Fluctuation Effects on Propagating Waves of Self-Assembly in Organosilane Monolayers.
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Wavefronts associated with reaction–diffusion and self-assembly processes are ubiquitous in the natural world. For example, propagating fronts arise in crystallization and diverse other thermodynamic ordering processes, in polymerization fronts involved in cell movement and division, as well as in the competitive social interactions and population dynamics of animals at much larger scales. Although it is often claimed that self-sustaining or autocatalytic front propagation is well described by mean-field “reaction–diffusion" or “phase field” ordering models, it has recently become appreciated from simulations and theoretical arguments that fluctuation effects in lower spatial dimensions can lead to appreciable deviations from the classical mean-field theory (MFT) of this type of front propagation. The present work explores these fluctuation effects in a real physical system. In particular, we consider a high-resolution near-edge x-ray absorption fine structure spectroscopy (NEXAFS) study of the spontaneous frontal self-assembly of organosilane (OS) molecules into self-assembled monolayer (SAM) surface-energy gradients on oxidized silicon wafers. We find that these layers organize from the wafer edge as propagating wavefronts having well defined velocities. In accordance with two-dimensional simulations of this type of front propagation that take fluctuation effects into account, we find that the interfacial widths $w(t)$ of these SAM self-assembly fronts exhibit a power-law broadening of in time $w(t) \sim t^\beta$, rather than the constant width predicted by MFT. Moreover, the observed exponent values accord rather well with previous simulation and theoretical estimates. These observations have significant implications for diverse types of ordering fronts that occur under confinement conditions in biological or materials-processing contexts.