Thermodynamics of carbon in iron nanoparticles at low temperature: reduced solubility and size-induced nucleation of cementite

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Abstract

In this manuscript we present the thermodynamics of iron-carbon nano particles at low temperature. By combining classical molecular dynamics simulations, \textit{ab initio} calculations, finite temperature thermodynamics modeling, and the “size/pressure approximation”, we address carbon-induced fluidization, size-induced eutectic point shift, and reduced solubility at the nanoscale. The results are used to describe, as functions of particle size, three scenarios in the catalytic chemical vapor deposition growth of single single-walled carbon nanotubes, corresponding to steady state-, limited- and no-growth. © 2010 Published by Elsevier Ltd.

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1. Introduction

Low temperature catalytic chemical vapor deposition (CVD) is the most appropriate technique, among the established methods for growing single-walled carbon nanotubes (SWCNTs) [1, 2], on a substrate at a target position and can thereby accelerate the integration of this unique material in hybrid electronics. Reported synthesis of SWCNTs by CVD at reactor temperature as low as \(\sim 350-450^\circ C\) was achieved by using hydrocarbons with extremely exothermic catalytic decomposition reaction [3, 4], which may release significant free energy (e.g. for acetylene 260 kJ/mol at \(650^\circ C\) [5]), affecting the temperature of the catalyst under certain conditions. For instance, if all produced heat is stored in the particle, the calculated temperature rise is \(\Delta T = 6834 K\) [5]. Thermal coupling with the substrate and with the surrounding gases has significant impact and, eventually, defines the catalyst local temperature.

Consider the vapor-liquid-solid model (VLS) as the most probable mechanism for SWCNT growth [8, 9, 10]. An alternative approach for lowering the growth temperature can be the reduction of the catalyst size, since the Gibbs-Thomson model predicts a decrease of the melting temperature with decreasing cluster size [11, 12, 13] and the synthesis temperature is correlated to the catalyst-carbon melting and eutectic points [14, 15, 16]. While small catalyst particles nucleate small diameter tubes, they also affect the morphology of the formed carbon structures [17], the kinetics of the growth [18, 19], and the solubility of carbon available for the growth process. The latter requires understanding the thermodynamic state [12]. The main challenges are the un-exposed features of small catalysts
and their binary phase diagrams with carbon. In this manuscript, we address the carbon solubility problem in Fe nanoparticles by summarizing briefly our experiments of the size-dependent growth of SWCNTs by CCVD, and by presenting detailed thermodynamic modeling of competing phases in Fe-C clusters with *ab initio* calculations.

2. V-shape and role of Fe$_3$C

In reference [10], Harutyunyan *et al.* have performed combined *in situ* studies of the Fe-catalyst activity during SWCNT growth by mass spectrometry with differential scanning calorimetry (DSC) and Raman spectroscopy. By sequentially introducing $^{12}$C- and $^{13}$C-based methane, the authors have revealed the influence of catalyst composition on the lifetime and termination path of the growth. The authors concluded that the presence of a “V”-shape liquidus line at the nanoscale was necessary to explain the experimental results.

![Figure 1](color online). a). Evolution of liquidus of Fe and Fe:Mo supported catalysts during nanotube growth, measured by DSC. b). Hydrogen concentration normalized evolution during SWCNT growth, with Fe:Al$_2$O$_3$, obtained with a mass spectrometer. The insets correspond to experiments with a sequential introduction of $^{12}$CH$_4$ and $^{13}$CH$_4$ gas, for (b1) 3 and 17, (b2) 7 and 13, (b3) 10 and 10 min, respectively. Reproduced from Ref. [10].

Figure 1 (reproduced from Ref. [10]) summarizes the results. By comparing the region of high $H_2$ concentration in the exhaust of the reactor, the continuous *in situ* measurement of the liquidus of the nanocatalyst and the outcome of the growth performed with normal ($^{12}$CH$_4$) or “heavy” methane ($^{13}$CH$_4$), it is evident that the growth is associated with the region in which $T_{\text{synth}}$ is higher than $T_{\text{melting}}$. In other words, the figure implies that the particle, upon pollution with C, undergoes a process of fluidization with an associated eutectic point (the minimum in the blue line of panel (a)). Further pollution causes an increase of the liquidus, with concomitant nucleation of a stable phase (cementite, a Fe$_3$C carbide), which is inactive and terminates the process. By looking at the usual Fe-C phase diagram [20, 21],
it is possible to realize that the mechanism described above is congruent with an isotherm at temperature higher than the eutectic, crossing twice the \textit{liquidus}, by going from the $\gamma$-Fe phase, to the liquid, and then to the Fe$_3$C carbide.

3. Molecular Dynamics calculations of eutectic points for Fe-C nanoparticles

Chemical vapor deposition experiments of SWCNT growth from small particles (diameter $\sim$0.6-2.1 nm) indicate that the diameter of the nanotube is similar to that of catalyst particle from which it grows [22, 23, 24, 25, 26, 27, 28]. In some experiments where the growth mechanism is thought to be root-growth, the ratio of the catalyst particle diameter to SWCNT diameter is $\sim$1.0 [25], whereas in experiments involving pre-made floating catalyst particles this ratio is $\sim$1.6 [27, 28]. It is therefore clear that, to reduce the SWCNT diameter, one has to reduce the size of the catalytic particle. In addition, the Gibbs-Thomson phenomenon predicts decrease of the melting point, $T_m$, of a particle [29, 30, 31] in function of bulk melting temperature $T_{\text{bulk}}$, effective diameter of the particle $d$, latent heat of melting $\Delta H_{m}^{\text{eff}}$, and solid-vapor interfacial energy $\gamma_{sv}$ [32].

![Figure 2](color online). Melting temperature versus the inverse of particle diameters. Free non-magic sizes (\textbullet) and their linear fit (dashed line); supported non-magic sizes (▲) and their linear fit (solid line); Supported clusters have higher melting temperatures due to the decreased curvature of the surface as shown on the two right particles where $R_S > R_F$, [33]. Melting temperatures of free magic sizes (◦) and supported magic sizes (△) clusters are compared with the linear fit lines of non-magic sizes (inset). Figure adapted from Ref. [12].

To study the “V”-shape \textit{liquidus} of Fe-C nanoparticles, we use Molecular-Dynamics (MD) simulations. The simulations are carried out in an \textit{NVT} ensemble using the Verlet algorithm [34, 35] with a time step $\Delta t = 1.0$ fs and Nosé-Hoover thermostats [12]. The Fe-Fe, Fe-C, and C-C, interactions are described by Born-Mayer [36, 37], Johnson [38, 39], Lennard-Jones [40] potentials, respectively. These interaction models are discussed in detail elsewhere [39, 12]. We use a Morse potential to model the Fe:C-Al$_2$O$_3$ interaction, as introduced by us in Ref. [12]. To avoid excessive kinetic energy fluctuations in the MD simulations of the nanoparticles one should start from the most stable configurations. We search for the best possible energy minima by randomly arranging atoms in a spherical nanoparticle, carefully optimizing the positions of iron and carbon atoms and finally annealing the nanoparticles for $6 \times 10^6$ MD iterations. In our work, the melting phenomenon is analyzed by performing several MD simulations starting at about 300 K below the expected melting point with temperature increments of 10 K for small ($N < 100$) and 20 K for large clusters (with 5 K upon approaching the transition). Only the lowest-temperature simulations begin from the annealed initial structures: the others start from the final configurations (positions, forces, velocities) of the preceding temperature simulations. Data gathering of the energies and other averages are performed over $10^6$ MD steps.
Several dynamical and structural properties such as total energy, Lindemann index, diffusion coefficients, and pair correlation functions can be used to identify phase transitions in nanoparticles [41, 42]. We characterize the melting phenomenon by the temperature dependence of the total energy (caloric curve), by the change in the total energy with time, and by the variation of the Lindemann index with respect to temperature [43]. The Lindemann index represents the root-mean-square relative bond-length fluctuation:

\[
\delta \equiv \frac{2}{N(N-1)} \sum_{i<j} \frac{\sqrt{(r_{ij}^2) - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle},
\]

where \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( N \) is the number of atoms and the average is calculated over an MD run at a given \( T \).

The melting point, which defines the temperature at which a solid becomes liquid, is a macroscopic concept for pure and bulk systems. Both finite-size and presence of more than one atomic species make the melting transition a continuous phenomenon that occurs over a range of temperatures, \( \Delta T_m \), in which solid and liquid phases coexist with different fractions [29, 44, 45]. To have a specific value of \( T_m \) instead of a range, we define the melting temperature \( T_m \) as the “max-solid point” which represents the maximum temperature at which the solid and the liquid phases coexist (the locus of all the max-solid points is the liquidus). Above \( T_m \), no solid phase is present. Note that within this definition of \( T_m \), we also identify plastic-viscous nanoparticles as “liquid” [46]. Similarly, the min-liquid point is the minimum temperature at which the solid and the liquid phases coexist (the locus of all the min-liquid points is the solidus). The difference between the energies of the particle at the max-solid and at the min-liquid points defines the enthalpy of melting \( \Delta H_m \) [12]. Figure 2 shows \( T_m \) of pure Fe nanoparticles in the whole range of sizes (\( N_{Fe} = 80 - 1000 \)) for free and Al2O3-supported clusters. Our results, in agreement with other theoretical [47, 48], computational [49, 50, 51], and experimental studies [52, 53, 54, 30, 55], predict a decrease in the melting temperature inversely proportional to the cluster diameter [56]. The behavior of \( T_m \) is described by the aforementioned Gibbs-Thomson model.

Figure 3: (color online). Fe-C phase diagrams obtained with addition of C (up to \( \sim \) 16%) to particles with \( N_{Fe} = 80, 100, \) and 200. The “GT” arrows represent the reduction of \( T_m \) as a function of the size of the particles. The “J” arrow represent the shift of the eutectic point toward lower C concentrations, as described in the text and in Jiang et al. [12]. Figure taken from Ref. [12].
To understand how inclusion of C influences the thermal behavior of the catalyst nanoparticles, we determine the melting temperature as a function of carbon concentration \( x^C \) ranging from zero to \( \sim 16 \% \). Figure 3 shows the phase diagrams (\( T_m \) versus \( x^C \)) for particles \( N_{Fe} = 80, 100, \) and 200 based on calorimetric curve and Lindemann index analysis. All the data sets show a similar trend in function of C concentration: \( T_m \) decreases almost linearly at low \( x^C \) and then increases for all the higher \( x^C \) considered. The exact functional form is difficult to determine because of the dispersion in the data, however the observed “V”-shape dependence is consistent with that in the bulk Fe-C phase diagram [20, 21]. Hence, by using the least square method we approximate the liquidus by a set of two straight lines, the intersection of which gives the eutectic point \((x_{eut}^C, T_{eut})\) [57]. This procedure allows us to estimate this invariant point with an accuracy of 1% and 12 K for \( x_{eut}^C \) and \( T_{eut} \) respectively. We observe that as the particle size is reduced, the eutectic point moves toward lower temperatures and lower concentrations. Due to the high energetic cost for bringing bulk cementite off-stoichiometry (in the Fe-C phase diagrams Fe3C forms two-phase regions with austenite (\( \gamma \)) and ferrite (\( \alpha \)) without going off-stoichiometry [20, 21]), the most probable cause of the shift of \( x_{eut}^C \) is a reduced solubility of C. This does not necessarily imply that the total amount of C (either dissolved in Fe or forming cementite) present in the nanoparticle decreases, because solubility counts only the carbon dissolved randomly in the solid Fe-rich phases, (in equilibrium with Fe3C (below \( T_{eut} \)) or with the liquid/viscous phase (above \( T_{eut} \))).

Figure 4 shows the bulk Fe-C phase diagram with arrows indicating the shift of boundary lines as a function of reduced nanoparticle size. “GT” arrow indicates the Gibbs-Thomson phenomenon while “J” represents the results of our molecular dynamics calculations [12]. Due to the fact that Fe3C is a line compound as summarized by the “crossed” arrow, the only plausible mechanism responsible of the shift of the eutectic point is a concomitant reduction of C solubility, in both the \( \gamma \) and \( \alpha \) phase (“must” arrows).

Figure 4 shows the bulk Fe-C phase diagram with arrows indicating the shift of boundary lines as a function of reduced nanoparticle size. By following the “GT”, “J”, and “must” arrows, one realizes that the only plausible mechanism responsible of the shift of the eutectic point is a concomitant reduction of C solubility, in both the \( \gamma \) and \( \alpha \) phases. The solubility reduction can be caused by excess free energy for interstitial C defects in \( \gamma FeC \) and \( \alpha FeC \) at the nanoscale, or the nucleation of a new phase at low temperature in small particles. The latter has a stronger impact on the amount of unordered-solute C inside the catalyst because it tends to segregate and order C by lowering its chemical potential and, hence, reducing its concentration in the random phases \( \gamma FeC \) and \( \alpha FeC \).

Figure 5 shows the MD-averaged radial distribution function \( N_{total}/r^2 \), calculated with respect to the geometrical center of the cluster, for two nanoparticles Fe80C6 and Fe320C24 at temperatures 25% higher than their melting points.
The panels \(N/N_{\text{total}}\), devising the fraction of species C and Fe, indicate that while the larger particle tends to be homogeneous, the smaller cluster has a strong ordering tendency. The phenomenon, typical of liquid/viscous systems in which a solid phase is competing for stability, corroborates the aforementioned observation of reduced solubility caused by nucleation of a carbide at the nanoscale.

Figure 5: (color online). Radial distribution function \(N_{\text{total}}/r^2\), calculated with respect to the geometrical center of the particle, for two nanoparticles Fe\(_{80}C_6\) and Fe\(_{320}C_{24}\) at temperatures 25\% higher than their melting point \(T_m\). The panels \(N/N_{\text{total}}\) indicate the fraction of species, C and Fe.

4. *Ab initio* calculations of Fe\(_3\)C stability in Fe-C nanoparticles at low temperature

Additional experimental results suggesting loss of carbon solubility in Fe-C nanoparticles are reported in Ref. [58, 59]. In this manuscript, the authors show that, by changing Fe:Al\(_2\)O\(_3\) molar ratio 1:15, 1:25, 1:50 and 1:100 [60], corresponding to particles of diameters \(\sim 3 \pm 0.6\), \(\sim 2 \pm 0.8\), \(\sim 1.4 \pm 0.7\), and \(\sim 1.3 \pm 0.7\) nm, the minimum synthesis temperature for SWCNT growth, \(T_{\text{min}}^{\text{synth}}\), increases contrary to what may be expected from the Gibbs-Thomson model [12]. This is summarized in Figure 1 of Ref. [58], where \(T_{\text{min}}^{\text{synth}}\) is plotted as a function of the Fe:Al\(_2\)O\(_3\) molar ratio.

The observation indicates that decomposition of the hydrocarbon alone is not enough to grow nanotubes and that the temperature must be increased to ensure that a certain amount of carbon dissolves into the particle. In fact, temperature must be increased to overcome the loss of solubility of C in the catalytically-active phase competing for thermodynamical stability with a nucleating carbide, and not only to enhance diffusion of C. Therefore, the on/off phenomenon should be addressed only through phase transformation within the particle, because a kinetic mechanism, such as diffusion, would be described by Arrhenius-type equations that are incapable of representing the temperature dependent on/off observation. The authors conclude that the origin of this apparent paradox lies in a novel phenomenon, i.e., a reduced solubility of C in Fe nanoparticles. Within the VLS-mechanism framework with bulk diffusion as the rate-limiting step [61, 62, 63, 64, 10], this implies an increase of temperature to achieve comparable amount of dissolved carbon to allow growth.

The accurate analysis of the phenomenon is achieved by calculating the interplay between the phases competing for stability at the temperatures of the process. For nanoparticles, this task is generally unsolvable, although qualitative information can be extracted from approximate zero-temperature first-principles modeling. In such approaches, by
comparing the formation energies of the candidate phases, we can determine the stability of the system at low-T and give indications for higher temperature behavior. The ab initio simulations presented here are performed with VASP [65, 66], using projector augmented waves (PAW) [67] and exchange-correlation functionals as parameterized by Perdew, Burke, and Ernzerhof (PBE) [68] for the generalized gradient approximation (GGA). Simulations are carried out with spin polarization, at zero temperature, and without zero-point motion. All structures are fully relaxed and numerical convergence is ensured to within about 2 meV/atom.

![Size-pressure approximation diagram](image)

**Figure 6**: Size-pressure approximation. Given a spherical particle, the pressure due to the surface curvature is obtained from the deviation of the average bond length inside the cluster, $\Delta d_{\text{nn}} \equiv d_{\text{nn}}^x - d_{\text{nn}}$ and mapped onto a fictitious hydrostatic pressure producing the same bond deviation in the bulk material.

The following four assumptions form the ansatz of the model. (i) *Mechanism*. The behavior of carbon is determined by the interplay of four competing phases as a function of catalyst size: pure bcc-Fe, C dissolved in ferrite ($\alpha$FeC$_x$), ordered cementite (Fe$_3$C), and carbon SWCNTs. The pure-Fe phase is taken to be bcc because our simulations are aimed to explore the low temperature regime of catalytic growth. The $\alpha$FeC$_x$ phase is simulated by taking samples of bcc supercells with different concentrations of interstitial carbon (Fe$_{23}$C, Fe$_{24}$C, Fe$_{16}$C). In addition, higher concentrations of C are not required to be explored, because even in bulk $\alpha$FeC$_x$ the solubility is small [20, 21]. (ii) *Carbon source*. Free carbon atoms come from the dissociation of the feed-stock on the surface of pure-Fe and random FeC$_x$ catalysts only. The formation of cementite stops the process due to its different activity and diffusion properties. (iii) *Nanotubes diameter*. To minimize the curvature energy of the tube, active catalysts produce nanotubes that have the same diameter as the particle. (iv) *Size-pressure approximation*. In nanoparticles, surface curvature and superficial dangling bonds are responsible for internal stress fields which modify the atomic bond lengths inside the particles. For spherical clusters the phenomenon can be modeled with the Young-Laplace equation $\Delta p = 2\gamma/R$ where the proportionality constant $\gamma$ (surface tension for liquid particles) can be determined with ab initio methods. As a first approximation, by neglecting all the surface effects not included in the curvature, the study of phase diagram for spherical particles can be mapped onto the study of phase diagrams for bulk systems under the same hydrostatic pressure produced by the curvature, as depicted in Figure 6 [69]. It is important to mention that $\gamma$ is not a real surface tension but an ab initio fitting parameter describing size-induced stress.

Figure 2 of Ref. [58] shows the implementation of the “size-pressure approximation” for Fe particles. On the left hand side the average distortion of the bond length inside the cluster $\Delta d_{\text{nn}} \equiv d_{\text{nn}}^x - d_{\text{nn}}$ is plotted for a variety of spherical bcc particles as a function of the inverse radius (1/R). On the right hand side the compression of the bond length is calculated as function of hydrostatic pressure for the bulk system. The combination of the two interpolations leads to the approximated $P \leftrightarrow R$ relation:

$$P \cdot R = 2.46 \text{ GPa} \cdot \text{nm} \quad (\gamma = 1.23 \text{J/m}^2). \quad (2)$$

By performing ab initio simulations of bulk systems under pressure and with the use of relation (2), we calculate the stability of all competing phases for particles with $R \sim \infty, 1.23, 0.62,$ and 0.41 nm corresponding to $N \sim \infty, 600, 150,$ and 40, respectively. Formation Energies, $E_F$, are calculated with respect to decomposition into the most stable configuration of the pure elements under investigation (bcc-Fe and SWCNTs)

$$E_F[Fe_{1-x}C_x] \equiv E[Fe_{1-x}C_x] - (1 - x) \cdot E[Fe] - x \cdot E[C]. \quad (3)$$
Figure 7: (color online) Gibbs Free Energies at $T = 500, 600$ and $723 \degree C$ for Fe-C nanoparticles with two different sizes, $R \sim 0.62$ nm and $R \sim 0.41$ nm, respectively (panels (a) and (b)). The convex hull, calculated with respect to the most stable structures, determines the phase boundaries. The insets show the formation energies (in meV/atom) for the two cases (figures adapted from Ref. [58]). The black stars represent the solubility of C in $\alpha - \text{FeC}_x$ calculated at the presented temperatures.

The Gibbs Free Formation Energy of each phase, $G_F$, is obtained from $E_F$ upon subtraction of the entropic term $T \cdot S_{\text{tot}}$. For simplicity, only configurational entropies $S_{\text{conf}}$ are taken into consideration, since the vibrational contributions $S_{\text{vib}}$ can be neglected in first approximation (typical vibrational entropy differences between phases are around $0.1-0.2 k_B/\text{atom}$, smaller than typical values of configurational entropy differences in binary alloys, at most $0.6932 k_B/\text{atom}$ [70]). In our model, the only phase allowed to go off-stoichiometry is $\alpha - \text{FeC}_x$. For $\alpha - \text{FeC}_x$ we use the ideal solution model and obtain

$$S_{\text{conf}}[\alpha - \text{FeC}_x] = -k_B \left[ x \cdot \log(x) + (1 - x) \cdot \log(1 - x) \right],$$

where $x$ is the concentration of carbon. For the other phases we have $S_{\text{conf}}[\text{Fe}_3\text{C}] = S_{\text{conf}}[\text{SWCNT}] = 0$.

A structure at a given composition is considered stable if it has the minimum $G_F$ for any structure at this composition, and, if on the binary phase diagram, it lies below the convex hull of tie lines connecting all the other stable structures [71, 72, 73, 74]. Phases lying above the convex hull and with small positive formation energies, might be explored by the thermodynamics of the system through entropic promotion.

Figure 7 shows the Gibbs Free Energies at $T = 500, 600$ and $723 \degree C$ for two size particles, $R \sim 0.62$ nm and $R \sim 0.41$ nm, panels (a) and (b), respectively. The insets (taken from Ref. [58]) show the evolution of the formation
energies at $T = 0$ K. The conservation of the chemical potential of carbon, implied by convex hull construction, gives the range of solubility of phases. The black stars of figure 7 represent the maximum solubility of C in $\alpha$FeC$_x$ at $T = 500, 600$ and $723^\circ$C. In big nanoparticles, $R > R_{\text{min}} \sim 0.58$ (calculated in Ref. [58]), $\alpha$FeC$_x$ competes for stability against SWCNTs. In smaller clusters, $R < R_{\text{min}} \sim 0.58$, $\alpha$FeC$_x$ competes with Fe$_3$C. The phenomenon has an important consequence for SWCNT growth. As mentioned before, Fe$_3$C is not catalytically active, therefore its nucleation terminates the growth process.

Concerning CVD growth of SWCNTs, we identify three scenarios. **I. Scenario I with $R > R_{\text{min}}$** (Figure 7(a)). Fe$_3$C has Gibbs free energy higher than the combination $\alpha$FeC$_x$ ↔ SWCNT. Hence, pollution of carbon at low and medium temperature does not promote cementite nucleation. Therefore such particles remain in the catalytically-active random $\alpha$FeC$_x$ state, (solubility is unaffected and similar to the bulk value). The balance between in- and out-flows of carbon can guarantee the steady state growth of nanotubes. Thermodynamically, in this regime, SWCNTs, MWCNTs and carbon fibers could be grown indefinitely and the only limitation is the availability of carbons feed-stock [75]. In addition, experiments performed with particles of these sizes would be described by Arrhenius equations governing the catalytic activity and diffusion properties. **II. Scenario II with $R \sim R_{\text{min}}$.** For particles of size $R \sim R_{\text{min}}$, the $\alpha$FeC$_x$ phase and Fe$_3$C have similar Gibbs free energies. Latter causes depletion of C in $\alpha$FeC (reduced solubility) and nucleation of ordered cementite, which reduces the amount of catalytically active random Fe. If exposed to hydrocarbons at elevated temperatures, such particles would be capable of dissociating carbon and growing SWCNTs with concomitant nucleation of the carbide. Such nucleation slowly terminates the growth. In this regime, SWCNTs can be produced up to a certain critical length depending on the net flow of carbon. **III. Scenario III with $R < R_{\text{min}}$** (Figure 7(b)). By further reducing the size of the particle, $R << R_{\text{min}}$, the Gibbs free energy of cementite becomes negative. Practically, over the range $0 < x < 25\%$ in the phase diagram, any available unbonded carbon will tend to form Fe$_3$C, because the maximum solubility of C in the random phase $\alpha$FeC$_x$ is negligible. The nucleation of Fe$_3$C occurs simultaneously with the carbon pollution (as rapidly as the availability of feed-stock allows) and no out-flow of carbon occurs. Particles with $R < R_{\text{min}}$ cannot grow SWCNTs, and $R_{\text{min}}$ can be considered as a lower limit for SWCNTs’ size in low-temperature CVD growth with Fe nano-catalysts. Experiments performed with such particles would result in Fe$_3$C nanoparticles and no appreciable nanotube productions. The rapid reduction of C solubility in small particles ($R < R_{\text{min}}$) is shown in Figure 8. By reducing the size of the particle, the solubility lines shift toward lower C concentration, in agreement with the molecular dynamics calculations and thermodynamic predictions shown in Figures 3-4-5.

We have not yet explored other phenomena which can induce modifications in the phase diagrams of Fe-C nanoparticles. The effect of substrate, smooth, rough or porous, can be studied with Density Functional or Monte Carlo methods [76, 77, 78, 79, 80, 81]. Bimetallic alloyed nanocatalysts, which can be studied with the “size/pressure

Figure 8: (color online) Maximum C solubility in small Fe-C nanoparticles. The rapid reduction of the amount of available unbounded carbon prevents the growth of very thin SWCNTs at low temperature. Concentration is expressed in atomic %.
approximation”, are interesting because they offer chemical and thermodynamical advantages (Fe-Mo in Ref. [59]).

5. Conclusions

In this paper we have addressed thermodynamics of Fe-C nano catalysts with classical molecular dynamics and quantum mechanical methods. We have introduced a novel approach, called “size-pressure approximation” which allow an estimation of the effect of particle size on phase boundaries. We show that size-induced nucleation of cementite Fe₃C is responsible for the loss of C solubility in bcc Fe nano-catalysis. The implications of the phenomenon on low temperature CVD growth of SWCNTs are addressed. Our theoretical modeling is corroborated by the increased minimum synthesis temperature experimentally observed in SWCNT growth with CVD and very small iron catalysts.

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[34] L. Verlet, Phys. Rev. 159, 98 (1967).
[57] We use the least square method to determine the four parameters of the fitting function ($\gamma_{C_{x}}^{2}, T_{C_{x}}$, and the slopes of the two straight lines).
[69] Since the amount of carbon present in the Fe particle is limited, we take $\gamma$ to be independent of the carbon concentration, and we construct the $R \leftrightarrow P$ relation by calculating pure Fe systems only.