Phase Diagram and Sublimation Enthalpies of Model C$_{60}$ Revisited

Fernando M. S. Silva Fernandes,* Filomena F. M. Freitas, and Rui P. S. Fartaria

Laboratory of Molecular Simulation and CECUL, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Lisboa, Rua Ernesto de Vasconcelos, Bloco C8, Piso 3, 1749-016 Lisboa, Portugal

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The objective of the present paper is to reassess our previous results and conclusions on the simulation of model C$_{60}$ and other fullerenes, in view of the results recently reported by other authors. We report new sublimation enthalpies in good agreement with the available experimental data and recent theoretical results. Special attention is given to the pressures along the coexistent phases. We also present a comparative study, by NVT and NpT simulations, of supercritical isotherms for Lennard-Jonesium and C$_{60}$, in order to clarify the Gibbs ensemble and Gibbs–Duhem Monte Carlo calculations. It is suggested that even in the case of C$_{60}$ the stable fluid–solid transitions can be detected through the visual analysis of the equations of state. Finally, we critically review our previous works on model fullerenes.

1. Introduction

In recent articles[1–3] we have reported the phase diagrams and enthalpies of sublimation of model C$_{60}$ by Gibbs ensemble (GE) and Gibbs–Duhem (GD) Monte Carlo simulations based on the Girifalco potential (GP)[4] and on the ab initio potential (PRP) of Pacheco and Ramalho.[5] Starting from different initial conditions, however, using the same simulation procedures, we have suggested that both interaction potentials show the existence of two sets of apparently conflicting triple-point properties. One, in which the triple point is approached from fluid–solid states at high temperatures, agrees well with free-energy-based calculations.[6,7] The other, in which the "triple point" is reached by extending the GE vapor–liquid lines to low temperatures, is in a reasonable accordance with the results of the modified hypernetted chain (MHCN) theory[8,9] combined with computer simulations and the one-phase freezing criterion (OPFC).[10] The triple-point temperature of the first set is considerably higher than the temperature of the second set. Conversely, the triple-point density of the first set is lower than the density of the second one. We have also argued that the high-temperature results correspond to local minima of the Gibbs free energy, whereas the low-temperature results correspond to the free energy global minima. Moreover, the enthalpies of sublimation obtained from the vapor–solid coexistence, starting at the low-temperature "triple point", are in good agreement with the available experimental data.

In recent investigations, Costa and co-workers[7,11] have suggested an explanation for the discrepancy between the prediction of several structural indicators and the results of full free energy calculations to locate the fluid phase boundaries. They have calculated the high-temperature phase diagram of the GP model, based on extensive absolute free energies, Monte Carlo simulations, and several theoretical approaches. In parallel, the entropy of the fluid phase has also been systematically analyzed, given that in their earlier articles[8,9,12] the onset of freezing was associated with the vanishing of the residual entropy, $\Delta S = 0$, following the prescription of OPFC. They have also reported the freezing line of the hard-sphere fluid

corresponding to the C$_{60}$ model, according to the Weeks, Chandler, and Andersen (WCA) theory.[13] Some of their conclusions are (i) the model C$_{60}$ has, confidently, a narrow stable liquid-phase interval ($\sim$1875–1940 K); (ii) due to the strong attractive and rapidly decaying potential well, the onset of the solid–liquid transition is mainly driven by "energetic" rather than entropic effects, resulting in the anticipation of the freezing threshold to lower densities than those predicted by solely structural conditions; and (iii) the OPFC freezing line almost coincides with the WCA line, suggesting that the $\Delta S = 0$ locus tends to overestimate the coexisting fluid density, thus affecting the location of the triple point.

This scenario has motivated us to reanalyze our previous results and conclusions. Meanwhile, more recently, Chen and co-workers[14] have showed that "the saturated vaporization pressures are higher than the saturated sublimation pressures below the "high-temperature" triple points. Because the chemical potential of the vapor phase increases with pressure, it is obvious that the phase with lower saturation pressure also have the lower Gibbs free energy". This, of course, refutes our arguments regarding the free energies of model fullerenes.[2,3]

The objective of the present paper is to reassess our previous results and conclusions on the simulation of model C$_{60}$ in view of the results of the authors referred to above. We report new sublimation enthalpies for the GP and PRP interaction models, now based on the vapor–solid coexistence starting from the high-temperature triple points. Special attention is given to the pressures along the coexistent phases. We also present a comparative study, by NVT and NpT simulations, of super-critical isotherms for Lennard-Jonesium and C$_{60}$, in order to clarify the Gibbs ensemble and Gibbs–Duhem Monte Carlo calculations and to show that even in the case of C$_{60}$ the stable fluid–solid transitions can be detected through the visual analysis of the equations of state. Finally, we critically review our previous works on model fullerenes.

2. Phase Diagram, Enthalpies of Sublimation, and Pressure Lines

The calculations have been carried out using the GP and PRP interaction models and the simulation procedures described

* To whom correspondence should be addressed. E-mail: fsilva@fc.ul.pt.
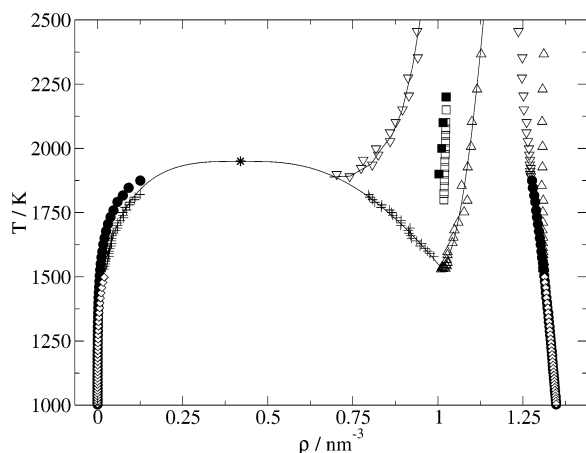
Figure 1. Temperature−density phase diagram of the GP model. Estimated critical point (∗), Gibbs ensemble (vapor−liquid, +). Gibbs−Duhem method: solid−fluid from high-temperature (▽), solid−fluid from low-temperature (△), solid−vapor from high-temperature triple-point (●), solid−vapor from "low-temperature triple-point" (◇). OPFC (■) and WCA (□) from ref 7. Solid lines are guides to the eye.
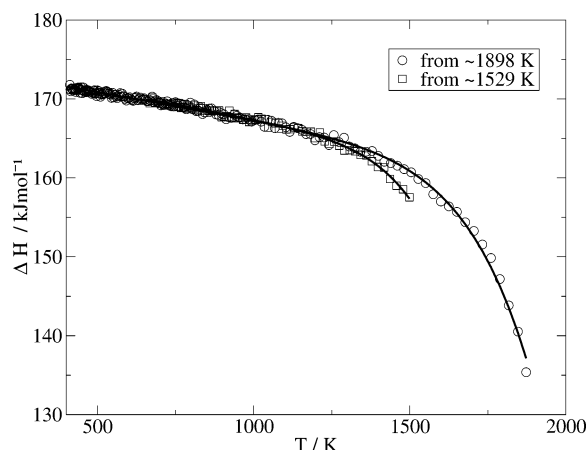

Figure 2. Enthalpies of sublimation as a function of temperature for the GP model. Fit to eq 1 (−).

elsewhere.[2,3] Figure 1 displays the whole temperature−density phase diagram of GP. Our previous fluid−solid results, corresponding to the low-temperature "triple point" (named GD-up), and the OPFC and WCA freezing lines of Costa et al.[7] are also included. The fluid−solid results corresponding to the high-temperature triple point are named GD-down. The temperature−density phase diagram of PRP is similar to the GP one and it is not represented. Figures 2 and 3, show the enthalpies of sublimation as a function of temperature, calculated from the high- and low-temperature triple points for GP and PRP, respectively. The results were fit to the equation[15]

$$\Delta_{sub}H = ZRT^2\frac{d(\ln p)}{dT} \qquad (1)$$

with

$$\ln p = A + \frac{B}{T} + C \ln T + DT^E \qquad (2)$$

Table 1 contains some simulated and experimental values. The error bars affecting the simulated results at 700 K are root mean square (rms) deviations. The values at 298 and 0 K are extrapolations of the fitting of eq 1.

The results apparently suggest the existence of two sets of triple point properties for the GP and PRP interaction models.
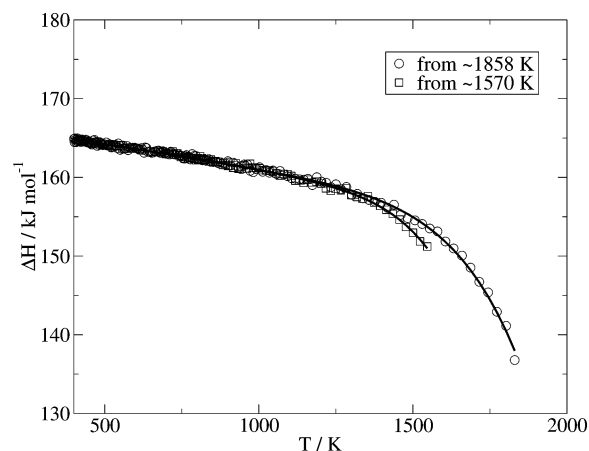

Figure 3. Enthalpies of sublimation as a function of temperature for the PRP model. Fit to eq 1 (−).

TABLE 1: Enthalpies of Sublimation in kJ mol^{-1}

		simulated results	
		GP	
	700 K	298 K	0 K
from ∼1529 K	170 ± 12	173	174
from ∼1898 K	170 ± 12	172	174
		PRP	
	700 K	298 K	0 K
from ∼1570 K	163 ± 9	166	167
from ∼1858 K	163 ± 10	166	167
	experimental results		
NIST[16]	Markov et al.[17]		
∼700 K	298 K	0 K	
176 ± 2	181 ± 2	175 ± 14	

However, as we shall see, the low-temperature set is not thermodynamically stable.

The narrow, stable, liquid-phase intervals [1880−1980, 1875−1940, and (1876 ± 13)−(1946 ± 4) K] predicted respectively by Hasegawa and Ohno,[6] Costa et al.,[7] and Chen et al.[14] for GP are, within the error bars, in very good agreement with our simulation result[2] corresponding to the high-temperature triple point [(1898 ± 21)−(1951 ± 28) K].

Both freezing lines depend on density and temperature, though the line from the high-temperature triple point spans a wider range of density versus temperature. The GD-up freezing line does not entirely coincide with the OPFC and WCA lines. Nonetheless, their extrapolation approaches our "low-temperature triple-point" density and temperature. The structural indicators do appear to identify a very restricted range of density versus temperature over which structural reorganization of the fluid phase should be established in order to mainly satisfy entropic demands, as proposed by Costa and co-workers.[7,11]

Hoover and Ree,[18] many years ago, determined that the hard-sphere system has a fluid−solid transition for densities, relative to the close-packing, in the range 0.667−0.736. Thus, a fluid of hard spheres with a diameter of 0.9599 nm (the effective diameter of the C_{60} molecule used in the present simulations) should freeze at a density ∼1.07 nm^{-3}. This value is just inside the range of density versus temperature of the GD-up freezing line. We have overlooked this important result in the conclusions of one of our previous articles,[2] where we have suggested the approach to hard-sphere behavior for the GD-down freezing line.

The present simulations clearly show that the vapor−solid lines, calculated from the two triple points and interaction
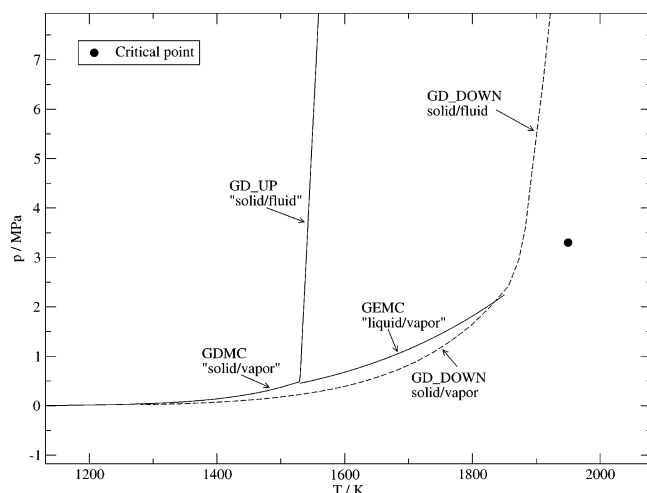
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Figure 4. Pressure−temperature phase diagram of the GP model.

Figure 5. Supercritical equations of state for Lennard-Jonesium.

Figure 6. Supercritical equation of state for the GP model at 2100 K.

potentials, coincide for temperatures below ∼1250 K. Consequently, the model sublimation enthalpies are equal below that temperature and they are in good agreement with the available experimental data, particularly the ones corresponding to GP. Thus, the experimental data cannot be used to discard one of the simulation triple-point estimates, contradicting what we have conjectured in our previous articles.[2,3] Incidentally, Zubov et al.[19] have reported, in a recent theoretical study, sublimation enthalpies in excellent agreement with our simulation results at 700 K. However, the noticeable discrepancy (on the vapor side) of the vapor−solid lines above ∼1250 K (see Figure 1), which is also reflected in the sublimation enthalpies above that temperature (see Figures 2 and 3), called for a further thorough analysis of our pressure−temperature diagrams, displayed in Figure 4 for GP. A similar diagram is observed for PRP. It is clear that the saturated sublimation pressures are systematically less than the saturated vaporization pressures, but below ∼1250 K they coincide. Thus, the corresponding Gibbs free energies definitely have the inverse order of what we have claimed in our previous articles.[2,3] This agrees with the Clausius−Clapeyron plots recently reported by Chen et al.[14] Therefore, the behaviors detected below the high-temperature sublimation curve are metastable or unstable. Indeed, this had already been suggested, for the first time, in the 1993 pioneering work of Hagen et al.[20]

3. Supercritical Isotherms for Lennard-Jonesium and C_{60}

The apparent persistence and reproducibility of the fluid−solid coexistence obtained from the metastable "low-temperature triple point" needs, however, a further investigation in an attempt to trace its origin and meaning. To this end, we have simulated, by NVT and NpT Monte Carlo as well as by NVT molecular dynamics, supercritical isotherms for Lennard-Jonesium (at reduced temperatures 2.0 and 2.74) and for C_{60} with GP (at 2100 K). For each point of the Lennard-Jonesium, the calculations, with 256 and 108 molecules, always started from face-centered-cubic (fcc) lattices. The density was increased by steps of 0.05, spanning the interval 0.7−1.3. In NpT, the pressure was slowly increased, always from a lattice at density 0.7, spanning the same range of densities. For each point of the C_{60}, the NVT calculations, with 256 and 2048 molecules, always started from fcc lattices, the densities being increased by steps of 0.05 nm^{-3}, spanning the interval 0.6−1.4 nm^{-3}. In NpT, however, two initial conditions were used: fcc lattices at different densities and the last configurations of production runs
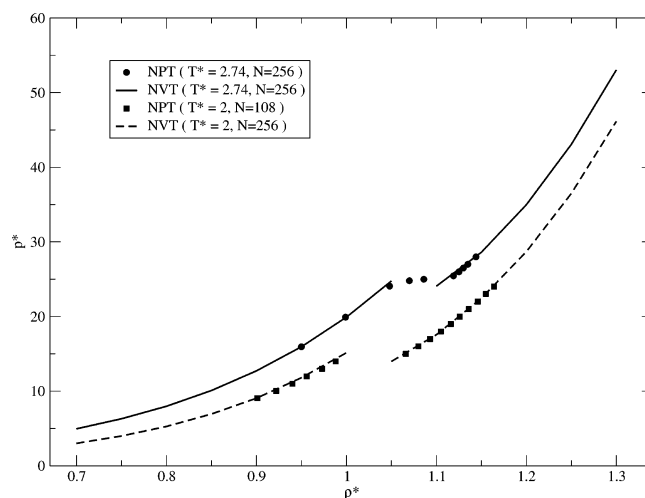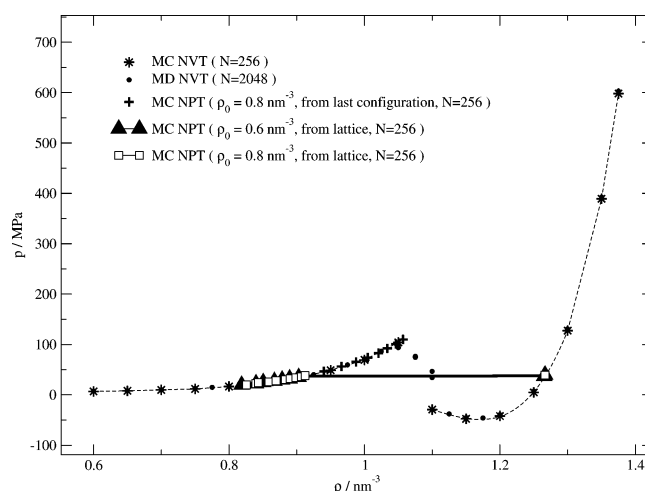
for previous states. The pressure was slowly increased. Cubic periodic boundary conditions were applied to both systems, with the potential cutoff at half of the simulation box length and applying long-range corrections. A total of 50 000 MC cycle production runs followed equilibration runs with 10 000 cycles. The canonical MD simulations, with 2048 molecules, were carried out with similar statistics, a cutoff at about three molecular diameters and using the linked-list technique. The results, displayed in Figures 5 and 6, suggest that

(a) for Lennard-Jonesium, the fluid−solid transitions are clearly detected by the direct observation of the equation of state, either in NVT or in NpT. The transition at $T^* = 2.74$, for example, is located in the density interval 1.05−1.13, the pressure being $p^* \sim 25$. These values agree well with the results of Street et al.[21] and Hansen and Verlet.[22] The supercooling of the fluid is slight because the starting configurations are fcc lattices. If the initial configurations are disordered, then a pronounced supercooling will be observed, as showed by Street et al.[21] years ago. It appears that the remains of the ordered initial configurations induce the presence of seeds for solidification.

(b) As for the C_{60}, two kinds of behavior are detected. In the NVT calculations, even starting always from the lattice, a pronounced supercooling of the fluid is observed and a transition is only detected at density ∼ 1.05 nm^{-3}. This value is in accordance with our GD-up calculations. The equation of state is, also, in excellent agreement with that recently reported by

Costa et al.[7] and Hasegawa and Ohno.[23] Incidentally, the production of metastable states by computer simulation is extremely useful in full free energy calculations, for it enables a correct double-tangent construction,[7] as well as in the study of metastable real systems.[24] The NpT calculations starting from the lattice, though, show a transition at the density interval $\sim 0.9-1.25$ nm^{-3}, in accordance with our GD-down simulations and full free energy calculations.[6,7] On the contrary, the NpT simulations starting from disordered configurations present the same pronounced supercooling of the fluid as observed in the NVT calculations. Constraint of fixed volume, and the anticipation of the freezing threshold to lower densities due to the potential form,[7] seems to prevent, in the case of C_{60}, a proper sampling of the phase space in the NVT calculations. This may explain the reason for Hasegawa and Ohno[23] not having detected the location of the stable fluid−solid boundary in their recent study on the isotherms of C_{60} by NVT Monte Carlo.

We should emphasize that we do not mean, at all, that straight Monte Carlo or molecular dynamics simulations can exactly determine the fluid−solid boundaries. Indeed, these can only be precisely established by appropriate simulation methods, free energy calculations, or both. However, it appears that, even in the case of C_{60}, the location of the stable boundaries can approximately be detected by direct observation of the equations of state.

This study indicates that the analogies between Lennard-Jonesium and C_{60}, or other systems that interact through short-range forces, must be taken with care. Furthermore, it clarifies the GE and GD simulations and it reconfirms that our so-called GD-up "freezing-lines" for C_{60} are metastable. It also recalls the well-known importance of the initial conditions when simulating states that are not thermodynamically stable.

4. Determination of the Triple Point by Gibbs Ensemble

The GD-up "freezing-lines" are based on a method recently proposed by us.[25] The method has its roots in a previous work[1] and it was mainly intended to avoid full free energy calculations. As it worked very well for Lennard-Jonesium,[25] we then applied it to C_{60} and other fullerenes.[2,3] An important detail has, however, been overlooked. That is, the method relies on the Gibbs ensemble vapor−liquid curve which, for C_{60}, is metastable in the simulated range of temperatures and densities (see Figures 1 and 4). This fact and the results of the previous section seem to suggest that the so-called low-temperature "triple point" and the corresponding "freezing lines" should be no more than the limit of metastability and the onset of the absolute instability of the system.

But why has this not turned out to be the case in our previous GD-up simulations? Another detail has been overlooked: the importance of the initial conditions. In fact, our original Gibbs−Duhem simulations (up and down) were performed always starting from the last configurations of the production runs for previous state points. We have recalculated the GD-down and GD-up curves, but now starting from lattice configurations. The GD-down curve is totally reproduced (indicating that stable states do not depend on the initial configurations), whereas the GD-up curve is not. In the last case, the "liquid box", after a few state points, reaches solid configurations. This can be tested, in a simpler way, by performing an independent NpT simulation at a "liquid state point" on the original "freezing-up line". The "liquid" does not withstand the applied pressure and jumps to a solid.

In view of the present results, it should be concluded that our method, in the case of C_{60} and other fullerenes, has just

extended the metastable GE vapor−liquid curve down to the point of absolute instability of the system. This point, initially detected with 108 and 256 molecules in each simulation box, has been confirmed by performing simulations with a larger number of molecules/box, namely 500 and 1000. The method was accepted for publication in July 2001.[25] At that time, we were not aware of the method by Chen and co-workers[26] published in the same year. Their method allows the direct simulation of the solid−vapor equilibria, in the spirit of extending the Gibbs ensemble technique and avoiding full free energy calculations. It appears to be general and robust.

We should also comment on the correlations that we have previously reported,[3] between the intermolecular potentials and the phase properties of C_{60} and other fullerenes, based on a kind of "corresponding states" rule. Apart from the "low-temperature triple points" being metastable, the correlations seem to be valid. Indeed, even the onset of absolute instability should directly depend on the underlying potential functions.

5. Final Remarks

We have critically reviewed our previous works on the phase behavior of C_{60} and other fullerenes. An explanation has been suggested regarding some important aspects that have not turned out in our original calculations.

The simulated sublimation enthalpies are in very good agreement with the available experimental data and recent theoretical results, particularly the enthalpies calculated from the Girifalco potential.

Finally, in view of the present results, it seems that the origin of the discrepancies on the fluid−solid equilibria, previously reported by us, has been resolved.

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