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Hull, CJ

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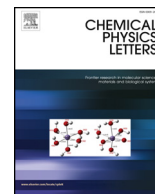
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The liquid state of carbon

C.J. Hull, S.L. Raj, R.J. Saykally*

Department of Chemistry, University of California, United States
Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States



ABSTRACT

While carbon provides the basis for all of organic chemistry and biology, *elemental* carbon compounds themselves play vital roles in our world. Graphite, diamond, fullerenes, graphene, and amorphous carbon solids are used in myriad modern applications, and a number of new, metastable states of carbon with unusual and promising properties have recently been proposed and created. Furthermore, liquid carbon and warm dense carbon are of astrophysical interest, and been proposed to exist in the cores of large planets and stars (Ross, 1981) [1].

While much is known about the solid forms of carbon, its liquid state remains very poorly understood. Due to difficulties in preparing and studying this material, its structure and properties remain essentially unknown. In this review, we describe recent technological advances which have enabled new experiments on liquid carbon samples, prepared with laser melting and shock compression techniques.

1. Introduction

The unique properties exhibited by the known allotropes of carbon make this element essential in an increasingly wide variety of industrial and technology contexts, ranging from industrial lubricants [2,3] and abrasives [4], to nuclear reactor moderators [5], and to the anodes in lithium ion batteries [6]. The economic importance of carbon technologies is only expected to grow, as newly-emergent carbon materials are applied in modern technology contexts; for example, the market for advanced carbon materials (graphene and carbon nanotubes, foams, fibers) is expected to reach ca. \$13 billion by 2025 [7], a growth of ca. 10% in only a few years. This appeal of carbon materials for technology applications derives from the broad array of properties exhibited by carbon allotropes; these, in turn, are engendered by the ability of carbon to form single, double, and triple covalent bonds. This unmatched flexibility in bonding motifs endows carbon materials with a multitude of available atomic structures with widely varying mechanical and chemical properties. By varying the bonding in the solid, these properties can be tuned for a specific application.

As would be expected for such a critical class of materials, a great deal of effort has been devoted to studying the fundamental properties of carbon in its many forms. Beyond the common graphite and diamond allotropes, which have been extensively investigated [8–11], newer solid carbon materials and nanostructures like nanotubes, graphene, and fullerenes, have increasingly received both experimental and theoretical attention [12–15]. The properties of the carbon vapor phase have likewise been carefully analyzed via plume studies of ablated carbon plasmas [16,17] and through spectroscopic studies of various C_n

chains [18].

Unlike the solid and gaseous states, liquid carbon has received comparatively little attention, and our understanding of its properties accordingly remains limited. This lack of research on the liquid phase emanates from the difficulty in both preparing and interrogating the liquid state. In fact, as we discuss in detail later, carbon in its liquid form exists only under extreme temperatures and pressures, like those found in planetary and stellar cores. As such, it is very difficult to generate samples of the liquid in the laboratory under equilibrium conditions. Due to that impediment, coupled with the fact that the liquid state is seemingly irrelevant in terrestrial chemistry and physics, the liquid has largely been ignored in modern carbon research. Despite this esoteric nature, it has become increasingly apparent that there are important fundamental and practical reasons to address this knowledge gap, and thus to advance our understanding of liquid carbon properties. This article describes the efforts made thus far to that end.

2. The carbon phase diagram

As can be seen from its position on the phase diagram shown in Fig. 1, producing carbon in the liquid state presents a formidable challenge. The liquid phase of carbon is favored only under extreme conditions, requiring a temperature of ~ 5000 K and pressures of ca. tens of megapascal to produce an equilibrium sample. The complexity of achieving these conditions is the chief impediment to studying liquid carbon. Known container materials cannot survive such extreme conditions; hence, maintaining the liquid under equilibrium conditions in a laboratory setting is nearly impossible. All experiments seeking to study

* Corresponding author.

E-mail address: saykally@berkeley.edu (R.J. Saykally).

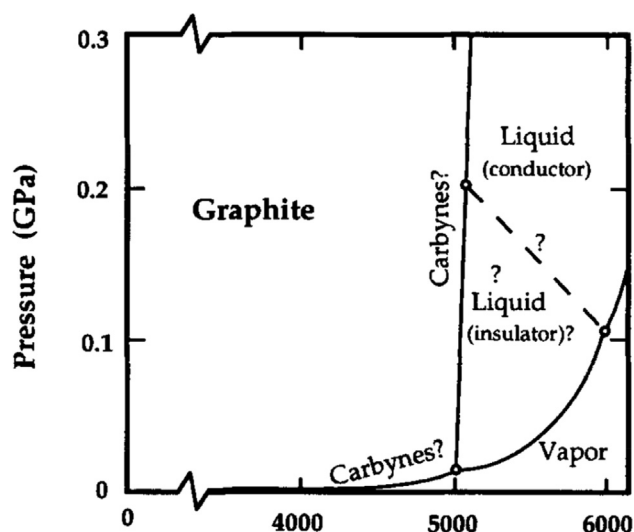


Fig. 1. The carbon phase diagram at low pressure. Graphite sublimes to the gas phase when heated at ambient pressure. Reproduced from Reference 19.

the liquid state of carbon are thus ostensibly forced to produce the liquid a transient manner. As the gas phase is favored under conditions of high temperature and low pressure, even these transiently produced liquids are very short-lived and quickly evaporate. This short sample lifetime is another of the many difficulties that arise in performing experiments on the liquid.

Beyond the position of the melt line, the shape of the curve has also drawn considerable attention from those studying the carbon phase diagram. The graphite melt line shows an inflection point near 4800 K and 5 GPa [19]. The existence of this inflection point has been the origin of much speculation regarding the structure of the liquid. The slope of the melt line is given by the Clapeyron equation:

$$\frac{dP}{dT_m} = \frac{\Delta S_m}{\Delta V_m} \quad (1.1)$$

Here P and T_m are the pressure and melting temperature, and ΔS_m and ΔV_m are the changes in entropy and volume upon melting. As can

be seen in the high pressure phase diagram (Fig. 2), [19] due to the existence of the inflection point, the sign of the slope of the graphite melt line changes [19,20]. As the entropy change upon melting should be positive, the change in sign is then due to a change in volume attending the phase transition. At low pressure, the melt line slope is positive, indicating a liquid which is less dense than graphite, while at high pressure the liquid is denser than graphite, evidenced by the negative slope of the melt line. This change in the slope of the melting line has been interpreted by several investigators as evidence that the liquid may undergo a first-order liquid-liquid phase transition (LLPT) from a low density liquid to a higher density liquid [21,22]. Such transitions have been predicted to occur in other tetrahedral liquids [23], including silicon [24,25], phosphorous [26,27] and water [28,29]. The existence of such a liquid-liquid phase transition in liquid carbon remains a point of contention and further experiments are clearly necessary to determine whether or not such a phase transition actually exists.

3. Why study liquid carbon?

As liquid carbon is a material naturally found in only the most extreme environments, it might seem as though there is little reason to undertake a detailed study of its properties—save for scientific curiosity. However, although rarely observed, understanding the properties of the liquid is potentially important in the modelling of both terrestrial and astrophysical systems, as well as being critical for the manufacture of emerging carbon materials.

3.1. Astrophysical phenomena

While the requisite conditions for the existence of liquid carbon are rarely found in terrestrial environments, such extremes of temperature and pressure are relatively common in astrophysics. Stellar and planetary interiors routinely reach the extreme conditions necessary for liquid carbon to exist in equilibrium [30]. Since carbon is the 4th most abundant element in the universe [11,31], the existence of the liquid state in the cores of stars and gas giants is quite probable. As noted by Ross for instance [1], the thermodynamic conditions in the liquid central layers of planets like Uranus and Neptune favor the pyrolysis of

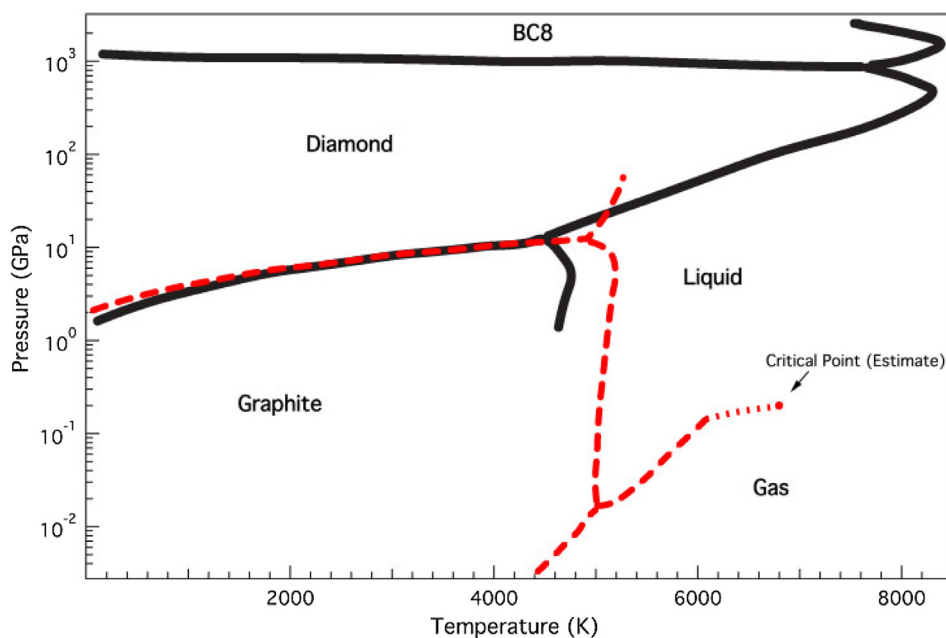


Fig. 2. Phase diagram of carbon. Our current understanding of the carbon phase diagram is shown. The black solid line is taken from Zhao et al. and the red dashed line is from Bundy et al. (References 20 and 19). The critical point has been estimated to be 6743 K by Horvath (Ref 21).

methane gas into a mixture of elemental carbon and hydrogen. Accordingly, understanding the properties of liquid carbon is critical in planetary and stellar physics. It has been proposed that a highly conducting layer of metallic liquid carbon could be the source of the magnetic fields detected in gas giant planets [1,32,33]. However, the question of whether liquid carbon is indeed metallic has long been debated, and other explanations for the origin of these planetary magnetic fields have become more widely accepted, viz. metallic hydrogen [34]. Clearly, a better understanding of the properties of the liquid phase of carbon is necessary if we are to model this substance and evaluate its importance in planetary magnetic field generation. More generally, our currently primitive understanding of the liquid state makes it difficult to predict how important liquid carbon is in various astrophysical phenomena.

3.2. Tetrahedral liquids

Liquid carbon is of fundamental interest as a prototypical tetrahedrally bonded liquid. While most liquids are icosahedrally coordinated, with up to twelve nearest neighbors, tetrahedral liquids are highly structured, with only four nearest neighbors on average [35]. These liquids are of much experimental and theoretical interest, as they often manifest unusual properties as a result of their unique structure. The tetrahedrally bonding liquid most commonly encountered is water, for which the famously unusually complex phase diagram is a direct manifestation of its tetrahedral hydrogen-bonding structure.

Carbon is well-known for its ability to form up to four bonds with neighboring carbon atoms, as in its diamond phase. Simulations have predicted that liquid carbon typically forms four bonds to its nearest neighbors, but can actually exceed that number in some cases [36–38]. Accordingly, it may serve as a model system for testing general theoretical predictions made for tetrahedral liquids. The possible existence of a liquid-liquid phase transition, for instance, is a unique property of tetrahedral fluids [39,40]. As of yet, however, there exist little experimental evidence for the widespread existence of such phase transitions, although a vigorous debate of this subject is ongoing [41–43]. Confirming the existence of such a transition in liquid carbon would therefore provide valuable evidence for the possibility of such transitions in other tetrahedral liquids. Other properties may emanate from the tetrahedral structure as well. Calculations from a Stillinger-Weber model predict that liquid carbon should exhibit an anomalous increase in constant pressure heat capacity upon supercooling, but that the liquid should not exhibit the density anomaly found in some other tetrahedral liquids [23]. As of yet, no experimental data exist to test these predictions. Additional characterization of the structure and properties of liquid carbon could greatly help to refine such models for tetrahedral liquids, which would advance our understanding, not only of liquid carbon, but of water and other tetrahedral liquids as well.

3.3. Advanced carbon materials

In terms of practical applications, liquid carbon has been proposed to be an intermediate in the synthesis of a variety of carbon nanomaterials of interest in modern technology, including nanotubes [11,14], nano-diamonds [44,45] and other novel materials. Liquid carbon is especially relevant to any process that injects large amounts of energy into the carbon substrate on short timescales, since this can transiently drive the material to the portion of the phase diagram where the liquid is thermodynamically stable [46]. As synthesis of carbon nanostructures and thin films via femtosecond and picosecond laser ablation grows in popularity due to low cost and high product yields, understanding this liquid intermediate may be vital for controlling the properties and uniformity of the resulting products.

Carbon nanotubes are already a widely used novel carbon material [11,14]. Commercialization of carbon nanotubes, however, has been hindered by the difficulty in producing them with well-controlled

uniform properties [11] like diameter and chirality. To address these difficulties, the physics of nanotube formation has been an area of fundamental interest [47,48]. Recent evidence suggests that liquid carbon may be a vital intermediate in some common synthetic routes. De Heer et al. studied the formation of carbon nanotubes by the catalyst-free arc discharge method, with an emphasis on elucidating the mechanism of nanotube formation [49]. In post-synthesis TEM images, large spherical droplets of amorphous carbon were observed to have deposited along the length of the arc-produced carbon nanotubes. He interpreted the presence of these droplets as evidence that the carbon nanotubes were nucleating from a liquid carbon intermediate state [49]. It remains unclear, however, why nanotubes are formed rather than the more thermodynamically stable graphite phase, [50]. As De Heer's mechanism cites the surface of liquid carbon droplets as the point of nanotube growth, perhaps undercooling of the liquid is important. To understand the role of the liquid during nanotube synthesis, more data on the properties of the liquid and its surface are clearly needed.

Nano-diamonds are emerging as a critical new carbon technology, with applications in manufacturing [51,52], medicine [53,54], and sensing [44,45]. The most common procedure for nano-diamond synthesis involves the detonation of a mixture of 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazinane (RDX) in a container of liquid water or inert gas. This method has high yield, but results in a mixture of carbon products, requiring extensive purification to yield the desired nano-diamonds [44]. As such, newer, cheaper synthesis routes are desirable.

One promising new route for nano-diamond synthesis involves the ablation of a carbon target immersed in a liquid medium, commonly water. Termed "laser ablation in liquid" or LAL, in this approach to laser ablation synthesis, the liquid acts to confine the laser produced plasma, increasing the temperature and pressure of the plume after laser irradiation [55]. In a recent study, Gorrini et al. synthesized nano-diamond from a graphite target irradiated in water with a 20 ns, 248 nm laser pulse. The resulting nano-diamonds were then analyzed using Raman and electron spectroscopies [56]. Applying Fabbro's [57] model to map the thermodynamic trajectory of the carbon in the confined plume, they proposed that the nano-diamonds nucleate from supercooled liquid carbon; under the confinement of liquid water, the laser-irradiated carbon target reaches the extreme temperatures and pressures at which liquid carbon is thermodynamically stable. The liquid carbon plume then expands and supercools, nucleating the nano-diamonds as a stable colloid. This same mechanism was also described in the synthesis of N-vacancy doped nano-diamonds produced in a similar manner [58]. As with nanotubes, better understanding of the properties of the liquid may help with refining this synthetic process, resulting in better yields, higher degrees of homogeneity, and reduced cost.

Laser synthesis of carbon materials is being increasingly applied to create novel phases of carbon with interesting properties. One exciting new carbon material is Q-carbon, an amorphous carbon with a high degree of sp^3 content, first synthesized and reported by Narayan et al. [59]. As with the nano-diamonds discussed previously, the Q-carbon is believed to be synthesized from an undercooled liquid carbon state, prepared via nanosecond excimer laser irradiation of a graphite target. It has a wealth of very interesting and potentially useful properties, including a predicted hardness higher than that of diamond, ferromagnetism, and high temperature superconductivity [59–61]. Critically, the successful synthesis of Q-carbon, as opposed to the more typical diamond or graphite phases, requires careful control of the incident laser power and the starting film morphology [61]. This is an example of how controlling the properties of the intermediate liquid can tune the properties and phase of the end product.

The many available bonding arrangements of carbon result in many different possible structures with potentially unique properties. One novel class of carbon-based materials, called novamenes, was proposed

and modelled using DFT calculations by Birchfield et al. [62]. This new class of carbon materials comprises a combination of graphitic and diamond lattice structures with a combination of sp^2 carbon rings fully surrounded by diamondlike sp^3 carbon. Simulations carried out on the simplest of these structures, the single ring novamene, predicted it to be a small bandgap semiconductor with a density between that of graphite and diamond. These authors speculated that the previously discussed Q-carbon could perhaps be one of these novamene-class materials, although there was insufficient evidence to determine whether or not that was the case. Even if Q-carbon is not directly related to the novamenes, with careful tuning of the liquid properties by varying melt fluence and starting substrate density, it is possible that these interesting novamene materials could be synthesized in an analogous manner. The most recently discovered carbon allotrope, cyclo [18] carbon was reported in a cover article in Science [60]. This sp -hybridized structure was synthesized by atom manipulation with STM/AFM technology, using a functionalized STM tip to decarboxylate $C_{24}O_6$ adsorbed on an inert NaCl surface. Other interesting forms of carbon are likely to be produced by this novel synthetic method.

4. Computer simulations of liquid carbon

4.1. Structural simulations

With the high temperatures and pressure necessary to generate equilibrium liquid carbon being so difficult to maintain in a laboratory setting, simulations have become a principal tool for elucidating its properties. One of the earliest simulations of liquid carbon was carried out by Galli and Martin in 1989 [63]. In their molecular dynamics study, an amorphous carbon precursor with an initial density of 2 g/cm^3 was heated to a temperature of 5000 K. The material was observed to melt at a temperature of around 4500 K, as judged by diffusion of the carbon atoms in the simulation; this melting temperature is consistent with predictions from early carbon phase diagrams. The liquid in their simulation proved to be metallic, with the energies of the π and π^* bands beginning to overlap and then merge as the carbon underwent the solid/liquid phase transition. Structurally, the liquid in the simulation was observed to be a mixture of two-, three- and four-coordinated carbon atoms, with the recorded ratio detailed in Table 1. The average coordination in the system was measured to be 2.9 nearest neighbors per atom [63]. While the fourfold coordinated carbon was quite unlike diamond, with variable bond lengths and bonding angles, the threefold coordinate sites could be regarded as slightly distorted sp^2 hybridized carbons, with bond angles near 120° and bond lengths near 1.5 \AA . The twofold coordinate carbons were mostly found as sp -bound chains, similar to the proposed carbyne phase in early carbon phase diagrams.

Subsequent studies on the structure of the liquid elaborated on the correlation between the liquid structural properties and density. Wang et al., [64] carried out molecular dynamics simulations on the liquid and found good agreement with Galli et al. for a carbon material of density near 2 g/cm^3 , noting that the system was dominated by threefold coordination. However, the liquid structure was found to change dramatically with its density. At low densities, ca. $\sim 1.5 \text{ g/cm}^3$, twofold coordinate carbon was found to dominate the liquid, accounting for 60–70% of all atoms in their simulation box. Meanwhile, at densities of ca. 3.5 g/cm^3 , the three-fold coordinate carbon was the

dominant species, while the share of twofold carbon dropped off quickly and fourfold-coordinated carbon atoms began to make up a significant portion of the total species [64]. At all densities studied, the liquid was found to exhibit metallic character, providing further support for the growing consensus that liquid carbon is indeed a metal. Later studies did observe that the conductivity increased, and then decreased with increasing density of the liquid, probably due to the shifting degree of sp^2 bonding in the liquid [65].

A common observation in most simulations of liquid carbon is that the average coordination is quite low for a liquid. In Wang's simulation, the average coordination was found to vary from ~ 2.1 at low densities of 1.2 g/cm^3 to 3 at higher densities of 2.68 g/cm^3 [64]. Harada et al. [36] studied the electronic structure of the liquid with a particular interest in its dependence on the system pressure. At low densities, a pronounced anisotropic electronic density surrounding the carbon atoms in the liquid was found, a sign that covalent bonding persists in the liquid phase at these densities. This is a characteristic that liquid carbon shares with liquid silicon and explains the unusually low coordination in the melt. Bonding in liquid carbon, as with liquid silicon, is generally very short-lived, with an average bond lifetime of 100–200 fs. Simulations of the liquid as it cools, however, imply that the bonds can have lifetimes that approach 1 ps or longer at lower temperatures, allowing for evolution of sp^2 domains in the solid He et al., 3635 [66]. At higher densities, ca. 10 g/cm^3 , the electron density is more uniformly distributed throughout the system, and the covalent character is lost. Under these high-density conditions, more traditional metallic bonding dominates in the liquid.

4.2. A liquid-liquid phase transition?

Based on the inflection point in the melting line of graphite, it has long been proposed that liquid carbon might exhibit a liquid-liquid phase transition (LLPT), like those previously predicted for phosphorus and silicon [67]. As for silicon, it was proposed that the liquid structure should undergo a shift from a high density, highly conductive liquid to a low density insulator with a higher degree of sp bonding. Some of the first theoretical support for the existence of a liquid-liquid phase transition was provided by Glosli and Ree [68], who performed a molecular dynamics study of carbon at high temperature and pressure using a Brenner potential model. In their simulation, Glosli and Ree observed a transition from a fourfold coordinate-dominated liquid to a twofold coordinate-dominated fluid as a function of temperature. The graphite-liquid-liquid triple point was predicted to exist at 5133 K and 1.88 GPa. The simulation also found that sp^2 bonding was rare in the liquid, as the torsional barrier in π -bonded systems led to low entropy. The absence of threefold coordination in the simulation was at odds with previous molecular dynamics studies [63]. These results were later improved upon by Wu et al. [22], who employed an *ab initio* molecular dynamics approach similar to that used by Galli. Contrary to Glosli's previous results, the simulated liquid carbon exhibited substantial degrees of sp^2 bonding and showed no evidence for an LLPT. Previous calculation of a LLPT in their MD simulations was attributed to the overestimation of the torsional barrier between threefold coordinate carbons. Instead, and in agreement with prior studies, the liquid coordination was found to vary smoothly as a function of pressure from sp -dominated liquids at low pressure to sp^3 -dominated diamond-like liquid at high pressure.

The most recent investigation into the existence of an LLPT in liquid carbon occurred in 2014, when He et al. once again found evidence for it He et al., 3635 [66]. In a study using classical molecular dynamics with long-range carbon bond order potentials, they observed a shift from a twofold coordinate dominated liquid to a threefold coordinate dominated liquid as the system temperature dipped below 7900 K. The three-fold coordinated carbons that make up the low temperature liquid were observed to have a structure analogous to sp^2 carbons in graphite and served as nucleation seeds for the eventual transition back to the

Table 1

Carbon coordination in simulations of liquid carbon described in Reference 63.

Coordination	Simulation population
Twofold coordinated	32%
Threefold coordinated	52%
Fourfold coordinated	16%

solid state.

To conclude, while many simulations of liquid carbon have been carried out, consensus on the properties of the liquid remains mixed. It is now well-accepted that the coordination of the liquid is highly dependent on the liquid density and that the liquid displays metallic character. Other properties, like the existence of an LLPT remain contentious however, with simulations finding evidence both for and against it. To validate the various theoretical models for the liquid and test their predictions, it is critical that experimental measurements of the liquid be obtained. As we discuss in the next section, there has been little success in studying the liquid due to the difficulties inherent in the experiments. Moreover, the results of experimental studies are often contradictory, and have thus far done little to facilitate consensus regarding the properties of liquid carbon.

5. Experimental studies of liquid carbon

5.1. Flash heating experiments

Preparing liquid carbon in a manner compatible with appropriate characterization tools has been and remains a significant challenge. As the conditions necessary to transition to the liquid state are essentially impossible to sustain in the laboratory, due to the extreme temperature and pressure required, liquid samples must be generated transiently and are generally very short-lived. This puts significant constraints on the types of experiment that can be performed on the material, as these transiently generated samples usually only persist for picoseconds [46]. Additionally, as the density and temperature, which strongly influence the structure and properties of the liquid, are expected to change as the prepared liquid carbon expands and cools, most experimental measurements tend to average over a range of differing liquid structures [46]. As a result, the apparent properties of the liquid may be strongly dependent on the timescales of both the liquid preparation and measurement. Nevertheless, and despite these challenges, several experimental studies have successfully characterized some properties of the liquid state, as discussed in a previous review [69].

One of the earliest attempts to produce and characterize the liquid state of carbon was Bundy's flash heating experiment in 1962 [70]. In this approach, a graphite filament contained in a high pressure cell was rapidly heated via a pulse of electrical current and the voltage drop across the graphite filament was measured as a function of injected power. Heating was carried out using a bank of capacitors, which could deliver the input energy on a timescale under 10 ms, allowing the graphite to be heated and subsequently cooled before significant damage to the containment cell could occur. By performing the experiment over a range of different pressures, the graphite melting curve was mapped out, revealing an inflection point at ~ 4600 K and 5 GPa. The measured resistivity of the liquid was found to be lower than that of the initial graphite fibers, which was interpreted as evidence for the liquid being metallic.

Subsequent flash heating experiments carried out by Heremans et al. improved on Bundy's initial efforts, using a faster capacitor bank that could deliver the necessary electrical current on microsecond, rather than millisecond, timescales [71]. As in the Bundy experiment, there was an observed decrease in the carbon resistivity following pulse heating. The measured resistivity for the liquid in Heremans' experiment was an order of magnitude lower than that obtained by Bundy, as evident in Table 2. This lower resistivity may be a result of the different measurement timescales in the two experiments, but based on the results from this pair of experiments, there was growing evidence that, as expected from earlier predictions, carbon in its liquid state was a metal.

The consensus on the properties of liquid carbon extracted from flash heating experiments was short lived. Newer laser melting experiments (discussed below) revealed conflicting evidence regarding the nature of the liquid. In 1997, Togaya et al. carried out another series of flash heating measurements that seemed to imply that the liquid was,

Table 2

Liquid carbon resistivity as measured in various studies.

Experiment	Measured resistivity
Bundy (Ref 69, 1962)	150 $\mu\Omega$ cm
Heremans et al. (Ref. 70, 1988)	30–70 $\mu\Omega$ cm
Togaya et al. (Ref 21, 1996)	600–1000 $\mu\Omega$ cm
Reitze et al. (Ref 75, from optical reflectivity) (1991)	625 $\mu\Omega$ cm
Cavalleri et al. (Ref 71 [72], optical reflectivity) (1992)	2 m Ω cm

in fact, an insulator. Using a system similar to that used by Heremans, Togaya mapped out the melting curve for graphite, just as Bundy had previously [67]. His results for the phase diagram were in good agreement with Bundy's, revealing an inflection point at 4790 K and 5.6 GPa. His measured resistivity was markedly different, however, with a value that ranged from 600 $\mu\Omega$ cm at 0.4 GPa to 1000 $\mu\Omega$ cm at a pressure of 30 GPa- a full order of magnitude higher than Bundy's values. Although successful in mapping out the thermodynamically stable range for liquid carbon, these flash heating experiments served to create more controversy regarding the liquid's putative metallic character.

5.2. Optical reflectivity experiments

With the advent of high-powered ultrafast laser systems came a new method for preparing liquid carbon via non-thermal melting. Earlier investigations using nanosecond lasers had established the capability to optically melt the sample surface, as evidenced by surface cratering following illumination. The properties of the melt could not be studied in these early experiments, however, as the ablation of the melted carbon layer began on timescales shorter than the pulse duration and obscured the surface [73]. However, newly available picosecond and femtosecond lasers provided sufficiently short pulses that it was assumed the optical properties of the melted carbon could be studied before significant surface ablation could occur. The first experiments on the ultrafast laser melting of carbon were carried out by Malvezzi et al. [74] in the mid-1980s. Graphite targets were melted using a 20 ps, 532 nm pulse from a YAG laser, and the resulting liquid reflectivity was probed using time delayed pulses at 532, 1064 and 1900 nm wavelengths. It was observed that above a critical melting threshold of 0.14 J/cm² there was a fluence-dependent decrease in the optical reflectivity, with higher input fluence resulting in a larger reflectivity loss. The change in the material reflectivity was taken as evidence that the laser had successfully induced a phase transition in the target, in accord with earlier investigations into the ultrafast melting of silicon [75]. The decrease in reflectivity observed after laser irradiation of the graphite was taken as evidence that liquid carbon was an *insulator*, rather than a metal.

These results were later challenged by Reitze et al., who carried out a similar experiment using a femtosecond, rather than a picosecond, laser system as both the pump and probe. In contrast to Malvezzi's results, Reitze [76] first observed a short-lived instantaneous *increase* in the optical reflectivity, followed by a long lived decay. The initial increase in reflectivity, which persisted for several ps, was attributed to the production of a metallic liquid carbon state. The observed reflectivity decay, Reitze argued, was the result of the development of a plume as the liquid carbon ablated. The reflectivity loss observed by Malvezzi was therefore deemed a result of the low time resolution of the 20 ps laser pulse used as the probe in those experiments. Using a Drude model, Reitze was able to extract a dc resistivity of 625 $\mu\Omega$ cm for the liquid, which compared favorably with some of the earlier resistivity measurements from flash heating. The experiment was also carried out using diamond as the melting target instead of graphite, with similar results for the observed reflectivity. Reitze argued that the initial increase in reflectivity upon melting of graphite and diamond indicated a transition to a liquid metal state. This opinion continued to be controversial, however, as further laser melting experiments performed by

Mavezzi et al. [77] and Chauchard et al. [78] found further evidence for the liquid being an insulator rather than a metal.

The most recent laser reflectivity measurements were performed by Mincigrucci et al. [79] on laser-melted amorphous carbon using femtosecond extreme UV (EUV) pulses generated by the FERMI free electron laser in Trieste, Italy. Carrying out reflectivity measurements at wavelengths between 19 and 30 nm, their results showed a decrease in reflectivity beginning at about 0.8 ps after laser excitation. As the high frequency of the EUV laser pulses in these experiments resulted in their pulses being insensitive to the hot electron plasma initially created by the melting pulse, they argued that the observed reflectivity decrease must be a result of hydrodynamic expansion, as was proposed by Reitze. They estimated that the liquid had a high free electron density of ca. $\sim 10^{21}/\text{cm}^3$, with the corresponding plasma frequency in the visible. The authors concluded, as did Reitze, that interpreting the results of optical reflectivity in the study of liquid carbon can be difficult, as the electronic and liquid expansion dynamics are inextricably linked.

5.3. X-ray studies of the liquid state

Experimental studies of liquid carbon have historically been more concerned with the liquid's electronic properties than with its structure. This is because, until recently, there was a lack of x-ray sources with the appropriate time resolution and flux needed to observe the short-lived liquid state. A few x-ray studies have nonetheless been conducted on liquid carbon. In 2005, Johnson et al. studied the bonding in laser-melted carbon using x-ray absorption spectroscopy at the Lawrence Berkeley National Lab ALS synchrotron light source [80]. To compensate for the low time resolution of the x-ray pulses from the synchrotron source, which had durations of 70 ps, their amorphous and diamond-like carbon targets were coated (tamped) with a thin layer of LiF, which served to temporarily delay the ablation of the liquid after melting. Results from the tamped and untamped samples were compared. The resulting x-ray absorption spectra were fit with peaks corresponding to the sigma and pi states of carbon solids, allowing for an estimate of the relative amounts of sigma vs. pi bonding in the liquid. The liquid was found to exhibit a higher degree of pi bonding than was observed in the unmelted carbon films, in agreement with the simulation results of Galli [63] for the melting of amorphous carbon at intermediate densities. It was also observed that, in agreement with previous simulations of the liquid, density played a central role in determining bonding in the liquid. The untamped, low density liquid was found to favor primarily sp bonding, with an average of ~ 2.3 pi bonds per site. The higher density tamped targets, in contrast, had an average pi bonding per site of 1.5. These results provided the first experimental evidence that the liquid structure depended on the system density, although only three different density points were examined in these experiments. Unfortunately, the low 70 ps time resolution of the synchrotron source precluded dynamics studies of the liquid.

In an attempt to more directly probe the atomic structure of the liquid, Kraus et al. performed x-ray scattering on a graphite target shock-compressed to 100 GPa with a ns laser [81]. Both elastic and inelastic scattering contributions were measured in a backscatter geometry at two different scattering angles, 105° and 126° . These angles were chosen because it was predicted that scattering at these angles should be especially sensitive to the shock-induced phase change. The authors indeed observed an increase in the scattering intensity upon shocking the target, evidencing the successful transition to the liquid phase. They found that their derived structure factor for the liquid could not be fit using simple Lennard-Jones or repulsive pair potentials, but compared favorably to the results of DFT-MD simulations. This result was interpreted as proof that the bonding in liquid carbon is complex and likely includes significant contributions from different covalent interactions, as had been predicted by earlier simulations. The fact that only two scattering angles were measured precluded a more detailed characterization of the liquid structure.

6. Conclusions

Clearly, many intriguing unanswered questions remain regarding the properties of liquid carbon. While theory has produced a wide array of predictions regarding the structure, phase diagram, and electronic nature of the liquid, as of yet, few of these predictions have been experimentally tested, and several of the predicted properties of the liquid remain controversial. On the experimental side, the results of measurements are often conflicting and provide little concrete insight into the true nature of the liquid. Many of these apparent contradictions emanate from the fact that the liquid structure is highly dependent on its temperature, pressure, and density at the time of measurement. In order to attain a better understanding of the liquid state, additional experiments designed to probe the electronic structure and bonding in the liquid as a function of its thermodynamic state are urgently needed. However, the extreme conditions necessary to generate the liquid, coupled with its short-lived nature, make such experiments on the liquid difficult to both carry out and to interpret. Nevertheless, there is hope that by embracing new tools-like x-ray free electron lasers and non-linear spectroscopies [82,83]-we may soon resolve some of the intriguing questions regarding the nature of the liquid state of carbon.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Richard Saykally is the Class of 1932 Endowed Professor of Chemistry at the University of California, Berkeley. He received his B.S. in Chemistry from the University of Wisconsin, Eau Claire and his Ph.D. from the University of Wisconsin, Madison. Prof. Saykally has been the recipient of over 75 awards from 15 different countries, including the Irving Langmuir Award in Chemical Physics and Peter Debye Award in Physical Chemistry from the American Chemical Society and the Faraday Lectureship Prize from the Royal Society of Chemistry. He has been an author of over 400 scientific papers that have been cited over 45,000 times. Prof. Saykally and his students have pioneered many important advances in spectroscopy, including velocity modulation spectroscopy of ions, terahertz laser vibration–rotation–tunneling spectroscopy of clusters, infrared photon counting spectroscopy, cavity ringdown spectroscopy, and X-ray spectroscopy of liquid microjets.



Christopher Hull received his Ph D. in Physical Chemistry in the Fall of 2019 and his B.S from Northwestern University.



Sumana Raj received her PhD. in physical Chemistry in the Fall of 2019 and her B.S degree in Chemistry from Cornell University.