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Predicted Anomalous Behavior of C_{60} Fullerenes on Graphite at Low Temperature: A New Hindered Cooperative Rotational Transition

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All-atom molecular dynamics (MD) computer simulations of C_{60} fullerene patches adsorbed onto graphite are conducted at various coverages for very low temperatures. There appears to be a hindered tumbling rotational transition through $T \leq 20$ K seen in the simulations that accompanies dramatic lattice expansion and configurational energy change with temperature in the adlayer. Moreover, the transition is unique in that it appears to be continuous and understandable on the basis of very simple dynamical arguments. The results suggest that such behavior could be present and influential in a wide range of molecules whose dynamical (time averaged) shapes are very close to their static symmetry, in contrast to surface systems with lower symmetry constituents and sharp rotational transitions. The transition is also observed in annealed, percolating adlayers and its dependence on lattice topology is discussed.

Keywords: Fullerenes, Molecular Dynamics, Surface Thermodynamics.

C_{60} Fullerenes have been of experimental and theoretical interest since their discovery almost thirty years ago. Their elastic properties and high degree of symmetry coupled with the interesting behavior of endohedral fullerenes make them ideal systems for study and innovation. When placed on a surface such as graphite or graphene, the interactions of the C_{60} adlayer with the graphite[1–7] result in a wide range of epitaxial characteristics and phase transitions dependent upon the area density of the system, which have been studied theoretically[3–7] and experimentally.[7–17] Fullerene layers on graphitic structures[18–21] as well as fullerenes in nanomechanical systems[22–24] have also been studied computationally. Experimentally, the C_{60}/gr system presents a single layer lacking strong orientational epitaxy over a wide temperature range[5–17] and a second layer which exhibits dendritic growth.[10] At all temperatures investigated so far the molecules themselves behave essentially as free rotors. Mainly because most of the interesting physics takes place for C_{60}/gr systems at room temperature and much higher, the low-temperature behavior of these systems has not been explored. Computational studies have provided a wealth of insight into the behavior of C_{60}/gr systems-complete with a prediction about structural ordering[21]-but the preponderance of work has been done with spherically averaged potentials which are known not to address the low-temperature behavior of the system.[4, 18] In addition the all-atom work that has been published deals with the high temperature regime or specific dynamics related to nanoscale bearings and nanodevices.[22–24] The purpose of this Letter is to report results of ultra-low-temperature ($T \leq 20$ K) all atom Molecular Dynamics simulations of fullerene patches on graphite, which predict anomalous behavior of the adlayer as the system evolves through a hindered rotational transition. Because the static symmetry of the adsorbate molecules is so close to their dynamic symmetry, the rotational transition couples with dramatic configurational energy changes and results in dramatic low-temperature thermal expansion.

An explicit atom model of the fullerenes is utilized in this study. Since simulations including bonded interactions generally require a smaller time step, computational time cost increases dramatically. For our simulations we utilized the NAMD code[25]—a parallelized MD simulation package which has been carefully and thoughtfully

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