

Methane's Elaborate Phases and Where to Find Them

A systematic exploration of the phase diagram of methane resolves inconsistencies of earlier studies, with potential ramifications for our understanding of planetary interiors.

By **Helen Maynard-Casely**

As a gas, methane is very simple. But as a liquid and as a solid, it is perplexingly complex. Ambiguity has long plagued our observations and measurements of its structure at different pressure–temperature combinations. Yet, understanding methane's phase diagram is vital for predicting its behavior deep within our and other planets. In a *tour de force* contribution Mengnan Wang at the University of Edinburgh in the UK and her colleagues have now charted the turbulent seas of the methane phase diagram [1]. By comprehensively mapping its phases and melting curve, they have resolved the legion of discrepancies of earlier studies.

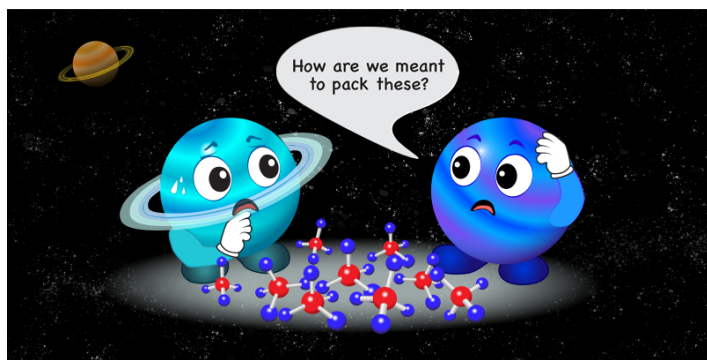


Figure 1: Methane's molecular structure makes it notoriously difficult for researchers to predict how the molecule packs into a crystalline form. There are many ways to solve this puzzle, as methane can take many forms depending on temperature or pressure. Knowing methane's behavior at high density is critical to understanding ice-giant planets such as Uranus and Neptune. Credit: H. Maynard-Casely/ACNS and ANSTO; APS/Carin Cain

Methane—one of the simplest of all molecules—is sometimes the subject of flatulence jokes (of which it is odorlessly innocent) but is also a powerful driver of climate change on Earth (of which it is very guilty [2]). The extraction of gaseous methane from Earth drives multibillion-dollar industries, which use the molecule both as a fuel and as a source of hydrogen. Out in the Solar System, methane in planetary atmospheres absorbs red light, which makes Uranus and Neptune shine blue, while icy methane damaged by radiation paints dwarf planets red.

Although most of us will only ever encounter methane as a gas, this is only one possible state for this molecule. Liquid methane is abundant on Saturn's moon Titan, where its evaporation–condensation cycle drives the weather on this alien world. Colder still, the surface of Pluto is carved by glaciers of solid methane. But what exactly is solid methane?

The methane molecule comprises four hydrogen atoms arranged around a carbon atom. This tetrahedron—an awkward shape to represent on a 2D chalk board—is one of five Platonic solids, and the one that cannot easily be stacked in larger structures (Fig. 1). Finding the most efficient way to arrange an infinite number of tetrahedrons—an optimization problem known as long-range packing—is a mathematical puzzle that has frustrated mathematicians for millennia [3]. When methane first crystallizes, either at a low temperature of $-182.5\text{ }^{\circ}\text{C}$ or at a high pressure of 1.3 GPa, it circumvents this structural conundrum by forming a plastic solid. In this form, known as phase I, each molecule rotates about its central carbon atom. This rotation has the effect of making the molecules behave like

spheres. The overall structure of the solid resembles the stacking of oranges by a fastidious grocer—a face-centered cubic arrangement, as crystallographers would put it.

On the basis of its quasispherical molecular behavior, researchers in the 1990s theorized that solid methane would share similarities with the noble gases. That is indeed the case for phase-I methane, which looks and reacts like solid argon (a very wobbly solid that doesn't like to be pushed). But there's a whole phase diagram of pressure and temperature conditions to be explored. Many researchers speculated that—under a broader set of conditions—methane could be regarded as a “bad noble gas,” retaining a spherical, albeit disordered, structure. They expected that at higher pressures it would transform to a hexagonal-close-packed structure similar to that of xenon [4] or krypton [5]. These are nice, simple, “well-behaved” structures that could straightforwardly be fed into geophysical and planetary models of our Solar System.

But methane wasn't having any of that. In 1995, researchers used spectroscopy methods to chart the molecule's arrangements at low temperatures and up to moderately large pressures, showing that it could adopt nine different solid forms [6]. Thirty years later, not all these structures are fully characterized. As the pressure is increased on phase-I methane, the compound shows increasingly inventive ways to pack its molecules [7],[8].

As high pressure research advanced, more measurements of the phases of methane were reported, but conclusions started to diverge about which of the nine forms were stable at given temperatures and pressures. The experimental divergences led researchers to dispute the reliability of methane's melting curve. Disagreements arose on what is the sequence of phases induced by increased pressure, on what phase forms under what conditions, and even on how to name the phases. Compounding the problem were several observations that under more extreme temperatures and pressures, methane would dissociate to hydrogen and carbon, the latter possibly in the form of diamond. Since methane, along with water and ammonia, makes up the bulk of Uranus's and Neptune's interiors, its possible dissociation would have a major impact on models of these ice giants. However, the lack of reproducibility of these findings substantially hindered the incorporation of methane's behavior into planetary models.

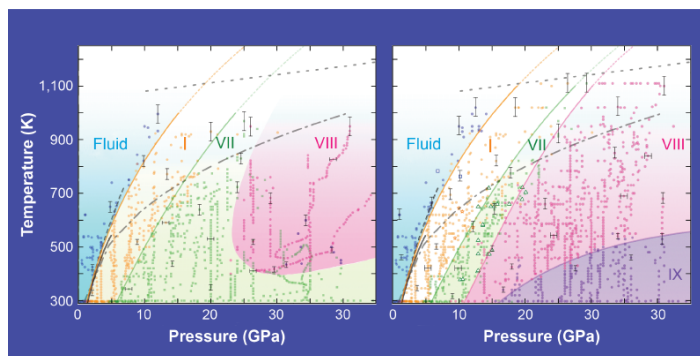


Figure 2: Experiments yield two distinct diagrams to fully describe methane's solid phases. One demonstrates kinetic transformations that depend on the pathways of temperature–pressure changes (left). The other represents equilibrium states usually reached over longer times (right). Dark blue represents methane's fluid state; the other colors represent different solid phases. Solid lines indicate measurements and dashed lines their extrapolations; gray lines represent different reported melting curves.

Credit: M. Wang *et al.* [1]; adapted by APS/Carin Cain

In a series of high pressure experiments that systematically chart methane's structure up to pressures of 45 GPa and temperatures of 1100 K, Wang and colleagues present results that clear up much of the confusion around methane's transformations. The researchers provide two versions of the phase diagram (Fig. 2). The first depicts the kinetic phase transformations—phase transitions controlled by the pathway of pressure and temperature changes. The second captures equilibrium states determined by allowing samples to equilibrate for months. The experiments allowed the team to identify two factors that caused previous confusion.

The first, which impacts the pressure and temperature regions at which each of methane's nine solid forms is stable, is time. Notably, their experiments overcome methane's long-known “sluggish” kinetic behavior by allowing the system sufficient time to evolve. For instance, the kinetic transformation phase diagram shows no phase IX, a structure that has not been fully characterized but is purported to be related to hexagonal close packing. The equilibrium phase diagram demonstrated that this phase forms at pressures above approximately 16 GPa.

The second factor that—according to Wang and her

colleagues—confused studies of dense methane is the molecule's sensitivity to light. Their equilibrium phase diagram indicates that methane is solid at pressure and temperature regions where other studies have reported it to be liquid or even decomposed into carbon and hydrogen. Their simple explanation for this result is that, in previous studies, methane didn't melt or decompose because of the high-pressure and -temperature conditions, but actually did so because of the intense light (usually synchrotron x rays) used to examine the samples. They demonstrate the significance of this phenomenon by showing that fluid methane decomposes under intense light at even low pressures. Still, this light sensitivity is perhaps exacerbated by high-pressure and -temperature conditions.

Wang and colleagues' experiments suggest that Uranus is unlikely to be the glittering diamond world that some had envisioned. Still, the researchers can take pride in having moved the understanding of solid, dense methane to much surer footing. The work, through its equilibrium phase diagram, has also led to a revised melting curve for methane. The curve's trajectory implies that that pressure-temperature conditions within the ice-giant planets might allow for solid layers of methane to form within Uranus and Neptune [9]. Future research could explore methane at even higher pressures and temperatures, perhaps revealing phases even more exotic than the superionic states of water and ammonia.

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REFERENCES

1. M. Wang *et al.*, "Revisiting the phase diagram of methane," *Phys. Rev. Lett.* **136**, 046101 (2026).
2. M. Saunio *et al.*, "Global Methane Budget 2000–2020," *Earth Syst. Sci. Data* **17**, 1873 (2025).
3. J. C. Lagarias and C. Zong, "Mysteries in packing regular tetrahedra," *Notices Amer. Math. Soc.* **59**, 1540 (2012).
4. H. Cynn *et al.*, "Martensitic fcc-to-hcp transformation observed in xenon at high pressure," *Phys. Rev. Lett.* **86**, 4552 (2001).
5. H. Shimizu *et al.*, "High-pressure fcc-to-hcp phase transition in solid krypton studied by Raman spectroscopy," *Phys. Rev. B* **79**, 132101 (2009).
6. R. Bini *et al.*, "High pressure crystal phases of solid CH₄ probed by Fourier transform infrared spectroscopy," *J. Chem. Phys.* **103**, 1353 (1995).
7. H. E. Maynard-Casely *et al.*, "The distorted close-packed crystal structure of methane A," *J. Chem. Phys.* **133**, 064504 (2010).
8. H. E. Maynard-Casely *et al.*, "The crystal structure of methane B at 8 GPa—An α -Mn arrangement of molecules," *J. Chem. Phys.* **141**, 234313 (2014).
9. R. Redmer *et al.*, "The phase diagram of water and the magnetic fields of Uranus and Neptune," *Icarus* **211**, 798 (2011).