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Thermodynamic and Kinetic Study of Germanium Crystal Growth by Computer Simulations

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Abstract: Monocrystalline germanium (Ge) is a key material in the fields of semiconductors, infrared optics and high-frequency electronics. In its crystalline form Ge has a diamond structure, whereas in the amorphous state it forms a random and distorted tetrahedral network. The experimental evaluation of its crystallization kinetics in the supercooled liquid is complicated by the fact that it occurs very fast within the interior of a dense liquid [1] and the critical nucleus size is usually too small to be detected. Therefore, the computational study of the molecular origins and microscopic mechanism of homogeneous crystal nucleation can provide relevant molecular insight on this system [2] and can also be useful to other materials. In this work we have carried out standard molecular dynamics simulations using the Tersoff potential [3] for Ge (~4,000 atoms). The crystalline phase was characterized by a tetrahedral order parameter (q) [4], whose values for a unique atom range between -3 and 1 (q=1 in a perfect tetrahedral arrangement and q=-3 for a linear configuration). Individual Ge atoms were considered to be in the crystalline state whenever q>0.92. Spherical crystalline nuclei were created into an amorphous Ge matrix in order to find the critical size of the crystalline nucleus (*Figure 1, left*) in a few temperatures at very deep undercooling conditions. The simulations allowed the calculation of free energy terms related to the formation of a crystalline nucleus with radius r in an amorphous matrix (*Figure 1, right*), to be used latter in the classical nucleation theory (CNT) calculations. Both results are consistent with a critical size of the Ge nucleus at 2000 K of *ca.* 22 Å (Figure 1). The crystallization of Ge is pictured on *Figure 2*, where all atoms in red represent those in tetrahedral configuration (q> 0.92). The initial structure had a seed crystal of diameter equal 24 Å (Figure 2, left), and after 5000 ps nearly all atoms evolved into a crystalline structure (Figure 2, right). The measurement of the crystal growth velocity is being carried out using a tenfold larger system in the SDumont supercomputer, in order to minimize finite-size effects which have been detected in the simulations with these smaller models.

Key-words: molecular dynamics simulations, crystal growth, germanium, entropy, order parameter

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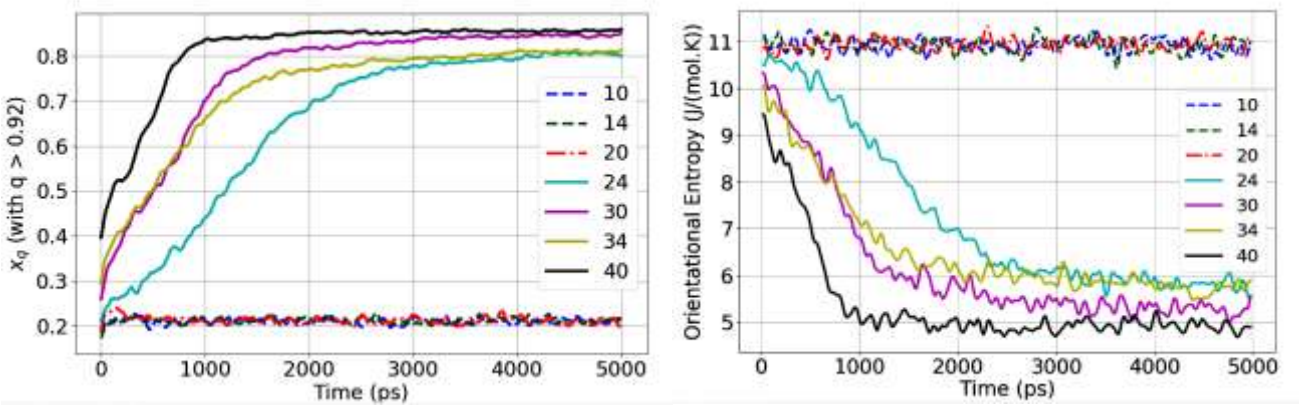

Figure 1: Fraction of Ge atoms with tetrahedral order parameter larger than 0.92 (left) and orientational entropy at 2000 K (right). Different colors stand for the size of the seed used for nucleating the crystal growth (diameters in Å).

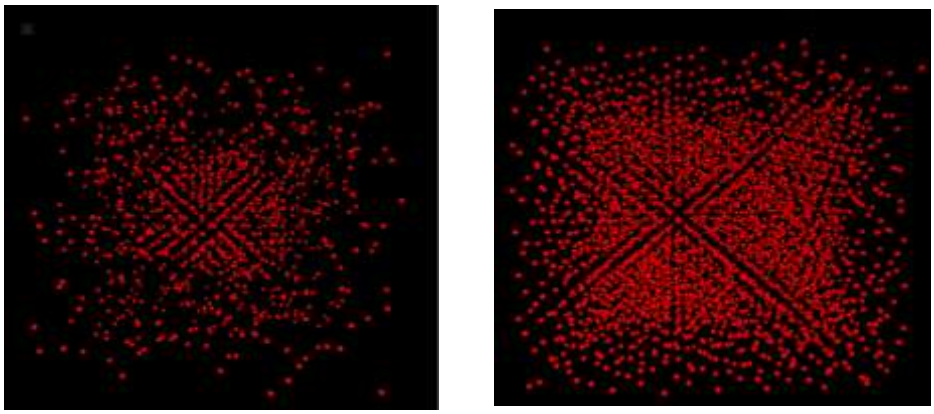

Figure 2: Atoms wit q>0.92 at the beginning of the simulation (left) and after 5 ns (right). Atoms with q<0.92 are not shown for clarity (seed diameter of 24 Å, T=2000 K).

References:

[1] SOSSO, G. C. et al. Crystal Nucleation in Liquids: Open Questions and Future Challenges in Molecular Dynamics Simulations. Chem. Rev., 2016, n. 12, p. 7078–7116, 2016.

[2] ZANOTTO, E. D.; MAURO, J. C. The glassy state of matter: Its definition and ultimate fate. Journal of Non-Crystalline Solids, 490-495, 2017.

[3] CHAU, P. L.; HARDWICK, A. J. A New Order Parameter for Tetrahedral Configurations. *Mol. Phys.* 1998, 93, 511−518.