Computer Simulations of Glasses

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Kyoto, January 2008

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Outline and collaborators

Outline:

- What are computer simulations?

- Watch out for these problems!

- Some results for SiO_2, NaO_2-SiO_2

- Summary

Magali Benoit (Toulouse)

Kurt Binder (Mainz)

Jürgen Horbach (Köln)

Remi Jullien

Philippe Jund

Anke Winkler (Mainz)

Sidoine de Wispelaire

What are computer simulations?

- Given: Interesting effect; technological problem; theoretical prediction

  Simulations: Use an atomistic/microscopic approach to find answers

  (atoms rule the world!)

  IMPORTANT: Here atomistic means that we have a Hamiltonian (=energy function) that can be used to apply the machinery of statistical mechanics

  $\Rightarrow$ No "reverse Monte Carlo" which is a method to move around particles in a simulation box in an *ad hoc* way in order to find a configuration/ arrangement of the particles that is compatible with experimental data

  $\Rightarrow$ No finite elements

Why computer simulations ?

- Simulations are relatively simple, inexpensive, and everything can be measured (in principle!)

- NOT to reproduce experimental results!! (exception: verify potential etc.)

- Help to understand experimental results (by considering ideal systems, measuring "exotic" quantities,..)

- Help to make better experiments (determine multiple scattering processes,…)

- Test of theoretical predictions or theories

- Investigate systems on a level of detail which is not possible in real experiments or analytical theories (local structure, mechanism of transport, "exotic" compositions, …)

Interaction potentials

Hamiltonian approach $\Rightarrow$ We need a potential that describes

the interactions between the particles

Three possibilities:

1. Postulate interactions *ad hoc*

2. *Ab initio* calculation

3. Effective potentials

Interaction potentials 2

1. Interactions postulated *ad hoc*

Universal phenomena (phase transitions, glass transition, …) or the behavior on large length scales (hydrodynamics,…) are independent of the details of the microscopic interactions

$\Rightarrow$ Use interaction that is as simple as possible

Example 1: Ising model on a lattice to investigate the universal (!) nature of second order phase transitions

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j \qquad \sigma_i \in \{-1, +1\}$$

Example 2 : Lennard-Jones potential; can be used to simulate, e.g., a simple glass-forming liquid

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Interaction potentials 3

- If one wants to obtain the properties of a real material (T_m, viscosity,…) the interactions need to correspond to the real ones

2. Interactions from *ab initio* calculation:

Potential is calculated from the instantaneous positions of the ions $\Rightarrow$ electronic structure of the system is obtained using the density functional theory (Kohn-Sham)

$\Rightarrow$ interaction between the atoms   Due to the necessity to deal with the many (valence) electrons this approach is computationally very expensive $\Rightarrow$ typical system sizes are O(200) particles

Program codes are *very* large and sophisticated: Car-Parrinello (CPMD); VASP; ABINIT; SIESTA; ….

Various codes have different advantages/disadvantages: Scaling of computational efficiency with system size; accuracy; quantities that can be calculated; …

Interaction potentials 4

• Since *ab initio* is too expensive one tries to come up with an *effective* potential that is specific for the material but less accurate than *ab initio*

3. Interactions from effective potentials (classical simulations):

 -One assumes a functional form for the potential (Lennard-Jones, Buckingham, Coulomb, …)

Example: Sim. of SiO_2 using pot. of van Beest, Kramer and van Santen (BKS)

$$\phi_{\alpha\beta}(r) = \frac{q_\alpha q_\beta e^2}{r} + A_{\alpha\beta} \exp\left(-B_{\alpha\beta}r\right) - \frac{C_{\alpha\beta}}{r^6} \quad \alpha, \beta \in [\text{Si}, \text{O}]$$

 -The free parameters of the potential are obtained by fitting experimental data or to results from *ab initio* calculations

 -Simulations are relatively cheap $\Rightarrow$ O(10^6) particles can be simulated 9

Propagating the system

- Given the interaction potential we must decide how to move the particles in configuration space

Two possibilities

1. Molecular Dynamics: Solve Newton's equations of motion

2. Monte Carlo: Pick a random configuration and apply a Boltzmann criterion

Stuctural and dynamical information

Propagating the system: MD

- Molecular dynamics = Solve Newton's equations of motion numerically

- One simple but surprisingly good algorithm is the one proposed by L. Verlet:

Velocity form of the Verlet algorithm:

1. Let $r_i(t)$ and $v_i(t)$ be the position and velocity of particle i at time t

2. Calculate the force $f_i(t)$ that acts on particle i (will depend on the positions of all the other particles)

3. Let h be a small time increment (typically 0.2-1.0 fs)

$$r_i(t + h) = r_i(t) + hv_i(t) + h^2 f_i(t)/2m_i$$

$$v_i(t + h) = v_i(t) + h[f_i(t) + f_i(t + h)]/2m_i$$

4. t $\Rightarrow$ t+h

5. goto 2.

$\Rightarrow$ trajectory of the system in phase space

Propagating the system: MC

• Monte Carlo = Pick a random configuration and apply a Boltzmann criterion

There are many different MC algorithms: A famous one is the one proposed by Metropolis

Metropolis algorithm:

1. Get a starting configuration R_{old} ={$r_1(t)$, $r_2(t)$, …, $r_N(t)$}

2. Calculate the potential energy for the configuration $R_{old} \Rightarrow E_{old}$

3. Displace "randomly" a (or several) particle(s) $\Rightarrow R_{new}$

4. Calculate the potential energy for the configuration $R_{new} \Rightarrow E_{new}$

5. if $E_{new} \leq E_{old}$ accept the new config.; set $R_{old} = R_{new}$; advance clock by 1

6. if $E_{new} > E_{old}$ accept the new configuration with probability

   $\exp[-(E_{new} - E_{old})/k_B T]$,   where k_B is the Boltzmann constant and T is temperature; if you accept set $R_{old} = R_{new}$; advance clock by 1

7. goto 3.

$\Rightarrow$ trajectory of the system in configuration space

Propagating the system: MC 2

- Important: In order for a Monte Carlo algorithm to be correct, it has to fulfill the condition of detailed balance

$$\exp(- E_{old}/k_BT) \; W(old \Rightarrow new) = \exp(- E_{new}/k_BT) \; W(new \Rightarrow old)$$

Transition probability (=how do you pick the new configuration)

This condition guarantees that the probability that a configuration occurs is given by its Boltzmann weight from statistical mechanics

$$P(\{r_1(t), r_2(t), \ldots, r_N(t)\}) \; \propto \; \exp[- H(\{r_1(t), r_2(t), \ldots, r_N(t)\})/k_BT]$$

An algorithm for which detailed balance does not hold is likely to give wrong results!

Present day computer simulations

- Processor speed doubles every 18 month!
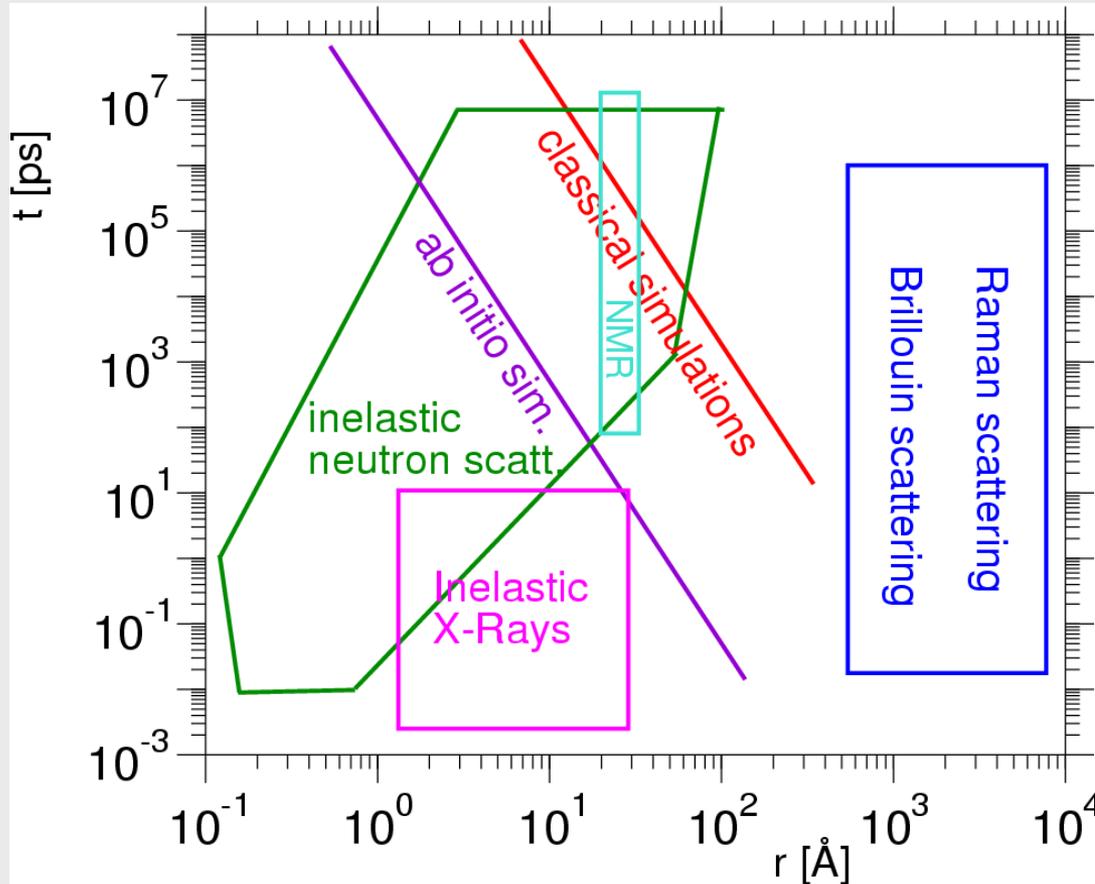
Large scale computer simulations (= several month of CPU time)
- 10^{10} time steps for 100 particles ($10\mu s$, 10Å) for effective potentials**!!**
- 10^5 time steps for 10^7 particles (100ps, 400Å)

Tricks of the trade

- Periodic boundary conditions

- Random number generators

- Equilibration

- Finite size effects

- …..

See Frenkel and Smit "Understanding Molecular Dynamics Simulations" for details

The real art is to use the trajectory of the system in configuration space in order to evaluate *efficiently* the quantities of interest

- Pressure, specific heat, elastic constants, …

- Radial distribution functions, coordination numbers, structure factors, …

- Diffusion constant, viscosity, ...

- Raman spectra, NMR spectra, optical and electrical properties, …

Problems: Don't get fooled!

- Simulations are hampered by relatively small time and length scales

    $\Rightarrow$ "hidden'' problems

Know these problems in order to make better simulations (and to avoid to be cheated by your colleagues)

Importance of potential

- What is the influence of the potential on the results?
- Hemmati and Angell calculated for various models for SiO_2 the structure and the diffusion constant at different temperatures

- Structure for the different models is quite similar

- The diffusion constant can be calculated via the Einstein relation

$$D = \lim_{t \to \infty} | r(t) - r(0) |^2 / 6t$$
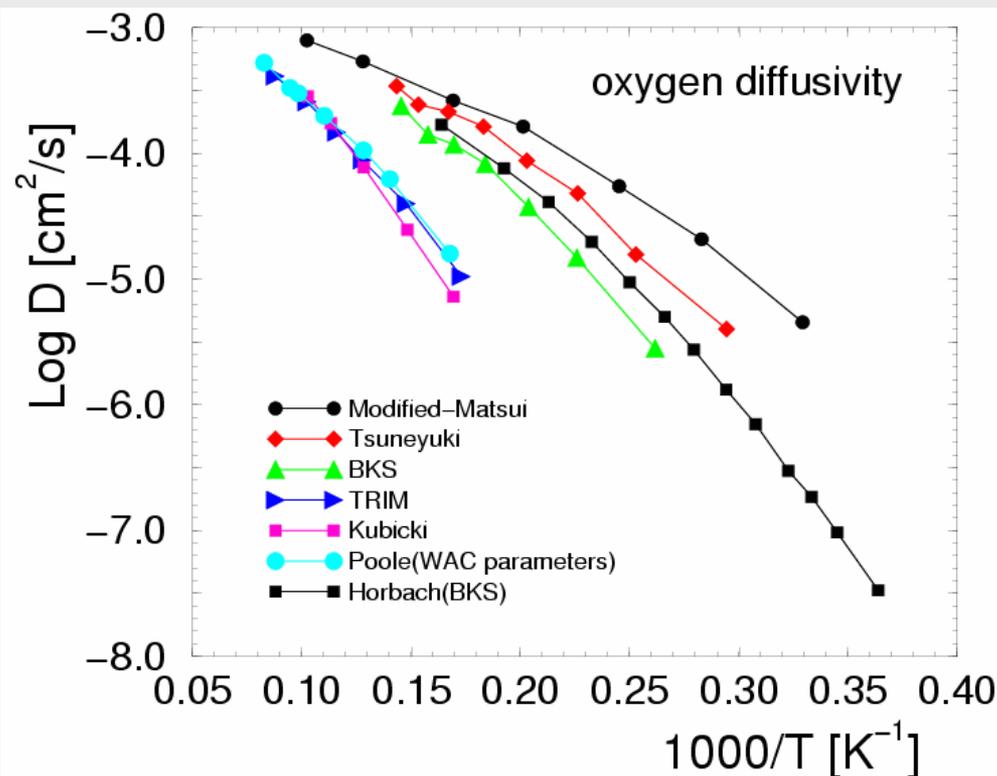
- Large discrepancy between the different potentials

$\Rightarrow$ use dynamics to validate potential (and not structure)

Importance of potential: II

- The same effect can be seen in the glass: e.g. vibrational density of states (vDOS) (measured in neutron or Raman scattering)
- Compare vDOS for two potentials of SiO_2 whose structure is very similar
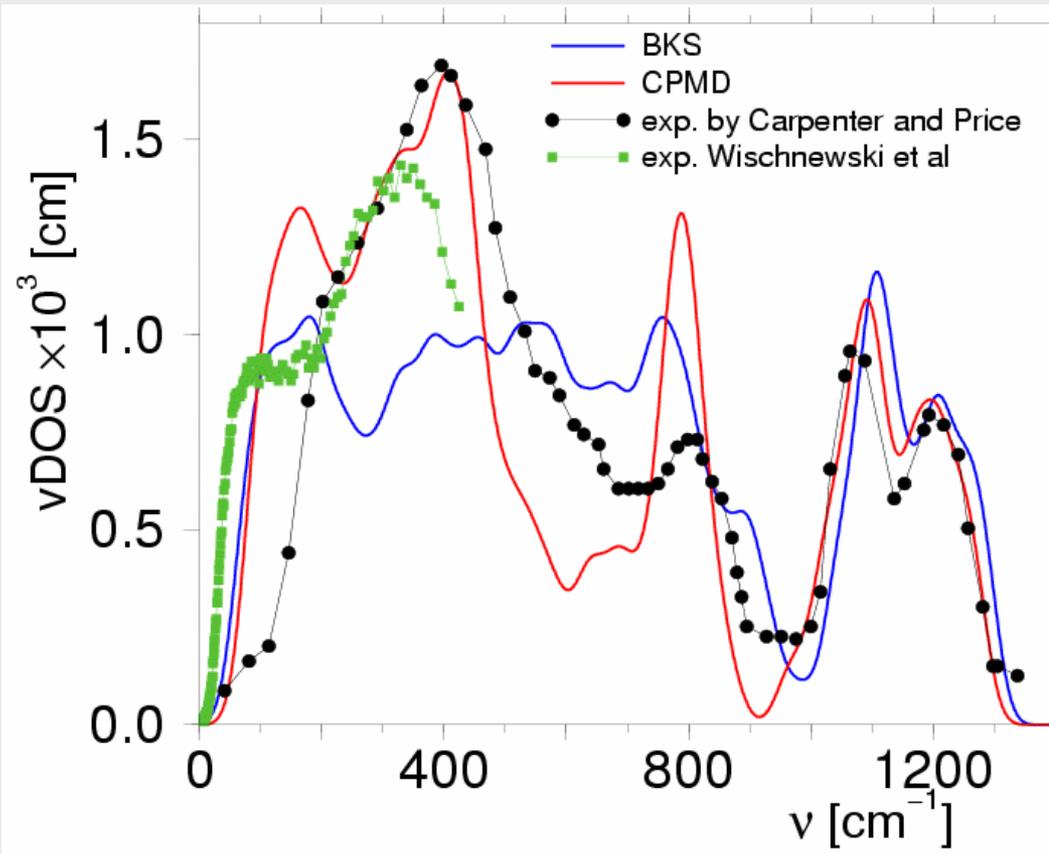
- Compare classical force field (BKS) with *ab initio* force field (CPMD)

- Although the BKS potential is usually quite reliable, there are situations were it fails badly!

$\Rightarrow$ use even better potentials or *ab inito*

Not all glasses are the same!

- To produce a glass a liquid has to be cooled below the glass transition temperature with a certain cooling rate γ [K/s]

Recall that the properties of glasses depend on their history!
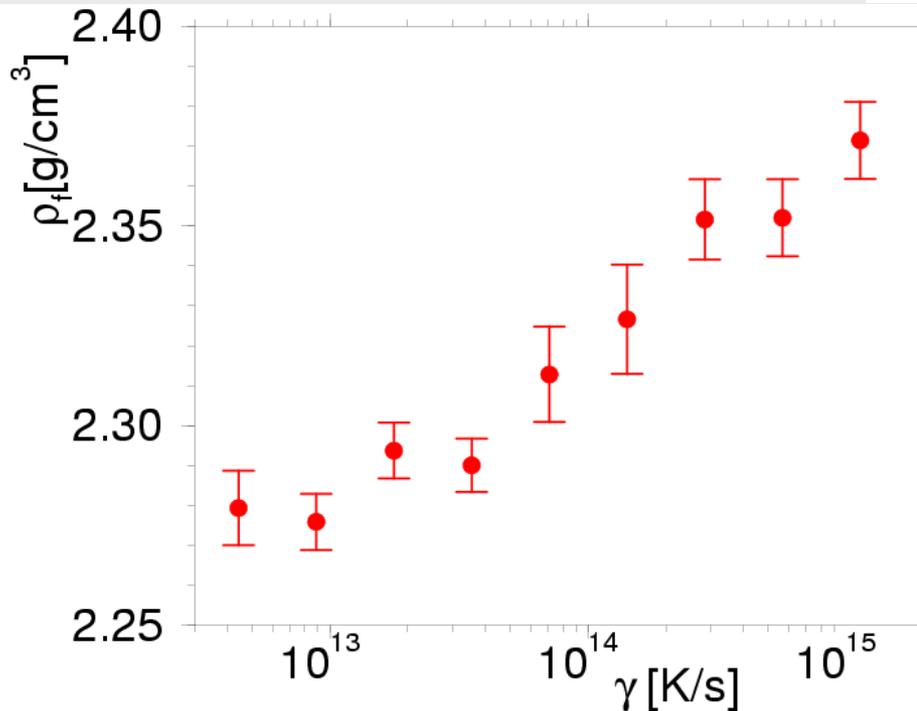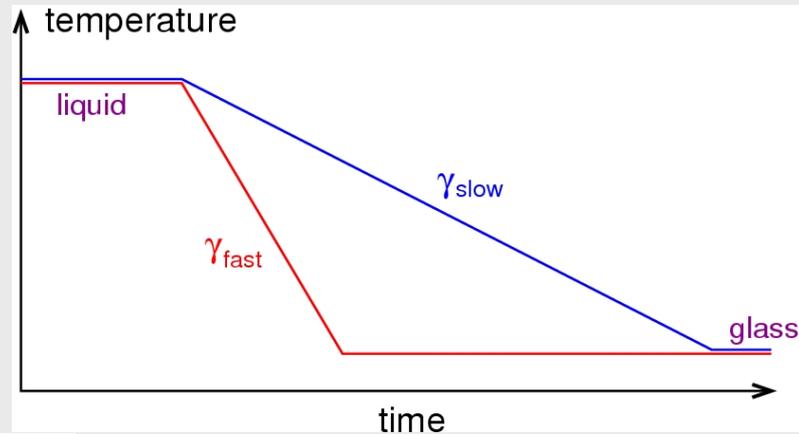
- Cooling rate dependence of the density of amorphous SiO_2 after a quench to 0K (ambient pressure)

- How to extrapolate to experimental cooling rates is not always obvious

Importance of system size

- Is system size important?

Static quantities:
Consider partial static
structure factor $S_{OO}(q)$ of SiO_2

$$S_{\alpha\beta}(q) = \frac{1}{N} \sum_{j=1}^{N_\alpha} \sum_{k=1}^{N_\beta} \langle \exp\left(i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)\right)\rangle$$

O–O

N=8016
N=336

$S_{OO}(q)$

SiO_2 at 3250K

q [Å^{-1}]
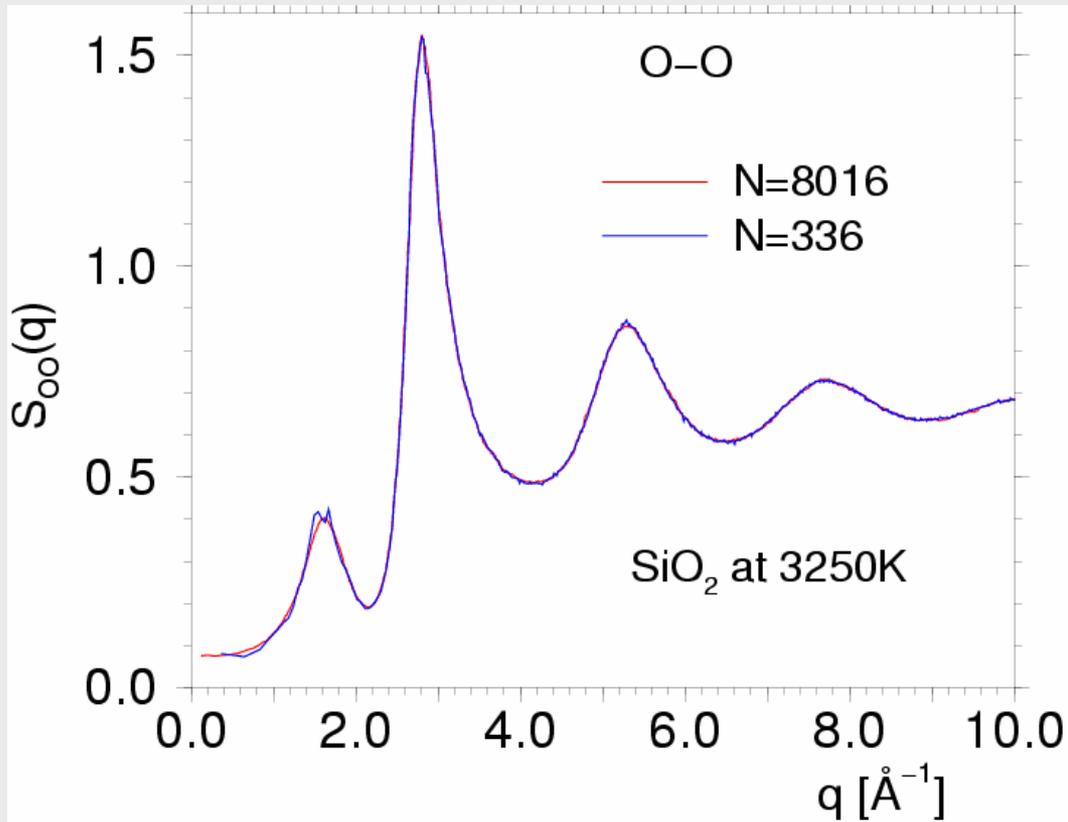
$\Rightarrow$ No (or only weak) finite size effects in static quantities

20

Importance of system Size: II

- Consider the vibrational density of states (vDOS), $g(\nu)$

- At small ν, $g(\nu)$ is expected to scale like ν^2 (Debye); many glass-forming systems shown an anomalous increase of $g(\nu)$ over the Debye-level $\Rightarrow$ Boson peak
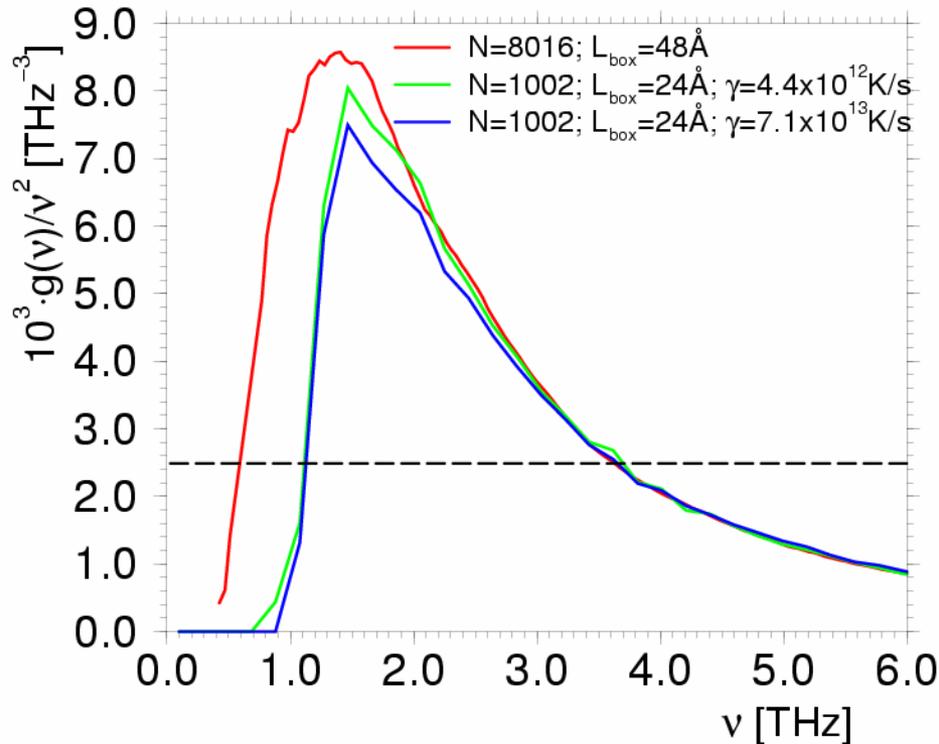
- Even for the largest systems $g(\nu)$ does not show the expected Debye behavior at small ν!

- $g(\nu)$ depends strongly on system size and on cooling rate

- **It is difficult to compare such results with real experiments**

Model and simulation of silica

- Interaction potential proposed by van Beest, Kramer, and van Santen (BKS) (PRL (1990))

$$\phi_{\alpha\beta}(r) = \frac{q_\alpha q_\beta e^2}{r} + A_{\alpha\beta}\exp\left(-B_{\alpha\beta}r\right) - \frac{C_{\alpha\beta}}{r^6} \quad \alpha, \beta \in [\text{Si}, \text{O}]$$

- 8016 particles in box with L=48.36Å;
- up to 12 mio. time steps (=19ns)

Static structure factor

- Characterize the structure by means of the partial structure factors:

$$S_{\alpha\beta}(q) = \frac{1}{N} \sum_{j=1}^{N_\alpha} \sum_{k=1}^{N_\beta} \langle \exp\left(i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)\right)\rangle$$
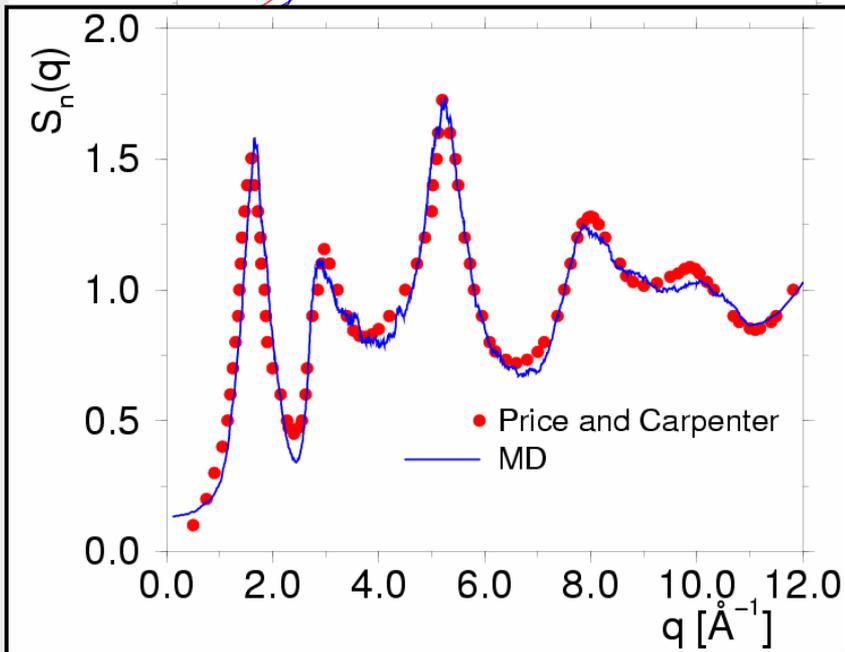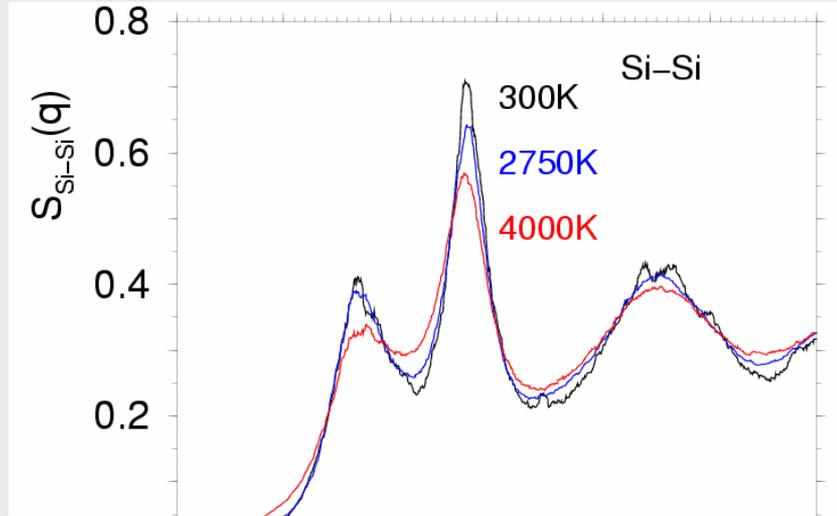
- $S_{SiSi}(q)$ shows a peak at q=1.6Å⁻¹ which corresponds to the distance between neighboring tetrahedra
- this pre-peak is already seen at very high T $\Rightarrow$ open tetrahedral network exists also at high T

- Use partial structure factors to calculate static neutron scattering function $S_n(q)$ (use experimental neutron scattering length b_α)

$$S_n(q) = \frac{1}{\sum_\alpha N_\alpha b_\alpha^2} \sum_{kl} b_k b_l \langle \exp\left(i\mathbf{q} \cdot [\mathbf{r}_k - \mathbf{r}_l]\right)\rangle$$

- No fit parameters!

Good agreement with experiments

$\Rightarrow$ **Structure is realistic**

23

Time correlation functions

- Investigate the dynamics by means of the mean squared displacement of a tagged particle:

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{j=1}^{N} \langle |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2 \rangle$$
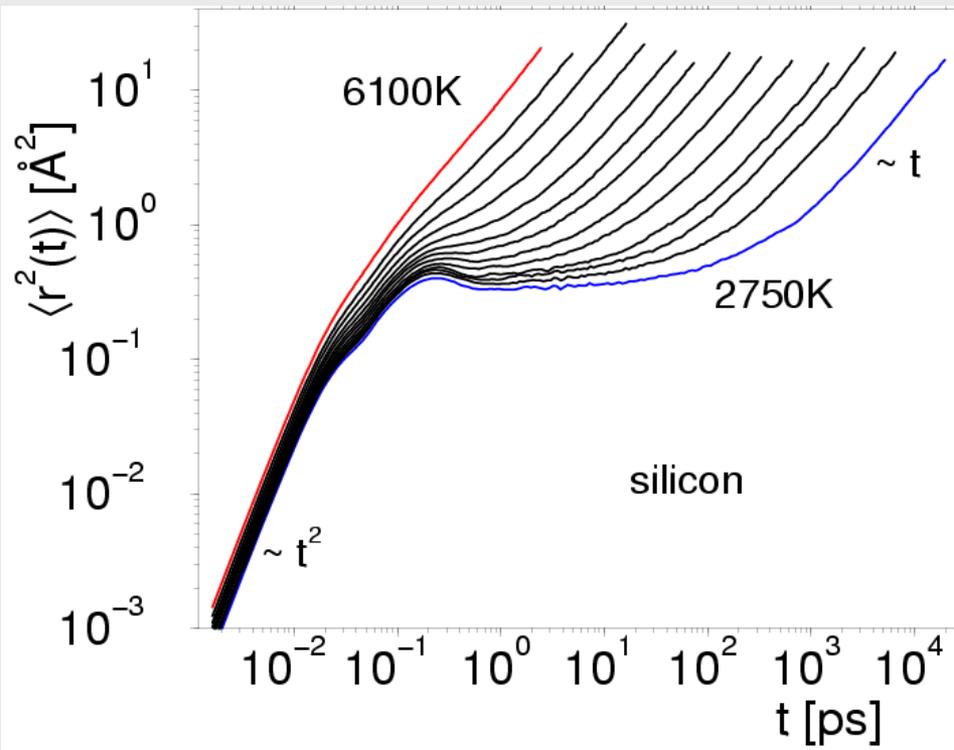
- short times: ballistic regime, $\langle r^2(t) \rangle \propto t^2$
- long times: diffusive regime, $\langle r^2(t) \rangle \propto t$
- intermediate times and low T:
  plateau due to cage effect

- dynamics slows down quickly with decreasing T because the life time of the cage increases
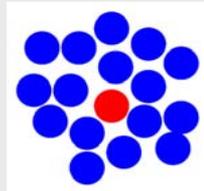
Diffusion constants

- Use the mean squared displacement to calculate the diffusion constant D_α

$$D_\alpha = \lim_{t \to \infty} [\mathbf{r}_\alpha(t) - \mathbf{r}_\alpha(0)]^2 / 6t$$
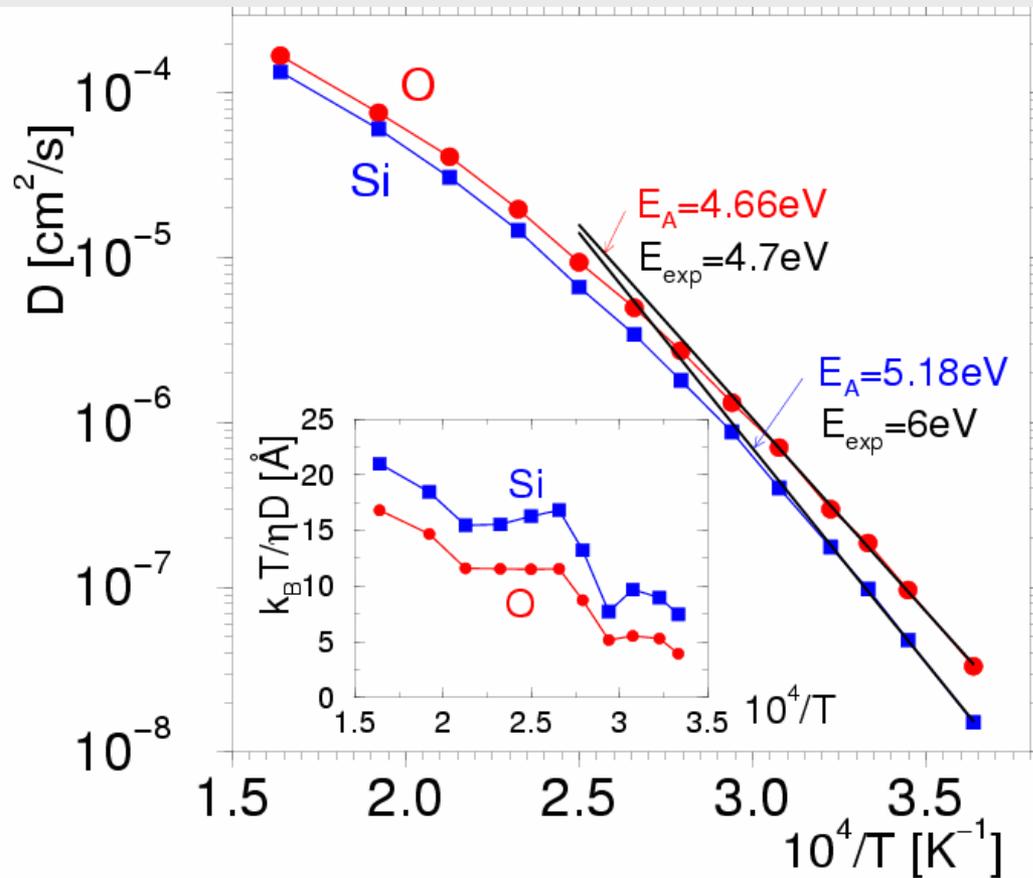
- low T: Arrhenius dependence with activation energies close to experimental values

- high T: cross-over to non-Arrhenius dependence !

- relaxation times and viscosity show the same behavior

- evidence for the existence of non-Arrhenius behavior also from high T viscosity experiments (Hess, Rössler, Dingwell)

- Stokes-Einstein relation is not valid at high T

Strong and fragile glass-formers?

- Is there really a fundamental difference between strong and fragile glass-formers?
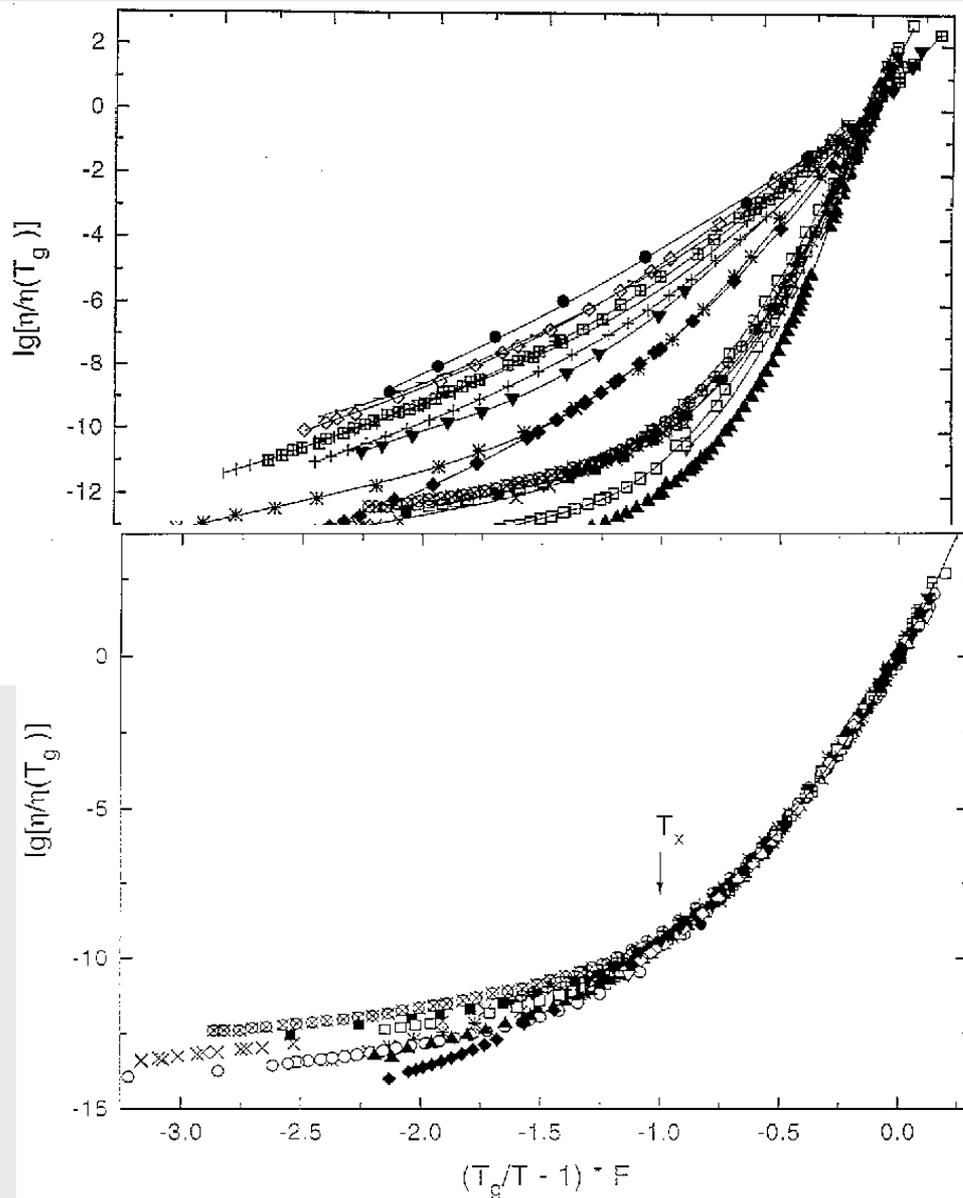
Scale T-axis such that the slope of the different curves at T_g is the same

Rössler, Hess, and Dingwell (1998):

Not really! (perhaps)

NB: $T_x = T_c$ from Mode Coupling Theoy

26

Model and simulation of Na_2O-$x(SiO_2)$

- Motivation:

- Pure SiO_2 is a fully connected network of tetrahedra; the addition of sodium leads to a partial breaking up of the network.

- At low T the motion of the Na atoms becomes decoupled from the one of Si and O $\Rightarrow$ ion conducting glass

$\Rightarrow$ **Use computer simulations to study the structure and dynamics of Na_2O-$x(SiO_2)$**

- Potential:

- Adaptation of BKS potential (Horbach *et al*. Chem. Geol. (2001))

- $\approx$ 8000 atoms

- Up to 4ns real time

Diffusion constants

- Use mean squared displacement of a tagged particle to calculate the diffusion constants D_α ($\alpha \in \{Si, O, Na\}$)
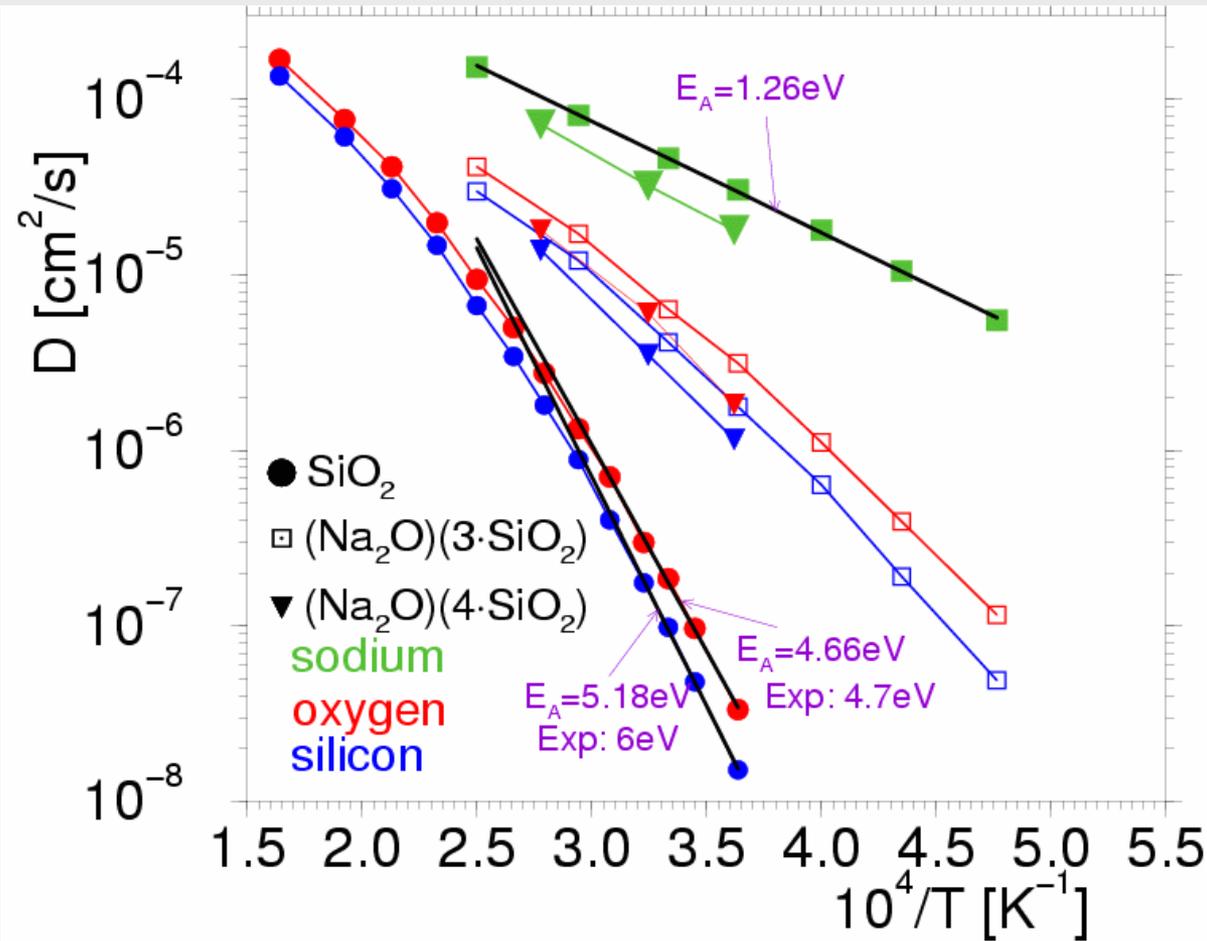
- strong acceleration of dynamics as compared to pure SiO_2

- Na shows an Arrhenius dependence for all T

- at low T the dynamics of Na is much faster than the one of Si and O

  $\Rightarrow$ at low T sodium is diffusing in a frozen SiO_2-matrix

Spatial correlations of Na in Na_2O-$x(SiO_2)$

- What is the spatial arrangement of the Na atoms?

Single snapshot:

- single snapshot looks quite homogeneous (no channels/clumps/clusters)

- no special ("good" sites in the matrix)
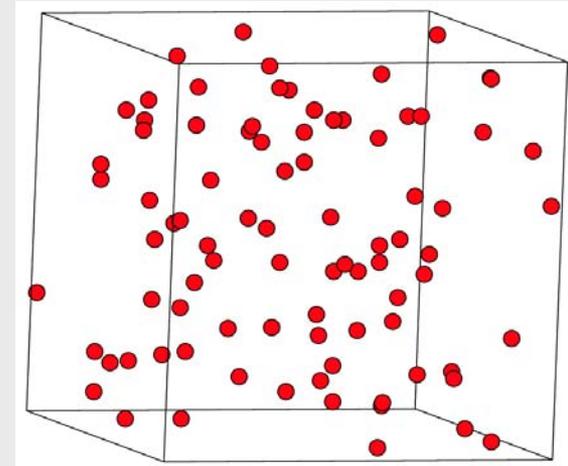
Is this really true? $\Rightarrow$ superpose many of these images and determine a (coarse grained) density of *different* Na atoms
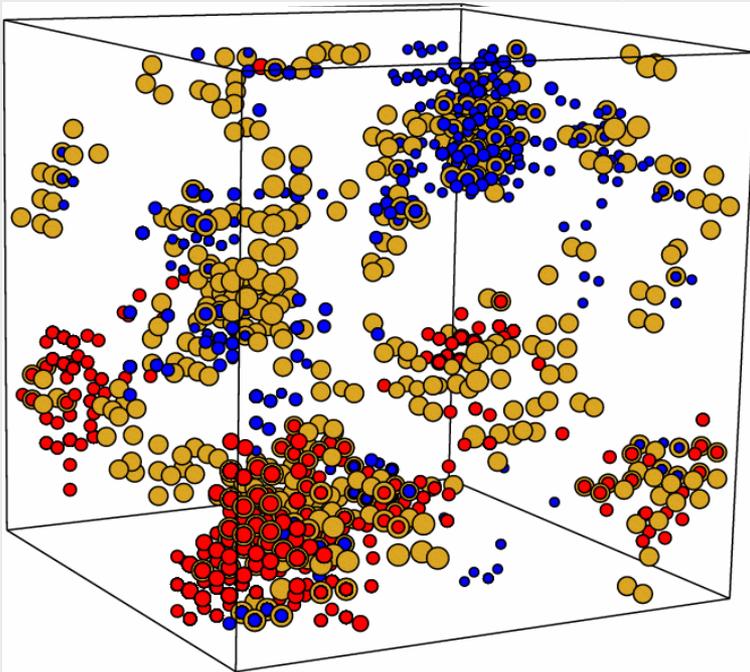
- structure with blobs of size 6-8Å and weak connections (yellow spheres); compare distance between neighboring Na atoms $\approx$ 3.4Å

- channels are quickly explored by most of the Na atoms (red and blue spheres)

Structure factors of Na$_2$O-2(SiO$_2$)

- Does one see these channels in the structure factor?
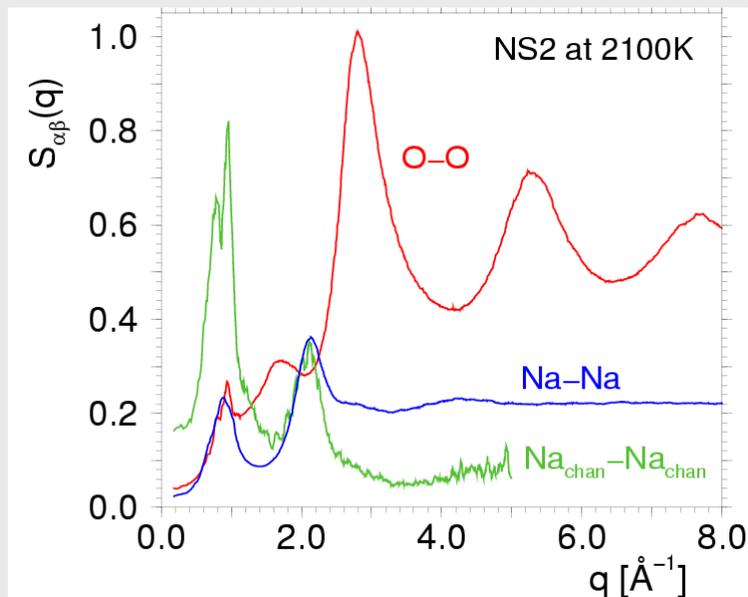
- Partial structure factors show a pronounced peak at $\approx 0.9\text{Å}^{-1}$
- Calculate structure factor of Na atoms that are *in the channels* (=have a high density of diffent Na atoms)

$\Rightarrow$ Peak at 0.9Å^{-1} corresponds to distance between the blobs
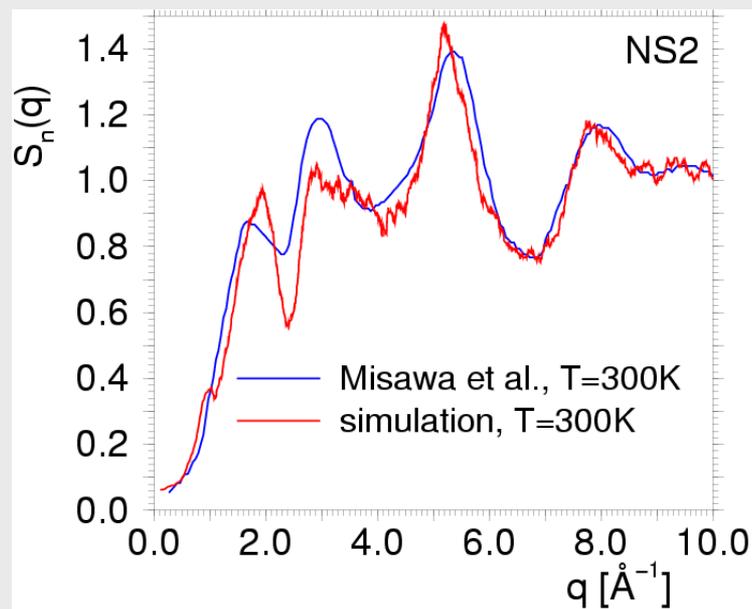
- HOWEVER: neutron scattering structure factor shows only a weak shoulder (due to cancellation effects of the 6 partial structure factors)

End of the story??

Structure factors in $Na_2O-2(SiO_2)$: II

• Problem at *room* temperature: cancellation effects

BUT: cancellation will in general depend on temperature!
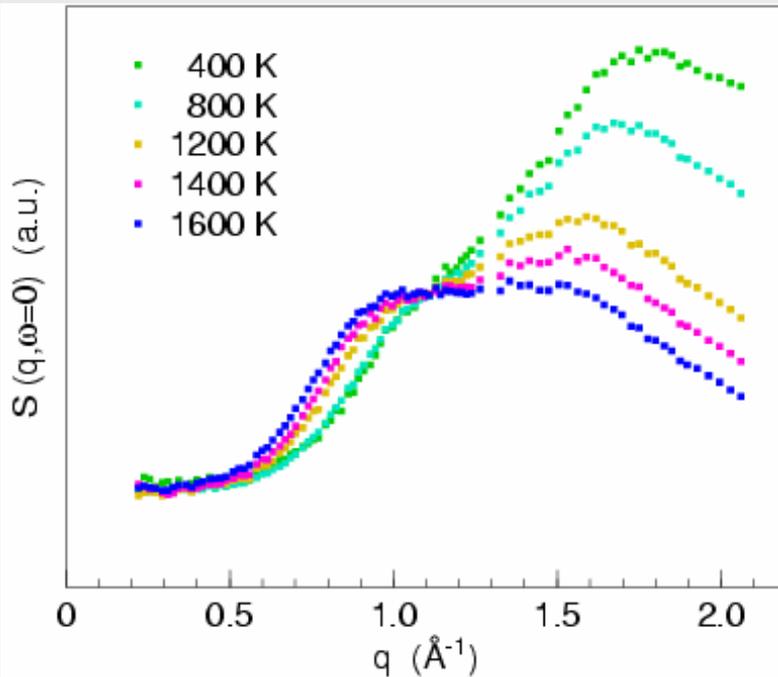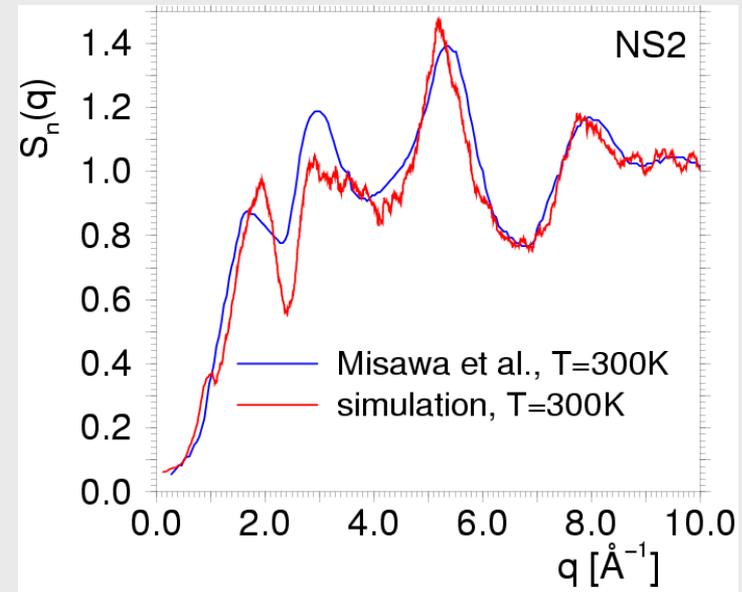
• n-scattering results of $Na_2O-2(SiO_2)$ by Meyer, Schober, Dingwell at high T

$\Rightarrow$ peak in elastic signal at $\approx 0.9 \text{Å}^{-1}$!
$\Rightarrow$ evidence that channels exist also in real NS2 and that they can be seen

Dependence of structure on Na concentration

- Are the channels only seen at high concentration of Na?
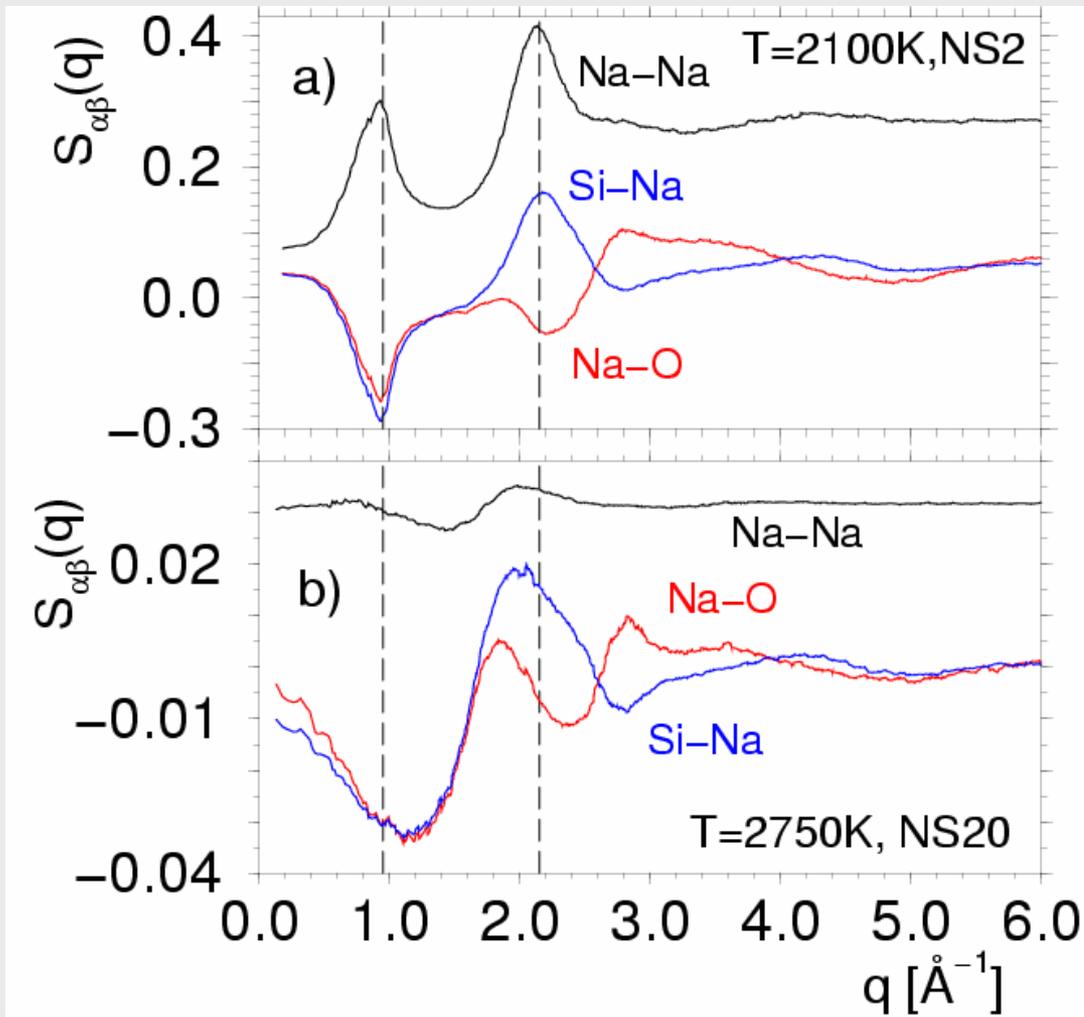
- Pre-peak at 0.95 Å^{-1} is seen also in Na_2O-20(SiO_2)

⇒ evidence that channels exist also at very low concentration of Na

Summary

- Simulations can be a very effective tool to obtain a better understanding of complex systems like liquids and glasses

- They allow to investigate (and predict!!) features of the structure and dynamics that are experimentally hardly accessible but that are important to obtain a better understanding of the material

- Although a reasonable potential will in many cases give a correct qualitative result, it is sometimes necessary to use *ab initio* simulations (and to pay the price in computer time)

- In simulations of glassy systems one has the problem of the huge time scales; need to investigate carefully how the results depend on the history of the sample.

- Not everything that looks reasonable is correct (and sometimes seemingly unreasonable things *are* correct)!

Dependence of dynamics on Na concentration

• How does the relaxation dynamics of the Na depend on their concentration?

Na$_2$O$-$x(SiO$_2$), ρ=2.37g/cm^3

NS1.5
NS2
NS3
NS5
NS20
NS40
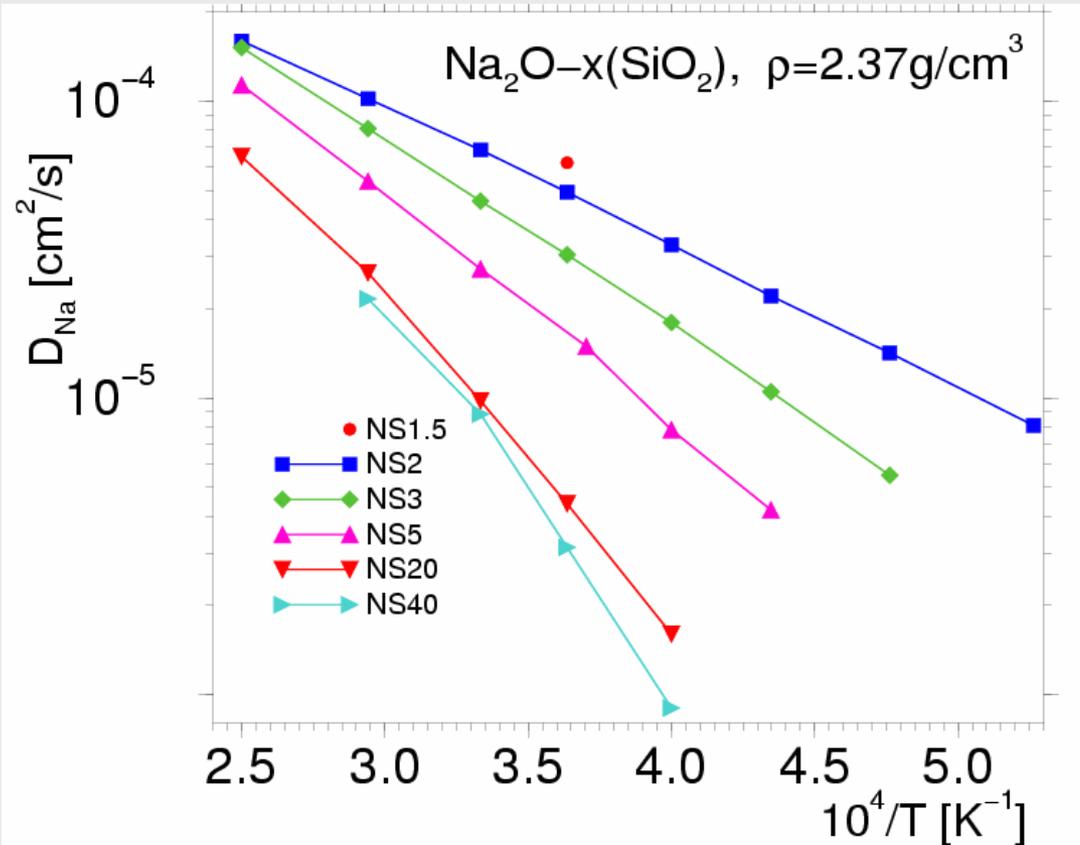
• high Na concentration: Arrhenius law for all T

• low Na concentration: deviation from Arrhenius law at high T

• low T: activation energy increases with decreasing concentration

$\Rightarrow$ motion of Na becomes stronger coupled to the one of the SiO$_2$-matrix

Model and simulation of Na_2O-Al_2O_3- SiO_2

• Motivation:

-pure SiO_2 is a fully connected network of tetrahedra; the addition of sodium leads to a partial breaking up of the network; but Al is a network former

- investigate Albite (=NaAlSi3O8)

$\Rightarrow$ **use computer simulations to study the structure and dynamics**

•Potential:

- adaptation of potential by de Man *et al.*

- $\approx$ 1000 atoms

- up to 1.4ns real time

Model and simulation of Na_2O-Al_2O_3- SiO_2

- Do the pre-peaks/channels found in NSx still exist?

$\Rightarrow$ Investigate the partial structure factors:
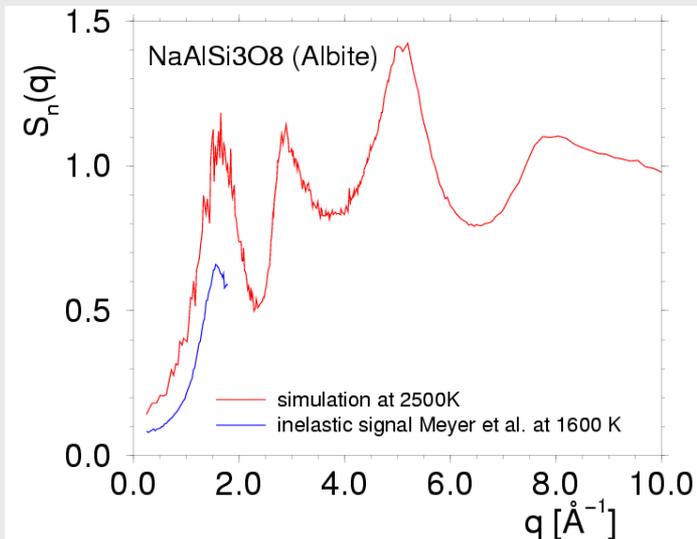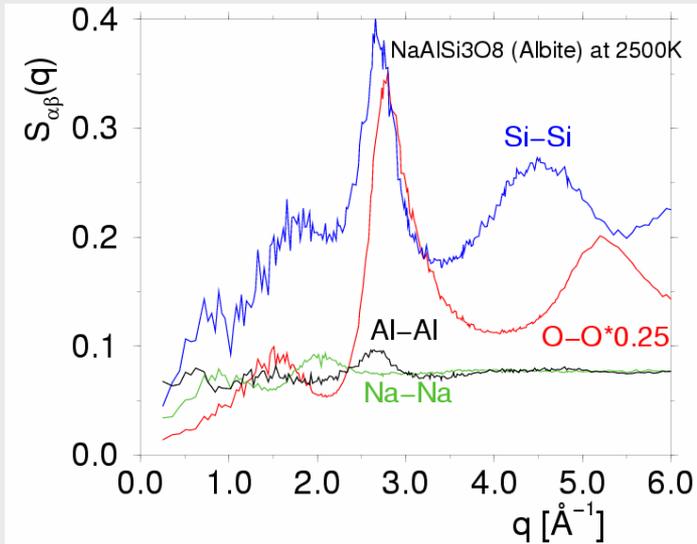
- pre-peaks at 0.9 Å^{-1} are still visible, although they are less pronounced than in the NSx systems
- in addition there is a peak at 0.5 Å^{-1} from the Al-Al correlation

- are these peaks visible in a neutron scattering experiment?

- pre-peaks are very difficult to see in a neutron scattering experiment and are in fact not seen in the inelastic signal of the real experiment

- same results for x-rays

Dynamics of individual Na atoms

• Characterize the dynamics by means of the self part of the van Hove correlation function $G_s(r,t)$:

$$G_s(r,t) = \frac{1}{N}\sum_{j=1}^{N}\langle\delta\left(\mathbf{r} - (\mathbf{r}_j(t) - \mathbf{r}_j(0))\right)\rangle$$

•N.B.: $G_s(r,t)$ is just the Fourier transform of $F_s(q,t)$
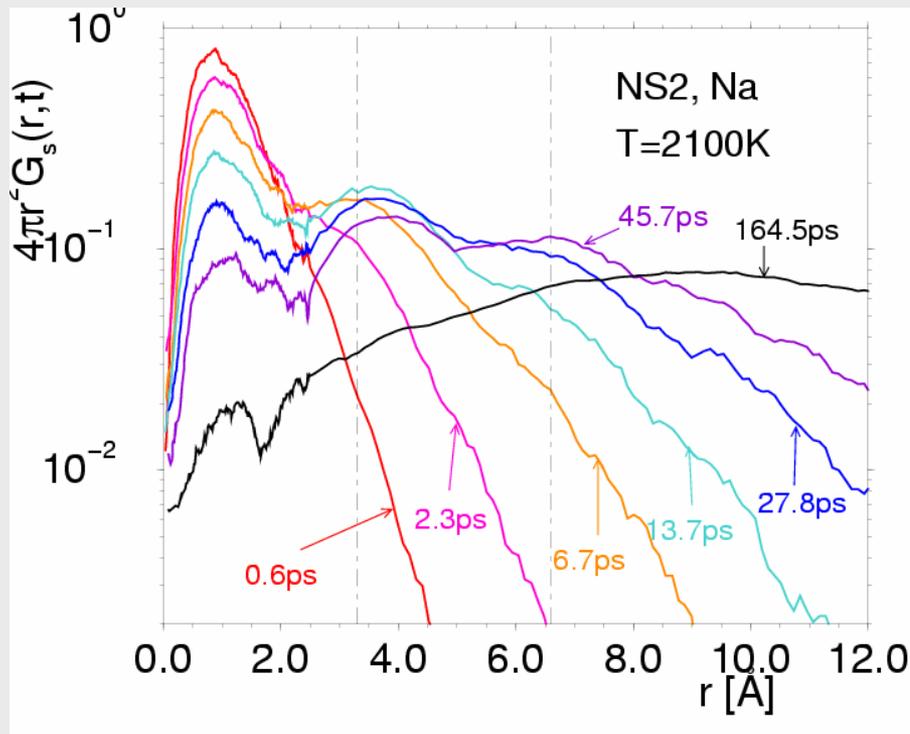
•low T: rattling and hopping motion on the length scale of nearest neighbors ≈ 3.4Å
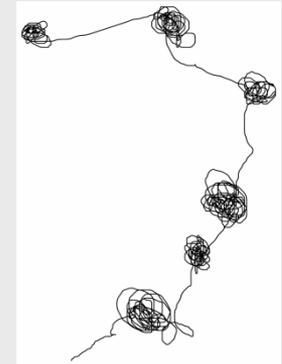
•dynamics of Si and O show only a very weak signature of hopping

Spatial correlations of Na in Na$_2$O-3(SiO$_2$)
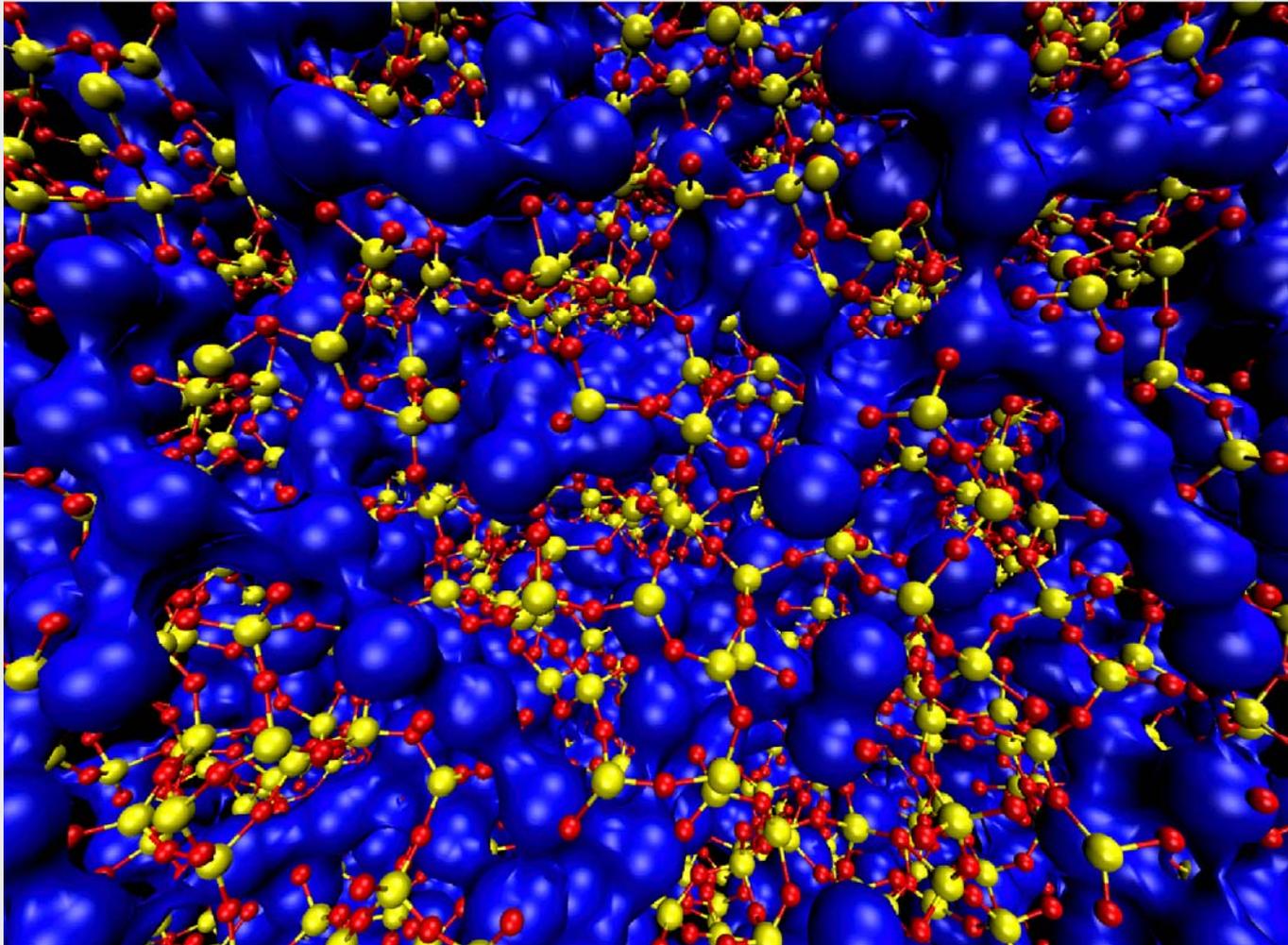
- Structure with Na channels forming a mesh with mesh size 6-8Å
- Compare distance between neighboring Na atoms ≈ 3.4Å

38