Two-level tunneling systems in amorphous alumina

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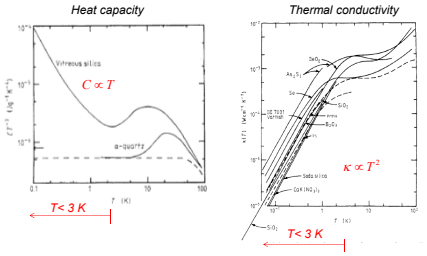
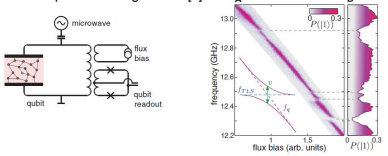
Experimental evidence for two-level systems

- Anomalies in low-temperature behavior of amorphous materials [1]



- Noise in superconducting circuits [2]



Model of two-level systems

Among all models proposed for explanation to account for anomalious thermal data for amorhous materials, the most successful one is the model of two-level systems (TLSs) [1]. In this model, atoms occupying two adjacent minima of the double-well potential tunnel quantum mechanically to the other, leading to the splitting of the ground state.

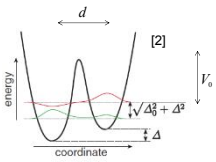
The energy splitting of TLS $E = \sqrt{\Delta^2 + \Delta_0^2}$

Δ is relative shift in energy for two wells (in the case of identical wells)

Δ_0 is the tunneling energy

$\Delta_0 \approx \hbar\Omega \exp(-\lambda) \qquad \lambda \approx d\sqrt{\frac{2mV_0}{\hbar}}$

Ω is frequency of vibrations about the energy minima
d is the distance between the energy minima
V_0 is the barrier separating the energy minima
m is the mass of the tunneling particle



TLS that incluence the properties at temperature $T \sim 1$ K have $\Delta_0 \approx k_B T \approx 10^{-4}$ eV For an Al atom, $\Omega \sim 10^{13}$ s^{-1} and $d \sim 0.5$ Å, we get $V_0 \sim 5$ - **10 meV**.

Assuming the distribution of energy splittings of two-level systems in energy is constant and has the density n_0, the heat capacity of amorphous solids at low temperature can be found as [1]

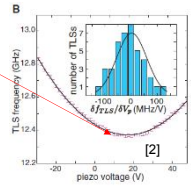
$$C(T) = \frac{\pi^2}{6} n_0 k^2 T$$

Thus, from the experimental data on the heat capacity, the density of TLSs with the energy splitting below 0.1 meV can be estimated as

$n_0 \sim 1$ TLS per 600 000 atoms or 1 TLS per cubic cell with 20 nm side

Applying stress, tuning of the relative energy of two minima is possible [2]. The experiments with superconducting circuits allow to distinguish response of individual TLSs and determine their parameters.

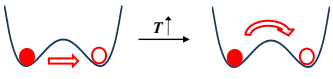
$E = \Delta_0 = hf$
$\Downarrow$
$V_0 \sim 7.5$ meV



In these experiments,

$n_0 \sim 1$ TLS per 2 000 000 atoms or 1 TLS per cubic cell with 60 nm side

Our goal: To identify structural motifs that can be responsible for TLSs in amorphous alumina by detection of low-temperature structural rearrangements in classical molecular dynamics simulations.



Computational approach

- Molecular dynamics simulations were performed using MD-kMC, LAMMPS and CP2K computational packages [3]
- Classical potentials were used

I. Matsui potential [4, 5]

$$V(r_{ij}) = \frac{q_i q_j}{r_{ij}} - \frac{C_{ij}}{r_{ij}^6} + A_{ij} \exp\left(-\frac{r_{ij}}{r_{ij}^0}\right)$$

The potential has been shown to reproduce experimental properties of crystalline aluminum oxide, such as structure, density, bulk modulus, thermal expansivities, and melting temperatures as well as properties of liquid phase (see Ref. 5 and references therein).

II. Potential of Beck et al [6]

$$V(r_{ij}) = \frac{q_i q_j}{r_{ij}} + D_{ij}\left[\exp\left[\gamma_{ij}\left(1 - \frac{r_{ij}}{\rho_{ij}}\right)\right] - 2\exp\left[\frac{\gamma_{ij}}{2}\left(1 - \frac{r_{ij}}{\rho_{ij}}\right)\right]\right]$$

The potential was fitted to the *ab initio* data on liquid alumina [6].

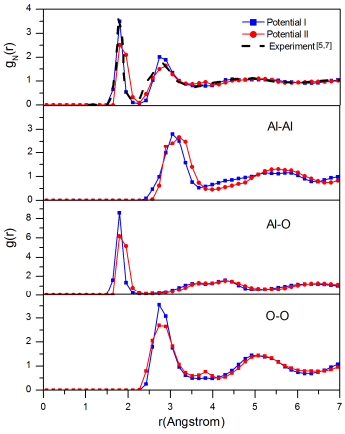
- The long-range Coulomb interactions were calculated with the standard Ewald summation technique.
- The time step was 1 fs.
- The Berendsen thermostat was used to control temperature.

Simulation procedure:

- Liquid alumina is simulated at high temperature 5000 K and low density 2.75 g/cm^3 during 200 ps starting from the crystalline configuration.
- Then the sample is cooled down to 3000 K with the cooling rate 20 K/ps.
- The system is allowed to equilibrate at 3000 K during 100 ps.
- The system is compressed to the density of 3.2 g/cm^3 by reducing simultaneously the lengths of the MD cell and the positions of all the atoms and equilibrated again at temperature 3000 K during 100 ps.
- The system is cooled down to 25 K with the cooling rate 4K/ps.
- Finally the systems is equilibrated at 25 K and analysis of structure and detection of low-temperature structural rearrangements is performed.

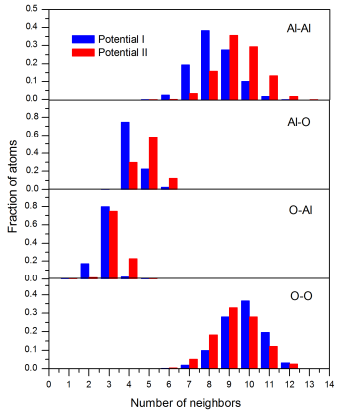
Analysis of structure of amorphous alumina

Radial distribution functions:



Radial distribution functions for amorphous alumina were calculated at 25 K for 20 samples consisting of 360 atoms. The neutron radial distribution function was calculated using parameters from paper [5]. The experimental data obtained from neutron diffraction spectra [7] are adopted from paper [5].

Nearest-neighbour coordination numbers:

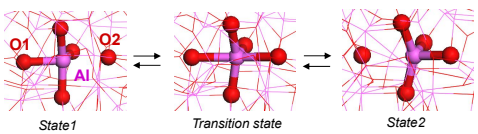


The coordination numbers were calculated within the cutoff distances of 3.7 Å for Al-Al pairs, 2.2 Å for Al-O pairs and 3.2 Å for O-O pairs.

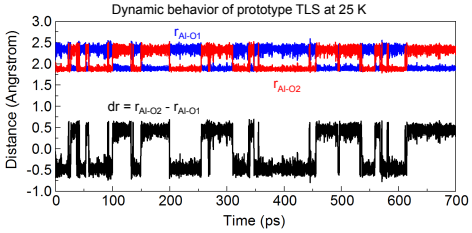
- The radial distribution functions and distributions of coordination numbers are quite sensitive to the potential used.
- Potential I provides the neutron radial distribution function in good agreement with the experiment.
- Potential II tends to overestimate the Al-O bond length and the average numbers of nearest neighbors.

Identified prototype TLS motifs

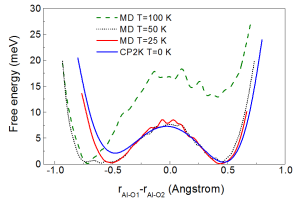
Potential I: An example of identified prototype TLS



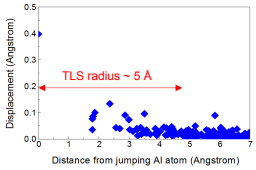
Dynamic behavior of prototype TLS at 25 K



Free energy surface of prototype TLS



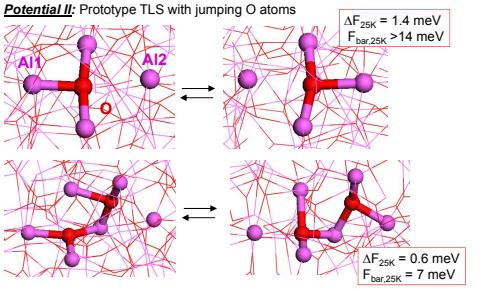
Displacements of atoms of prototype TLS



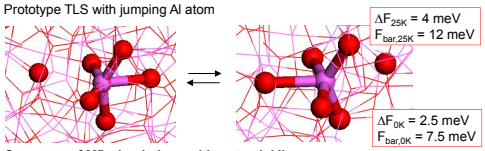
Summary of MD simulations with potential I:

- Bistable motifs with small energy difference ~ 1 - 2 meV and barrier ~ 4 – 7 meV were detected in 2 out of 100 systems with 360 atoms and in 1 system with 1500 atoms.
- In the both motifs, O atoms surrounding the jumping Al atom have the octahedral arrangement typical for crystalline alumina (though in two of the motifs, one of the O atoms from the full octahedron is missing).
- In all motifs, one Al atom jumps by the relatively large distance 0.4 – 0.6 Å, while the other atoms are displaced by less than 0.2 Å.
- Nevertheless, account of small displacements of atoms ~ 0.1 Å and less is important for existence of the second minimum. The characteristic radius of the motif is ~ 5 Å.

Potential II: Prototype TLS with jumping O atoms



Prototype TLS with jumping Al atom



Summary of MD simulations with potential II:

- Bistable motifs with small energy difference of a few meV were detected in 4 out of 20 systems with 360 atoms. Three of these motifs are related to jumps of O atoms and only one to a jumping Al atom.
- Though these motifs are different from the ones found using potential I, the characteristic energetic and geometrical parameters of these motifs are similar.
- The motif with a jumping Al atom resembles the one found using potential I.

Conclusions

- Structure and low-temperature dynamics of amorphous alumina were studied using classical molecular dynamics simulations with two different potentials.
- Potential I [4,5] was shown to be more reliable then potential II [6] in description of radial distribution functions in amorphous alumina.
- Prototype TLS motifs with only one atom jumping by considerable distance ~0.5 Å were identified. For the both considered potentials, the energy difference between two energy minima of detected motifs lies in the range from 0.5 to 2 meV. The barriers for transition between the minima are 4 – 15 meV.
- Account of displacements of atoms neibouring to the jumping atom was shown to be important for existence of bistability. The characteristic radius of the TLS motifs is estimated to be about ~ 5 Å.
- The density of prototype TLSs with the studied parameters was found to be about 1 motif per 10 000 atoms according to potential I and 1 motif per 2000 atoms according to potential 2.
- The estimated density of TLSs and TLS barrier are in agreement with the experimental data.

References

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Acknowledgements

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