Ab Initio Investigation of a Possible Liquid-Liquid Phase Transition in $MgSiO_3$ at Megabar Pressures

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Abstract

We perform density functional molecular dynamics simulations of liquid and solid $MgSiO_3$ in the pressure range of $120-700$ GPa and for temperatures up to 20000 K in order to provide new insight into the nature of the first-order liquid-liquid phase transition that was recently predicted on the basis of decaying laser shock wave experiments [Phys. Rev. Lett. **108** (2012) 065701]. However, our simulations did not show any signature of a phase transition in the liquid phase. We present and discuss different thermodynamic functions and then conclude by exploring alternative interpretations of the experimental findings including the formation of a Rayleigh-Taylor instability.

Keywords: density functional molecular dynamics, ab initio simulations, high pressure, shock wave experiments

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1. Introduction

The recent work by D. K. Spaulding *et al.* [1] reported results from decaying laser shock wave experiments which provided evidence of a liquid-liquid phase transition in $MgSiO_3$ at megabar pressures. The authors measured a reversal in the shock velocity and thermal emission and interpreted their findings in terms of a liquid-liquid phase transition that occurs when the sample changes from a high density to a low density fluid state during shock decay. Decaying shock experiments are a new experimental technique that allows one to map our the entire Hugoniot curve with a single shock wave experiment.

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The goal of this short paper is to perform density functional molecular dynamics simulations (DFT-MD) of dense liquids [2] in order to verify the predictions of a liquid-liquid phase transition by Spaulding *et al.* [1]. First order transitions in liquids are unusual but have been seen in experiments on phosphorus and in simulations of dense hydrogen [3].

2. Simulation Details

All simulations were performed with the VASP code [4] with pseudopotentials of the projector-augmented wave type [5], a cut-off for the expansion of the plane wave basis set for the wave functions of 500 eV, and the PBE exchange-correlation functional [6]. The Brillioun zone was only sampled with the Γ point to allow for efficient MD simulations. Our simulations were between 3 and 20 ps long and used a small time step of 0.2 fs. The electronic states were populated according to the Mermin functional [7].

We used an orthorhombic super cell with 60 atoms that we constructed by tripling the unit cell of the post-perovskite (PPV) structure that we relaxed at 120 GPa. The system was heated and melted using a Nosé thermostat. We then explored the liquid state by scaling the velocities and changing the density accordingly.

We also performed heat-until-it-melts simulations with 60 atoms starting a perfect PPV crystal at hydrostatic conditions. We then gradually increased the temperature in a fixed cell geometry.

3. Results and Discussion

The P-T conditions of our simulations are shown in Fig. 1 and the resulting equation of state (EOS) is given in Tab. 1. We focused our work on 7500 K and 12500 K in order to increase the likelihood of detecting a first order phase transition in the liquid. However, all the thermodynamic functions, that we analyzed, varied in a perfectly smooth way as function of temperature and pressure. Figure 2 shows the volume and the internal energy as function of pressure. The zero of energy was set equal to the energy of a collection of isolated atoms.

We computed the Hugoniot curve from the usual relation [13],

$$H = E - E_0 + \frac{1}{2}(V - V_0)(P + P_0) = 0, \tag{1}$$

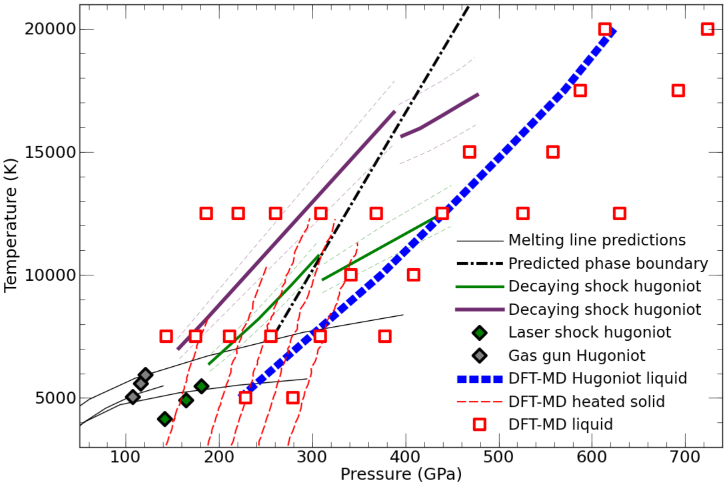

Figure 1: Phase diagram of $MgSiO_3$. The pressure-temperature conditions of our isothermal DFT-MD simulations of liquids and the solid portion of the heat-until-it-melts simulations are shown. The DFT-MD Hugoniot curve is derived from the simulation of liquid samples. Three earlier predictions of the melting line are included [8, 9, 10]. The experimental Hugoniot curves from decaying shock measurements in single crystal (green) and glass (purple) $MgSiO_3$ are plotted [1]. From the discontinuities in both curves, the phase boundary between a high and low density liquid was inferred. The diamonds indicate earlier shock measurements [11, 12].

where the initial volume, V_0=51.77 Å^3, and initial internal energy, $E_0 = -35.914$ eV per $MgSiO_3$ formula unit (FU), were taken from a DFT calculation of enstatite at 3.22 $\mathrm{g\,cm^{-3}}$ that we performed. P_0 was assumed to be zero because $P_0 \ll P$. The resulting DFT-MD Hugoniot curve for liquid $MgSiO_3$ is shown in Fig. 1. It agrees well with the experimental results at 450 GPa and 12500 K but the slope of the DFT-MD Hugoniot curve is different and it shows no sign of a phase transition.

We also investigated the possibility of the existence of a superionic phase between the solid and the liquid phases where some ions remain stationary while others diffuse throughout the material like in a liquid [14]. In Fig. 3, we plot the diffusion coefficients as a function of pressure. At 12500 K, all ions diffuse at the same rate approximately. At 7500 K, the diffusion is slower as one would expect in the fluid near the melting line. The oxygen ions diffuse

$T(K)$	time (ps)	V/FU (Å^3)	P (GPa)	E/FU (eV)
5000	5.43	27.360	279.3(5)	-17.99(2)
5000	5.02	29.106	228.7(5)	-20.10(4)
7500	4.90	34.786	143.3(5)	-19.23(7)
7500	4.99	32.818	174.4(5)	-17.97(9)
7500	4.93	30.925	211.1(4)	-16.66(8)
7500	4.66	29.106	255.4(5)	-15.01(8)
7500	4.67	27.360	308.9(7)	-13.12(9)
7500	5.94	25.686	377.9(6)	-10.31(7)
7500	5.60	24.081	456.5(8)	-7.40(9)
7500	5.78	22.544	557.3(7)	-3.26(9)
10000	5.30	25.686	408.5(9)	-5.10(13)
10000	4.94	27.360	341.2(7)	-7.63(6)
12500	22.94	34.786	186.2(3)	-9.61(4)
12500	17.24	32.818	220.3(3)	-8.38(6)
12500	12.72	30.925	260.8(3)	-6.88(7)
12500	17.99	29.106	309.4(3)	-4.98(5)
12500	15.74	27.360	368.7(3)	-2.63(6)
12500	3.52	25.686	439.3(1.0)	0.00(13)
12500	3.63	24.081	526.4(1.2)	3.39(18)
12500	4.36	22.544	629.7(1.0)	7.44(14)
12500	4.77	21.074	755.2(8)	11.78(6)
12500	4.72	19.670	908.8(1.2)	17.36(17)
12500	4.80	18.329	1094.4(1.8)	23.66(17)
12500	5.02	17.051	1326.5(1.7)	31.84(21)
12500	18.83	15.833	1604.8(1.1)	41.18(13)
15000	3.88	24.081	558.4(1.1)	8.56(14)
15000	3.75	25.686	468.9(8)	5.00(10)
17500	3.69	22.544	692.8(1.1)	16.96(14)
17500	3.65	24.081	587.5(1.1)	13.42(13)
20000	3.56	22.544	724.5(1.0)	22.06(14)
20000	3.38	24.081	614.1(1.2)	17.96(18)

Table 1: Temperature, MD simulation time, volume per formula unit, pressure and internal energy from our DFT-MD simulations. The 1σ uncertainties of the trailing digits are given in brackets.

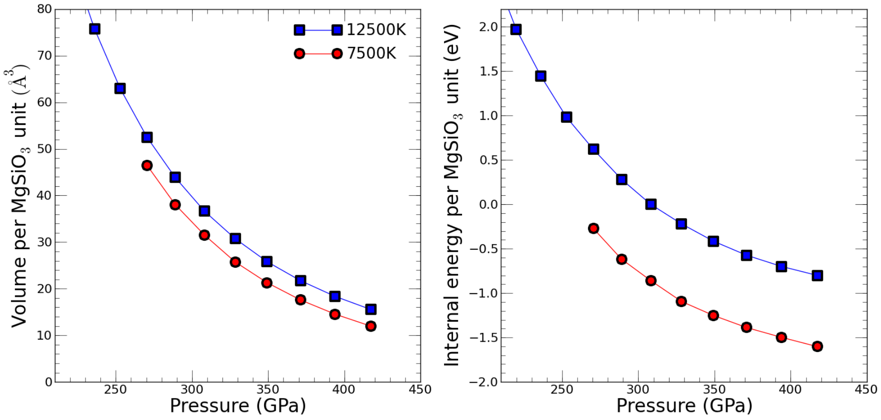

Figure 2: Volume and internal energy as function of pressure derived from DFT-MD simulations of liquid $MgSiO_3$. Both functions are smooth and exhibit no indication of a phase transition.

a bit faster than the magnesium and silicon ions but there is no evidence for a superionic state.

We also performed heat-until-it-melts simulations of solid samples (Fig. 1) that we isochorically heated at a rate of 1000 K per picosecond. This approach was used to predict the superionic state of water [14] but our sample always went into a fully fluid state after a substantial amount of superheating. Figure 4 shows that the liquid always exhibits a higher pressure than the solid when compared for the same density and temperature. This means, for given temperature and pressure, the solid is always denser than the liquid. Therefore the melting line of PPV $MgSiO_3$ is expected to have a positive Clapeyron slope.

We would now like to critically review our findings. We performed our simulations with only 60 atoms and the results would need to be confirmed with larger simulations that possibly also use more k-points. Our longest simulations ran for 20 ps, which is fairly long for *ab initio* calculations. So one would expect to observe a spontaneous phase transition as long as it does not involve any large-scale rearrangements of atoms. However, if liquid $MgSiO_3$ phase-separates into a MgO-dominated and a SiO_2-rich fluid, as was predicted for the solid at approximately 1000 GPa [15], then we would most likely not be able to observe this process in our simulations. One would

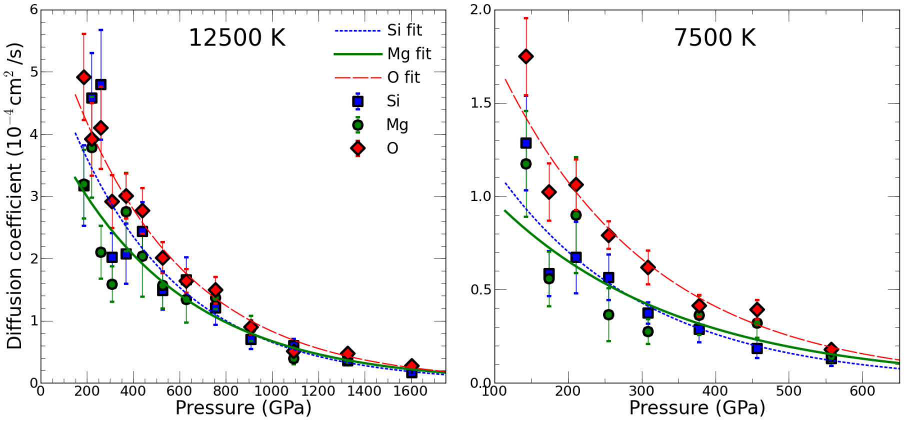

Figure 3: Diffusion coefficients of Mg, Si, and O ions as function of pressure for 7500 and 12500 K inferred from DFT-MD simulations. The lines show fits to an exponential function of pressure for each species.

instead need to perform more expensive Gibbs free energy calculations [16, 17, 18, 19, 20] but such a complex effort goes beyond this initial investigation.

Furthermore, if there existed a new, unknown phase in the $MgSiO_3$ phase diagram, it does not have to be a liquid. One could imagine a new stable solid phase that introduces a solid-solid-liquid triple point and lead to a sharp increase in the slope of the melting line. At zero temperature, existence of a post-post-perovskite phase has been intensely studied with *ab initio* random structure search algorithms and no such phase has been found but a new, entropy-stabilized phase may still exist at high temperature.

In principle, this triple point could also be between perovskite (PV) and PPV phases. The PV-PPV-liquid triple point has not been determined, neither with experimental no with theoretical means but PV-to-PPV transition pressure is known to increases with temperature.

One may also ask whether there exists an alternative interpretation for the experimental observations. Our first recommendation would be to repeat those measurements with steady shock wave experiments in order to verify the discontinuities on the principal Hugoniot curve of $MgSiO_3$. This may require a series of shock experiments with relatively small error bars but it would be an important confirmation.

There is also the possibility that observed shock velocity reversal is re-

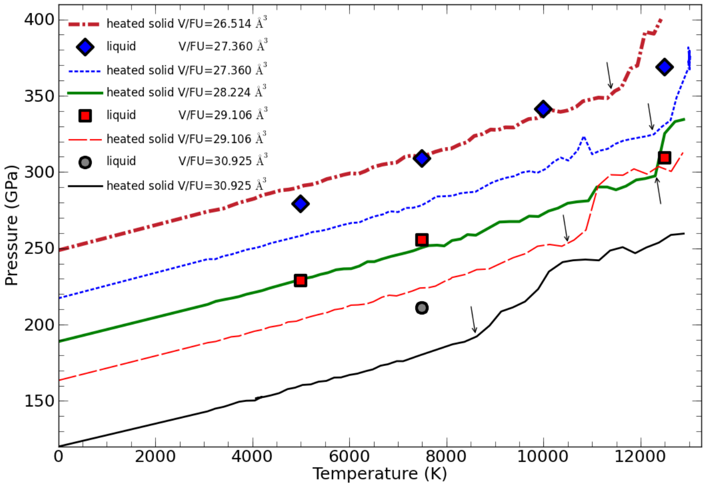

Figure 4: The pressure-temperature behavior during heat-until-it-melts simulations (lines) is compared with isothermal liquid simulations (symbols). The small arrows indicate the beginning of the melting transformation in the MD simulation. Liquid samples are found to always exhibit a higher pressure than solid ones at the same density.

lated to the melting transition of $MgSiO_3$. In principle, some material may freeze behind the shock front during the shock decay. This could introduce a secondary wave and affect the behavior of the shock front. For the predicted phase transition for single-crystal sample at 10000 K, this may be a more likely scenario than for the glass sample where the discontinuity was predicted at 16000 K. Nevertheless, we want to discuss the possibility of freezing during decaying shock wave experiments.

At the beginning of a decaying shock, the sample material is compressed to a state of high pressure and high temperature on the principal Hugoniot curve. As the shock decays, new material does not reach as high pressures and temperatures but stays on the Hugoniot curve, which allows one to map out the whole Hugoniot curve with just one shock measurement. The question is what happens to the material that had compressed to a higher P-T state earlier. Neglecting inertial forces, one may assume that the whole region behind the shock front will equilibrate to a new pressure, which we labeled P^* in Fig 5. Any parcel of material that was shocked to a high P-T state will adiabatically expand to reach P^* and slow down to travel at the new and

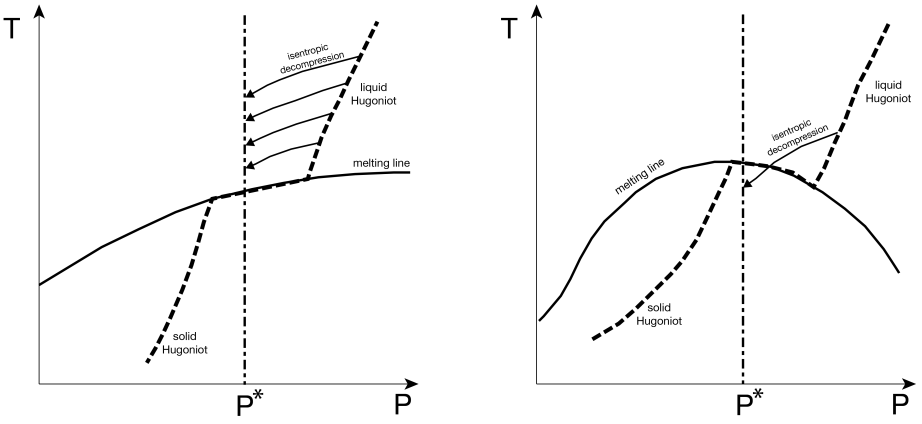

Figure 5: Temperature-pressure diagram with melting lines and shock Hugoniot curves. The arrows indicate the adiabatic and isentropic expansion of material during decaying shocks. The left graph shows a material with normal melting behavior, $dT_m/dP > 0$, while the right graph is for a material that exhibits a maximum along the melting line.

reduced shock velocity. Since this expansion is gradual and not associated with any shock, one typically also assumes that this expansion is isentropic (arrows in Fig. 5). While one assumes a new pressure, P^*, is established, the entire sample behind the shock front is not expected to reach thermal equilibrium during the experiment. This leads to the situation where hot material at a lower density is pushing on colder material at a higher density. This could lead to a fluid dynamic instability of Rayleigh-Taylor type if the density contrast becomes too high and the time scale is long enough for such an instability to develop.

Furthermore, it is important to note that Hugoniot curves are steeper in P-T space than isentropes, $\frac{\partial T}{\partial P}\big|_{\text{Hug}} > \frac{\partial T}{\partial P}\big|_{S}$. This makes explaining the observed shock velocity reversal very difficult if one wants to assume local thermodynamic equilibrium. The shock front on the Hugoniot curve would always enter any new thermodynamic phase, that may exist at lower temperature, before the hotter material behind the shock front reaches it.

Alternatively one may entertain the idea of non-equilibrium scenarios that involve supercooled liquids. In case of $dT_m/dP < 0$ that is shown on the right in Fig. 5, the material behind the shock wave enters a supercooled state before the shock front reaches the melting line. In this case, the entropy of the supercooled liquid is too high to be accommodated by any solid state at P^* and the material consequently freeze only partially. Since the solid would be at a lower density than the liquid, this could lead to an increase of the shock velocity if this information can be communicated to the shock front.

If a decaying shock wave reaches the melting line with a normal slope $dT_m/dP > 0$, a two-wave structure may still develop behind the shock front as parcels of material in a high entropy state are decompressed and partially freeze. A two-wave structure may occur for materials with normal melting behavior and for those with melting line maximum that we compare in Fig. 5. In both cases, the entropy of the liquid is always greater than in the solid. In regions with $dT_m/dP < 0$, the liquid is denser than the solid.

Whether a Rayleigh-Taylor instability exists, a new solid phase appears, a supercooled liquid introduces a secondary wave, or indeed a liquid-liquid phase transition is reason for the observed shock velocity reversal remains to be determined with future experiments. Concluding this theoretical investigation, we can report that our DFT-MD simulations to not support the hypothesis of a first-order liquid-liquid phase transition in $MgSiO_3$. We were not able to give an obvious alternative interpretation of the experimental findings but we do, however, suggest the measurements be repeated with steady shock waves. The experimental findings are very interesting nevertheless and will lead to a better understanding of magnesiosilicates at high temperature.

Acknowledgments

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References

[1] D. K. Spaulding *et al.*, Phys. Rev. Lett. 108 (2012) 065701.

[2] B. Militzer, F. Gygi, G. Galli, Phys. Rev. Lett. 91 (2003) 265503.

[3] M. A. Morales, C. Pierleoni, E. Schwegler, D. M. Ceperley, Proc. Nat. Acad. Sci. 107 (2010) 12799.

[4] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.

[5] P. E. Blöchl, Phys. Rev. B 50 (1994) 17953.

[6] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

[7] N. D. Mermin, Phys. Rev. 137 (1965) A1441.

[8] N. de Koker, L. Stixrude, Geophys. J. Int. 178 (2009) 162.

[9] G. Shen, P. Lazor, J. Geophys. Res. 100 (1995) 17699.

[10] A. Zerr, R. Boehler, Science 262 (1993) 553.

[11] J. A. Akins, S.-N. Luo, P. D. Asimow, T. J. Ahrens, Geophys. Res. Lett. 31 (2004).

[12] S.-N. Luo, J. A. Akins, T. J. Ahrens, P. D. Asimow, J. Geophys. Res. 109 (2004).

[13] Y. B. Zeldovich, Y. P. Raizer, Elements of Gasdynamics and the Classical Theory of Shock Waves, Academic Press, New York, 1968.

[14] C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, M. Bernasconi, M. Parrinello, Nature 283 (1999) 44.

[15] K. Umemoto, R. M. Wentzcovitch, P. B. Allen, Science 311 (2006) 983.

[16] D. Alfè, M. J. Gillan, G. D. Price, Nature 405 (2000) 172.

[17] M. Morales *et al.*, Proc. Nat. Acad. Sci. 106 (2009) 1324.

[18] H. F. Wilson, B. Militzer, Phys. Rev. Lett. 104 (2010) 121101.

[19] H. F. Wilson, B. Militzer, Astrophys. J 745 (2012) 54.

[20] H. F. Wilson, B. Militzer, Phys. Rev. Lett. 108 (2012) 111101.