

1 **On the liquid-liquid phase transition of dense hydrogen**

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Until recently the consensus theory/computation interpretation of the challenging liquid-liquid phase transition (LLPT) of high-pressure hydrogen was first order [1-5]. Cheng *et al.* [6] developed a machine-learned potential (MLP) that, in larger molecular dynamics (MD) simulations, gives a continuous transition instead. We show that the MLP does not reproduce our still larger MD density-functional theory (MD-DFT) calculations as it should. Since the MLP is not a faithful surrogate for the MD-DFT, the Ref. 6 prediction of a supercritical atomic liquid is unfounded.

Prior MD-DFT calculations differ but, for example, our results on $700 \leq T \leq 3000$ K are a curve along $320 \leq P \leq 70$ GPa [2]. Driven by molecular H_2 dissociation, transition signatures include density jumps, qualitative sharp changes in ionic pair correlation functions (PCFs), and abrupt dc conductivity and reflectivity changes. Coupled-electron ion Monte Carlo (CEIMC) [5] results concur at least roughly and there is reasonable agreement with experiment.

The continuous transformation found in Ref. [6] has an atomic liquid that goes supercritical above $P \approx 350$ GPa, $T \approx 400$ K. They attributed the dramatic differences versus MD-DFT to two causes which the MLP is expected to address. One is finite size effects that foster the formation of defective solids, with the common use of NVT dynamics tending to increase defect concentration compared to that from the NPT ensemble. The other is much shorter simulation times in the MD-DFT and CEIMC calculations than possible for MD-MLP runs.

Those diagnoses implicate other issues. Most of the MLP training was on $N \leq 108$ atoms

(1,833 512-atom configurations were used out of 38,716 total per Cheng et al. Supp. Info.[6]). That raises questions of large-system transferability. Conceptually the issue is whether a single MLP can represent two chemically distinct regimes (molecular, atomic) correctly. An unambiguous test is to do longer MD-DFT runs on significantly larger systems. If the MD-MLP represents the underlying theory (*ab initio* MD) faithfully and if the diagnosis based on MD-MLP is correct, results from the two simulation types should match. To test that, we have done much larger, longer MD-DFT calculations. The results are consistent with earlier MD-DFT calculations, thus qualitatively different from the MD-MLP results. Neither the large system nor longer run diagnosis from MD-MLP is sustained.

Our *NPT* MD simulations were driven by DFT forces with PBE exchange-correlation (XC) [7]. (Ref. [6] used PBE to train the MLP.) We used from 256 through 2048 atoms per cell. Brillouin zone sampling used the Baldereschi mean value point for the simple cubic crystal structure $\mathbf{k} = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ [8]. Vasp [9, 10] was used for 1024 and 2048 atom systems, while the i-PI interface [11] with QuantumEspresso [12] was used for 256 and 512 atoms. Consistent results from the two confirm that the MD code and technical choices (thermostat, barostat, etc.) are inconsequential.

Our new large-system MD-DFT results agree with prior MD-DFT and CEIMC simulations [2, 3, 13]: there is a sharp molecular-to-atomic transition. Fig. 1 shows the qualitatively different character versus the MD-MLP prediction. The left-column panels show density profiles $\rho_H(T)$ along isobars. At 350 and 300 GPa, the large-scale MD-DFT $\rho_H(T)$ values jump $\approx 1\%$ near $T = 650$ K. At 300 GPa, that is above the experimental melting temperature T_m [14]. In contrast, the 300-GPa MD-MLP isobar has a steep density increase near $T = 500$

K (in the stable solid phase) [6], but passes smoothly through both the melt line and the LLPT. Except for a systematic offset, the MD-MLP $\rho_H(T)$ matches the MD-DFT $\rho_H(T)$ in the atomic fluid region.

Figure 1 also shows clearly that there are *no important finite-size effects* on the calculated LLPT. The MD-DFT density profiles on each of the isobars ($P = 250, 200, 150$, and 100 GPa) are almost identical *irrespective* of atom count, 256 – 2048. The MD-MLP profiles.

FIG. 1. Comparison of MD results from the PBE XC-based MLP and *ab initio* MD-DFT (DFT) *NPT* simulations. Left column panels (a): Hydrogen density as function of T along six isobars. Experimental melting temperature T_m for each isobar is shown by a vertical dashed line [14]. Middle column panels (b): Molar heat capacity as a function of T along the isobars. Right column panels (c): Pair correlation function (PCF) for each isobar for two temperatures below the density jump and two above.

are *qualitatively* different. We find the transition character to be insensitive to system size while the transition temperature T_{LLPT} is affected only modestly. For example, at $P = 200$ GPa (for which T_{LLPT} is distinctly away from the melting line) going from 256 to 2048 atoms decreases T_{LLPT} by less than 100 K; ρ_H values jump $\approx 3\%$ in MD-DFT simulations for all system sizes. Computational resources limited us to 512 atoms for 300 and 350 GPa but that does not vitiate the clear finding on the other four isobars: the MLP-DFT does not reproduce the underlying MD-DFT. Note that a 512 atom system seems to be the smallest sufficient to control finite-size effects. That agrees with Ref. [15]: four well-defined molecular shells in the PCF of a 3456-atom system were captured well in a 500-atom supercell calculation.

The molar heat capacity from MD-DFT as a function of T is shown in Fig. 1, middle column. All the isobars exhibit divergent heat capacity character across the transition. Evidently

finite-size effects on T_{LLPT} are small and do not modify that character. To check on the possibility that finite-size effects trapped our simulations in defective solid configurations, we calculated the mean-squared displacement (MSD) of the 512 atom systems as a function of time along the 150 and 200 GPa isobars for $1100 \leq T \leq 1400\text{K}$ and $900 \leq T \leq 1200\text{K}$ respectively. The MSD grows near-linearly with time, as is characteristic of a liquid but not a solid. See Supplemental Information for details and figures.

Figure 1 right-hand column shows the PCF on each isobar at temperature pairs below and above the density jump. Above, the first PCF peak virtually disappears, confirmation of the density jump being in conjunction with the molecular dissociation [2].

To test possible long simulation duration effects on T_{LLPT} or its character, we did up to six sequential MD-DFT runs of roughly 1.8-ps duration each for a total of ≈ 10 -ps duration. This was at 200 GPa with 512 and 2048 atoms. There were no meaningful differences in the results in either case. This outcome agrees with that of Geng et al. [15] who did runs up to 6 ps and found no meaningful differences with respect to 1.5 ps (after equilibration).

To investigate whether the nanosecond timescale might make the simulated transition smooth, we performed a set of 2048-atom MD-DFT *NPT* simulations beginning with the atomic fluid at 200 GPa. Starting at 950 K, we cooled the system in sequential runs to

FIG. 2. The LLPT boundary from the present large-scale MD-DFT (DFT/PBE) simulations compared to MLP (MLP/PBE) C_p^{max} and ρ^{max} curves.

899, 849, and 824 K with simulation duration around 8 ps for each temperature. If the nanosecond timescale were to yield a smooth transition, the hydrogen density during such

a fast cooling curve would not drop sharply below the hypothetical smooth long-duration curve. But, as evident in the Fig. 1 density plot at 200 GPa (left column), the cooling curve (thin blue curve, circles), is almost identical to the one from MD-DFT simulations when the molecular fluid T is increased gradually (sharp transition shown by the solid orange curve).

Figure 2 shows the LLPT curves associated with density jumps, heat capacity peaks, and PCF peak disappearance. For the new large-scale MD-DFT calculations, those three criteria give one curve (virtually identical P, T values; small differences in the transition temperature (less than 100 K for $P \leq 150$ GPa) are caused by numerical errors in calculating the molar heat capacity using finite differences), shown in red with squares at data points. Two MD-MLP curves emerge from the analysis, however, one for the location of molar heat capacity maxima C_P^{\max} , and another for the maximum density, ρ^{\max} . Consistent with the foregoing discussion, there are striking differences. The MLP C_P^{\max} curve lies well below the MD-DFT curve. The MLP ρ^{\max} curve is flatter than the MD-DFT reference curve and lies close to it only at about $P = 70$ GPa, $T = 2800$ K and then again for P between about 170 and 300 GPa.

Given that neither the finite-size nor simulation duration diagnosis advanced in Ref. 6 is sustained by direct calculation, the only plausible remaining source of the different physics they found must be the MLP. The detailed origins seem obscure. We did find evidence (see Supplemental Information) in the Supp. Info. to Ref. 6 that the MLP does not reproduce the behavior (be it physical or not) of several MD-DFT calculations. In addition to the stark LLPT differences discussed here, such deviations are consistent with the assessment that the MLP is not systematically related to the physics of a well-defined Born–Oppenheimer electronic structure treatment of the H system. Instead it seems to be consistent, at least, with the MLP

being a single interpolative, approximate representation of the electronic structure of two chemically distinct regimes (molecular, atomic) of the hydrogen liquid.

We conclude that the MD-MLP results for the LLPT do not reproduce the fundamental MD-DFT results as they should. Up to 2048 atoms and 10 ps simulation duration, our results are consistent with the earlier sub-critical behavior predictions. The basic inconsistency of the MD-MLP numerical data with the MD-DFT results would seem to make any subsequent analysis of the MD-MLP data ill-founded. It is at least plausible that the supercritical behavior finding may be an artifact of a disconnect of the MLP from electronic structure differences inherent in the chemistry of the LLPT.

Data availability

The data that support the findings shown in the figures are available from the corresponding author upon reasonable request.

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Conflict of interests The authors declare that they have no conflicts of interest.

Additional information

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