Theoretical study of the thermal behavior of free and alumina-supported Fe-C nanoparticles

Aiqin Jiang\(^1\), Neha Awasthi\(^1\), Aleksey N. Kolmogorov\(^1\), Wahyu Setyawan\(^1\), Anders Börjesson\(^2\), Kim Bolton\(^2\), Avetik R. Harutyunyan\(^3\) and Stefano Curtarolo\(^1,4\)

\(^1\)Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708, \(^2\)University College of Borås, SE-501 90, Borås, and Physics Department, Göteborg University, SE-412 96, Göteborg, Sweden, \(^3\)Honda Research Institute USA Inc., 1381 Kinneir Road, Columbus, OH 43212, \(^4\)corresponding author: stefano@duke.edu

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The thermal behavior of free and alumina-supported iron-carbon nanoparticles is investigated via molecular dynamics simulations, in which the effect of the substrate is treated with a simple Morse potential fitted to ab initio data. We observe that the presence of the substrate raises the melting temperature of medium and large Fe\(_{1-x}\)C\(_x\) nanoparticles (\(x = 0 - 0.16\), \(N = 80 - 1000\), non-magic numbers) by 40-60 K; it also plays an important role in defining the ground state of smaller Fe nanoparticles (\(N = 50 - 80\)). The main focus of our study is the investigation of Fe-C phase diagrams as a function of the nanoparticle size. We find that as the cluster size decreases in the 1.1-1.6-nm-diameter range the eutectic point shifts significantly not only toward lower temperatures, as expected from the Gibbs-Thomson law, but also toward lower concentrations of C. The strong dependence of the maximum C solubility on the Fe-C cluster size may have important implications for the catalytic growth of carbon nanotubes by chemical vapor deposition.

I. INTRODUCTION

Catalytic chemical vapor deposition (CVD) is a widely used method for the production of carbon nanotubes (CNTs) by decomposition of hydrocarbons (such as CH\(_4\), C\(_2\)H\(_2\) etc.) or carbon monoxide on supported metal catalysts (Fe, Ni, Co, FeMo, etc.) \(^1\)\(^2\)\(^3\)\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\). Despite numerous studies, the growth mechanism of nanotubes is still not well understood. Among the most studied factors that control the growth process are the kinetics of carbon transport \(^2\)\(^3\)\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\), the thermodynamics of the catalyst particles \(^11\)\(^12\)\(^13\)\(^14\)\(^15\), and their interaction with substrates (oxides or zeolites) \(^16\)\(^17\)\(^18\).

The vapor-liquid-solid (VLS) model \(^19\) for the CNT growth by CVD implies that the catalytic particle should be in a liquid state which allows rapid diffusion of carbon atoms throughout the particle. The bulk diffusion of carbon through the metal nanoparticle is driven by concentration gradients \(^20\), and it is considered to be the rate-limiting step in the growth of filaments or carbonaceous deposits \(^21\)\(^22\). The activation energies (\(~1.2-1.8\) eV) measured for thermal CVD growth of nanofibers or nanotubes are consistent with those for the carbon diffusion through the corresponding metals \(^2\)\(^3\)\(^4\)\(^22\)\(^23\), hence further supporting the bulk diffusion VLS model. Another mechanism, the surface-mediated carbon transport model, has been proposed \(^6\)\(^7\). The low temperature nanotube synthesis by plasma-enhanced CVD \(^8\)\(^9\)\(^10\)\(^16\)\(^24\)\(^25\) implies that the catalyst could be in a solid state. However, the temperature of the active nanoparticles is extremely difficult to measure during the growth process. In fact, the bombardment of energetic species in plasma and the exothermic dehydrogenation reactions of hydrocarbon can increase the local temperature of the catalyst, even if the substrate is kept in thermal equilibrium. This phenomenon can promote the surface melting of the nanoparticle and, concurrently, facilitate the growth of the nanotube \(^13\)\(^14\).

Because the overall catalytic capability of nanoparticles strongly depends on whether they are in the liquid or solid states, their thermal behavior has been extensively investigated with experimental \(^11\)\(^12\)\(^26\)\(^27\)\(^28\)\(^29\)\(^30\)\(^31\)\(^32\)\(^33\)\(^34\)\(^35\)\(^36\)\(^37\)\(^38\)\(^39\)\(^40\) and theoretical means \(^13\)\(^14\)\(^33\)\(^34\)\(^35\)\(^36\)\(^37\)\(^38\)\(^39\)\(^40\). Under CVD experimental conditions, the melting temperatures of catalytic particles are strongly reduced because of the dissolved carbon (liquidus and solidus slopes in the metal-C phase diagram) and the relatively high surface energy with respect to the bulk materials (Gibbs-Thomson phenomenon). Unusually low melting points of 600-700°C have been observed for oversaturated solutions of carbon (up to 50 at.% at 700°C) in Fe, Ni, and Co metals \(^31\). In these cases, the fluidization of the metal catalytic particles at low or moderate temperature was attributed to the creation of highly dispersed unstable solutions oversaturated with carbon, with concentrations well above the limit of the stable carbide \(^32\)\(^41\).

With so many factors influencing the catalytic growth of CNT, the role of the substrate on the thermal properties of the particle is often overlooked. In fact, there are experimental indications that the presence of substrate could be an important factor in the thermodynamics of
the particle and in regulating the growth of nanotubes \[16, 17, 18\]. Most of the theoretical research has been
focused on the melting behavior of free-standing pure
\[14, 32, 34, 35\] or bimetallic \[36, 37, 38, 39, 40\] clusters. A phase diagram of free-standing Fe-C clusters of fixed size
\[\sim 2.4 \text{ nm}\] has been recently calculated \[12, 42\]. There
have been investigations performed on supported cata-
lysts \[15, 38, 43, 44\], showing that the cluster-substrate
interaction strongly affects the melting temperature of
particles and thus could influence the nanotube growth
rate. A more general picture, capturing the particle-
substrate interaction and size effects on the phase dia-
gram, is still lacking and is the main subject of our study.

In this paper we investigate thermal behaviors for free
and alumina-supported Fe-C nanoparticles with molec-
ular dynamics (MD) simulations. In Section II we de-
scribe the \textit{ab initio} development of a simple interaction
between Fe and Al\(_2\)O\(_3\) which is essential for the calcula-
tions of supported clusters of reasonable sizes. In Section
III, by using MD simulations we explore the thermody-
namics of Fe nanoclusters and the phase diagrams of Fe-
C binary nanoparticles focusing on the effects of cluster’s
size and interfacial interactions on the thermal properties
(Fe-C up to \(\sim 16\%\) carbon concentration). In the same
Section we show that not only the eutectic temperature
but also the eutectic composition are size- and substrate-
dependent. Section IV is devoted to the exploration of
the peculiar characteristics of very small clusters. Con-
clusions are described in Section V.

II. THE FE-AL\(_2\)O\(_3\) POTENTIAL

In this section we model the many-body Fe-Al\(_2\)O\(_3\) in-
teraction with a simple classical potential. If the cal-
culation of this interaction energy involved the sum-
mation over all substrate atoms (e.g., using modified
charge transfer potential \[45, 46\]) the simulation would
be computationally very expensive (a 200-atom nanopar-
ticle would require a 1000-atom substrate patch). Ideally,
a suitable potential for MD simulations would depend on
three integral variables, or even one (the distance from
an iron atom to the surface) if the potential corrugation
is small. The validity of such simplification critically de-
ponds on how weak the Fe-Al\(_2\)O\(_3\) interaction is compared
to those of Fe-Fe and Al\(_2\)O\(_3\)-Al\(_2\)O\(_3\).

There are three possible terminations for (0001) \(\alpha\)-
Al\(_2\)O\(_3\) surfaces \[47, 48, 49, 50\]: stoichiometric Al-
terminated, Al-Al-terminated (two top Al layers), and
O-terminated. These are depicted in Figure 1(a). The-
oretical calculations have predicted that the most stable
surface is the stoichiometric one, terminated by a sin-
gle layer of Al \[47\]. This type of surface is also believed
to be the most often observed under ultra high vacuum
conditions \[48, 49, 50\]. Therefore in this work we will re-
strict our analysis of Fe over Al\(_2\)O\(_3\) using only the stable
stoichiometric Al-termination.

A. Details of Calculation

To develop the interaction between Fe clusters and
Al\(_2\)O\(_3\) surfaces, we perform density functional theory
\textit{ab initio} calculations with Vienna Ab-Initio Simulation
Package VASP \[51, 52\] with projector augmented waves
(PAW) \[53, 54\] and exchange-correlation functionals as
parameterized by Perdew, Burke, and Ernzerhof (PBE)
\[55\] for the generalized gradient approximation (GGA).
Simulations are carried out at zero temperature, with
spin polarization and without zero-point motion. We
use an energy cutoff of 500 eV and a \(6 \times 1 \times 1\) \(k\)-point
Monkhorst-Pack mesh \[56\]. The force tolerance for struc-
tural relaxation is set to 0.1 eV/Å. The unit cell is hexag-
onal with lattice parameters \(a = 4.767\) Å and \(c = 29.143\)
Å. The length of the lattice vector normal to surface is
kept large enough to minimize the neighboring supercell
interaction. Vertically, there is at least 12 Å of empty
space. In addition, a dipole layer is applied in \(z\) direc-
tion to minimize electrostatic effects. A schematic of the unit
cell is shown in Figure 1(b).

FIG. 1: (color online). (a) Possible surface terminations of \(\alpha\)-
Al\(_2\)O\(_3\) (side view). (b) Schematic of the hexagonal unit cell.
(c) The two different high symmetry positions “1” and “2” of
the inner layer of adsorbed iron (top view), each Fe layer has
four atoms.

B. Results and Discussion

The calculated lattice parameters of the bulk alumina
(space-group \# 167) with a hexagonal unit cell \((hR30)\),
\(a = 4.767\) Å and \(c = 12.994\) Å, are in good agree-
ment with the experimental values, \(a_{exp} = 4.742\) Å and
\(c_{exp} = 12.919\) Å \[57, 58\]. Our \(\alpha\)-Al\(_2\)O\(_3\) slab consists of
four oxygen layers as shown in Figure 1(b). The structure is relaxed from the bulk \( \alpha-Al_2O_3 \) configuration while keeping one oxygen and one aluminum layers at the bottom frozen. The surface undergoes considerable relaxations; the interlayer spacings for the top four layers become \( d = 0.117, 0.899, 1.019 \) and 0.264 Å, differing from the corresponding bulk values by \(-87.3\%\), 7.8\%, -47.1\%, and 22.1\%\), respectively. These values compare well with the previous 18 oxygen-layer simulations (-87.4\%, 3.1\%, -41.7\%, 18.9\%) [47], suggesting that an alumina slab with four layers of oxygen is thick enough to be a realistic model of the \( Al_2O_3 \) surface. On the top of the relaxed \( \alpha-Al_2O_3 \) substrate we place a few close-packed layers of iron while keeping the in-plane lattice vectors of Fe identical to the bulk value of alumina. Because of the fortunate match between the natural Fe and the \( \alpha-Al_2O_3 \) surface lattice spacings (within 3\%), the effect of the interface strain energy on the total binding is insignificant. Close-packed iron layers can be put in different ways on top of alumina. Thus, we consider the two high symmetry positions labeled as “1” and “2” in Figure 1(c).

\[ E_b \equiv \frac{1}{4} [E_{Fe-Al_2O_3} - E_{relaxed[Al_2O_3]} - E_{Fe}] \]

where \( E_{deformed[Al_2O_3]} \) is the energy of an artificially isolated alumina slab with the same geometry as that of the optimized Fe-AI_2O_3 system but without adsorbed iron. Figure 2 shows a schematic of the definitions of the two energies, \( E_b \) and \( E_{deform} \). In our calculations only the surface is allowed to relax: iron atoms are kept at their ideal positions because we assume that a reliable Fe-Fe interaction (e.g. Born-Mayer potential [59, 60]) will be able to properly describe their energetics.

To determine how many layers of Fe must be included in the calculations, we evaluate the Fe-AI_2O_3 interaction for systems with different number of Fe layers situated at the same distance above the alumina surface. As summarized in Table I, the binding energy converges reasonably well once the iron film contains three or more layers. Therefore, we limit our calculations to the absorption of only three Fe layers. In addition, due to the corrugation of the surface, the binding energy depends on where the adsorbants are positioned in the \( x-y \) plane. Figure 1(c) shows the two high symmetry configurations of the inner layer of adsorbed film. The corrugation, calculated as the difference between the binding energies of the most and least stable configurations (position “1” and “2” in Figure 1(c), respectively), is less than 15\% of the total energy. Such little sensitivity to the lateral position of iron allows us to consider the surface essentially flat.

\[ E_{deform} \equiv \frac{1}{4} [E_{deformed[Al_2O_3]} - E_{relaxed[Al_2O_3]}] \]

![Figure 2](color online). The definition of the binding and deformation energies.

The binding energy between one Fe column (one Fe per layer) and \( Al_2O_3 \) is defined as

\[ E_b \equiv \frac{1}{4} [E_{Fe-Al_2O_3} - E_{relaxed[Al_2O_3]} - E_{Fe}] \]

where \( E_{Fe-Al_2O_3} \) is the total energy of the optimized system, \( E_{relaxed[Al_2O_3]} \) and \( E_{Fe} \) are the energies of the relaxed \( Al_2O_3 \) slab and Fe layers, respectively (note that the factor 1/4 appears because there are four Fe per adsorbed layer). The presence of adsorbed Fe strongly modifies the alumina surface, and the deformation of the surface may affect the total binding considerably. To evaluate this effect, we define the substrate deformation energy as

\[ E_{deform} \equiv \frac{1}{4} [E_{deformed[Al_2O_3]} - E_{relaxed[Al_2O_3]}] \]

Figure 3(a) shows the binding (\( E_b \)) and deformation (\( E_{deform} \)) energies as a function of the distance \( z \) from the surface. Since the \( Al_2O_3 \) slab experiences surface rearrangement, \( z \) must be defined with respect to a fixed reference, in our case, the bottom of the unit cell (see Figure 2). For convenience, we use a constant shift \( z_{ref} \) to have the minimum of the interaction energy at a reasonable distance of 2.25 Å. The strong contribution of \( E_{deform} \) to \( E_b \), shown in Figure 3(a), is caused by the considerable rearrangement of the surface atoms to accommodate the absorbed iron. The origin of the nonmonotonic variation of the deformation energy is clarified in Fig. 3(b), in which we show the vertical shifts of the outer Al and O layers, \( z^{Al} \) and \( z^O \), with respect to the O position when Fe is not present (\( z \rightarrow \infty \)). The outer positively charged Al layer first rises above the substrate to be closer to the approaching Fe film and accept more charge (as has been shown previously for the Zr-
terminated Ni/ZrO2 system\cite{61}, the charge transfer between the outer Zr and Ni, as well as the accumulation of charge in the gap between them, is significant). The maximum rise for the Al layer happens at the interlayer Al-Fe distance of 2.7 Å (z=2.8 Å in Fig. 3(b)), which corresponds to the kink in the deformation energy curve. After that point, both Al and O layers are pushed downwards. For z < 1.5 Å, one can also expect noticeable deformation of the Fe film, and the decomposition of the total Fe binding into the independent Fe-Fe and Fe-Al contributions may not be accurate anymore.

Fitting gives $D = 153$ meV, $\alpha = 1.268$ Å$^{-1}$, and $z_0 = 2.219$ Å. Figure 3(a) shows the fit of $E_b$ calculated as a sum of three Morse interactions.

The strength of the Fe-Al$_2$O$_3$ interaction (153 meV) amounts to only ~10% of the Fe-Fe interlayer binding energy (~1.24-1.42 eV, depending on the thickness of the Fe film), which implies that the latter is not significantly affected by the presence of the substrate. Hence, the assumption of decomposing the total Fe binding into the separate Fe-Fe and Fe-Al$_2$O$_3$ interactions is justified a posteriori. Our simple Fe-Al$_2$O$_3$ Morse interaction naturally incorporates the whole alumina surface deformation, since the binding energy has been defined with respect to an ideal Al$_2$O$_3$ slab and an isolated Fe film, as described in equation (1) and Figure 2. Within this framework, MD simulations on supported particles can be efficiently performed with reasonable accuracy by considering the z component of the particle interaction with the flat substrate.

As we are interested in the properties of binary Fe$_{1-x}$C$_x$ nanoparticles, we need to evaluate the interaction between carbon surrounded by iron and the alumina substrate (Fe-embedded-C-Al$_2$O$_3$ interaction). Starting from three layers of adsorbed Fe, we substitute one Fe with one C atom bringing the concentration to $x \sim 8.3\%$. Depending on the position in which the substitution takes place, the binding energy $E_b[Fe_{11}C_1-Al_2O_3]$ fluctuates while remaining similar to $E_b[Fe_{12}-Al_2O_3]$, which suggests some importance of many-body effects in the Fe-embedded-C-Al$_2$O$_3$ interaction. Because the substrate represents only a small perturbation to the total binding of the nanoparticle and the concentration of C in our simulations is small, we choose to treat the C-Al$_2$O$_3$ and Fe-Al$_2$O$_3$ interactions in the same way, i.e. we use the Fe-Al$_2$O$_3$ Morse potential for both atom types. The validity of this approximation has been addressed by performing MD simulations, similar to those described in Section III but here we vary the Morse parameters for the C-Al$_2$O$_3$ interaction. Our tests for supported Fe$_{30}$C$_{30}$ nanoparticles reveal that the thermodynamics of the systems is not very sensitive to the particular value of the C-Al$_2$O$_3$ binding. For example, increasing or decreasing the strength of the C-Al$_2$O$_3$ interaction for the Fe$_{30}$C$_{30}$ nanoparticles by a factor of two changes the melting temperature by 1–2 %, the amount comparable to the statistical error of the melting temperature determination in our simulations (see Section III). We conclude that the simple approximation of employing the same description for the Fe and C interactions with the substrate is suitable for this study.

III. MOLECULAR DYNAMICS

Among the taxonomy of thermodynamics phenomena for nanoparticles, melting has been subject of considerable interest. The characteristics of the melting process depend on a variety of parameters such as size \cite{26,62}. 

![FIG. 3: (color online). (a) The binding energy of Fe-Al$_2$O$_3$ (\textit{ab initio} values with fitted Morse potential) and deformation energy of the Al$_2$O$_3$ slab as functions of the distance from the surface. (b) Vertical coordinates of the outer Al and O layers of Al$_2$O$_3$ as function of the distance from the surface.](image)
and shape of the particles [64], concentration of impurities [65], and presence of substrates [43, 44].

In this section we are interested in the effect of size, carbon presence and Al₂O₃ substrate on the melting and solidification of binary Fe-C nanoparticles. We address these tasks by analyzing, with classical MD simulations, the liquidus and solidus lines of their phase diagrams, in function of the aforementioned parameters.

A. Methods

Molecular Dynamics Simulations. MD simulations are carried in the NVT ensemble using the Verlet algorithm [66, 67] with a time step \( \Delta t = 1.0 \) fs. Of the several methods developed for controlling the temperature in MD simulations [68, 69, 70, 71, 72], Berendsen and Nosé-Hoover thermostats are most commonly used. In Fig. 4 we compare the temperature dispersion \( \Delta T \) of the two thermostats with respect to that of the canonical distribution \( \Delta T_{\text{canonical}} \) at \( T = 400 \) K for small nanoparticles \( (N_{\text{Fe}} = 50) \). We observe that the widely used Berendsen thermostat is more sensitive to the choice of the coupling constant. Inset in Figure 4 shows the distribution of instantaneous kinetic temperature for Berendsen thermostat for the typical value of \( \Delta t/\tau = 0.1 \) [74], the Nosé-Hoover thermostat for \( \tau = 25 \) fs, and the canonical distribution at \( T = 400 \) K. The Nosé-Hoover thermostat (\( \sigma_T \sim 47 \) K) reproduces the canonical distribution (\( \sigma_T \sim 46 \) K) much better than the Berendsen thermostat (\( \sigma_T \sim 17 \) K), making it a better choice for our constant temperature simulations.

Interatomic interaction. Fe-Fe, Fe-C, and C-C interactions are described by Born-Mayer [53, 60], Johnson [73, 76] and Lennard-Jones [77] potentials, respectively. These interaction models are discussed in detail elsewhere [76]. The Morse potential, introduced in Section 11 is used to model the Fe-Al₂O₃ interaction; the Fe-embedded-C-Al₂O₃ interaction (C is diffused in Fe) is taken to be identical to Fe-Al₂O₃ as discussed before.

Initial configurations. To avoid excessive temperature 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 (6 ns). The annealing is performed in the following way: the nanoparticle is first heated to high temperature (from 1000 K to 1400 K depending on the size of the particle) for \( 0.6 \times 10^6 \) steps, kept at constant temperature for another \( 0.6 \times 10^6 \) iterations, and finally cooled to 0 K during the remaining \( 4.8 \times 10^6 \) MD steps.

Definition and determination of melting temperature. 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 simulation. 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 [78, 79]. Here, melting is characterized 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 [80]. The Lindemann index \( \delta \) represents the root-mean-square relative bond-length fluctuation:

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

where \( r_{ij} \) is the distance between atom \( i \) and \( j \). \( N \) is the number of particles 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 dif-
different fractions [81, 82, 83]. 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” [84]. Figure 5 shows an example of $T_m$ calculated from the caloric curve (panel a) and from the Lindemann index plot (panel b). 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 $\Delta H_m$.

B. Melting of nanoparticles

With the aforementioned method, we investigate pure nanoparticles of size $N_{Fe} = 80 - 1000$ atoms (diameter $d \sim 1$-3 nm). Caloric curves for particles with $N_{Fe} > 100$ show small melting intervals ($\Delta T_m \lesssim 10$ K). For smaller clusters ($N_{Fe} \sim 80 - 100$ atoms, $d \sim 1$ nm) the characterization becomes difficult because both the caloric curves and the Lindemann indices fluctuate over wide intervals of temperatures in which the liquid and solid phases coexist in dynamic equilibrium. This well known phenomenon, called dynamic coexistence melting [78] and shown in Figures 5(a) and 5(b), is caused by the multitude of different metastable solid phases present at the nanoscale, which have similar free energies, similar volumes (at constant pressure volumes are allowed to change) and different surface arrangements. The particles are quasi-plastic by continuously changing their state while alternating metastable configurations and liquid states (bi-stability). Thus, the observations of thermal properties inside the dynamic coexistence melting interval $\Delta T_m$ are affected by two types of fluctuations: physical, due to coexistence of phases (cannot be avoided), and statistical (can be reduced by increasing the total time of the MD simulation). In particular, the fluctuations of the Lindemann index can be captured by analyzing the standard deviation $\sigma_{LI}$. Figure 5(c) illustrates the phenomenon: by plotting $\sigma_{LI}$ versus $T$, we can estimate the dynamic coexistence melting interval $\Delta T_m$, the max-solid and min-liquid points. Pure liquid and solid temperature ranges will be the ones with negligible $\sigma_{LI}$.

Figure 7 shows $T_m$ of pure Fe nanoparticles in the whole range of sizes ($N_{Fe} = 80 - 1000$) for free and supported clusters. Our results, in agreement with other theoretical [33, 34], computational [13, 35], and experimental studies [26, 27, 28, 29, 30], predict a decrease in the melting temperature inversely proportional to the cluster diameter [85]. The behavior of $T_m$ can be described by the model based on the Gibbs-Thomson equation [29, 81, 80] in function of bulk melting temperature $T_{m}^{bulk}$, effective diameter of the particle $d$, latent heat of melting $\Delta H_{sv}$, and solid-vapor interfacial energy $\gamma_{sv}$ [87].

The melting point of bulk Fe, obtained by extrapolating the fit to $d \rightarrow \infty$ ($T_{m}^{bulk}(N_{Fe} = \infty) \sim 1416$ K) is $\sim 20\%$ below the real one [88], indicating that our Fe-Fe Born Mayer many body potential is slightly underbinding. The systematic shift in melting temperatures should not affect the main conclusions of our study since we are interested in the trends of the liquidus lines in the phase diagrams rather than their precise values. The supported particles considered here have higher melting point than that of the free clusters. In fact, the attractive interaction with the substrate ($Al_2O_3$) induces flattening of the particle and increases the effective diameter in agreement with previous studies [13].

Melting temperatures for magic-size clusters ($N = 55, 147, 309, 561, 923$) in our range of simulations are shown in the inset of Figure 7. Due to their inherent
FIG. 6: Melting phenomenon for small nanoparticles (N_{Fe} \sim 80-100 atoms, d \sim 1 nm): a) caloric curve, b) Lindemann index with respect to temperature, c) standard deviation σ_{LI} of the Lindemann index to identify the max-solid and min-liquid points.

FIG. 7: (color online). Melting temperature versus the inverse of particle diameters. Free non-magic sizes (■) and their linear fit (dashed line); supported non-magic sizes (▲) and their linear fit (solid line); Supported clusters have higher melting point due to the decreased curvature of the surface[13]. Melting temperatures of free magic sizes (○) and supported magic sizes (△) clusters were compared with the linear fit lines of non-magic sizes (inset).

C. Phase diagram of free and supported Fe-C nanoparticles

Analysis of phase diagrams. To understand how inclusion of carbon atoms influences the thermal behavior of the catalyst nanoparticles, we determine the melting temperatures as a function of carbon concentration x^C ranging from zero to up to \sim 16 %. To appropriately model the nanocatalyst in a nanotube growth process, instead of substituting Fe with C to increase the concentration of carbon, we add N_C atoms to the Fe particle.
Since $N_{Fe}$ remains constant and $N_C$ increases, the concentration of carbon is defined as $x^C = N_C / (N_{Fe} + N_C)$. We plot the locus of the max-solid points which represent the liquidus of the Fe-C phase diagram. In small Fe nanoparticles one might expect the average radius to increase noticeably with the addition of a few C atoms ($r^2 \propto N$) and hence their melting temperature would also increase ($T^m_{bulk} / T^m_{bulk} \propto d^{-1}$). However, our tests show that addition of C ($x^C \lesssim 16\%$) does not significantly change the volume of the nanoparticle indicating that C behaves as an interstitial solute in Fe nanoparticles as it does in bulk Fe \cite{93}.

Figure 8 shows phase diagrams ($T_m$ versus $x^C$ in atomic \%) for free and Al$_2$O$_3$-supported particles with $N_{Fe} = 80, 100,$ and 200 based on caloric 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 \cite{88}. Hence, by using the least square method we approximate the liquidus with a set of two straight lines, the intersection of which gives the eutectic point ($x^C_{cut} , T_{cut}$) \cite{96}. This procedure allows us to estimate this invariant point with an accuracy of 1 \% and 12 K for $x^C_{cut}$ and $T_{cut}$, respectively.

We observe that as the particle size is reduced, the eutectic point for free and supported nanoparticles moves toward lower temperatures and lower concentrations, indicating that the solubility of C decreases as well. To the best of our knowledge this phenomenon has never been reported before. Explanation of its origin will require a more detailed study of the behavior of dissolved C at various concentrations (changes in the distribution of C across the particle, possible formation of stable carbides etc.).

Implications for carbon nanotube growth. The “V”-shape liquidus feature of Fe-C nanoparticles observed in our simulations allows for the VLS interpretation of experimental results for catalytic activity of Fe. For a given temperature above the eutectic temperature $T_{cut}$, the dissolution of carbon in a metal catalyst initially induces the liquefaction of the particle by lowering its melting temperature \cite{11, 97}. As the catalyst becomes less viscous, the diffusion of carbon in the particle increases. High catalytic activity has been observed with associated liquefied particles during the growth of SWNT by CVD method \cite{97}. Some experiments have shown presence of liquid-like features and liquid layers on nanoparticles \cite{98, 99} before complete melting. These features would enhance the diffusion of carbon and the subsequent melting of the particles. In our case, the nanoparticles are so small that the surface effects on the melting temperature should be dominant. In fact, one cannot distinguish between surface and bulk layers in a particle with 200 atoms of radius $\sim 0.8$ nm, which is approximately three close-packed layers.

According to the data in Fig. 8 if during CVD experiments the size of the catalyst particle were in a given range ($d \sim 1 - 2$ nm), the smaller Fe nanoparticles ($d \sim 1$ nm) would liquefy earlier then the bigger ones ($d \sim 2$ nm). Consequently, if liquefaction was a prerequisite for catalytic activity, the small particles would begin to produce nanotubes earlier. Experimental verification of this hypothesis is challenging: very small catalyst nanoparticles ($d \sim 1$ nm) have a fast rate of coalescence during the reaction and coagulate to form bigger clusters \cite{100, 101}. Following the VLS model, the growth of very small nanotubes using metallic catalyst would be possible only if the reaction temperature were above $T_{cut}$ (to liquefy the particle) and below the temperature at which particles begin to coalesce. Hence, controlling the diameter of nanotubes grown with CVD in the small size range might be difficult. So far, the smallest reported nanotube ($d = 4$ Å, the most internal tube in a multiwalled nanotube) has been grown by arc-discharge method without any metallic catalyst \cite{102}. 

[FIG. 8: (color online). Fe-C phase diagrams obtained with addition of C (upto $\sim 16\%$) to particles with $N_{Fe} = 80, 100,$ and 200: a) free nanoparticles and b) Al$_2$O$_3$ supported nanoparticles.]
In the $x^C > x^C_{eq}$ region, our results also show that once
the dissolved carbon concentration reaches a point where
the corresponding melting temperature (from the phase
diagram) exceeds the reaction temperature, the particle
starts solidifying as a two-phase system composed of
solid carbide and Fe-rich liquid. This solidification gradu-
ally reduces the average surface mobility of the catalytic
species (Fe) and might affect the catalytic activity of the
nanoparticle. During the process of nanotube growth,
conditions such as sufficient carbon concentration and
temperature can induce the formation of stable carbides.
Cementite (Fe$_3$C) and other iron carbides have been ob-
served in experiments after the reaction of hydrocarbon
or carbon monoxide with iron catalysts [103, 104, 105]. It
has been reported that such stable carbides act as poison
by terminating the growth of nanotube [12, 106].

IV. PECULIARITIES OF SMALL FREE AND
SUPPORTED FE CLUSTERS

In this section we analyze the structural properties of
pure small Fe clusters, free and supported on Al$_2$O$_3$. We
find that as the size decreases Fe clusters assume sta-
ble polyhedron configurations [107, 108]. The same MD
technique described in the previous section is adapted
for searching the stable configurations of small clusters
($N \sim 50 - 80$). Twenty random configurations are gen-
erated per each size and optimized by annealing. The
whole annealing process contains $10^7$ MD iterations (10 ns)
. Free and supported clusters are heated to 1200 K
and 1400 K, respectively, before being slowly cooled to
0 K. Among the twenty annealed structures, we consider
the lowest energy configuration as the global minimum
for each size. For free clusters with $N < 72$, the lowest
5 energies are nearly degenerate (inset in Fig. 9) which
validates our approach. For bigger particles the found
minima might be sub-optimal as the difficulty of finding
the global minima rapidly increases.

The minimum energies per atom are fitted to the
$E_{ave} = a + bN^{-1/3}$ dependence, where, in the case of
spherical particles, the parameters $a$ and $b$ would rep-resent
the bulk energy per atom and the surface-creation
destabilization energy cost, respectively [109, 110, 111].
Our fit uses only two parameters $(a, b)$ instead of the
four of the more general formula $E_{ave} = a + bN^{-1/3} +
cN^{-2/3} + dN^{-1}$ [109, 110, 111] to avoid overfitting due to
the limited number of energy points. We include the best
available minima obtained with the aforementioned pro-
cedure for bigger ($N = 100, 120, 160$ and 200) clusters to
ensure the correct asymptotic behavior for the nanopar-
ticles of large sizes. To capture the size dependence only
we exclude sizes $N \sim 55$ ($N = 54, 55, 56$) from the
fit, because these nanoparticles achieve additional stability
by forming highly symmetric icosahedra (see Fig. 9).
We obtain $a_{free} = -4.29 \pm 0.01$ eV, $b_{free} = 2.42 \pm 0.03$
eV and $a_{supp} = -4.30 \pm 0.01$ eV, $b_{supp} = 2.34 \pm 0.02$
eV for free and supported clusters, respectively. The two
values of $a$ are very close to the bulk fcc cohesive en-
ergy of $-4.29$ eV/atom; the two values of $b$ slightly differ
because of the reduced total energy cost to create and
modify surface for the supported cluster [13].

Figures 10 and 11 illustrate the differences between
the calculated and the fitted energies for free and sup-
ported clusters. The prominent negative peaks in Fig.
10 for sizes $N \sim 55, 61, 64, 71, 75$, and 77 correspond to
the magic size structures in our sequence. The evolution
of the nanoparticle configuration with size is depicted in
the same picture. By comparing Figures 10 with 11 we
observe that the attractive substrate has little or no effect
on the internal structure of small clusters ($N \leq 70$). Due
to the spherical (or nearly-spherical) arrangements, such
small icosahedra are not significantly deformed by attrac-
tive substrates, unless the adsorption potentials is com-
parable to the internal atomic binding energy of the clus-
ter. Big supported particles behaves differently. In fact,
as the size increases beyond $N \geq 70$, alumina-supported
clusters form fcc arrangements (Fig. 11) with the \{111\}
planes at the particle/substrate interface. Elsewhere the
particles have simple close-packed facets or local arrange-
ments of them.

Big unsupported particles are different than the sup-
ported ones. Unsupported clusters of sizes between $N \sim
70$ and $N \sim 200$ have decahedra or icosahedra arrange-
ments (multi-twinned structures [112, 113]). Decahedra
are more frequent for medium size particles ($N \sim 70$ to
$\sim 100$) while icosahedra appear more often for bigger sizes
($N \sim 100$ to $\sim 200$). Figure 11 shows three particular ex-
amples of decahedra clusters with $N = 71, 75$, and 77.
As the size exceeds $N \sim 200$, the particles approach the
bulk configuration and the fcc and icosahedra structures
tend to become degenerate. For instance, the cluster at
$N = 500$ is a good example of an fcc particle with ap-

![FIG. 9: (color online). The minimum energies of free clusters and the fitting curve using $E_{ave} = a + bN^{-1/3}$. The 5 lowest energies are shown in the inset for cluster’s sizes from 50 to 80.](image-url)
The polyhedron→fcc transition that occurs at lower sizes for supported clusters can be explained in terms of surface/interface and elastic strain energies [114, 115]. In a groundstate configuration, the former (latter) energy dominates over the other for a small (big) particle. Particles with radii of \( r < r_0 \) (\( r_0 \) is the critical size for the polyhedron-fcc transition [116]) tend to form polyhedral structures (icosahedra or decahedra) to minimize the surface/interface energy, while clusters with \( r > r_0 \) will prefer the bulk configuration (fcc) to minimize the elastic strain energy [115]. This is true for free and supported clusters. However, for supported particles, the fcc configuration with flat facets (along the directions of minimum surface energy given by the Wulff plots [117, 118]) has a larger contact area with the substrate than the polyhedra do. Therefore, the attractive substrate interaction reduces the surface/interface energy of fcc the most, resulting in a lower critical \( r_0 \) (even though the overall surface area of the fcc structures could be larger than that of the icosahedra).

Our simulations reveal that the substrate attractive interaction tends to preserve the bulk structure for small particles. This demonstrates that although the Fe-Al₂O₃ interaction is relatively weak, it is able to influence the balance between the bulk and surface energies in competing configurations and ultimately determine the particle’s ground state. One can also expect to observe this effect in simulations with different models of the Fe-Fe and Fe-Al₂O₃ interactions, as long as their relative strength is comparable with ours.

V. CONCLUSIONS

In this paper we have investigated the behavior of free and alumina-supported Fe-C nanoparticles. We observe interesting phenomena that can be attributed to the presence of the substrate. The main results of the present study can be summarized as follows:

(i) The total Fe binding can be conveniently decomposed into independent Fe-Fe and Fe-Al₂O₃ parts: according to our ab initio calculations the two differ by about an order of magnitude. Moreover, the corrugation of the Fe-Al₂O₃ interaction is much smaller than the average adsorption energy. This allows us to parameterize the Fe-Al₂O₃ interaction as a Morse potential, which includes the deformation energy of the substrate.

(ii) The thermal behavior of pure-Fe particles is simulated with classical MD techniques. We observe the reduction of melting temperature as a function of the diameter, in agreement with the Gibbs-Thomson law. We also show that supported particles have higher melting points than the unsupported ones.

(iii) We calculate the liquidi on the phase diagrams for a range of Fe-C nanoparticles (\( d \sim 1.1-1.6 \) nm) and show that they are characterized by the presence of eutectic points in which the eutectic concentration depends on the size of the particles. These phenomena may have important effects on the growth of carbon nanotubes by CVD, as discussed in Section III C.

(iv) We find that the optimized configurations of very small pure Fe clusters (down to \( N_{Fe} \sim 50 \)) have icosahedron or decahedron structures. Bigger clusters tend to have close-packed configurations. We show that the size at which the cluster undergoes the polyhedron→close-packed transition depends on the substrate. In particular, Al₂O₃ supported Fe clusters have \( N_{Al_2O_3} \sim 70 \) while free cluster have \( N_{tr}^{free} \sim 200 - 500 \).
The thermodynamic study of nanoparticles will be extended with future ab initio characterizations carried out in this laboratory, and with experimental investigations performed by our collaborators. This work stimulates more comprehensive studies of the role of substrates on the thermodynamics of small particles, to understand the fundamental factors controlling the catalytic properties of small clusters.

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