Four atoms A, B, C, and D are involved;**
- **Before, bonds AB, BC, and CD exist**
- **After, bonds AC, BC, and BD exist:**
  bonds AB and CD are replaced by bonds AC and BD

Elementary mechanismns in network glasses (2)



- Top and bottom: colored atoms change their bonding
- middle: colored atoms move more than 0.1 Å(typical amplitude of vibrations)
- energy difference is 0.57 eV
- energy barrier is 3.47 eV
- total displacement is 2.27 Å

Wooten–Winer–Weaire (WWW) approach (1985)

1. **Start: a periodic diamond cubic structure**
2. **Randomization through bond transpositions at $T = \infty$**
3. **Simulated annealing (successively lower T)**

Keating potential:

$$E = \frac{3}{16}\frac{\alpha}{d^2}\sum_{l,i}\left(\mathbf{r}_l i \cdot \mathbf{r}_{l,i} - d^2\right)^2 + \frac{3}{8}\frac{\beta}{d^2}\sum_{l\{i,i'\}}\left(\mathbf{r}_l i \cdot \mathbf{r}_{l,i'} + \frac{1}{3}d^2\right)^2$$

- **α, β are bond-stretching, bond-bending force constants**
- **$d = 2.35$ Å is the Si-Si bond length in crystal**
- **Usual values: $\alpha = 2.965$ eV/Å^2 and $\beta = 0.285\,\alpha$.**

WWW approach (continued)

In one move:

1. **reconnect atoms (bond transposition)**
2. **relax configuration**
3. **accept/reject, Metropolis algorithm:**
   $P_{acc} = \mathbf{Min}\left[1, \exp\left(-(E_{\mathbf{aft}} - E_{\mathbf{bef}})/k_b T\right)\right]$

Our improvements (Barkema & Mousseau, PRB 2000):

1. **Quit relaxing a.s.a.p.**
2. **Start truly random**
3. **first local relaxation**
4. **efficient quenching**

Properties of our a-Si samples

	DTW$^{(1)}$	DTW$^{(2)}$	Conf. 2	Conf. 3	4096
E(eV)/atom	0.336	0.367	0.267	0.264	0.304
ρ/ρ_0	1.000	1.000	1.043	1.040	1.051
$\langle r \rangle / r_0$	0.996	0.997	0.982	0.982	0.980
$\Delta r / r_0$ (%)	2.52	2.65	3.94	3.71	4.17
$\langle \theta \rangle$	109.24	109.25	109.30	109.27	109.28
$\Delta\theta$	10.51	11.02	9.21	9.20	9.89
Rings/atom					
4	0.015	0.000	0.000	0.000	0.000
5	0.491	0.523	0.472	0.480	0.490
6	0.698	0.676	0.761	0.750	0.739
7	0.484	0.462	0.507	0.515	0.467
8	0.156	0.164	0.125	0.116	0.148
9			0.034	0.033	0.035

DTW=Djordević, Thorpe and Wooten, PRB 52, 5685 ('95)
other confs: Barkema & Mousseau, PRB (2000)

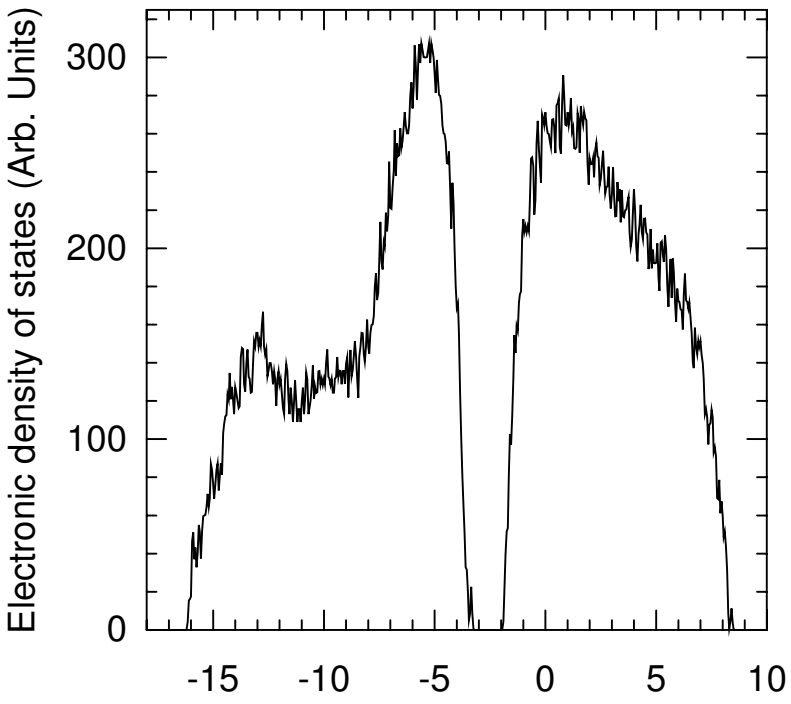
After minimization with modified SW potential

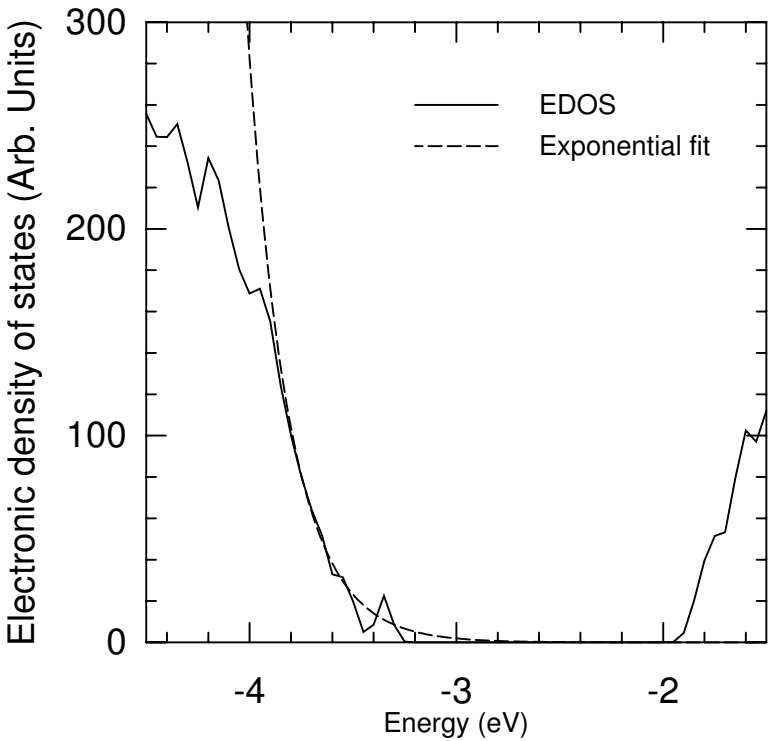
	Sample 2	Sample 3	4096
E(eV)/atom (mSW)	-4.026	-4.034	-3.990
E(eV)/atom (SW)	-4.126	-4.133	-4.106
ρ/ρ_0	0.947	0.950	0.936
$\langle r \rangle / r_0$	1.018	1.017	1.020
$\Delta r / r_0$ (%)	2.9	2.7	3.2
$\langle \theta \rangle$	109.25	109.24	109.20
$\Delta\theta$	9.77	9.70	10.51
Rings/atom			
4	0.000	0.000	0.001
5	0.472	0.480	0.489
6	0.840	0.847	0.830
7	1.011	1.023	0.979
8	2.025	2.002	2.064

comparison with ART: -4.14 eV/atom (SW) and -4.04 eV/atom (mSW) with 0.5% three-fold and 1.1% five-fold coordinated atoms

comparison with MD: -4.088 eV/atom (SW)

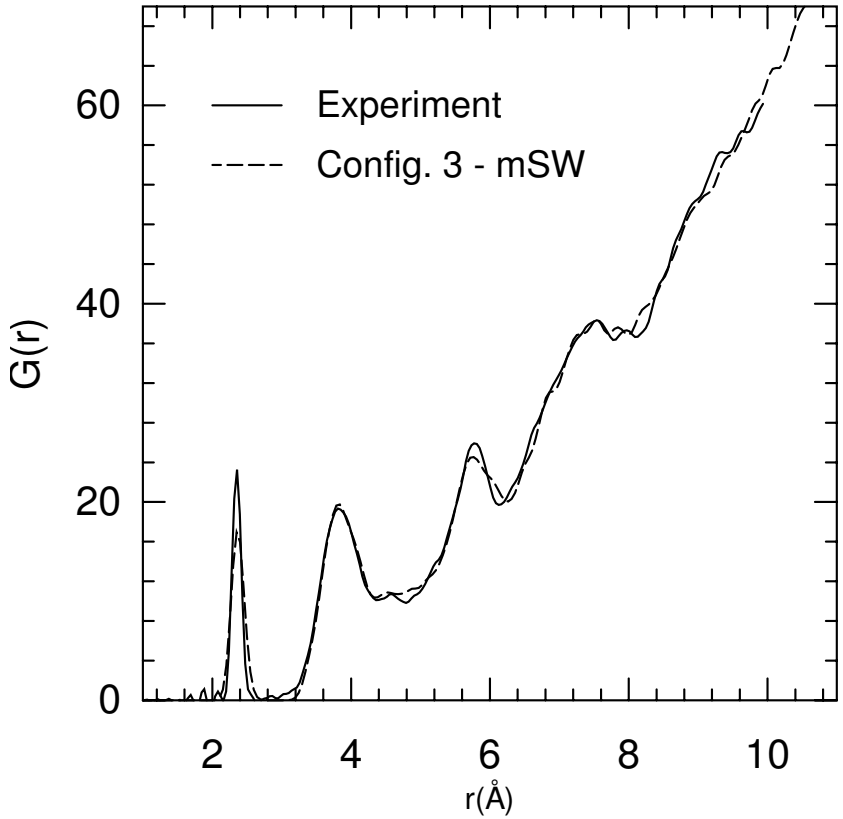
Electronic density of states (EDOS)





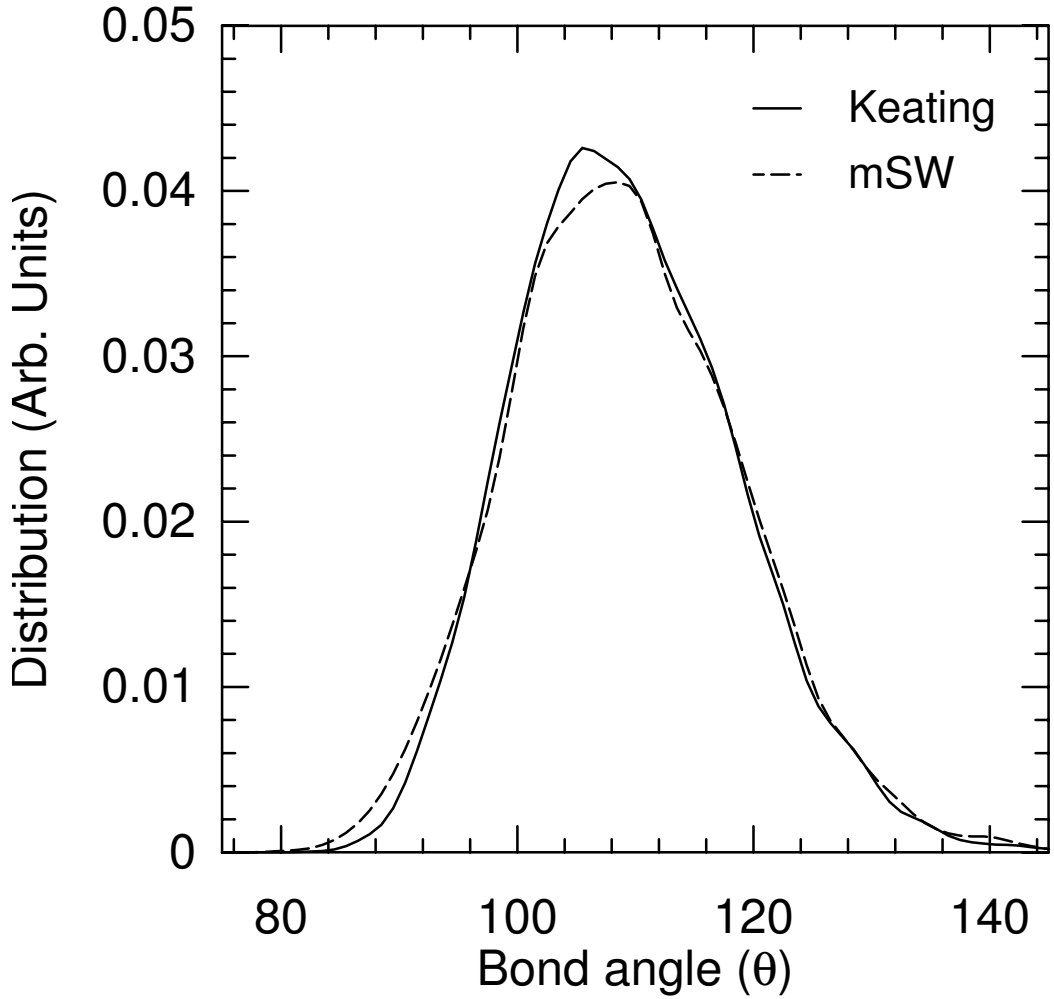
***calculation by S. Nakhmanson**

Radial Distribution Function (RDF)



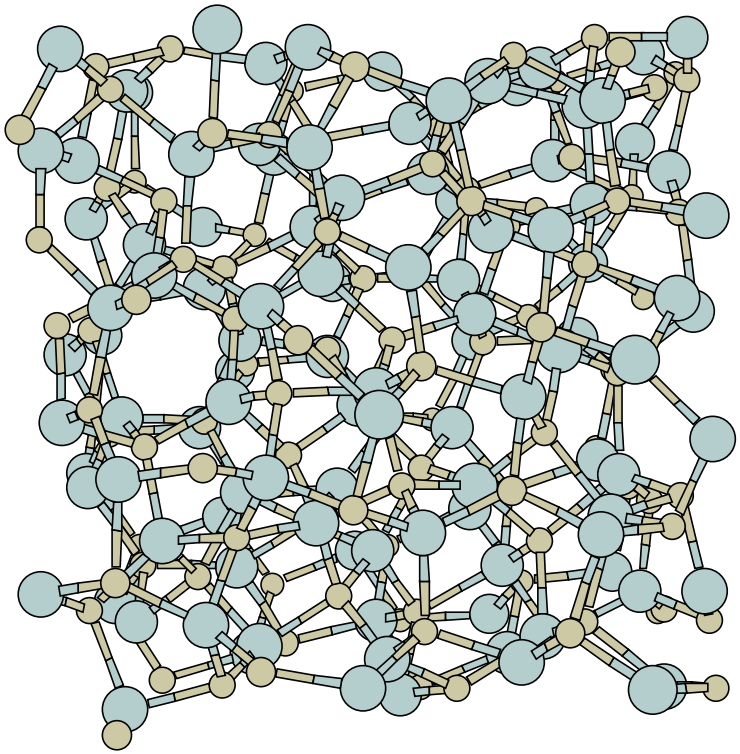
dashed line: sample 3, relaxed with mSW, scaled by 0.99
solid line: experiment

Bond Angle Distribution



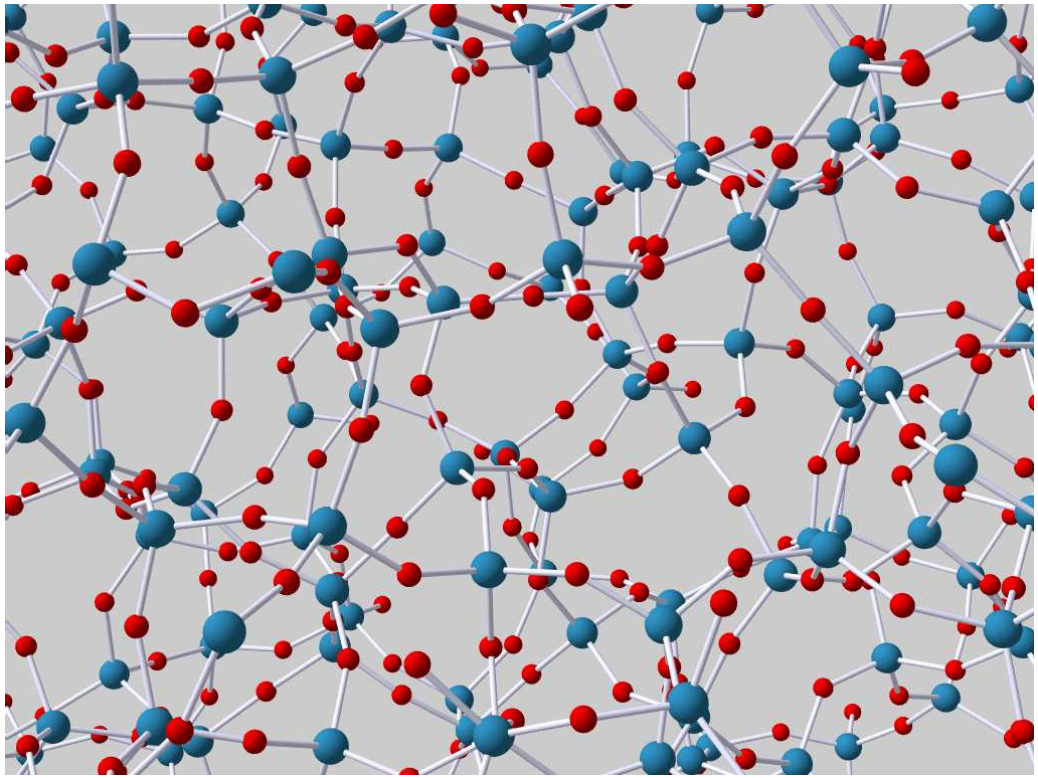
Connell-Temkin networks (a-GaAs)

- **Tetrahedrally coordinated network with two types of atoms**
- **no bonds between like atoms**

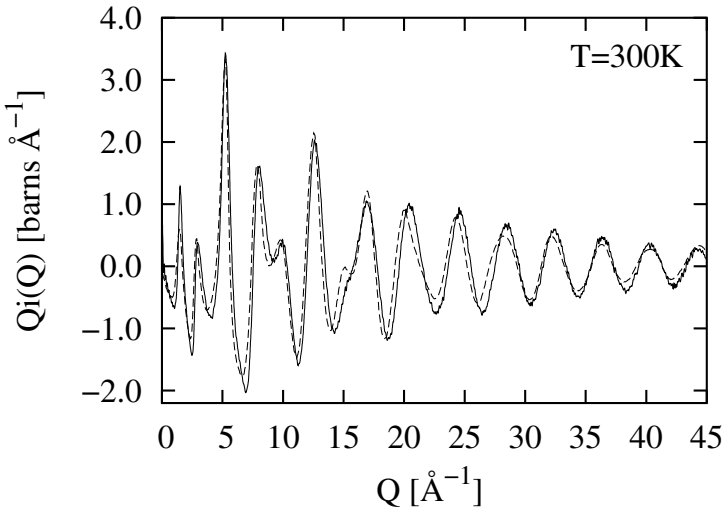


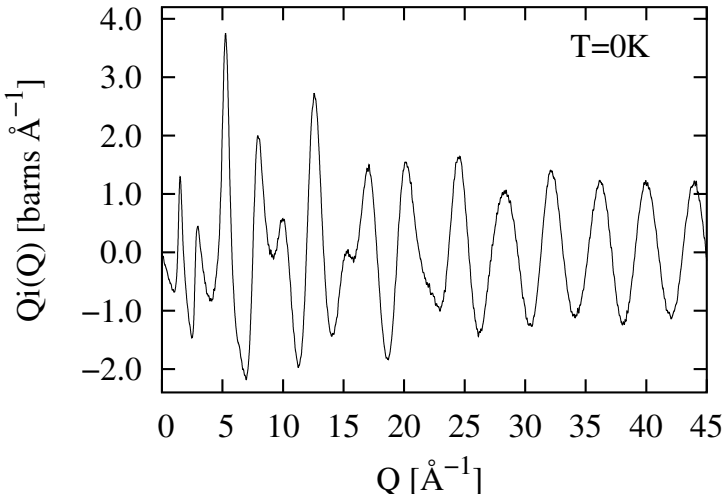
Silica glass (vitreous SiO_2), Vink & Barkema 2003

- Start with a large, well-relaxed fourfold coordinated CRN
- place oxygen atoms in the middle of each bond
- continue bond-exchanges with the Tu-Tersoff potential
- relax the configuration with an interatomic potential for silica (BKS)

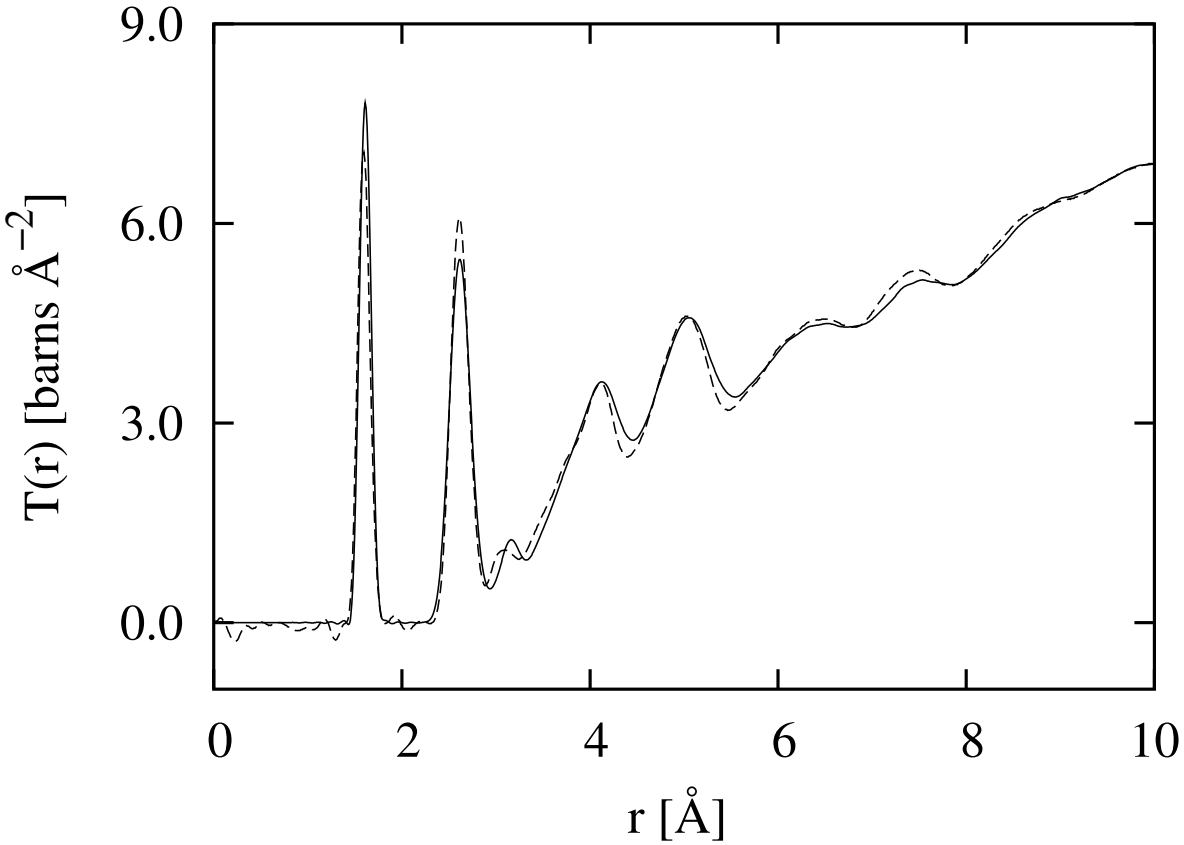


Results on silica vs. expt (Wright 1994)





Results on silica vs. expt (Wright 1994)



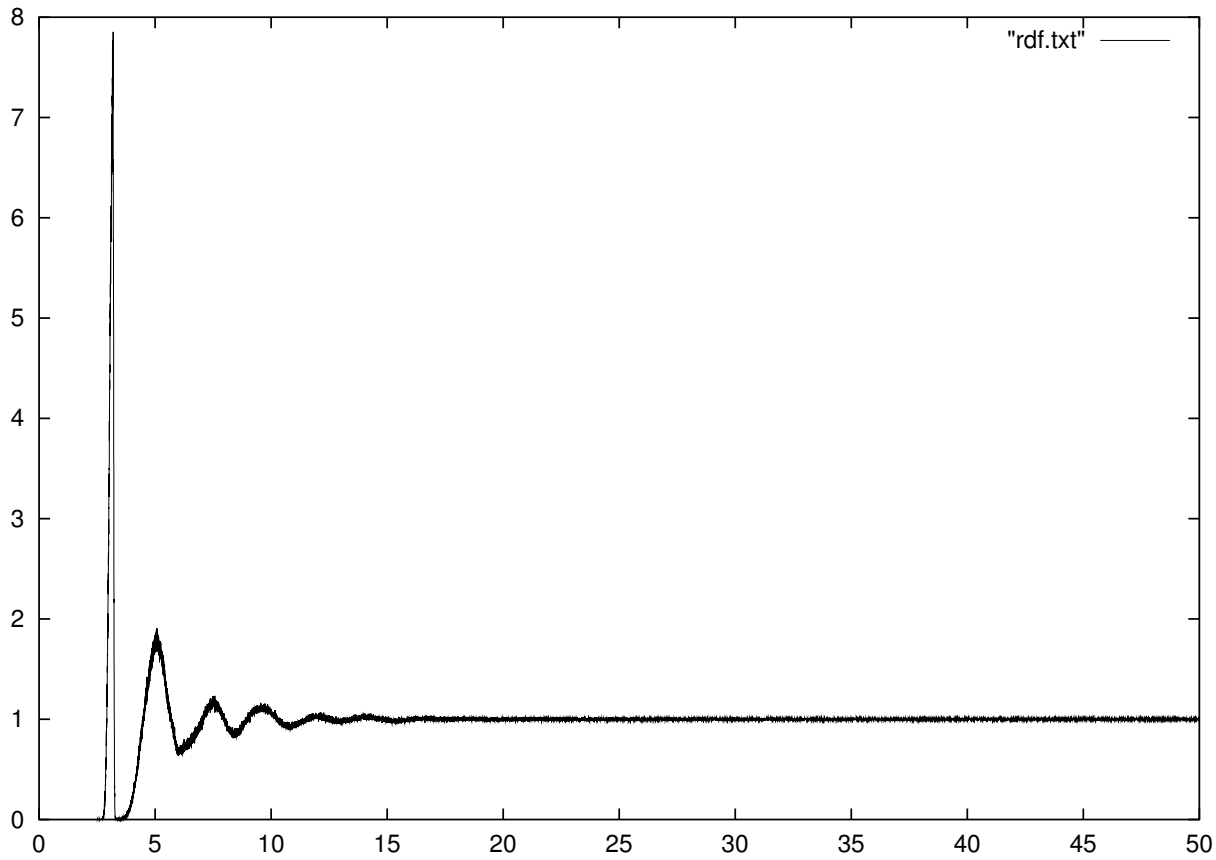
Obtained after temperature- and Fourier-broadening

$$T_b(r) = r + \frac{2}{\pi}\int_{Q=0}^{Q=Q_{max}} M(Q)Qi(Q)\sin(Qr)dQ \qquad \textbf{with} \qquad M(Q) = \frac{Q_{max}}{\pi Q}\sin\left(\frac{\pi Q}{Q_{max}}\right).$$

Results on silica vs. MD (Horbach&Kob)

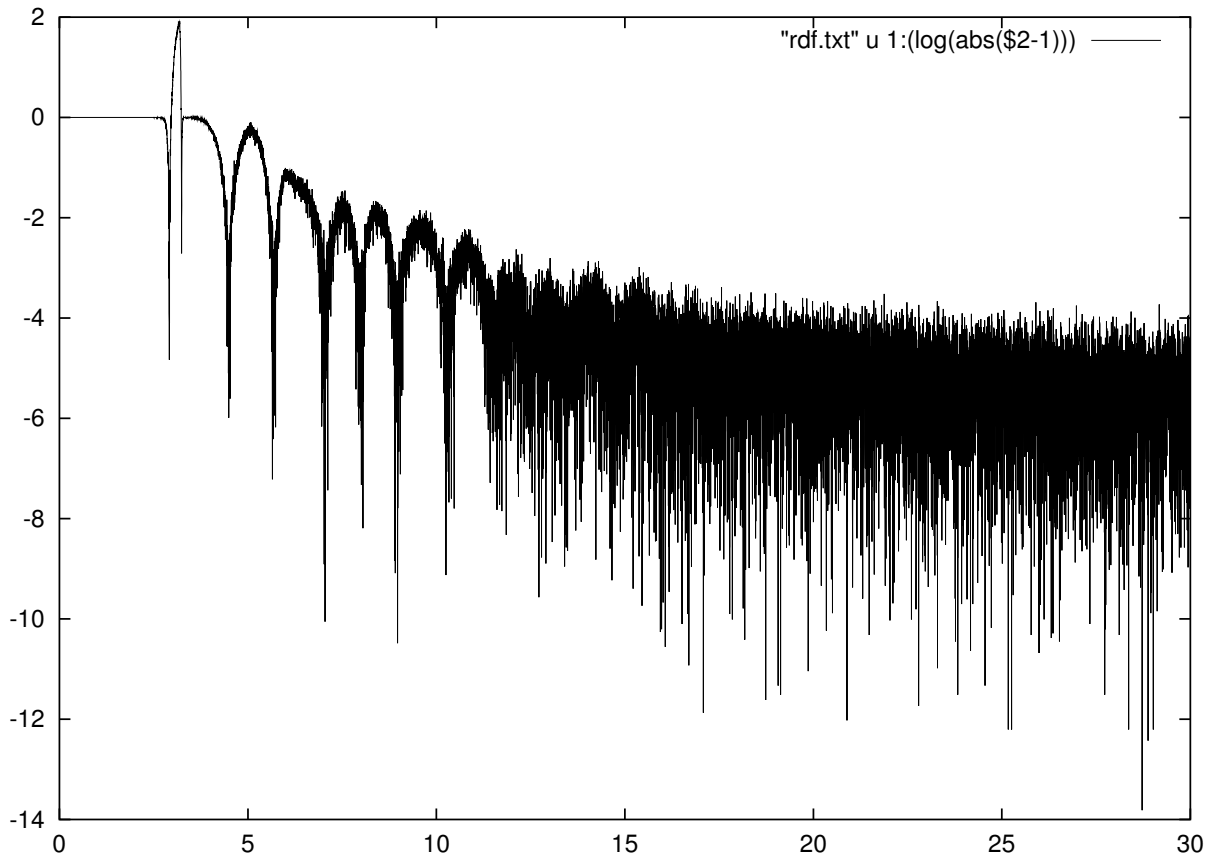
	3k	60k	300k	MD
N	3000	60,000	300,000	1002
E	-58.12	-58.10	-58.09	–
ρ	2.20^*	2.20^*	2.20^*	2.27-2.37
Si-O				
mean	1.606	1.608	1.606	1.595
rms	0.010	0.011	0.011	–
O-Si-O				
mean	109.44	109.43	109.43	108.3
rms	3.95	4.59	4.32	–
FWHM	8.3	9.3	9.8	12.8
Si-O-Si				
mean	153.89	153.57	153.00	152
rms	11.75	11.72	11.94	–
FWHM	34	33.3	34.5	35.7
z_4	100%	100%	99.997%	99.8%
z_2	100%	100%	99.998%	99.8%
R_χ	-	4.7%	4.9%	9%

Results on silica: long-range correlations?



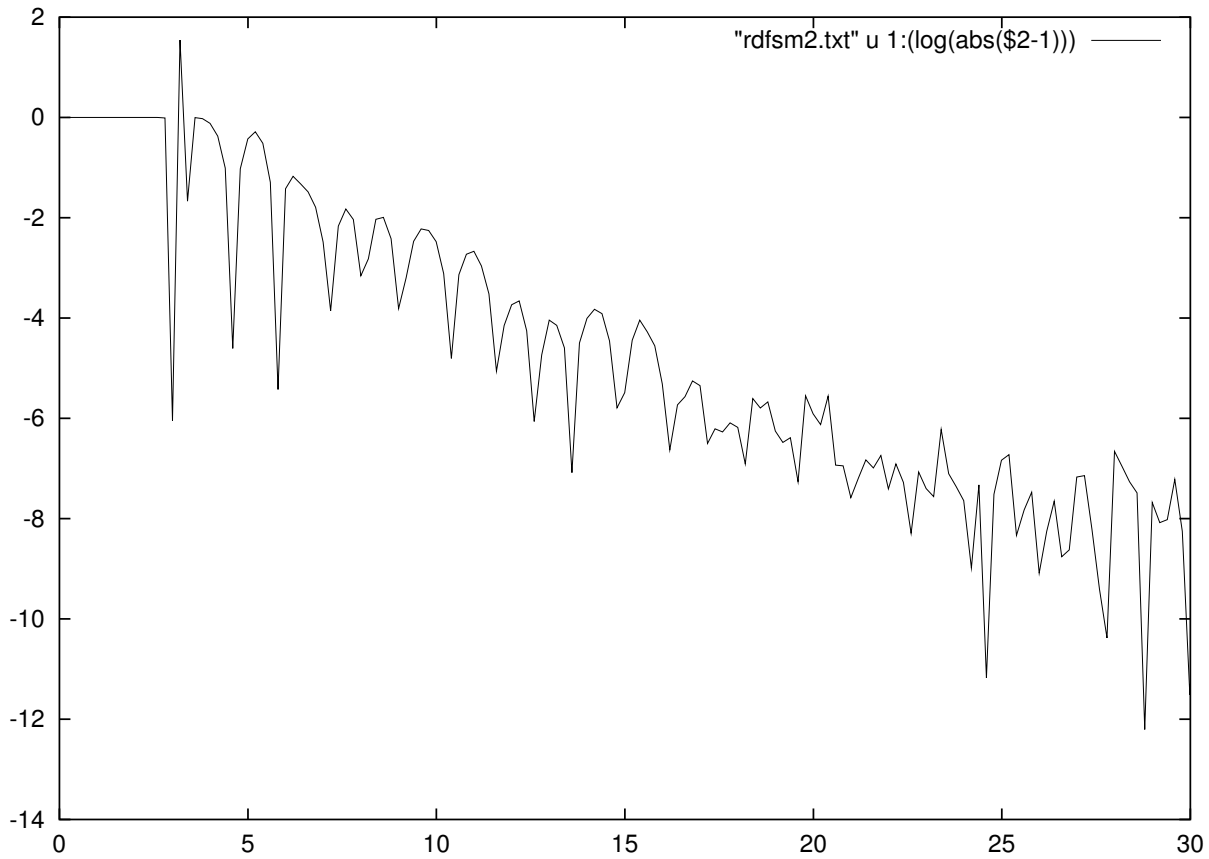
Si-Si radial distribution function

Results on silica: long-range correlations? (2)



Si-Si radial distribution function, plotted differently

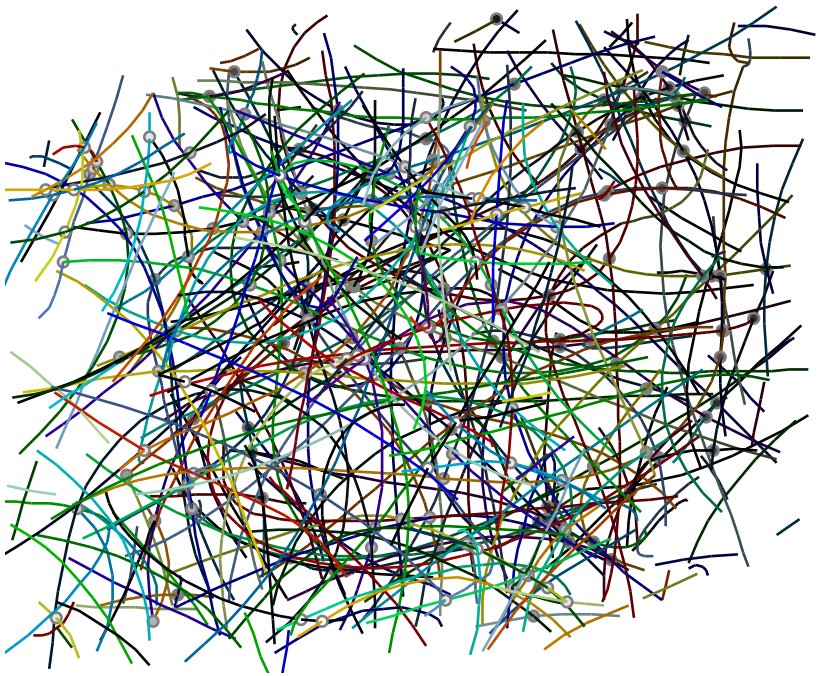
Results on silica: long-range correlations? (3)



smoothed Si-Si radial distribution function, plotted differently

Crosslinked polymer networks (actin skeleton)

- **semiflexible polymers, connected by crosslinkers**
- **$\Rightarrow$ Tetrahedrally coordinated network, with pair-wise preferred angle of 180°**



Summary

- sufficiently long time scales can only be reached with a crude simulation of the microscopic dynamics
- ART is an alternative for MD, for structural relaxation
- for network glasses (a-Si, silica, ...) high-quality sample configurations can be obtained with bond-switching simulations

Future work

- What makes glass so glassy?
- Understanding ART better
- Generation of undercoordinated networks
- mechanical properties of crosslinked polymer networks