

Does C₆₀ have a liquid phase?

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ABOVE a substance's liquid–vapour critical point (T_c), the distinction between the liquid and vapour phases disappears. Below the triple point (T_t), meanwhile (at which solid, liquid and vapour coexist), only the solid and vapour are stable. The liquid range, T_c/T_t , depends on the nature of the intermolecular forces: for argon, $T_c/T_t = 1.8$, whereas for sodium the ratio is 7.5. But might there be molecular substances that have no liquid phase at all? Here we present results which suggest that C₆₀ is such a substance. We map out the phase diagram using computer simulations in which the C₆₀ molecules are represented by spheres interacting via Lennard-Jones potentials summed over all 60 carbon atoms. We find that the sublimation line passes above the metastable liquid–vapour coexistence curve. By drawing an analogy with the aggregation of colloidal particles, we expect that solid C₆₀ formed by nucleation from the vapour phase will be amorphous rather than crystalline.

The phase behaviour of C₆₀ might be expected to differ qualitatively from that of simple fluids such as argon or methane. As is well known, the equations of state of such simple molecular systems obey the law of corresponding states. This means that if the temperature T , the pressure P and the density ρ are expressed in units of the critical temperature, pressure and density respectively, the equations of state of such fluids can (very nearly) be superimposed. The reason why the law of corresponding states works for these systems is that, to a good approximation, the pair potentials of noble gases and simple spherical molecules all have the same shape. A good approximation to the effective pair potential of noble gas atoms is the so-called Lennard-Jones 12–6 potential (Fig. 1). Although C₆₀ is also a fairly inert, nearly spherical molecule, its intermolecular potential is not Lennard-Jones-like. A simple pair potential that should describe the intermolecular interactions of C₆₀ at high temperatures, has recently been proposed by Girifalco¹. This potential was constructed by assuming that the carbon atoms on two different C₆₀ molecules interact through a simple Lennard-Jones potential. At high temperatures we may average these interactions over all relative orientations of the C₆₀ molecules, giving the spherically averaged potential shown in Fig. 1.

As may be seen in Fig. 1, the pair potential of C₆₀ differs significantly from the Lennard-Jones form. In particular, we see that the ratio of the width of the attractive well to the diameter of the repulsive core of the potential is much less for C₆₀ than for noble gases. This is because the carbon–carbon interaction determines the range of the attractive well, whereas the diameter of the repulsive core is fixed by the size of the C₆₀ 'cage'. In this respect C₆₀ and *a fortiori* the larger spherical fullerenes differ qualitatively from all smaller molecules. We should not expect C₆₀ to obey the same law of corresponding states as the noble gases.

What is the effect of the short range of the intermolecular interaction in C₆₀? As there are no other molecular systems with a similarly short-ranged potential, we turn for comparison to supra-molecular fluids, namely colloidal suspensions (for a review, see ref. 2). Uncharged colloidal particles in a nonpolar, refractive-index-matched solvent behave effectively like hard spheres. If we add non-adsorbing polymer to such a suspension, the polymer induces an effective entropic attraction between the

colloidal particles. The range of this attraction is comparable to R_g , the radius of gyration of the polymer. If R_g is larger than about one third of the radius of the colloidal particles, the phase diagram of the colloids includes a dense and a dilute disordered phase ('liquid' and 'vapour'), in addition to a colloidal crystal ('solid'). However, for shorter-ranged polymer-induced interactions, the 'liquid' phase disappears. In view of the short range of the pair potential shown in Fig. 1, it is natural to ask if something similar happens for C₆₀.

The phase behaviour of solid C₆₀ has been studied extensively, both at low³ and high⁴ temperatures. But there are, to our knowledge, no experimental data on the melting line of C₆₀ in the temperature range of the critical point ($\sim 1,800$ K, see below). We therefore decided to predict this part of the phase diagram by computer simulation. In fact, such simulations require a combination of several techniques that we briefly describe below.

To study the liquid–vapour coexistence of C₆₀, we used the 'Gibbs-ensemble' technique⁵. In this scheme, Monte Carlo simulations of the liquid and vapour phase are performed in separate periodic boxes. The two boxes can exchange volume and mass. This ensures that the liquid and vapour phase reach thermodynamic equilibrium. Using the techniques described in ref. 6, we could estimate the critical temperature to be $1,798 \pm 10$ K. We checked that only 15 K above this temperature, both boxes contain the same supercritical fluid phase.

But the Gibbs-ensemble technique can not be used to study solid–fluid coexistence: the mass-exchange between the fluid and the solid phase requires the addition or removal of molecules in an otherwise perfect crystal and this would necessarily result in the creation of point defects. In order to compute the melting line of C₆₀, we therefore used another approach. From thermodynamics we know that the condition for two-phase equilibrium is that both phases have the same temperature, pressure and chemical potential. In our simulations we can impose the temperature and the pressure. The chemical potential, however, must be computed separately. To this end, we performed absolute free-energy calculations^{7,8} in which we computed the chemical potential of the (face-centred-cubic) solid and the fluid phase at several temperatures. This allowed us to locate several points on the melting line, both above and below the estimated liquid–vapour critical point. The complete melting line was determined

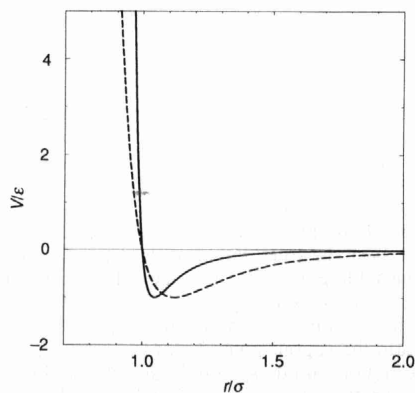


FIG. 1 A comparison of the 12–6 Lennard-Jones potential that describes the pair interaction of noble gases (dashed line), and the pair potential for C₆₀ proposed in ref. 1 (solid line). The potential energy V has been expressed in units of the well depth ϵ . For C₆₀, $\epsilon/k_B = 3,218$ K, where k_B is the Boltzmann constant. The intermolecular distance r is expressed in units of the effective diameter σ , defined as the distance where the pair potential crosses zero. For C₆₀, $\sigma = 0.959$ nm. In all simulations, we truncated the potential at $r = 2\sigma$ where the interaction energy is only 0.76% of the well depth.

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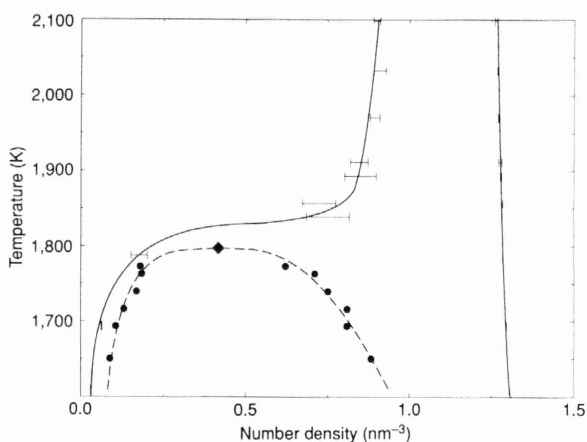


FIG. 2 Computed temperature-density phase diagram of C_{60} for temperatures in the region of 1,800 K. The solid lines are the solid-fluid coexistence lines. They were obtained by a fit to the data points (indicated by error bars) derived from free-energy calculations^{7,8} at 3,218, 1,893, 1,839, 1,788 and 1,694 K and 'Clausius-Clapeyron' integration⁹ between 3,218 and 1,893 K. The area between the two solid lines is a two-phase region where solid coexists with fluid. The dashed line denotes the (metastable) liquid-vapour coexistence line. It was obtained by a fit to the data points (solid circles) that were computed using the Gibbs-ensemble simulation technique of ref. 5. The solid diamond indicates the estimated location of the critical point. The fact that the critical point is located below the solid-fluid coexistence line implies that C_{60} has no liquid phase.

by integrating the Clausius-Clapeyron equation, following the scheme developed by Kofke⁹.

Figure 2 shows our prediction for the phase diagram of C_{60} . The sublimation line passes 35 ± 10 K above the liquid-vapour critical point. All phases that occur below the sublimation line in Fig. 2 have a higher Gibbs free energy than the coexisting solid and vapour phases. It may be possible to reach the liquid-vapour coexistence curve by supercooling the fluid below the sublimation line. But the liquid phase that would then form is necessarily less stable than the coexisting solid and vapour phases. Our results therefore suggest that C_{60} has no stable liquid phase. To our knowledge, this would be the first example of a pure substance that has no triple point. Of course, these findings assume that the interaction potential for C_{60} proposed in ref. 1 is accurate. An improved description of the intermolecular interactions would presumably result in small shifts of the predicted phase boundaries, but this will do little to change the highly anomalous appearance of the C_{60} phase diagram. Specifically, we expect the (metastable) critical point to remain very close to the sublimation line. This has interesting consequences for the formation of solid C_{60} from the vapour phase. If C_{60} is cooled below the sublimation line, it will probably not nucleate crystals from the vapour phase because, as soon as it is cooled below the liquid-vapour spinodal (that is, the line where the homogeneous fluid becomes absolutely unstable), metastable liquid-like aggregates will form. One might think that the formation of these aggregates would assist subsequent crystallization. However, experiments¹⁰ and simulations¹¹ on colloids with short-ranged attractions indicate that such aggregates do not crystallize but gelate to form rather open fractal structures. By analogy, we expect that solid C_{60} that is formed by homogeneous nucleation from the vapour phase will form an amorphous, rather than a crystalline phase. This may explain why the high-temperature synthesis of C_{60} in the gas phase often results in sooty deposits.

After we had completed this work, A. Cheng *et al.*¹² reported a similar simulation study of C_{60} in which the phase boundaries were located using a series of approximations. As a result of these approximations, a narrow liquid range was seen above 1,800 K. □

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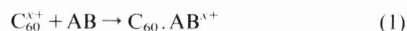
Enhanced reactivity of fullerene cations containing adjacent pentagons

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GEOMETRICAL constraints, first identified by Euler, dictate that all of the closed carbon cages known as fullerenes must contain twelve pentagonal rings of carbon atoms¹. In all of the fullerenes synthesized so far, each pentagon is surrounded by hexagonal rings². Indeed, this has been proposed as a criterion for fullerene stability—the 'isolated-pentagon rule'^{1,3}—on the basis that adjacent pentagons are expected to be chemically reactive. Buckminsterfullerene (C_{60}) is the smallest fullerene for which the isolated-pentagon rule can be satisfied; smaller, adjacent-pentagon fullerenes have not been formed in bulk, but have been identified previously as cations⁴⁻⁶. Here we report experimental evidence for the heightened chemical reactivity of cations of the adjacent-pentagon fullerenes C_{56} and C_{58} , relative to C_{60}^{x+} , which provides support for the basic assumptions underlying the isolated-pentagon rule. Our findings suggest that, if fullerenes such as C_{56} and C_{58} are produced as intermediates or byproducts of C_{60} generation either in the laboratory or in natural environments, they should form derivatives readily.

Using a selected-ion flow tube (SIFT) described elsewhere^{7,8}, we have observed many examples of addition reactions



for the ions C_{60}^{2+} , C_{60}^{3+} and C_{60}^{4+} , and have determined that several factors influence the efficiency of reaction (1) for different charge states (x) and for different reactants (AB)^{9,10}. The ions C_{60}^{x+} are generated by the impact of electrons upon vaporized C_{60} , a technique which also produces ions C_n^{x+} ($n < 60$) by the dissociative ionization of buckminsterfullerene. The molecules chosen for reaction with these latter ions were several (CH_3CN , NH_3 , C_2H_4 , $n-C_4H_{10}$) which showed little reactivity with C_{60}^{x+} , because such reactions provide scope for observable rate enhancement.

The increased reactivity of C_{56}^{x+} and C_{58}^{x+} , compared to that of C_{60}^{x+} , can be readily seen from the kinetic measurements reported in Table 1 and illustrated in Figs 1 and 2. There is a considerable amount of experimental evidence to support the assumption that C_{56}^{x+} and C_{58}^{x+} are fullerene ions. For example, collisions of