Prediction of Liquid C_{60} from *ab-initio* Inter-Molecular Potential

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Abstract. Since its discovery that fullerite - the bulk form of fullerene C_{60}- has been eluding scientists in what concerns its existence in a stable liquid phase. Whereas experiments have been unable to provide, so far, an unambiguous answer to this question, theories have arrived at conflicting conclusions. Making use of an ab-initio inter-fullerene interaction developed recently, we show that fullerite exhibits a well defined and stable liquid phase in a small region of its phase-diagram, at number densities between 0.468and 0.845 $nm^{-3}$and temperatures between 1881and 2012 K.

Admittedly one of the most important elements of nature, Carbon has been able to hide from Mankind many of its interesting forms, both as a bulk material as well as a finite cluster of atoms. Indeed, one had to wait until 1985 in order to witness the discovery [1] of buckminsterfullerene C_{60} and the tremendous implications it brought along in our understanding of the ingenious ways via which atoms bind into molecules, clusters and solids. Since then, several solid forms of pure carbon have been found [2], some of which with exciting technological potential [3]. In spite of the significant advances which took place in this context, the existence or not of liquid C_{60} has remained an open question with interesting consequences. For instance, if a stable liquid phase exists, then one may imagine fullerite to constitute an excellent lubricant, taking into account its chemical and mechanical properties. On the other hand, if there is no stable liquid phase, then one is facing the first pure substance exhibiting such a behaviour [4]. At a more fundamental level, the existence of a stable liquid phase and its detailed study from the experimental side may provide, via the determination of the structure factor at low momentum transfer q, valuable information in what concerns the nature of bonding between C_{60} clusters in fullerite [5].

Until now, it has not been possible to obtain an unambiguous answer to this quest from experiment [6]. Theoretically, one may address this issue, e.g., via computer simulations of the phase diagram of fullerite in the region of interest. This is the approach adopted here. To this end, we shall use at profit a recently

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developed inter-fullerene interaction, which has been derived from first principles Density Functional Theory (DFT) calculations in reference [7], and has been shown to reproduce very well the pressure-volume isotherm data of fullerite up to very high pressures (up to 20 GPa). Contrary to the more phenomenological approaches used in deriving the inter-fullerene interaction used in the simulations reported below, the first-principles interaction derived in ref. [7] takes into account the quantum mechanical nature of the C_{60} fullerene as a whole, both in the repulsive regime at short inter-fullerene distances, as well as in the asymptotic regime, in which one includes the (very large) dipole and quadrupole polarizabilities of individual C_{60} clusters calculated from first-principles. As a result, one finds that the canonical R^{-6} asymptotic dependence is insufficient to correctly account for the asymptotic behaviour of the inter-fullerene interaction.

In order to explore the phase-diagram of C_{60} in the region of interest we carried out computer simulations at different values of temperature and number density. Because of the exotic [7] shape of the inter-fullerene potential, stringent tests were imposed in our computer simulations. Furthermore, and wherever possible, more than one computational technique has been used in order to provide bias-free results. In keeping with this discussion, we have used a new method recently developed by one of us – the generalization of multiple histograms to volume and temperature extrapolations [10] (GMH) – which allows us to compute both the liquid-vapor and the solid-fluid coexistence curves (an account of the underlying technical and computational details together with the associated convergence tests will be published elsewhere [11]). In short, we have carried out simulations involving several numbers of C_{60} clusters placed in the simulation boxes, for which we took a cubic shape. We found that convergence was fully reached for simulations carried out with 500 clusters, and all results presented here will correspond to the results obtained via such simulations. As usual, the range of the inter-fullerene interaction was taken to be half of the linear dimension of the simulation box. Finally, standard long-range corrections have been applied as well [11]. The liquid-vapor coexistence curve was determined using relative free-energy calculations. Calculating the same curve using the well-known Gibbs-Ensemble [9] method (GE) leads to a very good agreement with our GMH results (see figure 1 below). The solid-fluid coexistence curve was also studied within the GMH method. Instead of using the relative free-energies determined directly by the GMH method, we have computed absolute free-energy values of the fcc solid phase and of the fluid phase at appropriately chosen thermodynamic reference points. The reason for this procedure is due to the fact that we have encountered ergodic problems – related with the appearance of metastable disordered solid phases – in the thermodynamically unstable region between the solid and the fluid phases. The results obtained in this way for the solid-fluid as well as for the liquid-vapor coexistence curves all agree when determined for different system sizes and for different simulation temperatures, giving us a very strong confidence that our results are indeed bias-free.

The resulting phase diagram of fullerite is shown in Fig. 1. Filled dots correspond to the results obtained in simulations using the GMH method, whereas the open circles

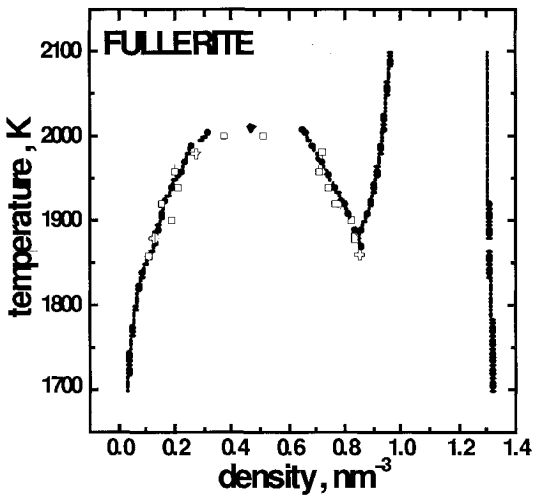

FIGURE 1. Phase diagram of fullerite. The solid circles represent the results of the computer simulations carried out using the GMH method. The hollow circles show the corresponding results obtained with the GE method. The solid diamond represents the estimated critical point. One can clearly observe a stable liquid phase in a small region of its phase-diagram.

correspond to the results of the GE method. As stated before, very good agreement between the two methods is obtained. Finally, the full-diamond corresponds to our estimate of the critical point.

Fig. 1 clearly shows a well developed dip characteristic of a substance exhibiting a stable liquid phase. Our estimate leads to a triple point temperature of 1881 K, more than 100 K higher than the value obtained by Cheng et al., reflecting the different inter-fullerene interaction used. The critical point is estimated to occur at 2012 K. Overall, our results predict that the liquid phase is expected to occur for temperatures between 1881 and 2012 K and for number densities between 0.468 and 0.845 nm^{-3}. It would be very interesting to conduct experiments at such values of temperature and density in order to verify our results.

In summary, we obtain a stable liquid phase for fullerite in a temperature interval of $\approx$ 100 K at around 1950 K. These results were obtained making use of an inter-fullerene interaction derived from first-principles DFT calculations. As such, we expect the numbers advanced here to constitute the best theoretical estimate available to date in what concerns this quest. Furthermore, and since our results favor the occurrence of a liquid phase for fullerite, one has the hope to obtain further experimental information on the nature of bonding between such unconventional quantum systems. On the other hand, we should not overlook the role played by additional physical effects which have been left out of our simulations, notably the three-body inter-fullerene interactions [12]. We argue that such effects, while contributing to modify the phase-diagram of fullerite - in particular changing the

triple and critical temperature values obtained here - will not be able to destroy the stable liquid phase obtained here. Indeed, in ref. [7] the leading three-fullerene interactions have been determined using Time-Dependent DFT calculations, and their role in the description of the pressure-volume isotherm of fullerite was shown to amount to $\approx 6\%$. Furthermore, simple phase-space considerations show that the three-fullerene interaction is mostly repulsive (although, as is well known, there are regions of attraction), a feature which is expected to contribute to an overall lowering of the triple point temperature of fullerite (and also the value for the critical point). Analysis of Fig. 1 shows that this effect would have to be abnormally large in order to destroy the liquid phase of fullerite, a feature one does not expect based on the results of ref. [7]. Of course, these considerations can be confirmed by introducing the three-body terms in our simulations. While such action is technically trivial to implement in the unified GMH approach, the computational cost involved, together with the nature of the inter-fullerene(s) interaction, has turned such simulations into a long-term project. Nevertheless, work along such lines is in progress.

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