Characterizing Surface Segregation in Fe-Ni nanoclusters using Monte Carlo Simulations

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Controlling the chirality of carbon nanotubes and by extension their apparent physical properties, especially conductivity, is of prime importance for industrial applications of semiconductors. Bimetallic nanoclusters have been found to impart such tuning properties to the growth of carbon nanotubes when adsorbed before propagation, and current research has been focused on understanding the effects of the Fe-Ni system, specifically at which compositions control of certain desired chiralities is optimized. However, these Fe-Ni nanoclusters by themselves present a problem for straightforward analysis not only because of the lattice mismatch between Ni and Fe but also due to their different bulk crystal structures, face-centered cubic (fcc) and body-centered cubic (bcc), respectively. Monte Carlo simulations provide an inexpensive way to probe the properties of a range of alloy compositions without the need for synthesis and purification in the laboratory, and are used here to study the surface segregation of Fe-Ni alloys as a function of composition and cluster size for the minimum energy configurations. Two potentials were used, an embedded-atom model (EAM) and an angular-dependent potential (ADP), both designed specifically for the Fe-Ni system. Analysis of the equilibrated nanoclusters reveals that Fe prefers core sites, while Ni prefers surface sites, with the relationship between overall concentration and site occupation differing for each potential.

1. INTRODUCTION

The Fe-Ni system has been among the most studied by researchers over the last several decades, not only due to its importance in the manufacture of steels [1] and catalysts [2-4], but also because it exhibits many novel physical properties, such as the Invar effect present at 35\% Ni-65\% Fe, described concisely by Rancourt and Dang as ‘large and positive magnetovolume expansion that can cancel normal thermal contraction’ [5]. Another subject of much research has been the phase transition from $\alpha$-bcc to $\gamma$-fcc [1,6], ascribed to a loss of magnetic energy upon heating through the $\alpha$-$\gamma$ transition temperature [6-10], and upon cooling, the low temperature bcc phase cannot be recovered, a manifestation of hysteresis [6-7]. More recently, certain alloys of Fe$_x$Ni$_{1-x}$ nanoclusters have successfully been used to control the chirality of single-wall carbon nanotubes (SWCNT) in a development that is almost certain to have implications in related industries such as semiconductors [11].

In terms of catalysts as a group, bimetallic catalysts are the most commonly studied, perhaps due to their relative simplicity of treatment as opposed to trimetallic or higher-order systems. Perhaps the most important of the various physical phenomena peculiar to such systems is surface segregation, defined as the preferred occupation of low-coordinated surface sites by atoms of one element, while atoms of the other element remain in high-coordinated bulk or core sites [12]. While the description of
the resulting surface structure may depend on the a) energy of mixing, b) surface energies, c) entropy, and d) atomic size differences, the elements’ respective surface energies usually dominate the nature of segregation, especially at lower temperatures [13]. In general, the element with the lower surface energy will occupy sites on the surface, while the element with the higher surface and, hence, lower cohesive or bulk energy, will occupy sites at the core [13]. Ni (2.364 J/m²) possesses a slightly lower surface (free) energy than Fe (2.939 J/m²) [14], so it is expected that Ni will preferentially segregate to the surface, while Fe mostly remains at the core. But since the difference in surface energies is not too large, this segregation should not be that pronounced.

In this paper, Monte Carlo (MC) simulations are used to both qualitatively and quantitatively assess surface segregation in these Fe-Ni nanoclusters. The backbone of any such simulation is the type and quality of the potential used to describe interactions between atoms. Two different potentials are considered: an angular-dependent potential [7], and a recent tabulated EAM [8], both specific to the Fe-Ni system. Though these bimetallic potentials are designed to reproduce the stability of certain composition-specific structures, namely Fe₀.₅Ni₀.₅ and Fe₀.₂₅Ni₀.₇₅, their major deficiency is an inability to predict the aforementioned phase transitions due to the lack of terms representing thermal and/or magnetic contributions [7-9].

Explicit magnetic models using the Ising approximation have been implemented in MC simulations to better explain the interplay between temperature and magnetism [15], but unfortunately these are quite limited in that non-magnetic interactions are ignored and, more generally, during the simulation magnetic and non-magnetic effects are not simultaneously considered. On the other hand, Meyer has shown that phase transitions can still be simulated as long as thermal data, such as specific heat, are included in the fitting procedure [9], and additionally observed that it is possible to artificially preempt a bcc-fcc transition by including a large number of vacancies in the lattice structure [6,16], perhaps since the atoms have more room to preferentially rearrange. For the purposes of this investigation, however, the possibility of phase transitions was precluded by the relatively low temperatures at which the simulations were performed (300 K), though in future work this would certainly pose an interesting research problem.

II. INITIAL CONFIGURATION SETUP

For the purposes of this paper, the system size for the Fe-Ni nanoclusters was limited to approximately 2.0 nm in diameter, which puts the simulations within the molecular regime where the number of atoms is less than 500. Cubic blocks of atoms, initialized as either fcc or bcc depending on the respective trial with a lattice parameter aₒ were created by replicating the respective unit cell in the ABC directions, following Sankaranarayanan et al [17]. Subsequently, spherical nanoclusters were generated by implementing an arbitrary cutoff radius rₒ to control the number of atoms. In most studies dealing with fcc-fcc metal systems, a cubo-octahedral configuration is used for ease of analyzing segregation to specific planes [13,18], but for bcc-bcc metals systems none such canonical structures have been proposed, and for mixed fcc-bcc systems the picture becomes more complicated due to the rise of defect sites. In any case, it was felt that, for reasons of robustness, spherical nanoclusters would allow for straightforward analysis. For all tests, the cluster size was set as N=459 atoms because it was
possible to generate both bcc and fcc-initialized clusters that had exactly that number of atoms and, therefore, reduce the numbers of parameters that varied. The corresponding dispersion for both bcc and fcc nanoclusters was approximately 50%, i.e. 50% of the atoms were on the surface, while 50% were at the core.

Compared to fcc-fcc bimetallic systems such as Cu-Ni and Ni-Al, where the only parameter to vary is the choice of lattice parameter (a0), in Fe-Ni nanoclusters one must consider not only lattice parameter but also lattice structure, i.e. fcc or bcc. In theory, the choice of lattice parameter should have a minimal effect on the stability of the equilibrium configuration, as preliminary tests indicated, this is not necessarily the case. While an initial approach took values of the alloy lattice parameter in between those of pure Fe and pure Ni with respect to the chosen lattice structure, i.e. lower a0 for bcc structures and higher a0 for fcc structures, in reality such an arbitrary trial-and-error scheme to optimize the given combination of parameters with respect to stability (i.e. lower overall energy) for a particular simulation loses track of the true physical picture. For this reason, an amended procedure for choosing parameters was subsequently implemented, using data available from the literature [11]. From this point forward, all compositions xFe are reported in atom percent.

Experimental plots of lattice parameter versus alloy composition reveal three important phenomena: a) Fe-Ni alloys take on a bcc structure for xFe>0.73 and an fcc structure for xFe<0.73, with a phase transition occurring at xFe=0.73, b) a0 of the fcc lattice increases from 3.5 A to 3.6 A at higher Fe concentrations, and c) a0 of the bcc lattice decreases from 2.9 A to 2.8 A at lower Fe concentrations [11]. Consistent with this data, FeNi1-x nanoclusters where 0≤xFe≤0.73 were initialized with an fcc lattice with a0=3.5 A, and with an bcc lattice with a0=2.9 A where 0.73<xFe≤1. In this way, one can be sure the initial configurations are as close to the experimental results as possible, ensuring that the equilibrium structures outputted by Monte Carlo are physically valid. While the usefulness of fitted potentials diminishes if the input parameters must be controlled to allow for a reasonable result, it is better to accurately simulate physical phenomena first before attempting to generalize the process.

For a given composition and nanocluster size, there were n1 atoms of Fe and n2 atoms of Ni, yielding a total of n1+n2=N atoms. With the number of sites (N total) set by the desired initialization (fcc or bcc), lattice parameter a0, and cutoff radius rc, these N atoms were placed at random at these sites until all were filled. In this way each test, even if of the same composition as another test, would be distinctly initialized, and checks could be performed to check whether the trajectories converged to the same or approximately the same equilibrium regardless of initialization, with all other parameters controlled.

III. POTENTIALS:

Two distinct types of metal potentials were used during the course of the simulations: an angular-dependent potential (ADP) [7] and a standard EAM potential [8]. Semi-empirical potentials, beginning with EAM, have been circulating in the literature since the 1980’s [19-20], with early efforts initially focused on fitting pure fcc metals as a group [21-23]. The EAM model is simple in form,
\[ E_{tot} = \sum_{i} F(\rho_i^o) + \frac{1}{2} \sum_{i} \sum_{j \neq i} \Phi(r_{ij}), \text{ where } \rho_i^o = \sum_{j \neq i} \rho(r_{ij}) \]

where one has the traditional pair potential term \( \Phi(r) \) in addition to an embedding function \( F(\rho) \), which signifies the energy associated with insertion of a metal atom in a host electron density \( \rho_i^o \) of all other atoms, i.e. the classical description of metallic bonding as a ‘sea of electrons’. This was soon expanded in order to deal with alloys of these metals [24], and sporadic attempts were made to additionally fit bcc metals [25-26]. The modified EAM (MEAM) potential expanded the terms associated with electron density and introduced a ‘screening procedure’ to more accurately reproduce bulk quantities [27], which rendered MC codes based on MEAM computationally expensive compared to the regular EAM [7]. A subsequent bond-order simulator (BOS) method explicitly parametrized the local coordination of each atom by making use of mixing parameters [13,18], and has successfully been applied to several systems, including Cu-Ni [12] and Pd-Pt [17].

Numerous surface segregation studies have been conducted based on MC, MD, or a combination of both (termed MD-MC/CEM [28]), mostly focused on fcc-fcc bimetallic nanoclusters such as Cu-Ni [12,29], Ni-Al [30], Pd-Ni [28,31], and Pd-Pt [17]. Several papers have sought to understand bcc Fe [32-33] and the phase transition phenomena peculiar in the Fe-Ni system [6,9], and recently thought has been given to modifying the standard EAM potential, which was originally designed for use with fcc metals. The angular-dependent potential (ADP) adds terms accounting for bond angle, as shown below:

\[
E_{tot} = \sum_{i} F(\rho_i^o) + \frac{1}{2} \sum_{i} \sum_{j \neq i} \Phi(r_{ij}) + \frac{1}{2} \sum_{i} \sum_{\alpha} (\mu_{i}^\alpha)^2 + \frac{1}{2} \sum_{i} \sum_{\alpha} \sum_{\beta} (\lambda_{i}^{\alpha\beta})^2 - \frac{1}{6} \sum_{i} \nu_i^2
\]

bringing the number of functions required for parametrization from 7 (2 electron density functions, 2 embedding functions, and 3 pair-potentials) to 13 (7+3 dipoles and 3 quadrupoles) [7]. Mishin suggested this form to move away from the purely “central force character” of EAM potentials, which do not properly account for the covalent nature of bonding in Fe. Both this ADP potential, along with a new EAM potential for the Fe-Ni system, are fitted using ab initio DFT calculations, with more weight given to the stable structures at a given alloy composition [7-8].

**IV. MONTE CARLO SIMULATIONS**

In order to characterize the minimum (potential) energy configurations of the Fe-Ni bimetallic alloy, Monte Carlo simulations coupled to the potentials described earlier were run across numerous compositions from pure Ni to pure Fe. At each Monte Carlo step, there was an equal probability of swapping two atoms or randomly displacing one atom, with the swaps usually completed after several hundred thousand steps for all alloy compositions. The Metropolis acceptance criterion was used to accept or reject moves (swaps or displacements) as follows:

a) if the move resulted in a lower configurational energy, then it was immediately accepted, or

b) if the move resulted in a higher configurational energy, then it was accepted proportionate to its Boltzmann weight \( e^{-\Delta U} \) in the probability distribution.
Mathematically speaking, assuming a uniform distribution of a variable ‘x’ on the interval [0,1], if $x \leq \exp(-\beta \Delta U)$ then the move is accepted, otherwise the move is rejected.

Control of acceptance ratios was accomplished by scaling the maximum possible displacement every 5000 steps to restrict values to between 0.47 and 0.53; that is, increasing the displacement if acceptances were too high, and vice versa. Various initial values of maximum displacement were tried and cross-checked with the equilibrium energies in order to allow the lattice to relax to the point where increasing the maximum displacement further would have little or no effect, with the general observation being that too small of a displacement essentially limits the energy minimization to swaps (≈0.05 Å), while too large of a displacement leads to rejection of most moves until it can be scaled down (≈0.75 Å). An intermediate value of 0.50 Å was subsequently implemented for the remainder of the simulations.

A cutoff for energy calculations was eventually set as slightly more than $4r_0$, where $r_0$ is the atomic radius of one of the elements present in the bimetallic cluster, in order to only account for 2nd as well as 1st nearest neighbors, though a reduced cutoff of $2.5r_0$ was tried as well for comparison purposes. Either atomic radius may be used because Fe and Ni have essentially identical atomic radii and thus roughly identical cutoff distances, though that of Ni is slightly larger. Simulations were terminated after several million steps, at which point the energy change between steps had usually converged to less than $10^{-5}$ eV, and repeated for several random initial configurations to ensure that the global energy minimum for a given alloy composition was found. In addition, all clusters were simulated at 300 K: tests at higher temperatures will be performed in future work. Simulations were coded in FORTRAN, and tests submitted as array tasks on a Linux OS to the GridEngine environment used by the Research Computing cluster at the University of South Florida.

V. RESULTS

Energy profiles:

Before comparing energy or segregation profiles between potentials, it was necessary to first establish the effect of using small or large cutoff radii for energy calculations. The below figure shows the average energy per atom across compositions for two different cutoffs: ≈3.1 Å (≈2.5$r_0$) and ≈5.0 Å (≈4$r_0$), where $r_0$ is the atomic radius. Since $r_{0, Ni} \approx r_{0, Fe}$, either radius may be used, though it is better to use $r_{0, Ni}$, which is slightly larger.
As can be seen, the effect of energy cutoff is dramatic: the shape of the energy profile changes completely. While a smaller cutoff essentially shows monotonically increasing fcc energies, a larger cutoff shows the exact opposite, while bcc energies appear unaffected. It seems that the presence of Ni impurities somewhat stabilizes bcc Fe, as is evidenced by the lower energy of 80% Fe as opposed to 100% Fe, and the fcc energies indicate that Fe impurities stabilize fcc Ni (here, ‘stabilize’ is used in the rough sense of possessing a lower overall (potential) energy). These differences may be explained quite simply: while a ≈3.1 A cutoff takes into account only 1st nearest neighbors, the ≈5 A cutoff takes into account 2nd nearest neighbors as well. Because including more of the surrounding atoms in energy calculations yields a more accurate answer, the ≈5.0 A cutoff was used for the remainder of the calculations

Radial distribution function and coordination:

The radial distribution function (RDF) provides an effective way to characterize the average spacing between atoms in a given structure. To construct an RDF, the distances between each atom and the remaining atoms are placed in a histogram with a set number of bins describing concentric spheres in the radial direction, averaged over all atoms, and then weighted by the shell volume corresponding to each bin in the radial histogram [35]. The peaks correspond to the spacing between any given atom and its neighbors in the surrounding coordination shells, but in general we are interested in only the first peak and trough, which indicate the average nearest neighbor distance and the maximum nearest neighbor distance, respectively. Once the latter is known, the coordination numbers of all atoms can be determined by calculating how many atoms lie inside the maximum nearest neighbor distance [28]. A sample RDF is shown below:
Figure 2: Sample radial distribution function, with maximum nearest neighbor distance as 2.88 Å.

Probably because only a single RDF was constructed after completion of the simulation rather than several during the simulation, in some cases this distance yielded some coordination numbers greater than 12 for fcc structures or 8 for bcc structures, which means that the calculated distance is larger than the maximum nearest neighbor distance. If such occurred, this distance was scaled down in small increments (0.01 Å) until the maximum coordination number observed was either 12 (fcc) or 8 (bcc).

The surface segregation of a particular bimetallic alloy can be determined from resulting distribution of coordination numbers because certain sites, such as faces and corners, will have characteristic coordinate values. The equilibrium structures produced by MC were analyzed for only two types of sites: a) core or bulk sites, and b) surface sites, both classified on the basis of coordination number. The table below summarizes the coordination (Z) of these sites for both fcc and bcc structures. This simplified nomenclature has been reported for fcc structures [28], the only difference here being that edge and corner sites were not categorized as separate from surface sites. It is straightforward to define corresponding quantities for bcc structures, as seen below.

<table>
<thead>
<tr>
<th>Type of site</th>
<th>Z for fcc structures</th>
<th>Z for bcc structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk/core</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Surface</td>
<td>Z&lt;12</td>
<td>Z&lt;8</td>
</tr>
</tbody>
</table>

Table 1: Coordination of different types of sites for fcc [28] and bcc structure used to categorize site occupations.
Though it may be expected that alloys would exhibit core coordination numbers in between those of bulk fcc and bulk bcc because of lattice distortion, tests indicated that the initialized core coordination remains, e.g. if a cluster was initialized as bcc, with Z=8 for the core, the equilibrated cluster also had Z=8 for the core. This conclusion was arrived at by scaling r_{\text{max,NN}} to intermediate Z, generating the corresponding segregation profile, and then checking the dispersion, or (100-% of sites at the core). For the case of intermediate Z, the calculated dispersion did not come close to approaching 50%. But for Z=8 or Z=12, depending on if the initialization was bcc or fcc, a 50% dispersion was arrived at. Thus it was concluded that the coordination was well-described by the initialized values, which simplified subsequent analyses significantly. In future work, bond order parameters such as Q4 and Q6, with predefined values for various crystal structures [38], will be used to impart more rigor to this procedure.

In Figure 3a, the simulated maximum nearest neighbor distance r_{\text{max,NN}} is plotted against composition. Technically, plotting a_0 instead of r_{\text{max,NN}} would have provided a more clear picture of the lattice structure, because though Ni and Fe have essentially the same r_{\text{max,NN}}=2r_0 in their respective bulk forms, their a_0 vary greatly due to geometrical differences between fcc and bcc. However, if one back-calculates a_0 using the below r_{\text{max,NN}} as:

$$r_{\text{max,NN}} = \frac{a_0 \sqrt{2}}{2} \text{ for fcc, and } r_{\text{max,NN}} = \frac{a_0 \sqrt{3}}{2} \text{ for bcc [37]}$$

it is evident that the simulated a_0 are distorted from their experimental/literature ranges (2.8-2.9 A for bcc, 3.5-3.6 A for fcc). Therefore, it may be more appropriate to simply observe trends in r_{\text{max,NN}} as mirroring those of a_0, rather than trying to get the simulated a_0 to match the experimental a_0.

When compared qualitatively to the experimental/literature plot of a_0 vs x_{Fe} (Figure 4b), the respective trends described earlier mostly agree. Both plots show: a) a decrease in a_0 or r_{\text{max,NN}} with increasing x_{Ni} for bcc structures, and b) an increase in a_0 or r_{\text{max,NN}} with decreasing x_{Ni} for fcc structures, though the behavior for 0.3Sx_{Ni}\leq0.5 defies this trend. In general, for nanoclusters and other finite size systems, it is sometimes difficult to know how much weight to give to comparisons with bulk data because properties can differ significantly [36]. At least for the bulk data plotted in Figure 3b), it seems that Ni impurities in Fe lead to a structural contraction, while Fe impurities in Ni lead to an expansion,
Figure 3a: $r_{\text{max,NN}}$ from EAM plotted against alloy composition, with standard deviations included as error bars. The data is in fair agreement with that plotted in Figure 4b, though the behavior varies considerably for $0.3 \leq x_{\text{Ni}} \leq 0.5$, perhaps a consequence of these nanoclusters being of finite size.

Figure 3b: Bulk lattice parameter vs alloy composition. $a_0$ decreases with increasing $x_{\text{Ni}}$ up to the fcc-bcc phase transition at $x_{\text{Ni}}=0.27$, rises dramatically, and then somewhat decreases once more. Alloys are of fcc structure at higher Ni concentrations, and of bcc structure at $x_{\text{Ni}} \leq 0.27$. Figure 1.h reproduced from [11].

Segregation profiles:

Upon implementing the various categories of coordination described earlier to the equilibrated nanoclusters, the following type of profile results:

Figure 4a): Segregation profile for EAM. Key: core sites (blue), surface sites (red)  
Figure 4b): Segregation profile for ADP. Key: core sites (blue), surface sites (red)
The EAM potential shows a nonlinear relationship between site occupation and $x_{Fe}$ for $x_{Fe}<0.50$, and a roughly linear relationship for $x_{Fe}\geq 0.60$. At lower $x_{Fe}$, Fe exhibits a stronger presence at bulk sites and a weaker presence at surface sites, perhaps an effect of differences in surface energy at low impurity (Fe) concentrations, while at higher $x_{Fe}$ the occupation of sites simply follows $x_{Fe}$ and surface energy differences appear not to play a pronounced role. Bulk and surface occupations appear to switch places for $x_{Fe}>0.73$, perhaps as it becomes more energetically favorable for fcc Ni to cede surface sites completely to Fe within the bcc lattice.

The ADP potential shows a roughly linear relationship for $x_{Fe}\leq 0.60$, with core sites saturated with Fe above and surface sites depleted of Fe around the phase transition at $x_{Fe}=0.73$. Such behavior makes sense for the bcc structures predominant for $x_{Fe}\geq 0.73$, because Fe can be expected to prefer core sites over lower coordinated sites at the surface in general, and especially those core sites with $Z=8$. On the other hand, for fcc structures, the linear relationship signifies that Fe has no particular strong preference for the core beyond simple proportionality arguments. In this region, the surface sites are unexpectedly slightly enriched in Fe, and core sites slightly depleted of Fe, with core sites only becoming preferred over surface sites for $x_{Fe}\geq 0.6$. As a comparison, when using a cutoff of ≈3.1 Å, core sites are always enriched in Fe except for low concentrations ($x_{Fe}<0.30$), which seems to make more sense with respect to surface energies.

VI. CONCLUSIONS

Most research into the Fe-Ni system has been concerned with the development of suitable potentials, though recent innovations in using Fe-Ni nanoclusters to control chirality during the growth of carbon nanotubes (CNT) showcase a need for simulations in order to offer reasonable comparisons to experiment. In this paper, Monte Carlo (MC) simulations were used to characterize the structures of these nanoclusters, especially the surface, because it is these surface sites that would most likely affect the particular mechanism of CNT growth. The resulting minimum energy, equilibrium clusters were analyzed for segregation using arguments based on coordination number, with the simulated results mostly agreeing with predictions based on surface energy differences between Fe and Ni. Both potentials show an overall preference of Fe for core sites, while Ni migrates to the surface, though the exact relationship of site occupation with concentration depends on the potential. The embedded-atom model (EAM) exhibits a linear relationship at higher Fe concentrations, while the angular-dependent potential (ADP) exhibits the same at lower Fe concentrations. Nonlinear relationships may arise from surface energy differences at lower Fe concentrations for EAM and from bulk coordination preferences for ADP.

VII. FUTURE WORK

With regards to simulations involving the Fe-Ni system, much remains to be studied. MC simulations will be carried out at higher temperatures, not only with an eye to segregation phenomena, but also to sample the different regions of the phase diagrams, specifically, the particular crystal structure(s) present at a given composition and temperature. The resulting equilibrated nanoclusters can then be simulated using MD with an annealing cycle in order to probe time- and temperature-
dependent properties such as melting point and diffusion coefficients. The low-coordinated sites present on the surface of the nanoclusters can be isolated, placed in the presence of a carbon cap, and DFT (density-functional theory) calculations used to gain a first-principles look at possible mechanisms for chirality control. In addition, MD simulations of these nanoclusters and carbon nanotubes will allow for a quantitative comparison with recent experiments by Chiang and Mohan. Lastly, if a more effective potential could be developed, one that a) accounted for both thermal and magnetic properties of Fe-Ni over large temperature ranges such that phase transitions were observed when expected, and b) gave proper weight to the stable lattice structure present at a given temperature (e.g. fcc Fe at higher temperatures), the aforementioned MC-MD process could be repeated, and more confidence placed on the segregation results.

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REFERENCES


