Lecture 3, Part 3: Computer simulation of glasses

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Computer Simulations of Glasses

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Outline and collaborators

Outline:
• What are computer simulations?
• Watch out for these problems!
• Some results for SiO₂, NaO₂-SiO₂
• Summary

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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

⇒ 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

⇒ 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 ⇒ 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

⇒ 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

\[
H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j \quad \sigma_i \in \{-1, +1\}
\]

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

\[
V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]
• If one wants to obtain the properties of a real material \((T_m, \text{ viscosity}, \ldots)\) 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; …
• 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 SiO₂ using pot. of van Beest, Kramer and van Santen (*BKS*)

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

- 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
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
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)

\[
\begin{align*}
  r_i(t + h) &= r_i(t) + hv_i(t) + h^2 f_i(t) / 2m_i \\
  v_i(t + h) &= v_i(t) + h[f_i(t) + f_i(t + h)] / 2m_i
\end{align*}
\]
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 $R_{\text{old}} = \{r_1(t), r_2(t), \ldots, r_N(t)\}$
2. Calculate the potential energy for the configuration $R_{\text{old}} \Rightarrow E_{\text{old}}$
3. Displace “randomly” a (or several) particle(s) $\Rightarrow R_{\text{new}}$
4. Calculate the potential energy for the configuration $R_{\text{new}} \Rightarrow E_{\text{new}}$
5. if $E_{\text{new}} \leq E_{\text{old}}$ accept the new config.; set $R_{\text{old}} = R_{\text{new}}$; advance clock by 1
6. if $E_{\text{new}} > E_{\text{old}}$ accept the new configuration with probability $\exp[-(E_{\text{new}} - E_{\text{old}})/k_B T]$, where $k_B$ is the Boltzmann constant and $T$ is temperature; if you accept set $R_{\text{old}} = R_{\text{new}}$; 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

\[
\exp(-E_{\text{old}}/k_B T) W(\text{old} \Rightarrow \text{new}) = \exp(-E_{\text{new}}/k_B T) W(\text{new} \Rightarrow \text{old})
\]

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

\[
P(\{r_1(t), r_2(t), ..., r_N(t)\}) \propto \exp[-H(\{r_1(t), r_2(t), ..., r_N(t)\})/k_B T)]
\]

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

- Processor speed doubles every 18 months!

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
  => “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 SiO₂ 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

\[ D = \lim_{t \to \infty} \frac{|r(t) - r(0)|^2}{6t} \]

• Large discrepancy between the different potentials

⇒ 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!
  ⇒ use even better potentials or *ab initio*
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 $\gamma$ [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$_2$

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

$⇒$ No (or only weak) finite size effects in static quantities
Importance of system Size: II

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

- At small $\nu$, $g(\nu)$ is expected to scale like $\nu^2$ (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 $\nu$!

- $g(\nu)$ 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))

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

- 8016 particles in box with L=48.36\text{Å};
- up to 12 mio. time steps (=19ns)
**Static structure factor**

- Characterize the structure by means of the **partial structure factors**:
  
  \[ S_{\alpha\beta}(q) = \frac{1}{N} \sum_{j=1}^{N_{\alpha}} \sum_{k=1}^{N_{\beta}} \langle \exp \left( i q \cdot (r_j - r_k) \right) \rangle \]

- \( S_{\text{SiSi}}(q) \) shows a peak at \( q=1.6\text{Å}^{-1} \) 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 \( b_{\alpha} \))
  
  \[ S_{n}(q) = \frac{1}{\sum_{\alpha} N_{\alpha} b_{\alpha}^2} \sum_{k,l} b_{k}b_{l} \langle \exp \left( i q \cdot [r_k - r_l] \right) \rangle \]

- No fit parameters!

Good agreement with experiments

\( \Rightarrow \) **Structure is realistic**
Time correlation functions

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

\[ \langle \mathbf{r}^2(t) \rangle = \frac{1}{N} \sum_{j=1}^{N} \langle |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2 \rangle \]

• short times: ballistic regime, \( \langle \mathbf{r}^2(t) \rangle \propto t^2 \)
• long times: diffusive regime, \( \langle \mathbf{r}^2(t) \rangle \propto t \)
• 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 $D_\alpha$
  \[ D_\alpha = \lim_{t \to \infty} \frac{\langle [r_\alpha(t) - r_\alpha(0)]^2 \rangle}{6t} \]

- 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?

Rössler, Hess, and Dingwell (1998):

Not really! (perhaps)

NB: \( T_x = T_c \) from Mode Coupling Theory

Scale T-axis such that the slope of the different curves at \( T_g \) is the same
Model and simulation of Na$_2$O-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 ⇒ ion conducting glass

⇒ Use computer simulations to study the structure and dynamics of Na$_2$O-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 $D_\alpha (\alpha \in \{\text{Si}, \text{O}, \text{Na}\})$

- 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$_2$O-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? ⇒ 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 $\approx 3.4\text{Å}$
- 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 different Na atoms)

  $\Rightarrow$ Peak at $0.9\,\text{Å}^{-1}$ 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$_2$O-2(SiO$_2$): II

• Problem at *room* temperature: cancellation effects

BUT: cancellation will in general depend on temperature!

• n-scattering results of Na$_2$O-2(SiO$_2$) by Meyer, Schober, Dingwell at high T

⇒ peak in elastic signal at $\approx$0.9Å$^{-1}$
⇒ 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\(_2\)O-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?

- 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

\[ \Rightarrow \text{motion of Na becomes stronger coupled to the one of the SiO}_2\text{-matrix} \]
Model and simulation of $\text{Na}_2\text{O}$-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$

• Motivation:
  - pure $\text{SiO}_2$ 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 ( =$\text{NaAlSi}_3\text{O}_8$ )

$\Rightarrow$ 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$_2$O-Al$_2$O$_3$- SiO$_2$

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

⇒ 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 $G_s(r,t)$:

$$G_s(r, t) = \frac{1}{N} \sum_{j=1}^{N} \delta(r - (r_j(t) - r_j(0)))$$

• 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 $\approx 3.4\text{Å}$

• 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 $\approx$ 3.4Å