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The Influence of Magnetic Moment on Carbon Nanotube Nucleation

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Abstract

We demonstrate the impact of magnetic moment on single-walled carbon nanotube (SWCNT) nucleation, using quantum chemical molecular dynamics simulations. The mechanism of SWCNT cap formation on Fe₃₈ nanoparticle catalysts can be manipulated by altering the total magnetic moment. When the magnetic moment is low, large cap structures dominated by pentagons are formed. Increasing the magnetic moment leads to smaller, "flatter" sp² carbon networks with a higher proportion of hexagons, which are incapable of lifting away from the catalyst surface. These results demonstrate that SWCNT (n,m) chirality distributions can be potentially manipulated via altering the magnetic moment of the catalyst-carbon interface. We also show that higher magnetic moments leads to slower SWCNT nucleation. This is a consequence of the extent of Fe→C charge transfer, which is proportional to the total magnetic moment. As the magnetic moment is increased, the Fe₃₈ nanoparticle has higher catalytic activity and is able to stabilise carbon in its subsurface region, thereby impeding the nucleation process.

1. Introduction

Single walled carbon nanotubes (SWCNTs) possess remarkable physicochemical, electronic and mechanical properties [1–4], which give them great potential in diverse technological applications [5]. The electronic and optical properties of a SWCNT are dependent on its (n,m) chiral indices. Since their initial characterisation [6, 7], traditional SWCNT synthesis methods, such as the arc discharge and chemical vapor deposition (CVD), have struggled to produce *in situ* (n,m) chirality SWCNTs selectively (so-called "chirality controlled growth"). This problem has represented the single largest hurdle in producing new SWCNT-based technologies over the last 20 years.

CVD growth of CNTs is currently believed to be the most promising approach for producing larger quantities of CNTs with controlled chiralities, since it enables more direct control over the physicochemical parameters that govern the nucleation/growth mechanism. The most widely used catalysts in this respect have traditionally been iron-group metals (Fe, Co and Ni) [8]. Recent advances based on catalyst design approaches (*i.e.* by tailoring the catalyst's elemental composition, phase and surface morphology) have enabled exclusive/near-exclusive growth of single (n,m) SWCNTs [9, 10]. Similar advances have also been made with cloning/vapor-phase epitaxy approaches [11–14], and the use of organic templates for SWCNT growth (*e.g.* cycloparaphenylenes) [15, 16].

At the molecular level, CNT nucleation and growth is an immensely complex process controlled by experimental parameters including temperature [17], catalyst type [18–23], catalyst particle size [24, 25], the type of carbon feed stock and feedstock pressure [19, 26, 27], the presence of reducing agents [28] (notably hydrogen [23, 29–34]), and applied

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electric [35, 36] and magnetic [37–39] fields. Understanding the relationships between these parameters and the CNT nucleation/growth mechanism has been the focus of the CNT growth community since the 1990s. It is now widely accepted that the vapor-liquid-solid (VLS) mechanism governs nucleation and growth on transition metal catalysts, particularly the iron-group metals [8]. More recent investigations have demonstrated a vapor-solid-solid (VSS) mechanisms on metalloid, main-group and solid oxide catalyst nanoparticles [23, 40–50].

Detailed understanding of how many of these parameters can be exploited for chirality-controlled growth is currently lacking. For example, magnetic fields have been shown to increase CNT purity and enable diameter selectivity [39] during arc-discharge synthesis. CNT length distributions are also decreased [37–39], suggesting that applied magnetic fields leads to slower nucleation kinetics. Greater control over CNT nucleation and growth obtained using applied magnetic fields has been attributed to the induced Landau spin currents and Dirac spin waves in the catalyst [51]. Applied magnetic fields could therefore be coupled with other experimental parameters to provide new routes for chirality-control. However, for such routes to be realised, a detailed atomistic understanding of the SWCNT nucleation mechanism is required.

In this work, we address this shortcoming by investigating how magnetic fields influence SWCNT nucleation on Fe_{38} nanoparticles, using non-equilibrium quantum chemical molecular dynamics (QM/MD) simulations. We approximate the influence of different magnetic field strengths by varying the total magnetic moment. We demonstrate that both the mechanism and kinetics of SWCNT cap formation on Fe_{38} is dependent on the total magnetic moment. For low magnetic moments, pentagon formation dominates hexagon formation during nucleation, leading to highly curved SWCNT cap structures. For higher magnetic moment, the kinetics of this reaction are significantly impeded, with pentagons and hexagons being formed in equal ratios, leading to smaller, more planar carbon structures. The presence and longevity of subsurface carbon are both proportional to the magnetic moment, with higher magnetic moments leading to more stable subsurface carbon species. This increased stability is a result of increased $\text{Fe} \rightarrow \text{C}$ charge transfer present at higher magnetic moments.

The simulations presented here demonstrate, in principle, that the proportion and pattern of pentagons formed in SWCNT cap structures can be manipulated *via* the magnetic moment of the carbon/catalyst interface, and thus demonstrate a potential route to manipulation of SWCNT (n, m) chirality during growth.

2. Computational Methodology

2.1. Quantum Chemical Molecular Dynamics Simulations

We simulate SWCNT nucleation here using non-equilibrium QM/MD, whereby the classical equations of motion are propagated in conjunction with a quantum chemical potential. For the former, we use the velocity-Verlet algorithm [52] ($\Delta t = 1$ fs) and an NVT ensemble. Temperature is maintained at 1,500 K in all simulations *via* a Nosé-Hoover chain thermostat (chain length = 3) [53, 54] coupled to the degrees of freedom of the system. The quantum chemical potential was calculated on-the-fly at each MD step using the spin-polarised self-consistent density functional tight-binding method (SDFTB), in conjunction with the trans3d parameters [55] for Fe-C and Fe-Fe interactions, and the mio-0-1 parameters for the C-C interactions [56]. An electronic temperature (T_e) of 10,000 K was employed for all QM/MD simulations. Molecular orbital populations near the Fermi level may therefore vary continuously between 0 and 2, and are determined by a Fermi-Dirac distribution function. This electronic temperature is employed here so that our simulations conform to those reported previously, enabling direct comparison between QM/MD simulations with and without spin-polarisation.

All QM/MD simulations reported here were performed using the DFTB+ program [57].

To elucidate the impact of magnetic moment on the SWCNT nucleation mechanism, QM/MD simulations with magnetic moments held constant at $1.08\mu_B/\text{atom}$, $2.39\mu_B/\text{atom}$ and $3.71\mu_B/\text{atom}$ were performed. These magnetic moments correspond to the presence of 40, 90 and 140 unpaired electrons in the catalyst-carbon complex, and are referred to as low, intermediate and high total magnetic moment, respectively.

2.2. SWCNT Nucleation Model System

The model system employed for these QM/MD simulations consisted of an ensemble of 30 C_2 moieties adsorbed on a $\gamma\text{-Fe}_{38}$ nanoparticle. An Fe_{38} nanoparticle was chosen here, since previous studies have established the SWCNT nucleation mechanism under identical conditions [58] *in the absence of magnetic moment*. Thus, we are able to perform direct comparisons here with these established results. We note also that, for surface-molten and liquid iron catalyst nanoparticles, the SWCNT nucleation mechanism itself is largely invariant to the size of the nanoparticle [59–61]. The diameter of this nanoparticle is ~ 0.7 nm, and such is pertinent to SWCNT diameters reported using arc discharge and CVD synthesis (~ 1 nm). The geometry of this nanoparticle was initially optimised at 0 K, before being equilibrated at 1,500 K for a period of 10 ps. Initial nuclear velocities in each of these trajectories were defined randomly *via* a Maxwell-Boltzmann distribution, to ensure statistical independence. Following equilibration, the C_2 fragments were adsorbed onto the surface of the nanoparticle during 30 ps QM/MD simulation at a constant rate of $1 \text{ C}_2 / \text{ps}$. The magnitudes of each C_2 fragment's velocities satisfied a Maxwell-Boltzmann distribution at 1,500 K, and were directed towards the Fe_{38} center of mass. Following this adsorption period, the metal-carbon complex was equilibrated at 1,500 K for 500 ps. To ensure a reliable statistical representation of the SWCNT nucleation mechanism/kinetics was obtained, 20 independent trajectories were calculated for each magnetic moment (*i.e.* 60 trajectories in total). These trajectories will be referred to as 1 – 20_{L,I,H}, for the low, intermediate and high total magnetic moment simulations, respectively.

3. Results and Discussion

3.1. Fe-Catalyzed SWCNT Nucleation Mechanism

We begin our discussion by summarising Fe-catalyzed SWCNT nucleation mechanisms reported previously in the literature [8]. SWCNT nucleation begins with the formation of extended polyyne chains *via* the coalescence of individual C_2 moieties. This process is driven by C_2 surface diffusion, which is rapid due to the high thermal energies present under typical synthesis conditions. Polyyne chain formation occurs quickly, over timescales on the order of ~ 10 ps. This is apparently independent of the type of catalyst, temperature, and catalyst diameter/morphology [60, 62–69]. Following polyyne chain formation, their oligomerization on the catalyst surface leads to the formation of polygonal carbon rings, predominantly pentagons and hexagons. Heptagons are also formed to a very small extent, which is consistent with their relative thermodynamic instability (compared to pentagons and hexagons). Ohta *et al.* [58] demonstrated that this key step in the nucleation process occurs *via* a "pentagon-first" mechanism: the first ring to be formed in a SWCNT is a pentagon, and this is unaffected by a number of pertinent experimental factors. This pentagon formation step requires the coalescence of two independent carbon chains, forming a "Y-junction" structure. Following the formation of this first pentagon ring, subsequent oligomerization and ring condensation proceeds rapidly, with SWCNT caps typically being generated within 500 ps. For liquid and surface molten catalyst nanoparticles, the arrangement of pentagons and hexagons in these caps is

essentially random, and this is consistent with the wide (n,m) chirality distribution obtained in typical CVD syntheses.

There is wide consensus that SWCNT nucleation is essentially a surface-mediated process. A number of investigations have observed iron carbide phases during and after SWCNT nucleation [70–76]. However, previous MD simulations have demonstrated that Fe/Ni/Co subsurface carbide structures are metastable, at least for nanoparticle diameters less than $\sim 1\text{-}2\text{ nm}$ [60, 63–68, 77]. Subsurface carbide phases are partially stabilised by carbon $\rightarrow$ metal charge transfer (back-donation). However, this effect leads to weakened metal-metal bonding and the partial disintegration of the catalyst surface morphology [58]. Combined with high temperature, this weakened catalyst structure enables rapid carbon precipitation to the catalyst surface. The stability of the subsurface carbide structure can therefore be assessed by the extent of carbon $\rightarrow$ metal charge transfer, and how this charge transfer evolves over time.

We now turn to a discussion of the influence of total magnetic moment on each of these aspects of SWCNT nucleation. In particular, we address how the key aspects of SWCNT nucleation – carbon diffusion/polyyne formation, carbon ring condensation and subsurface carbon stability – are affected by varying total magnetic moment.

3.2. Influence of Magnetic Moment on SWCNT Nucleation

3.2.1. SWCNT Nucleation Mechanism

Snapshots from representative QM/MD annealing simulations at low, intermediate and high magnetic moments are shown Figure 1. The final structures of all computed trajectories are given in ESI[†] (Figures S1, S2 and S3, respectively).

At low total magnetic moment (Figure 1(a)) polyyne formation proceeds rapidly (*e.g.* $< 5\text{ ps}$), such that by 30 ps several polyyne chains extend over the Fe_{38} nanoparticle surface. By 64.9 ps, the first polygonal carbon ring is observed, being a pentagon. Pentagons were also the first rings to be formed in all other low magnetic moment trajectories, indicating that a small magnetic moment does not interfere significantly with the pentagon first nucleation mechanism. Subsequent condensation of polygonal carbon rings proceeds in a very similar manner to simulations reported previously [58–60]: a distinctive SWCNT cap structure is formed within $\sim 400\text{ ps}$, and this structure consists only of pentagons and hexagons. Heptagons were observed (*e.g.* the cap structure at 400 ps, shown in Figure 1(a)), however were very short-lived due to their relatively high thermodynamic instability. We return to a more detailed discussion of ring condensation kinetics below.

Trajectory 20_I is depicted in Figure 1(b). At intermediate magnetic moment, polyyne chain formation and diffusion again occurs rapidly, and the first polygonal carbon ring (a pentagon) is formed at 44.2 ps. Further polyyne coalescence and ring formation appears to proceed at a comparable rate to that observed using a low magnetic moment (*i.e.* Figure 1(a)). The mechanism and kinetics of SWCNT cap nucleation using these two different magnetic moments are similar in this respect. The atomic structures of the simulated cap structure obtained here with low and intermediate magnetic moments are consistent with those previously observation by different groups using comparable time scales [23, 47, 58, 60, 63, 68]. However, comparison of the final "cap" structures in Figure 1(a), (b) and (c) shows that sp^2 network formation at high magnetic moment is significantly smaller than those observed at low and intermediate magnetic moments. Furthermore, the curvature of this network is "flatter" at high magnetic moments. Simulations at high magnetic moment also frequently deviated from the pentagon-first mechanism, with hexagons forming the initial SWCNT cap structure (this is not the case for Trajectory 20_H in Figure 1(c), but is evident in Figure S3 for other trajectories). The smaller, flatter cap structures formed in trajectories 1_H-20_H will exhibit a larger π interaction with the catalyst surface.

Figure 1 Representative SWCNT mechanism observed with (a) low, (b) intermediate and (c) high total magnetic moments on an Fe_{38} nanoparticle. (a), (b) and (c) depict trajectories 20_L , 20_I and 20_H , respectively. Cyan and brown spheres represent C and Fe atoms, respectively.

This could potentially prevent the subsequent "lift-off" of the cap structure from the catalyst surface over longer timescales, which is essential for the continued growth of the SWCNT.

It has previously been shown [78] that the (n,m) chirality of a SWCNT is determined by the arrangement of pentagons in the initial cap structure. The simulations presented here demonstrate, in principle at least, that this arrangement can be manipulated *in situ* during nucleation by changing the total magnetic moment of nanoparticle/carbon system. Further work investigating this possibility are ongoing in our research group.

These differences in the nature and kinetics of SWCNT cap formation are a consequence of (1) reduced rates of C_2 "consumption"/polyne formation, (2) slower ring condensation kinetics, and (3) an increased preference for hexagon formation, at higher magnetic moments. In the absence of a magnetic moment, intercalation of catalyst atoms into the nucleating cap structure is seldom observed [58]. However, with increasing magnitude of the total magnetic moment, intercalation of catalyst atoms into the nucleating cap structure occurs frequently, shown in Figures 1 and S1-3. This observation suggests that (1-3) are a result of the total magnetic moment influencing the stability of surface and subsurface carbon species during nucleation.

In the discussion below, we elucidate the relationship between the total magnetic moment and these kinetic and mechanistic aspects of SWCNT nucleation.

3.2.2. SWCNT Nucleation Kinetics

Figure 2 shows the evolution of polygonal carbon rings observed at low, intermediate and high total magnetic moment. At low magnetic moment (Figure 2(a)), cap structures formed consisted of (on average) ~ 5.4 pentagons and ~ 2.7 hexagons following 500 ps, while heptagon formation was limited. An intermediate total magnetic moment (Figure 2(b)) led to slightly lower average populations of pentagons (~ 4.4) and hexagons (~ 2.2) over the same timescale. Thus, the average pentagon:hexagon ratio for low and intermediate total magnetic moment are both $\sim 2:1$. Figure 2(a) shows the kinetics of ring condensation are initially fastest at low total magnetic moment, with pentagon and hexagon formation plateauing after *ca.* 200 ps and 400 ps, respectively. By comparison, the rates of pentagon and hexagon formation are both slower at intermediate magnetic moment (Figure 2(b)); pentagons formation ceases at *ca.* 400 ps, while hexagon formation continues beyond the timescales employed here. Increasing the total magnetic moment decreases the average number of heptagons formed, however this reduction is not statistically significant due to the near-zero heptagon population at low and zero total magnetic moments.

At high total magnetic moment, only ~ 2 pentagons and ~ 2 hexagons are formed within 500 ps (Figure 2(c)). The extent of ring condensation is therefore notably reduced, compared to low and intermediate total magnetic moments, indicating a reduction in the kinetic rate of SWCNT cap nucleation. Furthermore, the pentagon:hexagon ratio is reduced from $\sim 2:1$ to $\sim 1:1$, indicating that cap curvature at high magnetic moments should be reduced, compared to low and intermediate magnetic moments, as noted above (see Figure 1(c) and Figure S3). The change in the pentagon:hexagon ratio reflects the fact that pentagon formation decreases significantly with increasing magnetic moment, whereas the reduction in hexagon formation is less noticeable. This means that increasing magnetic moment impedes the formation of the initial pentagon ring, but does not impede subsequent ring condensation to the same extent. Thus, increasing the total magnetic moment increases the SWCNT nucleation barrier, which we rationalise in terms of the increased stability of subsurface carbon, below. However, once the pentagon nucleus of the SWCNT is formed however, the condensation of subsequent rings remains likely on a thermodynamic basis, due to the strength of the C–C bond, which is far stronger

than the carbon-catalyst interaction for iron catalysts [79].

Figure 2 Carbon ring populations observed using (a) low, (b) intermediate and (c) high total magnetic moments. All data averaged over 20 trajectories.

Figure 3 Populations of (a) C₂ and (b) C₃, C₄, C₅ and C₆, observed during QM/MD simulations of SWCNT nucleation on an Fe₃₈ nanoparticle with low, intermediate and high magnetic moments. The shaded regions correspond to the period of C₂ addition to the Fe₃₈ nanoparticle surface. In (a), C₂ consumption can be described using power laws, kt^α , where the exponent α is determined by the magnetic moment. All data averaged over 20 trajectories.

Figure 2 indicates an inverse relationship between the magnitude of the total magnetic moment and the rate of cap nucleation. This relationship is also evident from an analysis of C_n polyyne population dynamics during the cap nucleation process. Figure 3 shows how populations of (a) C₂ and (b) C₃, C₄, C₅ and C₆ moieties evolve during SWCNT cap nucleation. Longer polyyne chains have negligible populations (Figure S4), and are not discussed further here. Figure 3(a) shows that C₂ consumption proceeds effectively immediately for all magnetic moments considered. For example, even during the initial C₂ adsorption process (< 30 ps), surface-adsorbed C₂ units aggregate to form larger chains (predominantly C₄, as shown in Figure 3(b)). The extent of this C₂ aggregation is inversely proportional to the total magnetic moment. At 30 ps, low, intermediate and high magnetic moment simulations have, on average, ~ 18, 21 and 22 C₂ moieties adsorbed to the catalyst surface. Following a further 500 ps of simulation, ~ 5, 6 and 10 C₂ units remain on the Fe₃₈ nanoparticle surface. Thus, the C₂ populations using low and intermediate magnetic moments are ultimately comparable,

and approximately half that observed at high magnetic moment.

Figure 3(b) shows that the C_3 population during this period is also proportional to the magnitude of total magnetic moment; with low, intermediate and high magnetic moments, average C_3 populations of ~ 0.9 , 1.4 and 2.5 are observed after 530 ps. The formation of C_3 from C_2 moieties requires C–C bond cleavage, and so higher magnetic moments evidently improves the catalytic performance of the Fe_{38} nanoparticle. The same trend is evident for C_4 populations, albeit to a lesser extent. Figure 3(b) shows that after 530 ps, ~ 0.5 , 0.8 and 1.0 C_4 chains are observed (on average) using low, intermediate and high total magnetic moments. This trend quickly disappears with increasing chain length (see Figures 3(b) and Figure S4), and is not observable for carbon chains longer than C_6 . Thus, while higher magnetic moment evidently improves the catalytic performance of the Fe_{38} nanoparticle, this effect is potentially limited to the smallest carbon fragments present on the catalyst surface. We discuss the origin of this effect in the following section.

After 30 ps, C_2 population during SWCNT cap nucleation decreases according to a power law kt^α , where both the power law coefficient k and exponent α are dependent on the total magnetic moment (for low, intermediate, high magnetic moments: $k = 100.0, 113.7, 67.3$ and $\alpha = -0.481, -0.466, -0.292$, respectively). The dynamics of C_2 consumption therefore resemble a phase transition, as do the dynamics of 2-dimensional carbon nanostructure formation [80]. However, C_2 consumption rates derived from these power laws show no direct dependence on the magnitude of the total magnetic moment (Figure S5).

3.2.3. Stability of Subsurface Carbon

Figure 4 demonstrates the stability of subsurface carbon species at low, intermediate and high total magnetic moments. Subsurface carbon stability is measured here by comparing the Fe_{38} nanoparticle radius with the minimum distance between the nanoparticle centre and all carbon atoms. The initial adsorption period (0 – 30 ps) is characterised by a sharp contraction in the carbon – Fe_{38} -centre distance. The Fe_{38} nanoparticle radius increases during this period in response. Figure 4(a) shows that, for low magnetic moment, all carbon atoms then remain adsorbed on the Fe_{38} for the remainder of the simulation. Subsurface carbon in this instance is therefore never thermodynamically stable. Conversely, at intermediate magnetic moment (Figure 4(b)) the carbon – Fe_{38} -centre distance continues to decrease, to a minimum of 3.7 at ~ 60 ps. It takes a further ~ 90 ps for this carbon to be expelled from the nanoparticle subsurface. This trend is more exaggerated for the highest total magnetic moment considered here. Figure 4(c) shows that carbon species are stabilised in the Fe_{38} nanoparticle subsurface beyond the timescale of this simulation. Projecting Figure 4(c) forward suggests that all carbon finally precipitates from the Fe_{38} nanoparticle after *ca.* 1.5 ns. The stability of subsurface carbon species in this case is also consistent with the intercalation of iron atoms into the nucleating sp^2 carbon networks, discussed above.

Figure 4 indicates that subsurface carbon species are metastable in Fe catalysts, and that this metastability is proportional to the total magnetic moment. This is consistent with the high magnetic saturations of iron carbide nanoparticles, notably nanoparticle Fe_3C , which are known to approach that of the bulk (~ 140 emu/g) [81, 82]. However, the subsurface carbon structure obtained here is not a crystalline phase, since the simulation temperature is above the melting point for nanoparticle iron carbides [60]. We anticipate that the metastability of these subsurface carbon species will also increase in larger diameter nanoparticle catalysts, and crystalline/surface-molten iron phases, *i.e.* as the surface energy of the catalyst/carbide nanoparticle decreases.

The increased stability of subsurface carbon species shown in Figure 4 is responsible for the slower SWCNT cap nu-

Figure 4 Fe_{38} nanoparticle radius (dashed lines) and minimum distance between carbon and nanoparticle centre (solid lines) observed using low, intermediate and high magnetic moments. The shaded region corresponds to the period of C_2 addition to the Fe_{38} nanoparticle surface. The stability of subsurface carbon is proportional to the magnitude of the total magnetic moment, and high magnetic moment leads to the stabilisation of subsurface carbon over the timescales employed here. All data averaged over 20 trajectories.

cleation discussed above. It is also correlated to the extent of $\text{Fe} \rightarrow \text{C}$ charge transfer. This is because subsurface carbon receives a larger spin density from the catalyst nanoparticle as it is surrounded by iron atoms (thus increasing $\text{Fe} \rightarrow \text{C}$ charge transfer), whereas surface-adsorbed carbon has less extensive contact, and thus lower spin density by comparison. Figure 5 shows that $\text{Fe} \rightarrow \text{C}$ charge transfer is proportional to the total magnetic moment. Therefore, at higher magnetic moments, Fe atoms donate more electron density into the π^* molecular orbitals of surface-adsorbed C_2 species. The anti-bonding character in the C_2 bond is consequently increased, and this weakens the bond and makes C–C bond cleavage more likely.

In the event that C–C bond cleavage takes place, the carbon atoms produced can either (1) undergo reaction with nearby C_2 species on the Fe_{38} surface, resulting in C_3 chains or (2) diffuse into the nanoparticle subsurface. (1) is corroborated by the greater population of C_3 chains observed on the Fe_{38} surface at higher magnetic moments, shown in Figure 3(b) and discussed above. (2) is supported by Figure 4. The cleavage of the C–C bond enables the diffusion of carbon into the nanoparticle subsurface; diffusion of single atoms into the subsurface is considerably more favourable, compared to the diffusion of C_2 units (due to steric factors). Subsurface carbon atoms are stabilised through Fe–C σ bonding, irrespective of the total magnetic moment. However, Figure 5 shows that electrostatic attraction between iron

and subsurface carbon, on average, increases at higher magnetic moments, due to the increasing and opposite partial atomic charges. This means that subsurface carbon species are more stabilised at higher magnetic moments.

Figure 5 Mulliken charges on carbon (solid lines) and iron (dashed lines) during Fe_{38} -catalyzed SWCNT nucleation. The extent of $\text{Fe} \rightarrow \text{C}$ charge transfer is proportional to the total magnetic moment, and leads to greater stabilisation of subsurface carbon. All data averaged over 20 trajectories.

4. Conclusions

We have presented a detailed investigation concerning the influence of applied magnetic moments on the mechanism and kinetics of SWCNT nucleation on Fe_{38} nanoparticle catalysts. Our simulations demonstrate that both the mechanism and kinetics of SWCNT nucleation can be manipulated by changing the total magnetic moment of the catalyst–carbon interface. When the magnetic moment is low, SWCNT cap nucleation proceeds *via* established reactive pathways (the pentagon-first mechanism). Under these conditions, SWCNT caps formed are dominated by carbon pentagons, and thus have high positive curvature and easily lift away from the nanoparticle surface. At higher magnetic moments, we observe SWCNT cap formation deviating from the pentagon-first mechanism, leading to smaller "cap" structures that are rich in hexagons. As they are flatter, and more tightly adsorbed to the catalyst surface, cap lift-off is prevented, at least on the timescales employed in this investigation. Nevertheless, these simulations demonstrate that the ratio and distribution of pentagons and hexagons in SWCNT cap structures can be manipulated by changing the magnetic moment. In principle therefore, it may be possible to exploit this relationship towards (n,m) chirality control.

The kinetics of SWCNT cap formation were shown to be inversely related to the magnitude of the total magnetic moment. Higher magnetic moments lead to increased $\text{Fe} \rightarrow \text{C}$ charge transfer, which in turn promoted C–C bond cleavage and the subsequent diffusion of carbon atoms into the nanoparticle subsurface. Higher electrostatic attractions between subsurface carbon and iron atoms lead to the stabilisation of these subsurface carbon atoms for longer time periods, thus impeding surface-mediated cap formation.

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Supplementary data

Final structures of QM/MD trajectories obtained using low, intermediate and high total magnetic moments; populations of C₇, C₈, C₉ and C₁₀ polyyne chains observed using low, intermediate and high total magnetic moments; C₂ consumption rates observed using low, intermediate and high total magnetic moments.

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