Effect of aggregation on adsorption phenomena

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Adsorption at an attractive surface in a system with particles self-assembling into small clusters is studied by Molecular dynamics (MD) simulation. We assume Lennard-Jones plus repulsive Yukawa tail interactions, and focus on small densities. The relative increase of the temperature at the critical cluster concentration near the attractive surface (CCCS) shows a power-law dependence on the strength of the wall-particle attraction. At temperatures below the CCCS, the adsorbed layer consists of undeformed clusters if the wall-particle attraction is not too strong. Above the CCCS, or for strong attraction leading to flattening of the adsorbed aggregates, we obtain a monolayer that for strong or very strong attraction consists of flattened clusters or stripes respectively. The accumulated repulsion from the particles adsorbed at the wall leads to a repulsive barrier that slows down the adsorption process, and the accession time grows rapidly with the strength of the wall-particle attraction. Beyond the adsorbed layer of particles, a depletion region of a thickness comparable with the range of the repulsive tail of interactions occurs, and the density in this region decreases with increasing strength of the wall-particle attraction. At larger separations, the exponentially damped oscillations of density agree with theoretical predictions for self-assembling systems. Structural and thermal properties of the bulk are also determined. In particular, a new structural crossover associated with the maximum of the specific heat, and a double-peaked histogram of the cluster size distribution are observed.