

Hydrogen-helium immiscibility boundary in gas-giant planetary interiors from machine-learning molecular dynamics

Received: 8 November 2025

Accepted: 14 August 2026

Published online: 01 September 2026

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The location of the hydrogen-helium (H/He) immiscibility boundary controls whether and where helium rain occurs in giant planets, yet it remains uncertain because high-pressure experiments are challenging and ab initio simulations are limited in system size and simulation time. We map this boundary by computing composition-dependent chemical potentials from large-scale molecular dynamics driven by machine learning potentials trained on three density functional approximations (PBE, vdW-DF, and the hybrid HSE). Across the pressure range of 100–1000 GPa, the demixing temperatures are typically ~2000 K lower than previous ab initio simulations using small system sizes, and this discrepancy is larger than the estimated error from the chosen density functionals, machine learning potentials, neglect of nuclear quantum effects, and statistical uncertainties. Fitting the H/He mixing free energy to a Redlich-Kister regular solution model rationalizes the thermodynamic driving force for phase separation, and provides a predictive representation of the boundary. Comparing with current planetary interior profiles indicates that helium rain is plausible in Saturn but unlikely in the warmer interior of Jupiter. Our results narrow the uncertainty in the H/He immiscibility boundary and provide inputs for planetary models that couple demixing, heat transport, and composition gradients in gas giants.

Gas giants such as Jupiter, Saturn, and Jovian extrasolar planets are composed predominantly of hydrogen and helium¹. In the deep interiors of these planets at hundreds of gigapascals and thousands of kelvins, helium is hypothesized to become immiscible in hydrogen and to precipitate as helium-rich droplets that sink toward the planetary interior under gravity. This phase separation and subsequent gravitational settling of helium-rich components are commonly referred to as “helium rain”^{2–5}. We use “helium rain” in the conventional astrophysical sense to denote the precipitation and gravitational settling of helium-rich droplets, not a cyclic meteorological process. This mechanism can help reconcile a spectrum of observations from Voyager⁶, Pioneer⁶,

Juno⁷, and Cassini⁸ missions: The rainout of He-rich droplets from outer envelopes would account for the atmospheric helium depletion⁹ in Jupiter¹⁰ and Saturn¹¹, relative to the protosolar helium atomic fraction of $x_{\text{He}} = 0.089$ ^{12,13}. The gravitational energy released by falling droplets provides an additional heat source that helps explain the excess luminosity of Jupiter¹⁴ and Saturn³. Moreover, the resulting compositional stratification of He-rich mixtures can create distinct layered structures within the planets, altering their internal structures, dynamics, and magnetic fields^{4,15–18}.

While the hypothesis of helium rain is incorporated into the current planetary models for Jupiter and Saturn^{16,18}, all these models

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remain speculative due to the large uncertainty about the H/He immiscibility boundary. For example, several Jupiter models suggest the presence of 3 to 6 distinct interior layers, all of which are consistent with the gravity field data of Juno, despite varying structural assumptions¹⁶. The extreme planetary P - T conditions pose tremendous experimental challenges, leading to limited data along the immiscibility boundary: Only one high-pressure experimental study on H/He demixing with laser-shock¹⁹ is currently available, which reports a demixing temperature of 10,200 K at 150 GPa for a H/He mixture of $x_{\text{He}} = 0.11$. Theoretical calculations based on quantum mechanics^{20–25} have thus played an important role in determining the immiscibility boundary: Most ab initio molecular dynamics (AIMD) studies based on density functional theory (DFT) predict that H/He demixing occurs at 5000–6000 K under 150 GPa^{23,24} for $x_{\text{He}} \approx 0.09$. There are several challenges in the ab initio modeling of H/He demixing. First, DFT relies on approximations of the exchange-correlation (XC) functionals which can cause systematic errors in describing atomic interactions^{26–30}, and the effect of such approximations on the H/He immiscibility remains unclear^{1,24,25,31}. Second, estimating the non-ideal entropy of mixing requires computationally demanding free energy calculations such as thermodynamic integration (TI)^{21,24}. Third, DFT studies are often constrained to system sizes of a few hundred atoms and simulation durations of a few picoseconds due to the computational expense. The finite size effects can be significant, especially for phase transition phenomena^{32,33}. Recently, machine learning potentials (MLPs) have been introduced to overcome this obstacle by first learning atomic interactions from DFT energies and forces of training configurations³⁴, and subsequently driving large-scale MD simulations. A recent study using MLPs reports much higher demixing temperatures up to 8500 K at 150 GPa²⁵.

Here, we perform large-scale MD simulations driven by three sets of MLPs that are trained based on three different DFT functionals: the Perdew-Burke-Ernzerhof (PBE)³⁵ and van der Waals density functional (vdW-DF)³⁶, which are both widely used for such high-pressure mixtures, and the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional^{37,38} for its inclusion of exact exchange and superior performance in benchmark studies³¹. We benchmark the MLPs based on energetic, structural, and thermodynamic properties, as detailed in Supplementary Table S1 and Supplementary Figs. S3–S8. We explore a broad range of P - T conditions (P : 100–1000 GPa; T : 1000–12000 K) that span the typical interior conditions of gas giants. We accurately account for the thermal fluctuations with entropic effects by computing the chemical potentials (μ) at different helium concentrations using the SO method³⁹. We then use a Redlich-Kister regular solution model⁴⁰ to rationalize the thermodynamic driving force behind H/He phase separation, and to help understand the discrepancies with previous AIMD studies^{21–24}. Finally, we discuss the implications of our findings for the evolution of Jupiter and Saturn by juxtaposing our results with current planetary models^{18,24,41–44}.

Results

Machine learning potentials for H/He mixtures

We constructed MLPs for simulating the phase behaviors of H/He mixtures under planetary conditions (10^2 – 10^3 GPa and 10^3 – 10^4 K). Separate MLPs were fitted to data generated with PBE, vdW-DF, and HSE, in order to understand the impact of the underlying XC approximations. The vdW-DF training set comprises 13,389 configurations with varying helium fractions across a broad range of P - T conditions (1–1200 GPa and 500–16000 K), which was generated via a combination of strategies: AIMD simulations, random structure searches, active learning, and adapting from previous AIMD calculations for high-pressure H/He mixtures²⁴. We obtained the training set for the PBE MLP by recomputing the PBE energies and forces for all these configurations, as well as supplementing with a previous pure hydrogen training set³². To make the DFT computational cost of generating the training

set for the HSE MLP tractable, we employed a Δ -learning strategy⁴⁵ that treats the vdW-DF MLP as a baseline and learns the difference between vdW-DF and HSE energy surfaces ($\Delta(\text{vdW-DF} \rightarrow \text{HSE})$). Specifically, we selected ~2000 configurations from the full training set, recomputed their HSE energies and forces, and fitted the Δ -learning HSE MLP. The production HSE MLP adds the Δ -learning MLP $\Delta(\text{vdW-DF} \rightarrow \text{HSE})$ to the baseline vdW-DF MLP. As a validation of this Δ -learning strategy, we built an analogous $\Delta(\text{PBE} \rightarrow \text{vdW-DF})$ potential using the PBE MLP as a baseline, and compared it to the direct-learning vdW-DF MLP.

There are many MLP architectures available⁴⁶, with different trade-offs between computational efficiency and predictive accuracy. For the vdW-DF dataset, we tested three MLP architectures: the parallelizable and CPU-efficient N2P2⁴⁵, the more recent and accurate MACE⁴⁷ and CACE⁴⁸ models, as detailed in Methods. The performance of each fitted MLP was validated by comparing its predicted equations of state (EOSs) and radial distribution functions (RDFs) against reference DFT data over a wide range of pressures (100–1200 GPa) and temperatures (2000–10000 K). Even though N2P2 gives approximately twice the energy and force errors as MACE and CACE, the three vdW-DF MLPs trained on these architectures, as well as the aforementioned $\Delta(\text{PBE} \rightarrow \text{vdW-DF})$ MLP, yield EOS and RDF results that are consistent with vdW-DF AIMD results, as detailed in the Supplementary Figs. S3–S8. As an illustration, the pressure-density (P - ρ) relationship is presented for five H/He mixtures ($x_{\text{He}} = 0, 0.25, 0.5, 0.75$, and 1.0, color coded) at $T = 2000$ K (Fig. 1a), 6000 K (Fig. 1b), and 10000 K (Fig. 1c), and these four MLPs produce nearly identical pressure values matching the vdW-DF AIMD data²⁴. These results confirm that all the MLPs are sufficiently accurate for these thermodynamic properties.

Chemical potentials of H and He in the mixtures

We applied the direct-learning vdW-DF MLPs based on N2P2, MACE, and CACE in large-scale MD simulations, and checked the influence of MLP architecture on predicting H/He demixing behaviors. Two sets of thermodynamic conditions representative of planetary conditions, $T = 5000$ K, $P = 150$ GPa, and $T = 7000$ K, $P = 800$ GPa, were used. The H/He mixture shows distinct behaviors: As illustrated in Fig. 1d, h, the system is fully mixed at $T = 5000$ K, $P = 150$ GPa, and shows phase separation at $T = 7000$ K, $P = 800$ GPa.

To compute the chemical potentials of the H/He mixture, we employed the SO method³⁹, which circumvents the convergence issue of traditional particle insertion methods⁴⁹. At certain P - T and for a given composition, the derivative of the chemical potential of helium (μ_{He}) with respect to composition $(\partial\mu_{\text{He}}/\partial \ln x_{\text{He}})_{T,P}$ is given by the SO method:

$$\left(\frac{\partial\mu_{\text{He}}}{\partial \ln x_{\text{He}}}\right)_{T,P} = \frac{k_{\text{B}}T}{x_{\text{H}}S_{\text{He-He}}^0 + x_{\text{He}}S_{\text{H-H}}^0 - 2\sqrt{x_{\text{H}}x_{\text{He}}}S_{\text{H-He}}^0}, \quad (1)$$

where $S_{\text{He-He}}^0$, $S_{\text{H-He}}^0$, and $S_{\text{H-H}}^0$ are the static structure factors between different pairs of atoms in the limit of infinite wavelength^{50,51}.

At $T = 5000$ K, $P = 150$ GPa, and $T = 7000$ K, $P = 800$ GPa, we ran equilibrium NPT MD simulations using a system size of 3456 atoms, driven by the three vdW-DF MLPs with different architectures. We sampled a series of compositions with the helium atomic fraction, x_{He} , ranging from 0.015 to 0.98 in 26 intervals. The computed chemical potential derivatives $(\partial\mu_{\text{He}}/\partial \ln x_{\text{He}})_{T,P}$ are shown in Fig. 1e, i. The N2P2, MACE, and CACE results agree well for both conditions. Notably, the computed $(\partial\mu_{\text{He}}/\partial \ln x_{\text{He}})_{T,P}$ at $T = 7000$ K, $P = 800$ GPa (Fig. 1i) exhibits a near-zero plateau between $x_{\text{He-poor}} = 0.19$ and $x_{\text{He-rich}} = 0.77$ (dashed black lines), signaling two-phase coexistence, consistent with the microscopic structural configuration observed in Fig. 1h. The chemical potentials of helium and hydrogen are shown in Fig. 1f, j, obtained by integrating these derivatives $(\partial\mu_{\text{He}}/\partial \ln x_{\text{He}})_{T,P}$ over composition. In the two-phase region at $T = 7000$ K, $P = 800$ GPa, μ_{He} and μ_{H} are constant, and only the proportions of the He-rich and He-poor phases change.

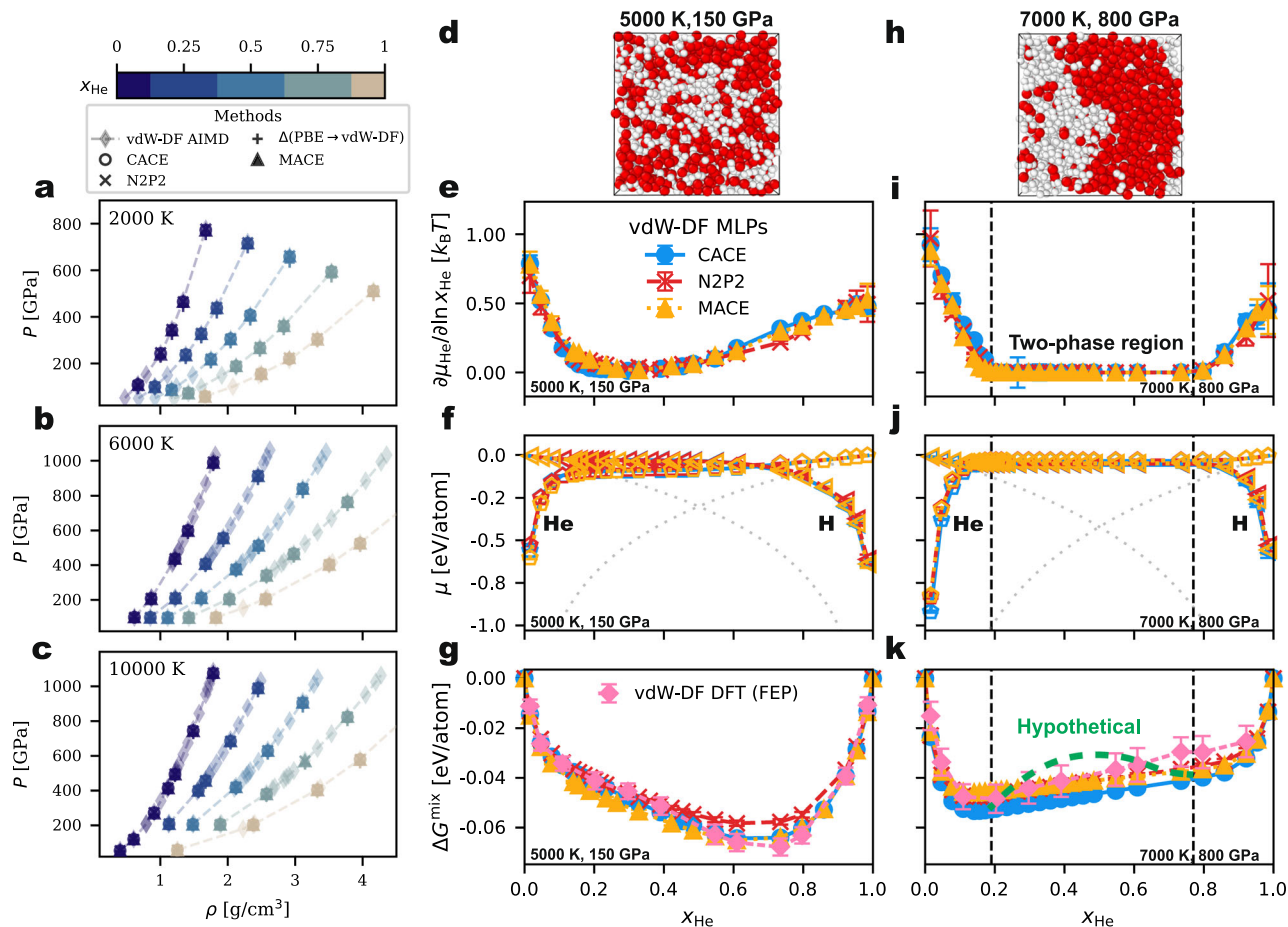


Fig. 1 | Thermodynamic behaviors of H/He mixtures predicted by different machine learning potentials (MLPs). **a–c** Pressure (P) as a function of density (ρ) for five H/He mixtures (helium atomic fraction $x_{\text{He}} = 0, 0.25, 0.5, 0.75$, and 1.0) at **a** 2000 K, **b** 6000 K, and **c** 10000 K. Results are from different vdW-DF MLPs: CACE (circles), MACE (triangles), N2P2 (crosses), and a Δ -learning vdW-DF model (pluses) built upon the PBE MLP baseline. All results are compared to reference vdW-DF data (dashed lines with diamonds) from AIMD calculations²⁴. **d, h** Snapshots from MLP MD simulations showing: **d** homogeneous mixture and **h** phase separation. White and red particles indicate hydrogen and helium atoms, respectively. **e, i** Derivative of the helium chemical potential ($\partial\mu_{\text{He}}/\partial\ln x_{\text{He}}$) _{T,P} computed from the S0 method³⁹ with error bars indicating ± 1 standard error propagated from the linear-fit covariance matrices for S^0 . The MD simulations were performed using MLPs trained on vdW-DF. Blue, red, and yellow symbols indicate MLP architectures employing

CACE, N2P2, and MACE, respectively. The vertical dashed black lines represent the equilibrium x_{He} of the He-poor ($x_{\text{He}} = 0.19$) and He-rich ($x_{\text{He}} = 0.77$) phases during demixing at 7000 K and 800 GPa. **f, j** Computed chemical potentials of H (triangles) and He (pentagons), compared with ideal solution behaviors (dotted light gray lines). Error bars indicate uncertainties propagated from $(\partial\mu_{\text{He}}/\partial\ln x_{\text{He}})_{T,P}$ through the numerical integration. **g, k** Mixing free energy per atom for H/He mixtures (ΔG^{mix}) as a function of helium fractions. Pink diamonds denote the ΔG^{mix} at the vdW-DF DFT level, promoted from the vdW-DF N2P2 MLP to DFT using free-energy perturbation (FEP), with error bars indicating ± 1 standard error of the mean across 100 uncorrelated configurations at each x_{He} . The schematic dashed green line in **k** represents the hypothetical ΔG^{mix} curve for a homogeneous H/He mixture inside the demixing region.

The per-atom Gibbs free energy of mixing (ΔG^{mix}) is:

$$\Delta G^{\text{mix}}(x_{\text{He}}) = x_{\text{He}}\mu_{\text{He}}(x_{\text{He}}) + (1 - x_{\text{He}})\mu_{\text{H}}(x_{\text{He}}). \quad (2)$$

At 5000 K and 150 GPa, the ΔG^{mix} curve in Fig. 1g is fully convex, indicating complete miscibility. In contrast, at 800 GPa and 7000 K, the mixing curve is linear in the demixing region ($x_{\text{He}} = 0.19\text{--}0.77$) that corresponds to $(\partial\mu_{\text{He}}/\partial\ln x_{\text{He}})_{T,P} = 0$ in Fig. 1i. A hypothetical homogeneous mixture there would be thermodynamically unstable, as its ΔG^{mix} (schematic dashed green line in Fig. 1k) exceeds that of the equilibrium phase-separated state (colored symbols). The phase separation also turns out to be kinetically rapid in our MD simulations: the separation completes within tens of picoseconds (Fig. 1h), implying a low activation barrier for H/He demixing.

To quantify whether the use of the MLP introduces bias in the predicted mixing free energies, we further promoted the MLP-derived ΔG^{mix} to the vdW-DF DFT level using free-energy perturbation (FEP).

As shown by pink diamond symbols in Fig. 1g, k, the ΔG^{mix} values at the DFT and at the MLP level show good agreement. In the Supplementary Fig. S15, we further show the agreement between MLP and DFT ΔG^{mix} at two other conditions. This suggests that the MLPs are able to accurately capture the thermodynamics of H/He mixing and demixing.

Taken together, all three vdW-DF MLPs produce consistent ΔG^{mix} results for H/He mixtures and hence consistent predictions of phase separation. Given the higher computational efficiency of the N2P2 MLP (see the Supplementary Information Section IV), in what follows, we use it to sample the large P - T - x_{He} parameter space relevant to gas giants via high-throughput MD simulations.

Phase separation of H/He mixtures

The immiscibility boundary is a two-dimensional surface in the P - T - x_{He} parameter space, as schematically shown as the blue surface in Fig. 2a. This boundary can be projected onto the T - x_{He} or the P - T planes. A

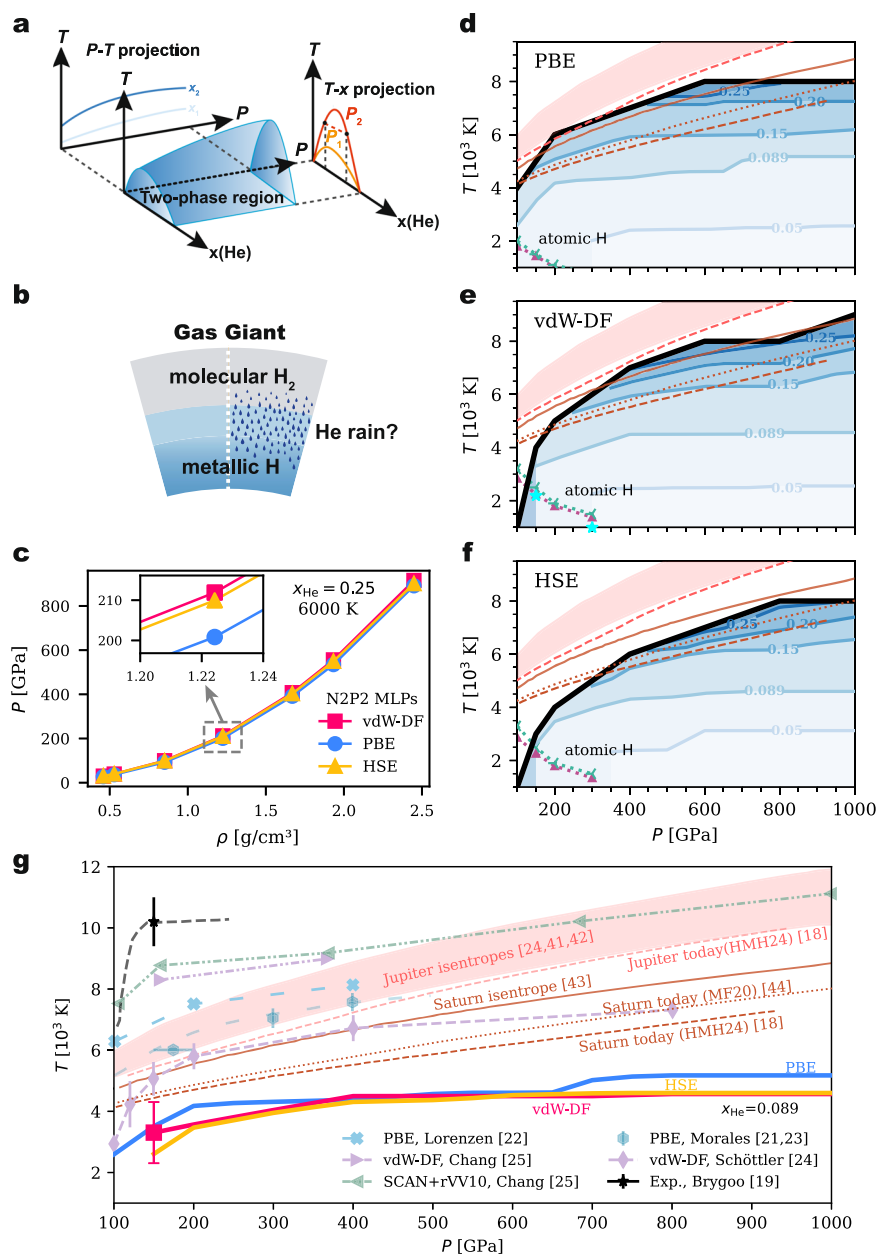


Fig. 2 | Immiscibility diagrams of H/He mixtures predicted using MLPs trained on PBE, vdW-DF, and HSE. **a** Schematic immiscibility diagram of the H/He mixtures with two projections. The blue surface denotes the upper bounds of the two-phase coexistence region. **b** A schematic of the possible scenarios of the H/He immiscibility and helium rain in the H/He envelope of gas giants. **c** Pressure (P) as a function of density (ρ) for $x_{\text{He}} = 0.25$ at 6000 K. **d–f** Composition-dependent immiscibility boundaries of H/He mixtures using MLPs trained on three XC functionals: **d** PBE, **e** vdW-DF, and **f** HSE. The dotted purple and green lines mark the estimated molecular-atomic transition boundaries for pure hydrogen and for a mixture with $x_{\text{He}} = 0.05$ based on classical MD simulations, respectively. In **e**, the cyan stars indicate the transition temperatures obtained from PIMD simulations driven by vdW-DF MLP for $x_{\text{He}} = 0.05$ at 150 and 300 GPa. Planetary isentropes for Jupiter^{24,41,42} (red band indicates the variation among these three studies) and

Saturn⁴³ (solid brown line) are indicated. The dashed lines denote the present-day thermal profiles of Jupiter and Saturn based on the HMH24 model¹⁸, while the dotted brown line denotes another thermal profile of Saturn from the MF20 model⁴⁴. **g** H/He immiscibility boundaries at $x_{\text{He}} = 0.089$. The bar on the red square at 150 GPa is a worst-case estimate of the MLP-induced uncertainty in the vdW-DF phase boundary, approximately ± 1000 K, obtained from the FEP analysis of 100 uncorrelated configurations at each x_{He} . For reference, previous studies at a similar composition ($x_{\text{He}} = 0.085\text{--}0.11$) with their reported uncertainties, where available, are included as follows: PBE AIMD results analyzed by assuming ideal entropy of mixing²², PBE AIMD results analyzed with non-ideal entropy^{21,23}, vdW-DF AIMD results analyzed with non-ideal entropy²⁴, vdW-DF MLP²⁵, SCAN+rVV10 MLP²⁵, and laser-shock experiments¹⁹.

state (P , T , x_{He}) above the surface is fully miscible (e.g., snapshot in Fig. 1d). Planets with interior conditions all above the immiscibility surface will not undergo H/He phase separation (left side of Fig. 2b). Conversely, planets with conditions below the surface may support helium rain (right side of Fig. 2b).

We computed ΔG^{mix} on a dense grid of P - T conditions, using the N2P2 MLPs trained on the three XC functionals (PBE, vdW-DF,

and HSE): 7 pressures (100, 150, 200, 400, 600, 800, 1000 GPa) and 12 temperatures from 1000 K to 12000 K in 1000 K increments. For each set of conditions, H/He phase separation was determined by identifying the point of thermodynamic instability, where $(\partial^2 \Delta G^{\text{mix}} / \partial x_{\text{He}}^2)_{T,P} = 0$. We then constructed continuous immiscibility boundaries at selected x_{He} values by linearly interpolating between the resulting discrete instability points in the P - T space.

We plotted the immiscibility boundaries for various helium fractions in the P – T projection in Fig. 2a. The boundaries for PBE, vdW-DF, and HSE are shown in Fig. 2d–f, respectively, with the upper bound indicated by a solid black line. Helium isopleths (blue curves) mark the demixing boundary of a given helium fraction, with darker shades corresponding to higher helium fractions. Phase separation occurs below a given isopleth.

Overall, the computed immiscibility boundaries depend on the XC functional, but the influence is relatively subtle. As another way to quantify the difference among the three functionals, we compared the EOS in Fig. 2c. At $T = 6000$ K and 1.225 g/cm³, vdW-DF (red square), PBE (blue circle), and HSE (yellow triangle) produce pressures of 212, 201, and 210 GPa, respectively, differing by approximately 5%. This small variation is consistent with quantum Monte Carlo (QMC) benchmarks³¹ that found these three functionals yield pressures that agree within 10% for H/He mixtures under Jovian conditions.

The immiscibility boundaries from the three functionals have similar characteristics: The demixing temperature generally increases with pressure and is highly sensitive to the helium fraction, particularly in He-poor compositions. This compositional sensitivity is further amplified at higher pressures, evidenced by the greater separation between isopleths in Fig. 2d–f.

We further considered two potential sources that could alter the computed boundaries using the MLPs: First, the difference between the MLP and the underlying DFT might cause a shift. However, as is seen in Fig. 1g, k and analyzed in detail in the Supplementary Fig. S15, such differences lead to very small changes in ΔC^{mix} , so the MLP-derived immiscibility boundaries remain consistent with the DFT reference. Second, we accounted for the nuclear quantum effects (NQE) on H/He demixing by performing path integral MD (PIMD) simulations based on the ring-polymer formalism using the vdW-DF N2P2 MLP. As shown in the Supplementary Fig. S28, we found that including NQEs would slightly enlarge the immiscibility region.

The precipitation of helium from the mixture is often regarded as being associated with the metallization of hydrogen¹. To investigate this connection, we computed the atomic-molecular transition boundaries for both pure hydrogen (dotted purple line) and a H/He mixture with $x_{\text{He}} = 0.05$ (dotted green line), as shown in Fig. 2d–f. Such a low helium fraction was chosen to quantify the influence of helium on the transition without complications from demixing that make helium concentrations heterogeneous in the system. We located the atomic-molecular transition as the P – T conditions where half the hydrogen becomes atomic, using an established order parameter³². This order parameter counts the fraction of hydrogen atoms with one bonded hydrogen neighbor, which is computed from H–H RDFs with a smooth cutoff function that is 1 within 0.8 Å and decays to 0 at 1.1 Å. Note that the atomic-molecular transition here is a smooth phase transition above the critical point of the first-order transition³². Within the H–He immiscibility region, atomic hydrogen dominates, but there is a narrow range of thermodynamic conditions ($T \lesssim 2000$ K and $P \lesssim 200$ GPa) where molecular hydrogen is stable.

Across all three functionals, the addition of $x_{\text{He}} = 0.05$ helium to pure hydrogen slightly raises the transition temperature by up to 500 K (Fig. 2d–f), indicating that helium stabilizes molecular hydrogen, in agreement with previous QMC MD⁵² and PBE AIMD⁵³ simulations. This is because the higher nuclear charge of He tightly localizes electrons and reduces the intermolecular electronic overlap between neighboring hydrogen molecules^{52,53}.

Moreover, the choice of XC functional affects the predicted H atomic-molecular phase transition. Both vdW-DF (Fig. 2e) and HSE (Fig. 2f) yield comparable boundaries at $x_{\text{He}} = 0.05$ that align with QMC MD results⁵² at $x_{\text{He}} = 0.085$. In contrast, PBE (Fig. 2d) gives lower transition temperatures relative to vdW-DF and HSE, likely due to its known underestimation of the hydrogen band gap²⁴.

Detailed comparisons for pure hydrogen and H/He mixtures of the atomic-molecular transition are provided in the Supplementary Figs. S19 and S20.

Note that the H atomic-molecular phase transition boundaries discussed above are based on classical MD simulations. To investigate the impact of NQEs, we performed PIMD simulations driven by the vdW-DF MLP for $x_{\text{He}} = 0.05$. As shown by the cyan symbols in Fig. 2e, compared to the classical MD results shown by the green line, the inclusion of NQEs lowers the hydrogen molecular-to-atomic transition temperature by up to 450 K. Such a decrease in the molecular-to-atomic transition temperatures mainly originates from the zero-point energy (ZPE) of the H–H bond in molecular hydrogen, and is consistent with previous DFT-based^{54–58} and MLP-based PIMD studies⁵⁹, which report that NQEs reduce the transition temperature by several hundred kelvin.

Our results reveal that the atomic-molecular transition of hydrogen may influence the H/He miscibility diagram: According to vdW-DF Fig. 2e and HSE Fig. 2f, hydrogen atomization drastically reduces helium solubility in hydrogen near 150 GPa. The mixture with $x_{\text{He}} = 0.089$ starts to demix only above this pressure, which is in agreement with previous vdW-DF AIMD results²⁴. These trends for vdW-DF and HSE suggest that helium is more soluble in molecular hydrogen than in atomic hydrogen, a mechanism that may promote the H/He demixing in planets^{22,25}. In contrast, because the PBE MLP predicts the atomic-molecular transition at lower temperatures (Fig. 2d), its miscibility diagram is less affected by the transition and exhibits continuous isopleths across the investigated conditions. Beyond the atomic-molecular transition ($P > 150$ GPa), the three XC functionals predict comparable H/He immiscibility boundaries that level off and increase gradually with pressure.

To relate our results to planetary models, we show in Fig. 2g the immiscibility boundaries at the protosolar helium abundance ($x_{\text{He}} = 0.089$) in the P – T projection. This specific x_{He} serves as the natural baseline because Jupiter and Saturn are often assumed to have formed from the same material as the solar nebula¹¹³. Previous experimental¹⁹ and theoretical^{22–25} results for similar compositions ($x_{\text{He}} = 0.085$ – 0.11) are included for comparison.

At the protosolar helium abundance, Fig. 2g shows that PBE (solid blue line), vdW-DF (solid red line), and HSE (solid yellow line) predict consistent immiscibility boundaries that differ by less than 500 K. In detail, at $x_{\text{He}} = 0.089$, the PBE MLP predicts the highest demixing temperatures across all pressures, while HSE yields the lowest temperatures at 200 GPa, and vdW-DF gives lower phase-separation thresholds above 600 GPa. These trends predicted by the MLPs are in line with previous AIMD studies demonstrating that PBE^{21,23} (blue hexagons) produces demixing temperatures up to 1000 K higher than vdW-DF²⁴ (purple diamonds).

As illustrated in Fig. 2a, b, helium rain begins where the internal P – T profile of a planet crosses into the two-phase region at the relevant composition. Accordingly, to investigate the occurrence of helium rain in Jupiter and Saturn, Fig. 2d–f illustrates their P – T profiles from two types of planetary models: classical adiabatic models (solid colored lines) and more recent evolutionary models (dotted/dashed colored lines). The red band in Fig. 2d–f reflects an uncertainty of ~ 1000 K in the isentrope of Jupiter, a range based on three earlier studies^{24,41,42}. Similarly, to address the uncertainty (~ 2000 K) in present-day P – T conditions of Saturn in evolutionary models, two references are included: a warmer interior (the MF20 model, dotted brown line)⁴⁴ and a cooler interior (the HMH24 model, dashed brown line)¹⁸. The black curves in Fig. 2d–f represent the upper boundary of the immiscibility region in the P – T projection, while the planetary profiles indicate possible paths through this projected boundary. A crossing of a planetary profile with the boundary marks where the local thermodynamic state enters or exits the two-phase region for the relevant helium concentration.

The formation of helium rain in a gas giant hinges on both its internal thermal profile and helium distribution. For Jupiter, the adiabatic models^{24,41,42} in Fig. 2d–f place the Jovian isentropes (red bands) largely above the immiscibility boundaries (black curves), suggesting that helium rain is unlikely. However, the interior of Saturn⁴³ (solid brown line) is ~2000 K cooler in the adiabatic model, making helium rain more likely, but whether it occurs would depend on the XC functionals used and the local helium concentration in Saturn: PBE (Fig. 2d) predicts helium rain is possible if $x_{\text{He}} > 0.20$ under 150–700 GPa, vdW-DF (Fig. 2e) requires a higher helium fraction of $x_{\text{He}} > 0.25$ at higher pressures (350–700 GPa), while the HSE MLP predicts no helium rain under the adiabatic conditions.

Recent studies in planetary evolution^{18,44,60–63} have challenged the adiabatic assumption for both Jupiter and Saturn and proposed that both planets have cooler interiors shaped by their evolutions. These newly developed models incorporate complex processes from the long-term cooling history of planets, including an inhomogeneous helium distribution, formation of helium rain, heavy-element compositional gradients, double-diffusive convection, and a non-adiabatic thermal structure. We compare our immiscibility boundaries with the thermodynamic conditions predicted by these models (dotted/dashed lines in Fig. 2d–g). For Jupiter, the interior profile predicted by the HMH24 model¹⁸ (dashed red lines) lies above the immiscibility boundaries at the protosolar helium abundance. Although helium rain may occur for $x_{\text{He}} > 0.15$ (Fig. 2d), recent planetary models^{18,44,61,62} suggest this composition requirement is not met in Jupiter, where the peak helium abundance is estimated to be $x_{\text{He}} = 0.09$, indicating that helium rain is unlikely in Jupiter.

On the contrary, the P – T conditions of Saturn (dashed brown line) from the same HMH24 model¹⁸ and the warmer MF20 profile (dotted brown line) from an alternative evolutionary model⁴⁴ both fall below the critical boundaries (black lines in Fig. 2d–f). For all functionals, helium rain requires $x_{\text{He}} \geq 0.15$, as shown in Fig. 2d–f. Given that Saturn may have a large helium gradient with x_{He} varying from 0.1 up to 1.0 based on recent studies^{18,44,62–65}, helium rain may occur throughout the interior of Saturn. However, this inference remains sensitive to the adopted models and the resulting thermal profile of Saturn.

Our H/He immiscibility boundaries (solid lines in Fig. 2g) are systematically shifted to lower temperatures by approximately 2000 K for $x_{\text{He}} = 0.089$, compared to prior AIMD studies using PBE^{22,23} (blue-coded symbols) and vdW-DF²⁴ (purple diamonds). According to our PBE MLP (solid blue line), at the protosolar helium abundance, demixing occurs only at much lower temperatures, such as 3511 K at 150 GPa. In contrast, prior PBE AIMD analyses reported demixing at 7500 K and 160 GPa by assuming ideal entropy of mixing²² (blue cross), and at 6000 K and 175 GPa including non-ideal effects on entropy²³ (blue hexagon). We will explore the possible origins of this discrepancy in detail in the next section. A recent large-scale MLP MD study²⁵ predicted even higher demixing temperatures, which are shown by the purple (vdW-DF) and green (SCAN + rVV10) triangles in Fig. 2g. While their immiscibility boundaries are robust with respect to the chosen functionals, the demixing temperatures are elevated by ~2000 K relative to previous AIMD studies and by ~4000 K relative to our predictions. A fundamental difference in methodology may contribute to this discrepancy: Whereas our method and prior AIMD studies compute the composition-dependent ΔG^{mix} , their approach defines phase separation in terms of changes in local atomic configurations.

Thermodynamic models of H/He mixtures

To rationalize the driving force behind H/He phase separation and understand the discrepancies with previous results, we fitted ΔG^{mix} to a Redlich–Kister (R–K) solution model⁴⁰. While previous AIMD studies^{22,24} employed fifth-order R–K models for ΔG^{mix} , here we adopted a third-order form, because including higher-order terms $\omega_i(T, P)$ with $i = 4, 5$ was found to provide no improvement in either fit accuracy or

predictive power (see the Supplementary Figs. S23 and S24 for the 5th-order fits and related analyses). Specifically, the solution model used is expressed as:

$$\Delta G^{\text{mix}} = k_B T (x_{\text{He}} \ln x_{\text{He}} + x_{\text{H}} \ln x_{\text{H}}) + x_{\text{He}} x_{\text{H}} \sum_{i=1}^3 \omega_i (1 - 2x_{\text{He}})^{i-1}, \quad (3)$$

where the parameters ω_i capture non-ideal interactions that lead to phase separation.

In accordance with the assumption of a homogeneous mixture in the R–K model, we fitted $\omega_i(T, P)$ parameters only to single-phase data above the immiscibility boundary, as shown in Fig. 2a. Results based on vdW-DF are exemplified in Fig. 3a, with PBE and HSE fits detailed in the Supplementary Figs. S21 and S22. The suitability of the R–K model for high-pressure H/He mixtures is demonstrated by the close alignment between the R–K fits (solid lines) and the direct MD results (colored pentagons). For the two-phase region, where the real free energy curve reduces to a straight line (e.g., as illustrated in Fig. 1k), we used dashed lines to denote the extrapolated ΔG^{mix} values for homogeneous mixtures from the individual R–K fits. At lower temperatures and higher pressures, however, the wide miscibility gap with linear mixing free energy (Fig. 1k) leaves insufficient data for an accurate local fit. To overcome this limitation, we performed a global fit of ΔG^{mix} to parameterize the P – T dependence of ω_i and extract their coefficients to model ΔG^{mix} , which is shown as dotted lines in Fig. 3a. Specifically, $\omega_1(T, P)$ and $\omega_2(T, P)$ parameters were fitted to the polynomial expression $\omega_i = c + a_1 T + a_2 T^2 + b_1 P + b_2 P^2$, with fits and uncertainties for vdW-DF presented in Fig. 3b. We treated $\omega_3(T, P)$ as constant for a given pressure, since it displays no discernible trends with temperature.

As shown in Fig. 3b, the ΔG^{mix} values and hence the thermodynamic stability of H/He mixtures are primarily controlled by the ω_1 term. Across all investigated conditions, ω_1 and ω_3 remain positive, increasing ΔG^{mix} and destabilizing the H/He mixture. With increasing temperature, the decrease of ω_1 lowers ΔG^{mix} of a homogeneous mixture and enhances H/He miscibility. The contribution of ω_2 to ΔG^{mix} depends on both composition and temperature; see the second panel of Fig. 3b. Below 6000 K, the second-order term $\omega_2 x_{\text{He}} x_{\text{H}} (1 - 2x_{\text{He}})$ in Eq. (3) increases ΔG^{mix} for He-poor compositions ($x_{\text{He}} < 0.5$), but decreases ΔG^{mix} for He-rich compositions ($x_{\text{He}} > 0.5$). Above 6000 K, ω_2 becomes negative, and the trend reverses: the second-order term now lowers ΔG^{mix} for He-poor components and increases it for He-rich components. Therefore, these trends indicate that H/He demixing is mainly driven by ω_1 and ω_3 at low temperatures, while higher temperatures and the sign reversal of ω_2 progressively favor complete miscibility, particularly for He-poor compositions.

Next, we used the fitted R–K model to analytically calculate the H/He immiscibility boundary for $x_{\text{He}} = 0.089$ by solving the P – T conditions that satisfy the equation $(\partial^2 \Delta G^{\text{mix}} / \partial x_{\text{He}}^2) = 0$. The resulting boundaries (dashed lines in Fig. 3c) agree well with our direct simulation results (solid lines). The uncertainty in the immiscibility boundary (shaded regions) is quantified via Monte Carlo sampling that propagates the error in the fitted parameters ω_i to ΔG^{mix} according to Eq. (3). The choice of functional has little impact on the results, as the predictions from different XC functionals fall within the uncertainty range of thermodynamic models. This analysis also shows that fitting the R–K model alone introduces an uncertainty of approximately 1000 K in the predicted phase boundary compared to direct MD results, due to uncertainties in the polynomial coefficients.

We then investigated the possible explanation for the ~2000 K discrepancy between our H/He immiscibility boundaries and previous AIMD results^{21–24}. First, we examined the effect of the thermodynamic model fitting protocol: In contrast to our global-fit approach described above, previous AIMD work^{23,24} used an individual fitting scheme: They performed individual R–K fits to ΔG^{mix} at each P – T condition, and used

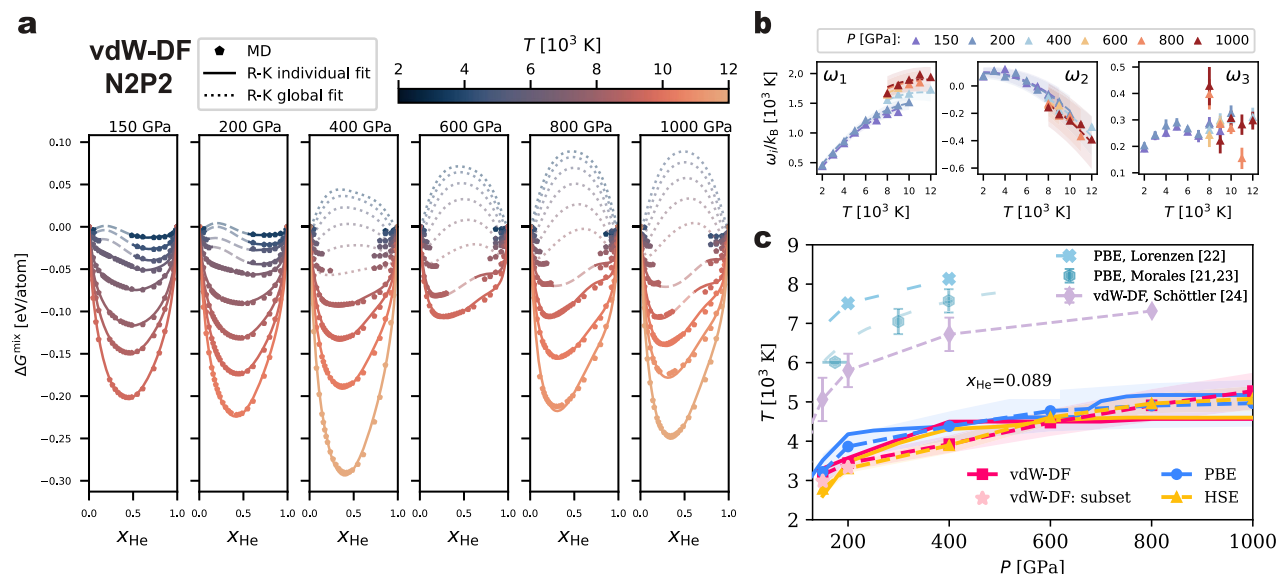


Fig. 3 | Redlich-Kister (R-K) model analyses of the mixing free energy (ΔG^{mix}) and the resulting immiscibility boundary in the H/He system. **a Mixing free energy per atom of H/He mixtures computed from 150 GPa to 1000 GPa and 2000 K to 12000 K, using the vdW-DF MLP. The solid lines denote the third-order R-K model fitted individually at each P - T . The dashed lines indicate the modeled ΔG^{mix} for assumed homogeneous H/He mixtures in the phase separation regime, derived from the individual fits. The dotted lines show ΔG^{mix} derived from a global R-K fit. **b** Pressure and temperature dependence of the R-K parameters (ω_i). Triangle symbols show ω_i values obtained from individual fits at each P - T state point, with error bars indicating ± 1 standard error. For ω_1 and ω_2 , the dashed lines represent the global polynomial fits in P and T to MD-derived values at 32 P - T state points with shaded bands indicating ± 1 standard error propagated from the fitted-coefficient variances. **c** Comparison of H/He immiscibility boundaries from**

different methods at a helium fraction of $x_{\text{He}} = 0.089$. The blue, red, and yellow solid lines correspond to direct MD simulation results based on PBE, vdW-DF, and HSE MLPs, respectively. The corresponding dashed lines show the immiscibility boundaries predicted by the globally fitted R-K model, and the shaded regions indicate the ± 1 standard deviation across 500 Monte Carlo samples generated by propagating the fitting uncertainties of ω_i values into the derived phase boundaries. The pink stars represent the immiscibility boundaries derived with the methodology of individual P - T fit in earlier AIMD studies^{23,24} for a vdW-DF subset at 150 GPa and 200 GPa. Previous studies at similar compositions ($x_{\text{He}} = 0.085$ – 0.09) are included: PBE AIMD results analyzed by assuming ideal entropy of mixing²² (blue crosses), PBE AIMD results analyzed with non-ideal entropy^{21,23} (blue hexagons), vdW-DF AIMD results with non-ideal entropy²⁴ (purple diamonds).

common-tangent analyses of the modeled ΔG^{mix} to identify phase separation and the compositions of any demixed phases. At a fixed pressure, these demixing temperatures were combined with the corresponding x_{He} of the demixed phases to map the T - x_{He} immiscibility diagram (right side of Fig. 2a). By treating the demixing temperature as a function of x_{He} , the demixing temperature at the protosolar helium abundance was linearly interpolated in the T - x_{He} projection. Applying the same protocol to our vdW-DF MLP MD results at 150 GPa and 200 GPa produces immiscibility boundaries (pink stars in Fig. 3c) that agree with our global-fit results (dashed red lines) within 500 K. The same agreement holds for the PBE and HSE results (detailed in the Supplementary Table S8), confirming the validity of both the global-fit and individual-fit approaches. Moreover, the inferred boundary is insensitive to the order of R-K models used; the fifth-order R-K fit yields immiscibility boundaries consistent with the third-order fit. Therefore, methodological differences in fitting and post-analysis procedures between our work and prior AIMD studies^{22,24} can only account for a shift of at most ~ 1000 K (see Fig. 3c and the Supplementary Fig. S24).

As such, the ~ 2000 K discrepancy cannot be attributed to R-K model fitting but can only originate from the computed ΔG^{mix} itself. Indeed, direct comparisons of ΔG^{mix} from MLP MD and AIMD based on vdW-DF at 400 GPa and 1000 GPa over 3000–10000 K show substantial deviations, irrespective of whether non-ideal effects in entropy are included in the analysis of AIMD results, as detailed in the Supplementary Fig. S25. We further speculate that the discrepancy in computed ΔG^{mix} may stem from the system size in the modeling of the mixtures. Our large-scale MD simulations allow macroscopic phase separation (Fig. 1h) and produce a demixed, linear segment in the derived ΔG^{mix} (Fig. 1k). In contrast, earlier AIMD studies^{21–24} use a

relatively small system ($N \leq 64$ atoms) to enforce complete mixing at all conditions. The single-phase assumption enables the evaluation of ΔG^{mix} for a homogeneous H/He mixture, analogous to our hypothetical green curve in Fig. 1k. As ΔG^{mix} comprises enthalpic and entropic contributions, the enthalpy is directly accessible from AIMD calculations, and the entropy is either taken as the ideal entropy of mixing (e.g.,²²) or evaluated by integrating changes in thermodynamic properties (e.g., internal energy and partial molar volume) over EOSs starting from a reference entropy for each x_{He} (e.g.,^{21,23,24}). This reference entropy can be computed via coupling-constant integration with force matching^{21,24}. However, if the small system is not perfectly mixed, or if the free energy of the finite-size system deviates from larger systems at the thermodynamic limit, errors can propagate into the calculated ΔG^{mix} and the inferred immiscibility boundary. In the Supplementary Figs. S9–S12, we examined finite-size effects and showed that the complete-mixing assumption may be violated even in small systems.

Discussion

By analyzing the thermodynamic behaviors of H/He mixtures with ΔG^{mix} computed from the S0 method, as shown in Fig. 1, we reported immiscibility diagrams of hydrogen and helium under planetary conditions in Fig. 2 using three MLPs trained on different XC functionals: PBE, vdW-DF, and HSE. The derived H/He immiscibility boundary (Fig. 2d–f) strongly depends on temperature and helium atomic fraction while exhibiting comparatively less sensitivity to the XC functional, consistent with previous AIMD and MLP MD studies^{21–25}. The immiscibility boundaries reported here should be interpreted within the accuracy of the underlying Born-Oppenheimer DFT framework, MLP fitting, MLP-driven classical MD, and the numerical free-energy

calculations. One systematic uncertainty arises from the exchange-correlation functional (PBE, vdW-DF, and HSE predict immiscibility boundaries that differ by less than 500 K at the protosolar helium abundance). Meanwhile, the MLP-to-DFT free-energy perturbation tests indicate the MLP error is not important: MLP and underlying DFT predict statistically indistinguishable mixing free energies at temperatures relevant to the immiscibility boundary, and MLP errors would lead to a shift of less than 1000 K in the worst-case scenario analysis (see the Supplementary Information Sections IV and VII). The PIMD simulations indicate that NQEs would only slightly affect the immiscibility boundaries by less than 200 K. Thus, although the absolute demixing temperatures remain condition-dependent and uncertain at the level of several hundred kelvin, the lowering of the H/He immiscibility boundary relative to previous small-cell AIMD estimates is robust across the three exchange-correlation functionals tested here. Moreover, the close match between immiscibility boundaries derived from the fitted R–K models (Fig. 3) and from direct MD simulations demonstrates the reliability of the thermodynamic model. This can make it a robust tool for the modeling of mass transport driven by chemical potential gradients in planets. Overall, as shown in Fig. 2g, our immiscibility boundaries shift to lower temperature regions compared to laser-shock experimental measurements¹⁹ and previous theoretical results^{22–25}.

Relating our results to planetary models reveals distinct scenarios for helium rain in Jupiter and Saturn, as sketched in Fig. 2b. As for Jupiter, both adiabatic and evolutionary models indicate helium rain is unlikely: First, the isentrope of Jupiter lies above the immiscibility boundary (Fig. 2d–f), implying that hydrogen and helium remain fully mixed. Second, although the latest evolutionary models (e.g., HMH24¹⁸) predict the interior of Jupiter to be about 1000 K cooler (dashed red lines in Fig. 2d–f), the predicted peak helium abundance of $x_{\text{He}} \approx 0.09$ ^{18,44,61,62} is still below the concentration threshold for helium rainout ($x_{\text{He}} \approx 0.15$) under the relevant conditions. Therefore, Jupiter has likely not cooled sufficiently for helium rain to initiate, and alternative mechanisms are required to explain its atmospheric helium depletion.

On the contrary, the cooler interior of Saturn predicted by the evolutionary models¹⁸ (dotted/dashed brown lines in Fig. 2d–f) may support extensive helium rain that potentially reaches the deeper interior ($P \approx 1000$ GPa). The substantial overlap between the present P – T condition of Saturn from HMH24/MF20 and the two-phase region, as illustrated in Fig. 2d–f, suggests that helium rain may have begun in Saturn long ago and could persist over an extended period of time. This is because demixing starts when the planetary thermal profile first intersects the immiscibility boundary, drives helium redistribution and modifies the thermodynamic conditions in the planet, and ceases once the evolved planetary profile no longer lies within the two-phase domain. This ongoing helium rain can help explain several unique characteristics of Saturn: The release of latent heat and gravitational energy during helium precipitation serves as an additional heat source in Saturn, which could account for its anomalous luminosity^{3,66}. Gravitational differentiation transports denser He-rich droplets inward and would explain the observed atmospheric helium depletion in Saturn⁹. The resulting stratification could establish a compositional gradient in Saturn that shapes its dynamo processes and axisymmetric magnetic field^{1,18,44,67,68}. As our calculated immiscibility boundaries shift to lower temperatures than those in previous studies^{19,22–25}, we predict a delayed onset of H/He demixing during the cooling history of Saturn.

The composition-dependent immiscibility boundaries derived here establish constraints for interpreting the distinct evolution and structures of Jupiter and Saturn^{3,66}. Once H/He demixing is triggered, a gas giant can no longer be modeled as a homogeneous adiabatic planet^{1,18,44,69}. Detailed P – T – x_{He} conditions for H/He immiscibility are thus critical inputs to future planetary studies to model the magnitude of helium rain, atmospheric helium abundances, planetary heat

budgets, emergent compositional gradients, and associated fluid dynamics. Beyond the solar system, resolving the phase behaviors of H/He mixtures and their role in the evolution pathways is fundamental to characterizing exoplanetary gas giants⁷⁰.

Methods

DFT calculations

We used the plane-wave code VASP⁷¹ for production DFT calculations using the exchange-correlation functionals of PBE³⁵, vdW-DF³⁶, and HSE^{37,38}. We sampled the Brillouin zone using a k -point grid resolution of at least $0.02 \text{ \AA}^{-1}$ for the PBE and vdW-DF calculations. The HSE calculations were performed using a resolution of $0.03 \text{ \AA}^{-1}$. We note that for the Δ -learning from the vdW-DF baseline to HSE, the vdW-DF energies and forces are recalculated at a resolution matching the HSE calculations ($0.03 \text{ \AA}^{-1}$).

The plane-wave energy cutoff was set to 1200 eV, after performing convergence tests for energy, forces, and pressure across a 700–1300 eV range. For the pseudopotentials, we used the hard version of the hydrogen PBE projector augmented wave (PAW) potential (PAW_PBEH_h06Feb2004), while for helium, we used the only available version (PAW_PBEHe05Jan2001) from the VASP library.

In the end, the DFT-generated training set for the PBE and vdW-DF functionals comprised 13,389 configurations (1,553,967 atoms) with varying x_{He} across a broad range of P – T conditions (1–1200 GPa and 500–16000 K). Subsets of approximately 2000 configurations each were used in fitting Δ -learning MLPs for vdW-DF and HSE.

In addition, we generated a dataset of 3500 configurations using vdW-DF DFT with the system size of $N = 64$ for three P – T conditions (150 GPa, 2000 K; 150 GPa, 5000 K; 800 GPa, 7000 K) and 12 helium compositions, as well as another set of 3500 configurations using vdW-DF DFT with the system size of $N = 1024$ at the same P – T – x_{He} conditions. These two datasets were used to assess finite-size effects in the DFT reference data and to further validate the fitted MLPs.

Construction of machine learning potentials

To construct MLPs for the high-pressure H/He system, we employed the Behler-Parrinello neural network⁷² via the N2P2 code⁴⁵ on CPUs, and the equivariant message-passing MACE⁴⁷ and CACE⁴⁸ models on GPUs.

In total, we developed 8 MLPs using three MLP architectures and two training strategies for three XC functionals (PBE, vdW-DF, HSE). Six MLPs were obtained by direct fitting: one for each of the three architectures for both PBE and vdW-DF. The other two MLPs were developed using a Δ -learning strategy in the N2P2 package: a vdW-DF MLP was trained on the Δ component $\Delta(\text{PBE} \rightarrow \text{vdW-DF})$ relative to the PBE MLP baseline, and an HSE MLP was trained on $\Delta(\text{vdW-DF} \rightarrow \text{HSE})$ relative to the vdW-DF MLP baseline. We evaluated the performance of all MLPs for H/He mixtures by comparing energetic and thermodynamic properties against AIMD results and one another. Dataset construction and training procedures are detailed in Supplementary Information Section II, with model errors reported in Supplementary Tables S1 and S2; the structural and EOS benchmarks are shown in Supplementary Figs. S3–S8.

Moreover, we compared the performance of these models with MLPs trained using alternative fitting protocols, including models trained with stress data and models trained on restricted subsets of the dataset. These comparisons further validate the training strategies and model architectures of our MLPs, as reported in Supplementary Tables S2 and S3.

MLP MD simulation details

All MD simulations for N2P2 MLPs were performed in LAMMPS⁷³ on CPUs. Following a 10 ps pre-equilibration for a 3456-atom system, each production run was performed for 60 ps with a timestep of 0.2 fs in the isothermal-isobaric (NPT) ensemble using the Nosé-Hoover thermostat and barostat. For MLPs constructed with MACE and CACE, MD

simulations were conducted with the ASE package⁷⁴ utilizing the Nosé-Hoover thermostat and Berendsen barostat. Sensitivity analyses on the timestep (0.1–0.2 fs) and simulation duration (40–80 ps) showed no discernible quantitative differences in computed chemical potentials and free energies. Further details are provided in the Supplementary Fig. S13.

Chemical potentials of H/He mixtures

We applied the newly established SO method³⁹ to compute the chemical potentials of H/He mixtures. For such a purpose, structure factors $S(\mathbf{k})$ were sampled every 10 fs from equilibrium MD trajectories at each P – T – x_{He} state. In the limit of wave-vector $\mathbf{k} \rightarrow 0$, the static structure factor for the H–He pair, $S_{\text{H–He}}^0$, is derived as:

$$S_{\text{H–He}}^0 = \lim_{\mathbf{k} \rightarrow 0} S_{\text{H–He}}(\mathbf{k}) = \lim_{\mathbf{k} \rightarrow 0} \frac{\langle \sum_i^{N_{\text{H}}} \exp(i\mathbf{k} \cdot \mathbf{r}_i(t)) \sum_j^{N_{\text{He}}} \exp(-i\mathbf{k} \cdot \mathbf{r}_j(t)) \rangle}{\sqrt{N_{\text{H}} N_{\text{He}}}} \quad (4)$$

In particular, $S_{\text{H–He}}^0$ was obtained by fitting small- $\mathbf{k}$ $S_{\text{H–He}}(\mathbf{k})$ to the Ornstein-Zernike form³¹ ($S_{\text{H–He}}(\mathbf{k}) = S_{\text{H–He}}^0 / (1 + a k^2)$) with a cutoff of $k_{\text{cut}}^2 = 0.01 \times 4\pi^2 / \text{\AA}^2$. By running multiple MD simulations at varying x_{He} , the chemical potential of helium (μ_{He}) was calculated through numerical integration based on Eq. (1):

$$\mu_{\text{He}}(T, P, x_{\text{He}}) = \mu_{\text{He, pure}}(T, P) + k_{\text{B}} T \int_0^{\ln x_{\text{He}}} d(\ln x_{\text{He}}) \left(\frac{\partial \mu_{\text{He}}}{\partial \ln x_{\text{He}}} \right)_{T, P}, \quad (5)$$

where the chemical potential of a pure helium liquid ($\mu_{\text{He, pure}}(T, P)$) was selected as a baseline for convenience, which does not affect the immiscibility diagram. Accordingly, the chemical potentials for hydrogen (μ_{H}) were derived based on the Gibbs-Duhem equation³⁹.

Equilibrium MD simulations were performed across a grid of P – T – x_{He} conditions: P set at 100, 150, 200, 400, 600, 800, and 1000 GPa, T ranging from 1000–12000 K in increments of 1000 K, and x_{He} varying from 0.015 to 0.98 in 26 intervals. Using the So method, chemical potentials at each P – T condition for each XC functional were computed and are shown in Supplementary Figs. S16–S18, and the corresponding miscibility gaps are listed in Supplementary Tables S4–S6.

Promoting MLP-derived ΔG^{mix} to the DFT level

To quantify the effect of the MLP error, we corrected the MLP-derived ΔG^{mix} to the DFT level using free-energy perturbation (FEP) at three P – T conditions (150 GPa, 2000 K; 150 GPa, 5000 K; 800 GPa, 7000 K). For each P – T – x_{He} condition, we sampled 100 uncorrelated configurations of system size $N = 1024$ from MD simulations using the vdW-DF N2P2 MLP. We recomputed the vdW-DF DFT energies and forces for these configurations, which constitute the $N = 1024$ vdW-DF DFT dataset described above. We then computed the energy difference, $\Delta U = U_{\text{DFT}} - U_{\text{MLP}}$, where U_{DFT} is the DFT energy of a given configuration, and U_{MLP} is the corresponding MLP energy evaluated for the same configuration. The free-energy difference per atom for the system at the DFT and the MLP level, Δg , can then be estimated as:

$$N \Delta g = -k_{\text{B}} T \ln \left\langle \exp \left(-\frac{\Delta U}{k_{\text{B}} T} \right) \right\rangle_{\text{MLP}} \quad (6)$$

Using such free energy correction terms Δg , we promoted the MLP-derived ΔG^{mix} to the DFT level for systems at fixed P – T – x_{He} .

PIMD simulation details

To account for NQEs in H/He mixtures, we performed PIMD simulations⁷⁵ based on the ring-polymer formalism via the i-PI interface (version 3.0)^{76,77} coupled with LAMMPS, using the vdW-DF N2P2 MLP.

Following prior convergence benchmarks^{56,57}, we employed eight beads over the investigated temperature range of 1000–3000 K. Consistent with earlier PIMD studies of dense hydrogen⁵⁷, each PIMD simulation began with a 10 ps equilibration in the NPT ensemble, followed by an 80 ps production run in the NVT ensemble. During the NPT equilibration stage, pressure was controlled with the isotropic stochastic barostat using a relaxation time of 500 fs. Temperature was controlled using the stochastic path integral Langevin equation thermostat (PILE_L) in i-PI⁷⁸, with a relaxation time of 50 fs. A system size of $N = 2560$ and a timestep of 0.2 fs were selected to ensure numerical convergence while maintaining computational efficiency. Further details are provided in the Supplementary Information Section VII.

Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability

The training data, fitted MLPs, MLP molecular dynamics results, and source data underlying all figures and tables in the main text and Supplementary Information have been deposited in the Zenodo repository: <https://doi.org/10.5281/zenodo.21632034>⁷⁹.

Code availability

The data-analysis and plotting scripts used to generate the figures and tables in the main text and Supplementary Information are available in the GitHub repository: https://github.com/ChengUCB/HighPressure_HHe.

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Acknowledgments

The authors are thankful to Armin Bergermann and Ronald Redmer for generously sharing AIMD trajectories and data, and for valuable discussions and feedback on the manuscript. The authors also acknowledge the research computing facilities provided by the high-performance computing (HPC) cluster at the Institute of Science and

Technology Austria (ISTA), Berkeley Research Computing (BRC) at the University of California, Berkeley (UCB), and Lawrence Livermore National Laboratory (LLNL).

Author contributions

B.C. conceived the idea; B.C. and X.W. designed the research; X.W., S.H., and B.C. performed the research; X.W., S.H. and B.C. wrote the paper.

Funding

B.C. was supported by the Laboratory Directed Research and Development (LDRD) Program at Lawrence Berkeley National Laboratory (LBNL) under project ID 110990-001. Part of this work was performed under the auspices of the U.S. Department of Energy by LLNL under Contract DE-AC52-07NA27344. S.H. was supported by the LDRD Program at LLNL under project tracking code 23-SI-006.

Competing interests

B.C. has an equity stake in AIMATX Inc. The remaining authors declare no other competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-026-77117-8>.

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Peer review information *Nature Communications* thanks the anonymous reviewers for their contribution to the peer review of this work. A peer review file is available.

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