

# Elucidation of the subcritical character of the liquid–liquid transition in dense hydrogen

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Determining the liquid–liquid phase transition (LLPT) in high-pressure hydrogen is a longstanding challenge with notable variation in experimental and calculated results. See Refs. 1–4 and works cited therein for both calculational and experimental developments. Until recently, the computational consensus was for a first-order transition. Calculated values differed but, for example, our results on  $700 \leq T \leq 3000$  K are a curve along  $320 \geq P \geq 70$  GPa [2]. Driven by molecular  $H_2$  dissociation, transition signatures include density jumps, qualitative and 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 with those from *ab-initio* molecular dynamics driven by consistent density functional theory (MD-DFT) [2] and show reasonable agreement with experiment also.

In marked contrast, Cheng et al. [6] found a continuous transformation from a molecular to an atomic liquid that goes supercritical above  $P \approx 350$  GPa,  $T \approx 400$  K. They used MD driven by a machine-learned potential (MLP). They attributed the dramatic differences versus MD-DFT to two causes. One is finite size effects that foster the formation of defective solids, with the common use of *NVT* dynamics tending to increased defect concentration compared to that from the *NPT* ensemble. The other is much shorter simulation times in the MD-DFT and CEIMC calculations than in the MD-MLP ones.

Those diagnoses implicate other issues. Almost all of the MLP training was on small systems ( $N \leq 108$  atoms). That raises questions of large-system transferability. Conceptually there is the question of whether a single MLP can represent two distinct chemical regimes (molecular, atomic) correctly. The straightforward way to test both the two diagnoses (system size and duration limits) and their implications is against much larger, longer MD-DFT calculations. We have done such calculations and find that neither diagnosis is sustained.

We investigated with *NPT* MD simulations driven by DFT forces with PBE exchange-correlation [7]. (PBE

was used in Ref. [6] to train the MLP.) We used system sizes 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 QUANTUM ESPRESSO [12] was used for 256 and 512 atoms. Consistent results from the two shows that the MD code and technical choices (thermostat, barostat, etc.) are inconsequential.

Our new large-system MD-DFT results agree with previous DFT-based and CEIMC simulations [2, 3, 13]: there is a sharp molecular-to-atomic transition. The qualitatively different character compared with what comes from the MD-MLP is shown in Fig. 1. 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, this is above the 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 that 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 unequivocally that there are *no important finite-size effects* on the calculated LLPT. The density profiles on each of the isobars ( $P = 250, 200, 150$ , and 100 GPa) are almost identical *irrespective of atom count* (256, 512, 1024, or 2048). The transition character is insensitive to system size and specific technical choices of the MD code used, while the transition temperature  $T_{LLPT}$  is affected only modestly. At  $P = 200$  GPa, for example, going from 256 to 2048 atoms decreases  $T_{LLPT}$  by less than 100 K;  $\rho_H$  values jump  $\approx 3\%$  in MD-DFT simulations for all system sizes. A 512 atom system seems adequate to eliminate any major finite-size effects. This outcome agrees with Ref. [15]. Those authors found that four well-defined molecular shells in the PCF of a 3456-atom system were captured quite 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. They confirm that finite-size effects on  $T_{LLPT}$  are small and do not modify that character.

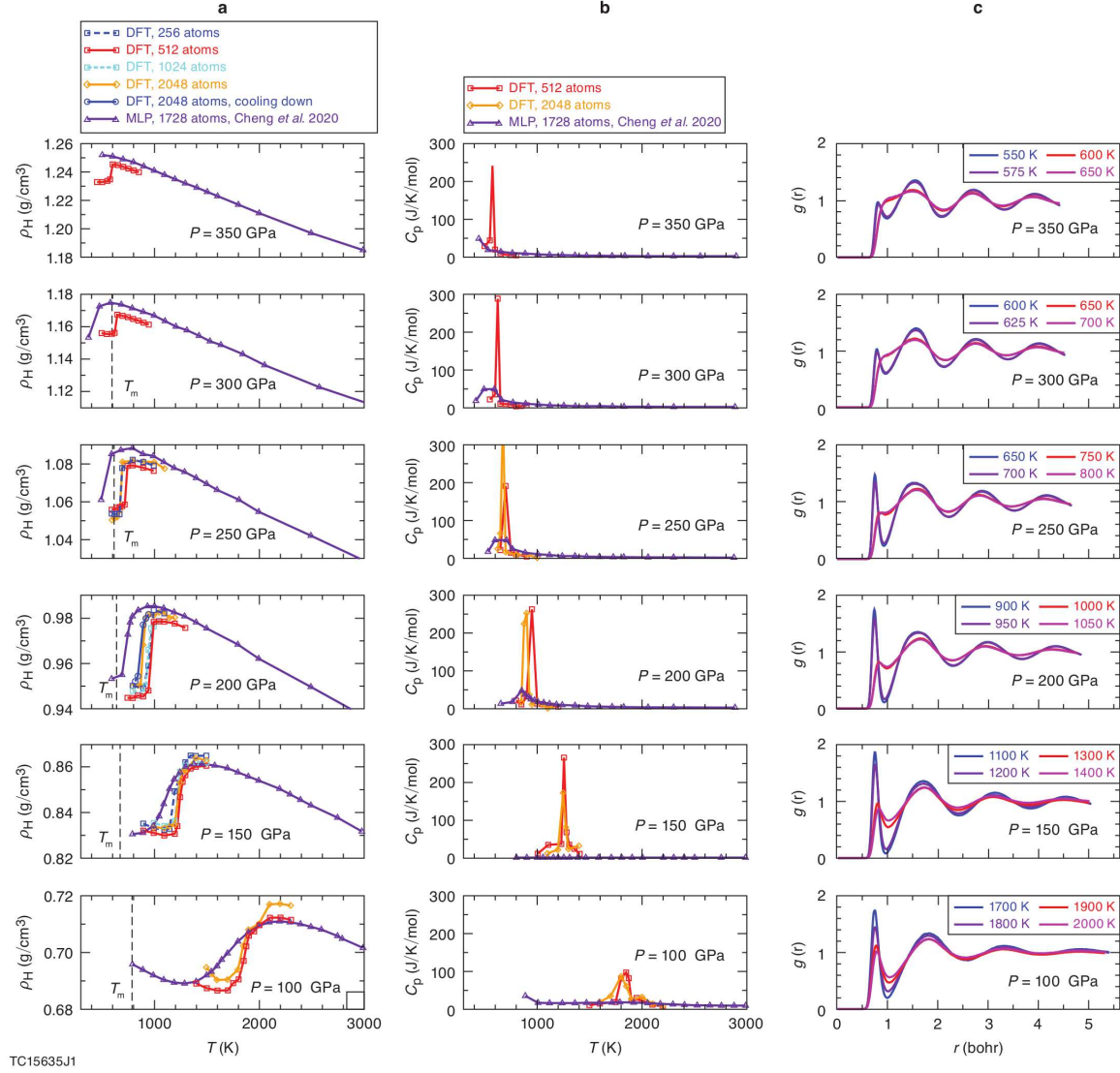


FIG. 1. Comparison of MD results from the PBE exchange-correlation-based machine-learning potential (MLP) and *ab initio* MD-DFT (DFT) *NPT* simulations. Left column panels (a): Hydrogen density as function of  $T$  along six isobars. Melting temperature  $T_m$  for each isobar is shown by a vertical 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.

Figure 1 right-hand column shows the PCF on each isobar at pairs of temperatures 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  $\approx 10$ -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 the results 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 899, 849, and 824 K with simulation durations 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

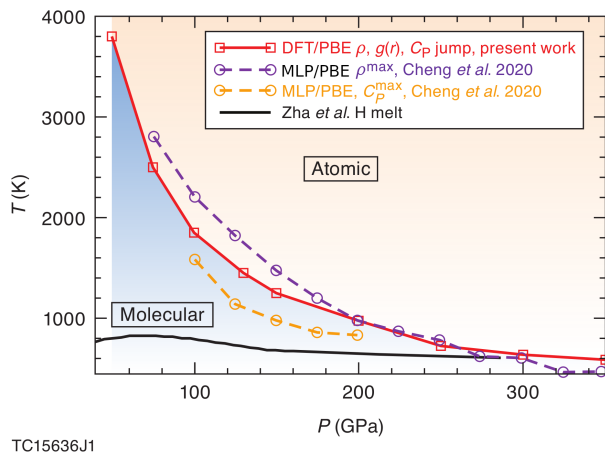


FIG. 2. The LLPT boundary from the present large-scale MD-DFT (DFT/PBE) simulations compared to MLP (MLP/PBE)  $C_P^{\max}$  and  $\rho^{\max}$  curves.

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 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), 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,  $\rho^{\max}$ . Consistent with the foregoing discussion, there are striking differences. The MLP  $C_P^{\max}$  curve lies well below the MD-DFT curve. The MLP  $\rho^{\max}$  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 effect nor simulation duration diagnosis advanced by Cheng et al. [6] is sustained by our direct exploration, the remaining plausible cause of the different physics they found must be in the MLP. The detailed origin of that different physics is a bit obscure. However, as discussed in our Supplemental Information, documentation in the Supplemental Information to Ref. 6 confirms that the MLP does not reproduce the behavior (be it physical or not) of several MD-DFT calculations. Those differences, in addition to the stark LLPT differences discussed here, confirm that the MLP is not systematically related to the physics of a well-defined Born–Oppenheimer electronic structure treatment of the H system. The MD-MLP results instead are consistent, at least, with the MLP being a single interpolative, ap-

proximate representation of the electronic structure of two chemically distinct regimes (molecular, atomic) of the hydrogen liquid.

We conclude that the numerical evidence for supercritical behavior of high-pressure liquid hydrogen based on the approximate MLP simulations is unsupported by MD-DFT simulations on much larger systems for significantly longer durations. The diagnosis of the difference between MD-MLP and MD-DFT calculations as being from size and duration effects is mistaken. Rather, the supercritical behavior found in the MD-MLP calculations seems plausibly to be an artifact of a disconnect of the MLP from underlying 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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**Author contributions** V.V.K. conceived the project initially and designed the study. V.V.K. and J.H. performed the MD-DFT simulations and post-processed the data. V.V.K. wrote the initial manuscript. S.B.T. revised the conception and scope. V.V.K. and S.B.T. rewrote the manuscript. All authors discussed the results and revised the paper extensively.

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

## Additional information

**Supplementary information** is available for this paper at <https://doi.org/10.1038/xx>

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