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Molecular dynamics strategies to determine the melting curve of CaO

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The thermodynamic properties of multicomponent liquids at high pressure and temperature (HP-HT) are of paramount importance to elucidate the melting and crystallization phase relations in geological systems. High-pressure melting experiments suffer from uncertainties of hundreds of K and rarely predict the ultimate nature of melting [1]. Ab initio molecular dynamics (AIMD) gave useful insights on the structure-energy properties of solid and liquid phases up to very HP-HT conditions, but the calculated melting temperature (T_m) depends critically on the simulation protocol and the computational cost increases proportionally with the number of atoms to process.

In this work we focus on the melting curve of CaO, not only because is a key phase in material and geological sciences, but also because the thermodynamic properties of the liquid phase are still controversial due to the very high melting point of the crystal [1,4]. The simplicity of its phase diagram makes it a good candidate for AIMD simulations. However, AIMD simulations are expensive, while classic MD with empirical potentials allows to employ different strategies at a reasonably low computational cost.

We simulate the melting process of CaO with classic molecular dynamics, by the means of the LAMMPS code [5]. We tested three different methods, which gave insights both on the melting temperature of the crystal and on the enthalpy of fusion (ΔH_f).

The two-phase solid-liquid coexistence method consists of running a solid-liquid interface at constant enthalpy [3,6]. The melting temperature is determined as the average equilibrium temperature.

The void-nucleated method exploits holes in the crystal structure to initiate the melting process, thus decreasing the unrealistic high melting point resulting from homogeneous heating simulations by introducing a defect [2].

Finally, to calculate the enthalpy of fusion, the temperature of the crystal is increased up until the solid melts, and then the temperature is lowered again until the liquid phase recrystallizes. The difference in energy between the liquid and the solid curves at the melting point represents the enthalpy of fusion, ΔH_f [2].

The values of T_m and ΔH_f obtained with these methods by the means of classic MD on CaO are found to be consistent with experimental data available in literature [7,8].

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