Effect of Surface Roughness, Etch Pits, and Adsorbates on the Surface Phonon Density of States of Graphite

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Gas-surface interaction processes are encountered in a wide variety of disciplines including heterogeneous catalysis, tribology, and thermal protection systems. A detailed understanding of the underlying physics of the interaction process is critical for the efficient design, modeling and control of these technological processes. The most common approach in modeling the gas-surface interaction processes has involved the use of simple models with a wide range of parameters that are calibrated to match experimental observations. Although such an approach can be used to reproduce the observed data *a posteriori*, the extension of such models for *a priori* prediction at conditions different from those of the experiments remains a great challenge.

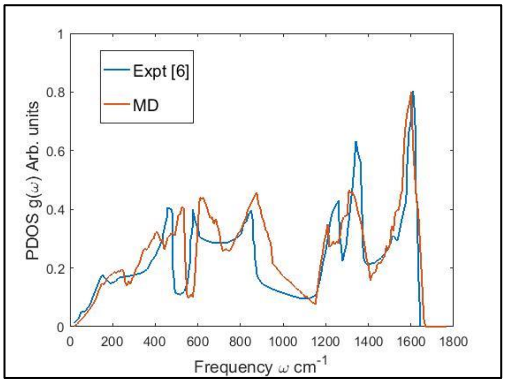

Fig.1: Comparison of experimental [6] and MD results for bulk PDOS of graphite carbon.

When a gas-phase particle strikes a surface, it can undergo adsorption, direct impact reactions, or inelastic scattering. These processes are coupled with the phonon bath at the material interface. During the interaction, energy transfer occurs both between and within the sub-systems (substrate and gas particle). A number of mechanisms including multi-phonon processes, translational and internal mode (rotational and vibration) excitations may be captured by the evaluation of the detailed scattering kernels and transition matrix of the gas-phonon interaction [1, 2]. Such a framework provides a powerful alternative to full molecular dynamics for computing various surface interaction quantities such as accommodation coefficients, adsorption and reaction probabilities, etc. Further, since this framework captures the underlying microscopic details, and can be extended to describe the system even in the state of extreme non-equilibrium, which are frequently encountered in high speed re-entry flows and nano-scale devices. Computational models based on this framework can be used to accurately model the gas-surface interaction process even within a transient non-equilibrium environment. These theoretical models have been shown to provide excellent agreement with the molecular beam experimental data for translational energy and angular distributions of the scattered products [3, 4].

In this work, we will focus on understanding the effect of (i) random surface roughness, (ii) etch pits, and (iii) adsorbates on the phonon density of states of carbon using Molecular dynamics (MD). The PDOS is calculated in MD using the velocity autocorrelation function shown below. The phonons at the surface are qualitatively and quantitatively different from the bulk due to the broken symmetry. In addition, the roughness of engineering material surfaces affects the phonon distributions. Furthermore, the gas-surface interactions also alter the PDOS due to the presence of adsorbates on the surface and removal of surface atoms due to surface participation reactions. This results in a highly coupled and dynamic system. Random surface roughness in MD will be obtained via irradiation with low energy particles. The effect of varying height and density of the defective region on the PDOS of this system will be investigated. The etch pits produced as a result of removal of surface atoms resembles a semi-ellipsoid with larger diameters and shorter depth [5]. Here, the phonon distribution will be characterized as a function of both diameter and depth of the etch pits. Finally, the effect of adsorbates on the PDOS will be studied in terms of bond strength (physisorbed vs chemisorbed) and surface coverage.

$$g(\omega) = \int dt\, e^{i\omega t} \frac{\langle \vec{v}(t) \cdot \vec{v}(0) \rangle}{\langle \vec{v}(0)^2 \rangle},$$

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