Atomistic Simulation of Metal Catalyst Nanoparticle Melting in Plasma-Enhanced Synthesis of Carbon Nanotubes

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Abstract: Classical molecular dynamics simulations are used to calculate the melting properties of Fe clusters under 100 atoms (1.2 nm). The presence of size-dependent second-order-like melting and sensitive surface and core melting temperatures may complicate the catalytic synthesis of carbon nanotubes (CNTs). The influence of carbon and sulfur (a common CNT growth promoter) on cluster melting will be investigated.

1. Introduction

Metal nanoparticles (NPs) under 100 nm have interesting properties desirable for catalytic applications like the growth of carbon nanotubes (CNTs) with floating catalyst chemical vapor deposition (FCCVD) [1]. FCCVD can be enhanced with plasma with spark discharge generation of nanoparticles with narrow size distributions [2]. While the mechanism of CNT production depends on many factors, it is accepted that carbon precursors interact with an NP with a disordered surface and ordered core: decomposing on, diffusing on, and dissolving inside the NP—eventually forming graphitic carbon that grows the CNT or encapsulates the NP, thereby terminating CNT growth [3]. These factors depend on the NPs melting characteristics, which are strongly size-dependent for clusters under 2 nm relevant to single-wall CNT growth [4]. Sulfur is often employed in FCCVD as a CNT growth promoter and is proposed to influence NP melting properties [5].

Here, classical molecular dynamics (MD) simulations are used to elucidate size-dependent Fe nanocluster melting alone and in the presence of FCCVD species like carbon and sulfur.

2. Methods

Classical MD with Embedded Atom Method Finnis-Sinclair (and soon ReaxFF) interatomic potentials are used to simulate NP melting thermodynamics and mechanisms for NPs up to 100 atoms in size. Parallel tempering simulations are employed to find global minimum energy configurations and energetic melting points (T_{Cv}) from cluster heat capacity curves. Core (T_{core}) and surface ($T_{surface}$) melting points are calculated from NVT simulations of cluster melting from minimum energy configurations.

3. Results and Discussion

Fig. 1 compares energetic, core, and surface melting points for cluster sizes between 10 and 100 atoms in size. At many cluster sizes where multiple core structures are close in energy, second-order-like melting without latent heat is observed. In these cases, structural isomerization occurs at temperatures well below T_{Cv}.

Single-shell cluster sizes with closed-shell structures have high $T_{surface}$, while cluster sizes with near-closed structures have lower $T_{surface}$ by hundreds of Kelvin. Small double-shell cluster sizes have high densities of low-energy configurations, showing mostly second-order-like melting behavior (2^{nd} order T_{Cv} in **Fig. 1**). Large double-shell cluster sizes exhibit premelting ($T_{surface} << T_{core}$) due to the presence of an ordered core structure with a less-ordered surface.

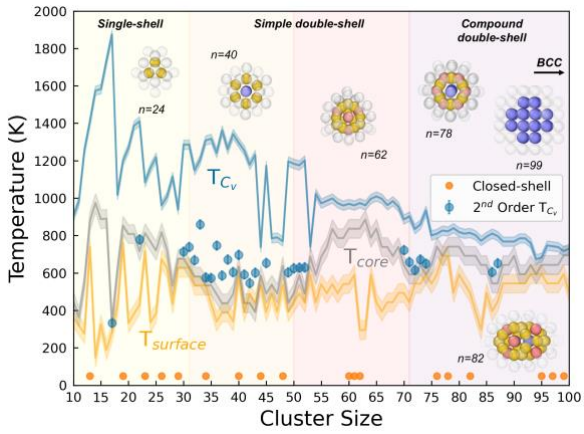

Fig. 1. Compares energetic, core, and surface melting points (T_{Cv}, T_{core}, and $T_{surface}$, respectively) for Fe clusters with $10 \leq n \leq 100$ atoms from classical MD simulations. Representative cluster structures (transparent surface atoms, core atoms colored by structure) and broad structural regimes (colorful fills) are depicted.

4. Conclusion

Size-dependent melting properties in Fe nanoparticles appear to have predictable trends in optimal structural configurations, second-order-like melting, and behavior of surface and core melting, within certain size regimes. These size-dependent properties may complicate the synthesis of single-walled CNTs. The influence of carbon and sulfur on Fe cluster melting properties is currently under investigation.

Acknowledgments

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References

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