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

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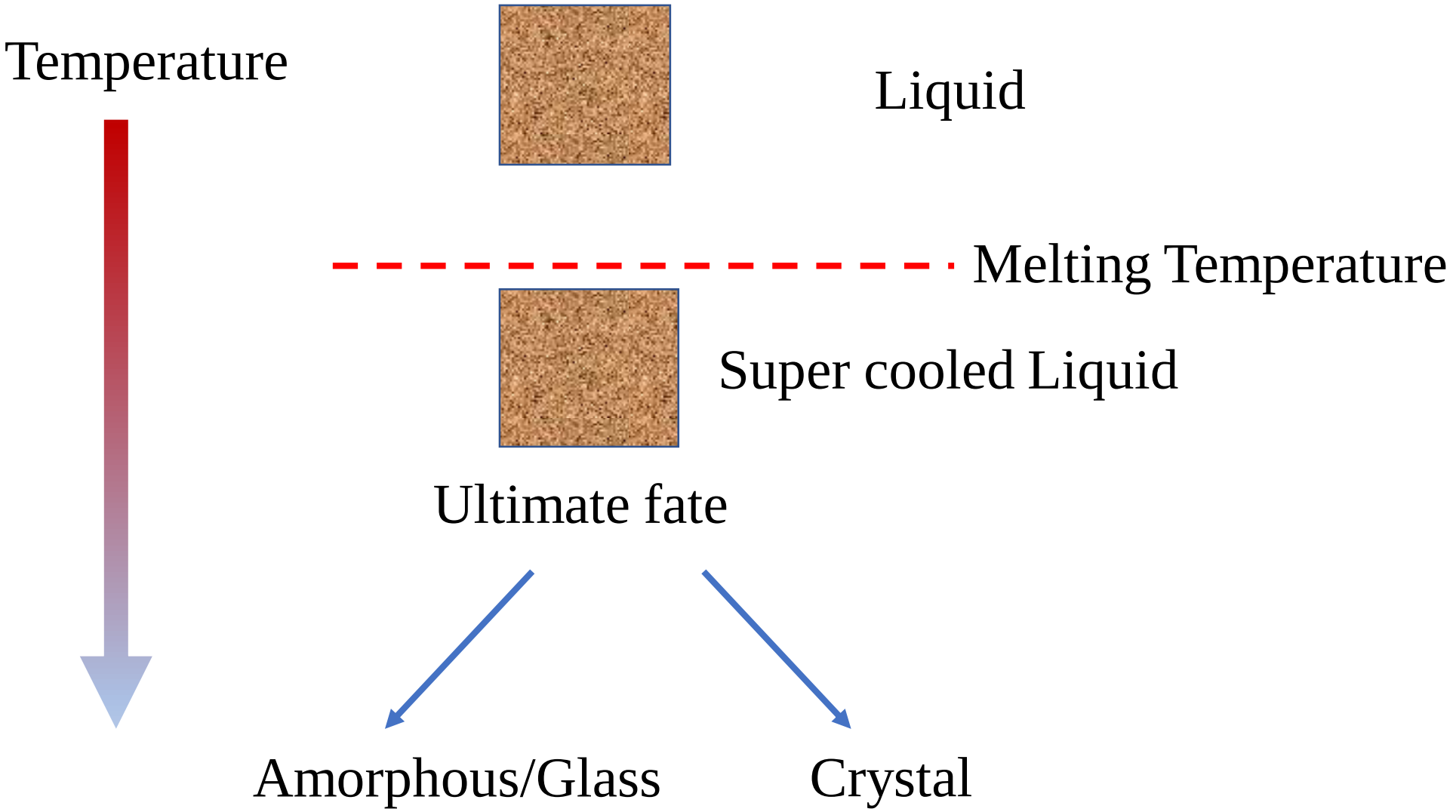
II ICTP-SAIFR Condensed Matter Theory in the Metropolis
São Paulo, November 9-11, 2022.


Temperature
Liquid
Melting Temperature
Super cooled Liquid
Ultimate fate
Amorphous/Glass
Crystal

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 - τ_R

  ✓ Average period need to spontaneously form the 1st crystalline critical nucleus – NUCLEATON TIME - τ_N

Race between the two relaxation times

If $\tau_N < \tau_R$ ⟹ crystallization

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

Temperature which $\tau_N = \tau_R$ ⟹ 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: $Li_2O.2B_2O_3$ and $Li_2O.2SiO_2$

Simulation:
- Pressurized SiO_2
- Supercooled Ni, Cu, Cu_5Zr
- Binary L-J mixture
- Cu_xZr_{1-x}, $0.15 \leqq x \leqq 0.645$
- 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

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

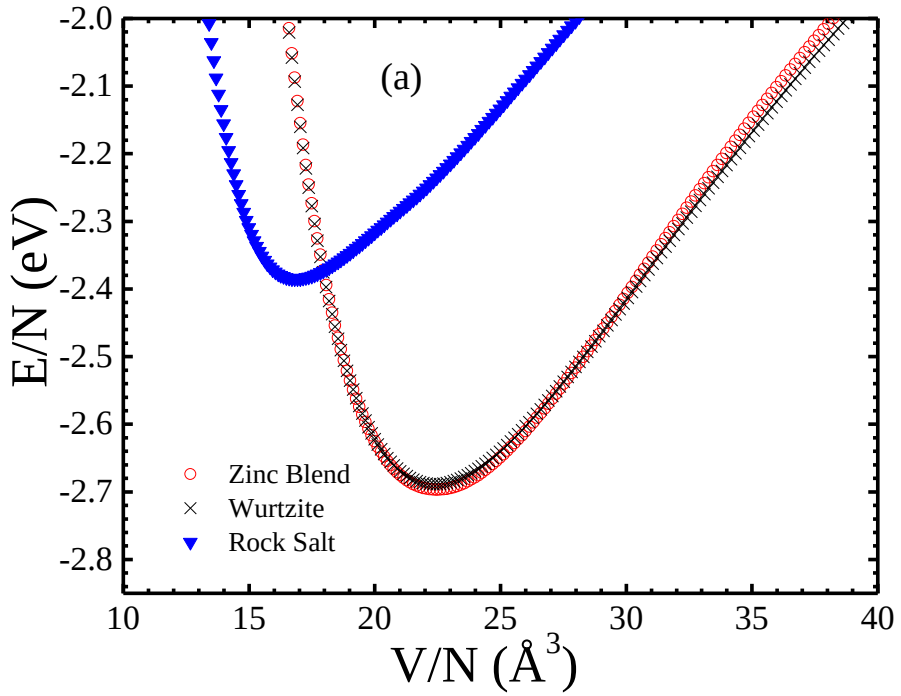
$$V_{ij}(r) = \frac{H_{i,j}}{r^{\eta_{i,j}}} + \frac{Z_i Z_j}{r} . e^{-r/\lambda} - D_{i,j}\left(\frac{\alpha_i Z_j^2 + \alpha_j Z_i^2}{2r^4}\right). e^{-r/\zeta} - \frac{W_{i,j}}{r^6}$$

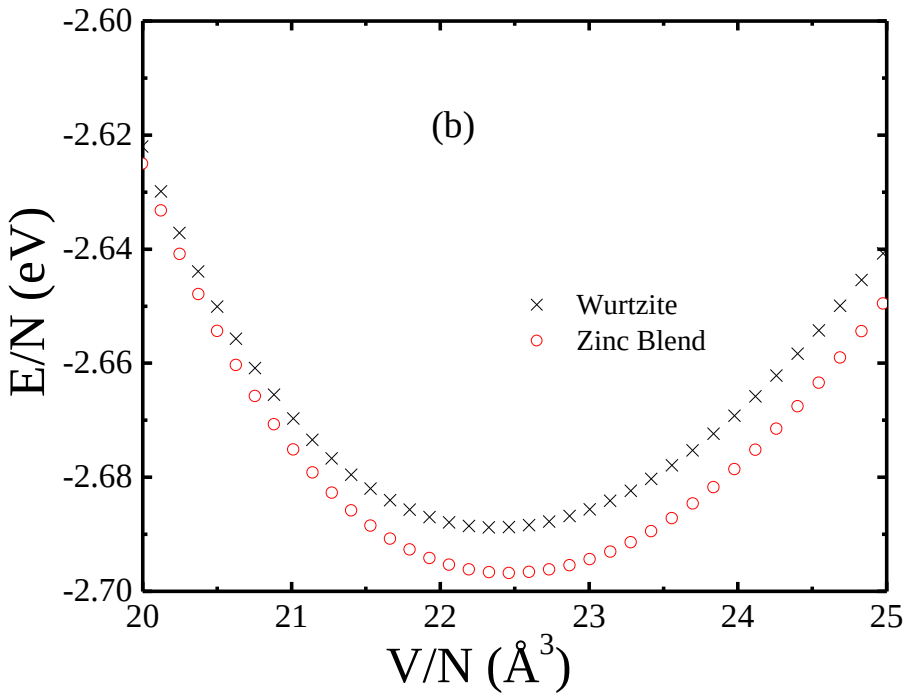
$$V_{jik}^{(3)}(\vec{r}_{ij}, \vec{r}_{ik}) = B_{jik}\exp\left(\left(\frac{1}{r_{ij}-r_o} + \frac{1}{r_{ik}-r_o}\right) \frac{\left(\cos\theta_{jik} - \cos\bar{\theta}_{jik}\right)^2}{1 + C_{jik}\left(\cos\theta_{jik} - \cos\bar{\theta}_{jik}\right)^2}\right.$$

Partial results

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

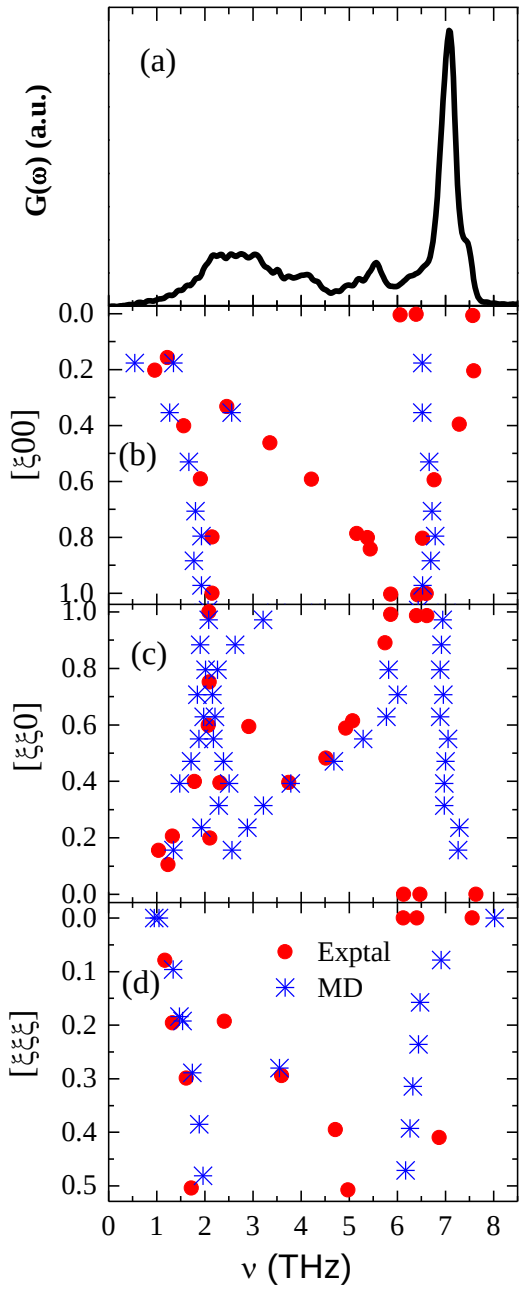
Partial results - Energetic

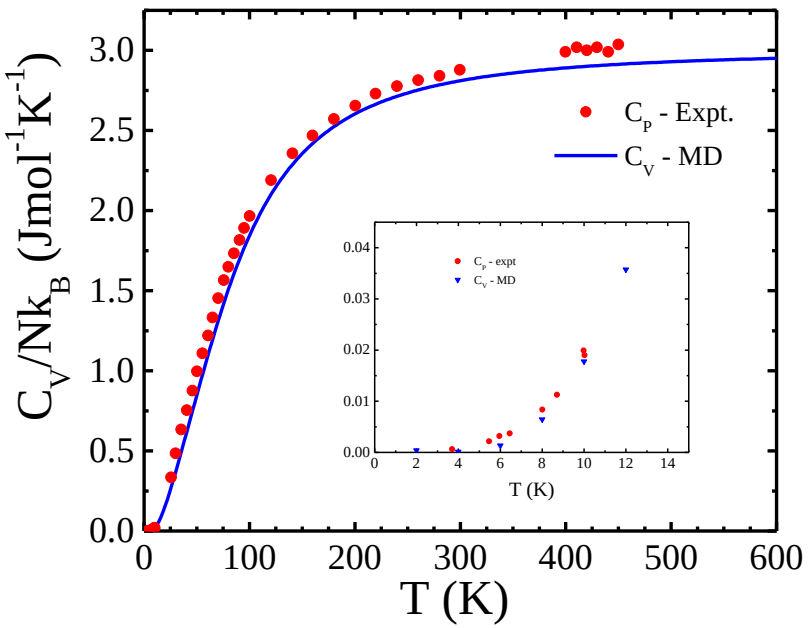


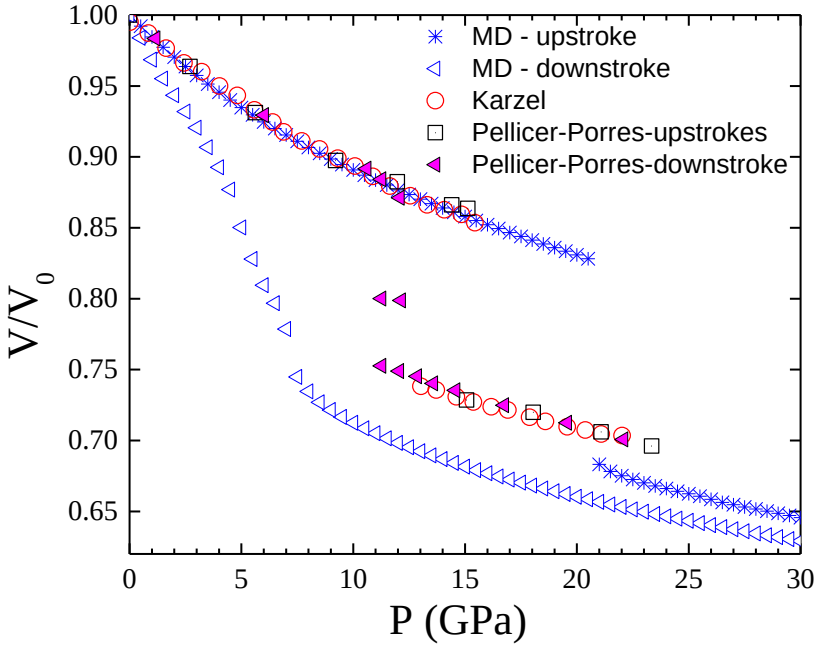


$$E_{ZB} - E_{WZ} = -8.5\ meV$$

Partial results







	MD	Expt*
Θ_{Debye} (K)	226 ± 1	237 ± 6 at room temperature 224± 2 at nitrogen temperature

- N.P. Sharma, Indian Pure Appl. Phys. 10, 478 (1972)
- R. Passler, Phys. Status Solid B 248, 904 (2011)
- J. Pellicer-Porres et al. Phys.Rev.B 65, 0.12109 (2001)
- H. Karzel et al. Phys. Rev. 53, 11425 (1996)

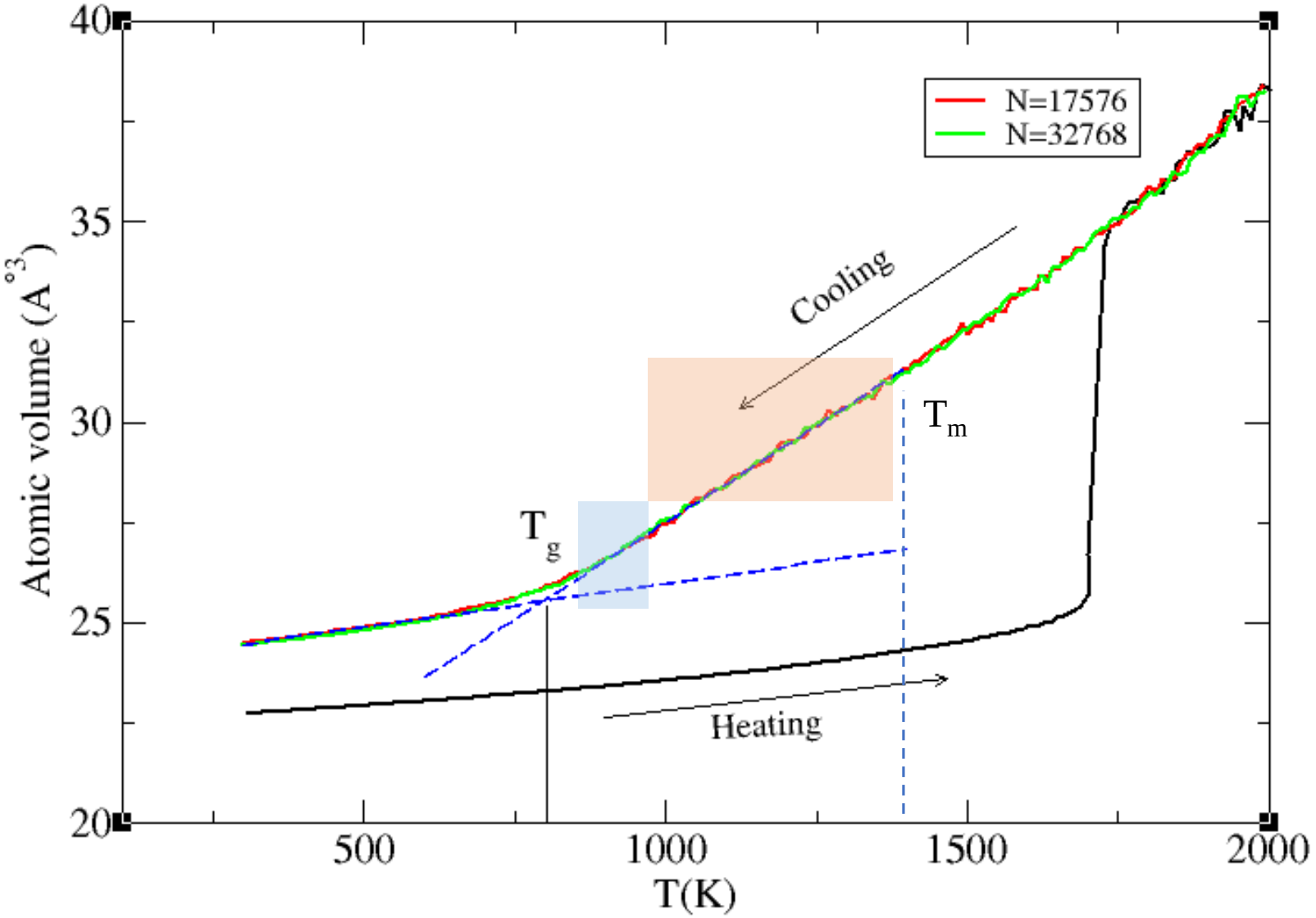
Partial conclusions

- ✓ 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 ≦ 1000K

Birth time, or nucleation time, τ_N

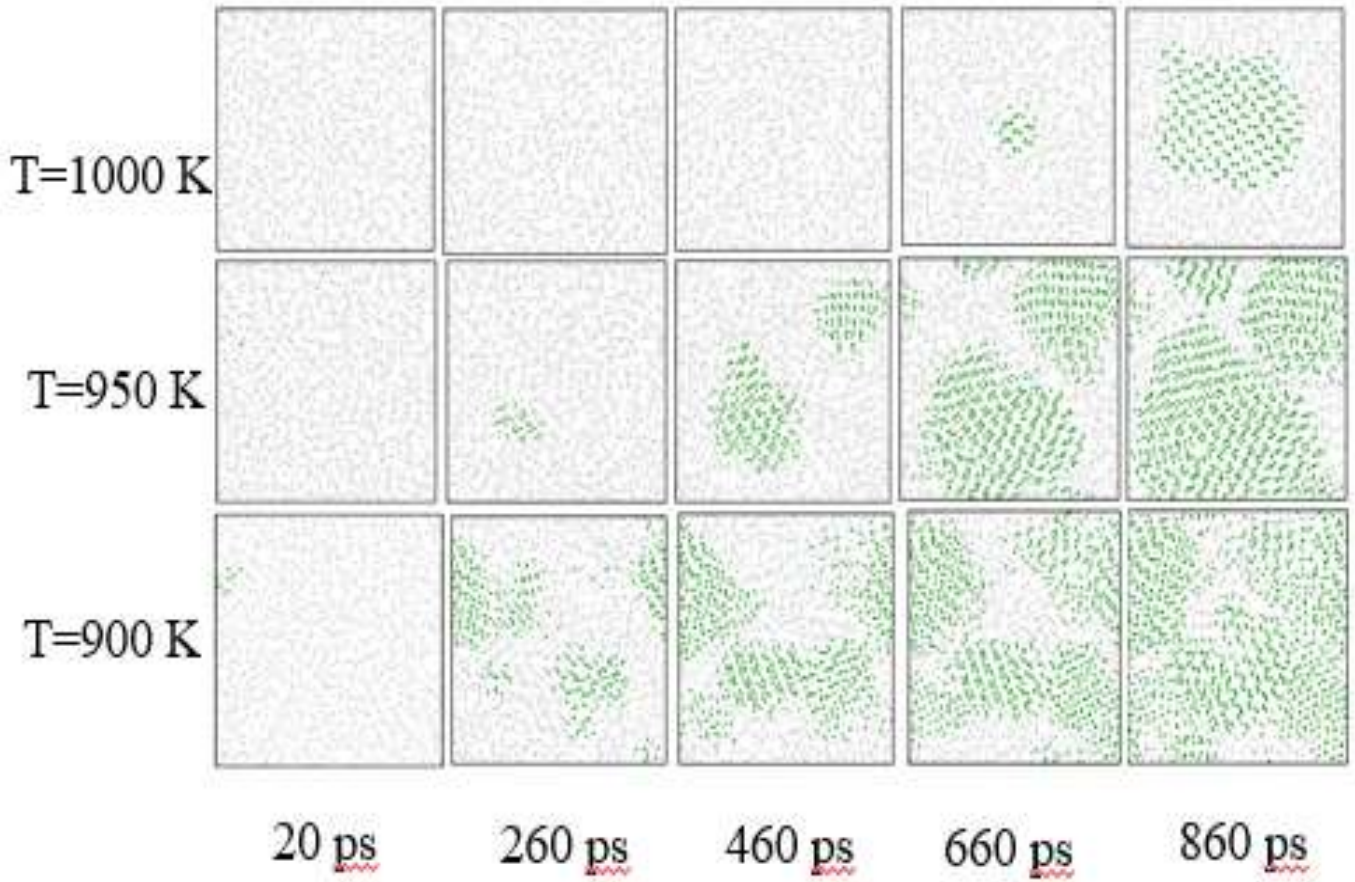
T = 1000K, 950K 900K

System sizes: 17,576 and 32,768 particles

Average over 15 samples

Solid like particles – Steinhart bond-order parameter

$$S_{ij} = \sum_{m=-6}^{m=+6} q_{6m}(i).q_{6m}^{*}(j); \quad q_{6m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{Nb(i)} Y_{lm}(\vec{r}_{in})$$


T=1000 K
T=950 K
T=900 K
20 ps
260 ps
460 ps
660 ps
860 ps

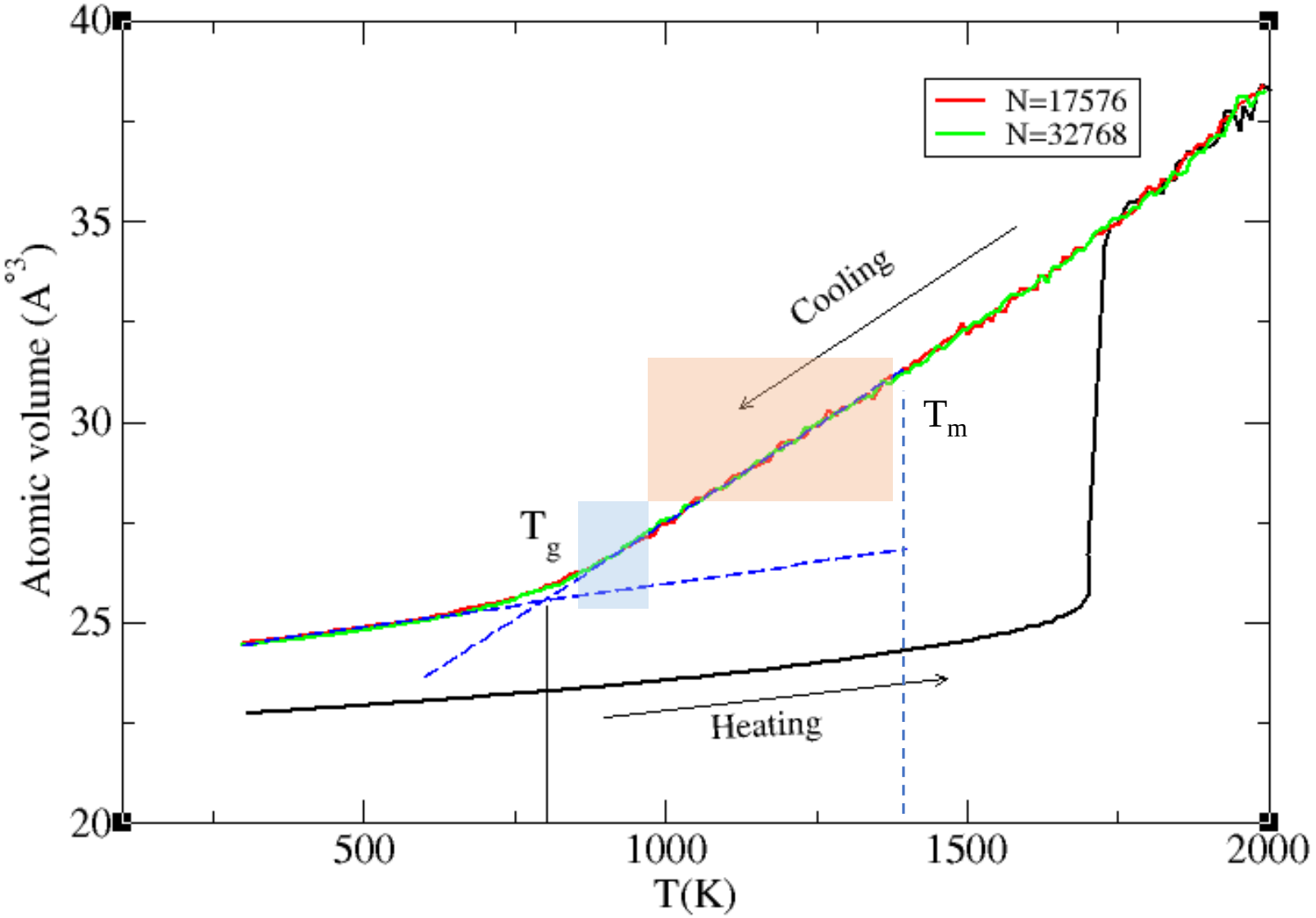
Spontaneous nucleation – T ≦ 1000K

T (K)	N	τ_N (ps)	J_{ss} ($ps^{-1}Å^{-3}$)
1000	17,576	803.8	$2.5x10^{-9}$
	32,768	740	$1.5x10^{-9}$
	$3.7x10^{10}$	$5.0x10^{-4}$	
950	17,576	224.7	$0.9x10^{-8}$
	32,768	168.3	$0.7x10^{-8}$
	$3.7x10^{10}$	$1.25x10^{-4}$	
900	17,576	161.2	$1.3x10^{-8}$
	32,768	78.8	$1.4x10^{-8}$
	$3.7x10^{10}$	$7.41x10^{-5}$	

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

$N=3.7x10^{10}$ particles ⟶ $V=1\mu m^3$

heating & cooling



Structural Relaxation time

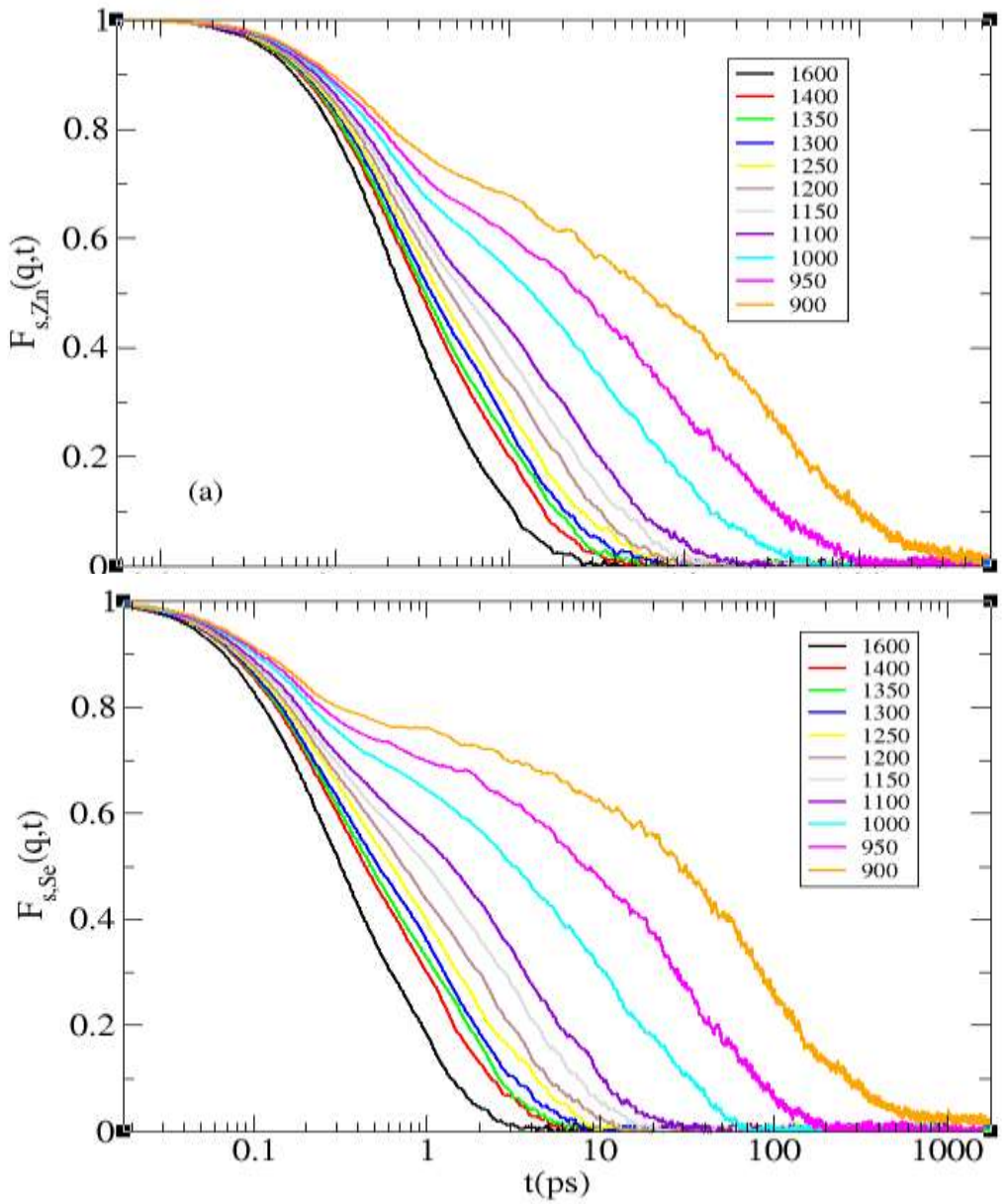
(1000 < T < T_m)

$$F_s(q,t) = N_\alpha^{-1} \sum_{j=1}^{N_\alpha} \left\langle \exp(i\vec{q} \cdot (\vec{r}_j^{\,\alpha}(t) - \vec{r}_j^{\,\alpha}(0)) \right\rangle$$

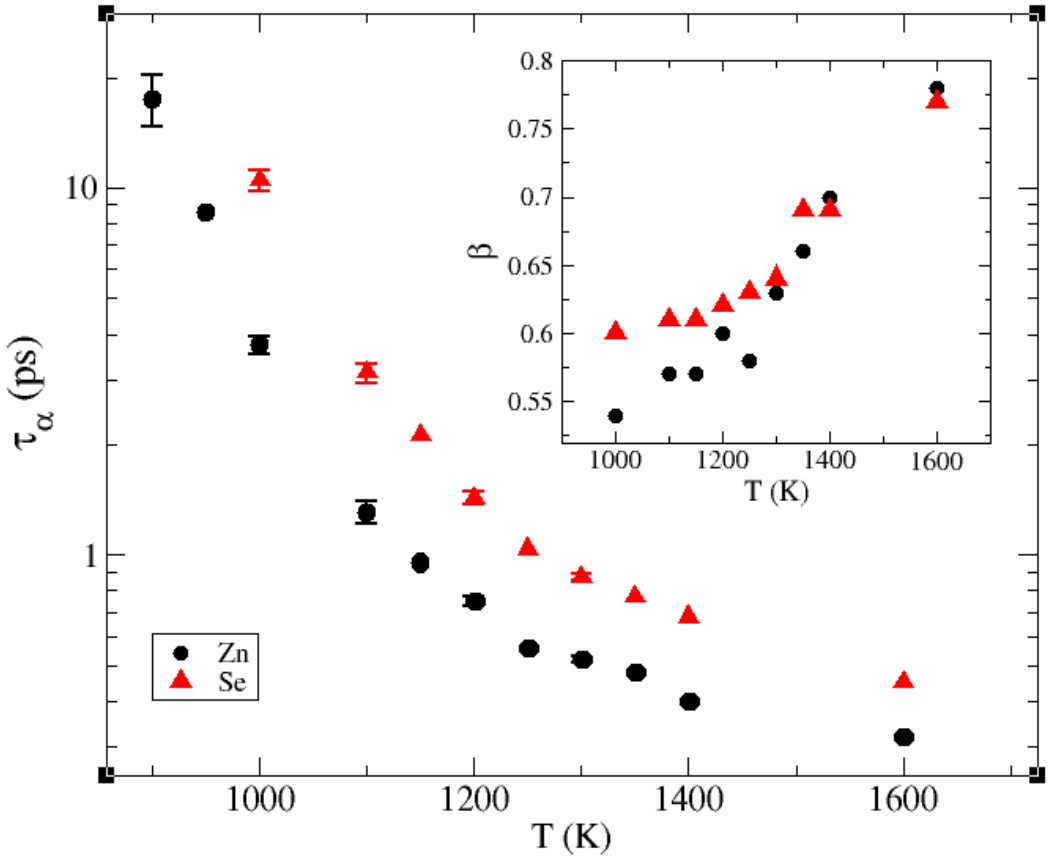
The tail (long time) is described by the KWW law
(Kohlrausch-Williams-Watts)

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

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 τ_R

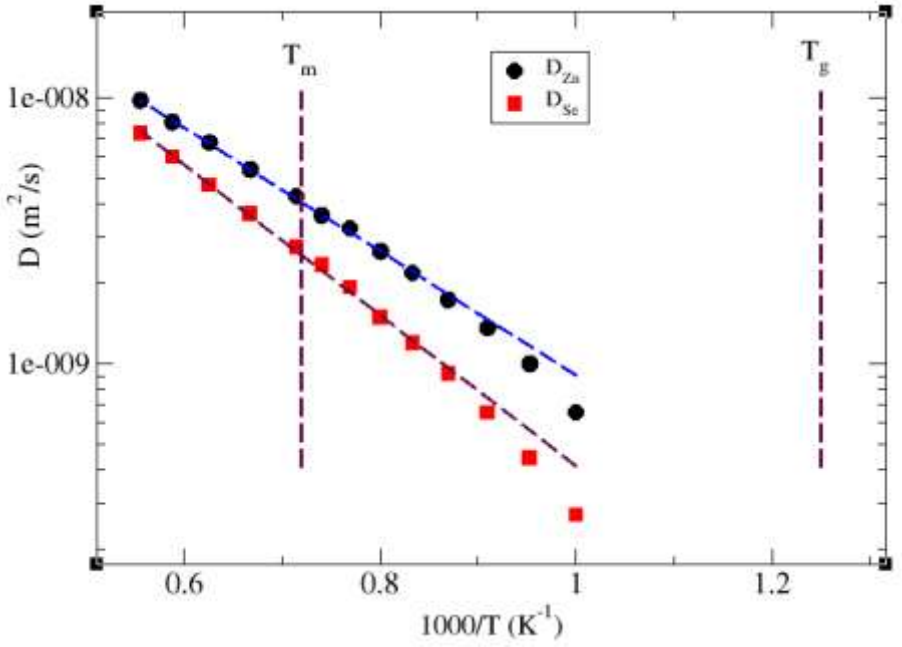
$$\tau_R\,(T) = \frac{\tau_\alpha(T)}{\beta(T)}\,\Gamma\left(\frac{1}{\beta(T)}\right)^{(a),(b)}$$

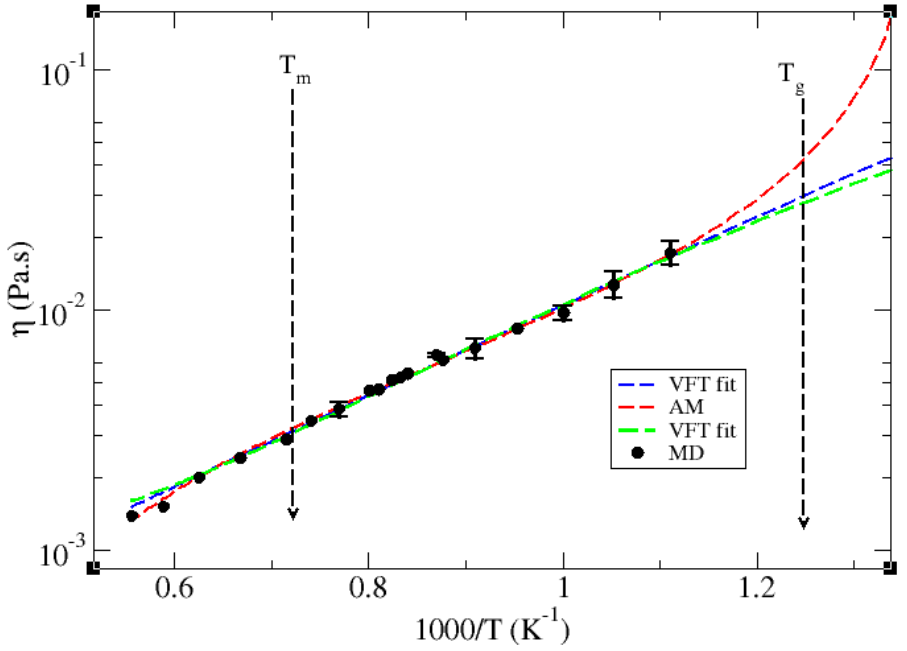
(a) Lancelotti, R.F. et al. J. Am. Ceram. Soc.104 (2021) 2066.
(b) Doss, K. et al. J. Am. Ceram. Soc.103 (2020) 23590.

Diffusion and viscosity

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

$$\eta = \frac{V}{Nk_B}\int_0^\infty \langle P_{ij}(0)P_{ij}(t)\rangle dt$$





Deep supercooling : spontaneous crystallization
(T: 1000K, 950K 900K)

→ τ_N

Shallow supercooling : relaxation time
(900K ≦ T ≦ 1600 K)

→ τ_R

How to compare ?

How to extrapolate to other temperatures?

- τ_N CNT
- τ_R MYEGA

τ_N - Classical Nucleation Theory

Recall that → $J_{ss} = {}^{1}/_{\tau_N V}$

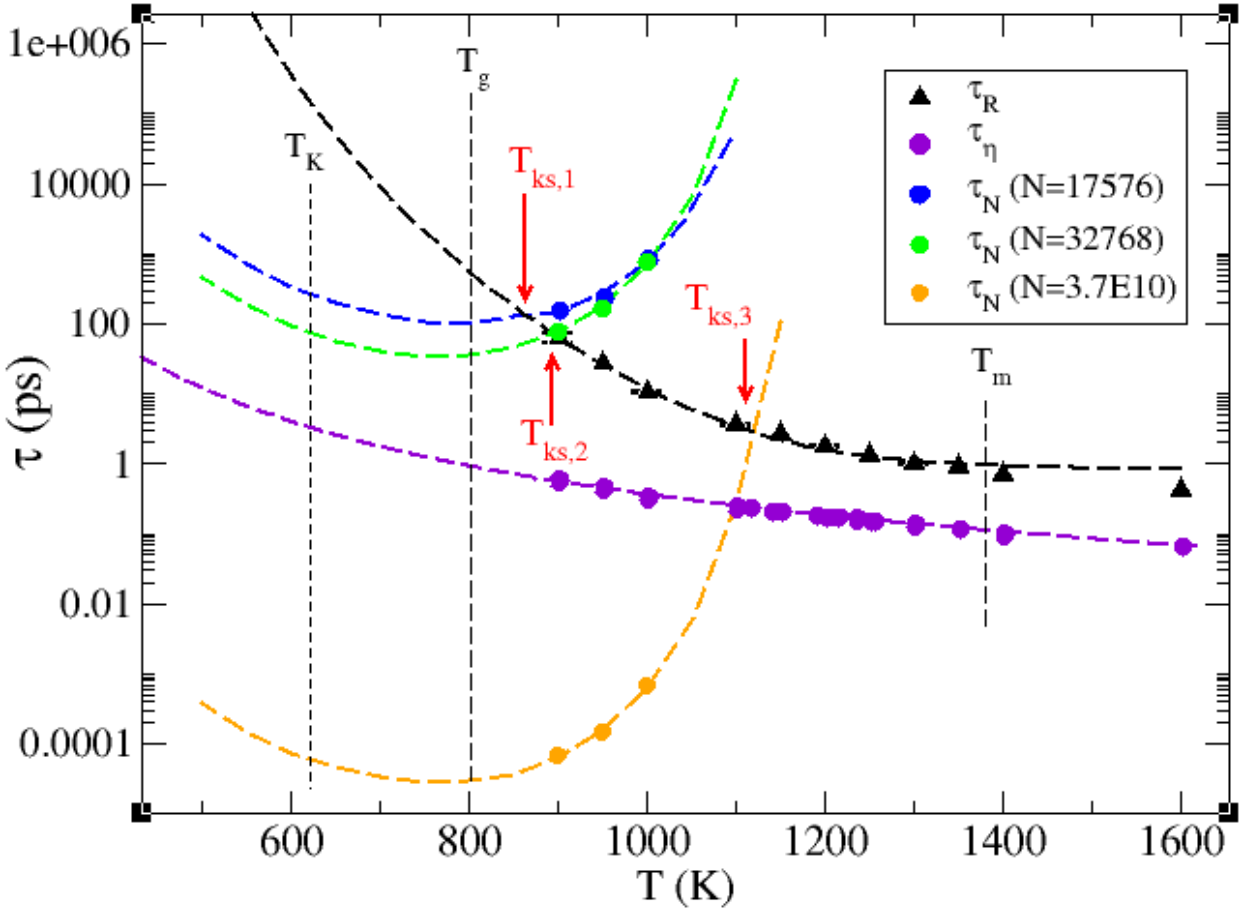
$$\frac{J_{ss}\sqrt{T}}{D} = Aexp\left(-\frac{B}{T}\right)$$ (A and B fitted parameters)

τ_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 ~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)

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

System size	Critical cooling rate (K/ps)
17576	5.5
32768	18.5

$cooling\ rate\ used\ 1K/ps$ → *spontaneous nucleation already in the cooling procedure*

Conclusions

- From MD we obtained both
  nucleation time, τ_N , (spontaneous crystallization)
  relaxation time, τ_R , from intermediate scattering function and viscosity

- Relaxation time using Maxwell relation, τ_η , gives a lower boundary.
  (this confirms recent experimental results – $Li_2O.2B_2O_3$ and $Li_2O.2SiO_2$)

- 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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Acknowledgments

- FAPESP - Fundação de Amparo à Pesquisa do Estado de São Paulo
- CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico

Brazil