Calculation of the Surface Pressure and the Contact Energy in the Adsorption of Alkanes on Aqueous Substrates

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An unusual sequence of two changes in the wetting state was found for the adsorption of alkanes on aqueous substrates, and it has been studied both experimentally [1, 2] and theoretically [2, 3] over the past decade. When droplets of an alkane are deposited on the surface of the water and the temperature is subsequently raised, one first observes a discontinuous transition which manifests itself in a sudden jump from a microscopically thin film to a mesoscopically thick layer of adsorbate. Upon further increase of the temperature, the layer thickness grows continuously and diverges at the critical-wetting temperature, which marks the ultimate transition to complete wetting. This sequence of transitions is now understood in terms of a competition of long-range and short-range forces acting between adsorbate and substrate. The long-range part, which governs the continuous transition to complete wetting, can be calculated within Dzyaloshinskii-Lifshitz-Pitaevskii theory, whereas a satisfactory theoretical account of the short-range interactions is still lacking. Based on a two-dimensional equation of state for the adsorbed alkane and an expression for the Henry's law constant derived by Hirasaki [4], the surface pressure is calculated and the contact energy, which accounts for the effective short-range interaction between adsorbate and substrate, is subsequently deduced using Dobbs' modified Cahn theory [5]. The theoretical description of sequential wetting is thus completed and uses only bulk properties of the isolated media.

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