

A New Molecular Model for Graphite to Model Adsorption Mechanisms of Non-Polar Gases and Associating Fluids - Isotherms and Isothermic Heats

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Characterization of carbon materials to determine surface area and pore size distribution conventionally uses models based on the Steele 10-4-3 potential (with Crowell-Steele molecular parameters) and the assumptions: (1) the collision diameter of a carbon atom in a graphene layer is 0.34nm and (2) the interlayer distance between the adjacent layers is 0.335nm. However, there is growing evidence from experiments and from quantum mechanical calculations, that challenges the parameters used in the Crowell-Steele 10-4-3 model. Experimentally, LEED and RHEED have shown that molecules are closer to the graphite surface than predicted by the Steele model, and theoretically, quantum DFT calculation of the van der Waals C_6 coefficient per carbon for a single graphene layer has been found to be much greater than that for C in bulk graphite. On these grounds, we propose an improved model for graphite that gives good descriptions of adsorption isotherms and isothermic heats, especially in describing the various transitions and the spike in the plot of the isothermic heat versus loading. The features of this new model are: (1) the collision diameter of carbon atom in the top graphene layer is 0.28nm: smaller than that for graphene layers in the bulk solid of 0.34nm, (2) the interlayer distance between the top layer and the second layer is 0.299nm compared to the spacing of 0.3365nm for lower layers, (3) the corrugation of the graphene surface is taken into account by using discrete carbon atom, rather than solid continuum calculations, and (4) the anisotropy of polarisability of carbon in graphite parallel and normal to the surface, is included in the potential model.

We have used grand canonical Monte Carlo (GCMC) and kinetic canonical Monte Carlo (k-CMC) simulations to evaluate the effects of the above modeling on the adsorption isotherm and isothermic heats of adsorbates commonly used for the characterization of carbon materials: argon, nitrogen, krypton, methane and water. Our proposed model successfully captures many fundamental features of how adsorbed molecules are and structured on graphite. For simple gases we consider: (1) the gas-liquid transition, (2) the transition of 2D liquid to 2D solid, (3) the transition from commensurate (C), to incommensurate (IC), packing, and (4) the cusp-spike signature in the isothermic heat versus loading. Water, which is an associating fluid, shows several distinct features: (1) formation of water-oxygen functional group complexes (at the edges of graphene layers), (2) growth of water clusters, and (3) merging of clusters, followed by filling of the interstices with condensate between graphite micro-crystallites. Simulation results for simple gases and water were validated with high resolution experimental data.

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