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ARTICLE

Enhanced Diffusive Transport in Fluctuating Porous Media

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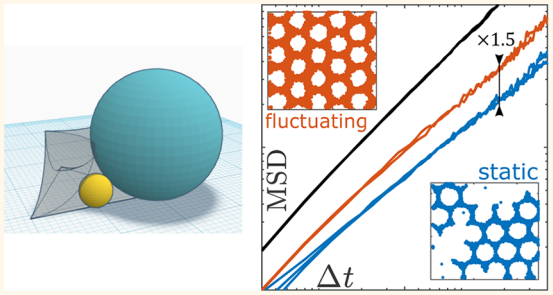
ABSTRACT: **Mass transport within porous structures is a ubiquitous process in biological, geological, and technological systems. Despite the importance of these phenomena, there is no comprehensive theory that describes the complex and diverse transport behavior within porous environments. While the porous matrix itself is generally considered a static and passive participant, many porous environments are in fact dynamic, with fluctuating walls, pores that open and close, and dynamically changing cross-links. While diffusion has been measured in fluctuating structures, notably in model biological systems, it is rarely possible to isolate the effect of fluctuations because of the absence of control experiments involving an identical static counterpart, and it is generally impossible to observe the dynamics of the structure. Here we present a direct comparison of the diffusion of nanoparticles of various sizes within a trackable, fluctuating porous matrix and a geometrically equivalent static matrix, in conditions spanning a range of regimes from *obstructed* to *highly confined*. The experimental system comprised a close-packed layer of colloidal spheres that were either immobilized to a planar surface or allowed to fluctuate locally, within the space defined by their nearest neighbors. Interestingly, the effective long-time diffusion coefficient was approximately 35−65% greater in the fluctuating porous matrix than in the static one (depending on the size of the nanoparticle probes), regardless of the geometric regime. This was explained by considering the enhancing effects of matrix fluctuations on the short-time diffusion coefficient and cooperative "gate-opening" motions of matrix particles and nanoparticle probes.**



KEYWORDS: *porous media, fluctuations, diffusive transport, obstructed diffusion, confined diffusion, hydrodynamic coupling*

Biological, geological, and industrial processes frequently involve complex and tortuous high surface area environments. For example, transport of molecular and particulate species (heavy metals, pesticides, microbes, colloids, *etc.*) within the fractured and granular Earth subsurface is critical to many processes associated with water treatment, environmental remediation, and energy production.[1,2] Transport of most biomolecular species takes place within the crowded and porous environments inside cells or tissues. And while high surface area materials are prized for their ability to enhance technological processes involving chemical reactions and separation or purification, transport within such materials remains an ongoing challenge to understand and optimize. Porous membranes used in water purification systems and filtration devices, for example, comprise a solid matrix embedding a percolated network of cavities, pores, and channels.[3,4] Diffusive dynamics in such structures can be challenging to describe, even qualitatively. For example, environments may range from a regime where species are merely obstructed—and transport is simply dominated by excluded volume effects—to the opposite extreme where species are strongly confined—and transport can be simplistically considered a sequential process of confinement within cavities punctuated by translocation through pores connecting neighboring cavities.

Materials engineering traditionally relies on the structure−function paradigm. In the context of porous materials, this implies that the matrix geometry and surface chemistry determine the transport properties of solutes and particles.[5] Within this framework, structure is implicitly assumed to represent a static or average property, although it has long been recognized that materials may fluctuate, rearrange, or evolve with time. Thus, while transport has been studied under the direction of various driving forces, including thermal motion (*i.e.*, diffusion), convective flow, and external fields, in most cases the porous matrix itself has simplistically been considered a static and passive participant, characterized sufficiently by its

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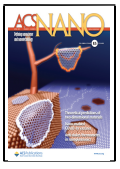

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