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From

Physics World

August 2006

© IOP Publishing Ltd 2009

ISSN: 0953-8585



**Institute of Physics Publishing
Bristol and Philadelphia**

Downloaded on Wed Jan 21 21:47:38 GMT 2009 [128.253.229.85]

A pressing matter

Under high pressures, some of the molecules and elements most familiar to us – water, hydrogen, oxygen and iron – behave in surprising ways, as **Russell J Hemley** explains

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It began some 400 years ago with a simple question: can water be compressed? At that time it was clear that gases were compressible, but liquids presented a greater experimental challenge. Francis Bacon and the Accademia del Cimento in Florence were the first to attempt an answer, by filling a metal sphere with water and sealing it with solder. Although able to indent the sphere by striking it with a hammer, the Florentines concluded that the volume lost was equal to that of the beads of water that forced their way through the insufficiently strong seal. Thus, they deduced that water is incompressible. A century later, however, John Canton overturned this finding with a more precise experiment, and the experimental science of high-pressure physics was set in motion.

We now know that the pressures encountered throughout the universe span a staggering range. Here on the Earth's surface we are subject to pressures of about 100 kPa, which is equivalent to a 10 000 kg mass sitting on an area of 1 m². But this is roughly at the centre of a scale that ranges over more than 60 orders of magnitude, from the near-vacuum of intergalactic space to the super-dense interior of a neutron star (figure 1). Indeed, most matter exists under extreme conditions, so it is clear that we cannot fully understand the natural world without knowing the fundamental physical and chemical forces at play in this broader domain.

Advances in experimental techniques mean that we can now create pressures of several hundred gigapascals in the lab, and the results continue to surprise. Under pressure, inert elements can become reactive, insulators can become superconductors, and unexpected complexity appears in the structures of materials. Even substances as familiar as water and hydrogen behave in surprising ways. Recent high-pressure experiments are therefore providing crucial tests of condensed-matter theory, with implications spanning the physical and biological sciences.

Energetics and electrons

As every student of physics should know, pressure is defined as the change in energy of an isolated system with its volume: $P = -(dE/dV)$. High-pressure experiments therefore allow us to study the energetics of materials – how the energy of a system varies with the distance between its constituent atoms and molecules. At ultrahigh pressures of tens of terapascals and above – which are currently beyond experimental reach – the atoms are so close together that their electronic structure is lost, greatly simplifying the description of matter. At the more modest pressures under which ordinary solids, liquids and gases exist, however, the properties of matter are determined almost entirely by the detailed distribution of electrons. This is the domain of chemistry and condensed-matter physics.

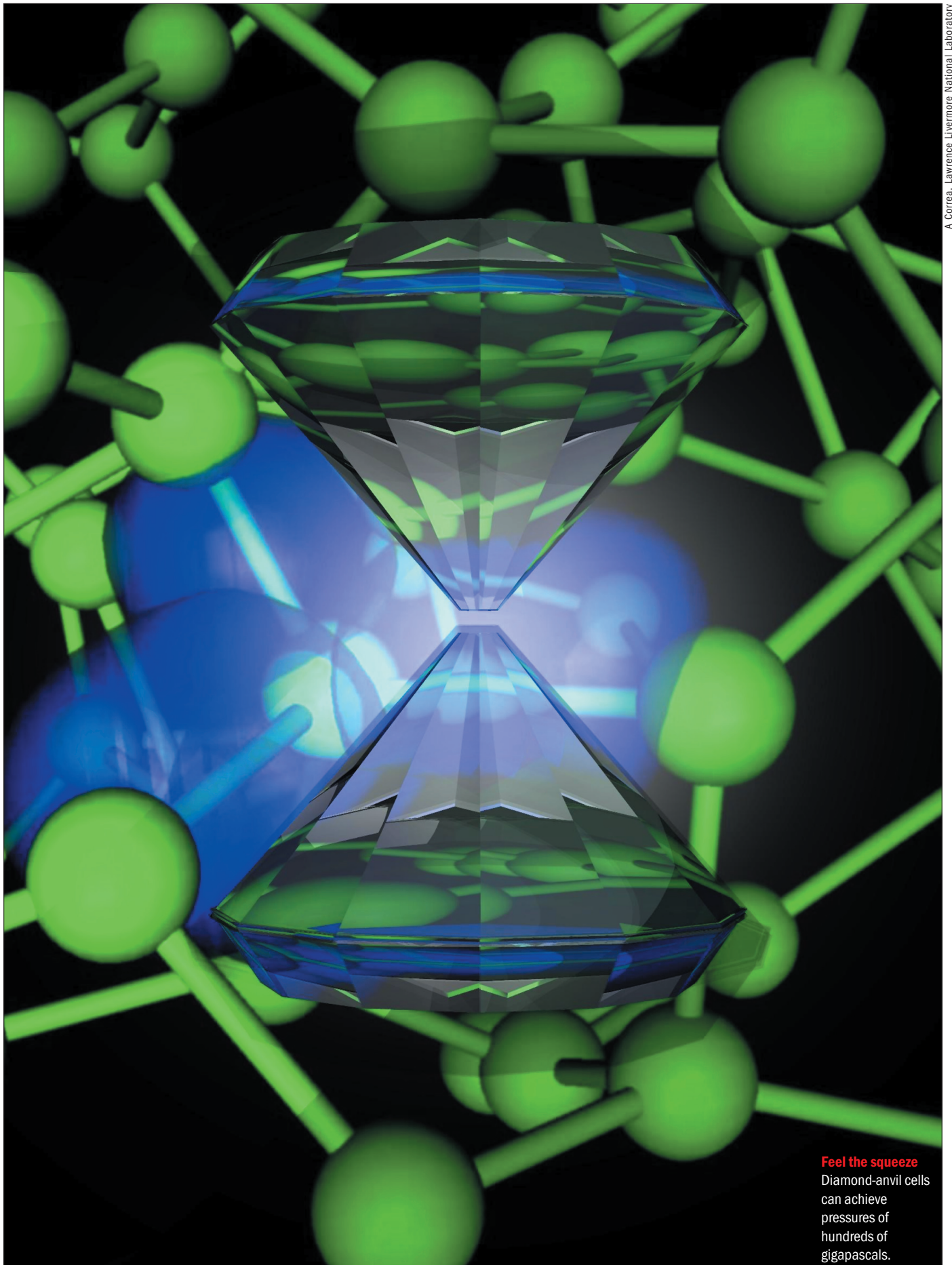
The periodic table describes how electrons populate atomic orbitals – the quantum “clouds” in which electrons are distributed around a nucleus – and puts the elements that have similar behaviours into families. Most of the elements crystallize in relatively simple structures determined by this electronic arrangement. Until quite recently we thought that under pressure the structure of materials became even simpler; high pressure was thought to pack atoms into denser structures, like stacked cannonballs. But in fact compression affects differently shaped atomic orbitals in different ways, leading to unexpected complexity; while other dramatic effects can arise from the subtle redistribution of electrons.

For example, applying pressure can make alkali metals behave like transition metals, lighter elements of a given family behave like heavier members, and noble elements become reactive. Furthermore, whole families of elements can transform from being insulators under ordinary conditions to being metals or even superconductors at high pressures. The configuration of electrons also determines how elements form molecules, and pressure can thus destroy some molecules and form others. Surprising effects also appear at low pressures, having implications for biological systems and also offering the prospect of new materials for hydrogen storage.

High-pressure experiments range in scale from bench-top laboratory instruments to major international facilities. But they adopt two basic approaches: static compression and dynamic compression (figure 2). In static-compression experiments, the pressure is sustained indefinitely at a controlled level by, for example, diamond-anvil cells. On the other hand, dynamic compression creates high pressures in a sample for only short periods of time, for instance by using shock waves. In static experiments, the temperature can also

At a Glance: High-pressure physics

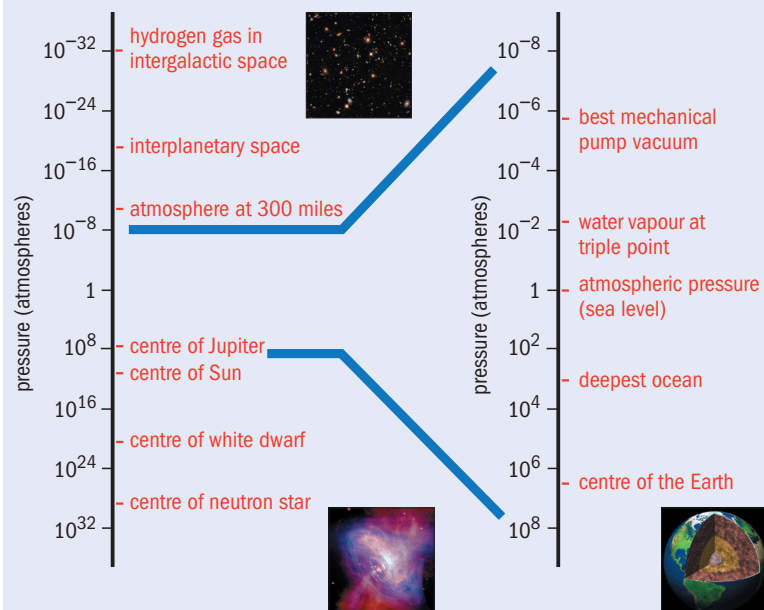
- Pressures in the universe span more than 60 orders of magnitude, with most matter in the universe existing under extreme pressures compared with those on Earth
- Applying pressure was once thought to simplify the structure of materials – in fact it can cause surprising complexity
- Water and hydrogen are among the simplest and most abundant molecules, but their high-pressure behaviour is still not fully understood
- The behaviour of materials under pressure offers important information for geophysics, chemistry and even biology
- New experimental techniques are extending both the range of pressures and temperatures that we can achieve and the type of measurements that can be performed



A. Correa, Lawrence Livermore National Laboratory

Feel the squeeze
Diamond-anvil cells can achieve pressures of hundreds of gigapascals.

1 Orders of magnitude



Naturally occurring pressures span an astonishing 60 orders of magnitude. At the low end is the non-equilibrium pressure of hydrogen in intergalactic space, while at the other extreme lie the pressures encountered inside neutron stars. At the Earth's surface we occupy a small niche near the centre of the range. High-pressure experiments can now recreate the pressures at the centre of the Earth, and recent technological advances will extend this to the conditions found in other planets and even stars.

be varied – from the millikelvin range to temperatures in excess of those at the surface of the Sun. Furthermore, some recent experiments combine both static and dynamic compression to access a broader range of conditions than either can achieve alone.

But generating extreme pressures and temperatures is only part of the story – we also need to probe the materials *in situ* under these conditions. Developing ways to do this, and therefore to investigate the atomic structures, dynamics and transport properties of materials, has been a major part of the revolution in high-pressure physics in the past few years, particularly when applied to static-compression experiments. Arguably the most important of these developments has been the steady increase in the brightness of beams from synchrotron sources. These can provide highly intense, collimated and even coherent light that can be focused inside the sample chambers of high-pressure devices.

Nature's abundance

Four centuries since the Florentines' early high-pressure experiments, water continues to surprise us. Take its solid form, ice, for example: around 1900 three forms of ice were known; now there are close to 20. The incredible complexity of water is evident from its phase diagram – a plot of pressure against temperature that shows which forms of a material are stable under different conditions (figure 3). At low pressures and temperatures, water molecules remain intact but can form into several different phases depending on how those molecules arrange themselves into a crystal structure. At higher pressures however, the molecules dissociate and a dense, essentially ionic crystal is formed.

The boundary between a solid and a liquid in a phase

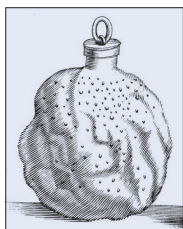
diagram is called the “melting curve” as it shows how the melting temperature varies with pressure. Normal ice – that is the low-pressure molecular form – has a melting curve with a negative slope, which means the melting temperature decreases with pressure. In contrast, for the non-molecular ionic form of ice created at high pressures there is a steep increase in melting temperature with pressure, as revealed in recent experiments with ice at pressures approaching 100 GPa and temperatures up to 1500 K.

Water can also become a very good conductor of electricity at high pressure. Initially the charge is carried by the protons, but at even higher pressures and temperatures the electrons become mobile and the water is “metallized”. The conductivity of water under extreme pressures has been studied in dynamic-compression experiments by impacting samples with a projectile or an intense laser beam. The metallization of water is important for understanding the magnetic fields of large “icy” planets, in which hydrogen and oxygen are believed to exist at pressures approaching the 10 TPa range.

The study of water at more modest pressures provides an insight into many of its peculiar properties at ambient conditions, such as its anomalous thermal expansivity and the fact that it is denser than normal ice. For example, some of these properties may be explained by a transition between a low-density liquid and a high-density liquid phase. This implies that there may be a second “critical point” in water's phase diagram where these two phases become indistinguishable, just as the liquid and gas forms of water do at its first critical point.

Water's principal component – hydrogen – has also remained a topic of great interest in high-pressure science. This lightest of gases has some very odd properties. For example, it is not clear where it should go in the periodic table, even at ambient pressure. Hydrogen forms a diatomic molecule like a halogen, so it would appear to belong in group VII. However, most representations of the periodic table place hydrogen at the top of group I, the alkali metals, because it has one electron. Under pressure, hydrogen is indeed predicted to break down to form an atomic metal. Thus, high-pressure experiments, together with theory, allow us to map out the phase diagram of this so-called simplest element.

Hydrogen is most familiar to us as a gas, in which the hydrogen molecules remain intact under pressures of up to 100 GPa. But recent results have shown that hydrogen forms a dense, non-molecular, conducting fluid at higher pressures. And at lower temperatures, hydrogen can also form a molecular solid with an unusual melting curve – at first the melting point increases with pressure, but then steadily declines. Extrapolating this melting curve to very high pressures implies that hydrogen's melting temperature would fall to zero, giving rise to a new state of matter – a “quantum liquid metal”. In other words, under these conditions the ground state of hydrogen would be a liquid. Recent work suggests that this state could be completely free of both electrical resistance and viscosity – a state known as a superconducting superfluid. Static-compression techniques are closing in on the pressure–temperature regime where this unique state is predicted to exist.

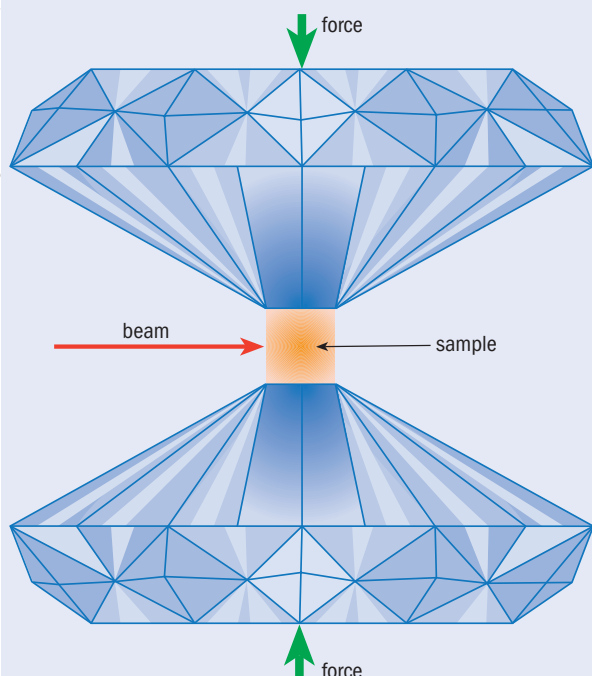


Early experiments

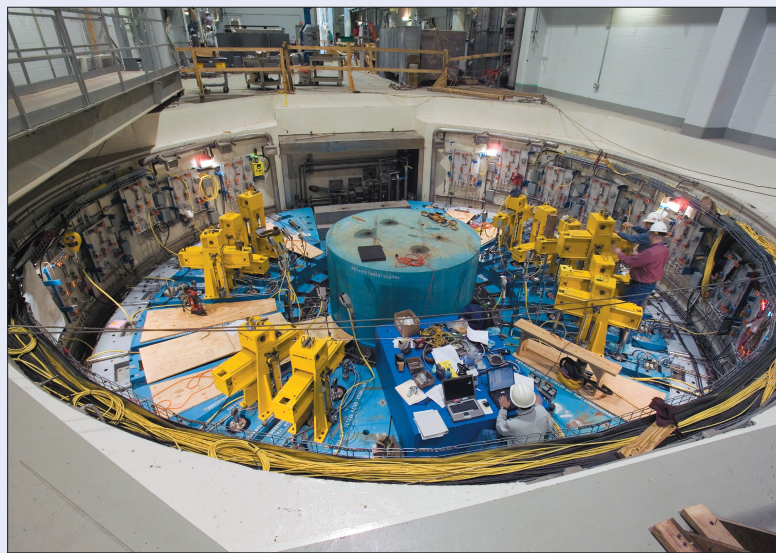
Scientists from the Accademia del Cimento in 17th-century Florence attempted to compress water by repeatedly striking a water-filled metal sphere.

2 Piling on the pressure

Argonne National Laboratory



High-pressure experiments fall into two categories: static compression and dynamic compression, although some experiments now use both. In static compression the pressure is sustained indefinitely by simply applying force to the sample in, for example, a diamond-anvil cell (above). Measurements can then be made *in situ*, often using beams of light or neutrons, such as those that will be available at the Spallation Neutron Source at the Oak Ridge National Laboratory (top right). Dynamic compression produces high pressure for very short periods of time, for example with a shock wave produced by an intense laser beam. The Lawrence Livermore National Laboratory's National Ignition Facility (bottom right) is the size of three football fields and houses 192 lasers that are focused on a tiny sample. Due for completion in 2009, it will be able to achieve pressures well into the terapascal range.



Oak Ridge National Laboratory



Lawrence Livermore National Laboratory

Surprising superproperties

While superconducting hydrogen remains a theoretical possibility, some 23 elements are already known to become superconducting under pressure, including iron, lithium, sulphur and oxygen. The pressures required range from a few tenths of a gigapascal to several hundred gigapascals depending on the element in question, and some remain superconductors up to temperatures as high as 20 K. Whether or not the “BCS theory” that explains conventional low-temperature superconductivity applies to these high-pressure superconductors is still an open question.

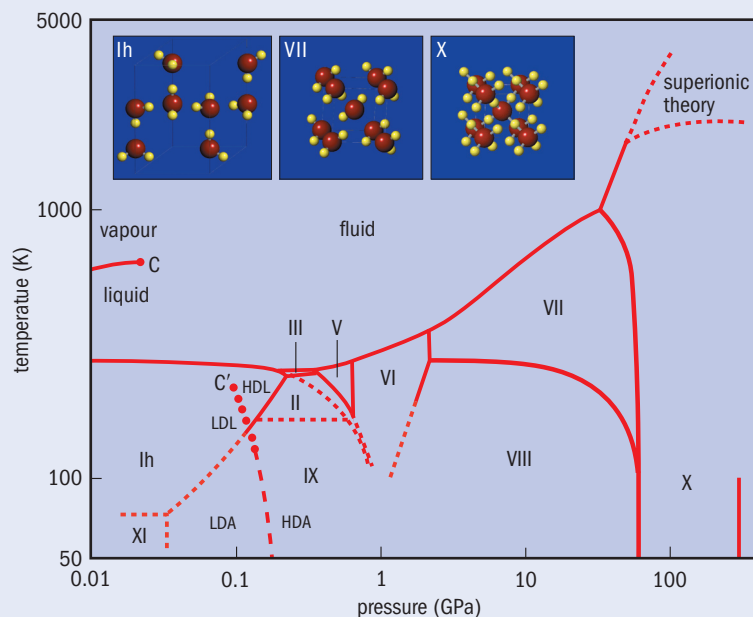
Just as for ice, the structures of metals under pressure can be surprisingly complex. A growing number of elements have been shown to form aperiodic “host-guest” structures under pressure, whereby atoms of the same element can behave very differently. Indeed, these structures look like alloys or compounds even though they are composed of only one element. These observations have overturned the conventional wisdom that one obtains simple, close-packed structures under pressure. Although these intriguing phenomena are not fully understood, answers may be found using concepts borrowed from the theory of metal alloys.

There are yet more surprises in store in the high pressure–temperature phase diagrams of metals. For example, recent X-ray measurements reveal that sodium has an unconventional melting curve. The melting point increases and decreases over a broad range of conditions, with the metal melting below room temperature at pressures of 100 GPa – behaviour that parallels that predicted for hydrogen, the lightest member of the alkali-metal family.

High-pressure research is by no means the sole preserve of condensed-matter physicists. Today's experimental facilities are achieving the pressures found in the centre of the Earth – up to 363 GPa – which is allowing geophysicists to address many puzzling observations from a materials-science point of view. For example, the melting point of iron – the major component of the Earth's core – under pressure provides information about the temperature at the centre of the planet, because we know that there is a transition within the core from a fluid outer zone to a solid region at the very centre.

Under these conditions, not only do the physical properties of iron change, but its chemical properties do too. Indeed, under pressure iron behaves as if it is

3 Complexity in the familiar



A phase diagram shows the stable states in which a material can exist as a function of pressure and temperature (and in principle other variables including composition). The phase diagram of water is remarkably complex, with numerous stable and metastable transitions (not all shown). The melting curve of normal ice (ice Ih) has a negative slope, which is the reason that ice is less dense than water and hence floats. In contrast, the melting curves of the high-pressure ice phases (e.g. ice VII) have positive slopes. Ice X is a non-molecular, ionic form of ice, while all the other phases have structures based on H_2O molecules (see insets). The transition between liquid and vapour ends at a critical point (C). A transition line between supercooled low-density liquid (LDL) and high-density liquid (HDL) that ends in a second critical point (C') has recently been proposed to explain some of water's peculiar properties. At lower temperature there is a transition between "low-density amorphous" (LDA) and "high-density amorphous" (HDA) phases. HDA is formed from ice Ih at low temperatures. At very high pressures and temperatures it is suggested that the protons in ice X become mobile, producing a "superionic" solid.

an entirely different element. Recent experiments have demonstrated pressure-induced transitions of iron from a high-spin to a low-spin state in both oxides and silicate compounds under the conditions found in the Earth's mantle. Indeed, the recent discovery of new iron-bearing silicate phases at very high pressures can explain a number of previously puzzling features in the boundary region between the core and the mantle.

Other open questions in geophysics include whether the solid inner core rotates faster than the planet as a whole, and how the Earth's magnetic field is generated. By determining physical properties of the materials that form the core at high pressures and temperatures we can begin to tackle these questions.

Soft matter to biology

Pressure-induced changes in the properties of materials can also occur under less extreme conditions, particularly with highly compressible "soft matter". For example, if you put hydrogen and water together at low pressures, the molecules mix very little, like oil and water; but under moderate pressures (less than a gigapascal in some cases), new compounds can form. These include host-guest structures, with an ice-like component forming the host and hydrogen molecules the guest, that have the potential to be important hydrogen-storage materials.

In the field of high-pressure organic chemistry, new methods for synthesis are being developed using a combination of high pressure and laser light to direct reactions. High-pressure research offers potential benefits for biological research too; for example, some microbes have been found that can survive an extraordinary pressure of 2 GPa. Such organisms provide the opportunity to study cell adaptation and evolution directly, while also raising new questions for biophysics: how proteins, membranes and nucleic acids are affected by pressure.

Given the broad range of pressures present in the universe, we are still operating in a very small domain – despite the many recent advances. One possibility for navigating these new areas is to do what nature can not: make larger and stronger diamonds than anything that the Earth can provide or that can be produced via conventional high-pressure synthesis. The process of chemical vapour deposition has the potential to create large, super-hard single-crystal diamonds for use in static-compression cells. This will be accompanied by new dynamic-compression facilities, such as large lasers; and X-ray and neutron sources for materials analysis. Such sources will be used in a new generation of experiments that will allow access to the conditions of giant and supergiant planets and even those of stars.

Modern high-pressure physics is an expanding and interdisciplinary field. Challenges remain at the pressure and temperature frontiers, but there are also important prospects for chemistry and biology under more modest conditions. The many recent surprises in the field reveal that we do not yet have a fully predictive paradigm of matter under extreme conditions. Advances in theory combined with the many technological developments now reaching the laboratory will significantly extend our understanding of matter and the forces that govern its behaviour.

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Around 1900, three forms of ice were known; now there are close to 20