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ELECTRONIC SUPPLEMENTARY INFORMATION for:

Nanoparticle diffusion in crowded and confined environments

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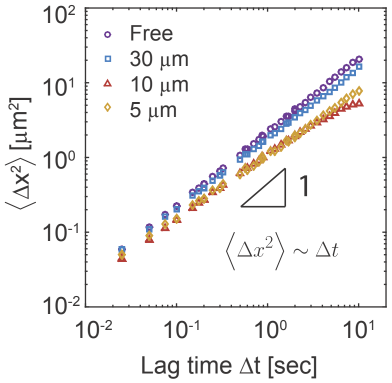

Figure S1. Mean-squared displacement of 400 nm polystyrene nanoparticles as a function of lag time in water. Symbols represent different media: free diffusion in solution (purple circle), confined diffusion in porous media with bead diameter of 30 μm (blue square), 10 μm (red triangle), or 5 μm (yellow diamond).

Table S1. Models describing the relative confined diffusivity in cylindrical and slit pores as a function of the dimensionless confinement length ξ.

Pore type	Model	Category	Validity
Cylindrical	$D/D_0 = (1-\xi)^2(1 - 2.104\xi + 2.09\xi^3 - 0.95\xi^5)$[1, 2]	Centerline approximation	$\xi < 0.4$
Cylindrical	$D/D_0 = 1 + \frac{9}{8}\xi \ln \xi - 1.539\xi + 1.2\xi^2 + O(\xi^2)$[3, 4]	Cross-section averaging	$\xi \to 0$
Cylindrical	$D/D_0 = 1 + \frac{9}{8}\xi \ln \xi - 1.539\xi + 0.528155\xi^2 + 1.915213\xi^3 - 2.81903\xi^4 + 0.270788\xi^5 + 1.10115\xi^6 + 0.435933\xi^7$[5, 6]	Cross-section averaging	$0 \le \xi \le 0.95$
Slit	$D/D_0 = (1-\xi)(1 - 1.004\xi + 0.418\xi^3 + 0.21\xi^4 - 0.169\xi^5 + O(\xi^6))$[7]	Centerline approximation	$\xi < 0.5$
Slit	$D/D_0 = 1 + \frac{9}{16}\xi \ln \xi - 1.9358\xi + 0.4285\xi^3 - 0.3192\xi^4 + 0.08428\xi^5$ [8]	Cross-section averaging	$\xi < 0.33$

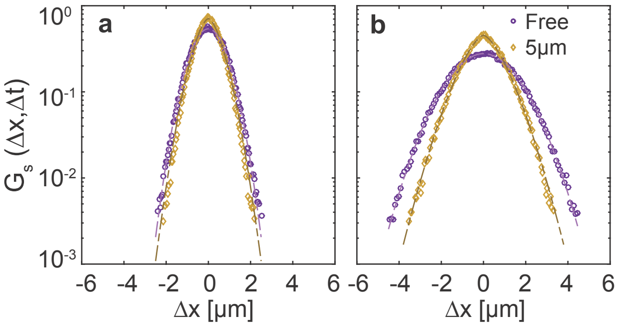

Figure S2. Probability density function of particle displacements at lag times of (a) 0.25 sec and (b) 1 sec for nanoparticles in water. Symbols represent different media: free diffusion in solution (purple circle) and confined diffusion in porous media with bead diameter of 5 μm (yellow diamond). The dashed line indicates a fit to the sum of a Gaussian and a stretched Gaussian.

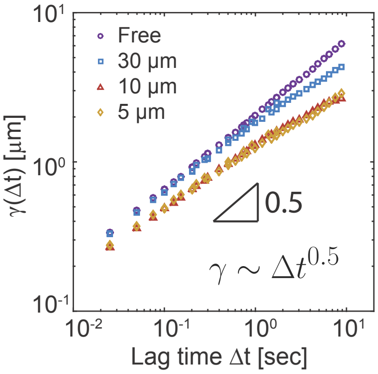

Figure S3. Decay length as a function of lag time for 400 nm nanoparticles in water. Symbols represent different media: free diffusion in solution (purple circle); confined diffusion in porous media with bead diameter of 30 μm (blue square), 10 μm (red triangle), or 5 μm (yellow diamond).

Calculation of interactions between nanoparticles and glass beads.

We treat the total interactions between nanoparticles and glass beads as the sum of an electrostatic interaction ΔG^{EL}, a Lifshitz-van der Waals interaction ΔG^{LW}, and a polymer mediated deletion interaction ΔG^{DEP}:

$$\Delta G^{total} = \Delta G^{EL} + \Delta G^{LW} + \Delta G^{DEP}. \qquad \text{S1}$$

The contribution of electrostatic and Lifshitz-van der Waals interactions is calculated using DLVO theory:[9, 10]

$$\Delta G^{EL}(h) = \pi\varepsilon\varepsilon_0 R\left[2\varphi_{NP}\varphi_{GB}\ln\left(\frac{1+\exp(-\kappa h)}{1-\exp(-\kappa h)}\right) + ({\varphi_{NP}}^2 + {\varphi_{GB}}^2)\ln(1-\exp(-2\kappa h))\right] \qquad \text{S2}$$

and

$$\Delta G^{LW}(h) = 2\pi R h_0 \Delta G_{d_0}^{LW} \frac{h_0}{h}, \qquad \text{S3}$$

where ε_0 is permittivity of the free space (8.85×10^{-12} s^4 A^2 m^{-3} kg^{-1}), $\varepsilon = 78$ is the relative permittivity of water, R is the particle radius, h is the distance between the particle and the wall, and h_0 is the minimum equilibrium distance. φ_{NP} and φ_{GB} are the surface potential of the nanoparticles and the glass beads, respectively, and are related to the corresponding zeta potentials. κ is the inverse of Debye length $\kappa = (4\pi l_B \sum_i c_i {z_i}^2)^{1/2}$, where $l_B = 0.7$ nm is the Bjerrum length in water, c is the ion concentration of polyelectrolytes, and z is the ionic charge.[11] $\Delta G_{d_0}^{LW}$ is calculated as:

$$\Delta G_{d_0}^{LW} = -2\left(\sqrt{\gamma_{NP}^{LW}} - \sqrt{\gamma_m^{LW}}\right)\left(\sqrt{\gamma_{GB}^{LW}} - \sqrt{\gamma_m^{LW}}\right), \qquad \text{S4}$$

where γ_{NP}^{LW}, γ_m^{LW}, and γ_{GB}^{LW} are the surface energy of the nanoparticles, water, and glass beads, respectively.

When the distance between a particles and a nearby confining surface (i.e. a glass bead) is less than the effective diameter of the polymer chains, the region between the particles and the surface is inaccessible to the centers of mass of the polymer chains and hence is depleted of polymer molecules. Depletion of polymer molecules inside this area creates an effective osmotic pressure, leading to a depletion attraction between particles and walls.[12] We follow the procedure for calculating the depletion interaction in the excluded volume regime established by ref [13]. Briefly, the potential interaction ΔG^{DEP} between a particle and a wall is calculated as

$$\Delta G^{DEP}(h) = -\int_0^{n_p} dn'_p \frac{1}{n'_p}\left(\frac{\partial \Pi}{\partial n'_p}\right)[\Gamma(h) - \Gamma(\infty)]. \qquad \text{S5}$$

where n_p is the polymer bulk concentration. From renormalization group theory, the osmotic compressibility Π can be written as

$$\frac{\partial(\beta \Pi)}{\partial n_p} = 1 + 2.63\,\phi_p \left(\frac{1 + 3.25\,\phi_p + 4.15\,\phi_p^2}{1 + 1.48\,\phi_p}\right)^{0.309} \qquad \text{S6}$$

where ϕ_p is the relative bulk polymer concentration and $\beta = 1/k_B T$. The overlap volume of the depletion layers in a semidilute solution is given by:[13, 14]

$$\frac{\Gamma(h)-\Gamma(\infty)}{n_p} = \begin{cases} \frac{4}{3}\pi(R+\Delta_s)^3 & h < \Delta_w - 2R - \Delta_s \\ \frac{1}{3}\pi(\Delta_s + \Delta_w - h)^2(3R + 2\Delta_s - \Delta_w + h) & \Delta_w - 2R - \Delta_s < h < \Delta_w + \Delta_s, \\ 0 & h < \Delta_w + \Delta_s \end{cases} \qquad \text{S7}$$

where Δ_s is the depletion layer thickness around the sphere and Δ_w is the depletion layer thickness near the wall. In the semidilute regime the depletion layer thickness depends on the polymer correlation length, which is in turn a function of the polymer concentration. The normalized depletion thickness around a sphere in semidilute solution is $\frac{\Delta_s}{R} = \left[1 + 3.213\frac{\xi}{R} + 2.607\left(\frac{\xi}{R}\right)^2 - 0.120\left(\frac{\xi}{R}\right)^3\right]^{1/3} - 1$ [refs [13, 15]], where ξ is the polymer correlation length. The depletion thickness near the wall in a semidilute solution is $\Delta_w = 1.071\xi$ [ref [13]].

Following ref [13], we apply the renormalization group theory approach of ref [16] to calculate the change in ξ as a function of n_p and use it to evaluate eqs S6 and S7. These expressions are then integrated to obtain the depletion interaction potential via eq S5, which accounts for the concentration dependence of the correlation length in the osmotic compressibility (eq S6), the overlap volume (eq S7), and the depletion thicknesses near a sphere and near a wall.

The electrostatic, Lifshitz-van der Waals, depletion, and total interactions between a nanoparticle and a glass bead are shown in Figure S6. Electrostatic repulsion prevents permanent adsorption of nanoparticles onto the surface of glass beads, whereas weak depletion interactions(~ 5kT) mediate particle-surface attractions at larger distances.

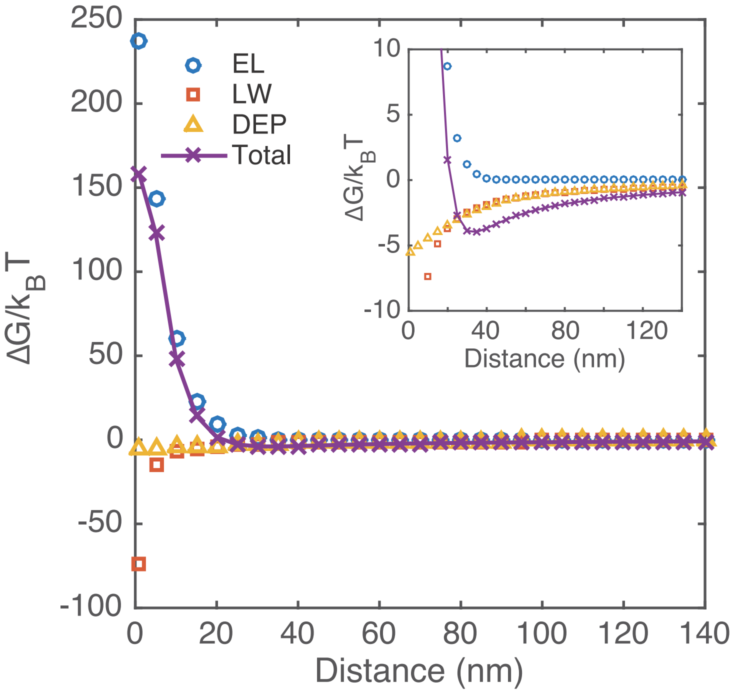

Figure S4. Electrostatic (blue circle), Lifshitz-van der Waals (red square), depletion (gold triangle), and total (purple line) interactions between a nanoparticle and a glass bead. The depletion interactions are calculated according to the renormalization group theory model following ref [13].

Table S2. Fitting parameters of a stretched exponential model ($G(\tau) = a\exp(-bx^c)$) for distributions of immobile time for nanoparticle diffusion in HPAM within porous media. Error is calculated from the confidence interval of the fitting parameters.

Fitting parameters	**Media**			
	5 µm	**10 µm**	**30 µm**	**Free**
a	5.5 ± 0.1	7.2 ± 0.2	7.1 ± 0.4	4.6 ± 0.7
b	2.53 ± 0.02	2.81 ± 0.03	2.80 ± 0.06	2.35 ± 0.02
c	0.63 ± 0.01	0.63 ± 0.01	0.66 ± 0.01	0.91 ± 0.01

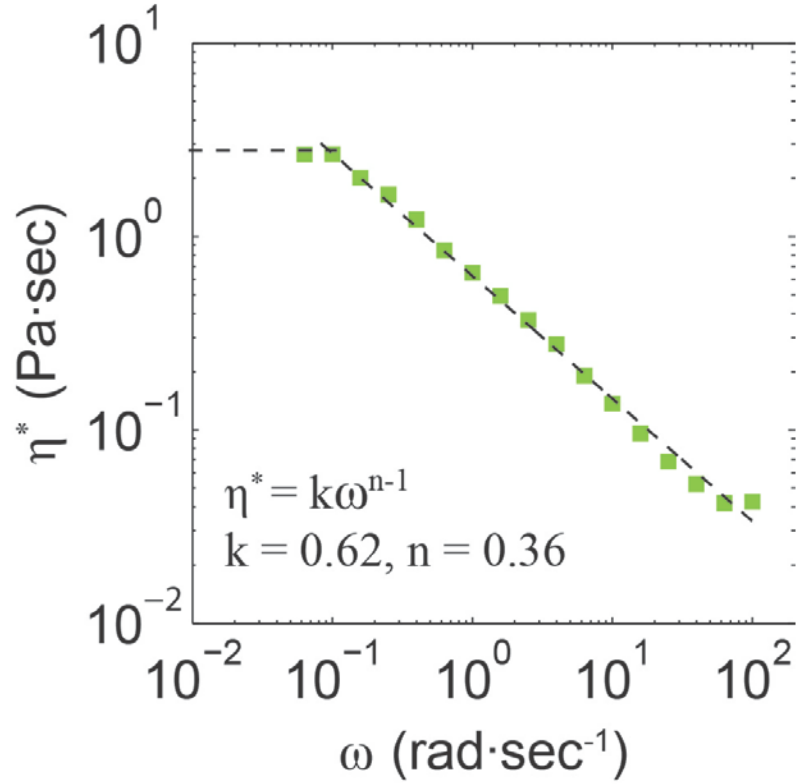

Figure S5. Complex viscosity η^* as a function of angular frequency ω of hydrolyzed polyacrylamide solution at concentration of 0.1 w/w%. The dashed line indicates a fit to a power law function $\eta^* = k\omega^{n-1}$.

Table S3. Glass bead properties and sintering protocol for borosilicate and soda lime glass beads.

Material	**Annealing point (°C)**	**Softening point (°C)**	**Sintering temperature (°C)**	**Sintering period (min)**
Borosilicate	560	821	810	5
Soda Lime	514	726	680	15

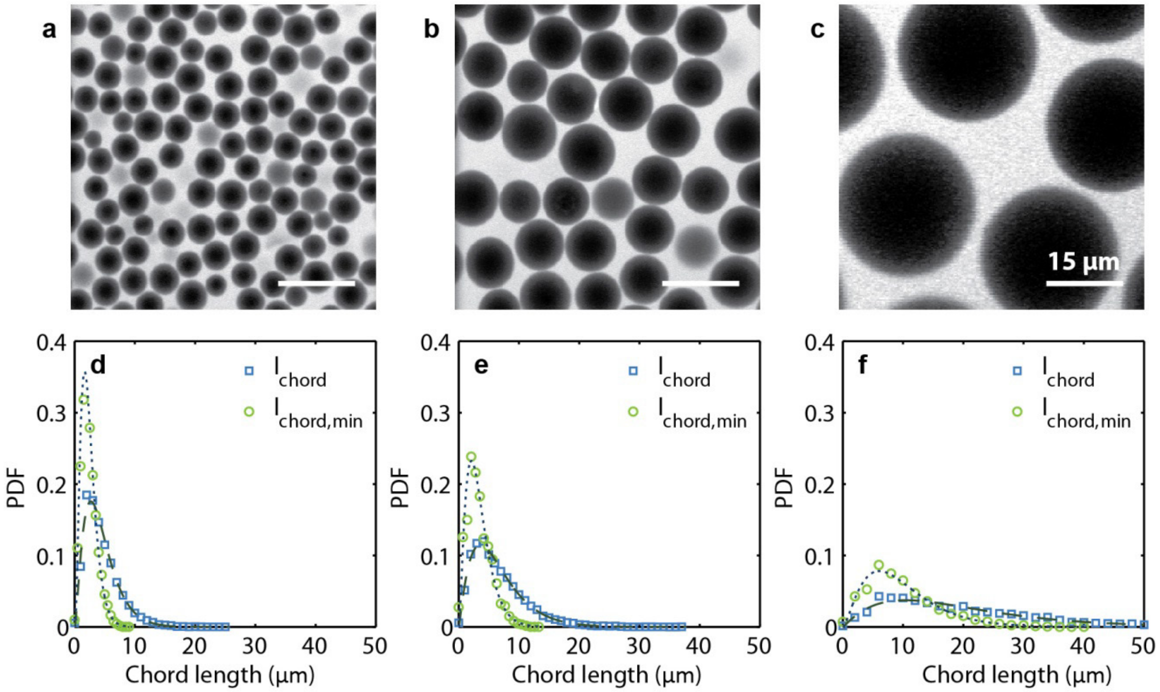

Figure S6. Characterization of the porous media. (a–c) Confocal images of porous media with bead diameters of (a) 5.4 µm, (b) 10 µm, and (c) 30 µm. (d–f) Probability distributions of the chord length and the minimum chord length for porous media with bead diameters of (d) 5.4 µm, (e) 10 µm, and (f) 30 µm. Dashed lines represent fits to a Gamma distribution function (equation 2 in the main text).

Table S4. Total number of trajectories of each bed configuration, fluid, and frame rate.

	HPAM		**Glycerol/water**		**Water**	
Frame rate (fps)	10	2	10	2	40	10
d_b=5 µm	111	113	44	81	2063	4628
d_b=10 µm	335	314	205	399	1260	2220
d_b=30 µm	67	113	499	427	1316	2377
Free diffusion	1088	765	1066	1144	1205	2741

Table S5. Total number of points at the shortest and longest time for each frame rate, bed configuration, and fluid.

HPAM				
	10 fps		2 fps	
	short time	long time	short time	long time
d_b=5 µm	159430	145468	152947	137919
d_b=10 µm	251967	232652	210154	187401
d_b=30 µm	61407	56879	50786	43213
Free diffusion	274046	250837	248081	211159
Glycerol/water				
	10 fps		2 fps	
	short time	long time	short time	long time

d_b=5 µm	10874	4596	7460	4706
d_b=10 µm	59238	46074	34707	18184
d_b=30 µm	87040	71113	31517	15715
Free diffusion	224728	188185	150809	104480
Water				
	10 fps		40 fps	
	short time	long time	short time	long time
d_b=5 µm	106374	18734	96209	39242
d_b=10 µm	96644	20435	102508	49892
d_b=30 µm	62936	6203	62440	24936
Free diffusion	115968	23280	96443	50305

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