

Temporally Anticorrelated Subdiffusion in Water Nanofilms on Silica Suggests Near-Surface Viscoelasticity

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Cite This: *ACS Nano* 2020, 14, 3041–3047

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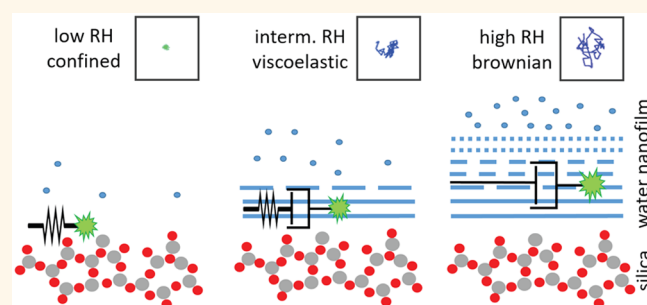
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ABSTRACT: Single-molecule tracking was used to probe the local rheology of interfacial water. Fluorescent rhodamine molecules were tracked on silica surfaces as a function of ambient relative humidity, which controlled the thickness of condensed water nanofilms. At low humidity, the molecules exhibited confined diffusion in the vicinity of isolated adsorption sites characterized by a broad distribution of binding stiffness constants; subsequent chemical or physical surface passivation selectively eliminated stiffer binding sites. At increased humidity, molecularly thin water films condensed, permitting near-surface transport of rhodamine molecules. Motion was subdiffusive, with an anomalous exponent increasing with the nanofilm thickness. Molecular trajectories were temporally anticorrelated, ergodic, but also featured transient binding and intermittent diffusion. Statistical modeling demonstrated that this complex motion in water nanofilms had the characteristics of fractional Brownian motion combined with a continuous-time random walk. This was consistent with diffusion within viscoelastic nanofilms, suggesting persistent molecular structuring in the vicinity of the silica surface.

KEYWORDS: silica, water nanofilm, single-molecule tracking, anomalous diffusion, confined diffusion, molecular structuring



The interface between water and silica (or related silicate minerals) is central to a wide range of geological and industrial processes,^{1,2} yet many of its properties remain elusive, notably in the nanoscale limit where molecules are highly confined and constrained. The different forms of Si–O groups at the surface are believed to interact strongly with water molecules through hydrogen bonding, leading to molecular ordering that extends several Å from the surface.³ Water structuring, in turn, may impact transport properties at the interface, by influencing the hydrodynamic slip or no-slip boundary conditions,⁴ and changing local rheology. The viscosity of water nanofilms remains hotly debated. While studies of water confined between two mica (an aluminosilicate mineral) surfaces separated by 5 nm or less found no substantial increase in viscosity,^{5,6} experiments using scanning-probe techniques on silica and other hydrophilic surfaces have reported viscosity enhancement by as much as 10⁶.^{4,7}

Hydrophilic surfaces exposed to water vapor become spontaneously coated by a thin film of water at the Å-to-nm scale, with the exact thickness depending on substrate chemistry, temperature, and vapor pressure. Water physisorption is therefore ubiquitous in the Earth's subsurface, surface,

and atmosphere, including on aerosol particles and ice (glacier and snow),⁸ with significant consequences for environmental processes, for example, in heterogeneous chemical reactions.⁹ Thus, there is significant interest in understanding molecular transport in water nanofilms, despite the uncertainty with respect to the structure of these thin films.¹⁰ Recent studies have elucidated the mechanisms of molecular interfacial transport through bulk-mediated diffusion, whereby molecules transiently bind to the surface and diffuse mostly in the bulk,^{11,12} describing a “hopping” diffusion which fits in the framework of continuous-time random walks (CTRWs). However, little is known about how extreme confinement, between two solids or between solid and vapor, perturbs this behavior.¹³ Presumably, confinement would increase the amount of interface available and modify the hydrodynamic properties of the fluid phase, which could result in different types of stochastic dynamics.

Received: October 7, 2019

Accepted: January 14, 2020

Published: January 14, 2020