Molecular Dynamics Simulation of supercooled ZnSe: Structural relaxation and Crystal nucleation

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The kinetics of crystal nucleation in SCLs are extremely important and play a crucial role in numerous natural processes such as

- snow precipitation
- crystallization of proteins and minerals

industrial technologies such as

- single crystals
- metal casting and solidification
- drug design and production
- glass-ceramics
• To properly understand the atomistic dynamics of SCL

- Two characteristic times

  - intrinsic atomic diffusivity that leads to structural rearrangement of the SCL - RELAXATION TIME - $\tau_R$

  - Average period need to spontaneously form the 1st crystalline critical nucleus – NUCLEATION TIME - $\tau_N$
Race between the two relaxation times

If $\tau_N < \tau_R$ $\Rightarrow$ crystallization

If $\tau_N > \tau_R$ $\Rightarrow$ liquid relax - glass

Temperature which $\tau_N = \tau_R$ $\Rightarrow$ kinetic spinodal temperature $T_{ks}$

OBS: $T_{ks}$ is not the classical thermodynamics spinodal, where the thermodynamic barrier for the liquid/crystal transformation vanishes
Race between the two relaxation times

The relationship between this characteristic time has been scarcely investigated.

Experimentally: \( \text{Li}_2\text{O}.2\text{B}_2\text{O}_3 \) and \( \text{Li}_2\text{O}.2\text{SiO}_2 \)

- Pressurized \( \text{SiO}_2 \)
- Supercooled Ni, Cu, Cu\(_5\)Zr

Simulation:
- Binary L-J mixture
- Cu\(_x\)Zr\(_{1-x}\), \(0.15 \leq x \leq 0.645\)
- BaS
Case studied: ZnSe

• Some properties:
  • direct wide band-gap
  • Low absorptivity at infrared wavelength
  • Preferred material for lenses, windows, output coupler, beam expander
  • Used laser-diodes
  • Green-blue LEDs
  • Crystallizes in both zinc-blende and wurtzite, under ambient conditions
Our Approach

Molecular Dynamics Simulation

• Interaction potential
• Spontaneous crystallization
Interatomic Potential – Vashishta/Rahman

\[ \Phi(r) = \sum_{i<j=1}^{N} V_{i,j}(r) + \sum_{i,j<k} V_{jik}^{(3)}(\vec{r}_{ij}, \vec{r}_{ik}) \]

\[ V_{ij}(r) = \frac{H_{i,j}}{r \eta_{i,j}} + \frac{Z_i Z_j}{r} e^{-r/\lambda} - D_{i,j} \left( \frac{\alpha_i Z_j^2 + \alpha_j Z_i^2}{2r^4} \right) e^{-r/\zeta} - \frac{W_{i,j}}{r^6} \]

\[ V_{jik}^{(3)}(\vec{r}_{ij}, \vec{r}_{ik}) = B_{jik} \exp\left( \frac{1}{r_{ij}-r_o} + \frac{1}{r_{ik}-r_o} \right) \frac{(\cos \theta_{jik} - \cos \bar{\theta}_{jik})^2}{1 + C_{jik} (\cos \theta_{jik} - \cos \bar{\theta}_{jik})^2}. \]
## Partial results

<table>
<thead>
<tr>
<th>Quantities used to find parameterization</th>
<th>MD</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cohesive energy (eV/N)</td>
<td>-2.697</td>
<td>-2.697</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>5.643</td>
<td>5.643 (extrapolated to 0K),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.667 at 300K</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>61.85</td>
<td>59.53 - 78.4</td>
</tr>
<tr>
<td>Elastic Constant $C_{11}$ (GPa)</td>
<td>83.70</td>
<td>81 – 104.6</td>
</tr>
<tr>
<td>Elastic Constant $C_{12}$ (GPa)</td>
<td>50.91</td>
<td>48.8 – 65.3</td>
</tr>
<tr>
<td>Elastic Constant $C_{44}$ (GPa)</td>
<td>31.02</td>
<td>44.1 – 46.13</td>
</tr>
<tr>
<td>Melting Temperature (K)</td>
<td>1388</td>
<td>1800</td>
</tr>
</tbody>
</table>
Partial results - Energetic

\[ E_{ZB} - E_{WZ} = -8.5 \text{ meV} \]
Partial results

<table>
<thead>
<tr>
<th>$\Theta_{\text{Debye}}$ (K)</th>
<th>MD</th>
<th>Expt*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>226 ± 1</td>
<td>237 ± 6 at room temperature&lt;br&gt;224 ± 2 at nitrogen temperature</td>
</tr>
</tbody>
</table>

- N.P. Sharma, Indian Pure Appl. Phys. 10, 478 (1972)
Partial conclusions

 ✓ Very good interatomic potential

 ✓ The system spontaneously crystallize when cooled down

Goal

 ✓ Nucleation rate, relaxation time

 ✓ Systems with 17,576 and 32,768 particles
heating & cooling
Spontaneous nucleation – $T \leq 1000K$

Birth time, or nucleation time, $\tau_N$

$T = 1000K, 950K, 900K$

System sizes: 17,576 and 32,768 particles

Average over 15 samples

Solid like particles – Steinhart bond-order parameter

$$S_{ij} = \sum_{m=-6}^{m=+6} q_{6m}(i) \cdot q^*_{6m}(j); \quad q_{6m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{Nb(i)} Y_{lm}(\vec{r}_{in})$$
Spontaneous nucleation – $T \leq 1000\text{K}$

$$J_{ss} = \frac{1}{\tau V}$$

<table>
<thead>
<tr>
<th>T (K)</th>
<th>N</th>
<th>$\tau_N$ (ps)</th>
<th>$J_{ss}$ (ps$^{-1}$Å$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>17,576</td>
<td>803.8</td>
<td>2.5x10$^{-9}$</td>
</tr>
<tr>
<td></td>
<td>32,768</td>
<td>740</td>
<td>1.5x10$^{-9}$</td>
</tr>
<tr>
<td></td>
<td>3.7x10$^{10}$</td>
<td>5.0x10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>950</td>
<td>17,576</td>
<td>224.7</td>
<td>0.9x10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>32,768</td>
<td>168.3</td>
<td>0.7x10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>3.7x10$^{10}$</td>
<td>1.25x10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>17,576</td>
<td>161.2</td>
<td>1.3x10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>32,768</td>
<td>78.8</td>
<td>1.4x10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>3.7x10$^{10}$</td>
<td>7.41x10$^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>

$N=3.7\times10^{10}$ particles $\rightarrow V=1\mu\text{m}^3$
heating & cooling

The graph illustrates the change in atomic volume (Å$^3$) as a function of temperature (T(K)). The curves represent different sample numbers (N=17576 and N=32768). The transition temperatures $T_g$ (glass transition temperature) and $T_m$ (melting temperature) are marked on the graph. The heating and cooling phases are indicated by arrows.
Structural Relaxation time

\[ (1000 < T < T_m) \]

\[ F_s(q, t) = N_{\alpha}^{-1} \sum_{j=1}^{N_{\alpha}} \exp(i\vec{q} \cdot (\vec{r}_j^\alpha(t) - \vec{r}_j^\alpha(0))) \]

The tail (long time) is described by the KWW law (Kohlrausch-Williams-Watts)

\[ F_s(q, t) = F_s(q)\exp\left[-\left(\frac{t}{\tau_\alpha}\right)^\beta\right] \]

By decreasing the temperature, a plateau appears which is related to the time needed by particles to break out of the cage created by neighboring particles.
Average relaxation time – structural relaxation time

\[ \tau_\alpha(T) = \left( \langle \tau_{\alpha,Zn} \rangle + \langle \tau_{\alpha,Se} \rangle \right) / 2 \]

\[ \beta(T) = \left( \langle \beta_{Zn} \rangle + \langle \beta_{Se} \rangle \right) / 2 \]

Relaxation time \( \tau_R \)

\[ \tau_R(T) = \frac{\tau_\alpha(T)}{\beta(T)} \Gamma \left( \frac{1}{\beta(T)} \right) \]

Diffusion and viscosity

\[ \langle R^2(t) \rangle = 6Dt; \quad D = D_0 \exp \left( \frac{-E_A}{k_B T} \right) \]

\[ \eta = \frac{V}{Nk_B} \int_0^\infty \langle P_{ij}(0)P_{ij}(t) \rangle dt \]
Deep supercooling: spontaneous crystallization
\((T: 1000K, 950K, 900K)\)

Shallow supercooling: relaxation time
\((900K \leq T \leq 1600 K)\)

How to compare?

How to extrapolate to other temperatures?

- \(\tau_N\) CNT
- \(\tau_R\) MYEGA
$\tau_N$ - Classical Nucleation Theory

Recall that

$$J_{ss} = \frac{1}{\tau_N} V$$

$$\frac{J_{ss}\sqrt{T}}{D} = A \exp \left( -\frac{B}{T} \right)$$

(A and B fitted parameters)

$\tau_R$ - MYEGA

Mauro-Yue-Ellison-Gupta-Allan - MYEGA

$$\log_{10}(\eta) = \log_{10}(\eta_\infty) + \frac{A}{T} \exp \left( \frac{B}{T} \right)$$
The ultimate fate of supercooled ZnSe

Maxwell equation,

$$\tau_\eta = \frac{\eta}{G_\infty}$$

1. $\tau_\eta < \tau_R$

2. above $\sim 1100K$ $\tau_R < \tau_N$

3. Large system below $\sim 1100K$ $\tau_N < \tau_R$

MYEGA: 

$$\log_{10}(\tau_R) = \log_{10}\tau_\infty + \frac{A}{T} \exp(B/T)$$
Critical cooling rate required to avoid nucleation

\[ \frac{\Delta T}{\Delta t} = \frac{T_m - T_{nose}}{\tau_{nose}} \]  

(Uhlmann D. R., J Non – Crystal Solids 7 (1972)337)

\( \tau_{nose} \) related to \( T_{nose} \) (minimum point in the Time-Temperature transformation curve)

<table>
<thead>
<tr>
<th>System size</th>
<th>Critical cooling rate (K/ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17576</td>
<td>5.5</td>
</tr>
<tr>
<td>32768</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Cooling rate used 1K/ps \( \rightarrow \) spontaneous nucleation already in the cooling procedure
Conclusions

- From MD we obtained both nucleation time, $\tau_N$, (spontaneous crystallization) relaxation time, $\tau_R$, from intermediate scattering function and viscosity.

- Relaxation time using Maxwell relation, $\tau_\eta$, gives a lower boundary. (this confirms recent experimental results – Li$_2$O.2B$_2$O$_3$ and Li$_2$O.2SiO$_2$)

- Shallow supercooling: $\tau_R < \tau_N$, relaxation occurs before nucleation.

- $T_{ks}$ increases as system size increases.

- $T_{ks} > T_g$, system crystallize (at least one critical nucleus) before become a glass.

- $T_g$, refer to a residual supercooled liquid which already contain several crystalline nuclei formed on the cooling path.
Collaborators

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Brazil