Supporting Information:

Enhanced Diffusive Transport in Fluctuating Porous Media

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Additional MSD curves

In Fig. S1 we show representative MSD curves, similar to those shown in Fig. 2c, for all other tracer sizes.

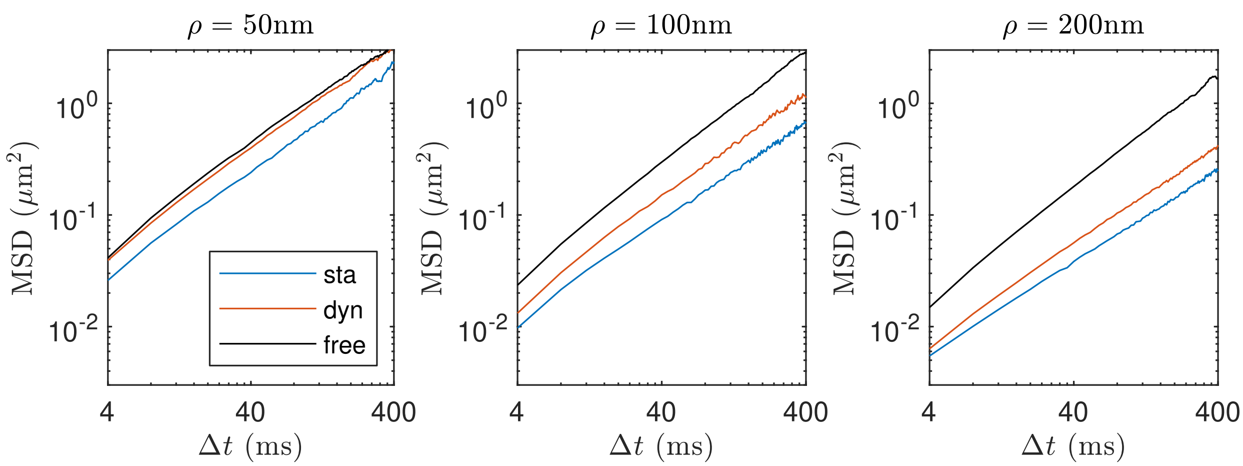

Figure S1: Representative MSD curves for tracers with $\rho = 50, 100, 200$nm. Black curves indicate diffusion in the free liquid, blue within the static lattice, and orange within the dynamic lattice.

Average lattice size and diffusivity enhancements

In the Main Text, we report diffusivity enhancements of about 50% in the dynamic lattice compared to the static lattice, for all tracer sizes. The static and dynamic lattices have similar time-averaged geometries; notably the distribution of nearest-neighbor distances d_{nn} are strongly overlapping (Fig. 1b). However, a typical dynamic lattice field-of-view (FOV) has a slightly larger average d_{nn} compared to a typical static lattice FOV, with $\langle d_{\mathrm{nn}}^{\mathrm{dyn}} \rangle \simeq 2.15\mu$m and $\langle d_{\mathrm{nn}}^{\mathrm{sta}} \rangle \simeq 2.10\mu$m. This corresponds to an increase of about 3%-5%. We demonstrate here that this small geometrical factor cannot explain the reported diffusivity enhancements by itself. We used kinetic Monte Carlo simulations with spacing between lattice spheres $S = 2R(1+s)$, for different values of s. We compare the asymptotic values of the MSD slopes at long times for increasing s values. We find in Fig. S2 that even for 200nm tracers, long-time diffusivities do not increase by more than 10% when $s = 0.05$, representing an upper limit for the magnitude of this effect.

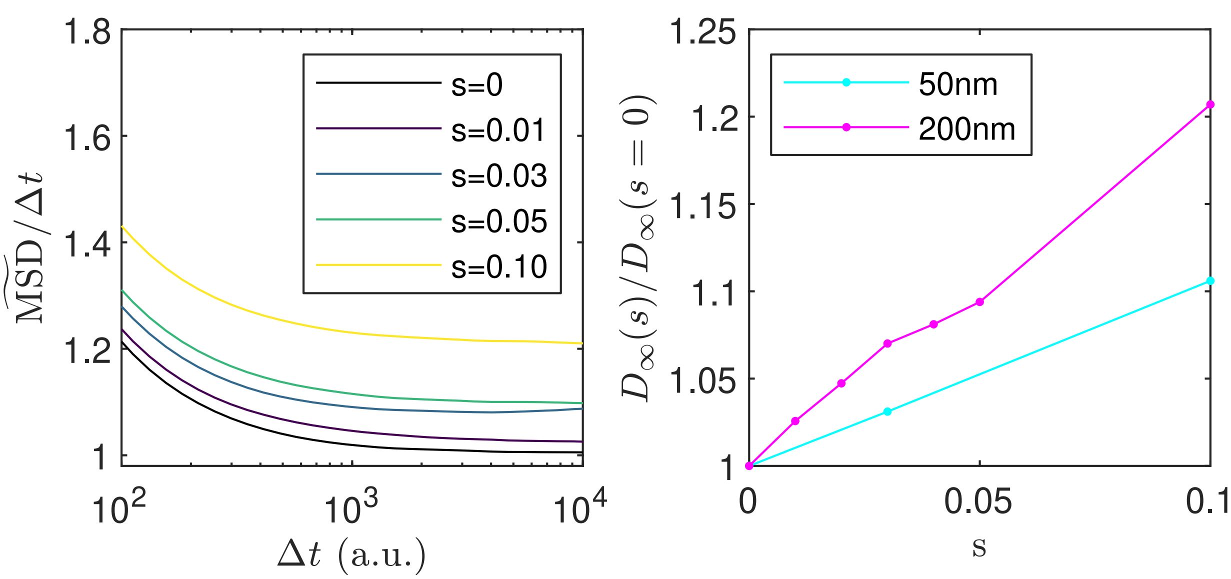

Figure S2: Influence of lattice spacing on long-time diffusivity. (a) Curves of mean-squared displacements over time-lag for different values of relative spacing s, renormalized by asymptotic value at $s = 0$, obtained from simulations for 200nm tracers. (b) Values of D_∞ at different s relative to D_∞ at $s = 0$, for 50nm and 200nm tracers, obtained from simulations.

Hydrodynamic interactions within the lattice

Compared to self-diffusion in the free liquid, tracer diffusivity within the static lattice is significantly hindered. There are two main contributions to this drop: 1) accessible volume effects; and 2) hydrodynamic interactions. Hydrodynamic interactions occur because of the viscosity of the fluid which couples the mobility of a particle to nearby no-slip boundaries, and are sometimes neglected in models of diffusion in porous media. We show here that hydrodynamic interactions significantly contribute to diffusivity drops, especially for large tracer particles. To do that, we compare the experimental long-time diffusivity measured in the static lattice relative to that of the free liquid with the expected results from simulations, which only account for geometrical effects, and neglect hydrodynamic contributions. We find in Fig. S3 that for tracers larger than 100nm, experimental diffusivities are about half of what is expected from pure excluded volume effects, demonstrating the preponderance of hydrodynamic interactions at large particle sizes.

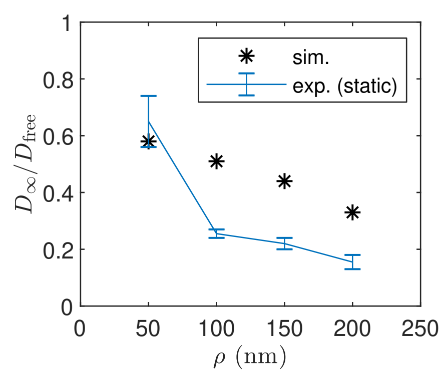

Figure S3: Long-time diffusion coefficients D_∞ relative to diffusion coefficients in the free fluid D_{free}. Compared to simulations (black asterisks), which only include geometrical effects, diffusivities measured in experiments (blue curve) are significantly lower, especially for large tracers.

Many-body effects in fluctuating cavities

In the Main Text, we show that tracer diffusivity is enhanced in a dynamic cavity compared to a static cavity (Fig. 4c). Although intuitive, this result is not immediate from common hydrodynamic considerations. For example, if we consider a system of two Brownian spheres (bb) of radius a and separated by a distance r, the classic calculation by Batchelor[1,2] shows that the diffusion coefficient *of* the center of mass is

$$D_C^{\rm bb} \simeq \frac{D}{2}\left[1+\frac{3}{2}\tilde{r}^{-1}-\tilde{r}^{-3}-\frac{15}{4}\tilde{r}^{-4}\right], \tag{1}$$

and *relative to* the center of mass is

$$D_R^{\rm bb} \simeq \frac{D}{2}\left[1-\frac{3}{2}\tilde{r}^{-1}+\tilde{r}^{-3}-\frac{15}{4}\tilde{r}^{-4}\right], \tag{2}$$

along the axis connecting the spheres centers, with $\tilde{r} = r/a$ and D the diffusion coefficient in the free fluid. This calculation, valid when $r/a \gg 1$, is obtained as a series expansion by considering sequentially the flow induced by one sphere on the other. In particular, the corrections in $\tilde{r}^{-1}, \tilde{r}^{-3}$ come from the flow created by the motion of sphere 2 on sphere 1. Therefore, if sphere 2 is immobilized, these terms disappear. For the system of one Brownian sphere and one fixed sphere (bf), this leads to

$$D_C^{\rm bf} = D_R^{\rm bf} = \frac{D}{2}\left[1-\frac{15}{4}\tilde{r}^{-4}\right] \tag{3}$$

Consequently, according to this model, immobilizing sphere 2 results in an increase in *relative* diffusivity ($D_R^{\rm bf} > D_R^{\rm bb}$), but a decrease in *collective* diffusivity of the two-sphere system ($D_C^{\rm bf} < D_C^{\rm bb}$). Therefore, if these far-field, pair-wise interactions were additive, one would expect that *relative* tracer diffusion within a fluctuating cavity be *slower* than in the static cavity, so it should stay confined in the cavity for longer times. This is not the case experimentally, suggesting hydrodynamic coupling within the lattice involves many-body interactions and other effects not captured in the simple model.

Supporting Movies

Movie S1

Diffusion of 200nm tracers in a *static* lattice. The distances between nearest-neighbor lattice spheres have mean 2.14μm and standard deviation 0.07μm. The movie is played at actual speed at 50fps.

Movie S2

Diffusion of 200nm tracers in a *dynamic* lattice. The distances between nearest-neighbor lattice spheres have mean 2.14μm and standard deviation 0.08μm, very similar to the distribution of distances in Movie S1. The movie is played at actual speed at 50fps.

References

1. Batchelor, G. K. Brownian Diffusion of Particles with Hydrodynamic Interaction. *J. Fluid Mech.* **1976**, *74*, 1

2. Crocker, J. C. Measurement of the Hydrodynamic Corrections to the Brownian Motion of Two Colloidal Spheres. *J. Chem. Phys.* **1997**, *106*, 2837

3. Marbach, S.; Dean, D. S.; Bocquet, L. Transport and Dispersion Across Wiggling Nanopores. *Nat. Phys.* **2018**, *14*, 1108–1113