Supporting Information

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SI Results and Discussion

Discussion of H2 Shock Hugoniot. At the time of our publication of the eFF description of the H2 shock Hugoniot in 2007, eFF agreed with experiments (2–4) and path integral Monte Carlo (PIMC) theory (5–7) up to 100 GPa, but eFF led to a compressibility 20% higher than PIMC for 100–200 GPa. More recent experiments in 2009 (8), shown as blue dots in Fig. S1 agreed with the eFF result that these is a large increase in the compressibility between 80 and 150 GPa, confirming the accuracy of eFF for extreme conditions. The initial Lawrence Livermore National Laboratory (LLNL) report (8) showed amazing agreement with the absolute compressibility predicted above 100 GPa, as shown in Fig. S1.

However more recently the Sandia National Laboratory (SNL) group Kudnuson and Desjarlais (9) reinterpreted the LLNL data, using a more accurate pressure standard based on a recalibration of the shock compression of quartz to 1.6 TPa: This ends up with the Hugoniot in Fig. S2, which retains the large increase in compressibility found in the eFF calculations, but now leads to disagreement with previous experiments in the region below 100 GPa. We are not aware that there has been any resolution of this disagreement in the experiments.

This increase in compressibility observed experimentally above 100 GPa was found in eFF to arise from the transition from molecular H2 to atomic H that occurs above 100 GPa in the Hugoniot. This LLNL experiments even with the SNL reinterpretation strongly supports the accuracy of eFF in predicting the phase transitions, but leaves open the question of the absolute accuracy of the eFF compressibility at high temperatures.

Comparison of Face-Centered Cubic (fcc) and Body-Centered Cubic (bcc) Phases. For the bcc structure, the electron force field (eFF) prefers to have each electron in a squashed octahedral site having six Li nuclei neighbors (four nuclei are \(\sqrt{2}/2a\) distant and two nuclei are 1/2u distant; a is the unit cell parameter), which is similar to the fcc phase where eFF leads to an electron in each octahedral site, with six Li nuclei neighbors at equal distances. For the fcc phase there is one such octahedral site per atom. However, in the bcc phase, there are three equivalent sites for each electron. Considering a \((4 \times 4 \times 4)\) bcc cell, there are 128 valence electrons to distribute among 384 octahedra, leading to a huge number of combinations. The exact quantum mechanical ground state would consider the optimum superposition (resonance) of these combinations, with correlations between them to prevent double occupation. The density functional theory (DFT) approximation would have approximately 64 occupied molecular orbitals per cell, leading to some problems with localized electrons interacting with themselves, which the exchange-correlation terms would aim to correct. The current eFF method keeps whole electrons in each localized orbital and must describe the resonance by hopping these orbitals from site to site. This will lead to some coupling of the electrons with the lattice, because each single configuration would like to distort the ions about the current positions of the electrons. Consequently, the current eFF leads to a minimized structure for finite supercells (e.g., 128 Li atoms) that distorts slightly. However the dynamical structure at 300 K for eFF leads to a pair correlation function and an X-ray diffraction pattern quite close to the bcc crystal structure but slightly distorted (Fig. S3). We anticipate that longer dynamics allowing cell dynamics with much longer cell damping constants would lead to an optimum structure with exactly the bcc overall cell size.

To assess how the structural distortion for the eFF description of bcc can be resolved by using a multiconfiguration wavefunction, we considered 500 different eFF electronic configurations. Here we fixed the nuclei positions at the bcc lattice sites, and carried out eFF minimizations only for the electrons using 500 randomly chosen initial electronic configurations. We then obtained the forces applied on the nuclei, which is the origin of the structural distortions. We compared these averaged forces to those from a single electronic configuration.

Fig. S4 shows the resolved forces on the 128 nuclei along x-direction (A), y-direction (B), and z-direction (C) for the single eFF configuration compared to the average over the 500 configurations. The forces from a single wavefunction fluctuate up to approximately 30 kcal/mol/Å, which would tend to distort the bcc structure. However, the consideration of multiple configurations (500 among 6128) dramatically reduces the applied forces to become almost zero, leading to a stable bcc structure.

For the fcc and cI16 phases more relevant to the high pressure phase, there is one available interstitial site per valence electrons, so that issues involving multiconfigurational wavefunction are negligible and eFF preserves the structures without distortions. This lack of distortion for model supercell sizes is the reason why we chose the fcc structure as our reference state for the Hugoniot calculation (but using the bcc density of 0.53 g/cm3).

We consider that this choice is reasonable because density functional theory studies show that the equilibrium density, equilibrium energy, bulk modulus, and its derivative with respect to pressure of bcc and fcc lithium are almost identical (11).

To clarify how different choices for the initial state affect the total shock Hugoniot curve, we show below the Hugoniot curve resulting from using the bcc structure as the initial structure. The bcc initial structure leads to a slightly larger pressure than for the fcc initial structure (Fig. S5). However, the differences are marginal (<8%) leading to a nearly identical shock Hugoniot curves.

Comparison of eFF Diffraction Pattern and Structure with Experiment. Fig. S6 compares the eFF predicted structures and calculated synchrotron X-ray diffraction patterns with experiment (10). We see excellent agreement.

eFF Isothermal Compression at Room Temperature Results. Fig. S7 shows the isothermal compression at room temperature. The black line in the top figure shows the equation of states (EOS) of more stable phase, which guides the eye to track the fcc-to-cI16 solid-solid transition curve during the isothermal compression (Lower). In the Inset, the EOS of fcc Li in the low pressure regime \((\rho \leq 0.9 \text{ g/cm}^3)\) is compared with the experimental results (11–13). At the bottom, we show the total energy per lithium atom during the 300 K isothermal compression is calculated using the initial structures of fcc Li and cI16 Li.

eFF Isothermal Compression at Room Temperature Results. The Pair correlation function \(g(r)\) in Fig. S8A shows a loss of order, with well-defined solid peaks vanishing as \(\rho\) is increased from 1.2 g/cm3 to 1.4 g/cm3. For consistency, \(g(r)\) is plotted as a function of the scaled distance, \(r/\rho\). The CN decreases from 12 (fcc) to 11 (cI16) to 9.29 (amor), showing the transition from fcc to cI16 to the amor phase. In contrast the CN of the liqd phase under low P is 16.1 indicating that the newly formed amor phase is distinct from the liqd phase. Fig. S8C shows that the third peak of \(g(r)\) disappears as \(\rho\) increases from 1.2 g/cm3 to 1.5 g/cm3.
which is quantified using the ratio of g(r) at the second minimum point to g(r) at the third maximum point. A rapid transition is observed at 1.32 g/cm³, which we consider as the transition point from cI16 to amor (intercept with the line y = 0.5).

**Diffusion.** Fig. S9 shows the mean square displacements (MSD) of nuclei of four different phases; The fluidity of amor phase is about 2/3 that of liqd phase, but 2.5 times larger than that of the solid fcc or cI16 phases.

**Isothermal Compression at 10,000 K, Case 2.** Fig. S10 shows the results of isothermal compression at 10,000 K (Case 2 of Fig. 2). The new distinctive peak appears at r/rs = 2.56, becomes more significant at higher compression. This indicates the formation of an inner shell structure during the liqd-to-amor phase transition. This is supported by the change of CN during the isothermal compression at 10,000 K, which drops near ρ = 1.0 g/cm³ due to the formation of the inner. Under low compression, valence electron of liqd phase is coordinated by approximately 6 Li⁺ nuclei. Under high compression, the Li CN increases until approximately nine suggesting that the compression induces more significant IE–Li interaction while sacrificing the Li–Li interaction (which results in inner shell formation). This is very similar to the phase transition from fcc to cI16 (compare Li CN of fcc and cI16 are six and eight, respectively).

**Diffusion of Electrons.** Fig. S11 shows the change of MSD of interstitial electrons (IEs) during liqd-to-amor phase transition at 10,000 K. The substantial suppression of MSD at the phase transition from liqd-to-amor suggests that the IEs of amor phase is more localized than that of liqd phase.

Reinterpretation of the LLNL data (8) by SNL (9). At the time of the report in 2007, the eFF agreed with experiments (2–4) and PIMC theory (5–7) up to 100 GPa, but eFF led to a compressibility 20% higher than PIMC for 100–200 GPa. More recent experiments in 2009 (shown as blue dots) (8), however, agree with the eFF results that there is a large increase in the compressibility between 80 and 150 GPa, confirming the accuracy of eFF for extreme conditions. This increase in compressibility observed experimentally above 100 GPa was found in eFF to arise from the transition from molecular H$_2$ to atomic H that occurs above 100 GPa in the Hugoniot.

Fig. S3. (Upper) Pair correlation function, g(r) is computed from the 0.5 ps eFF dynamics of 0.53 g/cm$^3$ bcc structure (red line). For the comparison, g(r) of the bcc crystal is shown simultaneously (black line). (Lower) Calculated synchrotron X-ray diffraction patterns ($\lambda = 0.4124$ Å) of 0.53 g/cm$^3$ bcc structure at 300 K. One hundred diffraction patterns from 100 snapshots generated from 0.5 ps eFF dynamics are averaged (red line). For the comparison, X-ray diffraction pattern of the bcc crystal is shown simultaneously (black line).
Fig. S4. Comparison of (A) x-directional, (B) y-directional, and (C) z-directional forces applied on the nuclei from the single wavefunction description and from the multiconfigurational wavefunction description. To generate multiconfigurational wavefunction, 500 randomly chosen initial electronic configurations were minimized using eFF, then, the averaged forces were calculated.

Fig. S5. Shock Hugoniot curve for solid Li computed from eFF dynamics when bcc is used as an initial phase (red circles and line) and fcc is used as an initial phase (black circles and line). Regardless of the initial phases, the shock Hugoniot curves are almost identical.
Fig. S6. The eFF predicted structures and calculated synchrotron X-ray diffraction patterns: (A) 0.53 g/cm$^3$ of fcc Li at 300 K; (B) 1.3 g/cm$^3$ of cI16 Li at 300 K. For each diagram, 100 diffraction patterns from 100 snapshots generated from 0.5 ps eFF dynamics are averaged. The wavelength is set by 0.4124 Å for the direct comparison to the experimental data from ref. 10.

Fig. S7. Isothermal compression at room temperature. (Upper) Black line shows the EOS of more stable phase, which guides the eye to track the fcc-to-cI16 solid-solid transition curve during the isothermal compression (Lower). In the Inset, the EOS of fcc Li in the low pressure regime ($\rho \leq 0.9$ g/cm$^3$) is compared with the experimental results (11–13) (Lower) Total energy per lithium atom during the 300 K isothermal compression is calculated using the initial structures of fcc Li and cI16 Li.
Fig. 58. (A) Pair correlation function $g(r)$. This shows a loss of order, with well-defined solid peaks vanishing as $\rho$ is increased from 1.2 g/cm$^3$ to 1.4 g/cm$^3$. For consistency, $g(r)$ is plotted as a function of the scaled distance, $r/\rho_s$. (B) The CN decreases from 12 (fcc) to 11 (cI16) to 9.29 (amor), showing the transition from fcc to cI16 to the amor phase. In contrast the CN of the liq phase under low P is 16.1 indicating that the newly formed amor phase is distinct from the liq phase. (C) The third peak of $g(r)$ disappears as $\rho$ increases from 1.2 g/cm$^3$ to 1.5 g/cm$^3$, which is quantified using the ratio of $g(r)$ at the second minimum point to $g(r)$ at the third maximum point. A rapid transition is observed at 1.32 g/cm$^3$, which we consider as the transition point from cI16 to amor (intercept with the line $y = 0.5$).

Fig. 59. MSD of nuclei of four different phases. (i) Blue solid line: fcc phase ($\rho = 1.0$ g/cm$^3$, $T = 1,718$ K). (ii) Green solid line: cI16 phase ($\rho = 1.3$ g/cm$^3$, $T = 4,009$ K). (iii) Red solid line: amor phase ($\rho = 1.5$ g/cm$^3$, $T = 9,347$ K). (iv) Orange dashed-double dotted line: liq phase ($\rho = 0.53$ g/cm$^3$, $T = 9,388$ K). The fluidity of amor phase is about 2/3 that of liq phase, but 2.5 times larger than that of the solid fcc or cI16 phases.

Fig. 510. Isothermal compression at 10,000 K (Case 2 of Fig. 2). (A) Change of pair correlation function during the isothermal compression at 10,000 K. At $\rho = 1.0$ g/cm$^3$, a new distinctive peak appears at $r/\rho_s = 2.56$, which becomes more significant at higher compression. This indicates the formation of an inner shell structure during the liq-to-amor phase transition. (B) Change of CN during the isothermal compression at 10,000 K. Due to the formation of the inner shell a large drop of the CN is observed near $\rho = 1.0$ g/cm$^3$. (C) Change of nuclei coordination number (CN) of the interstitial electron during the isothermal compression at 10,000 K. Under low compression, valence electron of liq phase is coordinated by approximately 6 Li$^+$ nuclei. Under high compression, the Li CN increases until approximately nine suggesting that the compression induces more significant IE-Li interaction while sacrificing the Li-Li interaction (which results in inner shell formation). This is very similar to the phase transition from fcc to cI16 (compare Li CN of fcc and cI16 are six and eight, respectively).
Fig. S11. Change of MSD of IEs during liq-d-to-amor phase transition at 10,000 K. The phase transition from liq-d-to-amor leads a substantial suppression of MSD, which infers that the IEs of amor phase is more localized than that of liq-d phase.