

Exotic helium compounds and new states under planetary conditions

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The variety of states that matter may take under extreme conditions of pressure and temperature—some of which are being discovered by theoretical computer simulations as well as by real experiments—sometimes exceeds and defies fantasy. Multi-megabar pressure conditions, quite hard to realize in the laboratory, are expected to prevail in the core of planets. While these high-pressure states determine to some extent the planetary evolution, our physical understanding is by necessity largely dependent on theory. It is thus fortunate that computer simulations of the first-principles kind, whose accuracy increases with density, can be put to work, leading sometimes to real discoveries, such as that of superionic water [1]. A very fresh and intriguing discovery—because it involves helium, the most inert element in the universe—has just appeared.

The gaseous atmosphere of icy giant planets such as Uranus and Nep-

tune is composed mostly of hydrogen and helium, while the inner mantle is mainly composed of water, ammonia and methane [2]. An open question is whether helium could penetrate into the mantle and react with molecular species found there giving rise to unheard of compounds that only exist under conditions of ultra-high pressure. Using first-principles simulations supplemented by machine-learning accelerated crystal structure prediction methods, Gao *et al.* [3] of Jian Sun's computational condensed matter group at Nanjing University investigated the possibility of stable helium-methane compounds. Amazingly, they predicted a He_3CH_4 compound that is stable over a wide range of pressures from 55 to 155 GPa.

The He_3CH_4 compound is predicted as a molecular crystal composed of helium atoms and methane molecules, which is a nice example of pure van der Waals crystals. The insertion of helium

atoms changes the original packing of pure methane molecules and also largely hinders the polymerization of methane at higher pressures. At high temperatures, this unexpected compound has a phase transition from a regular solid (Fig. 1a) to a plastic phase (Fig. 1b), where methane molecules rotate freely, to a further phase with coexistence of diffusive helium and plastic methane (Fig. 1c). Superionic-like, but with diffusive neutral atoms rather than ions, this kind of phase has never been discovered before.

With similar methods, Jian Sun's group also predicted helium-water [4] and helium-ammonia [5] compounds, including plastic and superionic phases under planetary conditions. Highly dependable, these density functional theory based predictions of chemically unlikely helium compounds will stimulate further experimental investigations, including shockwave compression used in the recent observations on superionic water

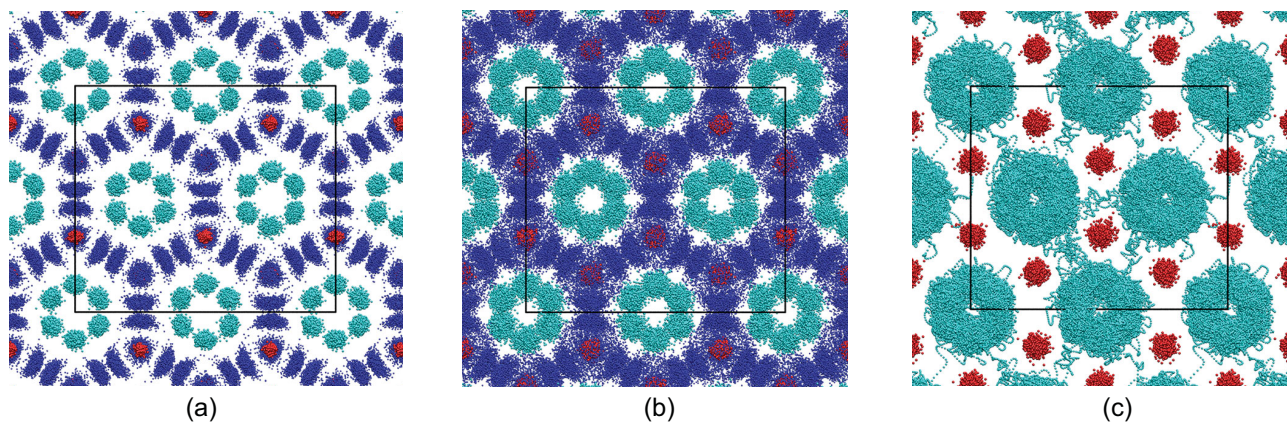


Figure 1. Trajectories of high pressure He_3CH_4 phases from *ab initio* molecular dynamics simulations at 50 GPa and 1000 K, 1900 K and 2350 K, respectively. (a–c) Blue, cyan and red dots represent H, He and C atoms, respectively. At 2350 K, the trajectories of H and He atoms overlap with one another, and therefore only the He and oxygen trajectories are shown here. (Figure is taken from [3].)

[6]. These results actually suggest that current models of icy giant planets may need to be updated, to include previously unexpected helium compounds and states of matter in the model of planet interiors.

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CHEMISTRY

When graphite meets Li metal

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Wetting, indicating the ability of a liquid to spread out over solid surfaces, is of vital importance in addressing the scientific issues related to energy and environment technologies. The study of wetting encompasses the academic disciplines of surface chemistry, nanotechnology, materials science and energy science. The past several decades have witnessed significant progress in achieving desirable wetting performance with water, which has resulted in broad technological applications, such as antifouling techniques, water–oil separation and water-harvesting [1]. In the field of energy storage, Li-ion batteries are widely used in portable electronics and electric vehicles, but the standard graphite anode is already near its theoretical capacity. Replacing graphite with Li metal (LM), the ‘holy grail’ anode with a high theoretical capacity of 3860 mAh/g, shows great promise in achieving more widespread applications [2]. However, LM suffers from low cycling efficiency, infinite volume change and uncontrollable dendrite growth. The method of using graphite to confine LM has been proved to be an effective solution. However, it is still challenging to composite LM with pure graphite directly, since carbon seems lithiophobic,

and surface coating is largely required to improve the wettability of carbon with Li via ‘reactive wetting’ [3].

Currently, it remains unknown whether graphite is essentially lithiophobic. To answer this fundamental question, recently Duan and co-workers carefully conducted contact angle (CA) measurements on several graphitic substrates and demonstrated that graphite is lithiophilic at low potentials free

of contaminants [4]. They observed that highly ordered pyrolytic graphite (HOPG) immediately shows a CA of 73° with molten Li (Fig. 1a). The *ab initio* molecular dynamics simulation further proved that graphite is intrinsically lithiophilic (Fig. 1b). However, further experiments with porous carbon paper (PCP) showed that surface contaminants on graphite would pin the contact line, causing contact-line hysteresis and

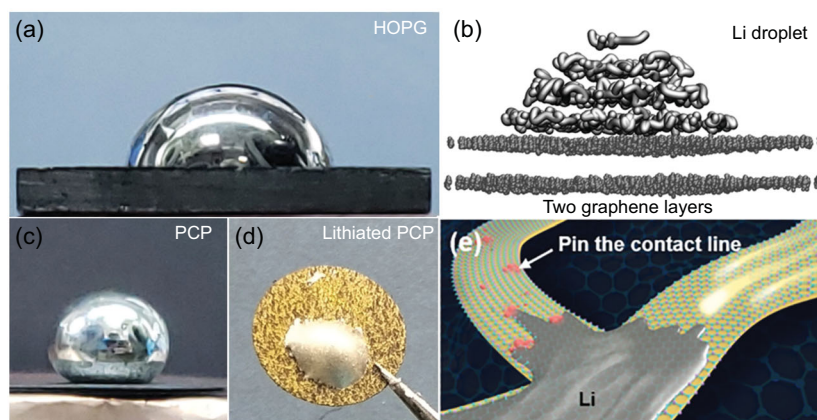


Figure 1. (a) Photograph of liquid Li droplet on HOPG with a small contact angle (CA). (b) *Ab initio* MD calculation of a Li droplet/graphene system at 500 K. (c) and (d) Digital photos of Li droplets on porous carbon paper (PCP) (c) and lithiated PCP (d). (a)–(d) are adapted from [4]. (e) Schematic of spreading Li metal on graphite and pinning the contact line by surface contaminants.